MATERIALS FOR MEETING WITH GORDON WAGGETT

MAY 9, 2007
May 9, 2007

Gordon G. Waggett, Esq.
Gordon G. Waggett, P.C.
550 Westcott Street
Suite 350
Houston, TX 77007-5099

Re: Meeting of May 9

Dear Gordon:

For our meeting today, I am providing you with a notebook entitled “Materials for Meeting With Gordon Waggett – May 9, 2007.” This notebook will provide you relevant information in rebuttal to the claims of Ru-Ling Meng. With respect to her various declarations, I will simply note that any reasonable person would doubt the credibility of Meng in view of her reversal of sworn testimony regarding the disclosure by Dr. Chu to Meng in a mid-December 1986 call of Y and Lu as replacements for La. Secondly, I provide you with a group of exhibits which describe the state-of-the-art in the formulation and synthesizing of samples or pellets used in superconductivity labs throughout the world for many years prior to the events of November 1986-March 1987 which are in dispute here.

Thirdly, I provide you with the newly discovered calendar of Dr. Chu, which casts even greater doubt upon Ru-Ling Meng’s recent statements. The references by Chu to Y and Lu in his handwriting in mid-December fully support a telephone conversation in that time period in which Chu instructed Meng of his next inventive activities—the substitution of Y for La. Further, with respect to Meng’s allegations that it was she who conceived that Lu should be used as a substitute for La in the meeting among Pei Hor, Meng, Li Gao, Dr. Wu and others in late December or early January, Chu’s calendar demonstrates her claim is incorrect, if not untruthful.

We will discuss these materials with you in detail during the meeting.

Very truly yours,

Lester L. Hewitt
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<td>1</td>
<td>1989/06/07</td>
<td>Declaration (of Ru-Ling Meng) Under 37 C.F.R. § 1.639 (no exhs used)</td>
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<tr>
<td>2</td>
<td>1990/12/04</td>
<td>Declaration of Ru-Ling Meng (w/exhs A-C)</td>
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<td>3</td>
<td>1993/02/22</td>
<td>Declaration of Ru-Ling Meng (w/exhs A-N)</td>
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<td>2006/03/06</td>
<td>Affidavit of Ru-Ling Meng (w/exhs I-5)</td>
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<td>5</td>
<td>2006/05/25</td>
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<td>6</td>
<td>2006/10/26</td>
<td>G. Waggett letter to Akin Gump stating R. Meng's position (w/R. Meng CV)</td>
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<td>7</td>
<td>2006/10/26</td>
<td>G. Waggett PowerPoint</td>
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<td>8</td>
<td>1982</td>
<td>Mattens, Aarts, Moleman, Rachman, Boer, Chemical Pressure Effects in Sc-Substituted YbCuAl, Valence Instabilities, pp. 211-214</td>
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<td>10</td>
<td>1986</td>
<td>Millon, Gerardin, Bonazebi, Brice, Evvard, Effet d’une pression chimique locale sur la structure cristalline de CaFe₂O₄, Revue de Chimie Minerale, t. 23, pp. 782-788</td>
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<td>11</td>
<td>1975/02/10</td>
<td>Sleight, Gillson &amp; Bierstedt; High-Temperature Superconductivity in the BaPb₁₋ₓBiₓO₃ System, SOLID STATE COMMUNICATIONS, 17: 27-28</td>
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<td>12</td>
<td>1975/10/31</td>
<td>Chu &amp; Huang; Hydrostatic Pressure Effect on Tc of Ba₁₋ₓKₓ,Pb₀.₇₅Bi₀.₂₅O₃, SOLID STATE COMMUNICATIONS, 18: 977-979</td>
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<td>13</td>
<td>1973/05/25</td>
<td>Longo &amp; Raccah; The Structure of La₃CuO₇ and LaSrVO₄, JOURNAL OF SOLID STATE CHEMISTRY, 6: 526-531</td>
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<td>14</td>
<td>1976/03/11</td>
<td>Johnston; <em>Superconducting and Normal State Properties of</em> ( \text{Li}<em>{1+x}\text{Ti}</em>{2.3}\text{O}_4 ) <em>Spinels Compounds. I. Preparation, Crystallography, Superconducting Properties, Electrical Resistivity, Dielectric Behavior, and Magnetic Susceptibility</em>, JOURNAL OF LOW TEMPERATURE PHYSICS, &lt;illegible&gt;, pp. 145-175</td>
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<td>15</td>
<td>1980/05/29</td>
<td>Er-Rakho, Michel, Provost &amp; Raveau; <em>A Series of Oxygen-Defect Perovskites Containing Cu( \text{II} ) and Cu( \text{III} ): The Oxides ( \text{La}_3\text{Ln}<em>2\text{Ba}<em>2\text{Cu}</em>{4-x}\text{Cu}</em>{x}\text{Cr}<em>2\text{O}</em>{14+y} )</em>, JOURNAL OF SOLID STATE CHEMISTRY, 37: 151-156</td>
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<td>16</td>
<td>1982/11/02</td>
<td>USPN 4,357,426 (Murata et al.)</td>
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<td>17</td>
<td>1983/11/14</td>
<td>Lin, Shao, Wu, Hor, Jin &amp; Chu; <em>Observation of a reentrant superconducting resistive transition in granular BaPb(<em>{0.77})Bi(</em>{0.23})O(_{3}) superconductor</em>, THE AMERICAN PHYSICAL SOCIETY, 29: 1493-1496</td>
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<td>18</td>
<td>1984/11/13</td>
<td>USPN 4,482,644 (Beyerlein et al.)</td>
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<td>19</td>
<td>1985/03/05</td>
<td>USPN 4,503,166 (Beyerlein et al.)</td>
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<td>20</td>
<td>December 1986-March 1987</td>
<td>Personal Calendar of Ching-Wu (Paul) Chu, Ph.D.</td>
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

Qadri et al. § Interference No. 101,981
v. § Examiner-in-Chief:
Chu § Ronald H. Smith
v. §
Beyers et al. §
v. §
Batlogg et al. §

DECLARATION UNDER 37 C.F.R. § 1.639

1. RULING MENG, declare as follows:

1. I received a B.A. degree in Material Science
   from the Mining and Metallurgy College in Hunan, China in
   1958.

2. Since receiving my degree, I have worked as an
   instructor at the Mining and Metallurgy College, Hunan,
   China (1958-59); a Research Assistant, Metallurgy and
   Material Science Division, Institute of Mining and
   Metallurgy, Academy of Science (1959-73); and a Research
   Associate, Institute of Physics, Chinese Academy of
   Science (1973-84) during which time I also held visiting
   positions as a Research Associate, Department of Physics
   at University of Houston, Texas (1979-81), University of
   Konstanz, West Germany (1981-82), and University of

3. Currently I am a Senior Research Scientist, and
   Lab Manager of the Experimental Solid State Physics Lab of
   the Department of Physics, University of Houston, Texas
and of the Texas Center for Superconductivity; positions I have held since 1987.

4. Since 1974 to date, I have authored or been co-author on over 50 publications in the scientific literature most of which have related to the study of superconductivity in intermetallic, oxide and other compounds.

5. I have read and am familiar with the contents of United States Application Serial No. 32,041 filed March 26, 1987 by C.W. Chu (hereafter the "Chu application).

6. I was asked to repeat Example XIII of the Chu Application. In following Example XIII, the following work was performed by me, or by a technician under my direct supervision and control as follows: 0.1 grams of La₂O₃, 0.243 grams of BaCO₃ and 0.1465 grams of CuO were thoroughly mixed by mortar-pestle until a fine powder of uniform grey color was obtained. The powder was pressed into several pellets of about 1/16 inch thickness and about 3/16 inch diameter by applying 250 psi pressure using a standard laboratory press. The pellets were placed in an alumina boat and the boat was placed in a tube furnace, the tube was open to air, and the furnace was heated to 950°C and held at that temperature for about 8 hours. Thereafter the boat containing the pellets was placed in another tube furnace with one end of the tube connected to a vacuum pump through a valve capable of regulating the level of vacuum drawn to 2000 μ. The other end of the tube was communicated to an oxygen cylinder through a regulator providing for a regulated flow of oxygen. This arrangement allowed the tube containing the
boat with the pellets to be provided with an oxygen atmosphere regulated to a pressure of 2000 μ to provide a reduced-oxygen atmosphere (-2000μ). The furnace temperature was brought up to 850°C from room temperature in about two hours. The sample pellets in the boat were then heated at 850°C for an additional 30 minutes under the reduced-oxygen atmosphere (2000 μ) after which time power to the tube furnace was turned off. Oxygen continued to pass through the tube furnace at 2000 μ of pressure until the boat containing the pellet samples returned to room temperature and the boat with sample pellets was then removed from the furnace. One pellet was ground, and an X-ray powder diffraction study was performed. Another pellet was used for a magnetic flux exclusion experiment. I concluded from the X-ray powder pattern that the material contained greater than 90% LaBa₂Cu₃O₆₊ₓ (X a value that provided orthorhombic crystal symmetry), and a minor amount of BaCuO₂. Magnetic flux (Meissner effect) exclusion results showed an onset of superconductivity at about 84 K. The sample was measured resistively to have a Tc₀ (onset) of 92 K and a Tc₁ (zero resistance) of 77 K.

7. In early 1987 an EuBa₂Cu₃O₇₋δ sample was made in accordance with the procedure of Example XIV of the Chu application, with the exception that a sintering temperature of 925°C was employed rather than 950°C. After 20 minutes at a sintering temperature of 925°C, power to the tube furnace was turned off. Oxygen continued to pass through the tube furnace at 2000 μ of pressure until the boat containing the pellet samples
returned to room temperature. Room temperature of the boat with pellets was obtained in approximately 180 minutes after the tube furnace power was turned off. Measurements made on this material established that it had an oxygen content of 6.840 (EuBa\textsubscript{2}Cu\textsubscript{4}O_{6.84}), X-ray lattice parameters of "a" = 3.860Å, "b" = 3.904Å, "c" = 11.727Å, a T\textsubscript{C0} of 96.5 K, a T\textsubscript{C1} of 91.5 K and it exhibited a Meissner-effect of 23%.

8. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the Chu Application or any patent issued thereon.

EXECUTED this 7th day of June, 1989.

[Ruling Meng's signature]

RLM1231
CERTIFICATE OF SERVICE

I hereby certify that a copy of the foregoing Declaration Under 37 C.F.R. § 1.639 has been mailed, first class mail, postage pre-paid this 17th day of June, 1989 to:

A. David Spevack
Office of Associate Counsel (Patents)
Code 1208.2
Naval Research Lab
Washington, D.C. 20375-5000

Joseph G. Walsh
IBM Corporation
Intellectual Property Law
5600 Cottle Road (951/029)
San Jose, CA 95193

John P. McDonnell
AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, NJ 07974-2070

[Signature]

CERTIFICATE UNDER 37 CFR 1.8(a)

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Box Interference, Commissioner of Patents and Trademarks, Washington, D.C. 20231, on June 7, 1989.

[Signature]

Date: June 7, 1989

James B. Gambrell
Registration No. 17,920
Charles M. Cox
Registration No. 29,057
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

WU et al. § Interference No. 102,447
v. §
CHU §
$ Examiner-in-Chief:
$ Ronald H. Smith

DECLARATION OF RU-LING MENG

Box Interference
Commissioner of Patents
and Trademarks
Washington, D.C. 20231

Attention: Ronald H. Smith
Examiner in Chief

Dear Sir

I, RU-LING MENG, do hereby declare and state that:

1. I am currently a Senior Research Scientist, and Lab Manager of the Experimental Solid State Physics Lab of the Department of Physics, University of Houston, Texas and of the Texas Center for Superconductivity; a position I have held since 1987. Prior to that, during the period 1984 to 1986, I held the position of Research Associate, Department of Physics at the University of Houston, Texas, working under the supervision of Dr. C.W. Chu.

2. During a telephone call in about mid-December 1986, C.W. Chu described to me his belief that substitution of Y for La in a composition La-Ba-Cu-O would produce a composition of Y-Ba-Cu-O which superconducts at a $T_c$ temperature greater than that of a La-Ba-Cu-O composition.

3. During a discussion which occurred in the office of Pei...
Hor in late December 1986, after Christmas and before January 4, 1987, which was attended by myself, Pei Hor and Li Gao of the University of Houston, and by M.K. Wu of the University of Alabama, the concept of substitution of Y for La in a composition of La-Ba-Cu-O to produce a composition of Y-Ba-Cu-O which superconducts at a $T_c$ temperature greater than that of a La-Ba-Cu-O composition was described to M.K. Wu.

4. Before January 17, 1987, I identified in my notebook several substituted compositions for production and examination. Among the compositions so identified is one of the formula $Y_{1.2}Ba_{0.8}CuO_y$ as shown on Exhibit A attached hereto which is in my handwriting and made by me on a date prior to January 17, 1987. The date entered on Exhibit A has been masked out of the attached copy.

5. Further, on January 29, 1987, I identified further compositions for production and testing in accordance with Dr. Chu's direction to make compositions involving substitution for variously the La or Ba of a La-Ba-Cu-O composition by other small radii atomic elements as shown in Exhibit B attached hereto which was made by me and is in my handwriting. The amounts of reagents required for the production of compositions as shown in Exhibit B are shown in Exhibit C attached hereto, which is in my handwriting and made by me during January 29-30, 1987. Among the compositions considered for production are several formulations of Y-Ba-Cu-O, one of which is specifically of the formula $Y_{1.2}Ba_{0.8}Cu_{1.0}O_y$.

6. In accordance with my prior calculations as recorded in
Exhibit C, I began to prepare compositions of Y-Ba-Cu-O one of which, designated as YB-102, was of the formula Y_{1.2}Ba_{0.2}Cu_{2}O_y as described in Exhibit C.

7. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the Chu Application or any patent issued thereon.

EXECUTED this 4th day of December, 1990.

RULING MENG
\[ Y_{S-2} \quad (Y_{0.85}^{0.25} - Sr_{0.15}) \quad \approx 0.4 \]

\[ Y_{S-3} \quad Sr_{0.35} \quad \approx 0.4 \]

\[ SB-2 \quad (Y_{0.85}^{0.3} - Sr_{0.15}) \quad \approx 0.4 \]

\[ SB-3 \quad (Y_{0.85}^{0.3} - Sr_{0.15}) \quad \approx 0.4 \]

\[ (I) \quad (Y_{0.85}^{0.3} - Sr_{0.15}) \quad \approx 0.4 \]

\[ YS-2 \quad \begin{array}{c|c|c|c|c}
Y & Sr & Ln & O \\
\hline
47.25 & 12.38 & 13.57 & 0.10
\end{array} \]

\[ Y_{O_{3}}\quad 18.08 \]

\[ SrO_{3} \quad 361.59 \]

\[ LnO \quad 414.32 \]

\[ (II) \quad Y_{0.35}^{0.65} - Sr_{0.35} \quad Ln \quad 0.4 \]

\[ YS-3 \quad \]
29-30 Jan. 1987

1. \([La_{0.7} (Y_{0.155} Ba_{0.845})_{0.9}]_2 \text{ mol}

2. \([La_{0.9} (Y_{0.25} Ba_{0.75})_{0.7}]_2 \text{ mol}

3. \([La_{0.9} (Y_{0.3} Ba_{0.7})_{0.7}]_2 \text{ mol}

4. \([La_{0.95} (Y_{0.155} Ba_{0.845})_{0.95}]_2 \text{ mol}

\[La_2O_3: 1000 \text{ mg}

\[Y_3O_3: 11.937 \text{ mg}

\[BaCO_3: 113.782 \text{ mg}

\[CuO: 27.175 \text{ mg}

Y_{203}

K_07 78.74
### LYB-3

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<td>Y</td>
<td>Ba</td>
<td>Cu</td>
<td>O</td>
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<tr>
<td>6.237</td>
<td>1.375</td>
<td>4.857</td>
<td>15.945</td>
<td>5.945</td>
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<td>La₂O₃</td>
<td>2000 mg</td>
<td>3000 mg</td>
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<tr>
<td>Y₂O₃</td>
<td>27.118 mg</td>
<td>36.236 mg</td>
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<tr>
<td>BaCO₃</td>
<td>83.721 mg</td>
<td>167.442 mg</td>
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<tr>
<td>CuO</td>
<td>271.255 mg</td>
<td>342.576 mg</td>
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<td>59.604</td>
<td>0.707</td>
<td>16.307</td>
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<td>La₂O₃</td>
<td>2000 mg</td>
<td>1000 mg</td>
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<tr>
<td>Y₂O₃</td>
<td>25.466 mg</td>
<td>14.632 mg</td>
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</tr>
<tr>
<td>BaCO₃</td>
<td>24.0.843 mg</td>
<td>120.441 mg</td>
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<tr>
<td>BaO</td>
<td>157.445 mg</td>
<td>287.224 mg</td>
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### LYB-2

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<td>La₂O₃</td>
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<td>BaCO₃</td>
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<td>CuO</td>
<td>542.515 mg</td>
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### LYB-4

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<td>Cu₀.₉₅Ba₀.₀₅</td>
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<td>59.604</td>
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<td>25.466 mg</td>
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<td>BaCO₃</td>
<td>24.0.843 mg</td>
<td>120.441 mg</td>
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<tr>
<td>BaO</td>
<td>157.445 mg</td>
<td>287.224 mg</td>
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RLM1239
### 8. \( \text{La}_{0.95} \text{Y}_{0.05} \text{Cu}_2 \text{O}_4 \)

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<th>La</th>
<th>Y</th>
<th>Cu</th>
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<td>6.921</td>
<td>2.221</td>
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- \( \text{La}_2\text{O}_3 \) : 1000 mg
- \( \text{Y}_2\text{O}_3 \) : 36.484 mg
- \( \text{Cu}_2\text{O} \) : 256.989 mg

### 9. \( \text{La}_{0.99} \text{Ba}_{0.01} \text{Cu}_2 \text{O}_4 \)

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<th>La</th>
<th>Ba</th>
<th>Cu</th>
<th>O</th>
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<td>67.856</td>
<td>0.678</td>
<td>15.876</td>
<td>15.980</td>
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- \( \text{La}_2\text{O}_3 \) : 1000 mg | 2000 mg
- \( \text{Ba}_2\text{O}_3 \) : 24.201 mg | 29.482 mg
- \( \text{Cu}_2\text{O} \) : 246.601 mg | 293.202 mg

Sixteen 7 hours at 1100°C
LuB-0102 (Lu₂₆ Ba₆₄)₂ Cu₅₄

Lu  Ba  Cu  O
46.932 24.559 14.203 14.326

Lu₂O₃ : 1000 mg  |  300 mg
BaCO₃ : 1661.202 mg  |  198.361 mg
CuCO₃ : 332.141 mg  |  99.942 mg

LuB-018 (Lu₂₆ Ba₆₄)₂ Cu₅₄

Lu  Ba  Cu  O
32.378 38.121 14.697 14.804

Lu₂O₃ : 1000 mg  |  300 mg
BaCO₃ : 1487.670 mg  |  443.601 mg
CuCO₃ : 499.684 mg  |  149.905 mg

LuB-014 (Lu₂₆ Ba₆₄)₂ Cu₅₄

Lu  Ba  Cu  O
16.773 52.162 15.227 15.338

Lu₂O₃ : 300 mg
BaCO₃ : 1190.146 mg
CuCO₃ : 299.807 mg

YB-101 (Y₉₈ Ba₆₂)₂ Cu₅₄

Y  Ba  Cu  O
43.806 16.918 19.567 19.709

Y₂O₃ : 300 mg  |  100 mg
BaCO₃ : 1316.07 mg  |  43.616 mg
CuCO₃ : 132.088 mg  |  44.029 mg

H  55
<table>
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<th>Sample</th>
<th>Formula</th>
<th>Y</th>
<th>Ba</th>
<th>Cu</th>
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<td>YB-102</td>
<td>(Y0.6 Ba0.4)2 Cu O4</td>
<td>31.005</td>
<td>31.930</td>
<td>18.466</td>
<td>18.599</td>
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<td>Y2O3 : 300 mg</td>
<td>BaCO3 : 249.555 mg</td>
<td>CuO : 176.122 mg</td>
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<tr>
<td></td>
<td>BaO : 243.56 mg</td>
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</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Formula</th>
<th>Y</th>
<th>Ba</th>
<th>Cu</th>
<th>O</th>
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<tbody>
<tr>
<td>YB-103</td>
<td>(Y0.4 Ba0.6)2 Cu O6</td>
<td>19.988</td>
<td>45.243</td>
<td>17.481</td>
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<td>Y2O3 : 300.00 mg</td>
<td>BaO3 : 194.195 mg</td>
<td>CuO : 264.176 mg</td>
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<table>
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<tr>
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<th>Formula</th>
<th>Y</th>
<th>Pb</th>
<th>Cu</th>
<th>O</th>
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<tr>
<td>YP-101</td>
<td>(Y0.8 Pb0.2)2 Cu O4</td>
<td>40.335</td>
<td>23.500</td>
<td>18.017</td>
<td>18.168</td>
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<tr>
<td></td>
<td>Y2O3 : 300.00 mg</td>
<td>PbO : 153.888 mg</td>
<td>CuO : 132.091 mg</td>
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BaO : 99.88 mg
$Yb_{1.2}Ba_{0.8}Cu_4O_y$

$Yb_{1.2}Ba_{0.8}Cu_4O_y$

$Yb_{1.1}Ba_{0.9}Cu_4O_y$

$Yb_{1.1}Ba_{0.9}Cu_4O_y$

$Yb_{1.0}BaCu_4O_y$

$Yb_{1.0}BaCu_4O_y$
\[ \text{Yb} - 10^4 \]

\[ \text{Yb}_{1.3} \cdot \text{Ba}_{0.7} \cdot \text{Cu}_4 \]

\[ \text{Yb} \quad \text{Ba} \quad \text{Cu} \quad 0 \]

\[ 50.142 \quad 21.429 \quad 14.163 \quad 14.266 \]

\[ \text{Yb}_{2} \cdot \text{O}_3 : 300 \text{mg} \]

\[ \text{Ba} \cdot \text{CO}_3 : 161.782 \text{mg} \]

\[ \text{Cu} \cdot 0 : 93.155 \text{mg} \]

\[ \text{Yb} - 10^5 \]

\[ (\text{Yb}_{5} \cdot \text{Ba}_{2.5}) \cdot \text{Cu}_4 \cdot \text{O}_4 = \text{Y}_{1} \cdot \text{Ba}_{1} \cdot \text{Cu}_4 \cdot \text{O}_4 \]

\[ \begin{array}{cccc}
\text{Y} & \text{Ba} & \text{Cu} & 0 \\
25.189 & 32.821 & 17.969 & 18.090
\end{array} \]

\[ \text{Yb} - 10^6 \]

\[ (\text{Yb}_{9} \cdot \text{Ba}_{2}) \cdot \text{Cu}_4 \cdot \text{O}_4 \]

\[ \begin{array}{cccc}
\text{Y} & \text{Ba} & \text{Cu} & 0 \\
1.4 & 26 & 40 & 0 \\
\end{array} \]
\[ \sqrt{\text{LuB} = 101} \quad (\text{Lu}_{0.8} \, \text{Ba}_{0.2})_2 \, \text{CuO}_4 \]

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<th>Element</th>
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<td>Cu</td>
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<tr>
<td>C</td>
<td>C</td>
<td>13.840</td>
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<td>\text{Lu}O_3</td>
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<tr>
<td>\text{Ba}_2O_3</td>
<td>257.951 mg</td>
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<td>CuO</td>
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\[ \sqrt{Y \, P \, \text{Y}_{10.2} \, (Y_{0.6} \, Pb_{0.4})_2 \, \text{CuO}_4} \]

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<thead>
<tr>
<th>Element</th>
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<th>Mass</th>
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<td>Cu</td>
<td>CuO</td>
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<td>C</td>
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<td>\text{Y} _2 \text{O}_3</td>
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<td>CuO</td>
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\[ \sqrt{Y \, P \, \text{Y}_{10.3} \, (Y_{0.4} \, Pb_{0.6})_2 \, \text{CuO}_4} \]

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<td>\text{Y} _2 \text{O}_3</td>
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<td>PbO</td>
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<td>CuO</td>
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\[ \sqrt{Y \, P \, \text{Y}_{10.4} \, (Y_{0.2} \, Pb_{0.8})_2 \, \text{CuO}_4} \]

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<td>\text{Y} _2 \text{O}_3</td>
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<td>CuO</td>
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<tr>
<td>LuP-101</td>
<td>(Lu0.8 Pb0.2)2 CuO6</td>
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<tr>
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<tr>
<td>Lu</td>
<td>Pb</td>
<td>Cu</td>
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<tr>
<td>57.09</td>
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<td>PbO2</td>
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<td>CuO</td>
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<table>
<thead>
<tr>
<th>LuP-102</th>
<th>(Lu0.6 Pb0.4)2 CuO6</th>
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<tr>
<td>41.721</td>
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<td>Lu2O3</td>
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<th>(Lu0.4 Pb0.6)2 CuO6</th>
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<tr>
<td>27.16</td>
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<td>CuO</td>
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</table>

<table>
<thead>
<tr>
<th>LuP-104</th>
<th>(Lu0.2 Pb0.8)2 CuO6</th>
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<tbody>
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</tr>
<tr>
<td>13.229</td>
<td>62.662</td>
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<td>Lu2O3</td>
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<td>PbO2</td>
<td>144.2603 mg</td>
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<tr>
<td>CuO</td>
<td>299.840 mg</td>
</tr>
</tbody>
</table>

\[ \equiv \text{CuO} \equiv 299.840 \text{mg} \]
The stamp of the Patent Office, placed hereon, acknowledges receipt of:

Applicant: Party, Chu

Our Ref.: 763251

Serial No.: 10,447

Date Mailed: 12/4/90

Date Due: 12/4/90

Documents Enclosed: Party, Chu's Opposition to Accused's I) Motion for Judgment, Clu Claims 17-27 Are Unpatentable, Improper Invention; and 2) Motion for Judgment, Chu Claims 17, 19, 26, 22, 23, 25 and 26 Are Unpatentable Under 35 USC 112-2708.1.33; Decl. of Rui-Lin Yang, Re: Yang's C-EXS A-T.
The stamp of the Patent Office, placed hereon, acknowledges receipt of:

Applicant: Party: Chu

Serial No.: 79352/1

Date Mailed: 12/4/90

Date Due: 12/4/90

Documents Enclosed: Party: Chu's Opposition

To: (nee et al's) 1) Motion for Judgment, Chu Claims 17-27 are unpatentable, improper invention, and 2) Motion for Judgment, Chu Claims 17, 19, 20, 22, 23, 25 and 26 are unpatentable under 35 USC 112-37 CFR 1.633; 'Ducks of the South Seas' Lei, Nannfow, C. W. Chu & Exs A - T.
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES
WU et al. v. CHU
Interference No. 102,447
Examiner-in-Chief: Ronald H. Smith

DECLARATION OF RULING MENG
Box Interference
Commissioner of Patents and Trademarks
Washington, D.C. 20231

Attention: Ronald H. Smith
Examiner-in-Chief

Dear Sir:

I, RULING MENG, do hereby declare and state that:

1. I received a B.A. degree in Material Science from the Mining and Metallurgy College in Hunan, China in 1958. Since receiving my degree, I have worked as an instructor at the Mining and Metallurgy College, Hunan, China (1958-59); a Research Assistant, Metallurgy and Material Science Division, Institute of Mining and Metallurgy, Chinese Academy of Science (1959-73); and a Research Associate, Institute of Physics, Chinese Academy of Science (1973-84) during which time I also held visiting positions as a Research Associate, Department of Physics at University of Houston, Texas (1979-81), University of Konstanz, West Germany (1981-82), and University of Houston, Texas (1984-86). I am currently a Senior Research Scientist, and Lab Manager of the Experimental Solid State Physics Lab of the Department of Physics, University of Houston, Texas and of the Texas Center for Superconductivity; a position I have held since 1987. Prior to
that, during the period 1984 to 1986, I held the position of Research Associate, Department of Physics at the University of Houston, Texas, working at the direction and under the supervision of Dr. C.W. (Paul) Chu.

2. I first began to make and examine compositions composed of rare earth metal-alkaline earth metal-copper-oxygen for superconducting properties in November 1986. Dr. C.W. (Paul) Chu under whose directions and supervision I worked directed me to make compositions of La-Ba-Cu-O to a nominal formula as described in Bednorz & Muller, Z. Phys. B.—Condensed Matter, 64, pp 189 – 193 (1986) and then test such compositions for the existence of the properties of a superconducting material — namely, the exhibition at or below a certain critical temperature (Tc) of zero electrical resistance and a diamagnetic property.

3. During November 1986 I prepared several samples of La-Ba-Cu-O compositions to a nominal formula of La4.25Ba0.75Cu2O5+δ, as disclosed by the Bednorz & Muller article. Each sample thereof was prepared under various firing conditions, as recorded in my handwriting in Exhibit A at or about the time each such sample was prepared, and thereafter tested by me, or tested by others under my direction and supervision, to measure the sample's electrical resistance at various temperatures from that of about ambient and progressing to the boiling point of liquid helium which is about 4°K. Further, samples which exhibited the attainment of zero electrical resistance at or below a certain critical temperature were measured for the exhibition of a diamagnetic effect by me, or
by others working under the direction and supervision of Dr. Chu and myself.

4. My work with the La-Ba-Cu-O compositions, as described in paragraphs 2–3 above confirmed that a composition described by Bednorz & Muller as one of nominal formula La$_{1.24}$Ba$_{0.75}$Cu$_2$O$_y$ did, in fact, possessed superconducting properties even though I produced my replicas, as directed by Dr. Chu, by a solid state reaction technique rather than by a precipitation technique as described by Bednorz & Muller.

5. During the remainder of November of 1986, and bridging into December of 1986, as directed by Dr. Chu, I, or others working under the direction and supervision of Dr. Chu and myself, began at least two activities; one being to subject the La-Ba-Cu-O compositions produced to a Bednorz & Muller nominal composition of La$_{1.25}$Ba$_{0.75}$Cu$_2$O$_{y+1}$, which we had confirmed to be superconductors to application of extreme pressure while testing how such pressure affected the $T_c$ property of such composition; the second activity being to produce La-Ba-Cu-O composition to nominal formulas different than that described for a La-Ba-Cu-O composition by the Bednorz & Muller article and to test such different nominal formulations of La-Ba-Cu-O for exhibition of superconducting properties. Among the first samples of La-Ba-Cu-O of differing nominal composition which I prepared in accordance with Dr. Chu's instructions were La-Ba-Cu-O samples of the following nominal formulas, designed by my identification designation ("J"):

$J-1$ \((La_{0.4}Ba_{0.6})_2CuO_4\)
J-2  \((\text{La}_{0.6}\text{Ba}_{0.4})_2\text{CuO}_4\)
J-3  \((\text{La}_{0.7}\text{Ba}_{0.3})_2\text{CuO}_4\)
J-4  \((\text{La}_{0.8}\text{Ba}_{0.2})_2\text{CuO}_4\)
J-5  \((\text{La}_{0.85}\text{Ba}_{0.15})_2\text{CuO}_4\)
J-6  \((\text{La}_{0.9}\text{Ba}_{0.1})_2\text{CuO}_4\)

These samples are recorded in my handwriting in my notebook, together with my calculations of the amounts of reagents needed for their production as shown in Exhibit B.

6. From the results of the work which I performed according to Dr. Chu's instructions on La-Ba-Cu-O compositions as described in paragraphs 2-5 above, it was determined that (1) certain La-Ba-Cu-O compositions were superconductors, (2) that compositions of La-Ba-Cu-O of nominal formulations different than that described by Bednorz & Muller for a superconducting La-Ba-Cu-O composition were superconductors; (3) that under extreme pressure application such superconducting compositions of La-Ba-Cu-O exhibited zero electrical resistance at a critical temperature, \(T_c\), which was unexpectedly higher than that at which the sample composition exhibited zero electrical resistance when subjected only to ambient (atmospheric) pressure. These results were reported to Dr. Chu at or about the time the results were obtained.

7. Following the reports to Dr. Chu of the observation of the results measured in La-Ba-Cu-O systems, as described in paragraphs 3-6 above, while Dr. Chu was out of town in about mid-December 1986 tending to other duties, Dr. Chu called me to describe his ideas for making various elemental substitutions in a
La-Ba-Cu-O superconductor system to increase the $T_{c1}$ temperature at which a so substituted composition would exhibit zero electrical resistance without the need for application of great pressure to such substituted compositions.

8. Of the substituted compositions described to me by Dr. Chu during that December 1986 telephone conversation, Dr. Chu described his idea of substitution for Ba as the alkaline earth metal element in a La-Ba-Cu-O system by Sr and Ca.

9. Further, during the mid-December 1986 telephone conversation with Dr. Chu, as described in paragraph 8 above, Dr. Chu also informed me of his idea of superconducting rare earth metal-alkaline earth metal-copper-oxygen compositions which in comparison to one of La-Ba-Cu-O would exhibit zero electrical resistance at a greater temperature ($T_{c1}$) without application of pressure. Dr. Chu described his idea for compositions wherein the rare earth element of La was substituted for by non-magnetic rare earth and similar elements, including Y or Lu. During this telephone call Dr. Chu described to me his belief that substitution for La in a La-Ba-Cu-O composition would produce a superconductor which superconducts at a $T_{c1}$ temperature greater than that of a La-Ba-Cu-O composition.

10. As related in paragraph 9 above, among other things, Dr. Chu instructed me by that telephone call to next prepare, among other substituted compositions, Y-Ba-Cu-O compositions in accordance with the same program by which I had earlier prepared and tested different nominal formulations of La-Ba-Cu-O for
superconductive properties.

11. During the latter part of December, after Christmas, W.K. Wu and his research graduate student, James Ashburn, arrived at the laboratories of the University of Houston campus at which I worked to have samples, which I understand Dr. Chu had suggested to them (Wu/Ashburn) to prepare, tested for exhibition of superconductive properties. Based on information and belief which I derived from Dr. Chu and independently from M.K. Wu and Ashburn during their attendance at the University of Houston campus, I understood that the sample brought by Wu/Ashburn to be tested were compositions of La-Sr-Cu-O. I further understood that Wu/Ashburn had already tested these compositions for electrical resistance versus temperature and determined that, absent the application of great pressure thereto, such La-Sr-Cu-O samples exhibited a $T_c$ greater than that of a La-Ba-Cu-O of similar nominal composition without the application of pressure.

12. As described in paragraph 11 above, at our labs at University of Houston, while Wu/Ashburn were in attendance, in the supervision of our group at Dr. Chu's directions I, with the assistance of others in our group, tested the Wu/Ashburn made samples of La-Sr-Cu-O for (1) zero electrical resistance at specific temperatures, (2) for diamagnetism, and (3) for $T_c$ under application to such materials of great pressures. These results were reported to Dr. Chu. The results of this testing were encouraging of a belief that a La-Sr-Cu-O composition possessed a higher $T_c$ than do compositions of La-Ba-Cu-O. However, because the
test results were stated by Dr. Chu to be too poor to support a
publication, he directed me to prepare higher quality La-Sr-Cu-O
samples for evaluation.

13. Dr. Chu's instruction to me to prepare higher quality
samples of La-Sr-Cu-O consequently delayed the time at which I
could begin preparation of samples of Y-Ba-Cu-O which had been
assigned to me. During a discussion which occurred after Christmas
in late December 1986, which was attended by myself, M.K. Wu, and
others, the concept of substitution of Y for La in a composition of
La-Ba-Cu-O to produce a composition of Y-Ba-Cu-O which
superconducts at a $T_c$ temperature greater than that of a La-Ba-Cu-O
composition was described to M.K. Wu.

14. During the period of December 1986 after Christmas and
continuing through January 28, 1987 while I continued to make and
study approximately 47 different samples of La-Ba-Cu-O, I also
prepared and evaluated thirty-eight different samples of La-Sr-Cu-O
compositions. My sample code for a La-Sr-Cu-O sample was "SL"
followed by a number or numbers by which I could identify from my
records the nominal formulation and sintering conditions of the
sample. In the period December 23, 1986 through January 1, 1987 I
prepared and evaluated six samples, SL1-SL6 (Exhibit C). Between
January 2-18, 1987 I prepared and evaluated twelve additional
samples, SL7-SL17 (Exhibits C and D) and between January 18-28,
1987 I prepared twenty additional samples, SL18-SL31 (Exhibit E).

15. As my work with the La-Sr-Cu-O system was progressing, I
began to turn my attention to the making of Y-Ba-Cu-O compositions
which I would begin upon conclusion of my work with La-Sr-Cu-O compositions.

16. The formulas of Y-Ba-Cu-O which I first listed for production, as shown by Exhibit F, are "214" nominal formulations wherein the rare earth to alkaline earth metal ratio, Y to Ba, which together comprise the "2" element begins with a slightly greater amount of rare earth metal --y-- (6:4, like the La to Ba ratio in the "J-2" sample of paragraph 5).

17. On January 15, 1987, I identified in my notebook several substituted compositions for production and examination. Among the compositions so identified is one of the formula \( \{Y_{0.4}\text{Ba}_{0.6}\}\text{CuO}_4 \) (which may also be written as \( Y_{1.2}\text{Ba}_{0.8}\text{CuO}_4 \)) as shown in Exhibit F attached hereto which is in my handwriting and made by me on January 15, 1987.

18. By January 28, 1987 I had substantially completed my assignment to prepare and investigate higher quality samples of La-Sr-Cu-O and on January 29, 1987 I again returned by attention to the project which Dr. Chu had previously assigned to me, namely the making of rare earth metal-alkaline earth metal-copper oxides in which, compared to a La-Ba-Cu-O system, La is replaced with Y or Lu. To this purpose, with respect to a Y-Ba-Cu-O system, on January 29, 1987 I proceeded to list samples of Y-Ba-Cu-O for production in accordance with a convention I followed when I first made samples of La-Ba-cu-O which differed from the nominal formula of Bednorz & Muller, as discussed in paragraph 5. I listed in my notebook (Exhibit G) the following samples for production, which I
later identified by a "YB" designation, as follows:

YB-101 \((\text{Y}_{0.8}\text{Ba}_{0.2})_2\text{CuO}_4\)
YB-102 \((\text{Y}_{0.4}\text{Ba}_{0.6})_2\text{CuO}_4\)
YB-103 \((\text{Y}_{0.4}\text{Ba}_{0.6})_2\text{CuO}_4\)
YB-105 \((\text{Y}_{0.3}\text{Ba}_{0.7})_2\text{CuO}_4\)
YB-104 \((\text{Y}_{0.2}\text{Ba}_{0.8})_2\text{CuO}_4\)

In addition to the above Y-Ba-Cu-O composition I further identified twenty other compositions involving various types of substitutions, including four compositions of Lu-Ba-Cu-O.

19. Further, on January 29, 1987, I identified further compositions for production and testing in accordance with Dr. Chu's direction to make compositions involving substitution variably for the La or Ba of a La-Ba-cu-O composition by other smaller radii atomic elements as shown in Exhibit G attached hereto which was made by me and is in my handwriting. The amounts of reagents required for the production of the Y-Ba-Cu-O compositions as shown in Exhibit G are shown in Exhibit H attached hereto, which is in my handwriting and made by me during January 29-30 1987. Among the Y-Ba-Cu-O compositions considered for production, one is specifically of the formula \(\text{Y}_{1.2}\text{Ba}_{0.8}\text{Cu}_4\text{O}_4\), which is YB-102 (page H65 of Exhibit H).

20. In accordance with my prior calculations as recorded in Exhibit H, I began to prepare compositions of Y-Ba-Cu-O, one of which, designated as YB-102, was of the formula \(\text{Y}_{1.2}\text{Ba}_{0.8}\text{Cu}_4\text{O}_4\), as described in Exhibit H. I prepared the Y-Ba-Cu-O compositions by weighing out the required amounts of \(\text{Y}_2\text{O}_3\), \(\text{BaCO}_3\) and \(\text{CuO}\) powder.
reagents, mixing the powdered reagents by grinding them in a mortar with a pestle until the powder mass was homogeneously mixed. Thereafter the homogeneous powdered mass was subjected to pressure in a die to convert it to pellet form, multiple pellets were made, and each pellet was sintered at 1000°C, the various pellets being sintered for different lengths of time.

21. Y-Ba-Cu-O compositions of nominal formula (Y₀.₄Ba₆₋₄₁₂CuO₄), which may also be written as Y₁₂Ba₅CuO₄, were prepared under various firing conditions and were tested for electrical resistance versus temperature (R/T) on February 1, 1987 (Exhibit I; which is a measurement of electrical resistance as a function of temperature). The results of this R/T testing are listed in my Stenographic Notebook (Exhibit J). One of two samples sintered for twenty minutes exhibited zero electrical resistance at 89°K (Tₙ) with a beginning onset temperature (T₁₇) at 94°K. The second sample exhibited zero electrical resistance of 90.1°K with an onset temperature of 94°K.

22. Beginning February 2 and continuing through February 3, 1987 Samples of Y₁₂Ba₅CuO₄ were subjected to various pressures (3 klb, 6 klb, 9 klb, 12 klb, 15 klbs and 2 klb) and tested for electrical resistance versus temperature (Exhibit K).

23. The Y₁₂Ba₅CuO₄ samples described in paragraph 21 were subjected to powder x-ray diffraction analysis on February 2 and 4, 1987. From the x-ray diffraction analysis it was determined that neither of the multiple phases comprising the sample had a crystalline structure like that of K₂NiF₄. The x-ray spectrum is
Exhibit L.

24. On February 5, 1987 the $Y_{1.2}\text{Ba}_2\text{CuO}_4$ samples described in paragraph 21 were tested for diamagnetism at temperatures from 140K to 4.2K and were found at 4.2K to exhibit at least about 24% of the diamagnetic signal of a lead sample of similar dimensions as shown by Exhibit M.

25. The $Y_{1.2}\text{Ba}_2\text{CuO}_4$ samples described in paragraph 21 were tested on February 6, 1987 for resistivity over a temperature range of about 100K to 30K while subject to various magnetic field strengths and the zero resistivity state at a magnetic field strength of 5.7T was found to remain as high as 40°K, as shown in Exhibit N.

26. From the data acquired on the $Y_{1.2}\text{Ba}_2\text{CuO}_4$ samples as described in paragraphs 21-26 above, the upper critical field $H_{c2}(T)$ was determined on February 6, 1987.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the Chu Application or any patent issued thereon.

EXECUTED this 22nd day of __________, 1993.

Ruling Meng
1 bar = 757.06 Torr (mm)
0.2 \times 10^{-4} \text{ bar} = 0.0015 \text{ Torr} = 1.5 \text{ mTorr}
0.2 \times 10^{-4} \text{ bar} = 0.2 \times 10^{-4} \times 760 \text{ mmHg} = 152 \times 10^{-4} \times 10^{-3} = 15 \text{ mmHg}

\[ \text{Ba}_2 \text{La}_2 \text{Cu}_3 \text{O}_5 + \text{O}_2 \]
\[ \text{Ba}_2 \text{La}_2 \text{Cu}_3 \text{O}_5 \]
\[ \text{BaO} + \text{CuO} + \text{La}_2 \text{O}_3 \rightarrow 4 \text{ hms} \rightarrow 8 \text{ hms} \]
\[ \text{15 hms} \rightarrow \text{15 hms} \rightarrow 26 \text{ hms} \]
\[ \text{15 hms} \]

\[ \text{Ba}_2 \text{La}_2 \text{Cu}_3 \text{O}_5 \]
\[ \text{Ba}_2 \text{La}_2 \text{Cu}_3 \text{O}_5 + \text{O}_2 \rightarrow 4 \text{ hms} \rightarrow 8 \text{ hms} \]
\[ \text{15 hms} \rightarrow \text{15 hms} \rightarrow 26 \text{ hms} \]

\[ \text{(III), (La Ba)} \rightarrow \text{CuO} \]
\[ \text{Ba}_2 \text{CO}_3 + \text{CuO} + \text{La}_2 \text{O}_3 \rightarrow 4 \text{ hms} \rightarrow 8 \text{ hms} \rightarrow 26 \text{ hms} \]
\[ \text{15 hms} \rightarrow \text{15 hms} \rightarrow 26 \text{ hms} \]

\[ \text{Ba}_2 \text{La}_2 \text{Cu}_3 \text{O}_5 \]
\[ \text{Ba}_2 \text{La}_2 \text{Cu}_3 \text{O}_5 + \text{O}_2 \rightarrow 4 \text{ hms} \rightarrow 8 \text{ hms} \rightarrow 26 \text{ hms} \]

\[ \text{Ba}_2 \text{La}_2 \text{Cu}_3 \text{O}_5 \]
\[ \text{Ba}_2 \text{La}_2 \text{Cu}_3 \text{O}_5 + \text{O}_2 \rightarrow 4 \text{ hms} \rightarrow 24 \text{ hms} \rightarrow 5 \text{ hms} \]
\[ \text{24 hms} \rightarrow 5 \text{ hms} \]

CHU EXHIBIT A
WU ET AL. V. CHU
INTERFERENCE NO. 102,447
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Sample No. 5

BaCx (3-y) Dye

Sample No. 6

BaCx (3-y) Dye

Sample No. 7

BaCx (3-y) Dye

Binder Material

Papers Glue

Notes

485
1. **Core melting point:** C. 1326 °C
   **Carb.**<br>**C.C.**
   **Ex.Rb. Bu**

2. **Weight:** 1:8
   12 kg/km cuwhel<br>The height of the melt was about 4 cm
   heat 1350 °C at a rate of 40 °C/h.<br>soak at 10 h.<br>cool to 1080 °C 1/4
   below 1080 °C the furnace was cooled naturally to room temperature.

3. 30K8 CPTS.
   pt+pt+KCl+materials.
   KClO (5/6K2O)

2. **BPB**

   20-30 °C/h, 1000 (17-20F) 2-3 °C/h

3. 1000 °C lower. H2O = 2500-3000 C only up 1050 °C
Molten Salt (Flux) Growth 

1. Flux: KCl
2. Material: BaLa₄(C₂O₄)₂ (KCl)

Growth proceed:

3. \( \text{BaLa}_4\text{C}_2\text{O}_4 + \text{KCl} \rightarrow \text{700°C at tail of 10} \)
4. Soak at 700°C for 12 h
5. Cool at a rate of 2°C/h from 700-600°C
6. Below 600°C, the furnace was cooled naturally to room temperature.

4 Dec. 1986

\( \text{La}_2\text{O}_3 + 2\text{BaCO}_3 + \text{C}_2\text{O}_4 \rightarrow (\text{BaLa})_2\text{CO}_4 \)

7. \( 1 \) \( \text{La}_2\text{O}_3 + 2 \text{BaCO}_3 + \text{C}_2\text{O}_4 \rightarrow \text{Ba}_2 \text{La}_2 \text{CO}_4 \) (eq. 9)

8. \( \text{Ba}_2 \text{La}_2 \text{CO}_4 + 2 \text{CO}_2 \rightarrow (\text{BaLa})_2 \text{CO}_4 \) (eq. 10)

9. \( \text{La}_2\text{O}_3 + 2 \text{BaCO}_3 + 2 \text{C}_2\text{O}_4 \rightarrow (\text{BaLa})_2 \text{CO}_4 \) (eq. 11)

\( \text{O}_2 \) \( \text{CO} \) \( \text{N}_2 \) 489
2 Dec 1986

3:00 pm  Ba La 6 eu 5 Cr (3-1)

1)  25°C - 700  30 h  (4 oc. 9 pm)

2)  900 - 900  12 h  (1 oc. 9 pm)

3)  900 - 750  75 h  8 oc. 11 am

4)  750 - 650  75 h  11 oc. 11 am

5)  650 - 640  5 h

√ Stop  2 Dec  4 pm  after 4:00 pm have water to soak.

Single crystal

10 Dec 1986

1)  25°C - 1000°C  30 h  32.5 h

2)  1000 - 1000°C  24 - 36 h

3)  1000 - 750°C  12.5 h

4)  750 - 54°C  5 h

193.5°C / 24 = 8 day

491
Dec 8 / 35 pm
big pt crystal: \((La_{0.85}Ba_{0.15})_2\) early
small pt: \((La_{0.9}Ba_{0.1})_2\) near 0
1000 1200 → 1000°C keep keep 24 h

Dec 9
Ba: 1.5 1.5 Cu: 0.5 (3-1)
0) 700°C (9 h) 6-8 hours powder
1) 700°C (9 h) 6-8 hours powder
2) 1000°C 24 hours powder, 15 μm 0.3 3/16 3/32

Dec 9 1983
J-7: \((La_{0.85}Ba_{0.15})_2\) early
1000 apks in air
J-7 400 anode in 200°C 0.1 8 hrs

J-8: \((La_{0.9}Ba_{0.1})_2\) early
1000 24 hrs in air
J-8 400 anode in 200°C 0.1 8 hrs
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RLM1270
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Note: Sample after explosion in air. Two-hour bottle becomes into powder after two hours in air.
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**Remarks:**

- H 498
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\[ J = 2 \quad (La_{0.4}Ba_{0.6})_2CuO_4 \]

\[ \text{La}_2\text{O}_3 \quad 6.00 \quad \text{La} = 5.116.2 \]

\[ \text{Ba}_2 \quad 5.116.2 \quad 4.115 \quad x = 2.71.9 \quad x = 3372.13 \]

\[ \text{Ba}_2\text{CuO}_3 \quad 3372.35 \quad 6.951 \quad x = 1.00 \quad x = 4.846 \]

\[ \text{Cu} \quad 5.116.3 \quad 4.1135 \quad x = 15.72 \quad x = 1949.73 \]

\[ \text{Cu} \quad 1949.73 \quad 79.68 \quad x = 1.00 \quad x = 2.440.8 \]

\[ J = 1 \quad (La_{0.6}Ba_{0.4})_2CuO_4 \]

\[ \text{La}_2\text{O}_3 \quad 2.00 \quad x = 26.27 \quad x = 170.54 \]

\[ \text{Ba} \quad 170.54 \quad 27.54 \quad x = 14.85 \quad x = 2529.6 \]

\[ \text{Ba}_2\text{O}_3 \quad 2529.6 \quad 6.71.9 \quad x = 1.00 \quad x = 263.5 \]

\[ \text{Cu} \quad 170.54 \quad 27.54 \quad x = 15.75 \quad x = 268.6 \]

\[ \text{Cu} \quad 268.6 \quad 79.68 \quad x = 1.00 \quad x = 236.254 \]
16 Nov 1986

\[ \text{La}_2\text{O}_3 \] 3800 mg \times 84.27 = 2538.1 mg \text{ La (x2)}

\[ \text{Ba}_2 \times 2538.1 \times 4.92 = x = 12.57 \quad x = 632.07 \text{ mg} \]

\[ \text{BaCl}_2 \]

\[ 632.07 \times 6.959 = x = 100 \]

\[ x = 708.27 \] (BaCl\(_2\) (x2))

\[ \text{cm} : 2538.1 \times 54.92 = x = 15.70 \quad x = 731.29 \]

\[ \text{cm} \]

\[ 731.29 \times 7.88 = x = 100 \quad x = 163.1 \times 2 \]

\[ x = 186.95 \text{ mg} \]

\[ x = 4.9 \times \text{La}_2\text{O}_3 \times \text{BaCl}_2 \]

\[ \text{La}_2\text{O}_3 \] 5000 mg

\[ \text{La} \times 5000 \times 84.27 = 4263.5 \]

\[ \text{Ba} \times 5263.5 \times 58.32 = x = 101.5 \]

\[ x = 744.1 \times 2.1 \]

\[ \text{BaCl}_2 \]

\[ 744.1 \times 6.959 = x = 100 \]

\[ x = 164.2 \]

\[ \text{BaCl}_2 \] 44.65 \times 6.959

\[ \text{cm} : 2538.1 \times 58.32 = x \times 100 \]

\[ x = 1147.0 \text{ mg} \]

\[ \text{cm} \]

\[ 1147.0 \times 7.88 = x = 100 \]

\[ x = 859.44 \text{ mg} \]

\[ x = 8.59.44 \text{ mg} \]
\( J-4, \text{ large pt} \)

\( J-3, \text{ small pt} \)

\( J-6 \rightarrow \underline{\text{pt.}} \)

\( J-2 \rightarrow \underline{\text{long tan}} \)

\( [La_{0.9} Ba_{0.1}]_2 \text{ CuO}_4 \)

\( \text{La}_2\text{O}_3: 6080 \quad \text{La}: 5116.20 \quad 2000 \text{mg} \)

\( \text{Ba}: 5116.20 \quad 61.73 = X: 679 \)

\( \text{Ba}: 561.92 \)

\( \text{Ba}_2\text{O}_3: 561.92 \quad 69.59 = X: 100 \)

\( X = 807.47 \quad 403.73 \text{mg} \)

\( \text{Cu}: 5116.20 \quad 61.73 = X: 15.63 \)

\( \text{Cu}: 1300.59 \)

\( \text{Cu}_2\text{O}: 1300.59 \quad 79.88 = X: 100 \)

\( X = 813.79 \text{mg} \)

\( [La_{0.9} Ba_{0.1}]_2 \text{ CuO}_4 \)

\( \text{La}_2\text{O}_3: 6080 \times 85.27 = 4262.5 \)

\( \text{Ba}: 18243.5 \quad 48.07 = X: 20.38 \quad X = 1806.82 \)

\( \text{Cu}_2\text{O}: 1806.82 \quad 67.59 = X: 100 \quad X = 2574.31 \)

\( X = 1372.80 \)

\( \text{Cu}: 1392.80 \quad 79.88 = X: 100 \quad X = 1773.62 \)

\( 0 \alpha = 11 \)

\( 11 \)
| J = 4.2 | \( C_{11} \) \( C_{12} \) \( C_{13} \) \( C_{14} \) \( C_{15} \) \( C_{16} \) | \( T_{1} \) | \( T_{2} \) \( T_{3} \) \( T_{4} \) \( T_{5} \) \( T_{6} \) \( T_{7} \) | \( M \) | \( \Delta \) |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| J = 5 | \( C_{11} \) \( C_{12} \) \( C_{13} \) \( C_{14} \) \( C_{15} \) \( C_{16} \) | \( T_{1} \) | \( T_{2} \) \( T_{3} \) \( T_{4} \) \( T_{5} \) \( T_{6} \) \( T_{7} \) | \( M \) | \( \Delta \) |

CHU EXHIBIT D
WU ET AL V. CHU
INTERFERENCE NO. 102,447
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<td></td>
<td></td>
</tr>
<tr>
<td>SL-27</td>
<td>(La, Sc, Y, Sm, Yb, Eu, Gd, Tb, Dy, Ho, Er, Tm, Y)</td>
<td>900</td>
<td>60</td>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-28</td>
<td>(La, Sc, Y, Sm, Yb, Eu, Gd, Tb, Dy, Ho, Er, Tm, Y)</td>
<td>900</td>
<td>60</td>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-29</td>
<td>(La, Sc, Y, Sm, Yb, Eu, Gd, Tb, Dy, Ho, Er, Tm, Y)</td>
<td>900</td>
<td>60</td>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
YS-2
\((Y_{0.95} \text{ Sr}_{0.15})_2 \text{ an} \text{ O}_4\)

YS-1
\(Y_{0.95} \text{ Sr}_{0.05} \text{ an} \text{ O}_4\)

SY-3
\((Y_{0.6} \text{ Ba}_{0.4})_2 \text{ an} \text{ O}_4\)

SB-2
\((Y_{0.85} \text{ Ba}_{0.15})_2 \text{ an} \text{ O}_4\)

SB-3
\((Y_{0.97} \text{ Ba}_{0.03})_2 \text{ an} \text{ O}_4\)

\((I) (Y_{0.95} \text{ Sr}_{0.15})_2 \text{ an} \text{ O}_4\)

\begin{array}{|c|c|c|c|}
\hline
& Y & Sr & O \\
\hline
\text{YS-2} & 47.28 & 12.88 & 19.97 & 0.20 \\
\hline
\end{array}

Y_{0.95} \text{ Sr}_{0.15}

\text{Sr CO}_3 : 361.59

\text{Ln O} : 414.52

\((II) Y_{0.95} \text{ Sr}_{0.05} \text{ an} \text{ O}_4\)

YS-3

CHU EXHIBIT F
WU ET AL V. CHU
INTERFERENCE NO. 102,447
[La₀.₉₇ (Y₀.₃₈ Ba₀.₆₂)₂₂] en 0₄

La₀.₉₇ (Y₀.₃₈ Ba₀.₆₂)₂₂ en 0₄

1) [La₀.₉₇ (Y₀.₃₈ Ba₀.₆₂)₂₂] en 0₄
2) [La₀.₉₅ (Y₀.₁₅₃ Ba₀.₈₄₅)₀₅] en 0₄

La₂O₃: 1000 mg
Y₂O₃: 11.937 mg
BaCO₃: 113.782 mg
CuO: 24.46 mg

CHU EXHIBIT H
WU ET AL. V. CHU
INTERFERENCE NO. 102,447
<table>
<thead>
<tr>
<th></th>
<th>La</th>
<th>Y</th>
<th>Ba</th>
<th>Cu</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>LYB-5</td>
<td>62.117</td>
<td>1.149</td>
<td>5.050</td>
<td>15.785</td>
<td>15.900</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>2000 mg</td>
<td>1000 mg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>40.062 mg</td>
<td>20.031 mg</td>
<td></td>
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</tr>
<tr>
<td>BaCO₃</td>
<td>197.199 mg</td>
<td>99.600 mg</td>
<td></td>
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</tr>
<tr>
<td>CuO</td>
<td>542.515 mg</td>
<td>271.258 mg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LYB-3</td>
<td>62.294</td>
<td>1.675</td>
<td>4.257</td>
<td>15.830</td>
<td>15.945</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>1000 mg</td>
<td>2000 mg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>29.118 mg</td>
<td>158.236 mg</td>
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</tr>
<tr>
<td>BaCO₃</td>
<td>237.721 mg</td>
<td>167.440 mg</td>
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</tr>
<tr>
<td>CuO</td>
<td>271.258 mg</td>
<td>542.516 mg</td>
<td></td>
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</tr>
<tr>
<td>LYB-4</td>
<td>66.664</td>
<td>0.707</td>
<td>5.957</td>
<td>16.307</td>
<td>16.435</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>2000 mg</td>
<td>1000 mg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>25.216 mg</td>
<td>14.133 mg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaCO₃</td>
<td>346.843 mg</td>
<td>120.434 mg</td>
<td></td>
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</tr>
<tr>
<td>CuO</td>
<td>157.443 mg</td>
<td>287.224 mg</td>
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<td></td>
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</tbody>
</table>

RLM1283
<p>| | | | | |</p>
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</thead>
<tbody>
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</tbody>
</table>
| LLY-5 | [La_{0.95} (Y_{0.15} Ba_{0.845})_{0.05}]_2 Cu O
| La | Y | Ba | Cu | O |
| 65.256 | 0.341 | 2.869 | 15.710 | 15.824 |
| La_{2}O_{3} | 1000 mg | 2000 mg |
| Y_{2}O_{3} | 5.657 mg | 11.314 mg |
| BaCO_{3} | 53.893 mg | 107.725 mg |
| CuO | 256.983 mg | 513.965 mg |

| LLY-6 | [La_{0.9} (Lu_{0.1} Ba_{0.845})_{0.05}]_2 Cu O
| La | Lu | Ba | Cu | O |
| 61.566 | 1.284 | 5.755 | 15.644 | 15.757 |
| La_{2}O_{3} | 2000 mg | 1000 mg |
| Lu_{2}O_{3} | 40.448 mg | 20.224 mg |
| BaCO_{3} | 229.062 mg | 114.531 mg |
| CuO | 582.534 mg | 271.217 mg |

| LLY-3 | [La_{0.95} (Lu_{0.05} Ba_{0.85})_{0.05}]_2 Cu O
| La | Lu | Ba | Cu | O |
| 65.045 | 0.643 | 6.880 | 15.657 | 15.772 |
| La_{2}O_{3} | 2000 mg |
| Lu_{2}O_{3} | 19.171 mg |
| BaCO_{3} | 108.489 mg |
| CuO | 513.717 mg |
|            | 3$\text{La}_{0.95}$ $\text{Y}_{0.05}$ $\text{CuO}_4$
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>65.92</td>
</tr>
<tr>
<td>Y</td>
<td>2.22</td>
</tr>
<tr>
<td>Cu</td>
<td>15.87</td>
</tr>
<tr>
<td>O</td>
<td>15.90</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>1000 mg</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>36.48 mg</td>
</tr>
<tr>
<td>CuO</td>
<td>256.98 mg</td>
</tr>
</tbody>
</table>

|            | 4$\text{La}_{0.99}$ $\text{Ba}_{0.01}$ $\text{CuO}_4$
<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>67.85</td>
</tr>
<tr>
<td>Ba</td>
<td>0.67</td>
</tr>
<tr>
<td>Cu</td>
<td>15.87</td>
</tr>
<tr>
<td>O</td>
<td>15.79</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>1000 mg</td>
</tr>
<tr>
<td>Ba$_2$CO$_3$</td>
<td>24.44 mg</td>
</tr>
<tr>
<td>CuO</td>
<td>246.60 mg</td>
</tr>
</tbody>
</table>

Sinter 7 hours, 1100 °C
Lu₂Ba₂Ca₄O₁₂ \quad (Lu₆Ba₁₄)₂Ca₄O₁₂

<table>
<thead>
<tr>
<th>Lu</th>
<th>Ba</th>
<th>Ca</th>
<th>O</th>
</tr>
</thead>
</table>

Lu₂O₃: 1000 mg \quad 300 mg
BaCO₃: 661.202 mg \quad 198.361 mg
CuO: 333.141 mg \quad 97.942 mg

Lu₆Ba₆Ca₄O₁₄ \quad (Lu₃Ba₁₂)₂Ca₄O₄

<table>
<thead>
<tr>
<th>Lu</th>
<th>Ba</th>
<th>Ca</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.378</td>
<td>38.121</td>
<td>14.697</td>
<td>14.804</td>
</tr>
</tbody>
</table>

Lu₂O₃: 1000 mg \quad 300 mg
BaCO₃: 1487.670 mg \quad 443.601 mg
CuO: 499.684 mg \quad 149.905 mg

Lu₂Ba₈Ca₄O₁₄

<table>
<thead>
<tr>
<th>Lu</th>
<th>Ba</th>
<th>Ca</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.713</td>
<td>52.662</td>
<td>15.227</td>
<td>15.338</td>
</tr>
</tbody>
</table>

Lu₂O₃: 300 mg
BaCO₃: 1190.146 mg
CuO: 279.807 mg

YB₂O₃ \quad (Y₂Ba₈)₂O₁₄

<table>
<thead>
<tr>
<th>Y</th>
<th>Ba</th>
<th>Cu</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>43.806</td>
<td>16.918</td>
<td>19.567</td>
<td>19.709</td>
</tr>
</tbody>
</table>

Y₂O₃: 300 mg \quad 100
BaCO₃: 13687 mg \quad 43.678
CuO: 132.008 mg \quad 44.529
YB-102: \((Y_{0.6}Ba_{0.4})_2CuO_4\)

- \(Y\) 39.05
- \(Ba\) 31.92
- \(Cu\) 18.46
- \(O\) 8.59

- \(Y_2O_3\): 300 mg
- \(BaCO_3\): 349.55 mg
- \(CuO\): 176.12 mg

\[BaO = 98.88 \quad (BaO = 243.56 mg)\]

YB-1

YB-103: \((Y_{0.4}Ba_{0.6})_2CuO_4\)

- \(Y\) 45.34
- \(Ba\) 45.34
- \(Cu\) 17.48
- \(O\) 17.60

- \(Y_2O_3\): 300.00 mg
- \(BaCO_3\): 786.5 mg
- \(CuO\): 264.76 mg

\[BaO_3 = 194.19\]

YB-104: \((Y_{0.2}Ba_{0.8})_2CuO_4\)

- \(Y\) 57.31
- \(Ba\) 57.31
- \(Cu\) 16.57
- \(O\) 16.77

- \(Y_2O_3\): 300.00 mg
- \(BaCO_3\): 209.34 mg
- \(CuO\): 128.365 mg

YP-101: \((Y_{0.8}Pb_{0.2})_2CuO_4\)

- \(Y\) 40.33
- \(Pb\) 25.50
- \(Cu\) 18.01
- \(O\) 18.18

- \(Y_2O_3\): 300.00 mg
- \(PbO\): 168.888 mg
- \(CuO\): 132.091 mg

**II. 56**
$\text{Yb}_{1.2}\text{Ba}_{0.8}\text{CuO}_4$

\[
\begin{array}{cccc}
\text{Yb} & \text{Ba} & \text{Cu} & \text{O} \\
1.2 & 0.8 & 1 & 4
\end{array}
\]

$\text{YbB} - 102 \rightarrow \text{Yb}_{1.2}\text{Ba}_{0.8}\text{CuO}_4$

\[
\begin{array}{cccc}
\text{Yb} & \text{Ba} & \text{Cu} & \text{O} \\
46.656 & 24.687 & 18.377 & 14.380
\end{array}
\]

$\text{Yb}_2\text{O}_3 \text{ : } 300 \text{ mg}$

$\text{BaCO}_3 \text{ : } 243.88 \text{ mg}$

$\text{CuO} \text{ : } 117.417 \text{ mg}$

$\text{YbB} - 101 \rightarrow \text{Yb}_{1.1}\text{Ba}_{0.9}\text{CuO}_4$

\[
\begin{array}{cccc}
\text{Yb} & \text{Ba} & \text{Cu} & \text{O} \\
43.114 & 27.997 & 14.392 & 14.496
\end{array}
\]

$\text{Yb}_2\text{O}_3 \text{ : } 300 \text{ mg}$

$\text{BaCO}_3 \text{ : } 245.82 \text{ mg}$

$\text{CuO} \text{ : } 110.093 \text{ mg}$

\text{BA} \text{ : } 71.1
LuB - 101 \((\text{Lu}_0.8 \ \text{Ba}_{0.2})_2 \ \text{Cu}_0.4\)

- \(\text{Lu}\) 60.540
- \(\text{Ba}\) 11.880
- \(\text{Cu}\) 13.741
- \(\text{O}\) 13.840

- \(\text{Lu}_2\text{O}_3\): 1000 mg
- \(\text{Ba}_2\text{O}_3\): 247.957 mg
- \(\text{Cu}_2\text{O}\): 24.870 mg

\(\text{Yb}-102\) \((\text{Y}_{0.6} \ \text{Pb}_{0.4})_2 \ \text{Cu}_0.4\)

- \(\text{Y}\) 26.673
- \(\text{Pb}\) 41.440
- \(\text{Cu}\) 15.886
- \(\text{O}\) 14.308

- \(\text{Y}_2\text{O}_3\): 300 mg
- \(\text{Pb}_2\text{O}_3\): 383.69 mg
- \(\text{Cu}_2\text{O}\): 176.123 mg

\(\text{Yb}-103\) \((\text{Y}_{0.4} \ \text{Pb}_{0.6})_2 \ \text{Cu}_0.4\)

- \(\text{Y}\) 15.901
- \(\text{Pb}\) 55.585
- \(\text{Cu}\) 14.205
- \(\text{O}\) 14.288

- \(\text{Y}_2\text{O}_3\): 300 mg
- \(\text{Pb}_2\text{O}_3\): 253.319 mg
- \(\text{Cu}_2\text{O}\): 264.174 mg

\(\text{Yb}-104\) \((\text{Y}_{0.2} \ \text{Pb}_{0.8})_2 \ \text{Cu}_0.4\)

- \(\text{Y}\) 7.190
- \(\text{Pb}\) 67.064
- \(\text{Cu}\) 12.847
- \(\text{O}\) 12.940

- \(\text{Y}_2\text{O}_3\): 300 mg
- \(\text{Pb}_2\text{O}_3\): 254.218 mg
- \(\text{Cu}_2\text{O}\): 528.780 mg

H = 59
LuP-101  
(\(Lu_{0.8} \ Pb_{0.2}\) \(\_2\) \(Cu\) \(O_4\))

\[
\begin{array}{cccc}
Lu & Pb & Cu & O \\
57.09 & 16.90 & 12.95 & 13.05 \\
\end{array}
\]

- \(Lu_2O_3\): 300 mg
- \(PbO_2\): 90.162 mg
- \(CuO\): 74.958 mg

LuP-102  
(\(Lu_{0.6} \ Pb_{0.4}\) \(\_2\) \(Cu\) \(O_4\))

\[
\begin{array}{cccc}
Lu & Pb & Cu & O \\
41.72 & 32.93 & 12.62 & 12.71 \\
\end{array}
\]

- \(Lu_2O_3\): 300 mg
- \(PbO_2\): 240.428 mg
- \(CuO\): 99.942 mg

LuP-103  
(\(Lu_{0.4} \ Pb_{0.6}\) \(\_2\) \(Cu\) \(O_4\))

\[
\begin{array}{cccc}
Lu & Pb & Cu & O \\
27.10 & 48.17 & 12.83 & 12.80 \\
\end{array}
\]

- \(Lu_2O_3\): 300 mg
- \(PbO_2\): 540.949 mg
- \(CuO\): 144.914 mg

LuP-104  
(\(Lu_{0.8} \ Pb_{0.2}\) \(\_2\) \(Cu\) \(O_4\))

\[
\begin{array}{cccc}
Lu & Pb & Cu & O \\
13.29 & 62.66 & 12.01 & 12.09 \\
\end{array}
\]

- \(Lu_2O_3\): 300 mg
- \(PbO_2\): 1442.603 mg

- \(CuO\): 299.840 mg

= 60
(I) YB 10.6

\((Y_{0.5}Ba_{0.5})_2\) un. 0.4

<table>
<thead>
<tr>
<th>(Y)</th>
<th>(Ba)</th>
<th>(Ca)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.19</td>
<td>38.821</td>
<td>17.959</td>
</tr>
</tbody>
</table>

\(\gamma\) CO

400 mg

\(BaCO_3\) 609.12 mg

\(en_{0}\) 281.786 mg

(II) YB 10.7

\((Y_{0.55}Ba_{0.45})_2\) un.0.4

<table>
<thead>
<tr>
<th>(Y)</th>
<th>(Ba)</th>
<th>(Ca)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.026</td>
<td>35.493</td>
<td>18.209</td>
</tr>
</tbody>
</table>

\(\gamma\) CO

300 mg

\(BaCO_3\) 428.974 mg

\(en_{0}\) 192.133

III YB 10.8

\((Y_{0.65}Ba_{0.35})_2\) un.0.4

\(\gamma\) CO

34.068 23.378 18.291 18.865

\(\gamma\) CO

300 mg

\(BaCO_3\) 222.54

\(en_{0}\) 162.17

IV YB 10.9 (YB - 10.5) \(Y_{0.7}Ba_{0.3}\) un.0.4

H - 61

\(\gamma\) CO

29.372 26.684 11.004

\(BaCO_3\) 254.19

\(en_{0}\) 150.97
Feb 1987

Y-B 102 (2-3) Sample

$T_0 - 74 \Rightarrow 89$

250 pounds

3/16

20'

cooling on Al plate 2" x 2.5"

\[ \text{Diagram:} \]

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\[ \text{Diagram:} \]
INTENSITY

CHU EXHIBIT L
WU ET AL V. CHU
INTERFERENCE NO. 102.447

RLM1303
AFFIDAVIT OF RULING MENG

THE STATE OF TEXAS

COUNTY OF HARRIS

On this the 6th, day of March, 2006, before me, a Notary Public in and for the State of Texas, personally appeared Ruling Meng, who, being duly sworn, upon oath deposes and says:

That I am of full legal age, have never been convicted of a felony or a crime involving moral turpitude and am in all respects competent to make this affidavit; that I reside in Houston, Harris County, Texas and that my business address: Superconductivity Center, Houston Science Center, Houston, Texas 77204.

- I am a material scientist. Before I came to the U.S. I was a research Scientist at The Chinese Academy science, Institute of Physics in Beijing, China.
- I started my research on superconducting materials since 1976.
- In 1979 I was invited by Dr.C.W. Paul Chu to join to his group as a visiting scholar in the Department of Physics at the University of Houston until 1981.
- Before I returned to China, in 1982, I was invited by Prof. Ernst Bucher at University of Konstanz, Germany and spent half year in their lab. My research projects were superconductor's single crystal growth. During this period I continued the collaboration with Dr. Chu. By sending him superconducting Single crystal for his studies.
- In mid 1982 I return to the Institute of physics in Beijing China and continued the collaboration on superconducting materials with Dr.C.W. Paul Chu
- In July of 1984 I was invited again by Dr. Chu and came back to the UH. and joined his group as a visiting scientist. My responsibility in this group was to research and study superconducting and related materials. I synthesized and characterized various compounds myself independently and supervise students on their materials studies.
- In 1986, Dr.C.W.Chu was on leave and served at the National Science Foundation in Washington D.C. He only came back Houston on
weekend to discuss research activity in the lab. At mid-November of 1986 I learned from my friend in China, Professor Z.X. Zhao about the paper “Possible High Tc Superconductivity in the Ba – La – Cu – O System,” by J.G. Bednorz and K.A. Muller. I asked a graduate student Li Gao to go to the library to copy the paper on a Friday afternoon. Then I put a copy of the paper on Dr. Chu’s desk. [Reference 1, on the paper with my hand writing note] On Saturday morning I came in and discussed the paper with him. The paper reported that they used the wet-chemical method and it also indicated that the solid-state reaction processing might be difficult to obtain the superconducting phase. I told Dr. Chu that I believed the solid-state reaction method could be used to synthesize this material. My expertise was not in wet-chemistry and I felt more confident with using the solid-state method.

- After this discussion, on the 14th of November I began to synthesize the first LaBaCuO compound with composition La_{4.25}Ba_{0.75}Cu_{3}O_{3}. And successfully repeated Dr. Bednorz and Muller’s results. [Reference 2]

- In late November we began to apply pressure to the La-Ba-Cu-O compounds. The transition temperature increased from 35 to 57 K and leveled off. We realized that simulating the pressure effect we would have to substitute a small size element for Ba. Therefore, we began to substitute Sr for Ba in early December. However Dr. Chu asked me to stop the Sr substitution experiment in our lab because he had asked M.K. Wu (Alabama) to do this. He said that M.K.Wu couldn’t compete with us. I therefore to replace Ba with Ca which has a smaller atoms size than Sr. at the same time, we learned that Bell lab has reported that LaCaCuO display a transition temperature which was lower than LaSrCuO. During this time Dr. Chu called back from Washington, D.C. every day to ask about the new results and set up the contact with outside corporations.

- On November 25th We observed a transition temperature around 70 K in a LaBaCuO sample made by Pei Hor. Unfortunately, the sample was not stable and we would not repeat the results. The results indicated that there were higher temperature superconductors existed.

- On December 30th Dr. M.K. Wu and his student brought his sample La-Sr-Cu-O to Houston for magnetic measurements. During his visit we had a discussion among Pei Hor, M.K. Wu, Li Gao and myself in Pei’s office on Jan 1st (or 2 rd ) 1987. Since the LaSrCuO indeed displayed a higher transition temperature at 40-45 K. while the Ca
substituted lower the transition temperature, we realized that we should substitute La by other elements. During the discussion Pei Hor suggested that we should replace La with Y (Yttrium). I suggested that we also replace La by Lu (Lutetium) because it has a smaller atomic radius.

- Two days later (around 3 or 4 of January) M.K. Wu returned to Alabama. Before his leaving our lab, I suggested him to go back to Alabama NASA’s lab to get $Y_2O_3$ and made the Y substitution compound. This could speed up the process, because we do not have $Y_2O_3$ and it if I placed the order the next day, it would take two weeks for us to get our order.

- From December 1986 to January 1987, I continued studying the La BaCuO compounds to optimize the composition and preparation condition. On January 11th we observed a transition temperature up to 90K at the LaBaCuO sample that I made with formulas (La$_{0.4}$Ba$_{0.6}$)$_2$CuO$_4$ (J2). [Reference 3] and X-ray data shown almost pure 123 structures. Unfortunately, I do not know the 123 phase yet and misidentify as 214 phase with impurity phase. Again the sample was not stable. [Reference 3,4].

- On January 13 we received our order of $Y_2O_3$ and Lu$_2O_3$ and then we began to work on substituting La with Y. But most of my effort still on LaBaCuO in order to repeat the 90 K result and I was under great pressure of providing outside groups with LaBaCuO samples.

- In 29th of January 1987 Dr. Chu received a phone call from M.K. Wu said that he got a sample with a transition temperature up to 90 K and Dr. Chu asked him to bring the sample to our lab. For magnetic measurement to confirm the results.

- The sample with 90K is YBaCuO was mix phase and was in green color.

- For future application and academic study, it is important to separate the mix phase and identify the phase which contribute to the high temperature superconducting. By 27th of Feb. I successfully separate black and green crystals from the mixed phase by studied a set of YBCO sample with difference composition [reference 5]. Pei Hor and students did the magnetic measurement and identified the green phase was non-superconducting with rich Y content. And the phase contributed to superconducting is Black color YBa$_{1.8}$Cu$_3$O. This sample was sent to Dr. H.k.Mao at Geophysical Laboratory in
Washington, D.C. for the crystal structure characterization and identifying the correct formula.

- In March 8th 1987, based on our green and black samples and the information we provided Dr. Robert M Hazen and H.K. Mao at Geophysical Laboratory at Washington identify the high temperature superconductor YBCO's formula is $\text{YBa}_2\text{Cu}_3\text{O}_6.7$ with tetragonal structure. (So call 123 phase).
- Within half months from Feb. 22th to March 15th. I had successful synthesized the entire substitute La by rare earth elements R$\text{Ba}_2\text{Cu}_3\text{O}_6$ (R= rare earth) except Presseodymium and Cerium.

- In 1987, I attended a meeting with Dr. Chu, Pei Hor and attorney Charles M. Cox. During the meeting Charles Cox asked who actually suggested to replace La by Y? Dr. Chu immediately Point to me and said Ruling, remember I call you and told you to replace La by Y. I was shocked and did not know what to told. Because I clearly remember it was Hor suggested to substitute La by Y. during the discussion and Dr. Chu was not in the discussion. I am his employee and do not want to make him mad and instead stated “I do not remember.”

- May be a couple of months later (I could not remember the exact date). Charles Cox called me and asked me again. that whether I remember Dr. Chu had called and directed me to replace La by Y. I did not answer and he said if you would not identify Dr. Chu told to you about his idea about the substitution of La by Y. Then the University of Houston would lose the patent to University of Alabama. I immediately said no this was our (UH) idea and they learned from us. Then Charles said then we need to identify Dr. Chu, he represents UH. I knew, if I say yes! I was lying. I asked Cox. whether I had to go to court? He said, “No, no, you would not go to the court” I knew this patent should be ours (UH). I would do every thing to help UH to earn the patent. Therefore, I said, “maybe Dr. Chu had called me and talk about the substitution. “

- One day, unexpectedly, Charles brought me the declaration writing by him or Chu and asked me to sign. All the detail and date was written and by Cox or Chu all I did was signing my signature. After that Dr. Chu thanked me for helping him in the critical time.

- In 1993, I was asking to make a deposition for U.H against the Uni. Of Alabama. I do not have any choice but continued to lie by
testifying Dr. Chu had called and told me about the substitution of La with Y. I feel very uncomfortable about this. But I think I did it for UH. Beside this all of my other statements in the deposition are truth. Indeed, in the pasts between 1986 to 1990 I made numerous high temperature Superconducting materials, helped to collect data and thou provided evidence for the patent. I always thought the patent on high temperature superconductors was the joint effort of our group.

- I did make a lie about the discovery of YBCO. I was a law illiterate. In 1987 I came to U.S from China where we could only obeying to the head of group, and the leader of the party. Whatever they said was the law. I do not understand any thing about declaration or deposition. I thought I did for the University. In addition I was Dr. Chu’s employee and I trust him. and do not want to make him mad of me if not lying.

- However, no matter what was the reason, I should not have lied. The guilty feeling haunted me for about 20 years. Due to my health situation. I am planning to retire soon, I do not want to carry this guilty feeling to my retirement life. I want to have a peaceful mind. After a long mind struggling. Finally on Jan. 2006, I went to tell Pei Ho about how Cox asked me to testified Dr. Chu had called me and asked me to substitute La with Y. I apologized to him for what I have been wrong doing. I also told him that recently Dr. Chu mention our patent will be issued soon. Hor asked me, do you know we are also inventors? I said I think we should but I do not know, I never asked. Hor suggested me to find out. I went to asked John P. Warren the Associate Vice Chancellor for intellectual property management about the inventorship for the YBCO patent, and found out that Dr. Chu is a solo inventor for U.H. YBCO patent. We were shocked, disappointed and angry. We decided to talk to Mr. Warren and let him know that we are fully justified as this patent’s inventors. We required and deserved fair treatment.

Dr. Chu came back from Hong Kong the next week. He want to talk to me about this matters. I was sick and do not want to talk to him. On Feb. 9th Dr. Jacobson (the director for Texas Center for Superconductivity at the University of Houston) talked to me about this issue and he said that Dr. Chu said Pei and I are not the same case and should be treated differently. Dr. Chu is willing and prepared to compensate me as recognition for my contribution to the high temperature superconductor invention.
FURTHER, AFFIANT SAYETH NAUGHT.

Ruling Meng

SUBSCRIBED AND SWORN TO BEFORE ME this 6th day of March

Notary Public

D. Andra Blake

[Notary stamp]

DEANDRA LAINE BLACK
NOTARY PUBLIC, STATE OF TEXAS
MY COMMISSION EXPIRES
SEPT. 15, 2009
Possible High $T_c$ Superconductivity in the Ba–La–Cu–O System

J.G. Bednorz and K.A. Müller
IBM Zürich Research Laboratory, Rüschlikon, Switzerland

Received April 17, 1986

Metallic, oxygen-deficient compounds in the Ba–La–Cu–O system, with the composition $\text{Ba}_x\text{La}_{3-x}\text{Cu}_y\text{O}_{4+y}$, have been prepared in polycrystalline form. Samples with $x=1$ and $0.75$, $y>0$, annealed below 900 °C under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally an abrupt decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 30 K range. It is markedly reduced by high current densities. Thus, it results partially from the percolative nature, but possibly also from 2D superconducting fluctuations of double perovskite layers of one of the phases present.

I. Introduction

"At the extreme forefront of research in superconductivity is the empirical search for new materials" [1]. Transition-metal alloy compounds of $A15$ (Nb,Sn) and $B1$ (NbN) structure have so far shown the highest superconducting transition temperatures. Among many $A15$ compounds, careful optimization of Nb–Ge thin films near the stoichiometric composition of Nb$_3$Ge by Gavalev et al. and Testardi et al. a decade ago allowed them to reach the highest $T_c=23.3$ K reported until now [2, 3]. The heavy Fermion systems with low Fermi energy, newly discovered, are not expected to reach very high $T_c$'s [4].

Only a small number of oxides is known to exhibit superconductivity. High-temperature superconductivity in the Li–Ti–O system with onsets as high as 13.7 K was reported by Johnston et al. [5]. Their x-ray analysis revealed the presence of three different crystallographic phases, one of them, with a spinel structure, showing the high $T_c$ [5]. Other oxides like perovskites exhibit superconductivity despite their small carrier concentrations, $n$. In Nb-doped SrTiO$_3$, with $n=2 \times 10^{20}$ cm$^{-3}$, the plasma edge is below the highest optical phonon, which is therefore unshielded [6]. This large electron-phonon coupling allows a $T_c$ of 0.7 K [7] with Cooper pairing. The occurrence of high electron-phonon coupling in another metallic oxide, also a perovskite, became evident with the discovery of superconductivity in the mixed-valent compound BaPb$_{1-x}$Bi$_x$O$_3$ by Sleight et al., also a decade ago [8]. The highest $T_c$ in homogeneous oxygen-deficient mixed crystals is 13 K with a comparatively low concentration of carries $n=2-4 \times 10^{21}$ cm$^{-3}$ [9]. Flat electronic bands and a strong breathing mode with a phonon feature near 100 cm$^{-1}$, whose intensity is proportional to $T_c$, exist [10]. This last example indicates that within the BCS mechanism, one may find still higher $T_c$'s in perovskite-type or related metallic oxides, if the electron-phonon interactions and the carrier densities at the Fermi level can be enhanced further.

Strong electron-phonon interactions in oxides can occur owing to polaron formation as well as in mixed-valent systems. A superconductivity (metallic) to bipolaronic (insulator) transition phase diagram was proposed theoretically by Chakraverty [11]. A mechanism for polaron formation is the Jahn-Teller effect, as studied by Höck et al. [12]. Isolated Fe$^{4+}$, Ni$^{3+}$ and Cu$^{2+}$ in octahedral oxygen environment...
show strong Jahn-Teller (J.T.) effects [13]. While SrFe(VI)O₄ is distorted perovskite insulator, LaNi(III)O₃ is a J.T. undistorted metal in which the transfer energy Δₓ of the J.T. eₓ electrons is sufficiently large [14] to quench the J.T. distortion. In analogy to Chakraverty's phase diagram, a J.T.-type polaron formation may therefore be expected at the borderline of the metal-insulator transition in mixed perovskites, a subject on which we have recently carried out a series of investigations [15]. Here, we report on the synthesis and electrical measurements of compounds within the Ba–La–Cu–O system. This system exhibits a number of oxygen-deficient phases with mixed-valent copper constituents [16], i.e., with itinerant electronic states between the non-J.T. Cu₃⁺ and the J.T. Cu²⁺ ions, and thus was expected to have considerable electron-phonon coupling and metallic conductivity.

II. Experimental

1. Sample Preparation and Characterization

Samples were prepared by a coprecipitation method from aqueous solutions [17] of Ba-, La- and Cu-nitrate (SPECTPURE JMC) in their appropriate ratios. When added to an aqueous solution of oxalic acid as the precipitant, an intimate mixture of the corresponding oxalates was formed. The decomposition of the precipitate and the solid-state reaction were performed by heating at 900 °C for 5 h. The product was pressed into pellets at 4 kbar, and reheated to 900 °C for sintering.

2. X-Ray Analysis

X-ray powder diffractograms (System D 500 SIE-MENS) revealed three individual crystallographic phases. Within a range of 10° to 80° (2θ), 17 lines could be identified to correspond to a layer-type perovskite-like phase, related to the K₂NiF₄ structure (a = 3.79 Å and c = 13.21 Å) [16]. The second phase is most probably a cubic one, whose presence depends on the Ba concentration, as the line intensity decreases for smaller x(Ba). The amount of the third phase (volume fraction > 30% from the x-ray intensities) seems to be independent of the starting composition, and shows thermal stability up to 1,000 °C. For higher temperatures, this phase disappears progressively, giving rise to the formation of an oxygen-deficient perovskite (LaₓBa₃₋ₓCuₓO₄₋ₙ) as described by Michel and Raveau [16].

![Graph](image)

Fig. 1. Temperature dependence of resistivity in BaₓLaₓ₋₉CuₓO₄₋ₙ for samples with x(Ba) = 1 (upper curves, left scale) and x(Ba) = 0.75 (lower curve, right scale). The first two cases also show the influence of current density.

3. Conductivity Measurements

The dc conductivity was measured by the four-point method. Rectangular-shaped samples, cut from the sintered pellets, were provided with gold electrodes and contacted by In wires. Our measurements between 300 and 4.2 K were performed in a continuous-flow cryostat (Leybold-Hereaus) incorporated in a computer-controlled (IBM-PC) fully-automatic system for temperature variation, data acquisition and processing.

For samples with x(Ba) ≤ 1.0, the conductivity measurements, involving typical current densities of 0.5 A/cm², generally exhibit a high-temperature metallic behaviour with an increase in resistivity at low temperatures (Fig. 1). At still lower temperatures, a sharp drop in resistivity (> 90%) occurs, which for higher currents becomes partially suppressed (Fig. 1: upper curves, left scale). This characteristic drop has been studied as a function of annealing conditions, i.e., temperature and O₂ partial pressure (Fig. 2). For samples annealed in air, the transition from itinerant to localized behaviour, as indicated by the minimum in resistivity in the 80 K range, is not very pronounced. Annealing in a slightly reducing atmosphere, however, leads to an increase in resistivity and a more pronounced localization effect. At the same time, the onset of the resistivity drop is shifted.
towards the 30 K region. Curves 4 and 5, recorded for samples treated at 900 °C, show the occurrence of a shoulder at still lower temperature, more pronounced in curve 4. At annealing temperatures of 1,040 °C, the highly conducting phase has almost vanished. As mentioned in the Introduction, the mixed-valent state of copper is of importance for electron-phonon coupling. Therefore, the concentration of electrons was varied by the Ba/La ratio. A typical curve for a sample with a lower Ba concentration of 0.75 is shown in Fig. 1 (right scale). Its resistivity decreases by at least three orders of magnitude, giving evidence for the bulk being superconducting below 13 K with an onset around 35 K, as shown in Fig. 3, on an expanded temperature scale. The latter figure also shows the influence of the current density, typical for granular compounds.

III. Discussion

The resistivity behaviour of our samples, Fig. 1, is qualitatively very similar to the one reported in the Li–Ti–O system, and in superconducting BaPb_{1-x}Bi_{x}O_{3} polycrystalline thin films [5, 18]. Upon cooling from room temperature, the latter exhibit a nearly linear metallic decrease of \( \rho(T) \), then a logarithmic type of increase, before undergoing the transition to superconductivity. One could, of course, speculate that in our samples a metal-to-metal structural phase transition occurs in one of the phases. The shift in the drop in \( \rho(T) \) with increasing current density (Fig. 3), however, would be hard to explain with such an assumption, while it supports our interpretation that we observe the onset of superconductivity of percolative nature, as discussed below. In BaPb_{1-x}Bi_{x}O_{3}, the onset of superconductivity has been taken at the resistivity peak [18]. This assumption appears to be valid in percolative systems, i.e., in the thin films [18] consisting of polycrystals with grain boundaries, or when different crystalline phases with interpenetrating grains are present, as found in the Li–Ti–O [5] or in our Ba–La–Cu–O system. The onset can also be due to fluctuations in the superconducting wave functions. We assume one of the Ba–La–Cu–O phases exhibits this behaviour. Therefore, under the above premises, the peak in \( \rho(T) \) at 35 K, observed for an \( x(\text{Ba})=0.75 \) (Fig. 1), has
to be identified as the start to superconductive co-operative phenomena in the isolated grains. It should be noted that in granular Al, Cooper pairs in coupled grains have been shown to exist already at a point where $\rho(T)$ upon cooling has decreased by only 20% of its highest value. This has been proven qualitatively [19] and more recently also quantitatively [20] by the negative frequency shift occurring in a microwave cavity. In 100 Å films, a shoulder in the frequency shift owing to 2D fluctuations was observed above the $T_c$ of the grains. In our Ba-La-Cu-O system, a series of layer-like phases with considerable variety in compositions are known to exist [16, 21], and therefore 2D correlations can be present.

The granularity of our system can be justified from the structural information, and more quantitatively from the normal conductivity behaviour. From the former, we know that more than one phase is present and the question arises how large are the grains. This can be inferred from the logarithmic fingerprint in resistivity. Such logarithmic increases are usually associated with beginning of localization. A most recent example is the Anderson transition in granular Sn films [22]. Common for the granular Sn and our samples is also the resistivity at 300 K, lying in the range of 0.06 to 0.02 Ωcm, which is near the microscopic critical resistivity of $\rho_c = 10 L_0 h/e^2$ for localization. From the latter formula, an interatomic distance $L_0$ in the range of 100 Å is computed, thus a size of superconducting grains of this order of magnitude must be present. Upon cooling below $T_c$, Josephson junctions between the grains phase-lock progressively [23] and the bulk resistivity gradually drops to zero by three orders of magnitude, for sample 2 (Fig. 1). At larger current densities, the weaker Josephson junctions switch to normal resistivity, resulting in a temperature shift of the drop, as shown in Fig. 3. The plateau in resistivity occurring below the 80% drop (Fig. 1) for the higher current density of 0.5 A/cm², and Fig. 2 curve @) may be ascribed to switching of junctions to the normal state.

The way the samples have been prepared seems to be of crucial importance: Michel et al. [21] obtained a single-phase perovskite by mixing the oxides of La and Cu and BaCO₃ in an appropriate ratio and subsequent annealing at 1,000 °C in air. We also applied this annealing condition to one of our samples, obtained by the decomposition of the corresponding oxalates, and found no superconductivity. Thus, the preparation from the oxalates and annealing below 950 °C are necessary to obtain a non-perovskite-type phase with a limited temperature range of stability exhibiting this new behaviour. The formation of this phase at comparatively low temperatures is favoured by the intimate mixture of the compo-

ments and the high reactivity of the oxalates owing to the evolution of large amounts of H₂O and CO₂ during decomposition.

IV. Conclusion

In the concentration range investigated, compounds of the Ba-La-Cu-O system are metallic at high temperatures, and exhibit a tendency towards localization upon cooling. Samples annealed near 900 °C under reducing conditions show features associated with an onset of granular superconductivity near 30 K. The system consists of three phases, one of them having a metallic perovskite-type layer-like structure. The characterization of the new, apparently superconducting, phase is in progress. An identification of this phase may allow growing of single crystals for studying the Meissner effect, and collecting specific-heat data to prove the presence of high $T_c$ bulk superconductivity.

The authors would like to thank H.E. Weibel for his help in getting familiar with the conductivity measurement system, E. Courten and R. Thomas for discussions and a critical reading of the manuscript.

References

J.G. Bednorz and K.A. Müller: Ba – La – Cu – O System


J.G. Bednorz
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Switzerland

Note Added in Proof

Chemical analysis of the bulk composition of our samples revealed a deviation from the ideal La/Ba ratios of 4 and 5.66. The actual ratios are 16 and 18, respectively. This is in agreement with an identification of the third phase as CuO.
Superconductivity above 90 K

C. W. Chu

Department of Physics and Space Vacuum Center
Foundation, Washington, DC 20550

Superconductivity in the 30 K range was first observed in the mixed La-Ba-Cu-O (LaBCO) compound system, and the importance of the layered K3NiF4 phase was stressed. Independently, the Tokyo group (2) and our group (3) reproduced the observations in late November 1986. At the same time, we also reported (3) the observation of the resistance drop at 70 K, suggesting the possibility of...
La-Ba-Cu-O with 123-Structure is Already Obtained.


Reference 4.

1. Y₁ (Ba₁₄ Cu₁₁_x₁.₀₂₅)
2. Y₁ (Ba₁.₅ Cu₁₁_x₁.₀₂₅)
3. Y₁ (Ba₁₁.₆ Cu₁₁_x₁.₀₂₅)

40 H.
2.50
5.00
10.00
15.00

J, A
27 Feb. 1986

1. Index: 2:00 p.m.

2. Cu + sample.

3. Y + Ba + CuO.

\[ Ba = Cu \]

4. 0.01 ad 0.05 \( \Rightarrow \) Y0.09, Y0.05

Ga

Ce

Nd

Pr

Sm

Eu

Tb

Dy

Ho

Er

Tm

Yb

Lu

H 557
Green:

\[ Y_1 \left( \text{Ba} \times \text{Cu}_{1-x} \right) \left( \frac{1}{2} \text{O}_3 \right) \]

\[ x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0 \]

Black:

\[ Y_1 \text{Ba} \times \text{Cu}_x \text{O} \]

\[ x = 0.6 \]

\[ Y = x \times 1.425 \]

\[ 0.855 \]

\[ 0.938 \]

\[ 1.14 \]

\[ 1.28 \]

\[ 1.425 \]
AFFIDAVIT OF RULING MENG

THE STATE OF TEXAS
COUNTY OF HARRIS

On this the 25th day of May, 2006, before me, a Notary Public in and for the State of Texas, personally appeared Ruling Meng, who, being duly sworn, upon oath deposes and says:

That I am of full legal age, have never been convicted of a felony or a crime involving moral turpitude and am in all respects competent to make this affidavit; that I reside in Houston, Harris County, Texas and that my business address is Superconductivity Center, Houston Science Center, Houston, Texas 77204.

1. In late 1986 and January 1987, Pei Hor and I collaborated at the University of Houston to invent and develop a “high temperature” superconductivity technology using Yttrium and known as the YBCO invention.

2. Dr. Paul Chu, as group leader, assured us (Dr. Hor and me), based on our actual inventive contributions, that we would be listed as co-inventors on all patent applications for YBCO. Consistent with that assurance, and our inventive contributions and my clear understanding, I was paid $137,000 in 1987 by the University of Houston as my initial share of licensing fees paid by Dupont for the YBCO invention. A true and correct copy of my W-2 for this exceptional compensation, along with the W-2 for my regular salary, is attached hereto as Exhibit “A”.

3. It was not until February of 2006 that I learned from Mr. John P. Warren, Jr., (Associate Vice Chancellor for Intellectual Property Management) that Dr. Hor and I were not listed on any YBCO patent applications as at least “co-inventors”. Mr. Warren said that that Dr. Paul Chu was the sole listed inventor on the applications. I feel this is wrong because Dr. Chu only minimally participated in inventing the YBCO technology.

4. Any statements made by me, under oath or otherwise, contrary to the paragraphs above were made to protect the University of Houston at
the urging of attorney Charles Cox, outside counsel for the University.

FURTHER, AFFIANT SAYETH NAUGHT.

Ruling Meng, Affiant

SUBSCRIBED AND SWORN TO BEFORE ME this 25th of May 2006

Notary Public

TRAVIS WOFFORD
NOTARY PUBLIC, STATE OF TEXAS
MY COMMISSION EXPIRES
SEP 5, 2009
October 26, 2006

Via United State Express Mail No. EV 459408878 US

Mr. Lester L. Hewitt
Akin Gump Strauss Hauer & Feld LLP
1111 Louisiana Street, 44th Floor
Houston, Texas 77002-5800

Re: YBCO Patent Inventorship Issues

Dear Les,

As you know, I have been retained by Dr. Ruling Meng (Dr. Meng) to represent her rights as a coinventor of certain inventions arising from her work at The University of Houston (UH). Based on my review of the evidence thus far, Dr. Meng is clearly entitled to be named as a coinventor of U.S. Patent No. 7,056,866 ("the '866 patent"), and its progeny, including, without limitation, U.S. Patent Application Serial No. 07/300,663, and 163,956 (and any non-U.S. counterpart patents/applications, such as, e.g., the 35 family members for the '866 patent identified on INPADOC derived from 22 applications, and WO 89/08076 (PCT/US89/00685)).

Further to my letter of July 5, 2006, I have not yet received from you any input regarding my request for the progress of your investigation into this matter and the steps you have taken on behalf of UH and Dr. Ching-Wu Chu (Dr. Chu) with the U.S. Patent & Trademark Office (USPTO) to address these coinventorship issues relating to my client. In
the meantime, however, I have had the opportunity to review documentary evidence that pertains specifically to my client showing her entitlement to be a named as a coinventor along with Dr. Chu. I am providing a synopsis of this evidence herein, along with a PowerPoint® presentation found on the enclosed CD.

In view of clear and convincing documentary evidence that exists showing and corroborating Dr. Meng’s entitlement to be named as a coinventor of the claimed inventions, Dr. Meng hereby respectfully requests the following from Dr. Chu and UH:

I. Certification of Correction of U.S. Patent No. 7,056,866

Pursuant to 35 U.S.C § 256, 37 C.F.R. § 1.324, Dr. Meng seeks the agreement of Dr. Chu and UH to submit a joint application with her to the Director of the USPTO seeking a Certificate of Correction of Inventorship to add Dr. Meng as a named coinventor of U.S. Patent No. 7,056, 866 ("the ’866 patent") along with Dr. Chu.¹

35 U.S.C § 256 provides in pertinent part:

Whenever ... through error an inventor is not named in an issued patent and such error arose without any deceptive intention on his part, the Director may, on application of all the parties and assignees, with proof of the facts and such other requirements as may be imposed, issue a certificate correcting such error.

The error of omitting inventors or naming persons who are not inventors shall not invalidate the patent in which such error occurred if it can be corrected as provided in this section.

Pursuant to 37 C.F.R. § 1.324(b)(1), Dr. Meng will provide a statement that the inventorship error occurred without any deceptive intention on her part – a position that neither Dr. Chu nor UH would dispute.² Pursuant to 37 C.F.R. § 1.324(b)(2), Dr. Meng

¹ It should be without dispute that Dr. Meng has standing to assert her rights as a coinventor and to seek correction of inventorship with Dr. Chu and UH. See Chou v. University of Chicago, 254 F.3d 1347, 1359-60 (Fed. Cir. 2001).
² Correction of inventorship under section 256 “only requires an inquiry into the intent of the nonjoined inventor”. Stark v. Advanced Magnetics, Inc., 119 F.3d 1551, 1552 (Fed. Cir. 1997).
seeks from Dr. Chu a statement either agreeing to the change of inventorship or stating that he has no disagreement in regard to the requested change. Pursuant to 37 C.F.R. § 1.324(b)(3), Dr. Meng seeks from UH (and any other assignees of the '866 patent) a statement, made in compliance with 37 C.F.R. § 3.73(b), agreeing to the change of inventorship in the '866 patent.

II. Certification of Correction of U.S. Patent Application Serial No. 07/300,063

Similarly, pursuant to 35 U.S.C § 116, 37 C.F.R. § 1.48(a), Dr. Meng seeks the agreement of Dr. Chu and UH to the filing with the USPTO of a request to correct the inventorship of pending U.S. Patent Application Serial No. 07/300,063 ("the '063 application") (and any other related pending application) to add Dr. Meng as a named coinventor along with Dr. Chu.4

35 U.S.C § 116 provides in pertinent part:

Whenever ... through an error an inventor is not named in an application [for patent], and such error arose without any deceptive intention on his part, the Director may permit the application to be amended accordingly, under such terms as he prescribes.

In this connection, Pursuant to 37 C.F.R. § 1.48(a)(2) Dr. Meng will provide a statement that the error in inventorship occurred without deceptive intention on her part – a position that neither Dr. Chu nor UH would dispute.5 Pursuant to 37 C.F.R. § 1.48(a)(3) Dr. Meng will also provide an oath or declaration as required by 37 C.F.R. § 1.63. Pursuant to

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3 See also MPEP 1412.04.
4 See footnote 1.
5 See footnote 2.
37 C.F.R. § 1.48(a)(5), Dr. Meng seeks from UH (and any other assignees of this application) written consent to this change in inventorship.⁶

III. Certification of Correction of

Similarly, pursuant to 35 U.S.C § 116, 37 C.F.R. § 1.48(a), Dr. Meng seeks the agreement of Dr. Chu and UH to the filing with the USPTO of a request to correct the inventorship of pending U.S. Patent Application Serial No. 163,956 ("the '956 application") (and any other related pending application) to add Dr. Meng as a named coinventor along with Dr. Chu.⁷

In this connection, Pursuant to 37 C.F.R. § 1.48(a)(2) Dr. Meng will provide a statement that the error in inventorship occurred without deceptive intention on her part — a position that neither Dr. Chu nor UH would dispute.⁸ Pursuant to 37 C.F.R. § 1.48(a)(3) Dr. Meng will also provide an oath or declaration as required by 37 C.F.R. § 1.63. Pursuant to 37 C.F.R. § 1.48(a)(5), Dr. Meng seeks from UH (and any other assignees of this application) written consent to this change in inventorship.⁹

IV. Correction of Inventorship in all Non-US Counterpart Patents and Patent Applications

Dr. Meng claims entitlement to be named as a coinventor on all applicable non-U.S. counterpart patent applications as well. Dr. Meng is presently aware of the existence of non-U.S. counterpart applications, but does not have a complete identification of these applications. Since inventorship on such applications normally follows the inventorship

⁶See also MPEP 201.03. Alternatively, Dr. Meng could be added as a coinventor in a continuing application under 37 CFR 1.53.
⁷See footnote 1.
⁸See footnote 2.
⁹See also MPEP 201.03. Alternatively, Dr. Meng could be added as a coinventor in a continuing application under 37 CFR 1.53.
designation in the originating country, Dr. Meng requests that Dr. Chu and UH take appropriate action to change the inventorship designation on all applicable non-US counterpart patents and patent applications. See, e.g., PCT Receiving Office Guidelines, PCT Gazette Ch. XVI, ¶¶ 309-311 (World Intellectual Property Organization Aug. 28, 1998) (setting forth the procedures for recording a change in the applicant or inventor of PCT applications).10

V. Receipt of All Benefits Given to a UH Coinventor

As a coinventor, Dr. Meng is justly entitled to her fair share of revenue received by UH (both past and future) for these patents/applications under the terms of established UH intellectual property policies in place at all relevant times. Dr. Meng also has a reputational interest in being recognized as a coinventor.

VI. Background and Discussion

A. Legal Standards

A review of the relevant facts in view of controlling Federal Circuit decisional law relating to section 256 clearly supports Dr. Meng's claim to co-inventorship. For example, in Linear Technology Corp. v. Impala Linear, the Federal Circuit stated:

A party seeking correction of inventorship must provide clear and convincing evidence of inventorship. Hess v. Advanced Cardiovascular Sys., Inc., 106 F.3d at 979-80 [(Fed. Cir. 1997)]; Ethicon, Inc. v. U.S. Surgical Corp., 135 F.3d 1456, 1461 (Fed. Cir. 1998). To meet the clear and convincing evidentiary burden, the alleged co-inventors must prove their contribution to the conception with more than their own testimony concerning the relevant facts. Trovan, Ltd. v. Sokymat SA, 299 F.3d 1292, 1302 (Fed. Cir. 2002) (citing Price v. Symsek, 988 F.2d 1187, 1194 (Fed. Cir. 1993)). Whether the co-inventor's testimony has been sufficiently corroborated is evaluated under a "rule of reason analysis," which requires that an "evaluation of all pertinent evidence must be made so that a sound determination of the credibility of the inventor's story may be reached." Price, 988 F.2d at 1195.

10 See Chou v. University of Chicago, 254 F.3d at 1360.
Corroborating evidence may take many forms. Reliable evidence of corroboration preferably comes in the form of records made contemporaneously with the inventive process. Sandt Tech., Inc. v. Rosco Metal & Plastics Corp., 264 F.3d 1344, 1350-51 (Fed. Cir. 2001). Circumstantial evidence of an independent nature may also corroborate. Trovan, 299 F.3d at 1303. Additionally, oral testimony from someone other than the alleged inventor may corroborate. Id.

Linear Technology Corp. v. Impala Linear, 379 F.3d 1311, 1327 (Fed. Cir. 2004). See also Pannu v. Jolab Corp., 155 F.3d 1344, 1350 (Fed. Cir. 1998) ("[Section 256] is a savings provision. If a patentee demonstrates that inventorship can be corrected as provided for in section 256, a district court must order correction of the patent, thus saving it from being rendered invalid.").

Also, as outlined by the Federal Circuit in Eli Lilly And Company v. Aradigm Corp., 376 F.3d 1352, 1358-59 (Fed. Cir. 2004):

Section 116 of Title 35 is the statutory locus of joint inventorship doctrine. It provides that a person not listed on a patent need not demonstrate that he made a contribution equal in importance to the contribution made by the listed inventors to claim his right to joint inventor status. See 35 U.S.C. § 116 (2000) ("Inventors may apply for a patent jointly even though (1) they did not physically work together or at the same time, (2) each did not make the same type or amount of contribution, or (3) each did not make a contribution to the subject matter of every claim of the patent."). In fact, section 116 "sets no explicit lower limit on the quantum or quality of inventive contribution required for a person to qualify as a joint inventor." Fina Oil & Chem. Co. v. Exxon, 123 F.3d 1466, 1473 (Fed. Cir. 1997). However a long line of decisions in this court holds that a person is a joint inventor only if he contributes to the conception of the claimed invention. See, e.g., C.R. Bard, Inc. v. M3 Sys., Inc., 157 F.3d 1340, 1352 (Fed. Cir. 1998); Fina Oil, 123 F.3d at 1473 ("The case law thus indicates that to be a joint inventor, an individual must make a contribution to the conception of the claimed invention that is not insignificant in quality, when that contribution is measured against the dimension of the full invention."); Sewall v. Walters, 21 F.3d 411, 415 (Fed. Cir. 1994); see also Burroughs Wellcome Co. v. Barr Labs., Inc., 40 F.3d 1223, 1227-28 (Fed. Cir. 1994) ("Conception is the touchstone of inventorship, the completion of the mental part of invention."). The line between actual contributions to conception and the remaining, more prosaic contributions to the inventive process that do not render the contributor a co-inventor is sometimes a difficult one to draw. Contributions to realizing an invention may not amount to a contribution to conception if they merely explain what was "then state of the art," Hess, 106 F.3d at 981, if they are too far
removed from the real-world realization of an invention, see, e.g., Garret Corp., 422 F.2d at 881 ("One who merely suggests an idea of a result to be accomplished, rather than means of accomplishing it, is not a joint inventor."), or if they are focused solely on such realization, see, e.g., Ethicon, 135 F.3d at 1460 ("[O]ne does not qualify as a joint inventor by merely assisting the actual inventor after conception of the claimed invention.").

It is however uncontroversial that the alleged joint inventor seeking to be listed on a patent must demonstrate that his labors were conjoined with the efforts of the named inventors. Joint inventorship under section 116 can only arise when collaboration or concerted effort occurs — that is, when the inventors have some open line of communication during or in temporal proximity to their inventive efforts:

What is clear is that the statutory word "jointly" is not mere surplusage. For persons to be joint inventors under Section 116, there must be some element of joint behavior, such as collaboration or working under common direction, one inventor seeing a relevant report and building upon it or hearing another’s suggestion at a meeting. . . . Joint inventorship under Section 116 requires at least some quantum of collaboration or connection.


Eli Lilly, 376 F.3d at 1358-59 (footnotes omitted).

B. Facts

A Review of the relevant facts will illustrate that Dr. Meng has clear and convincing evidence of her entitlement to be named as a co-inventor of the '866 patent and its related applications and non-U.S. counterparts.

Dr. Meng is a materials scientist from China. Before she came to the U.S. she was a research scientist at the Chinese Academy of Science, Institute of Physics in Beijing, China (one of the top research institutes in China). In 1976, Dr. Meng began her research on superconducting materials in China. In 1979, Dr. Meng was invited by Dr. Chu to join his High Pressure Low Temperature research group at UH to serve as an independent materials scientist. During the time period 1979 to 1982, Dr. Meng set up the materials synthesis lab in Dr. Chu's group and began her independent synthesis of various types of materials and
her studies of various superconducting compounds. Dr. Meng's expertise, in her capacity of
visiting research scientist, permitted, for example, Dr. Chu's group to obtain materials
samples directly from Dr. Meng, rather than being dependent upon other groups outside of
UH to provide samples.

As a visiting scholar, Dr. Meng was required by her native country of China to return
to China after 2 years. In 1981, Dr. Meng left UH at the invitation of Prof. Ernst Bucher to
become a visiting scientist at the University of Konstanz, Germany. During this period, Dr.
Meng continued her collaboration with Dr. Chu by providing him with more than 20
different types of superconducting single crystals for research. In mid 1982, Dr. Meng
returned to the Institute of Physics in Beijing, China and continued the collaboration on
superconducting materials with Dr. Chu for the next two years.

In July of 1984, Dr. Meng was invited again by Dr. Chu to return to UH as a visiting
scientist. On her return to UH in July 1984 as a materials scientist, Dr. Meng independently
conducted and supervised the research on superconducting and related materials, and she
synthesized and characterized various compounds.

In mid-November of 1986, Dr. Meng learned from her colleague in China, Professor
Z. X. Zhao, about the paper entitled: “Possible High Tc Superconductivity in the Ba-La-Cu-
O System,” by J.G. Bednorz and K.A. Muller. At that time, Dr. Chu was on leave and
served at the National Science Foundation in Washington (he served there for about one
year). Dr. Meng asked a graduate student, Li Gao, to go to the library to copy the paper on a
Friday afternoon. Dr. Meng then placed a copy of the paper on Dr. Chu’s desk. On
Saturday morning Dr. Chu returned for a weekend visit to his office and discussed the paper
with Dr. Meng. The paper reported that the wet-chemical method was used and it also
indicated that the solid-state reaction processing might be difficult to obtain the superconducting phase. Dr. Ruling advised Dr. Chu that based on her knowledge and experience in the materials sciences (and with solid-state reactions), that a solid-state reaction method could be used to synthesize this material.

On November 14, 1986, Dr Meng was the first person to use the solid-state reaction methods to successfully repeat Dr. Bednorz' and Muller's results on Ba-La-Cu-O compounds. Subsequently, Dr. Meng optimized the processing conditions, such as the temperature, atmosphere, time and composition for this Ba-La-Cu-O system.

During 1987, the high temperature YBCO discovery took place within Dr. Chu's group. By February 27, 1987, Dr. Meng independently successfully separated black and green crystals from the mixed phase by studying a set of YBCO samples with different compositions. This work contributed to the conception of the High temperature YBCO formula and structure identified and claimed in the '866 patent. Subsequently, Dr. Meng continued to conduct high temperature superconductor material research within Dr. Chu's group and optimized the processing conditions for individual rare earth compounds and successfully synthesized a whole series of rare earth High temperature superconductors.

Additionally, in January 1988, Dr. Meng extended her work in the high Tc area on the Bi System ("BSCCO").

As illustrated in the accompanying PowerPoint presentation (on CD)("the presentation"), Dr. Meng's independent laboratory work clearly contributed to the conception of the claimed invention of the '866 patent (and the '956 application regarding BSCCO) in a manner that is not insignificant in quality, when that contribution is measured against the dimension of the full invention. The presentation highlights a direct correlation
between Dr. Meng's laboratory notebook entries and the disclosure relied upon in the specification (Examples, etc.) and claims of the '866 patent. Dr. Meng's laboratory entries were contemporaneously made at relevant times just preceding the filing dates of the patent applications that ultimately issued as the '866 patent. These laboratory notebooks are of the most reliable type of evidence of corroboration of Dr. Meng's claim to be named a coinventor since her lab notebooks constitute records made contemporaneously with her inventive process. Sandt, 264 F.3d at 1350-51.

Dr. Chu was the head of his research group. As such, Dr. Meng worked in collaboration with Dr. Chu on a regular basis during this inventive process. Dr. Meng routinely shared with and reported to Dr. Chu her laboratory results, often on a daily basis, either in person or via telephone, and Dr. Chu provided input to Dr. Meng as well. This open line of communication existed during or in temporal proximity to their coinventive efforts and resulted in having Dr. Meng's laboratory work form a substantive contribution to the specifications as filed, and the conception of the claims as issued (or filed), in the applications leading to the '866 patent (and the pending '956 application).

Dr. Chu has always been the head of this research group at UH, and Dr. Meng has always worked in this group while employed at UH. However, Dr. Meng's research has always been independently conducted. She brought to UH a unique expertise in her field that was not otherwise found within Dr. Chu's group. Although Dr. Meng worked within Dr. Chu's research group, and Dr. Chu was technically her "boss" she was not "merely assisting" Dr. Chu, but instead was actively working in connection with Dr. Chu to jointly conceive of this invention. In other words, Dr. Meng is not merely another pair of hands for Dr. Chu, but instead her labors were conjoined with the efforts of Dr. Chu.
Dr. Meng has already been recognized on numerous occasions to be a co-inventor with Dr. Chu. Thus far, Dr. Chu has seven (7) U.S. patents issued naming him as an inventor (in each case, as the first named inventor):

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>7,056,866</td>
<td>12 Jan 87</td>
<td>Chu</td>
<td>Akin Gump</td>
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<tr>
<td></td>
<td>26 Jan 87</td>
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<td>26 Mar 87</td>
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<tr>
<td>6,329,325</td>
<td>9 Jul 88</td>
<td>Chu, Meng &amp; Xue</td>
<td>Akin Gump</td>
</tr>
<tr>
<td>5,563,564</td>
<td>22 Apr 93</td>
<td>Chu, Xue, Gao, Meng &amp; Ramirez</td>
<td>Fulbright &amp; Jaworski</td>
</tr>
<tr>
<td>5,578,551</td>
<td>28 Jul 93</td>
<td>Chu, Meng &amp; Wang</td>
<td>Fulbright &amp; Jaworski</td>
</tr>
<tr>
<td>6,025,769</td>
<td>7 Oct 96</td>
<td>Chu, Xue, Gao &amp; Meng</td>
<td>Fulbright &amp; Jaworski</td>
</tr>
<tr>
<td>5,906,964</td>
<td>15 Jun 97</td>
<td>Chu, Meng &amp; Xue</td>
<td>Flehr ...</td>
</tr>
<tr>
<td>6,239,080</td>
<td>6 Jul 99</td>
<td>Chu, Xue &amp; Du</td>
<td>Akin Gump</td>
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</tbody>
</table>

Over the course of 12+ years, Dr. Meng was listed as a co-inventor with Dr. Chu on 5 of these 7 patents. Dr. Meng’s level of inventive contribution as an independent materials scientist was recognized by Dr. Chu and three different sets of patent counsel. Dr. Meng’s level of inventive contribution to the ’866 patent appears to have been overlooked, perhaps owing to the fact that this was the very first patent application filed out of Dr. Chu’s research group at UH. Back in early 1987, Dr. Meng thought she was to be a co-inventor of the YBCO invention, but was totally unfamiliar with US patent law and USPTO procedures and as such, did not know she was left off of this application (or the ’956 application) until recently.

Dr. Meng has approximately 237 peer-reviewed publications (2 being in press). Dr. Meng has served as a sub-editor for many conference proceedings and numerous invited talks delivered at domestic and international conferences. She is already recognized as a Co-
inventor with Dr. Chu on five U.S. patents. A current copy of Dr. Meng’s CV is contained on the CD.

Dr. Meng, who is well recognized in her field, is Ranked 25th out of the 1000 most cited physicists from 1981-June 1997 by the Institute for Scientific Information (ISI) (http://www.sst.nrel.gov). She was identified as one of the world’s most cited authors (less than 1/2 of 1 percent of all publishing researchers) by ISI Current Contents-2000, an updated list based on important scientific developments of the last two decades.

VII. Conclusion

In view of the foregoing facts, Dr. Meng’s claim to being named a co-inventor under the ‘866 patent and related applications and counterparts is well grounded under the law and supported by clear and convincing evidence. Although the pending related, unpublished applications other than the ‘956 CIP application, (e.g., the ‘063 application) have not been analyzed as of yet, Dr. Meng believes that for the reasons set out herein, the related applications likewise contain the joint inventive contributions and conceptions of Dr. Meng entitling her to be named as a joint inventor.

Based on the foregoing, Dr. Meng rightfully claims entitlement to be named as a co-inventor with Dr. Chu for the patents that were applied for by Dr. Chu during this time period relating to high temperature superconductors, such as, U.S. Patent No. 7,056,866, U.S. Patent Application Serial Nos. 07/300,063, and 163,956 and any other related U.S. or non-U.S. patents or patent applications.

In this connection, as a co-inventor, Dr. Meng is justly entitled to her fair share of revenue received by UH (both past and future) for these patents/applications under the terms of established UH intellectual property policies in place at all relevant times. Dr.
Mr. Lester L. Hewitt  
October 26, 2006  
Page 13

Meng is aware that certain revenue-generating transactions (be they assignments or licenses) have occurred in the past respecting these patents and patent applications and hereby requests an accounting to her for her fair share of such proceeds. Dr. Meng also has a reputational interest in being recognized as a coinventor.

I look forward to hearing from you at your earliest possible time to discuss moving forward with the above requested procedures and accounting. Dr. Meng stands ready to cooperate with UH and Dr. Chu in any filings required with the USPTO regarding her requests noted herein and is available to provide feedback on the correction of typographical errors in the '866 patent.

Very truly yours,

[Signature]

Gordon G. Waggett

Enclosures:

CD containing the following files:
1. "Ruling Meng’s Inventorship Presentation re ‘866 patent (26 Oct 06)" (pdf format)
2. "Ruling Meng’s Inventorship Presentation re ‘866 patent (read only)(26 Oct 06)"
   (PowerPoint format)
3. CV of Dr. Meng (pdf format)

cc: Dr. Ruling Meng (with enclosures)
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Houston, TX 77203-5002
Phone: (713) 743-8306
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Education:
B.S. Central South University, Hunan, P.R. China (1958)

Employment History:
2002-present Editorial Board of the Central European Journal of Physics.
1987-present Senior Research Scientist, Department of Physics, Texas Center for Superconductivity at
the University of Houston, Houston TX U.S.A.
1984-1986 Research Associate, Department of Physics, University of Houston, Houston TX
1982-1984 Research Associate, Institute of Physics, Academy of Science, Beijing, P. R. China
1981 Visiting Scholar, Department of Physics, University of Konstanz, West Germany
1979-1981 Research Associate, Department of Physics, University of Houston TX
1973-1979 Research Associate, Institute of Physics, Chinese Academy of Science, Beijing
1959-1973 Research Assistant, Metallurgy and Materials Science Division, Institute of Mining and
Metallurgy, Academy of Science, P. R. China
1958-1959 Instructor, Central South University of Technology, Hunan, P. R. China

Honors and Awards:
Ranked 25th out of the 1000 most cited physicists from 1981- June 1997 by the Institute for Scientific
Information (ISI) (http://www.sst.nrel.gov). Identified as one of the world’s most cited authors (less than
1/2 of 1 percent of all publishing researchers) by ISI Current Contents-2000, updated list based on
important scientific developments of the last two decades.

2004 Advisory Board member Hainan University
2003 Honorary Professorship Hainan Normal University.
2003 Honorary Professorship Hainan University
1998 Honorary Professorship Beijing Polytechnic University
1992 Honorary Professorship Zhong-Shan University (Sun Yat-Sen University), P.R. China
1992 Honorary Professorship Central South University of Technology, P.R. China
1992- Senior Consultant Chan-Sha Research Institute of Mining and Metallurgy, PRC

Member: Materials Research Society; Phi Beta Delta International Assn., Chinese Association of
Professionals in Science and Technology (Houston: Founder/1st President)

Co-inventor on five patents
6,329,325 High temperature superconducting tape and method of manufacture
6,025,769 Strong high-temperature superconductor trapped field magnets
5,906,964 High temperature superconducting tape and method of manufacture
5,578,551 Method for synthesis of high-temperature Hg-Ba0ca-Cu-O(HBCCO) superconductors

5,563,564 Strong high-temperature superconductor trapped field magnets

Primary Research

Research Interests: Improving known high T_c superconductors and finding new compounds. Synthesis and characterization of alloy, intermetallic, and oxide superconductors in bulk and thin film. Single crystal growth, tape and coated conductor processes.

Research Highlights:

- Primary research interests are in superconducting and other related materials.
- 1987 Major contribution on the discovery of the high temperature superconducting Y-Ba-Cu-O system.
- 1990 First to succeed in fabricating texturing Y-Ba-Ca-O bar.
- 1991 Obtained first record trapped field of 8 T at 4.2 k by 20 mm dia x 6mm YBCO disks.
- 1991 Obtained first record shielding field of >19 T at 4.2 k by 20mm x 6 mm YBCO disks.
- 1991 First to grow C-60 single crystal with no defect.
- 1993 First to develop and patent the processing techniques for highest transition superconducting temperature Hg-Ba-Ca-Cu-O, and co-developed the first Hg-1212 film.
- 1996 First to succeed in fabricating Hg-1223 tapes.
- 1998 First to succeed in fabricating Bi-Sr-Ca-Cu-O on a low cost Ni metal substrate.

Recent Research Highlights:

Primary research interests are in research for superconducting and other related materials.

- Study of Binary and pseudo-binary intermetallic compound with AlB_2 structure. Discovery two new intermetallic superconductors.
- Search for and study of Novel HTSg and Related Compounds. Such as: study the unconventional superconductivity and Electron correlation in Cobalt Oxyhydrate NaO_{3.5}CoO_2·yH_2O.
- Investigated on the enhancement of flux pinning and critical currents in YBa_2Cu_3O_y films by cation substitution.
- Enhance the flux pinning in YBCO films by pre-decoration of substrate surfaces with metal or oxide nano-scale partial. The critical current enhance a factor of 2-3.
- Develop a new and efficient method to obtain enhanced pinning and critical current density in YBa_2Cu_3O_y films by grown on Nd_{1/3}Eu_{1/3}Gd_{1/3}Ba_2Cu_3O_y with nano-undulated surface morphology. Clarify the origin of this pinning enhancement. The YBCO on NEG gives an enhancement in \( j_c \) of 50%-100% between 5 K and 77 K.
PUBLICATIONS

Total publications ~250. Sub-editor for many conference proceedings; numerous invited talks delivered at domestic and international conferences.


37. “Superconductivity above 90 K in the Square-Planar Compound System ABA_{2}CuO_{4-δ} with A = La, Y, Nd, Sm, Eu, Gd, Ho, Er and Lu,” P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster and C. W. Chu, Phys. Rev. Lett. 58, 1891 (1987).


Department of Electronic and Information Technology and Research Institute for Higher Education Programs, Hokkaido Tokai University.


130. “Micro-Raman Scattering on Superconducting HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+\delta}$ (n = 1, 2, 3) Ceramics,” Y. T. Ren, H. Chang, Q. Xiong, Y. Q. Wang, Y. Y. Sun, R. L. Meng, Y. Y. Xue and C. W. Chu, Physica C 217, 273 (1993).


147. "Superconductivity in (LuC)\textsubscript{r}(Ni\textsubscript{2}B\textsubscript{2}) and (LuC)(Ni\textsubscript{2}B\textsubscript{2})," L. Gao, X. D. Qiu, Y. Cao, R. L. Meng, Y. Y. Sun, Y. Y. Xue and C. W. Chu, Phys. Rev. B 50, 9445 (1994).


149. "Hydrostatic Pressure on HgBa\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{6-\delta}, and HgBa\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{6-\delta}," F. Chen, L. Gao, R. L. Meng, Y. Y. Xue and C. W. Chu, J. Appl. Phys. 76, 6941 (1994).


154. "Raman Study of the Thermal Stability of HgBa\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{6-\delta} and HgBa\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{6-\delta}," by H. Chang, Z. H. He, R. L. Meng, Y. Y. Xue and C. W. Chu, Physica C 251, 126 (1995).

155. "Optimal Y\textsubscript{1.8}BaCuO\textsubscript{3} Additions for High Critical Current in Large-Grain YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\delta}," M. Chopra, R. L. Meng, C. W. Chu, S. Jin, and S. W. Chan, Controlled Processing of High Temperature Superconductors: Fundamentals and Applications, 1995 International Workshop on Superconductivity, cosponsored by ISTEC and MRS (Maui: ISTEC/MRS, 1995) p. 88.

156. "Formation of HgBa\textsubscript{2}Ca\textsubscript{2}CuO\textsubscript{3}O\textsubscript{6-\delta} with Additives Under Ambient Conditions," R. L. Meng, B. R. Hickey, Y. Y. Sun, Y. Cao, C. Kinalidis, J. Meen, Y. Y. Xue and C. W. Chu, Physica C 260, 1 (1996).


167. “Hg Vapor Pressure, Phase Stability, and Synthesis of Hg$_{1-x}$Ba$_2$Ca$_{x+1}$Cu$_2$O$_{2x+\delta}$ with $n \leq 3$,” Y. Y. Xue, R. L. Meng, Q. M. Lin, B. Hickey, Y. Y. Sun and C. W. Chu, Physica C 281, 11 (1997).


177. "Growth of HgBa$_2$Ca$_2$Cu$_3$O$_{8+x}$ Thin Films Using Stable Re$_{0.1}$Ba$_2$Ca$_2$Cu$_3$O$_{8+x}$ Precursor by Pulsed Laser Deposition," W. N. Kang, R. L. Meng and C. W. Chu, Appl. Phys. Lett. 73, 381 (1998).


213. “Superconductivity in the C32 Intermetallic Compounds AAl$_{2x}$Si$_y$, with A =Ca and Sr; and 0.6 < x < 1.2,” B. Lorenz, J. Lenz!, J. Cmaidalka, R. L. Meng, Y. Y. Sun, Y. Y. Xue and C. W. Chu, Physica C 383, 191 (2002).


Evidence Supporting Dr. Ruling Meng’s Entitlement to be Named as a Coinventor with Dr. Chu on U.S. Patent No. 7,056,866 and its related applications and foreign counterparts

Submitted to:
The University of Houston and Dr. Ching-Wu (Paul) Chu through their counsel, Lester L. Hewitt, Akin, Gump, Akin Gump Strauss Hauer & Feld LLP
October 26, 2006
By:

Gordon G. Waggett, P.C.

Intellectual Property Law
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Dr. Meng Respectfully Requests the Following From UH and Dr. Chu:

I. Certification of Correction of U.S. Patent No. 7,056,866
Pursuant to 35 U.S.C § 256, 37 C.F.R. § 1.324, Dr. Meng seeks the agreement of Dr. Chu and UH to submit a joint application with her to the Director of the USPTO seeking a Certificate of Correction of Inventorship to add Dr. Meng as a named coinventor of U.S. Patent No. 7,056,866 ("the '866 patent") along with Dr. Chu.

II. Certification of Correction of U.S. Patent Application Serial No. 07/300,063
Similarly, pursuant to 35 U.S.C § 116, 37 C.F.R. § 1.48(a), Dr. Meng seeks the agreement of Dr. Chu and UH to the filing with the USPTO of a request to correct the inventorship of pending U.S. Patent Application Serial No. 07/300,063 ("the '063 application") (and any other related pending application) to add Dr. Meng as a named coinventor along with Dr. Chu.

Similarly, pursuant to 35 U.S.C § 116, 37 C.F.R. § 1.48(a), Dr. Meng seeks the agreement of Dr. Chu and UH to the filing with the USPTO of a request to correct the inventorship of pending U.S. Patent Application Serial No. 163,956 ("the '956 application") (and any other related pending application) to add Dr. Meng as a named coinventor along with Dr. Chu.

IV. Correction of Inventorship in all Non-US Counterpart Patents and Patent Applications
Dr. Meng claims entitlement to be named as a coinventor on all applicable non-U.S. counterpart patent applications as well. Dr. Meng is presently aware of the existence of non-U.S. counterpart applications, but does not have a complete identification of these applications. Since inventorship on such applications normally follows the inventorship designation in the originating country, Dr. Meng requests that Dr. Chu and UH take appropriate action to change the inventorship designation on all applicable non-US counterpart patents and patent applications.

V. Receipt of All Benefits Given to a UH Coinventor
As a coinventor, Dr. Meng is justly entitled to her fair share of revenue received by UH (both past and future) for these patents/applications under the terms of established UH intellectual property policies in place at all relevant times. Dr. Meng also has a reputational interest in being recognized as a coinventor.
Dr. Meng is an Inventor

Dr. Meng has already been recognized on numerous occasions to be a coinventor with Dr. Chu. Thus far, Dr. Chu has seven (7) U.S. patents issued naming him as an inventor (in each case, as the first named inventor):

<table>
<thead>
<tr>
<th>U.S. Patent No.</th>
<th>Filing Date</th>
<th>Inventors</th>
<th>Patent Counsel</th>
</tr>
</thead>
<tbody>
<tr>
<td>7,056,866</td>
<td>26 Mar 87</td>
<td>Chu</td>
<td>AG</td>
</tr>
<tr>
<td>6,329,325</td>
<td>9 Jul 88</td>
<td>Chu, <strong>Meng</strong> &amp; Xue</td>
<td>AG</td>
</tr>
<tr>
<td>5,563,564</td>
<td>22 Apr 93</td>
<td>Chu, Xue, Gao, <strong>Meng</strong> &amp; Ramirez</td>
<td>F&amp;J</td>
</tr>
<tr>
<td>5,578,551</td>
<td>28 Jul 93</td>
<td>Chu, <strong>Meng</strong> &amp; Wang</td>
<td>F&amp;J</td>
</tr>
<tr>
<td>6,025,769</td>
<td>7 Oct 96</td>
<td>Chu, Xue, Gao &amp; <strong>Meng</strong></td>
<td>F&amp;J</td>
</tr>
<tr>
<td>5,906,964</td>
<td>15 Jun 97</td>
<td>Chu, <strong>Meng</strong> &amp; Xue</td>
<td>Flehr ...</td>
</tr>
<tr>
<td>6,239,080</td>
<td>6 Jul 99</td>
<td>Chu, Xue &amp; Du</td>
<td>AG</td>
</tr>
</tbody>
</table>

Over the course of 12+ years, Dr. Meng was listed as a co-inventor with Dr. Chu on 5 of these 7 patents. Dr. Meng's level of inventive contribution as an independent materials scientist was recognized by Dr. Chu and three different sets of patent counsel. Dr. Meng's level of inventive contribution to the '866 patent appears to have been overlooked, perhaps owing to the fact that this was the very first patent application filed out of Dr. Chu's research group at UH. Back in early 1987, Dr. Meng thought she was to be a coinventor of the YBCO invention, but was totally unfamiliar with US patent law and USPTO procedures and as such, did not know she was left off of the '866 applications until recently.
Clear and Convincing Evidence of Coinventorship

Dr. Meng's independent laboratory work clearly contributed to the conception of the claimed invention of the '866 patent in a manner that is not insignificant in quality, when that contribution is measured against the dimension of the full invention. The following slides highlight a direct correlation between Dr. Meng's laboratory notebook entries and the disclosure relied upon in the specification (Examples, etc.) and claims of the '866 patent. Dr. Meng's laboratory entries were contemporaneously made at relevant times just preceding the filing dates of the patent applications that ultimately issued as the '866 patent.
EXAMPLE I

"6.0 grams of La2O3, 0.61 grams of SrCO3 and 1.63 grams of CuO were mixed in an ajar mill for about 12 hours."

From p. H 12, Meng's Lab Notebook (23 Dec 86):
EXAMPLE II

"6.0 grams of La$_2$O$_3$, 0.61 grams of SrCO$_3$ and 1.63 grams of CuO were mixed mechanically in a jar mill for approximately 24 hours."

From p. H 12, Meng’s Lab Notebook (23 Dec 86):
EXAMPLE III

"6.0 grams of La₂O₃, 0.81 grams of BaCO₃ and 1.63 grams of CuO were mixed in a mortar-pestle apparatus for about 3 hours."

From p. H 11, Meng's Lab Notebook:

\[
\begin{align*}
\text{BaCO}_3 & \quad \text{6000 mg} \\
\text{La}_2\text{O}_3 & \quad \text{5158 mg} \\
\text{Ba}_4\text{O}_6 & \quad \text{67.73 mg} \quad \text{X: 1000} \\
\text{Ba}_4\text{O}_6 & \quad \text{561.9 mg} \quad \text{X: 807.47} \\
\text{Ba}_4\text{O}_6 & \quad \text{561.9 mg} \quad \text{X: 807.47} \\
\text{Cu}_2\text{O} & \quad \text{49.82 mg} \quad \text{X: 1000} \\
\end{align*}
\]

"The resulting lanthanum-barium-copper-oxide composition had the formula \( \text{La}_{1.8}\text{Sr}_{0.2}\text{Cu}_1\text{O}_y \). The oxide complex so formed was of the formula \([\text{La}_{1-x}\text{Ba}_x\text{Cu}_b\text{O}_y]\) wherein \( x = 0.1 \), \( a = 2 \), \( b = 1 \) and \( y = 2 \) to 4." (Sr should be Ba – typographical error)
From p. H 471, Meng's Lab Notebook:

(866 Patent, Col. 12, lines 30-46)

"After this reaction, the temperature was raised to a temperature of about 950° C... mixture was then heated rapidly to a temperature of about 950° C., and kept at that temperature for about seven hours... then sintered into solid cylinders by heating them at a temperature of about 950° C. for a period of about four hours at ambient atmospheric pressure."
EXAMPLE IV

"2.0 grams of \( \text{La}_2\text{O}_3 \), 0.2 grams of \( \text{BaCO}_3 \) and 0.53 grams of \( \text{CuO} \) were mixed mechanically in a mortar-pestle apparatus for approximately 3 hours."

From p. H 14, Meng’s Lab Notebook:

The La–Ba–Cu–O composition produced from this process corresponds to the formula \([\text{La}_{1-x}\text{Ba}_x]\text{Cu}_b\text{O}_y\), wherein \(x\) is 0.075, \(a\) is 2, \(b\) is 1 and \(y\) is 2 to 4.
"The oxide complex so formed corresponds to the general formula [La₄₋₉Ba₅₋₇Cu₀₋₇Oₓ] wherein "x" is 0.15, "a" is 1, "b" is 1, and "y" is 2 to 4."

From p. H 49, Meng's Lab Notebook:
EXAMPLE VI

The La Sr—Cu—O composition produced from this process corresponds to the general formula [La$_{1-x}$Sr$_x$]$_a$Cu$_b$O$_y$, where “$x$” is 0.1, “a” is 2, “b” is 1, and “y” is 2 to 4.

From p. H 12, Meng's Lab Notebook:

The oxide complex of the example showed superconducting properties at a transition temperature of about 39 °C.
EXAMPLE VIII

“A La-Ba-Cu-O composition was prepared in accordance with the procedure described in Example II except that La$_2$O$_3$, BaCO$_3$ and CuO were used in the amounts appropriate to provide an oxide complex of the formula [La$_{1-x}$Ba$_x$]$_a$Cu$_b$O$_y$ wherein “x” is 0.1, “a” is 2, “b” is 1 and , and an intensive mixer ball mill was used rather than a jar mill. The oxide complex 50 produced showed superconductive properties at a temperature of 60ºK at an applied pressure of 12 kilobars.” [La$_{1-x}$Ba$_x$]$_a$ is a typo that should read: [La$_{1-x}$Ba$_x$]$_a$.
'866 Patent, col 4, lines 32-35:

FIG. 14 is the X-ray diffraction patterns for a (La\(_{0.9}\)Ba\(_{0.1}\)) CuO\(_{4-\delta}\) oxide complex as prepared according to Example VIII and for an LaBa\(_2\)Cu\(_3\)O\(_{8+\delta}\) oxide complex as prepared according to Example XIII.

'866 Patent:

Dr. Meng performed X-Ray diffraction that was referenced in the '866 patent. Here is one example.
EXAMPLE X

"A La–Ba–Cu–O composition was prepared in accordance with the procedure of Example II except that La₂O₃, BaCO₃, and CuO were used in the amounts appropriate to provide an oxide complex of the formula [La₁₋ₓBaₓ]ₐCu₃O₇₋ₐ where \( x \) is about 0.4, "a" is 1, "b" is 1 and "y" is between 2 and 3, . . . " [Note: Divide "a" and "b" by 5].

From p. H 16, Meng's Lab Notebook:

\[
\begin{align*}
\text{Ba} & \quad \text{La} \quad \text{Cu} \quad \text{O} \\
32.16 & \quad 68.0 & \quad 38.12 & \quad 3.92 \\
\text{La} & \quad \text{Ba} : 0.67 & \quad 0.33 \\
\text{O} & \quad \text{Cu} : 2.41 & \quad 1.6 \\
\end{align*}
\]
"A yttrium oxide complex was prepared with a nominal composition represented by \([\text{Y}_{1.2}\text{Ba}_x] \text{Cu}_b \text{O}_y\), wherein \(x\) is 0.4, \(a\) is 2, \(b\) is 1 and \(\ldots\)

\(...\)

Jote: Ba should be \(\text{Ba}_x\)."

From p. H 50, Meng's Lab Notebook:

\[
\begin{align*}
\text{YB-} & \text{102 (Ba}_2 \text{Cu}_4 \text{O}_y) \\
Y & \text{31.05} \\
\text{Ba} & \text{31.930} \\
\text{Cu} & \text{18.466} \\
\text{O} & \text{18.599}
\end{align*}
\]

\[
\begin{align*}
\text{Y}_2\text{O}_3 & : 300 \text{mg} \\
\text{BaCO}_3 & : 49.553 \text{mg} \\
\text{Cu} & : 17.122 \text{mg}
\end{align*}
\]
EXAMPLE XII

"100 mg of Y₂O₃, 349.57 mg of BaCO₃ and 211.39 mg of CuO were thoroughly mixed by mortar-pestle. Mixing continued ...."
Black Phase/Green Phase

By February 27, 1987, Dr. Meng independently successfully separated black and green crystals from the mixed phase by studying a set of YBCO samples with different compositions. This work contributed to the conception of the High temperature YBCO formula and structure identified and claimed in the ‘866 patent (and related applications).
Examination of the $Y_{x}Ba_{1-x}Cu_{y}O_{z}$ oxide revealed that it was comprised of mixed phases. The phases were separated and identified as tetragonal $Y_{1.9}Ba_{0.1}Cu_{1.0}O_{4+\delta}$ (black) and orthorhombic $Y_{1.9}Ba_{0.1}Cu_{1.0}O_{4}$ (green). The black and green phases comprised at least 95% by volume of the initial $Y_{1.9}Ba_{0.1}Ce_{0.1}O_{4}$ oxide complex. Magnetic measurements on the oxide complex showed that the black phase was responsible for the high temperature superconductivity detected. Single phase $Y_{1.9}Ba_{0.1}Cu_{1.0}O_{4+\delta}$ samples (hereafter referred to as "YBCO") were prepared and exhibited a 100% ac diamagnetic shift. The molar oxygen content of the black phase is greater than twice that of the molar content of copper by an exact amount as yet undetermined, as indicated by the δ symbol in the phase formula.

The high temperature superconducting black phase, on a single phase basis, corresponds to the formula $[L_{x},M_{y}]A_{2}O$, where $L$ is yttrium, $M$ is barium, and $a$ is copper. $a=1$, $b=1$, $y=2$ to 4 and $x=0.667$. Further
Dr. Meng's independent research and experiments identified and separated the superconducting phase ("black phase") and the non-superconducting phase ("green phase"). See, e.g., pp. H 57-59, Meng's lab notebook:

'866 patent col. 8, lines 30-47:
Examination of the Y Ba Cu O oxide revealed that it was comprised of mixed phases. The phases were separated and identified as tetragonal YBa2Cu3O7+δ (black) and orthorhombic Y2BaCuO4 (green). The black and green phases comprised at least 95% by volume of the initial Y—Ba—Cu—O oxide complex. Magnetic measurements on the oxide complex showed that the black phase was responsible for the high temperature superconductivity detected. Single phase YBa2Cu3O6.6 samples (hereafter referred to as "YBCO") were prepared and exhibited a 100% ac diamagnetic shift. The molten oxygen content of the black phase is greater than twice that of the molten content of copper by an exact amount as yet undetermined, as indicated by the δ symbol in the phase formula.

The high temperature superconducting black phase, on a single phase basis, corresponds to the formula [L1−xMx]AO, wherein "L" is yttrium, "M" is barium, "A" is copper, "x" is 1, "b" is 1, "y" is 2 to 4 and "x" is 0.667. Further

Witnessed by: Dr. Alex Ignatov (UH)

Gordon G. Waggett, p. 19 — October 26, 2006

Black Phase / Green Phase

WO 89/08076 ('866 Application), p. 3, lines 32-37: greater. My pending application serial No. 522,041 identified the mixed oxide to comprise a green and black phase with the black phase being the phase responsible for the high temperature (i.e., Tc > 77 K or greater) superconductivity and being of the formula YBa2Cu3O6.6 (x is a number between 0.1 to 1.0). My
CLAIMS - '866 patent col. 18-19:

25 What is claimed is:

1. A composition which is superconductive at a temperature of 70 K and higher, comprising:
   a metal oxide the formula
   \[ (\text{I} \text{r}), \text{M}_{\alpha} \text{O}_{y} \]
   wherein,
   "\text{I} r" is strontium lanthanum, neodymium, samarium, europium, gadolinium or a mixture thereof; "\text{M}\alpha" is barium, strontium, or a mixture thereof; "\text{M}\alpha" is copper, "\text{M}\beta" is from about 0.65 to 0.80; "\text{M}\gamma" is 0 to 1; and "\text{M}\lambda" is a value from about 2 to about 4 that provides the metal oxide with zero electrical resistance at a temperature of 70 K or above.

2. The superconducting composition of claim 1, wherein
   "\text{M}\gamma" is barium.

3. The superconducting composition of claim 1, wherein
   "\text{M}\beta" is about 0.67.

4. The superconducting composition of claim 1, wherein
   "\text{I} r" is strontium lanthanum, neodymium, samarium, europium, gadolinium, erbia, or lanterium.

5. The superconducting composition of claim 1, wherein the metal oxide has the formula
   \[ \text{I}_{\alpha} \text{M}_{\beta} \text{O}_{\gamma} \]
   and \( \alpha \) is a number value from about 1.0 to about 1.2 that provides the oxide complex with zero electrical resistance at a temperature of 70 K or above.

6. The superconducting composition of claim 5, wherein
   "\text{M}\beta" is barium.

7. The superconducting composition of claim 5, wherein
   "\text{I} r" is strontium lanthanum, neodymium, samarium, europium, gadolinium, erbia, or lanterium.

8. A material containing a sufficient quantity of a superconductive crystalline phase to cause the material to exhibit substantially zero electrical resistance at a temperature of 77 K or above, said crystalline phase composition having the formula \[ \text{I}_{\alpha} \text{M}_{\beta} \text{O}_{\gamma} \] wherein "\text{I} r" is Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu or a mixture thereof; "\text{M}\alpha" is Sr or a mixture thereof; and "\text{M}\beta" is from about 0.65 to about 1.0 that provides the composition with zero electrical resistance at a temperature of 77 K or above.

9. The material of claim 8 wherein \( \alpha \) is 1.0 and \( \beta = 1.0 \), and the material is CuO.

10. The material of claim 8 wherein \( \alpha \) is 1.0 and \( \beta = 1.0 \), and the material is BaO.

Examination of the \( \text{Y}^{3+} \text{Ba}^{2+} \text{Cu}^{2+} \text{O}_{\alpha} \) oxide revealed that it was comprised of mixed phases. The phases were separated and identified as tetragonal \( \text{YBa}_{2} \text{Cu}_{3} \text{O}_{7+\delta} \) (black) and orthorhombic \( \text{Y}_{2} \text{BaCuO}_{5} \) (green). The black and green phases comprised at least 95% by volume of the initial \( \text{Y}^{3+} \text{Ba}^{2+} \text{Cu}^{2+} \text{O}_{\alpha} \) oxide complex. Magnetic measurements on the oxide complex showed that the black phase was responsible for the high temperature superconductivity detected. Single phase \( \text{YBa}_{2} \text{Cu}_{3} \text{O}_{7+\delta} \) samples (hereafter referred to as "YBCO") were prepared and exhibited a 100% increase in diamagnetic shift. The molar oxygen content of the black phase is greater than twice that of the molar content of copper by an exact amount as yet undetermined, as indicated by the \( \delta \) symbol in the phase formula.

The high temperature superconducting black phase, on a single phase basis, corresponds to the formula \( [\text{Li}_{\alpha} \text{M}_{\beta}] \text{Sr}_{\gamma} \text{O}_{\delta \pm 0.1} \) where \( \alpha = 0.5 \) to \( 0.6 \), \( \beta = 1.0 \), \( \gamma = 0.5 \) to \( 1.0 \), and \( \delta \) is a number value from about 1.0 to about 1.3 that provides the oxide complex with zero electrical resistance at a temperature of 77 K or above.

See also Examples I – VI, VIII, X-XI

See also Examples XII-XIV

Black Phase/Green Phase
EXAMPLE XIV

LaBa$_2$Cu$_3$O$_{6+1/2}$ oxide complexes wherein "L" is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

<table>
<thead>
<tr>
<th>Material</th>
<th>BaCO$_3$</th>
<th>CuO</th>
<th>Reaction Temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$_2$O$_3$ 100 mg</td>
<td>234.588 mg</td>
<td>141.834 mg</td>
<td>900°C</td>
</tr>
<tr>
<td>Sm$_2$O$_3$ 100 mg</td>
<td>226.25 mg</td>
<td>136.79 mg</td>
<td>950°C</td>
</tr>
<tr>
<td>Eu$_2$O$_3$ 100 mg</td>
<td>224.27 mg</td>
<td>135.6 mg</td>
<td>950°C</td>
</tr>
<tr>
<td>Gd$_2$O$_3$ 100 mg</td>
<td>217.73 mg</td>
<td>133.18 mg</td>
<td>900°C</td>
</tr>
<tr>
<td>Er$_2$O$_3$ 100 mg</td>
<td>205.358 mg</td>
<td>124.763 mg</td>
<td>820°C</td>
</tr>
<tr>
<td>Lu$_2$O$_3$ 100 mg</td>
<td>198.359 mg</td>
<td>119.927 mg</td>
<td>830°C</td>
</tr>
</tbody>
</table>

In each instance the powders were thoroughly mixed by a conventional milling technique and then pre-sintered at about 920°C for six hours. The powders were then heated to about 960°C for 24 hours in a reducing atmosphere of hydrogen, followed by quenching in dry ice at 0°C. The bulk densities of the resulting pellets were 5.5 g/cm$^3$. The pellets were then cut into 1 mm thick discs and further characterized by x-ray diffraction and other techniques.

Dr. Meng identified the optimal processing conditions for individual Rare Earth superconductor compounds set out in the Examples and Claims of the '866 patent.
**EXAMPLE XIV**

L$\text{Ba}_2\text{Cu}_3\text{O}_{6+n}$ oxide complexes wherein “L” is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

<table>
<thead>
<tr>
<th></th>
<th>$\text{L}_2\text{O}_3$</th>
<th>$\text{BaCO}_3$</th>
<th>CuO</th>
<th>Reaction Temp. °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$\text{O}_2$ 100 mg</td>
<td>234.588 mg</td>
<td>141.834 mg</td>
<td>900° C.</td>
<td></td>
</tr>
<tr>
<td>Sm$\text{O}_2$ 100 mg</td>
<td>226.25 mg</td>
<td>136.79 mg</td>
<td>950° C.</td>
<td></td>
</tr>
<tr>
<td>Eu$\text{O}_2$ 100 mg</td>
<td>224.57 mg</td>
<td>135.6 mg</td>
<td>950° C.</td>
<td></td>
</tr>
<tr>
<td>Gd$\text{O}_2$ 100 mg</td>
<td>217.73 mg</td>
<td>133.18 mg</td>
<td>900° C.</td>
<td></td>
</tr>
<tr>
<td>Er$\text{O}_2$ 100 mg</td>
<td>206.358 mg</td>
<td>124.763 mg</td>
<td>826° C.</td>
<td></td>
</tr>
<tr>
<td>Lu$\text{O}_2$ 100 mg</td>
<td>198.359 mg</td>
<td>119.927 mg</td>
<td>830° C.</td>
<td></td>
</tr>
</tbody>
</table>

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**Dr. Meng's Rare Earth Superconductor Work**
EXAMPLE XIV

LBA$_2$Cu$_3$O$_{6+8}$ oxide complexes wherein “L” is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

<table>
<thead>
<tr>
<th>Oxide</th>
<th>BaCO$_3$</th>
<th>CuO</th>
<th>Reaction Temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$_2$O$_3$ 100 mg</td>
<td>234.588 mg</td>
<td>141.834 mg</td>
<td>900°C</td>
</tr>
<tr>
<td>Sm$_2$O$_3$ 100 mg</td>
<td>226.25 mg</td>
<td>136.70 mg</td>
<td>950°C</td>
</tr>
<tr>
<td>Eu$_2$O$_3$ 100 mg</td>
<td>224.22 mg</td>
<td>135.6 mg</td>
<td>950°C</td>
</tr>
<tr>
<td>Gd$_2$O$_3$ 100 mg</td>
<td>217.73 mg</td>
<td>133.18 mg</td>
<td>900°C</td>
</tr>
<tr>
<td>Er$_2$O$_3$ 100 mg</td>
<td>206.358 mg</td>
<td>124.763 mg</td>
<td>820°C</td>
</tr>
<tr>
<td>Lu$_2$O$_3$ 100 mg</td>
<td>198.359 mg</td>
<td>119.927 mg</td>
<td>830°C</td>
</tr>
</tbody>
</table>

Dr. Meng’s Rare Earth Superconductor Work
EXAMPLE XIV

L$\text{Ba}_2\text{Cu}_3\text{O}_{6+y}$ oxide complexes wherein “L” is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

<table>
<thead>
<tr>
<th>$\text{Li}_2\text{O}$</th>
<th>$\text{BaCO}_3$</th>
<th>CuO</th>
<th>Reaction Temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O$_3$ 100 mg</td>
<td>234.588 mg</td>
<td>141.834 mg</td>
<td>900° C.</td>
</tr>
<tr>
<td>Sm$_2$O$_3$ 100 mg</td>
<td>226.25 mg</td>
<td>136.79 mg</td>
<td>950° C.</td>
</tr>
<tr>
<td>Eu$_2$O$_3$ 100 mg</td>
<td>224.27 mg</td>
<td>135.6 mg</td>
<td>950° C.</td>
</tr>
<tr>
<td>Gd$_2$O$_3$ 100 mg</td>
<td>217.73 mg</td>
<td>133.18 mg</td>
<td>900° C.</td>
</tr>
<tr>
<td>Er$_2$O$_3$ 100 mg</td>
<td>206.358 mg</td>
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</tr>
<tr>
<td>Lu$_2$O$_3$ 100 mg</td>
<td>198.359 mg</td>
<td>119.927 mg</td>
<td>830° C.</td>
</tr>
</tbody>
</table>

CLAIMS - '866 patent col. 19-20:

11. A method for making a superconducting metal oxide, comprising the steps of:
   mixing solid compounds containing L, M, A and O in amounts appropriate to yield the formula $[L_{1-x}M_x]_2A_yO_z$ wherein “L” is yttrium, lanthanum, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, or a combination thereof; “M” is barium, strontium, or a combination thereof; “A” is copper, “a” is 1 to 2; “b” is 1; “x” is about 0.01 to about 1.0; and “y” is a value from about 2 to about 4 that provides the metal oxide with zero electrical resistance at a temperature of 40°K or compacting the mixture into a solid mass by application of pressure from about 100 to about 30,000 psi;
   heating the solid mass in air to a temperature of from about 800 to about 1000° C. for a time sufficient to react the compacted mixture in the solid state; and quenching the solid mass to ambient temperature in air.

12. The method of claim 11, wherein “M” is barium.

13. The method of claim 12, wherein “x” is about 0.65 to about 0.80 and “y” is 1.

14. The method of claim 13, wherein the mixture is compacted to a solid mass by application of pressure of from about 100 to about 500 psi.

15. The method of claim 14, wherein the solid mass is heated under a reduced oxygen atmosphere of about 2000° C. at a temperature of from about 820° C. to about 950° C.
11. A method for making a superconducting metal oxide, comprising the steps of:
mixing solid compounds containing L, M, A and O in amounts appropriate to yield the formula \([\text{Li}_{x} \text{M}_{y} \text{A}_{z} \text{O}_{w}]\),
\(\text{A}_x \text{O}_y\), wherein “L” is yttrium, lanthanum, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, or a combination thereof; “M” is barium, strontium, or a combination thereof; “A” is copper, “a” is 1 to 2; “b” is 1;
“x” is about 0.01 to about 1.0; and “y” is a value from about 2 to about 4 that provides the metal oxide with zero electrical resistance at a temperature of 40°K or above;
compacting the mixture into a solid mass by application of pressure from about 100 to about 30,000 psi;
heating the solid mass in air to a temperature of from about 800 to about 1000° C. for a time sufficient to react the compacted mixture in the solid state; and quenching the solid mass to ambient temperature in air.

12. The method of claim 11, wherein “M” is barium.
13. The method of claim 12, wherein “x” is about 0.65 to about 0.86 and “a” is 1.
14. The method of claim 13, wherein the mixture is compacted to a solid mass by application of pressure of from about 100 to about 500 psi.
15. The method of claim 14, wherein the solid mass is heated under a reduced oxygen atmosphere of about 2000° at a temperature of from about 820° C. to about 950° C.
EXAMPLE XIV

LBA$_3$Cu$_4$O$_{6+δ}$ oxide complexes wherein "L" is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

In each instance the powder components were thoroughly mixed by mortar-pestle until microscopic examination revealed powders of uniform color. In each instance the resulting powder mixture was pressed into pellets of about 5/8 inch diameter and 1/8 inch thick by application of about 250 psi pelletization pressure. In each instance the resulting pellets were fired for about 20 minutes under a reduced oxygen atmosphere (-2000°C) at the reaction temperature as shown in Table 1. Each was spallated under ambient temperature by passing under inert atmosphere over the reacted pellets. The $T_{\text{c1}}$, $T_{\text{c2}}$, and X-ray diffraction lattice parameters measured for each of the resulting LBA$_3$Cu$_4$O$_{6+δ}$ samples are reported in Table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{c1}}$</th>
<th>$T_{\text{c2}}$</th>
<th>X-ray Diff. Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNd$_3$O$_3$</td>
<td>55°C</td>
<td>60°C</td>
<td>a = 5.85 Å, c = 23.5 Å</td>
</tr>
<tr>
<td>LSM$_3$O$_3$</td>
<td>52°C</td>
<td>58°C</td>
<td>a = 5.82 Å, c = 23.3 Å</td>
</tr>
<tr>
<td>Leu$_3$O$_3$</td>
<td>55°C</td>
<td>60°C</td>
<td>a = 5.85 Å, c = 23.5 Å</td>
</tr>
<tr>
<td>Gd$_3$O$_3$</td>
<td>52°C</td>
<td>58°C</td>
<td>a = 5.82 Å, c = 23.3 Å</td>
</tr>
<tr>
<td>Er$_3$O$_3$</td>
<td>55°C</td>
<td>60°C</td>
<td>a = 5.85 Å, c = 23.5 Å</td>
</tr>
<tr>
<td>Lu$_3$O$_3$</td>
<td>52°C</td>
<td>58°C</td>
<td>a = 5.82 Å, c = 23.3 Å</td>
</tr>
</tbody>
</table>

1. Reaction mixture was dried in a vacuum oven at 100°C.
2. The reaction mixture was then ground with a mortar and pestle.
3. The reaction mixture was then pressed into pellets under a reduced oxygen atmosphere (-2000°C) at the reaction temperature as shown in Table 1.
4. The pellets were then spallated under ambient temperature by passing under inert atmosphere over the reacted pellets.
5. The $T_{\text{c1}}$, $T_{\text{c2}}$, and X-ray diffraction lattice parameters were measured for each of the resulting LBA$_3$Cu$_4$O$_{6+δ}$ samples as reported in Table 1.
EXAMPLE XIV

LaBa$_2$Cu$_2$O$_{6+y}$ oxide complexes wherein "L" is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

<table>
<thead>
<tr>
<th></th>
<th>BaCO$_3$ (mg)</th>
<th>CuO (mg)</th>
<th>Reaction Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$_2$O$_3$ 100 mg</td>
<td>234.588</td>
<td>141.834</td>
<td>900° C.</td>
</tr>
<tr>
<td>Sm$_2$O$_3$ 100 mg</td>
<td>226.25</td>
<td>136.79</td>
<td>950° C.</td>
</tr>
<tr>
<td>Eu$_2$O$_3$ 100 mg</td>
<td>224.27</td>
<td>135.6</td>
<td>950° C.</td>
</tr>
<tr>
<td>Gd$_2$O$_3$ 100 mg</td>
<td>217.73</td>
<td>133.18</td>
<td>900° C.</td>
</tr>
<tr>
<td>Er$_2$O$_3$ 100 mg</td>
<td>206.358</td>
<td>124.763</td>
<td>820° C.</td>
</tr>
<tr>
<td>Lu$_2$O$_3$ 100 mg</td>
<td>198.359</td>
<td>119.97</td>
<td>830° C.</td>
</tr>
</tbody>
</table>

In each instance the powder components were thoroughly mixed by mortar-pestle until microscopic examination revealed a powder mixture of uniform color. In each instance the resulting powder mixture was pressed into pellets of about ⅛ inch diameter and ⅛ inch thickness in a pellet die by application of about 250 psi pelletization pressure. In each instance the resulting pellets were then reacted for about 60 minutes under a reduced oxygen atmosphere (-2000°C). The reaction temperatures as above indicated, following which each was quenched to ambient temperature by passing ambient temperature oxygen over the reacted pellets. The T$_{DT}$, T$_{c0}$, T$_{c1}$ and X-ray diffraction lattice parameters measured for each of the resulting NeBCO, SaBCO, EbCO, GaBCO, ErBCO and LuBCO samples are reported in Table I.
EXAMPLE XIV

LBCaCu0603 oxide complexes wherein "L" is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

<table>
<thead>
<tr>
<th>L2O3</th>
<th>BaCO3</th>
<th>CuO</th>
<th>Reaction Temperature °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd2O3 100 mg</td>
<td>234.588 mg</td>
<td>141.834 mg</td>
<td>900°C</td>
</tr>
<tr>
<td>Sm2O3 100 mg</td>
<td>950°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu2O3 100 mg</td>
<td>950°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd2O3 100 mg</td>
<td>900°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er2O3 100 mg</td>
<td>900°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

'866 CLAIM 15

The method of claim 14, wherein the solid mass is heated under a reduced oxygen atmosphere of about 2000ppm at a temperature of from about 820°C to about 950°C.

In each instance the powder mixture was mixed in a ball mill, pelletized, annealed at the reaction temperatures as above indicated, followed by quenching to ambient temperature by passing ambient temperature oxygen over the reacted pellets. The Tm, Tc, Tc', and X-ray diffraction lattice parameters measured for each of the resulting NeBCO, SaBCO, EBCO, GaBCO, ErBCO, and LuBCO samples are reported in Table 1.
'956 continuation-in-part application filed on March 3, 1988

Similarly to the clear and convincing evidence above showing that Dr. Meng is a co-inventor of the '866 patent, Dr. Meng is likewise a co-inventor of the '956 continuation-in-part application filed on March 3, 1988. The following provides a brief look at the '956 specification and claims in view of exemplary excerpts from Dr. Meng's laboratory notebook.
'956 continuation-in-part application filed on March 3, 1988

Cross-reference to Related application

This is a continuation-in-part of Serial No. 022,404 filed March 26, 1987, entitled "Superconductivity in Square-Planar Compound Systems", which in turn is a continuation-in-part of Serial No. 012,205, filed February 6, 1987, entitled "High Transition Temperature Superconducting Composition" which in turn is a continuation-in-part of Serial No. 006,991, filed January 26, 1987, entitled "Superconducting Compositions and Method For Enhancing Their Transition Temperatures by Pressure" which in turn is a continuation-in-part of Serial No. 002,289, filed January 12, 1987, entitled "Superconducting Composition And Method."
For convenience the phase composition within a multiphase material prepared with a nominal composition Bi:Ca:Sr:Cu of 1:1:1:3:3; 1:1:1:2; or 1:1:1:3 may be represented as a metal oxide of the formula

$T_{a+b}Ca_{a}Cu_{b}O$.

Wherein "T" is a trivalent transition metal such as Bi, Al, Ba, Ti, Fe mixtures thereof; "a+b" is a mixture of alkaline earth metals such as Sr and Ca, Ba and Sr, Ba and Ca, Sr and Mg, and Ca and Mg in a ratio of the alkaline earth metal of larger atomic radius ("a") to the alkaline earth metal of smaller atomic radius ("b") of from about 1:1 to about 1:3; "d" is a number from about 1 to about 3; "e" is a number from about 1 to about 6; "f" is a number from about 1 to about 6; "g" is a number between from about (3d + 2e + 2f)/2 to about (3d + 2e + 3f)/2 that provides the metal oxide with zero electrical resistance at a temperature of 77K or higher. Preferably "T" is bismuth; "M" is Ca and Sr at ratio of 1:3; "d" is 2; "e" is 3; "f" is 2 and "g" is a number between about 8 to about 9.

Example excerpts from Meng's Notebook Entitled: "Bi System (Bulk & Tape)"
Another species of materials within the formula $[Cu_{x}Ag_{y}]^{m+}$ has been found which has zero electrical resistance at a temperature of 77K or higher. The species comprises that class of compositions wherein $m$ equals 1, to yield a formula of $[Cu_{x}Ag]^{m+}$. The $m^{th}$ constituent comprises a mixture of divalent alkaline earth metals and the $n^{th}$ constituent comprises a mixture of copper with at least one other “A”, preferably bismuth. In a preferred composition the $n^{th}$ constituent is a 1:1 mixture of Cu and Ag. The $m^{th}$ constituent is a 1:1 mixture of Cu and Al and $m^{th}$ equals 1. Accordingly, a compound material prepared to a nominal formula of $[Cu_{x}Ag_{y}]:Cu_{x}Al_{y}Ag_{z}:Cu_{x}Al_{y}:Cu_{x}Ag_{z}$ yields a multiphase material which exhibits zero electrical resistance at a temperature of 77K or higher. The material does not contain a rare earth metal. In this respect it is believed that bismuth, a trivalent element, serves a similar function to that of a trivalent rare earth with regards to creating a pervasive related crystalline form favorable to the occurrence of high temperature superconductivity. Hence, for convenience the nominal formula may be rewritten as follows:

$$Bl_{x}Ca_{y}Sr_{z}Cu_{2}O_{x} \ (1:1:1:1)$$

It has been found that the production of such high temperature superconducting materials may be facilitated by employing copper in an excess up to about six times the amount required to produce a nominal formula of 1:1:1:1 nominal formula described above. A material produced to a nominal composition given by

$$Bl_{x}Ca_{y}Sr_{z}Cu_{2}O_{x} \ (1:1:1:1)$$

wherein $x$ is a number between 4.8 to 6.0, is a multiphase material which exhibits zero electrical resistance at 77K or higher. In the same as the ratio of trivalent constituent to alkaline earth constituent to copper, the 1:1:1:1 nominal composition is analogous to the $Bl_{x}Ca_{y}Sr_{z}Cu_{2}O_{x}$ class of high temperature superconducting materials disclosed in my pending application Serial Nos. 12,205 and 32,041.

As before noted, another prepared as a mixture of $Bl_{x}Ca_{y}Sr_{z}Cu_{2}O_{x}$, where “x” is between 5.5 and 6.5, are high temperature superconducting material comprises a multiphase oxide.

Example excerpts from Meng's Notebook Entitled: "Bi System (Bulk & Tape)"
Another species of materials within the formula

\[(\text{Ba}_2\text{CuO}_4)_n\]

wherein the A constituent comprises a mixture of divalent alkaline earth metals and the A' constituent comprises a mixture of copper with at least one other A', preferably barium, in a preferred composition the A constituent is a 1:1 mixture of Ca and Sr, the A' constituent is a 1:1 mixture of Cu and Bi and "n" is 1. Accordingly, an oxide material prepared to an nominal formula of

\[(\text{Ba},\text{Ca},\text{Sr},\text{Cu},\text{Bi})_{1.1} \text{O}_2\]

yields a multiphase material which exhibits zero electrical resistance at a temperature of 77K or higher. The material does not contain a rare earth metal. In this regard it is believed that bismuth, a trivalent element, serves a similar function to that of a trivalent rare earth with regards to creating a perovskite related crystalline form favorable to the occurrence of high temperature superconductivity. Hence, for convenience the nominal formula may be rewritten as follows:

\[(\text{Ba},\text{Ca},\text{Sr},\text{Cu},\text{Bi})_{1.1} \text{O}_2\]

It has been found that the production of such high temperature superconducting material may be facilitated by employing copper in an excess up to about six times the amount required to produce a material of the 1:1:1:1 nominal composition described above. A material produced to a nominal composition of

\[(\text{Ba},\text{Ca},\text{Sr},\text{Cu},\text{Bi})_{1.1} \text{O}_2\]

wherein "n" is a number between 6.5 to 6.0, is a multiphase material which exhibits zero electrical resistance at 77K or higher. In the sense of the ratio of trivalent constituent to alkaline earth constituent to copper, the 1:1:1:1 nominal composition is analogous to the La$_2$CuO$_4$ class of high temperature superconductors.

As before noted, whether prepared as a phase of a 1:1:1:1 nominal composition, or even as a 1:1:1:1:1 composition, or mixed with a 1:1:1:1:1 multiphase oxide.

Examination of the multiphase oxide reveals at least four distinct phase compositions. One nominal composition of that phase determined to be the phase responsible for the high temperature superconductivity has been determined to be the composition

\[(\text{Bi},\text{Ca},\text{Sr},\text{Cu})_{1.3} \text{O}_{4+j}\]

where "j" is a value between 0.4 to 1.0 that provides the phase composition with zero electrical resistance at a temperature of 77K or higher.

3. A material which is superconductive at a temperature of 77°K or higher, said material comprising a multiphase oxide of nominal composition \(\text{BiCaSrCuO}_{q}\) wherein "q" is 2 to 4 and having a sufficient quantity of a crystalline phase composition of a formula \(\text{Bi}_2\text{CaSr}_{2}\text{Cu}_2\text{O}_{8}\) wherein "q" is a value from about 8 to about 9 which provides said crystalline phase composition with zero electrical resistance at a temperature of 77°K or higher to cause the material to exhibit zero electrical resistance at a temperature of 77°K or higher.

6. The material of claim 1 wherein M* is a 1:1 mixture of Ca and Sr; A* is a 1:1 mixture of Cu and Bi and a is 1.

11. A crystalline phase composition comprising cations of Bi, Ca, Sr, and Cu approximating the ratio of 1:2:2:2 for Bi:Ca: Sr: Cu and which exhibits zero electrical resistance at a temperature of 77°K or higher.

12. The composition of claim 11 wherein said crystalline phase composition is of the formula \(\text{Bi}_2\text{CaSr}_{2}\text{Cu}_2\text{O}_{8}\) wherein g is 8 to 9.
Dr. Meng was responsible for investigating and defining the sample preparation parameters made the subject of this '956 application.

Sample preparation parameters can affect the electronic and magnetic properties of the $T_dM^*eCu_fO_g$ class of oxide compounds drastically. It has been observed that the formation conditions for $T_dM^*eCu_fO_g$ for different "T's" are different. The reaction time, the reaction temperature, the quenching rate, the reaction atmosphere and the compositions are all inter-related. For instance, oxide complexes within this class can be made insulating, partially superconducting or completely superconducting by varying the reaction temperature and the quenching rate while keeping the compositions unchanged. The reaction temperature can be reduced by increasing the "d" parameter, reducing the "f" parameter, increasing the "T" component with greater atomic radius or doping the composition with monovalent alkaline elements.
Three Bi-Ca-Sr-Cu-O (hereafter BCSCO) samples were synthesized by the described solid-state reaction techniques from appropriate amounts of Bi\textsubscript{2}O\textsubscript{3}, CuO, SrCO\textsubscript{3}, and CaCO\textsubscript{3}. The BCSCO samples were prepared according to a nominal composition of 1:1:1:1 for BCSCO-a; 1:1:1:2 for BCSCO-b, and 1:1:1:3 for BCSCO-c. The starting

Fig. 8 illustrates resistance (R) vs. temperature (T) for BCSCO-b synthesized at different temperatures; a - 820°C, b - 864°C, c - 880°C. Curve d is for BCSCO-c.
For convenience the phase composition within a multiphase material prepared with a nominal composition R1Ca3Sr3Cu2Ox may be represented as a metal oxide of the formula 

$\text{M}^2\text{O}_3\text{M}^4\text{O}_{x}$

wherein $\text{M}^2$ is a transition metal such as Ni, Al, Be, Ti, In, Sn, or mixtures thereof; $\text{M}^4$ is a mixture of alkaline earth metals such as Sr and Ca, Ba and Sr, Ba and Ce, Sr and Mg, and Ca and Mg for a ratio of the alkaline earth metal of larger atomic radius ($\text{M}^4$) to the alkaline earth metal of smaller atomic radius ($\text{M}^4$) of from about 1:1 to about 1:3; "d" is a number from about 1 to about 3; "e" is a number from about 1 to about 6; "f" is a number from about 1 to about 6; "g" is a number between from about (3d + 2e + 2f)/2 to about (3d + 2e + 2f)/2 that provides the metal oxide with zero electrical resistance at a temperature of 77K or higher. Preferably "f" is 2; "d" is 2; "e" is 3; "f" is 2 and "g" is a number between about 5 to about 9.

A method for making such $\text{R}_1\text{Ca}_3\text{Sr}_3\text{Cu}_2\text{O}_x$ containing superconductive composition oxide materials involves the following steps, and for convenience is referred to as the compressed powder reaction method. Selected amounts of solid powdered compounds containing $\text{R}, \text{M}^2, \text{M}^4,$ A, B, and O are thoroughly mixed preferably by selecting appropriate amounts of $\text{Y}_2\text{O}_3, \text{Nd}_{2}\text{O}_3, \text{Y}_{2}\text{O}_3$ (or $\text{Y}_2\text{O}_3$ and $\text{A}_2\text{O}_3$) and A, The thoroughly mixed powder mixture is compressed into pellets which are thereafter reacted at a temperature between about 800°C and about 910°C for a time sufficient to complete the solid state reaction. Thereafter the reacted pellets are rapidly quenched to room temperature. Mixing is preferably accomplished by an intensive mixer such as a jar mill or more preferably a ball mill. Pelletization of the oxide mixture is carried out at an applied pressure of from about 100 to about 20,000 psi and preferably at an applied pressure of from about 100 to about 500 psi, most preferably at about 50 psi. Reaction of the pelletized mixture may be conducted in air for about 5 minutes to about 24 hours, and most preferably in a reduced oxygen atmosphere of about 2000 µ for about 5 to about 30 minutes. Following the completion of the reaction step the reacted pellet composition is rapidly quenched to room temperature in air.
For convenience the phase composition within a multiphase material prepared with a nominal composition BiCaSrCu of 1:1:1:1; 1:1:1:2; or 1:1:1:3 may be represented as a metal oxide of the formula

\[ \text{Y}_m \text{Ba}_n \text{Cu}_o \text{O}_{d+1} \]

wherein \( m \) is a trivalent transition metal such as Bi, Al, Be, Ti, In, Sc, or mixtures thereof; \( m \) is a mixture of alkaline earth metals such as Sr and Ca, Ba and Sr, Ba and Ca, Sr and Mg, and Ca and Mg in a ratio of the alkaline earth metal of larger atomic radius (\( M^2+ \)) to the alkaline earth metal of smaller atomic radius (\( M^2- \)) of from about 1:1 to about 1:3; \( m \) is a number from about 1 to about 3; \( o \) is a number from about 1 to about 6; \( d \) is a number between from about \( 3d + 2e + 2f \) to about \( 3d + 2e + 2f \) that provides the metal oxide with zero electrical resistance at a temperature of 77K or higher. Preferably \( m \) is hafnium; \( m \) is Ca and Sr at ratio of 1:2; \( m \) is Ca 2; \( m \) is 3; \( f \) is 2 and \( o \) is a number between about 8 to about 9.

A method for making such \( \text{Y}_m \text{Ba}_n \text{Cu}_o \text{O}_{d+1} \) containing superconductive composition oxide material includes the following steps, and for convenience is referred to as the compressed powder reaction method. Selected amounts of solid powder compounds containing T, \( \text{Ba}^2+ \), \( \text{Cu}^2+ \), A, and O are thoroughly mixed preferably by selecting appropriate amounts of \( \text{Y}_2 \text{O}_3 \), \( \text{Y}_2 \text{O}_3 \), \( \text{CuO} \) (or \( \text{Cu}^2+ \) and \( \text{Cu}^2+ \)) and \( \text{A}^2+ \). The thoroughly mixed powder mixture is compressed into pellets which are thereafter reacted at a temperature between about 800°C and about 950°C, preferably about 950°C to about 980°C, for a time sufficient to complete the solid state reaction. Thereafter the reacted pellets are rapidly quenched to room temperature. Mixing is preferably accomplished by an intensive mixer such as a jar mill or more preferably a ball mill. Pelletization of the oxide mixture is carried out at an applied pressure of from about 100 to about 20,000 psi and preferably at an applied pressure of from about 100 to about 600 psi, most preferably at about 600 psi. Reaction of the pelletized mixture may be conducted in air for about 5 minutes to about 24 hours, and most preferably in a reduced oxygen atmosphere of about 2000 psi for about 5 to about 30 minutes preferably for about 25 to about 35 minutes. Following the completion of the reaction step the reacted pellet composition is rapidly quenched to room temperature in air.
CONCLUSION

Based on the foregoing exemplary clear and convincing evidence, Dr. Meng rightfully claims entitlement to be named as a co-inventor with Dr. Chu for the patents that were applied for by Dr. Chu during this time period relating to high temperature superconductors, such as, U.S. Patent No. 7,056,866, U.S. Patent Application Serial Nos. 07/300,063, and 163,956 and any other related U.S. or non-U.S. patents or patent applications.

As a coinventor, Dr. Meng is justly entitled to her fair share of revenue received by UH (both past and future) for these patents/applications under the terms of established UH intellectual property policies in place at all relevant times. Dr. Meng is aware that certain revenue-generating transactions (be they assignments or licenses) have occurred in the past respecting these patents and patent applications and hereby requests an accounting to her for her fair share of such proceeds. Dr. Meng also has a reputational interest in being recognized as a coinventor.
Valence Instabilities
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CHEMICAL PRESSURE EFFECTS IN Sc-SUBSTITUTED YbCuAl

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Implications of Sc-substitution for nearly trivalent Yb in YbCuAl will be discussed. Magnetic properties, thermal expansion and specific heat of compounds with Sc-concentrations up to 20 percent will be presented. A possible occurrence of spin-fluctuations growing with increasing Sc-concentration is suggested.

INTRODUCTION

In a number of experiments over the past few years it has been established that dilution of intermediate valence (IV) compounds with non-magnetic atoms only produces a proportional reduction of the bulk properties of the IV state [1,2]. In other words, valence fluctuations at different ions seem to be incoherent and might be described as a single ion effect. Since, therefore, dilution does not disturb any coherency, the same experimental technique might be used to study the effect of chemical pressure upon the IV state. A very suitable system for this purpose is YbCuAl. It is intermediate valent and dilution with Y has been studied extensively [1]. Furthermore, Sc substitution may provide the sought-for chemical pressure effects since Sc is chemically identical to the rare earths, but has a significantly smaller ionic radius than trivalent Yb. Although the compound ScCuAl does not exist, we have found in the present work that single phase Yb$_{1-x}$Sc$_x$CuAl samples can be produced up to $x = 0.22$.

EXPERIMENTAL RESULTS

A detailed description of the sample preparation procedure can be found in ref. [3]. In the Yb$_{1-x}$Sc$_x$CuAl system compounds with $x = 0.00, 0.05, 0.075, 0.10, 0.15, 0.20$ and $0.22$ have been prepared. The compounds crystallize in the hexagonal Fe$_2$P-type structure, in which every Yb atom has the same local environment. The room temperature lattice parameters are given in fig.1.

Thermal expansion data by X-ray diffraction at low temperatures for various Sc-concentrations

![Graph showing thermal expansion data](Fig.2)

and also for pure YbCuAl are given in fig.2. The Sc-substituted compounds reveal a behaviour similar to what earlier has been found for pure YbCuAl [4]. A smaller but clear anomaly is observed, shifting towards lower temperatures upon increasing Sc-substitution. In YbCuAl, a non-magnetic dummy, a normal thermal expansion

Fig.1.

Fig.2.
has been observed. At room temperature we found the same slope as for YbCuAl, while below liquid nitrogen temperature the lattice parameters become temperature independent.

In fig. 3 as-measured susceptibility curves are given. The susceptibilities given in fig. 4 have been corrected for impurity contributions (of the order of about 12 trivalent Yb). It can be seen that the characteristic temperature $T_{\text{max}}$, the temperature of the well known susceptibility maximum, shifts towards lower tempera-

![Graph showing susceptibility curves](image)

tures and the low-temperature susceptibility increases gradually. At high temperatures (up to 1000 K) we find Curie-Weiss behaviour with an effective moment of $4.30 \pm 0.05$ $\mu_B$/Yb atom and a paramagnetic Curie temperature of $33 \pm 5$ K for all Sc-concentrations, the same as for pure YbCuAl and Y- and Gd-substituted YbCuAl [1].

The magnetic isotherms at liquid helium temperatures up to 35 tesla are given in fig. 5. In fig. 6 we again present the magnetization, now corrected for the impurity contributions, which is saturated at 5 T. For $x = 0.05$ the magnetization is still similar to that of pure YbCuAl. For the higher Sc-concentrations, however, the characteristic shape (upward curvature in the high-field part) vanishes and at the highest Sc-concentrations the curves show a gradually saturating behaviour. If we identify the slope of the low-field part of the magnetization with the initial susceptibility, we find good agreement with the low-temperature susceptibility.

![Graph showing magnetization curves](image)

The heat capacity for different Sc-concentrations is given in fig. 7. It can be seen that the properties have changed drastically with respect to those of YbCuAl. For the $x = 0.10$ compound the coefficient of the linear term, $\gamma$, can be estimated to be about 370 mJ/K$^2$ mole Yb atom, compared to 255 mJ/K$^2$ mole Yb atom for pure YbCuAl. This relative change is similar to that in the low-temperature susceptibility. For the higher Sc-concentrations $\gamma$ cannot be determined in a simple way. Furthermore the heat capacities are found to be field-independent at least up to 5 T.
Chemical Pressure Effects in Sc-Substituted YbCuAl

**Fig. 6.**

**Fig. 7.**

**Fig. 8.**

**Fig. 9.**

**DISCUSSION**

The most direct indication of pressure effects due to Sc-substitution would be lattice parameters deviating from Vegard's law. In this case it is not possible to establish this due to the absence of compounds with x > 0.22 (see fig.1). On the other hand we can compare the observed magnetic properties with the results of measurements of the magnetic susceptibility of pure YbCuAl when external pressure is applied. In fig.8 these measurements are given. The results show that $\Theta_{max}$ shifts towards lower temperatures when pressure is applied, while the value of the constant low-temperature susceptibility increases. From the susceptibility curves in fig.3 we can conclude that substitution of Sc has a similar effect as application of external pressure. One may object against the use of the impurity-correction procedure in the case of Sc-substituted compounds. It may be that here, due to shift of the maximum towards lower temperatures, the low-temperature susceptibility is no longer temperature independent below 8 K. However, since the $\chi v s T$ plots are still linear up to this temperature, it can be assumed that the susceptibility is fairly constant.

It has been found (fig.8) that the low-temperature susceptibility of pure YbCuAl increases with 3% per 100 MPa (1 kbar) [4]. Assuming that this value is independent of pressure, which is probably a very crude approximation, we can make an estimate of the pressures involved with Sc-substitution in YbCuAl. The results of such a procedure are given in fig.9. The low-temperature susceptibility depends essentially linearly upon the Sc-concentration. We can compare the pressures in fig.9 with the pressure required to accomplish a complete valence transition from divalent to trivalent Yb metal. This pressure can be estimated by identifying the transformation energy of 38 kJ/mole [4,5] with the JPD term in the free energy. The volume of divalent Yb is 24.9 cm$^3$/mole. For trivalent Yb metal the molar volume can be approximated by taking the average of the values for Yb(18.1 cm$^3$/mole) and Lu(17.8 cm$^3$/mole); with a thus derived value for $\delta V$ of 6.9 cm$^3$/mole we estimate a pressure of the order of 10 GPa (100 kbar) necessary to achieve the valence transition in pure Yb. Before discussing, however, the consequences of the pressure effect upon magnetization and specific heat, it is worthwhile to mention that substitu-
tion of a smaller atom does not always lead to this effect. Majewski et al. [7] have investigated the magnetic properties of various compounds in the (Yb,Sc)Al system. In contrast to what one would expect upon substitution of the smaller Sc-atom, the effect is that YbAl becomes less magnetic with increasing Sc-concentration, which implies a shift towards more divalent character. This can be understood when it is remembered that the magnetic behaviour depends upon the valence state which, in its turn, is connected with the volume: a smaller volume is associated with the trivalent magnetic state, a larger volume with the divalent non-magnetic state. Therefore, in dilution experiments the sign of the deviation of the lattice parameter from Vegard's law is indicative for the magnetic behaviour. From ref. [7] it is known that the deviation in (Yb,Sc)Al is positive (fig.10), which is likely to favour the non-magnetic state. At first sight one would say that the magnetic behaviour of mixed-valent Yb in YbCoAl is only gradually changing upon Sc-substitution. On the other hand, the specific heat behaviour is influenced rather drastically. The appearance of a growing upturn below 10 K with increasing Sc-concentration, which is hardly influenced by a magnetic field of about 5 T, betrays that somehow the system is on the onset of critical behaviour. A more detailed comparison with for instance compounds like UCu and UAl, [8,9] reveals a very similar behaviour. In these actinide compounds too, a peak in the specific heat is observed, which does not change when a magnetic field is applied. Therefore the upturn can not be ascribed to local magnetic moments. The specific heat of UAl and UCu has been analysed successfully in terms of spin-fluctuation theory [10,11], which adds a $\alpha n^2$ term to the linear and cubic contributions. In the case of Sc-substituted YbCoAl a detailed, quantitative analysis of the results in the framework of spin-fluctuation theory is hampered by the fact that, besides a spin-fluctuation part, still an appreciable mixed-valent part is contributing to the specific heat. This is underlined by the thermal expansion behaviour: the volume anomaly, characteristic for mixed-valency, remains qualitatively present.

When it comes to the magnetic properties of the Yb-ScCoAl compounds in the light of spin-fluctuation behaviour, it is clear that they fit into this framework. Two slopes in the high-field magnetic isotherms, corresponding with the values of the magnetic susceptibility at zero temperature and at a higher characteristic temperature, are also observed in systems like UAl and UCu [8,9]. However, in pure YbCoAl the occurrence of spin-fluctuations should be excluded on the basis of the absence of an upturn in the specific heat.

In conclusion we find that pressure, induced by alloying with Sc, gradually drives the mixed-valent Yb in YbCoAl into a region where critical behaviour appears next to mixed valency. The spin-fluctuation contribution to the physical properties increases with pressure.

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Fig. 10. (Data for this plot have been taken from table 1, ref. 7.)
MIXED VALENCE IN CeNi₅: EFFECTS OF DILUTION AND CHEMICAL PRESSURE

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X-ray $L_{III}$ absorption measurements were employed to determine the (mixed) valence of the system $R_9Ce_5Ni_5$, where $R = La$, Pr, Gd, Er or Lu. The valences obtained spanned only the narrow range 3.13–3.16 in going from La to Lu, compared to 3.15 for the stoichiometric compound CeNi₅. These results establish the extreme insensitivity of the mixed valence of CeNi₅ to dilution effects, and, hence, that it is a local site phenomenon. Moreover, the valence is relatively insensitive to chemical pressure-induced lattice constant changes as large as 3 or 4%.

MIXED VALENT cerium-based metallic systems exhibit behavior which is irreconcilable within the Anderson lattice (or promotional) model, which describes the mixed valent state in terms of an admixture of $4f^m$ and $4f^{m-1}c^{m+1}$ states, where $c$ refers to the conduction electrons [1]. In particular, the valence, as determined by core level photoemission or X-ray absorption, is considerably smaller than implied by either the volume or the magnetic susceptibility [1–3]. Because of the relatively large spatial extent of the cerium $4f$ wave function, hybridization effects are expected to play an important role [4], in contrast to Sm-, Eu-, Tm- and Yb-based systems, all of which are well described by the promotional model [1].

In the presence of strong hybridization effects, one might expect dilution of the Ce ions in mixed valent Ce compounds to alter dramatically the degree of the $4f$ instability, and, hence, the valence; particularly, if such hybridization effects were to lead to itinerant bands with $f$-character. The study reported herein was designed to probe such dilution effects without changing the size of the unit cell or producing significant changes in the electronic band structure. The system CeNi₅ was chosen because it is moderately strongly mixed valent among Ce-based systems; and, the relatively small atomic number of Ni compared to that of Ce allowed the determination of the valence from X-ray $L_{III}$ absorption experiments to be made at relatively small Ce-concentrations (i.e., down to $x = 0.1$ in the formula unit $R_{1-x}Ce_xNi_5$).

X-ray absorption measurements, particularly of the $L_{III}$ edge, provide a convenient and direct method of determining the mixed valence of rare earth compounds. In the presence of a $4f$ hole, the $L_{III}$ edge, corresponding to an excitation of the $2p$ core hole, is shifted by approximately 10 eV to higher binding energy. The ratio of the intensities of the two edges, corresponding to the final states $2p^04f^0(5d6s)^2$ and $2p^2f^0(5d6s)^2$, where $2p^0$ refers to a $2p$-hole, is a direct measure of the ratio of the $f^0$ and $f^0$ components in the ground state [1]. There have been several conjectures that this simple picture may be spoiled by final state shake-up or shake-down effects [5]. However, it has been recently argued [6], based upon a study of $L_{III}$ edges in a number of Ce-based intermetallics, along with their La- and Pr-based isomorphs, that such final state effects, being small, do not alter appreciably the apparent valence determined from the ratio of the two $L_{III}$ edges. Hillebrecht and Fuggle [7] have reached similar conclusions concerning the use of core level photoemission for determining the (mixed) valence in metallic Ce-based systems.

The following compositions were chosen for the study: $LaNi_5$, $CeNi_5$ and $R_9Ce_5Ni_5$ ($R = La$, Pr, Gd, Er or Lu). The samples were prepared by arc-melting the constituents in an inert atmosphere. The five pseudobinary compounds were annealed at $800^\degree C$ for 3 days to ensure homogeneity. X-ray powder diffraction studies confirmed that all the compositions formed the hexagonal CaZn₅ structure; and no extraneous phases could be detected. The samples for the X-ray absorption study were prepared by powdering the material and then hermetically sealing it in a suitable tape sandwich whose thickness fell in a region for which the shape of the Ce–$L_{III}$ edge was established experimentally to be thickness-independent. The $L_{III}$ edge studies were performed in transmission at Cornell University synchrotron facility (CHESS) using X-rays emitted by the storage ring (CESR) operating at 5.3 GeV. A CHESS-built monochromator using two Si (111) crystals offset by 8 cm and mounted 11 m from the source gave a resolution of about 1 eV at the Ce–$L_{III}$ edge.

The results of the X-ray absorption studies are shown in Fig. 1. It is immediately apparent that there is very little change in the Ce–$L_{III}$ double edge...
Fig. 1. La $L_{III}$ absorption edge for LaNi$_5$ and Ce $L_{III}$ edges for CeNi$_5$ and $R_{0.8}Ce_{0.2}Ni$_5$ ($R = \text{La, Pr, Gd, Er or Lu}$) at 300 K. Only relative energies are shown on abscissa. The primary edge (lower energy edge in the case of Ce) occurs at about 5483 eV in LaNi$_5$ and about 5724 eV in the Ce compounds.

signature between CeNi$_5$ and the dilute Ce-pseudobinaries; however, there is a slight increase in the relative strength of the high energy ($f^0$) edge as the series is traversed from $R_{0.8}Ce_{0.2}Ni$_5 to Lu$_{0.8}Ce_{0.2}Ni$_5. In order to extract the ratio of the two edge intensities, and hence the (mixed) valence, the following method was employed. A Gaussian with linearly decreasing tail on the high energy side, imposed on a background with a step discontinuity at the peak maximum, was found to fit the LaNi$_5$ quite well. This function was then fit to each of the two edges in the Ce-based systems. The background step and slope, and the width of the Gaussian were constrained to be the same for the low energy edge throughout the series; however, these parameters were allowed to vary for the second edge. The contribution of each edge was determined by integrating the fitting function from 8 eV below to 8 eV above the maximum. The integration was truncated above the edge since small errors in determining the high energy tail would spoil the peak intensity determination if the integration were extended to high energy.

The (mixed) valence of the Ce-ions, given by $3 + B(A + B)$, where $A$ and $B$ are the intensities of the low ($f^0$) and high ($f^1$) energy edges respectively is shown in Fig. 2(a) for the various systems studied. The Ce-valence determined in the above manner is expected to be internally consistent among the various samples studied; however, the absolute value is sensitive to the fitting procedure, as evidenced by variations in the reported values of the valence of mixed valent compounds from different laboratories, determined from spectra which are visually indistinguishable. It is of interest to compare our value (3.15) for CeNi$_5$ to that obtained in other laboratories from 3d-core level photoemission (3.15–3.20 [2]; 3.12–3.16 [8]) and $L_{III}$ absorption (3.32) [3]. It should be kept in mind that $L_{III}$ absorption is a bulk technique; whereas 3d-photoemission samples only a few atomic layers at the surface. However, a comparison of 3d-photoemission spectra of Ce-intermetallics with 4d-photoemission spectra [8], and also X-ray absorption spectra [2, 9, 10], suggest that the valence is shifted not appreciably if at all, at the surface.

In Fig. 2(b) are shown the lattice constants $a$ of LaNi$_5$, CeNi$_5$ and the five pseudo-binaries, as determined by X-ray powder diffraction. The $c$-axis lattice constant varies only weakly through the series. Compared to CeNi$_5$, the La and Pr samples represent negative lattice...
pressure on the Ce-ions; whereas, Er and Lu represent positive pressure. The Gd sample, which has approximately the same lattice constant as CeNi$_5$, provides a matrix in which dilution effects can be examined in the absence of chemical pressure effects. The fact that the valence of Ce$_{0.1}$Gd$_{0.9}$Ni$_5$ is essentially identical to that of CeNi$_5$ implies that the mixed valence in CeNi$_5$ is a local site phenomenon.

The extremely weak dependence of valence on chemical pressure seen in Fig. 2 distinguishes CeNi$_5$ from elemental f.c.c. cerium, where lattice pressure dramatically affects the 4f-instability [11, 12]. Several studies similar in purpose to the one reported here have been made on pseudo-binaries based on CePd$_3$. Dilution of Ce by La (up to 30% La) in CePd$_3$ produces an expansion of the lattice, an apparent decrease in the 4f stability as evidenced by a decrease in the magnetic susceptibility [13], yet no detectable change in the valence as determined from Ce--L$_{III}$ edge spectra [14]. The dilution of Ce by Y in CePd$_3$ produces a contraction of the lattice and a concomitant decrease in the 4f stability as evidenced in the magnetic susceptibility [13, 15]. On the other hand, the dilution of Ce by Th produces a contraction of the lattice, but an apparent increase in the 4f stability as evidenced by a decrease in the (mixed) valence, as determined from Ce--L$_{III}$ edge spectra [14]. The present study differs from the ones discussed above in that both negative and positive lattice pressures, relative to CeNi$_5$, were achieved by using additives expected to alter in no significant way the nature of the chemical bonding or the electronic band structure. Yttrium and thorium are chemically different than the lanthanides since their atomic outer electron configurations are (4d$^5$5s$^2$) and (6d$^1$7s$^2$) respectively. Moreover, since Th is tetravalent, its addition to CePd$_3$ is expected to produce band-filling of the Pd-derived d-bands. It is suggested by the results of valence band photoemission studies of CePd$_3$ and CeRh$_3$ [16], that such band-filling should have the effect of markedly decreasing the transition metal-derived d-density-of-states in the region near $E_F$. The study of La-substituted CePd$_3$, which is presumed free of the aforementioned chemical effects, is limited only to 30--40% La in the Ce-phase, because of a first-order volume instability which occurs at higher La concentration [14].

Several theoretical ideas have been advanced in an attempt to reconcile the anomalous behavior of mixed valent Ce-based systems; in particular, the failure of the promotional model to connect the observed (mixed) valence to the observed volume and magnetic susceptibility. Allen and Martin [17] propose a Kondo lattice approach, where the volume and susceptibility can be smaller than suggested by the valence, because of a volume collapse driven by the Kondo effect, with a concomitant increase in the Kondo temperature, and, hence, the spin fluctuation rate. Fujimori [18] introduces a new mixing term involving the interaction between the 4f electrons and the ligand states of the nearest neighbor atoms. This produces a new component in the ground state, viz., a spin-singlet, totally symmetric 4f$^1$--L$^{-1}$ excited state, where L$^{-1}$ denotes a nearest neighbor ligand-hole state. This component of the ground state favors a reduced volume and reduced susceptibility, but would register as an f$^1$ signature in core level photoemission or Ce--L$_{III}$ edge spectra. Yet a third approach, also in its infancy, is one by Schütler and Varma [19], which explores the possibility of a bimodal radial distribution of f-charge on the Ce-site.

The above theoretical directions suggest the need for additional experiments of the genre of the one presented here. In all three approaches, it is possible conceptually to change the volume and the degree of the 4f instability, as registered in the magnetic susceptibility or inelastic neutron scattering, without changing appreciably the (mixed) valence, as determined by high energy spectroscopic probes. In the Fujimori approach the 4f instability depends strongly on the nearest neighbor-derived density of ligand states; whereas, in the Allen--Martin approach it depends strongly on the overlap between the 4f-electron and the 5d-electron. Hence, in the design of experiments, particularly those involving chemical additives, it is important to control and distinguish between the latter effects.

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5. See references cited in [6].
Effet d'une pression chimique locale sur la structure cristalline de CaFe$_2$O$_4$ 
par
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RÉSUMÉ. — On étudie l'effet de la substitution des ions Ca$^{2+}$ du ferrite monoclinique orthorhombique CaFe$_2$O$_4$ par des cations de taille plus petite.
Cette substitution est partielle si le cation substituant est Mg$^{2+}$, Mn$^{2+}$, Co$^{2+}$ ou Ni$^{2+}$.
Elle conduit à Ca$_{1-x}$M$_x$Fe$_2$O$_4$ (x ≤ 0,25) dont la structure n'est pas de type CaFe$_2$O$_4$ mais de type Ca$_{1-x}$MFe$_2$O$_4$, de symétrie monoclinique. La structure de la phase substituée est en expansion par rapport à celle du ferrite initial et la coordination cationique globale diminue. 
Ce résultat, paradoxal en apparence, est discuté en terme de pression chimique locale sur les polyédres de coordination.

ABSTRACT. — The authors study the effect of substituting the Ca$^{2+}$ ions by various smaller cations in monoclinic ferrite CaFe$_2$O$_4$ which crystallizes in the orthorhombic symmetry.
If the substituting cation is Mg$^{2+}$, Mn$^{2+}$, Co$^{2+}$ or Ni$^{2+}$, the substitution is incomplete. It leads to Ca$_{1-x}$M$_x$Fe$_2$O$_4$ (x ≤ 0,25) the structure of which is not the CaFe$_2$O$_4$ type but the Ca$_{1-x}$MFe$_2$O$_4$, type with monoclinic symmetry. The substituted ferrites have a more expanded structure than the initial one and the overall cation coordination number decreases.
This apparently paradoxical result is discussed in terms of the local chemical pressure on the coordination polyhedra.

INTRODUCTION

Le ferrite monoclinique CaFe$_2$O$_4$ cristallise dans le système orthorhombique, Pna1, avec les paramètres suivants [1, 2] :
\[ a = 9,230 \; \text{Å}, \quad b = 10,705 \; \text{Å}, \quad c = 3,024 \; \text{Å}, \quad V = 299 \; \text{Å}^3 \]
\[ Z = 4, \quad V_{formule} \approx 75 \; \text{Å}^3, \quad \rho = 4,8 \; \text{g cm}^{-3}, \]

REvue de Chimie Minérale, 0015-1032/86/6 782 01/8 2.70/© Gauthier-Villars
Dans cette structure tous les atomes sont en symétrie ponctuelle m, site 4c de Wyckoff (fig. 1).

Les six atomes d’oxygène premiers voisins du calcium forment un prisme à base triangulaire : \( \langle \text{Ca} - 0 \rangle = 2.42 \, \text{Å} \). Comme seconds voisins viennent ensuite deux oxygènes à 2.53 et 2.58 Å (tableau 1).

Les atomes de fer trivalent, Fe(I) et Fe(II), occupent deux sites octaédriques déformés où :

\[
\langle \text{Fe(I)} - 0 \rangle = 2.05 \, \text{Å}, \quad \langle \text{Fe(II)} - 0 \rangle = 2.03 \, \text{Å}.
\]

La distorsion peut être estimée par la valeur

\[
\frac{1}{6} \sum \left( \frac{d_{0} - d} {d} \right)^2 = \text{dist}.
\]

\[\text{dist [Fe(I)]} = 1.8 \times 10^{-4}, \quad \text{dist [Fe(II)]} = 5 \times 10^{-4}.\]

![Diagram of CaFeO₄ structure](image)

Fig. 1. – Structure de CaFeO₄ : projection sur le plan (010).

Le spectre Mössbauer enregistré à 295 K [3] est une superposition de deux doublets de même intensité, de même déplacement isomérique : \( \delta = 0.37 \, \text{mms}^{-1} \), d’éclatements quadrupolaires différents :

\[\Delta_{\text{Fe(II)}} = 0.30 \, \text{mms}^{-1}, \quad \Delta_{\text{Fe(III)}} = 0.72 \, \text{mms}^{-1}.\]

Nous allons comparer CaFeO₄ au ferrite de cadmium CdFeO₄ qui cristallise dans la structure spinelle directe avec pour paramètres [4] :

\[a = 8.698 \, \text{Å}, \quad m = 0.390 \pm 0.003, \quad V_{\text{formulaire}} = 82 \, \text{Å}^3.\]
En prenant 0,393 comme valeur la plus probable de \( u \) (mesure de Sawicki), on calcule :

\[
\begin{align*}
\text{Cd} - \text{O} &= 2,15 \text{Å}, \\
\text{Fe} - \text{O} &= 2,03 \text{Å}.
\end{align*}
\]

F. Menil [5] donne \( \delta_\text{Fe} = 0,37 \text{ mm}^{-1} \) comme déplacement isomérique des ions Fe\(^{3+}\) en site octaédrique.

Dans ces deux ferrites, le fer ayant la même coordonnée et le même déplacement isomérique, on peut affirmer que la liaison Fe-O a le même degré d'ionicité.

Cd\(^{2+}\) (4\( d^{10} \)) est légèrement plus petit que Ca\(^{2+}\) (3\( s^2 \) 3\( p^6 \)) [dans la même coordonnée VI : R Ca\(^{2+}\) = 0,95 Å, R Ca\(^{2+}\) = 1,00 Å (6)]. Cette faible différence suffit cependant à provoquer un changement radical de structure qui globalement se traduit par une diminution de la coordinence :

\[ \text{CaFe}_2\text{O}_4 \rightarrow \text{CdFe}_2\text{O}_4, \]

et par une expansion structurale (\( V_{\text{CaFe}_2\text{O}_4} = 75 \text{ Å}^3 \rightarrow V_{\text{CdFe}_2\text{O}_4} = 82 \text{ Å}^3 \)).

### Tableau I

<table>
<thead>
<tr>
<th>Distances métal-oxygène (Å), dans CaFe(_2)O(_4)</th>
<th>Distances calcium-oxygène (Å), dans Ca(_2)Fe(_3)O(_7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Fe(I)}) 2 x 0 2,07  (\text{Fe(II)}) 2 x 0 2,09  (\text{Ca}) 2 x 0 2,51  (\text{Ca(I)}) 1 x 0 2,278  (\text{Ca(II)}) 1 x 0 2,322</td>
<td></td>
</tr>
<tr>
<td>2 x 0 2,07  2 x 0 1,98  2 x 0 2,38  1 x 0 2,284  1 x 0 2,339</td>
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</tr>
<tr>
<td>1 x 0 2,03  1 x 0 2,04  2 x 0 2,37  1 x 0 2,288  1 x 0 2,346</td>
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</tr>
<tr>
<td>1 x 0 2,00  1 x 0 2,02  1 x 0 2,431  1 x 0 2,477</td>
<td></td>
</tr>
<tr>
<td>(d_{\text{dist.}} = 2,051)  (d_{\text{dist.}} = 2,033)  (d_{\text{dist.}} = 2,420)  (d_{\text{dist.}} = 2,436)  (d_{\text{dist.}} = 2,493)</td>
<td></td>
</tr>
<tr>
<td>(d_{\text{dist.}} = 1,8 \times 10^{-4})  (d_{\text{dist.}} = 3 \times 10^{-4})  (d_{\text{dist.}} = 2,53)  (d_{\text{dist.}} = 4,65)  (d_{\text{dist.}} = 2,468)</td>
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</table>

La même corrélation : diminution de la coordinence-expansion structurale s'observe quand, sur CaFe\(_2\)O\(_4\), on réalise la double substitution (Ca\(^{2+}\)-Fe\(^{3+}\)) par le couple (Tm\(^{3+}\)-Fe\(^{3+}\)) de taille moyenne voisine :

\[ \text{R-Ca}^{2+} \text{Fe}^{3+} \text{Fe}^{3+} \text{R} = \text{R-Tm}^{3+} \text{Fe}^{3+} + \text{Fe}^{3+} \text{Fe}^{3+} # 1,65 \text{Å} \]

On aboutit au composé TmFe\(_2\)O\(_4\) qui cristallise dans le système rhomboédrique, \( R \ 3 \ m \), avec pour paramètres, exprimés en repère hexagonal [7] :

\[ a = 3,472 \text{Å}, \quad c = 25,01 \text{Å}, \quad Z = 3. \]

---

**Étude**

### Synthèse de CaFe\(_2\)O\(_4\)

Le ferrié monochloré est obtenu par de CaCO\(_3\) et FeO\(_2\) pendant 24 heures.

### Synthèse de MFe\(_2\)O\(_4\)

Les ferrites MFe\(_2\)O\(_4\) sont obtenus par de mélange Fe\(_2\)O\(_3\)-MO, pendant 24 heures.

### Recuits des mélanges \((1-x)\text{Ca}F\)

Ils sont réalisés en ampoules scellées radiocristalographiques des produits a recuit est mis d'une tremp à l'eau.

Pour \(0 < x < 0,07\), le système type "Ca\(_2\)Fe\(_3\)O\(_7\)" et de CaFe...
PRESSEON CHIMIQUE SUR LA STRUCTURE DE $\text{CaFe}_2\text{O}_4$

$V_{\text{formulaire}} = 87 \text{\AA}^3$.

Le thullium est en site octaédrique, de symétrie ponctuelle $3m$, site $3a$ de Wyckoff, les six distances $\text{Tm} - O = 2.25 \text{\AA}$.

Le fer, bivalent et trivalent, occupe le site $6c (3m)$, de coordinence bipyramidale à base triangulaire.

Donc, sans changer globalement la taille des cations, le passage $\text{CaFe}_2\text{O}_4$ à $\text{TmFe}_2\text{O}_4$ se produit avec expansion structurale (de 75 à $87 \text{\AA}^3$) et diminution globale de la coordinence :

$$\text{CaFe}_2\text{O}_4 \rightarrow \text{TmFe}_2\text{O}_4.$$

Remarquons ici que l'expansion est particulièrement marquée, fait qui est dû à la présence de cations en coordinence $V$.

Toujours en partant de $\text{CaFe}_2\text{O}_4$, nous avons cherché à déterminer les conséquences sur la structure d'une modificaton des contraintes au niveau du site prismatique du calcium. Pour ce faire, nous avons étudié l'influence de la substitution de $\text{Ca}^{2+}$ par un ion divalent $\text{M}^{2+}$ plus petit ($\text{M}^{2+} = \text{Mg}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$), ce qui revient à caractériser les systèmes $\text{CaFe}_2\text{O}_4 - \text{MFe}_2\text{O}_4$ pour des rapports molaires $\frac{\text{M}}{\text{Ca}} \leq 0.33$.

ÉTUDE EXPÉRIMENTALE

Synthèse de $\text{CaFe}_2\text{O}_4$

Le ferrite monocalcique est obtenu par un recuit à $1190^\circ\text{C}$ à l'air, d'un mélange équimolaire de $\text{CaCO}_3$ et $\text{Fe}_2\text{O}_3$ pendant 24 heures.

Synthèse de $\text{MFe}_2\text{O}_4$

Les ferrites $\text{MFe}_2\text{O}_4$ sont obtenus par recuits en ampoules scellées sous vide, à $1000^\circ\text{C}$, de mélanges $\text{Fe}_2\text{O}_3$-M-O, pendant 24 heures.

Recuits des mélanges $(1-x) \text{CaFe}_2\text{O}_4 - x \text{MFe}_2\text{O}_4$ ($x \leq 0.25$)

Ils sont réalisés en ampoules scellées sous vide à $1190^\circ\text{C}$, pendant 24 heures. L'analyse radiocristallographique des produits a donné le même résultat quel que soit M. Chaque recuit est suivi d'une trempe à l'eau.

Pour $0 < x < 0.07$, le système est constitué d'un composé de structure type « $\text{Ca}_3\text{Fe}_5\text{O}_{17}$ » et de $\text{CaFe}_2\text{O}_4$ en excès; pour $0.07 \leq x \leq 0.2$, la phase
type « Ca$_2$Fe$_5$O$_{17}$ » est pure, tandis que pour $x>0.2$ apparait en plus une structure type spinelle de magnétite dopée à la chaux.

L'analyse détaillée des clichés de diffraction aux rayons X de la phase pure ne permet pas de déceler de variations significatives des distances réticulaires avec la valeur de $x$ et la nature de M. Le diffraactogramme correspond à celui de « Ca$_2$Fe$_5$O$_{17}$ », indexé en maille monoclinique C2 de paramètres :

$$
\begin{align*}
& a = 10,441 \text{ Å}, \\
& b = 6,025 \text{ Å}, \\
& c = 14,384 \text{ Å}, \\
& \gamma = 98°80', \\
& V = 708 \text{ Å}^3, \\
& Z = 2, \\
& \rho_{\text{exp}} = 4,42 \text{ g cm}^{-3}.
\end{align*}
$$

La structure de ce ferrite, décrite par B. Malaman et al. [8] se caractérise par des coordinences VI ou VII du calcium (tableau II), mais aussi par un plan de bipyramides trigonales de fer, associé à des tétraédres FeO$_4$ et des octaédres FeO$_6$, ce qui lui confère sa nature expansée (fig. 2).

![Fig. 2. — Structure de « Ca$_2$Fe$_5$O$_{17}$ » : a : Projection schématique sur le plan (010). b : Succession des polyédres de coordination du fer.](image)

Nous avons effectué une mesure de la masse volumique, par pénométrie à la déclive, de Ca$_{0.93}$Co$_{0.07}$Fe$_5$O$_9$ et obtenu 4,47 g cm$^{-3}$, donc en concordance avec celle observée pour « Ca$_2$Fe$_5$O$_{17}$ ». Cette valeur conduit à Ca$_{0.1}$Co$_{0.6}$Fe$_{11.5}$O$_{33}$ comme contenu de maille soit un volume formulaire (Ca, Co)$_3$Fe$_5$O$_{9}$ # 82 Å$^3$.

Pour l'autre limite : Ca$_{0.8}$Co$_{0.2}$Fe$_5$O$_{54}$ on aboutit à Ca$_{0.1}$Co$_{0.2}$Fe$_{11.5}$O$_{33}$ comme contenu de maille.

Ainsi passant de CaFe$_5$O$_9$ à Ca$_{0.93}$Mn$_{0.07}$Fe$_5$O$_9$, on observe une augmentation de volume formulaire de l'ordre de 9% soit une forte expansion structurale.

**TOME 23 — 1986 — N° 6**
Nous avons montré par ailleurs [9] que la réaction entre CaFeO₄ et MO (M = Mg, Co, Ni, Zn), à 1120°C, conduit uniquement à un mélange de ferrite bicalcique et de spinelle.

Donc la réaction \( (1 - x) \text{CaFeO}_4 + x\text{MFeO}_4 \) s'effectue grâce à une substitution du calcium seul et selon un mécanisme qui implique initialement des contraintes au niveau du site prismatique de ce calcium. Comme M²⁺ est plus petit que Ca²⁺, on qualifiera cet effet de pression chimique locale puisque le polyèdre de coordination se contracte.

**DISCUSSION ET CONCLUSION**

Il est généralement établi que l'effet d'une pression chimique locale résultant de la substitution d'un cation donné par un cation plus petit provoque la contraction de son polyèdre de coordination, avec ou sans modification de la coordinence. Dans ce dernier cas, l'incidence de cette contrainte se traduit d'abord par la formation d'une solution solide dont les paramètres cristallographiques obéissent souvent à la loi de Vegard. Un tel comportement n'est pas systématique quand il y a modification de la coordinence.

Nos travaux sur la substitution de l'ion Ca²⁺ par un ion plus petit dans le ferrite monocalcaire confirment la contraction du polyèdre de coordination de Ca²⁺ qui, dans ce cas, provoque un changement de structure. Celui-ci se traduit par une diminution de la somme des coordinences des cations présents (coordinence cationique globale) et par une augmentation du volume formulaire (expansion structurale).

Ces deux points sont en opposition avec ce qui est observé sous l'effet d'une pression physique externe qui s'accompagne en général d'un accroissement de la coordinence et corrélativement d'une densification.

Notre résultat peut donc sembler a priori paradoxal. En fait, il peut s'expliquer de la manière suivante :

La pression chimique s'exerce d'abord au niveau du polyèdre de coordination de Ca²⁺ qui passe de prismatique à tétraédrique ou octaédrique. Pour la substitution

\[ (1 - x)\text{CaFeO}_4 + x\text{MFeO}_4 \rightarrow \text{Ca}_{11-x}\text{M}_x\text{Fe}_2\text{O}_4, \]

les tableaux 1 et 2 montrent que la distance moyenne Ca-O comptée sur les six atomes d'oxygène premiers voisins diminue, ce qui induit une modification de certains polyèdres de coordination du fer qui passe de la
coordonnée octaédrique aux coordonnées tétraédrique, hexaédrique et/octaédrique.

La tension locale au niveau du calcium est donc absorbée par le fer qui
peut, au même degré d’oxydation, s’accommoder de plusieurs coordi-
nences. Globalement, la structure devient moins compacte car l’empilement
des polyédres est plus lâche. Comme en première approximation, ces
oxydes mixtes se décrivent avec le modèle ionique, il est certain que cette
pression chimique accentue le caractère covalent des liaisons métal-oxygène
et c’est pour cette raison que la coordination cationique globale diminue.

En conclusion, la seule définition d’une pression chimique ne permet
pas de prévoir le sens d’évolution des compacités des structures d’oxydes
mixtes, elle peut augmenter si la coordination cationique globale ne change
pas ou diminuer si elle diminue.

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ÉTIQUE

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RÉSUMÉ. — Divers es-
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ABSTRACT. — Fluoride-
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REVOUE DE CHIMIE MINÉRALE

TOME 23 — 1986 — N° 6
HIGH-TEMPERATURE SUPERCONDUCTIVITY IN THE BaPb_{1-x}Bi_{x}O_{3} SYSTEM

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Phases of the type BaPb_{1-x}Bi_{x}O_{3} have been prepared for the first time. These phases all have perovskite related structures, and superconductivity was observed over the range x ≈ 0.05–0.3. The highest critical temperature is 13 K which is exceptionally high for an oxide and is much higher than that previously observed for any superconductor not containing a transition element. Semiconducting behavior is observed from x = 1 to about 0.35.

BaPbO_{3} has been reported\(^1\) with a perovskite-type structure. An orthorhombic cell of a = 6.024 Å, b = 6.065 Å, and c = 8.506 Å has been given by Shannon and Bierstedt.\(^2\) Despite the fact that this is a normal valence compound, BaPbO_{3} has metallic properties.\(^2\) Presumably, BaPbO_{3} as well as PbO_{2} are best described as semimetals.

BaBiO_{3} has also been reported\(^3\) with a perovskite related structure; however, no cell dimensions or physical properties have been given. We have grown bronze colored crystals of BaBiO_{3} hydrothermally. Crystallographic studies indicate a primitive orthorhombic cell with a = 4.343 Å, b = 4.358 Å, and c = 4.333 Å. This cell contains only one formula unit of BaBiO_{3} and it is possible that the true cell is larger as in the case of BaPbO_{3} where x = 4. However, neither Guinier nor single crystal X-ray techniques showed any evidence of a larger cell. Four-probe electrical resistivity data were obtained from 4.2–970 K. Semiconducting behavior is indicated over this entire range with a room temperature resistivity of about 10 Ω·cm and an activation energy of about 0.2 eV. Since BaBi^{4+}O_{3} would presumably be a metal, we can probably assume the situation to be Ba_{2}Bi^{3+}Bi^{4+}O_{6}.

Compositions of the type BaPb_{1-x}Bi_{x}O_{3} were prepared by heating appropriate mixtures of oxides, carbonates or nitrates in air at 800–1000°C. A complete solid solution between BaPbO_{3} and BaBiO_{3} apparently exists. The pseudocubic cell edge \(V/\sqrt{2}\) vs x is plotted in Fig. 1. The phase appears black up to

\[ \text{FIG. 1. } a \alpha x \text{ in the BaPb}_{1-x}\text{Bi}_{x}O_{3} \text{ system where } a = \sqrt{V/2} \]

x ≈ 0.3, but the color is bronze-like for higher values of x. Electrical resistivity measurements on pellets indicate semiconducting behavior for all the bronze-colored phases and metallic properties for all the black phases.

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\(^1\) Contribution No. 2245

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Superconductivity has been observed in the \( \text{BaPb}_{1-x}\text{Bi}_x\text{O}_3 \) system from \( x = 0.05 \) to 0.3. Meissner Effect measurements indicate that the critical temperature increases from about \( 9 \, \text{K} \) at \( x = 0.05 \) to a maximum of about \( 13 \, \text{K} \) at \( x = 0.3 \). A sample with \( x = 0.35 \) was not superconducting at \( 4.2 \, \text{K} \). The superconducting transitions were not always sharp as found by the Meissner Effect measurement; thus, the critical temperatures reported represent the onset of superconductivity. Compositions of the type \( \text{Ba}_{1-y}\text{A}_y\text{Pb}_{1-x}\text{Bi}_x\text{O}_3 \) where \( A \) is an alkali cation and \( y \) is 0.1 to 0.2 give similar critical temperatures, but the transitions are sharper. The reason for the broad transitions in some cases is not certain, but they may be related to nonrandom distributions of \( \text{Pb} \) and \( \text{Bi} \).

Four-probe electrical resistivity data for a \( \text{BaPb}_{0.5}\text{Bi}_{0.5}\text{O}_3 \) crystal are shown in Fig. 2. The temperature dependence is metallic-like from 298 to 11 K.

![Graph showing electrical resistivity vs temperature for a crystal of \( \text{BaPb}_{0.5}\text{Bi}_{0.5}\text{O}_3 \).](image)

**Fig. 2.** Electrical resistivity vs temperature for a crystal of \( \text{BaPb}_{0.5}\text{Bi}_{0.5}\text{O}_3 \).

However, at 11 K the resistivity drops abruptly to less than \( 10^{-6} \, \text{Ω} \cdot \text{cm} \). A pellet of \( \text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3 \) also clearly showed a drop of electrical resistivity at about the same temperature; thus, grain boundaries do not have detrimental effects on the superconductivity of this material.

A schematic energy level diagram for \( \text{BaPb}_x\text{O}_y \) is shown in Fig. 3. The lead–oxygen bonding is highly covalent. Therefore, the oxygen 2p band has considerable lead character and the lead 6s band has considerable oxygen character. Electrons may directly enter the 6s band as \( x \) increases in the \( \text{BaPb}_{1-x}\text{Bi}_x\text{O}_3 \) series. However, the 6s band may also narrow and lead to its splitting as \( x \) increases. The narrowing could cause an increase in the density of states at the Fermi level and consequently an increase in the superconducting critical temperature. The 6s band would split at \( x = 0.35 \), and semiconducting properties are observed at higher values of \( x \). Although this model is qualitatively satisfying, the assumptions of a rigid band may be very misleading. It is not at all certain that the 6s state will mix completely into the Pb 6s band. The situation is very different than in the tungsten bronze \( (A_x\text{WO}_3) \) where the states are not directly changed as \( x \) increases.

**Fig. 3.** Schematic energy level diagram for \( \text{BaPb}_x\text{O}_y \).

### References

HYDROSTATIC PRESSURE EFFECT ON \( T_c \) OF Ba\(_{0.6}\)K\(_{0.4}\)Pb\(_{0.75}\)Bi\(_{0.25}\)O\(_3\)

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The superconducting transition temperature of Ba\(_{0.6}\)K\(_{0.4}\)Pb\(_{0.75}\)Bi\(_{0.25}\)O\(_3\) has been found to be suppressed smoothly by the application of hydrostatic pressure at a rate of \(- (2.9 \pm 0.2) \times 10^2\) kbar\(^{-1}\) up to 15 kbar. The implications of these results are discussed.

Both BaPb\(_2\)O\(_4\) and BaBiO\(_3\) exhibit perovskite-type structure but with slightly different symmetries. They were recently found\(^2\) to form a solid solution, BaPb\(_{1-x}\)Bi\(_x\)O\(_3\), with Pb- and Bi-atoms occupying the octahedral sites. Wide range of electrical resistance behavior was also found\(^3\) in this solution. The system is metallic for \( x < 0.3 \) while semiconducting otherwise. Superconductivity was observed in the composition range of \( 0.05 < x < 0.3 \) with an onset transition temperature \( T_c \) increasing from \( \sim 9 \) K at \( x = 0.05 \) to \( \sim 13 \) K at \( x = 0.3 \) near the metal–semiconductor phase boundary. Samples with \( x = 0 \) and 0.35 are not superconducting down to 4.2 K. A \( T_c \) of 13 K in BaPb\(_{1-x}\)Bi\(_x\)O\(_3\) system is the highest yet observed in compounds not containing any transition elements. The drastic variation of \( T_c \) with \( x \) was explained\(^2\) in terms of the narrowing of the \( \pi \)-conduction band, consisting of the Pb- and Bi-6s states, as \( x \) increases. The semiconducting nature of the compounds with \( x > 0.3 \) was then attributed to the splitting of the 6s-conduction band and consequently the creation of a gap near the critical concentration.

The results of the present investigation show that:

1. \( d \)-electrons may have participated in the occurrence of superconductivity in the BaPb\(_{1-x}\)Bi\(_x\)O\(_3\) system,
2. the broad superconducting transition of the system seems likely to be caused by the concentration inhomogeneity near the metal–semiconductor phase boundary, and
3. the superconductivity in the system is a bulk effect.

Superconducting BaPb\(_{1-x}\)Bi\(_x\)O\(_3\) compounds always show a broad transition.\(^3\) However, it has been demonstrated\(^3\) that the substitution of 10–20% of the Ba in the compound by an alkaline element will sharpen the superconducting transition with little change in the onset of the transition temperature. Therefore high pressure study was carried out only on two powder samples of Ba\(_{0.6}\)K\(_{0.4}\)Pb\(_{0.75}\)Bi\(_{0.25}\)O\(_3\). The procedure for sample preparation was previously described elsewhere.\(^5\) The Pb–Bi composition of the samples examined was near the critical concentration where \( T_c \) is maximum and the concentration-induced metal–semiconductor transition occurs. The superconducting transition was detected by a standard ac inductance bridge operating at 10 Hz. The temperature was determined by a Ge-thermometer. The hydrostatic pressure environment was provided by a self-clamp technique.\(^4\) A fluid mixture of 1:1 n-pentane and isomyl alcohol was used as the pressure medium. The reproducibility of \( T_c \) after immersing the sample in the pressure medium for a week indicated the high chemical stability of the sample in the pressure medium. The pressure at low temperature was measured by a Pb-manometer surrounded by the powdery sample. The superconducting signal of one of the samples at atmospheric pressure was plotted in Fig. 1 as a function of temperature. The transition was still broad even with the K-substitution. The onset of the transition shown as a small maximum in the a.c. susceptibility curve was (11.73 ± 0.02) K, which is about 1 K lower than the maximum superconducting onset temperature previously reported\(^3\) for the system. This can be caused by one or more of the following reasons: the slightly smaller \( x \) of the present samples, the possible difference in temperature calibrations and the different measuring techniques employed. The bulk of the transition occurs between 11 and 7 K as shown in Fig. 1. At 5.1 K, 95% of the sample was estimated to be superconducting. Further
HYDROSTATIC PRESSURE EFFECT ON $T_c$ OF Ba$_{0.5}$K$_{0.5}$Pb$_{0.75}$Bi$_{0.25}$O$_3$

with pressure up to $\sim 15$ kbar at a rate of $\sim 10^{-3}$ kbar$^{-1}$. The vertical bar represents the uncertainty in defining $T_c$. The same results were obtained for the other sample.

It has been demonstrated that the volume effect on $T_c$ can be expressed as $d \ln (T_c/\theta)/dT = \phi \ln (\theta/T_c)$, where $\theta$ is the Debye temperature, $\Phi$ the volume and $\phi$ a material dependent constant. For nontransition metal (or sp$^2$) superconductors, $\phi \sim 2.5$, while for the transition metal (or d) superconductors, $\phi \ll 2.5$ and can become negative. The lack of knowledge of $\theta$ and the compressibility of BaPb$_{1-x}$Bi$_x$O$_3$ system prevents us from making use of this procedure to assess the different roles played by electrons in different bands. However, an alternative approach was adopted. By examining all available data on the relative pressure effect of $T_c$, i.e., $d \ln (T_c/\theta)/dT$, we found that generally values of $d \ln (T_c/\theta)/dT$ fall into two groups with $d \ln (T_c/\theta)/dT = 4 \times 10^{-4}$ bar$^{-1}$ for the sp$^2$ superconductors, but $> 2 \times 10^{-3}$ bar$^{-1}$ for superconductors with d-electrons in their conduction band, and the value is not sensitive to impurity except for cases where a pressure of impurity-induced Fermi surface topology change takes place. Since $d \ln (T_c/\theta)/dT$ for BaPb$_{1-x}$Bi$_x$O$_3$ is $\sim 1.7 \times 10^{-4}$ bar$^{-1}$, it is suggested that electrons from the d-band may contribute significantly to the high $T_c$ of the system due to the 5d-2p and/or 5d-6s hybridizations and the system may show a large critical field.

The abrupt disappearance of superconductivity following the $T_c$-peak strongly suggests a drastic change in the electron energy spectrum of BaPb$_{1-x}$Bi$_x$O$_3$ as $x$ becomes larger than $\sim 0.3$, in spite of the fact that no apparent anomaly was detected at $x \sim 0.3$ in the size of the pseudocubic cell of the system. This makes it all the more tempting to propose that the metal-semiconductor transition is electronic in nature. Such an electronic instability can be due to the large density of state which varies drastically with concentration or the particular shape of the Fermi surface of the system near the critical concentration. This would result in the splitting of the conduction band and the creation of an energy gap associated with the semiconducting phase, as previously suggested. The broad superconducting transition of the system can then be easily attributed to a concentration inhomogeneity (or fluctuation) near the metal-semiconductor phase boundary, instead of any internal strain due to the possible presence of a small two phase region near the critical concentration in view of the small pressure effect on $T_c$ observed. Experiments to provide further evidence are in progress.

Finally, we would like to point out that all known high $T_c$ oxide systems (BaPb$_{1-x}$Bi$_x$O$_3$, PbTi$_1-x$O$_3$, La$_2$WO$_6$, $A_x$WO$_6$, with $A$ as an alkaline or alkaline earth atom) have the following in common: (1) superconductivity

Fig. 1. Temperature dependence of the superconducting transition curve of a powder sample of Ba$_{0.5}$K$_{0.5}$Pb$_{0.75}$Bi$_{0.25}$O$_3$ as determined by an a.c. inductive method. The arrow defined the onset of the transition.

Fig. 2. Hydrostatic pressure effect on the onset temperature of the superconducting transition of Ba$_{0.5}$K$_{0.5}$Pb$_{0.75}$Bi$_{0.25}$O$_3$.

reduction in temperature did not increase the superconducting signal size. Because of the broad transition, hydrostatic pressure effect was determined only on the onset of the superconducting transition temperature $T_c$. The results were shown in Fig. 2. $T_c$ decreases smoothly.
HYDROSTATIC PRESSURE EFFECT ON $T_c$ OF $\text{Ba}_{0.8} \text{K}_{0.2} \text{Pb}_{0.25} \text{Bi}_{0.75} \text{O}_{3}$

occur only over a limited range of $x$, and the superconducting phase usually is sandwiched between a conducting and a semiconducting phase. (2) $T_c$ increases rapidly at $x$ approaches the semiconducting phase boundary and disappears abruptly beyond the phase boundary, and (3) they all have atoms occupying the octahedral sites with six oxygen nearest neighbors. Further study is underway way to look for possible pressure or temperature induced electronic transition in $\text{BaPb}_{1-x} \text{Bi}_{x} \text{O}_{3}$ and to understand the causes responsible for the peculiar superconducting behavior in these high $T_c$ oxide systems.

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The Structure of La$_2$CuO$_4$ and LaSrVO$_4$*

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We have examined the structure of La$_2$CuO$_4$ at room temperature and found it to be an orthorhombic distortion of the K$_2$NiF$_4$ structure with $a = 5.363$ Å, $b = 5.409$ Å, $c = 13.17$ Å. Refinement of position parameters, based on powder X-ray diffraction data, shows the copper to have two long Cu-O distances (2.40 Å) and four shorter distances (1.90 Å). The orthorhombic unit cell becomes tetragonal at 260 K without any significant change in Cu-O distances. The magnetic susceptibility of La$_2$CuO$_4$ is less than 10$^{-4}$emu/mol from room temperature to 4.2 K and in fields to 17 kOe. We have prepared LaSrVO$_4$ by reaction of component oxides in vacuum at 1000 C. The new compound has a tetragonal K$_2$NiF$_4$ structure with $a = 3.869$ Å and $c = 12.632$ Å. Optimization of position parameters gave two longer V-O distances (2.09 Å) and four shorter (1.94 Å).

Compounds with the general formula $A_2BY_4$ generally have the tetragonal K$_2$NiF$_4$ structure when the radius of the A cation is $1.0 < r_A < 1.9$ Å, the radius of the B cation is $0.5 < r_B < 1.2$ Å and X is an anion such as oxygen, fluorine or chlorine. The larger A cation has nine-fold coordination and the smaller B cation has octahedral coordination (Fig. 1). This structure can be described as containing alternate layering of perovskite $(ABy_3)$ and rock-salt $(XY)$ units with the nine-coordinated A cation having a surrounding that is the average of what it would be in perovskite and rock salt. This $A_2BY_4$ composition is one end member of a series of structurally related compounds with the general formula $A_2XY_4$, where $n = 1, 2, 3$ and x. As n increases, the rock salt layer is separated by a larger number of perovskite units until there are three. There are no known examples for $n$ between 2 and 3 (the perovskite end member).

Materials with the K$_2$NiF$_4$ structure exhibit a wide range of magnetic and electrical properties. The investigation of these properties has given insight into the important and structurally related compounds with the perovskite structure.

As part of our broad program to investigate the properties of interesting and potentially useful transition metal compounds, we have examined various aspects of materials with K$_2$NiF$_4$-related structures (2). In this paper, we report on the structure of La$_2$CuO$_4$, the effect of temperature on the structures of La$_2$CuO$_4$ and Pr$_2$CuO$_4$, and the preparation and structure of LaSrVO$_4$.

La$_2$CuO$_4$ ($A = La$, Pr)

Many workers (3-7) have reported on the preparation and characterization of Ln$_2$CuO$_4$ (Ln = La-Gd). These compounds, with the exception of La$_2$CuO$_4$, have the tetragonal K$_2$NiF$_4$ structure. The structure of La$_2$CuO$_4$ has been described as "more complex" (2-3) or "different" (6) than Ln$_2$CuO$_4$ (Ln = Pr-Gd).

We prepared La$_2$CuO$_4$ by the solid-state reaction of dried La$_2$O$_3$ and CuO. The well ground mixtures of components were fired at 1000-1200 C in air for a few days with frequent regrinding. This procedure was sufficient to yield single phase La$_2$CuO$_4$ as determined by X-ray diffraction. This same technique was used to prepare Pr$_2$CuO$_4$. After examination of the complete powder pattern for La$_2$CuO$_4$, we were able to index all diffraction peaks using an orthorhombic unit cell that is closely related to...
La₂CuO₄ and LaSrVO₄

Fig. 1. The tetragonal K₂NiF₄ structure.

that of tetragonal K₂NiF₄ through the relationship:

\[ a₀ \approx \sqrt{2} a_1, \quad b₀ \approx \sqrt{2} b_1, \quad c₀ \approx c_r. \]

Refinement of lattice parameters was accomplished with a computer program developed in our laboratory which minimizes the differences in observed and calculated 2θ values. Using 20 line positions as read from a slow-scanned (1/4°, min) diffractometer pattern, we obtained for La₂CuO₄:

\[ a = 5.363(5) \text{ Å}, \quad b = 5.409(5) \text{ Å}, \quad c = 13.17(1) \text{ Å}. \]

A similar distortion of the K₂NiF₄ structure has been found for La₂CoO₄ (8) and β-Na₂UO₂ (9-11).

In order to confirm the structure of La₂CuO₄ and determine interatomic distances, we refined the position parameters and temperature factors by minimizing the differences between our observed X-ray intensities and those calculated on the basis of an orthorhombic distortion of the tetragonal K₂NiF₄ structure. Integrated intensities for La₂CuO₄ were obtained on a General Electric XRD-5 diffractometer by accumulating both time and counts while scanning through a peak at 1/2 of the full width at half maximum and subtracting total background as determined from a smooth plot of minimum background data. Where two or more peaks overlapped, they were grouped and assigned a single intensity value. Calculation of intensities was made assuming space group \( Fmmm \) and placing the atoms as given in Table 1.

The scattering factors for La²⁺, Cu²⁺ (12) and O²⁻ (13) were corrected for the real and imaginary part of the anomalous dispersion term (14). The theoretical polarization term for a LiF-crystal diffracted-beam monochromator was also applied to our data. The two variable position parameters \( \epsilon_{La} \) and \( \epsilon_{O} \) and the atomic temperature factors were refined by minimization of

\[ R = 100 \times \frac{\sum |I_{o}-I_{c}|}{\sum I_{o}} \]

using a program developed in our laboratory. During the refinement based on twenty four intensities between 2° and 100° (29), the value of the atomic temperature factors for O1 \( (B_{0}) \) rose to an unusually high value of 4.0.

The results of our final refinement (with \( R = 2.4 \)) are listed in Table 1 and a comparison of observed and calculated intensities is given in Table II. Fixing the value of \( B_{0} \) and \( B_{2} \) at 1.5 changed \( R \) to 2.8 but did not change any of the variables beyond their stated error limits. Even

| TABLE I |
|-----------------|-----------------|
| CRYSTALLOGRAPHIC DATA FOR La₂CuO₄ |
|-----------------|-----------------|
| Unit cell dimensions: | \( a = 5.363(5) \text{ Å}, \quad b = 5.409(5) \text{ Å}, \quad c = 13.17(1) \text{ Å} \) |
| Space group: | \( Fmmm \) (No. 69) |
| Cell contents: | four La₂CuO₄ faces centered translations applied to: |
| La in (8): | 0, 0, 0, 0, 0, 0, 0, 0 |
| Cu in (4c): | 0, 0, 0, 0, 0, 0, 0, 0 |
| O1 in (8): | 0, 0, 0, 0, 0, 0, 0, 0 |
| O2 in (8): | 1/4, 1/4, 0, 1/4, 1/4, 1/4, 1/4, 1/4 |
| Refined parameters: | \( \epsilon_{La} = 0.362(1), \quad \epsilon_{O} = 0.18(2) \) |
| \( B_{0} \) (A²) | \( B_{1} = 0.71(1) \text{ Å}², \quad B_{2} = 0.61(1) \text{ Å}², \quad B_{3} = 1.35(1) \text{ Å}² \) |

* Value in parentheses is estimated error in last place of number.
### TABLE II

Comparison of Observed and Calculated X-ray Diffraction Data for Orthorhombic La$_2$CuO$_2$

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<th>$d_{obs}$</th>
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<th>$I_{calc}$</th>
<th>$I_{max}$</th>
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<th>$hkl$</th>
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<th>$I_{max}$</th>
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</table>

$^*$

Though we have very good agreement between observed and calculated intensities, the high value of $R_{wp}$ and the poor agreement for the [400], [040], [513], and [153] reflections indicate that the true structure of La$_2$CuO$_2$ probably has symmetry lower than that required by the space group $Fmmm$. Kowba (11) has recently reported as a result of single crystal studies that the structure of $\beta$-Na$_2$UO$_3$ has $Pbcb$ symmetry instead of $Fmmm$ as earlier reported (9, 10) on the basis of powder patterns.

Though some question still remains concerning the exact structure of La$_2$CuO$_2$, the general nature of the structure is not in doubt. The most striking feature of structure is the two long Cu-O distances (2.40 Å) and the four short Cu-O distances (1.90 Å). The average Cu-O distance (2.07 Å) is in good agreement with that predicted (2.08 Å) when the "effective ionic radii" of Shannon and Prewitt (15) are used.

If we calculate $c/a_P$ where $a_P = (a + b)/(2 \times c)$, we obtain a value of 3.46. For the tetragonal K$_2$NiF$_4$ structure, $c/a_P$ is always found to be $3.30 \pm 0.05$ (16) except when there is a Jahn-Teller ion present. The unusually large $c/a$ value for La$_2$CuO$_2$ is consistent with a Jahn Teller configuration for Cu$^{2+}$ ($d^{9}$) and supports our finding of two longer and four shorter Cu-O distances.

In order to further show the structural relation...
of orthorhombic La$_2$CuO$_4$ to tetragonal K$_2$NiF$_4$, we have measured the lattice parameters of La$_2$CuO$_4$ as a function of temperature to 990°C using a Tempress high-temperature attachment on a General Electric XRD-5 diffractometer. The orthorhombic unit cell becomes less distorted with increasing temperature and transforms to tetragonal symmetry at 260°C. The lattice parameters for the tetragonal cell at 420°C are $a = 3.811(1)$ Å, $c = 13.245(5)$ Å, ($c/a = 3.47$). By following the position of the [006] and [200] reflections as the temperature is increased, the value of $c/a$ was found to remain constant at $3.47 \pm 0.01$ up to 990°C where $a = 3.853(1)$ Å and $c = 13.373(5)$ Å. This would indicate that there is little change in going from the orthorhombic to the tetragonal unit cell. Using the pseudo-tetragonal $a$ and $c$ of the orthorhombic unit cell we were able to calculate a coefficient of linear thermal expansion ($x$) for La$_2$CuO$_4$ between room temperature and 990°C. The values we obtain, $a_x = 12 \times 10^{-6}$°C$^{-1}$ and $c_x = 16 \times 10^{-6}$°C$^{-1}$, are in good agreement with those found for Sr$_2$TiO$_4$. $a_x = 14.6 \times 10^{-6}$°C$^{-1}$ and $c_x = 14.4 \times 10^{-6}$°C$^{-1}$.

We have prepared Pr$_2$CuO$_4$ and confirm that its structure is K$_2$NiF$_4$ (5). Refinement of lattice parameter based on 20 line positions between 23° and 74° (2θ) gives $a = 3.956(8)$ Å, $c = 12.24(2)$ Å, and $c/a = 3.09$. This no doubt indicates that the Jahn-Teller ion Cu$^{2+}$ has two shorter and four longer Cu-O distances. Knox (18) has found the same surroundings for Cu$^{2+}$ in isostructural K$_2$CuF$_4$ ($c/a = 3.07$). These Cu-O distances are opposite to what is found for La$_2$CuO$_4$ and reflects a change from a $d_{x^2-y^2} - d_{dz^2}$ (Pr$_2$CuO$_4$) to a $d_{x^2-y^2} - d_{xy}$ (La$_2$CuO$_4$) configuration. We have followed the $c/a$ ratio for Pr$_2$CuO$_4$ up to 900°C and find that it remains constant at 3.09 ± 0.01. At 900°C the tetragonal unit cell is $a = 4.00(1)$ Å and $c = 12.31(3)$ Å. The coefficients of linear expansion between room temperature and 990°C are $a_x = 9.5 \times 10^{-6}$°C$^{-1}$ and $c_x = 6.7 \times 10^{-6}$°C$^{-1}$. These values are much smaller than those found for La$_2$CuO$_4$.

We have investigated the magnetic properties of La$_2$CuO$_4$ using a vibrating sample magnetometer. The magnetic susceptibility of our sample (0.2142 g) was below the sensitivity of our instrument (10$^{-6}$ emu/g) from room temperature to 4.2 K and in fields to 17 kOe. Since Cu$^{2+}$ has an odd number of $d$ electrons, the absence of a normal magnetic moment probably indicates antiferromagnetism.

LaSrBO$_4$

An examination of the literature (7) of known materials with the K$_2$NiF$_4$ structure revealed that LaSrVO$_4$ and LaSrTiO$_4$ have not been reported as members of the series LaSrBO$_4$ where $B^{x+} = Al, Cr, Mn, Fe, Co, Ni, Ga, Rh. All of the known compounds have been obtained by reaction of oxides and carbonates in air, N$_2$, or O$_2$. We have attempted the preparation of LaSrVO$_4$ and LaSrTiO$_4$ by the reaction of stoichiometric amounts of dry La$_2$O$_3$, freshly prepared SrO and V$_2$O$_5$, or Ti$_2$O$_3$. The reagents were intimately mixed, pelleted, and fired in evacuated silica capsules at 1000°C for 24 hr. X-ray diffraction patterns of the reaction products in the case of the Ti compound revealed a mixed phase with no compound having the K$_2$NiF$_4$ structure. However, there was compound formation for LaSrVO$_4$ with only trace amounts of a second phase.

The X-ray pattern of LaSrVO$_4$ could be interpreted assuming the material has the tetragonal K$_2$NiF$_4$ structure. Refinement of the lattice parameters was based on 15 well-defined peaks whose positions were determined from a 1/4°/min scan over the 2θ interval 50°-125°. For LaSrVO$_4$, we obtained $a = 3.866(1)$ Å and $c = 12.652(3)$ Å. The $c/a$ ratio is 3.27 and is similar to those found for most materials with the K$_2$NiF$_4$ structure. To confirm our structural assignment, we have compared our observed intensities with those calculated for the K$_2$NiF$_4$ structure. 

### TABLE III

**Crystallographic Data for LaSrVO$_4$**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
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<td>3.866(1) Å, $c = 12.652(3)$ Å</td>
</tr>
<tr>
<td>(Tetragonal)</td>
<td></td>
</tr>
<tr>
<td>Space group:</td>
<td>$I4_1/mmm$</td>
</tr>
<tr>
<td>Unit cell contents:</td>
<td>Two LaSrVO$_4$ molecules centered translation applied to:</td>
</tr>
<tr>
<td>$A$ in (4e)</td>
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</tr>
<tr>
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<tr>
<td>$O_2$ in (4e)</td>
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</tr>
<tr>
<td>Optimized parameters:</td>
<td>$z_{max} = 0.357(2)$, $z_{min} = 0.165(5)$, $R_{int} = 1.0(3)$ Å$^2$</td>
</tr>
</tbody>
</table>

* $*$ Value in parentheses is estimated error in last place of number.
structure in space group $I4/mmm$. In a series of calculations, we have optimized the two positional parameters ($z_a$ and $z_o$) and cell temperature factor ($B$). It was assumed that the La and Sr are randomly placed on the $A$ site. The scattering factors for Sr$^{2+}$, La$^{3+}$, V$^{5+}$ (12) and O$^{2-}$ (13) were corrected for the real and imaginary parts of the anomalous dispersion term (14). The theoretical polarization term for a graphite crystal—diffracted beam monochromator was also applied to our data. A summary of the crystallographic data found for LaSrVO$_4$ is given in Table III. A comparison of observed and calculated intensities and $d$ values is given in Table IV. The good agreement

\[(R = 100 \times \frac{\sum |I_o - I_c|}{\sum I_o} = 9.4)\]

between observed and calculated intensities confirms the assignment of the K$_3$NiF$_3$ structure to LaSrVO$_4$. Along the $c$ axis of LaSrVO$_4$, a value of $z = 0.165$ gives two V-O1 distance of 2.09 Å while in the $a$-b plane, there are four

\[
\begin{array}{cccccccc}
  d_{oobs} & d_{calc} & h & k & l & I_{oobs} & I_{calc} & R \\
  6.334 & 6.326 & 0 & 0 & 2 & 2.603 & 1.82 & 1.091 & 1.091 & 2.19 & 0.950 & 0.991 \\
  3.696 & 3.700 & 1 & 0 & 1 & 18.33 & 17.31 & 1.069 & 1.069 & 3.21 & 1.097 & 1.27 \\
  3.162 & 3.165 & 0 & 0 & 4 & 12.29 & 11.82 & 1.059 & 1.059 & 2.010 & 1.272 & 7.29 \\
  2.852 & 2.851 & 3 & 3 & 0 & 100.00 & 91.12 & 1.058 & 1.058 & 3.16 & 5.597 & 8.75 \\
  2.739 & 2.736 & 1 & 1 & 0 & 73.48 & 71.06 & 1.054 & 0.012 & 12 & 0.035 & 0 \\
  2.511 & 2.511 & 3 & 3 & 2 & 4.32 & 4.01 & 1.050 & 1.050 & 3.70 & 7.633 & 2.34 \\
  2.110 & 2.118 & 1 & 0 & 5 & 4.28 & 24.60 & 1.040 & 1.040 & 3.23 & 3.920 & 8.75 \\
  2.109 & 2.100 & 0 & 0 & 6 & 14.84 & J & 1.035 & 1.035 & 2.28 & 2.912 & 4.19 \\
  2.068 & 2.069 & 1 & 1 & 4 & 33.47 & 31.89 & 0.9881 & 0.9882 & 3.25 & 1.476 & 1.45 \\
  1.934 & 1.935 & 2 & 0 & 0 & 38.22 & 38.73 & 1 & 0.9431 & 1.11 & 0.000 & 0 \\
  1.850 & 1.850 & 2 & 0 & 2 & 0.17 & 0.18 & 0.9676 & 0.9676 & 3.01 & 3.17 & 6.38 \\
  1.715 & 1.714 & 2 & 1 & 1 & 4.74 & 5.46 & 0.9617 & 0.9617 & 4.00 & 3.42 & 9.11 \\
  1.670 & 1.670 & 1 & 1 & 6 & 14.60 & 15.49 & 0.9579 & 0.9579 & 2.11 & 8.38 & 9.11 \\
  1.650 & 1.650 & 2 & 0 & 4 & 7.17 & 8.20 & 0.9567 & 0.9567 & 4.00 & 2 & 0.033 & 0 \\
  1.638 & 1.638 & 1 & 0 & 7 & 9.19 & 10.92 & 0.9505 & 0.9506 & 3.09 & 0.93 & 0.55 \\
  1.600 & 1.601 & 2 & 1 & 3 & 34.29 & 38.27 & 0.9442 & 0.9441 & 1.01 & 0.44 & 0.36 \\
  1.582 & 1.582 & 0 & 0 & 8 & 3.43 & 7.29 & 0.9358 & 0.9361 & 4.11 & 0.844 & 0.73 \\
  1.428 & 1.428 & 2 & 1 & 5 & 5.48 & 5.48 & 0.9297 & 0.9290 & 2.10 & 1.38 & 1.09 \\
  1.426 & 1.426 & 2 & 0 & 6 & 13.09 & J & 0.9250 & 0.9260 & 2.01 & 0.98 & 1.1 \\
  1.370 & 1.369 & 1 & 1 & 8 & 4.44 & 4.441 & 0.9252 & 0.9252 & 4.04 & 1.54 & 0.14 \\
  1.369 & 1.368 & 2 & 2 & 0 & 10.28 & J & 0.9229 & 0.9229 & 3.27 & 3.49 & 3.64 \\
  1.331 & 1.331 & 2 & 2 & 2 & 0.20 & 0 & 0.9160 & 0.9162 & 4.13 & 6.50 & 6.55 \\
  1.322 & 1.322 & 1 & 0 & 9 & 0.983 & 0.94 & 0.9121 & 0.9122 & 3.00 & 2.25 & 2.74 \\
  1.283 & 1.283 & 3 & 0 & 1 & 0.930 & 0.930 & 0.9039 & 0.9039 & 0.14 & 1.22 & 1.09 \\
  1.265 & 1.265 & 0 & 0 & 10 & 0.745 & 0.745 & 0.9028 & 0.9028 & 3.2 & 0.69 & 0 \\
  1.256 & 1.256 & 2 & 2 & 4 & 2.807 & 2.74 & 0.8880 & 0.8880 & 4.1 & 1.23 & 1.09 \\
  1.250 & 1.250 & 2 & 1 & 7 & 7.21 & 7.20 & 0.8795 & 0.8797 & 3.10 & 4.38 & 6.74 \\
  1.234 & 1.233 & 3 & 3 & 3 & 6.75 & 6.78 & 0.8794 & 0.8794 & 4.06 & 2.45 & 3.19 \\
  1.224 & 1.224 & 2 & 0 & 8 & 5.977 & 16.40 & 0.8763 & 0.8764 & 3.34 & 2.14 & 2.19 \\
  1.224 & 1.224 & 3 & 1 & 0 & 9 & 4.21 & 4.21 & 0.8652 & 0.8653 & 4.20 & 6.01 & 5.46 \\
  1.201 & 1.201 & 3 & 1 & 2 & 0.315 & 0 & 0.8549 & 0.8549 & 3.01 & 1.40 & 0.66 \\
  1.149 & 1.149 & 3 & 0 & 5 & 1.633 & 1.633 & 0.8547 & 0.8546 & 1.14 & 3.85 & 7.1 \\
  1.148 & 1.148 & 1 & 1 & 10 & 3.687 & 10.01 & 0.8530 & 0.8531 & 3.29 & 0.80 & 0.73 \\
  1.141 & 1.141 & 3 & 1 & 4 & 7.036 & 7.29 & 0.8483 & 0.8484 & 2.13 & 0.95 & 0.73 \\
  1.102 & 1.103 & 1 & 0 & 11 & 2.90 & 6.92 \\
\end{array}

* $a = 3.389$ Å, $c = 12.652$ Å
V-O2 distances of 1.94 Å. The average V-O distance in the elongated octahedron is 1.99 Å which agree exactly with that predicted from the effective ionic radii of Shannon and Prewitt (15).

Acknowledgments

We wish to thank Dr. J. B. Goodenough for many stimulating discussions and acknowledge the valuable technical assistance of Don Batson, Carl Anderson, and Jim Werner.

References

Superconducting and Normal State Properties of Li$_{1+y}$Ti$_2$O$_4$ Spinel Compounds. I. Preparation, Crystallography, Superconducting Properties, Electrical Resistivity, Dielectric Behavior, and Magnetic Susceptibility

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LiTi$_2$O$_4$ is one end member of the homogeneity range of the spinel phase Li$_{1+y}$Ti$_2$O$_4$ (0 ≤ x ≤ 1/3) and is superconducting at temperatures up to 13.7 K. Various measurements were carried out in order to characterize the superconducting and normal state properties of LiTi$_2$O$_4$ and of other compositions within the homogeneity range of the spinel phase. These measurements establish LiTi$_2$O$_4$ as a d-band superconductor and show that T$_c$ decreases to <1.3 K for x > 0.1. This disappearance of superconductivity with increasing x was found to be correlated with anomalous changes in the lattice parameter with composition, and, from electrical resistivity measurements, is tentatively attributed to the occurrence of a composition-induced metal–semiconductor transition at x = 0.1. The metallic character of LiTi$_2$O$_4$ and the composition dependence of the observed electrical properties are shown to follow from crystallographic considerations.

1. INTRODUCTION

Superconductivity in oxide compounds has been known for about a decade, and began with a report in 1964 of superconductivity in reduced SrTiO$_3$ ($T_c = 0.3$ K). However, the presently known number (23) of superconducting oxide compounds is still very small in comparison to the ~1000


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known superconducting intermetallic compounds. Apart from TiO$_2$ and NbO$_2$, all of these superconducting oxide compounds are ternary compounds. The importance of ternary compounds in the search for new high-temperature superconductors has recently been stressed.\footnote{19}

A brief preliminary report has been given concerning the superconductivity in one such ternary compound, Li$_{1+x}$Ti$_2$O$_6$, which becomes superconducting at temperatures up to about 13.7 K.\footnote{19} This compound is one end member of the homogeneity range of the spinel phase in the Li-Ti-O ternary system: Li$_{1+x}$Ti$_2$O$_6$ ($0 \leq x \leq 1/3$).\footnote{11} The other end member is a colorless electrical insulator. LiTiO$_3$ has a high $T_c$ compared with most other oxide superconductors and is the only oxide superconductor having the spinel structure. The reason that no other oxide spinel compounds have been found to be superconducting is related to the occurrence of metallic properties among members of this structure class. Of the several hundred known oxide spinel compounds, few are known to exhibit a metallic electronic ground state at low temperatures. One of these few is LiV$_2$O$_5$,\footnote{17} and this compound is not superconducting above 1.5 K.\footnote{12} The reason for lack of superconductivity in LiV$_2$O$_5$ is apparent from a consideration of the magnetic susceptibility data\footnote{14} for this compound: The susceptibility follows a Curie-Weiss law, and the Curie constant yields an effective moment of 1.93 $\mu_B$ per V cation, slightly greater than the value of 1.73 $\mu_B$ expected for a spin-only $d^1$ cation. Superconductivity in LiV$_2$O$_5$ is therefore precluded by the apparent large concentration of local moments inherent in this material. In contrast to LiV$_2$O$_5$, it will be shown here that although the susceptibility of LiTi$_2$O$_6$ is also relatively large, it is nearly temperature independent.

The unusual characteristics of LiTi$_2$O$_6$ noted above prompted a detailed investigation\footnote{11} into its superconducting and normal state properties. In addition, measurement of these properties was extended to other compositions within the homogeneity range of the spinel phase, and the results of these investigations are presented here and in the following paper.

2. SAMPLE PREPARATION

The assignment of the observed high-temperature superconductivity in the Li-Ti-O ternary system to the spinel phase\footnote{19} was initially hampered by the fact that the x-ray patterns of several of the phases in this ternary system are nearly identical in line positions and are similar in line intensities. Therefore, a careful consideration of the phase relations, crystal structures, and lattice parameters of the various phases was required. This information was also necessary in determining the best method of synthesis for the spinel phase and in searching for other superconducting phases\footnote{13} in the Li-Ti-O system. Since the previously published data are scattered and are nowhere
Apart from TiO$_3$ and Ti$_2$O$_7$, the compounds in the ternary Ti-O system were not investigated. These compounds are ternary compounds that have been synthesized using the superconducting niobate and superconductor systems. The superconductor systems have been shown to be stable in the superconducting state, and they have been used to study the superconducting properties of these compounds.

The superconducting properties of these compounds have been studied extensively, and the superconducting transition temperatures have been measured for a variety of compositions. The superconducting transition temperatures are generally low, and they range from a few millikelvins to several kelvins. The superconducting transition temperatures of these compounds are not known to be affected by the presence of impurities, and they are not known to be affected by the presence of defects.

The superconducting transition temperatures of these compounds are not known to be affected by the presence of impurities, and they are not known to be affected by the presence of defects.

The superconducting transition temperatures of these compounds are not known to be affected by the presence of impurities, and they are not known to be affected by the presence of defects.
superconducting properties of the samples deteriorated after being stored for periods of about one month or more. This behavior was not accompanied by observable crystallographic changes; the reason for the deterioration may be related to the sintered nature of the samples.

3. MEASUREMENT TECHNIQUES

X-ray powder diffraction data were obtained with a General Electric XRD-6 diffractometer using Cu Kα radiation and equipped with a diffracted beam crystal monochromator. Lattice parameters were determined by extrapolation to a Bragg angle 2θ = 180° using the extrapolation function \( \cos^2 \theta/\sin \theta \). The Cu Kα doublet was very well resolved at the higher Bragg angles for all samples investigated. Line intensities were determined by measuring the area under diffraction peaks on diffractometer tracings. When calculating line intensities, the atomic form factors were taken from Ref. 16.

Superconducting transition temperatures \( T_c \) were determined using standard ac inductance techniques at a frequency of 20 Hz. The volume fraction of superconducting material in a sample was determined by comparing a superconducting throw to that obtained from a known volume of lead. The transition temperatures were measured to an accuracy of better than 0.1 K, using a calibrated carbon resistor.

Electrical resistivity measurements were carried out below room temperature using standard four-probe ac or dc techniques. Absolute resistivity values were determined using the van der Pauw method\(^{17}\) or by direct calculation from the measured sample dimensions. For low-resistance samples (\( \approx 0.1 \Omega \)), an ac technique was employed. For samples showing high contact resistance or with a resistance greater than 0.1 \( \Omega \), dc techniques were used. In the latter cases, the current-voltage characteristics were checked at several temperatures to ensure that they were linear, and the currents were such that the power dissipated in the samples was always less than 1 \( \mu \)W. The electrical leads (0.002-in-diameter Pt wire) were attached to the samples with silver paint, and the bond of the silver paint to the samples was found to be satisfactory. All resistivity measurements reported here were carried out on samples in the form of sintered pellets. Temperatures were determined using calibrated Ge and Pt resistance thermometers.

The dielectric constant for sintered disks of \( \text{Li}_{1/2} \text{Fe}_{1/2} \text{O}_3 \) was determined at a frequency of 1 kHz. The ends of these disks were coated with silver paint, which was allowed to dry under a heat lamp. The capacitance of a sample prepared in this way was measured using the three-lead technique over the temperature range 2–295 K. A sample was suspended between two
deteriorated after being stored. The behavior was not accompanied by any reason for the deterioration of the samples.

**TECHNIQUES**

These obtained with a General Electric determination and equipped with a diffractometer, parameters were determined by the extrapolation function \( F \), using the extrapolation function \( y \) well resolved at the higher Bragg intensities were determined by peaks on diffractometer tracings. Single atom form factors were taken from tables \( T \); were determined using a frequency of 20 Hz. The volume a sample was determined by combining from a known volume of measured to an accuracy of better than 0.1 \( \Omega \); dc techniques were used. For low-resistance samples, the measurements were always less than 1 \( \mu \Omega \). Pt wire) were attached to the Pt lead to the samples was measured here were pellet and resistors. Temperatures were measured resistances thermostats.

Disks of \( \text{Li}_{42} \text{Ti}_{3} \text{O}_{8} \) were determined using the three-lead technique in a heat lamp. The capacitance of the disk using the three-lead technique was suspended between two gold-plated pressure contacts, which were connected via miniature low-thermal-conductivity coax cables to the terminals of a General Radio 1650-A impedance bridge. The coax shields were grounded to the case of the bridge. The temperature was measured with a calibrated 1/10-W Allen-Bradley carbon resistor.

Static susceptibility measurements were carried out using the Faraday technique in the temperature range 0.4–295 K in a field of 7.8 kG. Details of the apparatus are described elsewhere. The accuracy of the measurements reported here is 2% or 1 \( \times \) 10^{-6} cm^{3}/mole, whichever is larger. Magnetization versus field isotherms were determined by nulling the force on a sample at given values of applied field with a current flowing through a coil surrounding the sample. Alternatively, the isotherms were determined by measuring the force on a sample versus applied field.

**4. CRYSTALLOGraphy**

**4.1. General Considerations**

A unit cell of the face-centred-cubic (fcc) spinel structure of an oxide spinel with composition \( \text{AB}_{2} \text{O}_{4} \) consists of an approximately cubic close-packed array of 32 oxygen atoms, with one-eighth of the 96 tetrahedral holes per unit cell and one-half of the 32 octahedral holes per unit cell filled by the cations \( A \) and \( B \). The resultant unit cell contains 8 formula units of \( \text{AB}_{2} \text{O}_{4} \). The distribution of cations in the octahedral and tetrahedral sites of a spinel is usually indicated by putting the cations occupying the octahedral sites in brackets: \( \text{A[AB]} \text{O}_{4} \) is denoted a “normal” spinel, and \( \text{B[AB]} \text{O}_{4} \) an “inverse” spinel. Assuming a normal spinel configuration, the positions of the \( A \), \( B \), and \( O \) ions in the unit cell are as follows:

Origin at 43m

Equivalent positions 

\[ (0, 0, 0); (0, \frac{1}{2}, \frac{1}{2}); (\frac{1}{2}, 0, \frac{1}{2}); (\frac{1}{2}, \frac{1}{2}, 0); \]

8 A in (a): (0, 0, 0); (1, 1, 1); (1, 1, 1);

16 B in (d): (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}); (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}); (\frac{1}{4}, \frac{1}{4}, \frac{1}{4});

32 O in (b): (u, u, u); (u, u, u); (1, 1, 1 - u, 1 - u); (1, 1, 1 - u, 1 - u);

\[ (u, u, u); (u, u, u); (u, u, u); (u, u, u); \]

\[ (u, u, u); (u, u, u); (u, u, u); (u, u, u); \]

with \( u = 3/8 \).

If the oxygen parameter \( u \) is identically equal to 3/8 and the cations are in the normal spinel configuration, then an ideal spinel structure results, in which the oxygen atoms form a perfect fcc sublattice. This ideal spinel structure is shown in Fig. 1a, where it is seen that each oxygen anion is coordinated on one side with an equalateral triangle of three \( B \) cations, and on the other side by one \( A \) cation. Each \( A \) cation is at the center of an oxygen...
tetrahedron, and each B cation resides at the center of a perfect oxygen octahedron. The oxygen octahedra surrounding the B cations share edges with each other, and share corners with the oxygen tetrahedra surrounding the A cations. However, these tetrahedra do not make contact with each other.

The cation sublattice AB_2 is shown in Fig. 1b. The B cations form a network of tetrahedra connected at their corners. The A cations form a diamond-type lattice. An interesting aspect of the cation sublattice is that it is identical to the fcc C-15 (MgCu_2) structure. This latter structure class
contains compounds with rather high superconducting transition temperature (e.g., 9.6 K for HfV3)\textsuperscript{21} However, only one compound AB\textsubscript{2} in the C-15 structure class is also known to form the cation sublattice in a spinel compound: TiCo\textsubscript{2} = Co(CoTi)O\textsubscript{4}, which is an inverse spinel as defined above.

For most spinel compounds, the value of the oxygen parameter \( u \) is found to deviate slightly in a positive direction from the ideal value of 0.375, resulting in a small displacement of the oxygen anions in a [111] direction away from the nearest A cation, toward the center of the equilateral triangle of B cations on the opposite side of the oxygen anions. This displacement does not distort the tetrahedral coordination around the A cations, but does result in a distortion of the oxygen octahedra around the B cations. This trigonal distortion is shown in Fig. 1c, where the direction and length of the arrows correspond to the change in an oxygen octahedron as the value of \( u \) increases from the ideal value of 0.375 to a value of 0.425 (13–10 times the distortion normally found).

Because the cation sublattice is independent of \( u \), the cation–cation distances depend only on the lattice parameter \( a_0 \). However, the cation–oxygen distances are functions of both the lattice parameter \( a_0 \) and the \( u \) parameter. These distances are as follows:

**Distances (with \( u = 0.375 + \Delta \)):**

(a) Cation–oxygen distances

\[
\begin{align*}
\text{d}_{A-O} &= (3^{1/2}/8)a_0(1 + 8\Delta) = 0.2165a_0(1 + 8\Delta) \\
\text{d}_{B-O} &= 4a_0(1 - 8\Delta + 24\Delta^2)^{1/2} = 0.25a_0(1 - 4\Delta)
\end{align*}
\]

(b) Cation–cation distances

\[
\begin{align*}
\text{d}_{A-A} &= (3^{1/2}/4)a_0 = 0.43301a_0 \\
\text{d}_{A-B} &= d_{B-O} = 0.35355a_0 \\
\text{d}_{A-B} &= (11^{1/2}/8)a_0 = 0.41458a_0
\end{align*}
\]

The determination of the oxygen parameter \( u \) is therefore of interest in establishing the cation–oxygen distances and the extent of oxygen octahedron distortion around the B cations.

### 4.2. Results

The lattice parameters \( a_0 \) for single-phase samples are plotted versus the composition parameter \( x \) in Fig. 2. The data of Deschanvres et al.\textsuperscript{11} have been included for comparison. As the composition parameter \( x \) increases from 0, the lattice parameter decreases rapidly in the range 0 \( \leq x \leq 0.1 \), then linearly and at a lower rate as \( x \) increases further to its maximum value of
The behavior for $0 \leq x \leq 0.1$ may be associated with anomalous changes in the superconducting and electrical properties occurring in this composition range (Sections 5 and 6).

In Fig. 2 it is seen that for $x \neq 1/3$, there is considerable disagreement between the lattice parameters determined in the present work and those of Deschanvres et al. It is possible that the latter data were obtained for samples which were oxidized more than the nominal composition would indicate, thereby giving a true spinel composition corresponding to a larger $x$ value, and hence a lower lattice parameter. For the fully oxidized composition ($x = 1/3$), the lattice parameter determined here is identical to that found by Deschanvres et al. and by most other previous workers. 22-24

For determining the distribution of cations among the tetrahedral and octahedral sites, the diffracted intensities of lines having even indices and satisfying the following conditions were used:

$$h \neq 4n + 2 \quad k \neq 4n + 2 \quad l \neq 4n + 2$$

And $h + k + l = 4n$ for $h, k, l \neq 0$.

For the lines satisfying these relations [e.g., (220), (422), (620)], the line intensities depend primarily upon the form factor of the cations occupying the tetrahedral sites: Statistically distributed cations occupying octahedral

![Graph showing lattice parameter versus composition for $La_{1-x}T_{x}$O$\gamma$. The data of Deschanvres and co-workers have been included for comparison.](image-url)
sites make no contribution to the intensities of these lines; the contribution due to the oxygen anions is zero for the ideal oxygen parameter $u = 0.375$ and increases only slowly for $u \neq 0.375$. Since the atomic form factor for Ti is much greater than that for Li, the intensities of these lines are therefore very sensitive to the occupation of the tetrahedral sites by titanium cations. The observed intensities for these lines were found to be $-0$, and a quantitative calculation showed that the tetrahedral sites are at least 95% occupied by lithium cations.

Since the tetrahedral sites are occupied solely by Li cations, the octahedral site occupation is determined by the composition, and the general site occupation is given by $Li(Li, Ti)_{1-x}O_3$ ($0 \leq x \leq 1/3$). For $x \neq 0$, the observed line intensities are consistent with a statistical distribution for the Li and Ti cations on octahedral sites (see below). The two limiting compositions of the spinel homogeneity range correspond to the cation distribution $Li^{1+}(Ti^{3+}, Ti^{4+})O_4$ ($x = 0$) and $Li^{1+}(Li^{1+}, Ti^{4+})O_4$ ($x = 1/3$), where the formal valences of the cations have also been indicated. The homogeneity range is limited at $x = 0$ by the reluctance of Ti cations to occupy tetrahedral sites, and at $x = 1/3$ by the inability of Ti and Li to assume formal valences in the spinel structure greater than four and one, respectively. Attempts to synthesize samples with $x < 0.3$ resulted in multiphasic samples containing (Ti, Li)$_2$O or (Ti, Li)O phases in addition to the spinel phase (see the phase diagram in the appendix).

The oxygen parameter $u$ was determined for the two end members of the spinel homogeneity range by calculating the intensities for the particular pairs of strong, low-angle diffraction lines for which the intensity ratios were strong functions of $u$, and comparing these calculated ratios with those obtained experimentally. Figure 3 shows the theoretical calculations (solid curves) and the experimental points (filled circles). In the case of $Li(Li, Ti)_{1-x}O_4$, the curves of Fig. 3 were computed assuming a statistical distribution for the cations in the octahedral sites. From the consistency of the experimentally predicted values of $u$ for this compound, this assumption appears to be justified.

The values of the oxygen parameter obtained from Fig. 3 are in agreement with those found by Deschanvres et al. These values were then used to calculate the line intensities for the full diffraction pattern. The results of these calculations are compared with the experimental data in Table I. The calculated and observed lattice $d$ spacings have also been included in the table.

Using the lattice parameters and oxygen parameters found above, the interatomic distances in the Li-Ti-O spinel were computed and are listed in Table II, along with data on several other titanium-oxygen spinels for comparison.
5. SUPERCONDUCTING PROPERTIES

The superconducting transition temperature of spinel-phase samples \( \text{Li}_{1+x} \text{Ti}_{1-x} \text{O}_4 \) determined from ac susceptibility measurements are plotted vs. composition \( x \) and lattice parameter \( a_0 \) in Fig. 4. For compositions near \( \text{LiTi}_2 \text{O}_4 \) \((x = 0)\), the midpoints of the superconducting transitions are independent of composition, and for most samples are in the range 10–12 K. For three samples in the composition range \(0.05 \leq x \leq 0.15\), the \( T_c \) onsets were 11–12 K, but the volume fraction of superconducting material in the samples was small (<40%), even at the lowest temperatures (1.5 K). \( T_c \) data for these samples have therefore not been included in Fig. 4. For \( x > 0.15 \), no superconductivity was observed in any sample. Heat capacity measurements have been carried out \(^{5-9}\) which show that the superconducting transitions for \( x = 0 \) are indeed bulk transitions, and which substantiate the present findings concerning the composition dependence of the superconducting behavior.

Although most of the transition temperatures shown in Fig. 4 for \( x = 0 \) are in the range 10–12 K, for a few samples superconducting transitions were observed which showed onsets as high as 13.5–13.7 K. Despite much effort, the particular conditions necessary for the reproducible synthesis of samples with these higher transition temperatures have not yet been determined.
For the Cu-Kα radiation for \( \text{LaFeO}_3 \), \( m = 2.0174 \), and \( w = 0.0905 \) for \( \text{La}_2\text{CuO}_4 \), \( c_0 = 8.37 \text{Å} \).
<table>
<thead>
<tr>
<th>A[BO₃]O₄</th>
<th>Liat₄Ti₂O₇</th>
<th>Li₄/Mg₂Ti₂O₇</th>
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<td>Present work</td>
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*All accuracies are placed in parentheses.*
6. ELECTRICAL PROPERTIES

Measurements of the temperature dependence and absolute value of the electrical resistivity were carried out for several compositions within the homogeneity range of the spinel phase $Li_{1+x}Ti_{2-x}O_4$. Samples with composition parameter $x = 0.0, 0.1$ (nominal composition $Li_{1+1/2}Ti_{1+1/2}O_4$), and 0.2 were measured. X-ray analysis indicated that these samples were single-phase spinel compounds, with lattice parameters shown in Fig. 2. Resistivities for two samples with nominal compositions outside the homogeneity range of the spinel phase ($x = -0.1, -0.2$) were also determined. These two samples contained small quantities of the $(Ti, Li)_2O_3$ and $(Ti, Li)O_2$ phases in addition to the spinel phase.

The samples with composition parameters $x = 0.2$ and $x = 0.1$ showed high resistivities, and the measurements for these samples were therefore carried out using dc techniques. For the other samples, ac techniques were employed.

The results of the resistivity measurements are collected in Fig. 5. For the single-phase spinel samples ($x = 0, 0.1$, and 0.2), the room-temperature resistivity increases by nearly three orders of magnitude as the composition changes from superconducting $LiTi_2O_4$ to $Li_{1+1/2}Ti_{1+1/2}O_4$. For the latter sample and for $Li_{1+2}Ti_{1+1/2}O_4$, the resistivity shows a rapid increase as the
temperature is lowered from 300 K, in contrast to that for LiTiO$_4$, which increases slightly in the temperature range 300 to 100 K, but is temperature independent below 100 K (apart from the superconducting transition). The resistivities determined for the two samples with compositions ($x = -0.1, -0.2$) beyond the LiTiO$_4$ end of the spinel phase homogeneity range have about the same absolute magnitude as that for LiTiO$_4$. Although resistivity data obtained on sintered oxides are often only of qualitative significance, the present measurements do suggest the occurrence of a metal-semiconductor transition as the composition of the spinel phase changes from LiTiO$_4$ to Li$_{1-x}$Ti$_{2-x}$O$_4$. Attempts to grow single crystals of Li$_{1-x}$Ti$_{2-x}$O$_4$ in order to verify this behavior have not as yet been successful.

7. DIELECTRIC PROPERTIES

Besides the Li$_{1-x}$Ti$_{2-x}$O$_4$ spinel system, there are other classes of compounds which undergo composition-induced metal-insulator (semiconductor) transitions without change in crystal structure. One of these is the class of degenerate semiconductors in which metallic behavior is obtained by doping the parent semiconducting host with suitable dopants,
and in which metallic properties are initiated through impurity band conduction. These materials are characterized by high static dielectric constants relative to the charge carrier effective masses, and several of them are superconducting.

The electronic properties of this class of degenerate semiconductors are often treated within the framework of the theory of impurity states in semiconductors, in which the ground-state orbit radius \( a_{\text{H}} \) for a hydrogen-like donor impurity is

\[
    a_{\text{H}} = \frac{\varepsilon}{(m^*/m)}(0.53 \text{ Å})
\]

where \( \varepsilon \) is the static macroscopic dielectric constant of the host, \( m^* \) is the effective mass of the current carriers, and \( m \) is the rest mass of the electron.

It has been shown that a semiconductor to metal transition occurs when the donor concentration \( N \) attains a value \( N_{\text{min}} \) given by

\[
    N_{\text{min}}/a^2 = 0.3
\]

It should be noted that this theory describing electron delocalization and impurity band formation is only valid if the donor orbit radius defined in Eq. (1) is much larger than an interatomic distance.

Dielectric constant measurements were carried out for the electrically insulating spinel composition \( \text{Li}_{12/3} \text{Ti}_{12/3} \text{O}_4 \) in order to ascertain whether the formation of a degenerate Fermi gas in the \( \text{Li}_{1-x} \text{Ti}_{x} \text{O}_4 \) system as \( x \to 0 \) can be described within the framework of the theory cited above. The results of this measurement showed that the dielectric constant is independent of temperature for \( 2 \leq T \leq 295 \text{ K} \), and no dielectric anomalies were observed. The dielectric constant of \( \text{Li}_{12/3} \text{Ti}_{12/3} \text{O}_4 \) was found to be 11 ± 1. Utilizing this value of the dielectric constant along with the effective mass of 9.4m found for the current carriers in \( \text{Li}_{12/3} \text{Ti}_{12/3} \text{O}_4 \) from magnetic susceptibility measurements (see Section 8), \( a_{\text{H}} \) and \( N_{\text{min}} \) were computed from Eq. (1) and (2). The results of these calculations, along with similar calculations for several well-known degenerate semiconductor hosts, are shown in Table III. From the table, the calculated radius of a donor orbit in \( \text{Li}_{12/3} \text{Ti}_{12/3} \text{O}_4 \) is only about 0.6 Å, which is much smaller than an interatomic distance, and is in contrast to the values obtained for the known degenerate semiconductor hosts shown there. Therefore, the theory cited above is not applicable to the metal-insulator transition in the \( \text{Li}_{1-x} \text{Ti}_{x} \text{O}_4 \) system, and the metallic ground state for spinel-phase compositions approaching \( \text{Li}_{12/3} \text{Ti}_{12/3} \text{O}_4 \) does not occur through the formation of a distinct impurity band. The electronic properties of \( \text{Li}_{1-x} \text{Ti}_{x} \text{O}_4 \) are discussed further in Section 9.
TABLE III

<table>
<thead>
<tr>
<th>Material</th>
<th>(\alpha^{\text{e}} + m)</th>
<th>(\varepsilon)</th>
<th>(\varphi_B), Å</th>
<th>(N_{\text{max}}), cm(^{-3})</th>
</tr>
</thead>
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<tr>
<td>Ge</td>
<td>0.42(^{16})</td>
<td>11.5(^{11})</td>
<td>42</td>
<td>(4 \times 10^{17})</td>
</tr>
<tr>
<td>Si</td>
<td>0.34(^{16})</td>
<td>11.7(^{13})</td>
<td>21</td>
<td>(3 \times 10^{18})</td>
</tr>
<tr>
<td>SnTe</td>
<td>~1.3(^{13})</td>
<td>120(^{12})</td>
<td>420</td>
<td>(4 \times 10^{24})</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>(8 \times 10^{34})</td>
<td>300(^{12})</td>
<td>32</td>
<td>(8 \times 10^{17})</td>
</tr>
<tr>
<td>Li(<em>{1.2})Ti(</em>{1.8})O(_4)</td>
<td>9.2(^{14})</td>
<td>11(^{14})</td>
<td>0.6</td>
<td>(1 \times 10^{17})</td>
</tr>
</tbody>
</table>

\(^{13}\)At 100 K.

\(^{16}\)Present work.

\(^{14}\)For comparison only; see text.

8. MAGNETIC SUSCEPTIBILITY

Magnetic susceptibility measurements were carried out on several samples at room temperature and/or in the temperature range 0.4–295 K. The susceptibilities for three different single-phase samples of Li\(_{1.2}\)Ti\(_{1.8}\)O\(_4\) were determined, along with data for samples of composition Li\(_{1.2}\)Ti\(_{1.8}\)O\(_{3.95}\), Li\(_{1.2}\)Ti\(_{1.8}\)O\(_{4}\), and Li\(_{1.2}\)Ti\(_{1.8}\)O\(_{4.05}\). The three Li\(_{1.2}\)Ti\(_{1.8}\)O\(_4\) samples were previously determined by ac susceptibility measurements to be superconducting, with transition temperatures in the range 10–12 K. The Li\(_{1.2}\)Ti\(_{1.8}\)O\(_{3.95}\) sample also showed about 1% volume superconductivity below ~11 K, and the susceptibility measurement for this sample was therefore limited to higher temperatures. The Li\(_{1.2}\)Ti\(_{1.8}\)O\(_4\) sample showed no trace of superconductivity above 0.44 K.

Most of the samples showed small nonlinearities in the \(M\) vs. \(H\) characteristics at fields below about 1 kG, attributed to ferromagnetic impurities. The concentration of these impurities was estimated from the zero-field intercept of the extrapolated high-field linear portion of the \(M\) vs. \(H\) plots, and was found for various samples to be equivalent to 1–30 ppm of ferromagnetic iron impurities (saturation moment 2.2 \(\mu_B\)). The susceptibility data presented below were determined from the slope of the linear portion of the \(M\) vs. \(H\) curves.

The results of the susceptibility measurements are shown in Fig. 6, where the measured molar susceptibilities (Fig. 6a) and inverse molar susceptibilities (Fig. 6b) are plotted vs. temperature. Near room temperature, the susceptibilities are only weakly temperature dependent, with the magnitude of the susceptibility decreasing monotonically with increasing values of the composition parameter \(x\). At the lowest temperatures, however, the susceptibilities increase rapidly.

The analysis of the data is complicated by possible contributions due to paramagnetic impurities in addition to the intrinsic contribution due to the...
Adequate Susceptibility

were carried out on several temperature range 0.4–295 K.
ephase samples of LiTiO$_3$ were of composition Li$_2$Ti$_2$O$_4$,
TiO$_2$ samples were previously reported to be superconducting,
with 8 K. The Li$_2$Ti$_2$O$_4$ sample
activity below ~11 K, and the
was therefore limited to higher
and no trace of superconductivity

nolinearities in the $M$ vs. $H$
and was estimated from the
linear portion of the $M$ vs. $H$
be equivalent to 1–30 ppm
agent 2.2 $\mu_B$). The susceptibility
from the slope of the linear
ments are shown in Fig. 6.
(Fig. 6a) and inverse molar
perature dependent, with the
monotonically with increasing
the lowest temperatures, how-

possible contributions due to
trinsic contribution due to the

samples. From the low-temperature region of the $\chi_M^{-1}$ vs. $T$ plots (Fig. 6b),
the susceptibilities appear to approach a Curie-Weiss law. Therefore, the
temperature dependences of the susceptibilities shown in Fig. 6 are analyzed
in terms of the following equation:

$$\chi_M(T) = \frac{C}{T + \theta} + I(T)$$

where the first term is attributed to paramagnetic impurities and the second
term describes the susceptibilities of the impurity-free compounds. The
values of $\theta$ indicated by the data of the low-temperature region of Fig. 6b are
at most a few K, so at higher temperatures, the impurity terms are well
approximated by $C/T$. Therefore, above a few K, the above equation takes
the approximate form

$$T \chi_M(T) = C + TF(T)$$

Assuming that $F(T)$ is nearly temperature independent at low temperatures,
the Curie constants were obtained from the intercepts of $T \chi_M$ vs. $T$ plots
The deviation of the data from straight-line behavior at the higher temperatures is attributed to the temperature dependence of $F(T)$. In Fig. 7b, the temperature-dependent molar susceptibilities have been replotted, after subtracting out the Curie-like impurity term, and the data of this figure therefore represent the intrinsic susceptibilities of the compounds.

Assuming the Curie constants to result from the presence of spin-1/2 moments, with a $g$ factor of 2, the impurity concentration can be calculated from the relation

$$n \text{ (moles impurity/mole Li}_{1+x}, \text{Tl}_{2-x}, \text{O}_4) = C/0.375$$

From the Curie constants determined in Fig. 7a, the concentration of impurities is in the range 0.35 mole % for Li$_2$O to 1.63 mole % for Li$_{1.1}$Ti$_{1.9}$O$_4$. These impurity concentrations are much larger than the concentration of foreign magnetic impurities expected to be in the samples. It is therefore likely that the impurity susceptibilities arise from the presence of local Ti$^{3+}$ moments in the samples. The lowest number of these local

---

**Fig. 7**: (a) Determination of the Curie constants due to paramagnetic impurities in Li$_{1+x}$Ti$_{2-x}$O$_4$ samples from $T_H/T_H$ versus $T_H$. (b) Molar susceptibilities versus temperature for Li$_{1.1}$Ti$_{1.9}$O$_4$, after correction for the impurity Curie terms.
right line behavior at the higher temperatures. In Fig. 6, values have been replotted, and the data of this figure and the data of the compounds, from the presence of spin-1/2 concentration can be calculated.

\[ x_{\text{LiTi}_2\text{O}_4} = C/0.375 \]

In Fig. 7a, the concentration of \( \text{LiTi}_2\text{O}_4 \) to 1.63 mole % for are much larger than the concentrated to be in the samples. It is the case of the presence of nearest number of these local moments occurs in the samples that are superconducting and metallic \( \text{LiTi}_2\text{O}_4 \), even though all the samples were prepared in a similar fashion, using similar starting materials.

Because the \( \text{Li}_{1.5}\text{Ti}_{1.5}\text{O}_4 \) sample showed no trace of superconductivity, detailed low-temperature measurements were carried out to further characterize the nature of the local moments. In Fig. 8a, the inverse molar susceptibility for this sample is plotted for the temperature region below 4 K, after subtracting out the temperature-independent term found from Fig. 7b \( (60 \times 10^{-6} \text{ cm}^3/\text{mole at } T < 40 \text{ K}) \). From Fig. 8a, the impurity contribution to the susceptibility of the sample in the region 0.4 - 4 K is given by a Curie-Weiss law \( \chi_M = C/(T + \theta) \), with \( \theta = 0.8 \text{ K} \) and \( C = 0.005 \text{ cm}^3/\text{mole. Below 1.3 K, the impurity susceptibility begins to saturate in fields of 10 kG, so the susceptibility values for lower temperatures shown in Fig. 8a were determined from the linear portion of the } M \text{ vs. } H \text{ curves. This saturation is illustrated in Fig. 8b, in which } M \text{ is plotted vs. } H \text{.} \)

![Graph](image_url)
TABLE IV
Magnetic Susceptibility Data for Several Li$_{1+x}$Ti$_{2-y}$O$_4$ Compounds

<table>
<thead>
<tr>
<th>Composition</th>
<th>T, K</th>
<th>$H/T$</th>
<th>$\chi_m$</th>
<th>C, cm$^3$/mole</th>
<th>(\alpha_{\text{mag}}) molc %</th>
<th>$10^6\chi_m - C/T$, cm$^3$/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>{1.75}$Ti$</em>{3.25}$O$_4$</td>
<td>294</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$<em>{1.83}$Ti$</em>{3.17}$O$_4$</td>
<td>294</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$<em>{1.75}$Ti$</em>{3.25}$O$_4$</td>
<td>294</td>
<td>96</td>
<td>0.0013</td>
<td>1.15</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1130</td>
<td>0.0050</td>
<td>1.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$<em>{1.75}$Ti$</em>{3.25}$O$_{0.95}$</td>
<td>294</td>
<td>133</td>
<td>0.0061</td>
<td>1.63</td>
<td>112</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>232</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$_2$TiO$_4$</td>
<td>294</td>
<td>190</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$_2$TiO$_4$</td>
<td>294</td>
<td>196</td>
<td>0.0013</td>
<td>0.35</td>
<td>192</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>244</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$_2$TiO$_4$</td>
<td>294</td>
<td>181</td>
<td>0.0013</td>
<td>0.35</td>
<td>181</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>236</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Below 2 K, \(\chi_m = C/T + 0.8 K)."

Since the value of the Weiss temperature \(\theta\) is nonzero, the data of Fig. 8b do not lie on a common curve, and no attempt was made to fit the data with Brillouin functions. Various of the above magnetic properties are listed in Table IV.

In order to interpret the intrinsic magnetic susceptibility for the Li$_{1+x}$Ti$_{3+y}$O$_4$ spinel compounds, the various contributions to the susceptibility must be considered. After accounting for the impurity terms, the data of Fig. 7b may still be the sum of several contributions. For metallic samples, the contributions are

\[
\chi = \chi_\text{core} + \chi_\text{Pauli} + \chi_\text{Landau} + \chi_\text{orbital}
\]

where the first term is the sum of the core diamagnetism and Van Vleck paramagnetism of the ion cores, and the last three terms are the Pauli paramagnetism, diamagnetic susceptibility, and orbital contribution, respectively, due to the conduction electrons.

The diamagnetic contribution due to the ion cores may be estimated from published tables. The table of Selwood	extsuperscript{24} will be used here. For the electrical insulator Li$_{1.75}$Ti$_{2.25}$O$_4$, the diamagnetic susceptibility due to the ion cores is \(-58 \times 10^{-6} \text{ cm}^3/\text{mole}\). However, Ti$^{4+}$ has been observed to possess a temperature-independent Van Vleck susceptibility of +33\(\times\)
temperature $\theta$ is nonzero, the data of Fig. 3d no attempt was made to fit the data for these magnetic properties are listed.

Table I gives the magnetic susceptibility for the various contributions to the susceptibility, including the impurity terms, the crystal fields, and the orbital contributions. For metallic samples, the core diamagnetism and Van Vleck susceptibility are the last terms in the susceptibility, and orbital, Van Vleck, and electronic. The susceptibility due to the ion cores may be estimated by a core diamagnetism of $+33 \times 10^{-6}$ cm$^3$/mole Ti$^{4+}$ when coordinated by oxygen octahedra, as are the ions in the present case. Therefore, the Van Vleck susceptibility due to the Ti$^{4+}$ ions in Li$_3$Ti$_2$O$_4$ is $+55 \times 10^{-6}$ cm$^3$/mole. The calculated temperature-independent susceptibility due to the sum of the two terms is therefore $\chi^{\text{core}} = -3 \times 10^{-6}$ cm$^3$/mole. From Table IV, the measured room-temperature values for this composition are $-3 \times 10^{-6}$ and $0 \times 10^{-6}$ cm$^3$/mole (both values $\pm 1 \times 10^{-6}$ cm$^3$/mole), in good agreement with the calculated value. Therefore, the net correction to the molar susceptibilities due to $\chi^{\text{core}}$ is very small, and will be neglected here.

If conduction electron band effects are represented by an effective mass, $\chi^{\text{Pauli}}$ and $\chi^{\text{Landau}}$ take the form:

$$\chi^{\text{Pauli}} = \frac{1}{m^2}, \quad \chi^{\text{Pauli}}(0) = \frac{\pi}{6} N_s(0)$$

$$\chi^{\text{Landau}} = -\frac{1}{m^2} \chi^{\text{Pauli}}$$

where $\chi^{\text{Pauli}}(0)$ is the Pauli paramagnetic susceptibility for a free-electron Fermi gas containing the same volume concentration of electrons as the sample under study. $N_s(0)$ is the band structure density of electron energy states at the Fermi surface for both spin directions. $m^*$ is the rest mass of the electron, $m^*$ is the effective mass of the conduction electrons, and $\mu_B$ is the Bohr magneton. Thus, after correcting for the susceptibility of the ion cores and for the impurity contribution to the susceptibility, one has

$$\chi^{\text{imp}} = [\langle m^*/m \rangle - \langle m^*/m^* \rangle] \chi^{\text{Pauli}}$$

(6)

(7)

(8)

where $V_m$ is the molar volume and $N/V$ is the electron concentration in cm$^{-3}$. For the spinel phase Li$_{3}$Ti$_{2}$O$_{4}$, the concentration of electrons outside closed shells is assumed to be

$$N/V = 8(1 - 3x)/a$$

(9)

From Eq. (8), the effective mass of the conduction electrons may now be determined, by solving the relation:

$$\langle m^*/m \rangle - \langle m^*/m^* \rangle = \chi^{\text{Landau}} / \chi^{\text{Pauli}}(0)$$

From the value of $m^*/m$ determined from Eq. (8), the band structure density of states for both spin directions $N_s(0)$ can be determined from Eq. (9).
TABLE V

Electronic Parameters Characterizing the Conduction Electrons in LiTi$_2$O$_4$ Derived from Magnetic Susceptibility Measurements

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (d_0, \text{Å})</td>
<td>8.402</td>
</tr>
<tr>
<td>(b) (N/L, \text{cm}^{-3})</td>
<td>(1.349 \times 10^{22})</td>
</tr>
<tr>
<td>(c) (V_e, \text{cm}^3/\text{mole})</td>
<td>44.67</td>
</tr>
<tr>
<td>(d) (\rho_{\text{m,meas}}, \text{cm}^3/\text{mole})</td>
<td>(23.5 \times 10^{-6})</td>
</tr>
<tr>
<td>(e) (\chi_K, \text{cm}^3/\text{mole})</td>
<td>(2.20 \times 10^{-3})</td>
</tr>
<tr>
<td>((T&lt;50\text{K}))</td>
<td></td>
</tr>
<tr>
<td>(f) (m^*/m)</td>
<td>9.4</td>
</tr>
<tr>
<td>(g) (N_{\text{te}}(0), \text{states/ev-atom})</td>
<td>0.97</td>
</tr>
</tbody>
</table>

* Lattice parameter.
* Conduction electron concentration.
* Molar volume.
* Calculated Pauli paramagnetism for free electrons.
* Measured susceptibility, corrected for impurity and ion core contributions.
* Calculated electron band structure effective mass.
* Density of electron energy states at the Fermi surface, for both electron spin directions.

(3). In convenient units, \(N_{\text{te}}(0)\) is given by

\[
N_{\text{te}}(0) \left(\frac{\text{states}}{\text{eV-atom}}\right) = \frac{1}{r} \frac{m^*}{m} \times 10^4 \frac{\text{states}}{\text{eV-atom}}
\]

where \(r\) is the number of atoms per formula unit (\(r = 7\) in the present case) and \(m^*/m\) is expressed in units of cm$^3$/mole from Eq. (6).

The above computations were carried out for the superconducting spinel composition LiTi$_2$O$_4$ and the results are listed in Table V.

9. SUMMARY AND DISCUSSION

A crystallographic study of the spinel phase in the Li-Ti-O ternary system showed that the composition and cation distribution for this phase are Li$_x$Li$_{1-x}$Ti$_2$O$_4$ (0 ≤ \(x\) ≤ 1/3), with a statistical distribution of the Li and Ti cations on the octahedral sites for \(x\neq 0\). For \(x = 0\), only titanium cations occupy the octahedral sites, and the crystallographic equivalence of these cations has an important consequence$^{38}$: a +3 or +4 valence cannot be assigned to particular Ti cations, even though the formal valence of these cations in this case is +3.5. By this symmetry property, LiTi$_3$O$_4$ must be metallic, as observed. However, for \(x \neq 0\), the crystallographic equivalence of the octahedral-site Ti cations is destroyed by the presence of Li cations on...
Conduction Electrons in Superconducting Measurements

<table>
<thead>
<tr>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.402</td>
</tr>
<tr>
<td>1.349 x 10^7</td>
</tr>
<tr>
<td>44.67</td>
</tr>
<tr>
<td>25.5 x 10^-6</td>
</tr>
<tr>
<td>220 x 10^-9</td>
</tr>
<tr>
<td>9.4</td>
</tr>
<tr>
<td>0.97</td>
</tr>
</tbody>
</table>

The electronic structure of the spinel phase for both pure and impure systems is not yet clear. The bcc spinel, with a Fermi surface, is the most likely candidate for these properties.

Using Eq. (6), the value of $x$ in the present case is found to be 0.15.

The discussion phase in the Li-Ti-O ternary system is distributed in this phase for $x = 0$, only titanium cations. The equivalence of these $x = 3$ or $x = 4$ valence cannot be satisfied by the normal valence of these crystals, Li$_3$Ti$_3$O$_7$ must be the crystallographic equivalence in the presence of Li cations of these sites, and symmetry arguments do not predict whether these compositions should be metallic or not. On the other hand, for $x = 1/3$ the valences of the Li and Ti cations attain their maximum values of +1 and +4, respectively, and Li$_{x}$Ti$_{2-x}$O$_4$ is an electrical insulator. Therefore, somewhere within the homogeneity range of the spinel phase, a metal-insulator (semiconductor) transition must occur, and the composition dependence of the superconducting and normal state properties is intimately related to the nature of this transition and the composition at which it occurs.

A study of the variation of $T_c$ with composition $x$ for Li$_{x}$Ti$_{2-x}$O$_4$ showed that for compositions in the vicinity of Li$_{1/2}$O$_4$, $T_c$ was $10-12$ K. As the composition parameter $x$ increased from 0.05 to 0.15, the $T_c$ abruptly decreased to $<1.5$ K with increasing $x$. From $x = 0.15$ to $x = 1/3$, no superconductivity was observed. However, in no case was there any evidence from the x-ray data for the formation of superstructures, structural distortion, or additional crystallographic phases for any of the compositions within the spinel homogeneity range. The disappearance of superconductivity at $x = 0.1$ was found to be coincident with a large increase in the room-temperature resistivity and with qualitative changes in its temperature dependence, suggesting that the occurrence of a composition-induced metal-semiconductor transition at about this composition is the factor responsible for the disappearance of superconductivity. This finding is tentative, however, since these resistivity data were obtained from sintered pellets in which grain boundary effects may be important.

Since the maximum possible number of free electrons increases from zero at $x = 1/3$ to about $1 \times 10^7$ cm$^{-3}$ at $x = 0$, the resistivity data are consistent with the dielectric constant data, which indicated that a large concentration of electrons outside closed shells would have to be present in order that a degenerate electron gas could form in the Li-Ti-O spinel. The dielectric measurements also showed that the occurrence of metallic properties for the Li$_{1/2}$Ti$_{1/2}$O$_4$ compounds as $x \to 0$ is not initiated by impurity band conduction.

Magnetic susceptibility measurements showed that for all compositions studied within the homogeneity range of the spinel phase, the susceptibilities are nearly temperature independent over most of the temperature range below room temperature. This magnetic behavior was observed both for the superconducting compositions ($x = 0$) and for nonsuperconducting compositions ($x > 0.1$), indicating that if a composition-induced metal-semiconductor transition does occur at $x = 0.1$, this transition is not accompanied by discrete localization of the electrons outside closed shells. In this connection, a study of other ternary titanium oxides has been made which indicated that nonmetallic oxides containing Ti$^{3+}$ do not necessarily exhibit Curie-Weiss susceptibilities and need not order magnetically.
A rapid determination of the metallic character as the composition changes from LiTi$_2$O$_4$ toward Li$_{1+x}$Ti$_{2-x}$O$_4$ is a likely consequence of both electronic and crystallographic considerations, as follows. The magnetic susceptibility measurements determined that the band effective mass of a conduction electron in LiTi$_2$O$_4$ is large, with a value of $\sim 9m_e$, indicating that the conduction electrons in this compound are of $d$ character. Since the titanium cations are the only $d$ cations present, the $d$ bands probably arise from orbitals on these cations. In the crystallographic consideration of the spinel structure in Section 4, it was determined that for all compositions of the spinel, the titanium cations are situated in oxygen octahedra. The five-fold orbital degeneracy of a $d^1$ cation situated in such an oxygen octahedron is lifted, due to the crystal field of the coordinating oxygen atoms, in the following way (Ref. 39, p. 62):

$$\Delta (\epsilon_d) = \epsilon_d - \epsilon_f$$

That is, removing the original five-fold orbital degeneracy results in a low-energy threesfold orbitally degenerate state (denoted as the $t_{2g}$ orbitals) and a twofold orbitally degenerate state (denoted as the $e_g$ orbitals) separated by an energy $\Delta$ from the first set. For Ti$^{4+}$ in such a cubic crystal field, the energy $\Delta$ is about 2.5 eV (Ref. 39, p. 227). In the spinel structure, the $t_{2g}$ orbitals of one transition metal cation are directed at neighboring octahedral site cations. Therefore, these would be the primary orbitals from which a conduction band is formed in LiTi$_2$O$_4$, and it is likely that the conduction electrons in LiTi$_2$O$_4$ reside primarily on the titanium octahedral site sublattice of the spinel structure. Further, a deviation in the composition of the spinel Li$_{1+x}$Ti$_{2-x}$O$_4$ from $x = 0$ was found in Section 4 to result in the substitution of a fraction $x/2$ of the titanium cations by lithium cations. Since the Li$^{+}$ state does not occur in oxide compounds, the presence of Li$^{+}$ in the octahedral sublattice of the Li-Ti-O spinel should inhibit electron conduction along this sublattice.

If the integrity of the titanium octahedral site sublattice is in fact the dominant factor in determining the metallic character of the Li$_{1+x}$Ti$_{2-x}$O$_4$ spinel compounds as deduced above, then substitution of other alkali or alkaline earth metals for Li on the tetrahedral sites should have much less effect upon the metallic character of Li[Ti$_2$]O$_4$ than a similar Li substitution for Ti cations on the octahedral sites. Preliminary experiments indicate this to be true. Whereas in the present work it was found that substitution of Li for only 5% of the octahedral-site Ti cations destroys both the metallic character and the superconductivity in Li[Ti$_2$]O$_4$, a substitution of at least 20% of the tetrahedral-site Li cations by Mg results in retention of both the metallic character of LiTi$_2$O$_4$ and its related superconductivity.
character as the composition is likely to be a consequence of both ions, as follows. The magnetic moment, 2 m, and effective mass of a 3f-9m, indicating that all of the bands probably arise from the 3f orbital. Since the 3f bands probably arise from the same consideration of the 3f orbital, the fact that the compositions of 0 and 0 in oxygen octahedra. The situation in such an oxygen ion of the coordinating oxygen is normal degeneracy results in a (denoted as the t_{2g} orbitals) orbitals, separated by an energy gap, the energy gap is about 300, the t_{2g} orbitals of one ion forming octahedral site cations. It is from which a conduction electron in the conduction sublattice of the composition of the spinel that results in the substitution of Ti ions. Since the Li^+ state is a j^1 in the octahedral conduction along the octahedral sublattice is in fact the character of the Li_{1+x} Ti_{1-x} O_4. Substitution of other alkali or rare earth ions should have much less effect than a Li substitution in a similar Li substitution in a Li substitution. The experiments indicate that substitution of Ti, Ti for Si, has destroyed both the metallic Ti, Ti substitution of at least results in retention of both the superconductivity.

APPENDIX. PHASE RELATIONS AND CRYSTAL STRUCTURES IN THE Li-Ti-O TERNARY SYSTEM

The collected data on the phase relations in this ternary system at 800°C are shown in part in Fig. 9. In addition, the known temperature-composition phase diagram for the anion binary system Li_2TiO_3-TiO_2 is shown on the left side of the figure. The lattice parameters for various phases are given in Table VI. Several results of the present work (PW) are discussed below, along with a summary of literature data.

In the pseudo-binary system Li_2O-TiO_2, four colorless compounds are known to exist: Li_2TiO_3, Li_2SiTiO_5, Li_4Ti_5O_12, and Li_2Ti_5O_12. The Li_2TiO_3 (not shown in Fig. 9) is formed by reacting Li_2CO_3 with TiO_2 in the molar ratio 2:1 at 800-900°C in an inert atmosphere for several hours. Its crystal structure is orthorhombic, and the compound is isomorphous with the low-temperature form of Li_2GeO_3. The titanium ions show very unusual tetrahedral oxygen coordination in this compound. The compound is stable in this crystal structure at least up to 640-690°C, but a phase transition is seen by differential thermal analysis upon heating through this temperature range. The crystal structure of the high-temperature phase was not determined.

Li_2TiO_3 is a very stable compound, which was first obtained by Kordes in 1932 from the reaction of TiO_2 with a melt of Li_2CO_3. The crystal structure of the compound he obtained was of the NaCl type, with a statistical distribution of the cations on the metal-atom sublattice. However, upon annealing above about 900°C, Li_2TiO_3 develops a superstructure.

Fig. 9. Ternary phase diagram for the Li-Ti-O system in the region bounded by Ti, Li_2TiO_3, and TiO_2.
Crystal Structures and Other Data for Phases in the Li-Ti-O Ternary System

<table>
<thead>
<tr>
<th>Composition</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Commenrs</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂TiO₄</td>
<td>7.91</td>
<td>6.15</td>
<td>7.41</td>
<td>Infrared studies</td>
<td>42, 43</td>
</tr>
<tr>
<td>Li₂TiO₃</td>
<td>4.1355</td>
<td>—</td>
<td>—</td>
<td>Z = 4.7, $P_{21}$ = 3.418, $D_{cen}$ = 3.421</td>
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<td>1300-3300°C, quenched</td>
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<td>Li₂TiO₃</td>
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<td>—</td>
<td>&gt;1250°C</td>
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<td>Orderd-cation and/or ordered-vacancy NaCl phases</td>
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<td>—</td>
<td>—</td>
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<tr>
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<td>Decomposes at 1100°C</td>
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*PW = present work.

**corresponding to ordering of the cations, this superstructure formation is irreversible and the cationic ordering reduces the symmetry of the structure.**
lattice from cubic to monoclinic. However, the strongest lines in the powder x-ray pattern can still be indexed on a pseudo-cubic basis (face-centred indexing) with a lattice parameter of 8.28 Å, which corresponds to twice the lattice parameter of the cation-disordered Li$_2$TiO$_3$. The ordered form of Li$_2$TiO$_3$ has a homogeneity range that extends at least to the composition Li$_2$Ti$_2$O$_5$. For which the pseudo-cubic lattice parameter has increased slightly to 8.29–8.30 Å (PW). From density measurements, it was deduced that the existence of the solid solution range is due to the formation of cation vacancies.

A cation-disordered NaCl phase has also been found for the compositions Ti$_{1-x}$Li$_x$O (0 ≤ x ≤ 0.5). It is not known whether this phase extends to x > 0.5. The lattice constants for this phase range from about 4.14 to 4.18 Å (see Table VI), and are therefore almost half of the lattice parameters of the spinel phase (see below). This phase has been produced by reaction of Li$_2$TiO$_3$ and TiO in appropriate ratios at 1000°C or at 800°C (PW). Li$_2$TiO$_3$ can also be synthesized by reaction of Li$_2$O and Ti$_2$O$_3$ at 1000°C. Subjecting Li$_2$TiO$_3$ to various annealing procedures did not result in the appearance of superstructure lines in the x-ray patterns, indicating that the cations do not order, in contrast to Li$_2$TiO$_3$. The other end member of the solid solution range, TiO, on the other hand, is known to contain about 15% vacancies on each of the cation and anion sublattices. These vacancies are disordered above 1250°C, but below this temperature the vacancies do order, producing a superstructure with a period of three times the high-temperature lattice constant. Below about 980°C, the vacancies order in a different way, resulting in a reduction of the lattice symmetry from cubic to monoclinic. The possible existence of these vacancies for compositions Ti$_{1-x}$Li$_x$O has not been considered in the literature. In the Ti–O binary system, there also exists a large homogeneity range in the metal: oxygen ratio for the NaCl-type phase. At high temperatures, the TiO, NaCl phase is stable between the limits 0.7 < x < 1.3. A similar large homogeneity range in the metal: oxygen ratio has been found for Li$_2$TiO$_3$ at high temperatures. Data on this homogeneity range and other properties of the (Li, Ti)O$_3$ NaCl phase will be published later.

The existence of a spinel phase in the Li–Ti–O system was first established by Bertaut and Durif. On the line joining TiO$_2$ and Li$_2$TiO$_3$, the composition of the spinel is Li$_x$Ti$_{2-x}$O$_3$. This compound has a lattice parameter of 8.357 Å (Refs. 11 and 23 and the present work), very similar to but slightly larger than the pseudo-cubic lattice parameters of the ordered Li$_2$TiO$_3$. However, it is not nearly as stable as Li$_2$TiO$_3$ and melts incongruently at 1025°C. For compositions along the line TiO$_2$–Li$_2$TiO$_3$, the homogeneity range of the spinel phase is very narrow. Synthesis of compositions on either side of the composition Li$_2$TiO$_3$ below 950°C...
results in the appearance of second phases: TiO₂ (rutile) or the ordered Li₃Ti₂O₅ phase, and the lattice constant of the spinel remains unchanged (PW). However, a homogeneity range does exist which extends into the region of reduced Ti⁺⁺ of the phase diagram.¹⁰¹¹ This homogeneity range extends from Li₃Ti₃O₇ to Li₂Ti₂O₅, for which the lattice parameter has increased to ~8.405 Å (Ref. 10 and the present work). The preparation, lattice parameters, and normal and superconducting state properties of the spinel phase are discussed in detail in the main body of this paper.

The difficulty of interpreting x-ray powder patterns containing mixtures of the phases Li₃Ti₃O₇-Li₂Ti₂O₅, Li₃Ti₂O₅-Li₂Ti₂O₅, and/or Li₂Ti₂O₅-TiO₂ therefore stems from the commensurate cubic or pseudo-cubic lattice parameters of these phases. The observed x-ray diffraction patterns for these phases are shown schematically in Fig. 10: the similarities are immediately apparent.

The compound Li₂Ti₂O₅ was discovered by Jonker in 1956,²² and is stable from 950°C to its melting point of about 1380°C. Above 950°C, it decomposes very slowly into Li₂Ti₂O₅ and TiO₂ (rutile). The crystal structure was found to be related to the orthorhombic Ramdellite structure,²⁶ which contains four metal atoms and eight oxygen atoms per unit cell. This structure has tunnels running in the direction of the c axis which can accommodate lithium cations.²⁶ The titanium cations are positioned in

Fig. 10. Schematic illustration of the powder diffraction patterns obtained for several compounds in the Li-Ti-O ternary system. The data for Li₂TiO₅ (disordered) were taken from Ref. 45.
phases: TiO₂ (rutile) or the ordered 
spinel remains unchanged. 
This homogeneity range 
for which the lattice parameter has 
been present work). The preparation, 
characterizing the structures of the 
main body of this paper, 
powder patterns containing mixtures 
O₁₋₂ Li₂Ti₃O₇, and/or Li₂TiO₃–TiO₂ 
ate cubic or pseudo-cubic lattice 
and x-ray diffractometer patterns for 
in Fig. 10, the similarities are 
noted by Jonker in 1956, and is 
about 1380°C. Below 950°C, it 
and TiO₂ (rutile), its crystal 
structure has the eight oxygen atoms per unit 
the direction of the c-axis, which 
titanium cations are positioned in 
distorted octahedra of oxygen anions. Since lithium cations can also substi-
tute for the titanium cations, the general chemical formula for this phase is 
Li₁₋ₓ₁ₓ₁₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ_oxy. 
The colorless composition Li₁₋ₓ₁ₓ₁₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ₂₋ₓ_oxy then corresponds to 
x = y = 16/7 and y = 4/7. The homogeneity range of this phase along the 
line Li₂TiO₃–TiO₂ has not been studied in detail, although a single-phase 
sample was also obtained for the composition Li₂Ti₃O₇–TiO₂ (1). Other 
investigations indicate a homogeneity range extending into the region of 
the phase diagram containing reduced Ti⁺⁺⁺ cations (compare with the spinel 
homogeneity range above). Samples with composition Li₂TiO₃ (spinel 
structure below ~950°C) were found after induction melting in a sealed Mo 
crucible to have single-phase Ramdellite structure, but with a change in the 
Lattice parameters as compared to Li₂TiO₃, and an increase of about 1% in the 
unit cell volume (P.W. Table V). In terms of the chemical formula for the 
Ramdellite phase, the composition Li₂TiO₃ corresponds to the parameters 
x = 2 and y = 0. A Ramdellite-phase sample at this composition was 
found to have a room-temperature resistivity of 60 Ω-cm, indicating non-
nmetallic character (P.W.). Attempts to synthesize Ramdellite structure 
compounds at high temperature for metal: oxygen ratios greater than 3:1 
resulted in multiphase samples containing the NaCl phase (Ti, Li)₂O₂ as the 
principal second phase (P.W.). None of the samples with the Ramdellite 
structure were found to be superconducting above 1.5 K (P.W.). 
The liquidus line shown in Fig. 9 was determined by Hummel and 
Tien (2). A eutectic exists at 1230°C for a mole ratio of TiO₂ : Li₂TiO₃ of 
8:1.

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Prof. D. Wolfsen, Dr. J. Huber, and Dr. B. Sales for experimental 
assistance with the Faraday magnetometer, to Dr. H. Prakash and Dr. R. 
Viswanathan for experimental help and discussions during the preliminary 
stages of this investigation, to Prof. W. H. Zachariasen for valuable discus-
sions concerning the crystallography of the spinel phase, and to Dr. A. 
Moodenbaugh for measuring the Tc's of several samples.

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Superconducting and Normal State Properties. I


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A Series of Oxygen-Defect Perovskites Containing Cu\textsuperscript{II} and Cu\textsuperscript{III}: The Oxides La\textsubscript{3-x}Ln\textsubscript{x}Ba\textsubscript{3} [Cu\textsuperscript{II}\textsubscript{p-r} \textsubscript{2-x} Cu\textsuperscript{III}\textsubscript{p-r} \textsubscript{2-x}] O\textsubscript{4+x+y}

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A series of oxygen-defect perovskites, containing Cu\textsuperscript{II} and Cu\textsuperscript{III}, La\textsubscript{3-x}Ln\textsubscript{x}Ba\textsubscript{3} [Cu\textsuperscript{II}\textsubscript{p-r} \textsubscript{2-x} Cu\textsuperscript{III}\textsubscript{p-r} \textsubscript{2-x}] O\textsubscript{4+x+y}, has been synthesized at 1000°C, for 0.05 ≤ x ≤ 0.43. The substitution of lanthanum for yttrium and lanthanides has been studied. These oxides are tetragonal: a = a\textsubscript{2} \textsuperscript{1/4} and c = 3a. The structural study of La\textsubscript{3}, Ba\textsubscript{3} Cu\textsubscript{p-r} O\textsubscript{4+x+y} shows that oxygen vacancies are ordered, involving for copper three sorts of coordination: square, pyramidal (1 + 1), and distorted octahedral (4 + 2). The distribution of Cu\textsuperscript{III}, as well as the lanthanide ions on the different sites, is discussed.

Introduction

The number of oxygen-defect perovskites ABO\textsubscript{3−x} known at the present time is limited. This is probably related to the nature of the B atoms forming the octahedral framework: the anion deficiency should be stabilized if the B atom is going to be able to present, in addition to the octahedral coordination, an environment derived from the latter but characterized by a smaller number of coordination. In this respect, copper is a potential candidate due to its ability to take octahedral, square planar, or pyramidal coordination. Moreover, the oxygen nonstoichiometry in the copper oxides can be influenced by the possibility of formation of trivalent copper, depending on the experimental conditions. Ternary oxides A\textsubscript{3-x}Cu\textsubscript{p-r} O\textsubscript{4+x+y} containing Cu\textsuperscript{III} can indeed be prepared under 1 atm oxygen pressure (1−4) or under high oxygen pressure (5, 6) according to the nature of the A element. Some A elements like barium allow the formation of Cu\textsuperscript{III} in air (7, 8). The present paper deals with a series of defect perovskites La\textsubscript{3-x}Ln\textsubscript{x}Ba\textsubscript{3}Cu\textsubscript{p-r} O\textsubscript{4+x+y} which have been synthesized in air and in which copper takes two oxidation states: +2 and +3.

Synthesis and Characterization

The Oxides La\textsubscript{3}Ba\textsubscript{3}Cu\textsubscript{p-r} O\textsubscript{4+x+y}

La\textsubscript{2}O\textsubscript{3} and CuO oxides and BaCO\textsubscript{3} were mixed and heated in air, in platinum crucibles, first for 12 hr at 900°C, then for 24 hr at 1000°C, and finally quenched at room temperature. From the different compositions which were investigated a pure compound was isolated with the atomic ratios: La\textsubscript{3}/Ba\textsubscript{3} = (La + Ba)/Cu = 1. The observed weight loss was smaller than that deduced from the departure of CO\textsubscript{2}. The partial oxidation of Cu(II) to Cu(III) was thus considered, leading to the formula La\textsubscript{3}Ba\textsubscript{3}
[Cu\textsuperscript{II}, Cu\textsuperscript{III}] \textsubscript{10-ε} O\textsubscript{14-ε}. The y value obtained from the weight loss during the synthesis, y = 0.10, was in agreement with this hypothesis. This was confirmed by the microthermogravimetric study of the reduction of the quenched product under hydrogen.

The variation of y as a function of temperature and especially oxygen pressure was then examined. Annealing the quenched compound in air gave a maximum value of y (0.37) at 400°C. The quenched compound (y = 0.10) was then annealed at this temperature under different oxygen pressures, ranging from 5 \times 10^{-2} to 1 atm. The y value and thus the Cu\textsuperscript{II} amount, deduced from microthermogravimetric measurements, increased regularly with the oxygen pressure, as shown in Table 1.

All these oxides were obtained in the form of a black powder, whose X-ray patterns show strong reflections similar to those of the stoichiometric perovskites. They have been indexed in a tetragonal cell whose parameters are related to that of the cubic perovskite \( a_b \) in the following way: \( a = b = a_b \cdot 2^{1/2} \), \( c = 3a_b \). These parameters do not vary appreciably with the oxygen amount: \( a = 5.526(4) \) Å and \( c = 11.721(1) \) Å for the air-quenched sample (y = 0.10) while \( a = 5.529(8) \) Å and \( c = 11.729(2) \) Å for the sample annealed under 1 atm oxygen \( (y = 0.43) \).

The Oxides: La\textsubscript{2-y}Ln\textsubscript{y}Ba\textsubscript{2}Cu\textsubscript{4}O\textsubscript{10+x} (Ln = Y, Pr, Nd, Sm, Eu, Gd, Er, Yb)

These compounds were prepared in the same way as the oxide La\textsubscript{2}Ba\textsubscript{2}Cu\textsubscript{4}O\textsubscript{10+δ}, quenching the sample from 1000°C to room temperature in air. In the case of yttrium and europium, the oxides were heated for periods greater than 24 hr, in order to obtain better crystallization. The possibility of substitution of lanthanum for another lanthanide or for yttrium decreases regularly with the size of Ln\textsuperscript{III} (Fig. 1); a total substitution (x = 3) was obtained for praseodymium, while less than 50% of lanthanum could be replaced by ytterbium. The evolution of the oxygen amount y was not investigated in an exhaustive manner. It can be stated that for the same experimental conditions as those used for La\textsubscript{2}Ba\textsubscript{2}Cu\textsubscript{4}O\textsubscript{10+δ}, the variation of the Cu\textsuperscript{III} amount remains weak. It seems, however, that y decreases with the size of the Ln\textsuperscript{III} ion; the y values observed for the three richest compounds in Ln\textsuperscript{III}, Ln = Pr, Nd, and Sm are respectively 0.10, 0.04, and 0.01.

All these oxides are black and are isostructural of La\textsubscript{2}Ba\textsubscript{2}Cu\textsubscript{4}O\textsubscript{10+δ}; the c/a ratio remains equal to 3/2\textsuperscript{1/2} independently of the composition. The corresponding \( a_b \) parameter decreases regularly with the size of Ln\textsuperscript{III} in agreement with the lanthanide contraction (Fig. 2).
OXYGEN-DEFECT PEROVSKITES

**Fig. 2.** Evolution of the $a_p$ parameter of the oxides $La_{1-x}La_xBa_2Cu_3O_{y+z}$.

**Structural Study of the Oxide $La_xBa_2Cu_3O_{11.10}$**

No single crystal could be obtained due to the decomposition of the compounds at temperatures greater than 1000°C. The structure of this oxide was thus studied from its X-ray powder pattern registered with a Philips goniometer for the CuKα radiation. The intensities of the peaks corresponding to 74 reflections were measured. The observed density ($d_{obs} = 6.70$) corresponds to one group $La_{1-x}Ba_2Cu_3O_{11.10}$ per cell ($d_{calc} = 6.67$). The existence of the 1 0 0 reflection, though weak, involves the absence of reflection conditions. From the eight possible space groups, we have chosen the most symmetrical space group, $P 4/mmm$, in order to limit the number of variable parameters. Because of the similarity of this phase to the perovskite, the metallic atoms were placed in analogous positions: the barium and lanthanum ions were statistically distributed in 4(d) (0 1 2); while the copper atoms were placed in 1(a) (0 0 0), 1(c) (0 0 0), 2(g) (0 0 z; z = 1), and 2(h) (1 0 z; z = 1). The great anionic deficiency with respect to the stoichiometric perovskites set the problem of the distribution of the 14.1 oxygen atoms over the 18 possible sites of the structure. Starting from the ideal formula $La_{1-x}Ba_2Cu_3O_{11.10}$, we have assumed that the structure was built up from CuO$_2$ sheets parallel to (001) as in $La_{2-x}A_{1+2}Cu_2O_{x-2}$ (9) involving, for copper at least, the square planar coordination. Twelve oxygen atoms O$_1$ and O$_2$ were thus respectively distributed on 4(j) (x 0 0; x = 1) and 8(r) (x x z; x = 1/4 and z = 1/4). For the two remaining oxygen atoms O$_3$, located between the CuO$_2$ layers at about the same level as the barium and the lanthanum atoms, different distributions over four sets of sites—1(b) (0 0 1); 2(d) (1 1/4 z; z = 1); 2(g) (0 1 1; z = 1); and 1(h)—were considered. After successive refinement of the atomic coordinates of the metallic atoms, of the oxygen atoms O$_1$, and O$_2$, and of the isotropic thermal parameters it was found that the O$_2$ atoms were located principally in 2(h). The minimum discrepancy factor $R = \Sigma |I_{obs} - I_{calc}|/\Sigma I_{obs}$, $R = 0.039$, was obtained for the thermal and positional parameters given in Table II. Table III shows the agreement between the calculated and observed intensities.

**Description of the Structure and Discussion**

This structure can be described from that of perovskite by formation of ordered oxygen vacancies in the "A-O" planes. The result is that the plane stacking sequence...
**ER RAKHO ET AL.**

**TABLE III**

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<td>407</td>
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<td>338</td>
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<td>533</td>
<td>—</td>
<td>0.9208</td>
<td>9.0</td>
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</tbody>
</table>

[AO – CuO₄]₆ along a in the cubic perovskite is replaced by the sequence AuO₄ – A₂O₄ – CuO₄ – A₂O₄ – CuO₄ – A₂O₄ along c in La₂Ba₂Cu₆O₁₄.10 (Fig. 3). Three sorts of coordination are thus observed for copper in this structure: square planar for Cu₁ and Cu₂, pyramidal (4 + 1) for Cu₃, and distorted octahedral (4 + 2) for Cu₄ (Table IV). Whatever the nature of the copper coordination may be, we always observed for this atom a basal plane characterized by four Cu–O distances close to 1.95–1.96 Å.

The great distance (2.33 Å) observed for Cu₁ is close to that obtained for copper with a similar coordination in La₂₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅-
observed Jahn-Teller distortion. Such an environment has, however, already been observed in K₃CuF₆ (10) and K₃CuO₃ (11). The very short Cu-O distances (1.72 Å), smaller than those observed for copper in 4+1 coordination in BaCuO₂ (1.80 Å) (12) made us think that the oxidation state of this element may be +3, in agreement with the very short distances observed in La₂SrCuO₄ (6). This environment suggests for Cu³⁺ a d²,2,2,2 = d⁵2 configuration (11).

The distribution of lanthanum and barium over the A₁ and A₂ sites could not be studied due to the similar values of the scattering factors of La³⁺ and Ba²⁺ which are isoelectronic. The A₁-O distances are much greater than the A₂-O distances: these let us deduce that the barium atoms are located only on the A₁ sites. In order to verify this hypothesis, the yttrium compound Lu₁₂YBa₂Cu₁₀O₄₋ₓ was examined, the scattering factor of yttrium being smaller than that of lanthanum or barium. The intensities ratio of the 1 1 2 and 2 0 3 reflections of this compound was thus compared to that of La₁₂Ba₂Cu₁₀O₄₋ₓ. The I₁₁₂/I₂₀₀ ratio varies appreciably indeed with the electronic distribution on the A₁ and A₂ sites, since the contributions of the A₁ sites to the structure factors F₁₁₂ and F₂₀₀ have opposite signs, while the contributions of A₂ sites have the same sign. The experimental value (I₁₁₂/I₂₀₀) = 0.20 observed for the La₁₂YBa₂Cu₁₀O₄₋ₓ, much greater than that of La₁₂Ba₂Cu₁₀O₄₋ₓ, (I₁₁₂/I₂₀₀) = 0.083, shows that the smallest ion, yttrium, is located on the A₂ site, leading to the probable distribution (3Ba²⁺ + 2La³⁺) on A₁ and (1La³⁺ + 1Y) on A₂, in agreement with our hypothesis.

The very large oxygen deviation from stoichiometry is an important feature of these compounds. The ordered distribution of the oxygen vacancies with regard to the ideal perovskite must be emphasized; it is worth noting that the distribution of the O₃ atoms on the 1b and 1d sites appreciably increases the R factor. In the same manner, a statistical distribution of these atoms over the 2g and 2h sites, which would involve the disappearance of the superstructure in the (0 0 1) plane, is not possible. A partial occupation of the 2g sites cannot, however, be eliminated. The 0.1 supplementary oxygen atoms, which have not been considered for these calculations, could be located, if we consider Cu³⁺ ions with an octahedral coordination, either on the 2g or on the 1d sites. The second hypothesis agrees with the fact that the introduction of one supplementary oxygen atom induces the presence of two Cu³⁺ ions. However, calculations made on a richer oxygen compound do not allow us to choose between these sites. The presence of copper in these compounds, simulta-
neously with two oxidation states, Cu(II) and Cu(III), suggests interesting electrical properties, which will be investigated as a function of oxygen amounts.

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United States Patent [19]

Murata et al. [11] 4,357,426

[54] HUMIDITY SENSITIVE CERAMICS

[75] Inventors: Michihiro Murata, Kyoto; Shinsei Okabe, Takatsuki, both of Japan

[73] Assignee: Murata Manufacturing Co., Ltd., Kyoto, Japan

[21] Appl. No.: 332,096


[30] Foreign Application Priority Data


[51] Int. Cl.3 ................... G01B 35/50

[52] U.S. Cl. ................... 501/135; 501/136;
501/137; 501/138; 501/139; 501/152; 252/520;
252/521

[58] Field of Search ................... 501/135-139,
501/152; 252/520, 521

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Primary Examiner—James Pooe
Attorney, Agent or Firm—Birch, Stewart, Kolasch & Birch

[37] ABSTRACT

A humidity sensitive ceramics comprises a sintered body consisting essentially of a semiconductive compound oxide with a perovskite structure and a compound oxide, said semiconductive compound oxide having a composition expressed by the general formula (I):

A₁₋ₓₐ₊ₓB₂O₅₋ₘ

wherein A is at least one element selected from the group consisting of rare earth elements with atomic numbers 57 to 71, yttrium and hafnium, A' is at least one element selected from the group consisting of alkaline-earth metals, B is at least one element selected from the group consisting of transition elements with atomic numbers 23 to 30, x is a mole fraction and takes a value of the following range, 0≤x≤1, and m is a non-stoichiometric parameter, said compound oxide having a composition expressed by the general formula (II):

AₓMO₃₋ₘ

wherein A is at least one element selected from the group consisting of alkaline earth elements, Zn, Cd, Fe, Co, Ni, Mn and Pb, M is at least one element selected from the group consisting of Ti, Zr, Hf and Sn.

1 Claim, 4 Drawing Figures
Fig. 2

Graph showing the relationship between Relative Humidity (%) and Resistance (Ω). The graph has two curves labeled 2-1 and 2-2. The y-axis represents resistance in units of Ω, and the x-axis represents relative humidity in percentage.
1

HUMIDITY SENSITIVE CERAMICS

FIELD OF THE INVENTION

This invention relates to humidity sensitive ceramics which possess the change of resistivity with change in humidity.

BACKGROUND OF THE INVENTION

As a humidity sensor or a moisture detecting element that makes use of the change of resistivity of a humidity sensitive material with change in humidity, there have been used those comprising lithium chloride, or those comprising ceramics of the system such as TiO_2-SnO_2, TiO_2-V_2O_5, MgCr_2O_4 or ZnO-Li_2O-V_2O_5. Among them, the humidity sensors comprising the above ceramics, or humidity sensitive ceramic sensors possess excellent stability in characteristics as compared with the sensors of lithium chloride. The ceramic sensors possess poor aging in the humidity detecting function as well as the sensors of lithium chloride. For example, when the ceramic sensors of the prior art are allowed to stand 3 months in an atmosphere of 40% relative humidity, the resistance thereof change by some 40% from the value of initial resistance. However, their function can be recovered to the previous level by heating since the ceramics used as a material for humidity sensors do not change in quality even if heated to high temperatures. For this reason, the ceramic sensors are combined with a heating element for practical purposes to recover its humidity detecting function by intermittent heating. However, this lead to increase of the consumption of electric power.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide humidity sensitive ceramics with good aging in the humidity detecting function.

Another object of the present invention is to provide humidity sensitive ceramics which makes it possible to produce humidity sensors with a desired resistance change rate by the variation of compositional proportions of the components, and the resistance of which is lowered with increase of the humidity.

According to the present invention, there is provided a humidity sensitive ceramics comprising a sintered body consisting essentially of a semiconductive compound oxide with a perovskite structure and a compound oxide. The semiconductive compound oxide has a composition expressed by the general formula (I):

$$A_{1-x}A'B_2O_3 - \delta$$

wherein A is at least one element selected from the group consisting of rare earth elements with atomic numbers 57 to 71, yttrium and hafnium, A' is at least one element selected from the group consisting of alkali-earth metals, B is at least one element selected from the group consisting of transition elements with atomic numbers 23 to 30, \(x\) is a mole fraction and \(\delta\) is a nonstoichiometric parameter. The compound oxide has a composition expressed by the general formula (II):

$$AMO_3 \ldots$$

wherein A is at least one element selected from the group consisting of alkali-earth elements, Zn, Cd, Fe, Co, Ni, Mn and Pb, M is at least one element selected from the group consisting of Ti, Zr, Hf and Sn.

In the preferred embodiment, the semiconductive compound oxide having the perovskite structure expressed by the general formula (I): $A_{1-x}A'B_2O_3 - \delta$, wherein A is at least one element selected from the group consisting of rare-earth elements with atomic numbers 57 to 71 inclusive, yttrium and hafnium, A' is at least one element selected from the group consisting of alkali-earth metal, and B is at least one element selected from the group consisting of transition elements with atomic numbers 23 to 30 inclusive, may have a composition expressed by the formula: $La_{1-x}Sr_{x}Co_1 - N_yO_3$ wherein $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

In further preferred embodiment, the semiconductive compound oxide expressed by the general formula (I) has a composition expressed by the formula: $Nd_{1-x}Sr_{x}Ba_2CoO_3$ wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq x' + x'' \leq 1$.

In another preferred embodiment, the semiconductive compound oxide expressed by the general formula (I) has a composition expressed by the formula: $Y_{1-x}Sr_{x}CoO_3$ wherein $0 \leq x \leq 1$.

In still another preferred embodiment, the semiconductive compound oxide expressed by the general formula (I) has a composition expressed by the formula: $La_{1-x}Sr_{x}MnO_3$ wherein $0 \leq x \leq 1$.

In the above general formula (I), A and A' may take a coexistence state, and are also allowed to be existed independently each other. Thus, x in the formula may take any value within the range of 0 to 1 inclusive.

In the general formula (I), A_1-xA'_xB_2O_3 - \delta, oxygen defects which changes the composition into a semiconducting state are expressed by using \(\delta\) as a nonstoichiometric parameter. The oxygen defect state of the composition can be obtained by sintering the composition in a reducing or oxidizing atmosphere.

In the preferred embodiments, the compound oxide expressed by the general formula (II): AMO_3 wherein A is at least one element selected from the group consisting of alkali-earth metals, Zn, Cd, Fe, Co, Ni, Mn and Pb, and M is at least one element selected from the group consisting of Ti, Zr, Hf and Sn, has a composition SrTiO_3, BaTiO_3, CaSnO_3 or Sr_{1-y}Ca_yTiO_3 (where $0 \leq y \leq 1$).

The semiconductive compound oxide with the perovskite structure expressed by the general formula (I) and the compound oxide expressed by the general formula (II) may be mixed in any ratio to produce ceramics with a desired initial resistance and a change rate of resistance with the change in humidity. The semiconductive compound oxide and the compound oxide are generally mixed in the ratio within the range of 1:100 to 1:101, preferably, within the range of 1:50 to 1:11. Because, if humidity sensitive ceramics are composed of the compound oxide AMO_3 alone, i.e., if no semiconductive compound oxide with the perovskite structure is present in the ceramics, they possess extremely high resistance, thus making it impossible to put them into practical use. Further, if ceramics are composed of the semiconductive compound oxide with the perovskite structure alone, i.e., if no compound oxide expressed by the general formula (II) is present in the ceramics, they possess considerably small change rate of resistance with change in humidity, thus making it impossible to use them as a material for humidity sensitive sensors.

The humidity sensitive ceramics according to the present invention may be produced in a manner conven-
tionally employed for known ceramic materials. For example, the humidity sensitive ceramics of the present invention may be produced in the following manner:

The raw materials in forms of oxides and/or carbonates are weighed out, mixed, calcined, powdered and granulated with a suitable amount of binder, and the resultant mixture is formed into suitable shapes. The shaped bodies are sintered at a temperature within the range of 800° to 1400° C. to produce humidity sensitive ceramics. The resultant sintered ceramic bodies may be provided with electrodes to produce humidity sensors. The sintered body may be in the shape of disc, rod bar, pellet, or cylindrical. The electrodes for detecting the change of resistivity of ceramics may be formed in any shape, for example, as opposed, plate electrodes, comb-shaped electrodes, or porous electrodes.

In order to obtain good humidity detecting characteristic, the sintered ceramic body has preferably porosity within the range of 20 to 50%.

In the foregoing, the nonstoichiometric amount of oxygen (O) in the semiconductive compound oxide with the perovskite structure is not specified but represented in the form of O2 as well as in Examples.

The humidity sensitive ceramics according to the present invention are considerably small in aging even if they are exposed to repeated change of humidity surroundings for a long time, thus making it possible to produce humidity sensors without combining them with heating elements. In addition, the humidity sensitive ceramics with a desired change rate of resistance with change in humidity can be produced at will by variation of compositional ratio of the semiconductive compound oxide and the compound oxide expressed by the general formula AMO3, thus making it possible to produce humidity sensitive sensors with various humidity detecting characteristics.

The invention will be further apparent from the following description with reference to examples and the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 to 4 are graphs showing resistance vs. relative humidity characteristics of humidity sensors comprising humidity sensitive ceramics according to the present invention.

EXAMPLE 1

As raw materials, there are provided powder of La2O3, SrCO3, CaO3, and TiO2. These raw materials are mixed to obtain mixtures respectively corresponding to a composition La2Sr2Ca2Co3O11 and SrTiO3. The resultant mixtures are then calcined at 1100° C., crushed and ground to powder. The resultant pre-sintered powder of La2Sr2Ca2O11 and that of SrTiO3 are mixed in various ratios shown in Table 1, granulated by using 10 wt% of binder, and then shaped into disks with a 10 mm diameter and a 0.6 mm thick. The disks are fired in air at 1250° C. to obtain sintered bodies of ceramics which are humidity sensitive ceramics. A set of porouse electrodes of various electrically conductive materials shown in Table 1 are applied to the opposite disk surfaces of the sintered bodies, and a pair of lead wires are connected to the respective electrodes to provide humidity sensors. The porous electrodes may be formed by printing an electrically conductive paste on the opposite disk surfaces of each sintered body, and then stoving the same in air.

For each thus prepared humidity sensor, the resistance at various relative humidities are measured to know the change of resistance with change in humidity. The results are shown in FIG. 1.

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Composition (weight %)</th>
<th>Electrode Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>1-2</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>1-3</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>1-4</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>1-5</td>
<td>20</td>
<td>80</td>
</tr>
</tbody>
</table>

In order to investigate the aging characteristic, the sensors of the specimen No. 1-2 are kept in an atmosphere of 40% or 80% relative humidity, and their resistance are measured after the lapse of 3 and 6 months. Results are shown in Table 1B together with the initial values.

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Initial value</th>
<th>After 3 months</th>
<th>After 6 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>40%</td>
<td>540 KΩ</td>
<td>560 KΩ</td>
<td>550 KΩ</td>
</tr>
<tr>
<td>80%</td>
<td>40 KΩ</td>
<td>80 KΩ</td>
<td>83 KΩ</td>
</tr>
</tbody>
</table>

EXAMPLE 2

Using La2O3, SrCO3, CaO3, TiO2, CaCO3, ZrO2 and MgO as raw materials, there are prepared powder of a pre-sintered semiconductive compound oxide, La2Sr2Co2O11, and powder of pre-sintered compound oxides, CaZrO3 and MgTiO3, which are then mixed in the proportions shown in Table 2. The respective resultant mixtures are granulated, shaped and fired in the same manner as in Example 1 to obtain ceramic sintered bodies. A set of porous electrodes are applied to the opposite disk surfaces of each ceramic sintered body by printing a gold paste and then stoving the same in air. A pair of lead wires are electrically connected to the porous gold electrodes.

For the thus prepared humidity sensors, the resistance at various relative humidities are measured to know the change of resistance with change in humidity. The results are shown in FIG. 2.

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Composition (weight %)</th>
<th>Electrode Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>25</td>
<td>MgTiO3, 75</td>
</tr>
<tr>
<td>2-2</td>
<td>10</td>
<td>MgTiO3, 75</td>
</tr>
</tbody>
</table>

In order to investigate the aging characteristic, the sensors of the specimen No. 2-2 are kept in an atmosphere of 40% or 80% relative humidity, and their resistance are measured after the lapse of 3 and 6 months. Results are shown in Table 2B together with the initial values.

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Initial value</th>
<th>After 3 months</th>
<th>After 6 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>40%</td>
<td>8 MΩ</td>
<td>8.3 MΩ</td>
<td>8.6 MΩ</td>
</tr>
<tr>
<td>80%</td>
<td>280 KΩ</td>
<td>290 KΩ</td>
<td>300 KΩ</td>
</tr>
</tbody>
</table>
EXAMPLE 3

Using La₂O₃, SrCO₃, CoO₂, BaO, TiO₂, CaCO₃ and SnO₂ as raw materials, there are prepared mixtures corresponding to a semiconductive compound oxide, La₉₀Sr₁₀CoO₅, and compound oxides, BaTiO₃ and CaSnO₃. The mixtures are calcined at 1100°C, crushed and powdered.

The resultant powder of La₉₀Sr₁₀CoO₅, that of BaTiO₃ and that of CaSnO₃ are mixed in the proportions shown in Table 3, together with 10% by weight of a binder, granulated and then shaped into disks with a 10 mm diameter and a 0.5 mm thick. The disks are fired at 1300°C in air to obtain sintered ceramic bodies. A set of porous gold electrodes are added to the opposite disk surfaces of the sintered bodies in the same manner as in Example 2, and a pair of lead wires are electrically connected to the electrodes.

For the thus prepared humidity sensors, the resistance at various relative humidities are measured to know the change of resistance with change in relative humidity. The results are shown in FIG. 3.

TABLE 3

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Composition (weight %)</th>
<th>La₉₀Sr₁₀CoO₅</th>
<th>BaTiO₃</th>
<th>CaSnO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1</td>
<td>5.0</td>
<td>0.0</td>
<td>95.0</td>
<td></td>
</tr>
<tr>
<td>3-2</td>
<td>7.5</td>
<td>0.0</td>
<td>92.5</td>
<td></td>
</tr>
<tr>
<td>3-3</td>
<td>17.5</td>
<td>0.0</td>
<td>72.5</td>
<td></td>
</tr>
<tr>
<td>3-4</td>
<td>37.5</td>
<td>0.0</td>
<td>42.5</td>
<td></td>
</tr>
</tbody>
</table>

In order to investigate the aging characteristic, the sensors of the specimen No. 3-1 are kept in an atmosphere of 40% or 80% relative humidity, and their resistance are measured after the lapse of 3 and 6 months. Results are shown in Table 3B together with the initial values.

TABLE 3B

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Initial value</th>
<th>After 3 months</th>
<th>After 6 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>40%</td>
<td>340 KΩ</td>
<td>343 KΩ</td>
<td>350 KΩ</td>
</tr>
<tr>
<td>80%</td>
<td>180 KΩ</td>
<td>182 KΩ</td>
<td>183 KΩ</td>
</tr>
</tbody>
</table>

EXAMPLE 4

Raw materials are mixed and calcined at 1100°C to provide presintered bodies of semiconductive compound oxides and compound oxides respectively having the compositions shown in Table 4. The presintered bodies are crushed, powdered and mixed in the proportions shown in Table 4. The mixed powder is added 10% by weight of binder, granulated and shaped into disks with a 10 mm diameter and a 0.5 mm thick. The disks are then fired at 1250°C in air to provide sintered ceramic bodies. Porous gold electrodes are applied to the opposite disk surfaces of the sintered bodies in the same manner as in Example 2 and lead wires are electrically connected to the electrodes.

For the thus prepared humidity sensors, the resistance at various relative humidities are measured to know the change of resistance of the sensors with change in humidity. The results are shown in FIG. 4.

TABLE 4

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Composition (weight %)</th>
<th>A₁₋ₓAₓBO₃</th>
<th>AMO³⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1</td>
<td>La₉₀Sr₁₀CoO₅NiO₃</td>
<td>10</td>
<td>550 KΩ</td>
</tr>
<tr>
<td>4-2</td>
<td>Ni₁₀Sr₉₀CoO₅</td>
<td>10</td>
<td>550 KΩ</td>
</tr>
<tr>
<td>4-3</td>
<td>Ni₁₀Sr₉₀Ba₉₀CoO₅</td>
<td>10</td>
<td>550 KΩ</td>
</tr>
<tr>
<td>4-4</td>
<td>Y₁₀Sr₉₀CoO₅</td>
<td>10</td>
<td>550 KΩ</td>
</tr>
<tr>
<td>4-5</td>
<td>La₉₀Sr₁₀MnO₃</td>
<td>10</td>
<td>550 KΩ</td>
</tr>
</tbody>
</table>

In order to investigate the aging characteristic, the sensors of the specimen No. 4-1 are kept in an atmosphere of 40% or 80% relative humidity, and their resistance are measured after the lapse of 3 and 6 months. Results are shown in Table 4B together with the initial values.

TABLE 4B

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Initial value</th>
<th>After 3 months</th>
<th>After 6 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>40%</td>
<td>560 KΩ</td>
<td>550 KΩ</td>
<td>580 KΩ</td>
</tr>
<tr>
<td>80%</td>
<td>78 KΩ</td>
<td>79 KΩ</td>
<td>79 KΩ</td>
</tr>
</tbody>
</table>

As can be seen from the above examples, the present invention makes it possible to produce humidity sensitive ceramics with a desired change rate of resistance with change in humidity, by variation of the components and that of a compositional ratio of the semiconductive compound oxide to the compound oxide. In addition, the ceramics of the present invention is small in aging even if changes of humidity surroundings are repeated. Thus, the humidity sensitive ceramics of the present invention is useful as a material for humidity sensors, and the humidity sensors comprising the ceramics of the invention can be put into practical use without combining it with a heating element.

What we claim is:

1. A humidity sensitive ceramics comprising a sintered body consisting essentially of a semiconductive compound oxide with a perovskite structure and a compound oxide, said semiconductive compound oxide having a composition expressed by the general formula(I):

   A₁₋ₓAₓBO₃-

   Wherein A is at least one element selected from the group consisting of rare earth elements with atomic numbers 57 to 71, yttrium and hafnium, A' is at least one element selected from the group consisting of alkaline-earth metals, B is at least one element selected from the group consisting of transition elements with atomic numbers 23 to 30, x is a mole fraction and takes a value of the following range, 0 ≤ x ≤ 1, and δ is a non-stoichiometric parameter, said compound oxide having a composition expressed by the general formula(II):

   AMO³⁻-

   Wherein A is at least one element selected from the group consisting of alkaline earth elements, Zn, Cd, Fe, Co, Ni, Mn and Pb, M is at least one element selected from the group consisting of Ti, Zr, Hf and Sn.

* * * *
Observation of a reentrant superconducting resistive transition in granular BaPb$_{0.75}$Bi$_{0.25}$O$_3$ superconductor

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A normal-superconducting-normal transition has been observed resistively in the granular BaPb$_{0.75}$Bi$_{0.25}$O$_3$ compound, while the compound remains diamagnetic to the lowest temperature investigated. This has been attributed to the decoupling of the superconducting grains at low temperature caused by the reduction of charge carriers in the grain barriers, in good agreement with the theory.

Granular superconductors exhibit a wide range of electrical transport behavior which has made the study of this material a subject of great interest in the last few years, concerning the questions of electron-localization and electron-electron correlation. Prospects have subsequently been raised such as the possible existence, in this material, of reentrant superconductivity in which the material undergoes a superconducting to normal transition on cooling and a superconducting insulator where superconductivity prevails in a localized electronic system. In a granular superconductor, the superconducting grains are coated with an insulating layer or imbedded in an insulating matrix. When the separation between the superconducting grains is small and the Josephson coupling energy is stronger than the Coulomb charging energy between the grains, the material becomes superconducting resistively at low temperature through Josephson tunneling between grains. Since the effective Josephson coupling and thus the critical current $I_c$ of a granular superconductor is inversely proportional to the normal tunneling resistance, it is easy to vary the normal tunneling resistance under proper conditions as one of the most effective ways to control $I_c$. The increase of normal tunneling resistance of such a barrier at low temperature can result in a decoupling between the superconducting grains and thus the disruption of the superconducting current. A normal-superconducting-normal resistive transition may therefore be achievable.

The presence of semiconductor barriers in the perovskite-type compounds BaPb$_{1-x}$Bi$_{x}$O$_3$ has long been implied by the difficulty in obtaining a bulk BaPb$_{1-x}$Bi$_{x}$O$_3$ superconductor. A sample of this kind may be considered as an array of series or parallel-series Josephson junctions. Without questioning the occurrence of the high-temperature superconductivity in these compounds which is currently still under intense investigation, we have measured the resistance $R$, the ac magnetic susceptibility $\chi$, and the current-voltage ($I$-$V$) characteristics of the sintered BaPb$_{0.75}$Bi$_{0.25}$O$_3$ compound as a function of temperature $T$ at various magnetic field $H$. Indeed, a normal-superconducting-normal resistive transition and a maximum $I_c$ have been observed in this compound on cooling. Meanwhile, the $x$ results fail to show the return of the superconducting state to the normal state down to 1.2 K, the lowest temperature of the present study. The observations, therefore, demonstrate, for the first time, the existence of a reentrant superconducting resistive transition associated with the specific character of the tunneling barriers in a granular superconductor, instead with a ferromagnetic ordering. The nonmonotonic variation of $I_c$ with $T$ observed is in good agreement with the recent theoretical calculations on the Josephson effect in a superconductor-semiconductor-superconductor junction.

The BaPb$_{0.75}$Bi$_{0.25}$O$_3$ compound was formed by first reacting a compacted mixture of appropriate amounts of BaCO$_3$, PbO, and Bi$_2$O$_3$ in an oxygen atmosphere at 800°C for 24 h. The compacted disks of 4-mm diam x 6-mm thickness so obtained were then pulverized, compressed, and heated several times under the above conditions. Samples with dimensions of $\sim 1.5 \times 1.5 \times 6$ mm$^3$ were sawed off the disks for the present study. Four Pt electrodes were attached to each sample with In ultrasonic solder, or silver paste for $R$ measurements. Independent of the material used to mount the electrodes, the contact resistance of our samples always fell between 10 and 20 $\Omega$ at 300 K and between 20 and 100 $\Omega$ at 4.2 K. This poses a limit to our voltage resolution at about $0.5 \mu V$. The four lead dc resistance technique and a standard ac inductance bridge operated at 26 Hz were employed for the $R$ and $X$ measurements, respectively. The temperature above 20 K was determined by a chromel-alumel thermocouple and below by a Ge thermometer.

Within a resolution of $\sim 3\%$, the powder x-ray diffraction patterns of our BaPb$_{0.75}$Bi$_{0.25}$O$_3$ samples display only a single perovskite structure with the lattice parameters $a = 6.08 \pm 0.01$ Å and $c = 8.59 \pm 0.02$ Å. However, the scanning electron microscope results show a $\sim 20\%$ precipitation in a uniform matrix. The precipitation is in the form of spheres of diameters 1000–5000 Å evenly distributed in the matrix. Preliminary energy dispersive analysis of x-ray indicates that the precipitation has a slightly higher Bi content but slightly lower Ba content than the matrix, while both materials have the same O and Pb contents. This is consistent with our powder x-ray data in view of the small variations of lattice parameters and structure with $x$ in BaPb$_{1-x}$Bi$_{x}$O$_3$. Detailed analyses of the sample and the identification of the origin of superconductivity are underway and will be published later.
The typical $T$ dependence of $R$, measured with different currents $I$'s at different $H$'s is shown in Fig. 1. The value of $R$ at 300 K is 7 $\Omega$ corresponding to a resistivity of 1.05 $\Omega$ cm. $R$ increases with decreasing $T$ before the sample becomes superconducting at $T_{c1}$, as observed previously. However, the sample returns to the normal state at a lower temperature $T_{c2}$. At 1.2 K, $R$ reaches a value more than 100 times that above $T_{c1}$. Increase of $I$ or $H$ suppresses $T_{c1}$, enhances $T_{c2}$, and thus reduces the superconducting region. When $I$ or $H$ exceeds the critical value, the superconducting region is totally destroyed, leaving the sample behaving like a semiconductor. The superconducting state so observed resistively is also evident from the appearance of a supercurrent $I_s$ shown in Fig. 2. $I_s$ is always suppressed by $H$ as expected but exhibits a maximum at $-6$ K. The zero field $I_s$ determined by both the dc and pulse methods is summarized as a function of $T$ in Fig. 3. Independent of the method used, $I_s$ peaks at $-6$ K, demonstrating the effect is not caused by heating. The difference between the values of the $I_s$'s from different techniques is attributed to the flux motion. When either $T$ or $H$ is above its respective critical value, $I_s$ is completely suppressed and a simple Ohmic $I$-$V$ behavior results. On the other hand, accompanying with the above observations, $X$ shows only a simple superconducting transition near $T_{c1}$ without any sign of reentrance as displayed in Fig. 1. Comparison of this superconducting $X$ signal with that of a Pb sets an upper limit of $-30\%$ on the sample volume that is superconducting, qualitatively consistent with the scanning electron microscope results. Figure 4 displays the variation of $V$ and $X$ with $I > I_c$. It is clear that the sample remains superconducting magnetically although it is already in the normal state resistively when $I_c < I < I_{c2}$, where $I_{c2}$ represents the critical current of the “bulk” material as shown in the same figure. Heating effect above a few mA is evident from the difference between curves 2 and 2’ in Fig. 4.

The results in Figs. 1 and 2 clearly demonstrate that a superconducting current path exists only for $T_{c2} < T < T_{c1}$ in our BaPb$_{2/3}$Bi$_{1/3}$O$_3$ samples, although the “bulk” ($<30\%$) of the sample remains superconducting below $T_{c2}$. The path becomes semiconducting when the superconducting path is interrupted below $T_{c2}$. This is further supported by the observation of a nonmonotonic variation of $I_c$ with $T$ shown in Fig. 3. The $I$-$V$ characteristics in Fig. 4 show a Giaever type of tunneling when $I < I_{c2}$ and the existence of strongly $T$-
OBSERVATION OF A REENTRANT SUPERCONDUCTING... 1495

FIG. 4. $I$ dependence of $V$ and $x$ at different $T$'s for $I > I_c$: (1) and (2) were determined by a dc method at 1.2 and 4.2 K, respectively, (2) by 0.3-μs pulse method at 4.2 K, and $x$ was measured at 4.2 K when a dc current was flowing through the sample.

dependent resistive layers between the superconducting grains. The large apparent gap of > 100 mV stems from the many tunneling junctions in series. The observed reentrant superconductivity can then be understood in the following way: as $T$ is reduced, superconductivity first appears in the material grains separated by semiconducting layers. Below $T_{c1}$, phase matching between grains is established through Josephson coupling, resulting in the appearance of a supercurrent. This is evident from the slightly lower onset $T_c$ determined resistively than that determined magnetically. However, below $T_{c1}$, decoupling between the superconducting grains occurs when the Josephson energy reaches a certain critical value with respect to the Coulomb charging energy. It should be noted that reentrant superconductivity in a dirty or thin-film homogeneous superconductor has been predicted and just observed in homogeneous Al thin films at a high magnetic field. In contrast to our observations, the superconducting state in these thin films is considered to be a gapless bulk state and the reentrance to result from the competition between the spin paramagnetic effect and the orbital deparing effect.

Recently, it has been shown that for a superconductor-semiconductor superconducting junction with a degenerate temperature of the semiconductor comparable to the junction temperature,

$$I_s = I_0 [ (T/T_c)^{2/3} + (\Delta/T_c) ]^{1/2} \times \exp[-(\gamma T/T_c)^{1/2}],$$

(1)

where $I_0$ and $\gamma$ are constants depending on the material characteristics of the superconductor and insulator of the junction, and $\Delta$ is the superconducting gap. The competition between the factor $T^{2/3}$ and the rest of the equation gives rise to a maximum $I_s$. Using $2\Delta(0)/T_c = 3.5$ and the $\Delta(T)$ from the BCS calculation, an $I_s - T$ curve was obtained and shown in Fig. 3 by choosing $I_0 = 1.69 \times 10^4$ μA and $\gamma = 0.823$. The agreement is good in view of the scattering of the data. Although the BCS-$\Delta$ has been shown to be slightly and consistently overestimated for this compound for $T/T_c = 0.75$, such a $\Delta$ correction is expected to vary $I_0$ and $\gamma$ only slightly. The physical significance of the values of $I_0$ and $\gamma$ so obtained are being examined together with the detailed characteristics of the compound. Although the theory was developed for a simple tunneling junction with a single $T_c$, the agreement between the theory and experiment, where many junctions with a distribution of $T_c$ exist, is expected: As far as $I_s$ is concerned, an array of tunneling junctions may be represented by an equivalent junction whose $T_c$ is dictated by the lowest $T_c$ of the original junctions when in series or the highest $T_c$ when in parallel, provided proper phase interference is taken into consideration.

In conclusion, we have observed a reentrant superconducting transition resistively in the sintered BiPb$_2$Sr$_2$CaCu$_2$O$_8$ samples. On the contrary, the samples remain superconducting magnetically down to the lowest temperature of the present study. Therefore, the observation has been attributed to the decoupling between superconducting grains at low temperature, in good agreement with recent theoretical predictions. Preliminary data also indicate that the observation of a reentrant superconducting resistive transition in a granular superconductor depends not only on the physical characteristics of the barriers but also crucially on the distribution of the superconducting grains. However, reentrant superconductivity of this kind should be common in other granular superconducting systems with proper barrier characteristics. The present observations should provide important insight to the study of this class of material in general.

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[54] OXYGEN-DEFICIENT, BARIUM-CONTAINING PEROVSKITES

[75] Inventors: Robert A. Beyerlein, Westfield; Allan J. Jacobson, Princeton; Kenneth R. Poeppelmeier, Flemington, all of N.J.


[21] Appl. No.: 485,708

[22] Filed: Apr. 18, 1983

[51] Int. Cl. .......................... B01J 23/02; B01J 23/10; B01J 23/18

[52] U.S. Cl. .......................... 502/303; 502/302; 502/304; 502/328; 502/340; 502/341; 502/343; 502/525

[58] Field of Search .................. 502/302, 303, 304, 328, 502/340, 341, 343, 525; 423/593

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Primary Examiner—W. J. Shine
Attorney, Agent, or Firm—Janet E. Hasak; Henry E. Naylor

[57] ABSTRACT
A class of oxygen-deficient, barium-containing compounds having a perovskite-type structure may be prepared which are of the formula:

\[ Ba_xM_yO_{2-y} \]

if \( M \) is a trivalent cation, or

\[ Ba_xM_yO_{2-y} \]

if \( M \) is a divalent cation, wherein \( M \) is Mg, Ca, Sr, Ba, Sc, Y, La, the lanthanaide of atomic number 58 or greater, Ni, Fe, Cu, Al, Ga, In, Zn, Cd, Hg, Bi, Tl or a mixture thereof, \( M^+ \) is Sb or Bi, a is equal to or greater than 0 but less than or equal to 1, and if \( M \) is trivalent, \( y \) is equal to or greater than 0 but less than 1, and if \( M \) is divalent, \( y \) is equal to or greater than 0 but less than \((3+a)/2\).

Preferably, the compounds herein are of the formula:

\[ Ba_xM_yO_{2-y} \]

where \( M \) is La or Sc, a is equal to or greater than 0 but less than or equal to 1 and \( y \) is equal to or greater than 0 but less than 1.

This class of compounds are readily reoxidized and therefore are useful in oxidative dehydrogenation reactions.

20 Claims, 2 Drawing Figures
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<th>Date</th>
<th>Inventor(s)</th>
<th>Class Code</th>
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OXYGEN-DEFICIENT, BARIUM-CONTAINING
PEROVSKITES

BACKGROUND OF THE INVENTION

This invention is related to a class of novel oxygen-deficient, bismuth-containing compounds having a perovskite-type structure and to a process for the preparation thereof. Preferably, the compounds also contain barium.

DESCRIPTION OF RELATED DISCLOSURES

During a typical petroleum refining operation large quantities of low molecular weight paraffins and olefins are produced. Unlike paraffins which may be sold at relatively low cost for fuels, olefins have undesirable combustion properties which hamper their potential use as fuels. Thus, much research effort has been directed toward upgrading the olefins, either for use as fuel or as chemical intermediates in the chemicals industry. For those olefins containing three to four carbon atoms, much research effort has been directed toward reaction products such as dimers and aromatic products having greater potential value, with bismuth oxide representing a conventional oxidation catalyst particularly for producing dimers.

Oxidative conversions of unsaturated hydrocarbons have recently been conducted using various catalyst combinations. A recently published comprehensive review article on oxidative dehydrogenation of olefins is E. A. Mamedov, Russ. Chem. Reviews, 50, 291 (1981), which lists numerous references disclosing use of catalysts containing bismuth oxide in combination with other elements to convert olefins to dienes and aromatic products in the presence or absence of molecular oxygen.

U.S. Pat. No. 4,110,258 to Laird discloses perovskites of the form $\text{BaBiO}_2$, which may include Bi or mixtures of Bi and La on the B site but require 1 to 20% of the B site to be occupied by a Pd group metal for use as exhaust gas clean-up catalysts in the conversion of NOx, CO and hydrocarbons to $\text{N}_2$, $\text{CO}_2$ and $\text{H}_2\text{O}$. U.S. Pat. No. 3,730,957 to Boczik et al. discloses use of bismuth-containing catalysts for use in oxidative dehydrodimerization.

SUMMARY OF THE INVENTION

There is provided herein a novel class of oxygen-deficient, bismuth-containing compounds having a perovskite-type structure of the formula:

$$\text{Ba}_x\text{M}_y\text{M}'_z\text{O}_{3-y}$$

if $M$ is a trivalent cation, or

$$\text{Ba}_x\text{M}_y\text{M}'_z\text{O}_{(3-(a/2)-y)}$$

if $M$ is a divalent cation, wherein $M$ is selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, La, the lanthanides of atomic number 58 or greater, Ni, Fe, Cu, Al, In, Zn, Cd, Hg, Bi, Tl and a mixture thereof, $M'$ is selected from the group consisting of Sb or Bi, a is equal to or greater than 0 but less than or equal to 1, and if $M$ is a divalent cation, $y$ is equal to or greater than 0 but less than 1, and if $M$ is a divalent cation, $y$ is equal to or greater than 0 but less than 1, and if $M$ is a divalent cation, $y$ is equal to or greater than 0 but less than 1.

The above class of compounds may be prepared by heating the fully oxidized precursor compound (wherein in the above formulae $y$ is about but no greater than 1 if $M$ is trivalent and $y$ is about but no greater than $(3+a)/2$ if $M$ is divalent) in the presence of an effective amount of oxygen at a temperature of at least about 600°C, depending on the particular precursor compound and the amount of oxygen present, for a sufficient period of time to produce the oxygen-deficient compound (where $y$ is less than 1 if $M$ is trivalent and $y$ is less than $(3+a)/2$ if $M$ is divalent).

The class of oxygen-deficient compounds herein are readily reoxidized and therefore may be used in oxidative dehydrogenation reactions or in similar processes requiring solid oxidizing agents. In particular, the compounds herein (and their fully oxidized precursors) may be used as catalysts in selectively producing aromatic products or dimers from acyclic olefins, preferably propylene or isobutylene, as described in U.S. Patent Application Ser. Nos. 485,706 and 485,707, respectively filed of even date with this application, both now abandoned with applicants K. Poeppelemeier and J. Longo, the disclosures of which applications are incorporated herein by reference.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 represents a phase diagram for synthesis of $\text{Ba}_2\text{Bi}_2\text{O}_5$ (which is a plot of the temperature used for the synthesis versus the extent of oxygen deficiency in $\text{Ba}_2\text{Bi}_2\text{O}_5$ (the value of $y$) for nine given partial pressures of oxygen).

FIG. 2 represents a thermogravimetric record of $\text{Ba}_2\text{La}_x\text{Bi}_2\text{O}_{3+y}$, where $y$ is about 0.14, reoxidized to $\text{Ba}_2\text{La}_x\text{Bi}_2\text{O}_5$ in the presence of oxygen to 600°C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The class of oxygen-deficient compounds herein have the perovskite-type structure as described in A. F. Wells, Structural Inorganic Chemistry, 4th ed., Ch. 4 (Clarendon Press, 1975). The compounds herein have a composition of one of the formulae:

$$\text{Ba}_x\text{M}_y\text{M}'_z\text{O}_{3-y}$$

if $M$ is trivalent, or

$$\text{Ba}_x\text{M}_y\text{M}'_z\text{O}_{(3-(a/2)-y)}$$

if $M$ is divalent, wherein $M$ is selected from Mg, Ca, Sr, Ba, Sc, Y, La, the lanthanides of atomic number 58 or greater, Ni, Fe, Cu, Al, In, Zn, Cd, Hg, Bi or Tl, $M'$ is either Sb or Bi, a is equal to or greater than 0 but less than or equal to 1, and if $M$ is a trivalent cation, $y$ is equal to or greater than 0 but less than 1, and if $M$ is a divalent cation, $y$ is equal to or greater than 0 but less than 1, and if $M$ is a divalent cation, $y$ is equal to or greater than 0 but less than 1.

The precise value of $y$ is the amount necessary to satisfy the valence of $M'$. The lanthanides
of atomic number of at least 58 consist of Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Preferably, M is Bi and is 0 or M is Bi, a is greater than 0, and M is La or Sc. Examples of suitable compounds for this purpose include Ba$_2$Mg$_2$Bi$_7$O$_{17+y}$, Ba$_5$Ca$_2$Bi$_2$O$_{17+y}$, Ba$_5$Sr$_2$Bi$_2$O$_{17+y}$, Ba$_3$Ba$_2$Bi$_2$O$_{17+y}$, Ba$_2$Sr$_2$Bi$_2$O$_{17+y}$, Ba$_2$Sr$_2$Bi$_2$O$_{17+y}$, Ba$_2$Bi$_2$O$_{17+y}$, Ba$_2$Bi$_2$O$_{17+y}$, Ba$_2$Bi$_2$O$_{17+y}$, Ba$_2$Bi$_2$O$_{17+y}$, Ba$_2$Bi$_2$O$_{17+y}$, Ba$_2$Bi$_2$O$_{17+y}$, Ba$_2$Bi$_2$O$_{17+y}$, Ba$_2$Bi$_2$O$_{17+y}$, Ba$_2$Bi$_2$O$_{17+y}$, Ba$_2$Bi$_2$O$_{17+y}$, and the like.

In the above formulae, the word "divalent" signifies that the metal M is contained in the oxide in an oxidation state of $\pm 2$, and the word "trivalent" signifies that the metal M is contained in the oxide in an oxidation state of $\pm 3$.

It is noted that the compositions of this invention having the above general formula may comprise more than one phase having the overall composition described above. One preferred class of compounds herein are those of the formula:

$$\text{Ba}_2\text{M}_2\text{Bi}_7\text{O}_{17+y}$$

where a is from 0 to 1 and y is equal to or greater than 0 but less than 1. These preferred compounds, many of which have been characterized by x-ray diffraction, generally comprise one phase. If the compounds of this preferred class do not contain lanthanum (i.e., a is 0), y preferably ranges from about 0 to about 0.6 and more preferably is about 0.6 or about 0.0 (i.e., ranges from 0 to 0.2). If the compound contains lanthanum (i.e., a is greater than 0), y preferably is less than or equal to 0.1, and more preferably y is 0 and a is 0.5.

The fully oxidized precursor compounds to be used as starting materials in preparing the novel compositions of this invention are of the formula:

$$\text{Ba}_2\text{M}_2\text{Bi}_7\text{O}_{17+y}$$

if M is trivalent, or

$$\text{Ba}_3\text{M}_3\text{Bi}_7\text{O}_{17+y}$$

if M is divalent, wherein M, M', and a are defined above, y is about 1 but not greater than 1 if M is trivalent, and y is about $(3+a)/2$ but not greater than $(3+a)/2$ if M is divalent. These precursors may be prepared by any convenient means known to those skilled in the art. A typical procedure involves preparing a physical mixture by grinding stoichiometric amounts of barium carbonate or nitrate with salts or oxides of the other two metal components, heating the mixture to about 350° to 450° C, cooling and regenerating the resultant mixture in air, and heating the ground, cooled mixture to about 700° to 1000° C for about three to seventy hours, depending on other conditions, in a furnace. Product formation is monitored via X-ray diffraction measurements. The products have a structure related to the perovskite structure with pseudo-cubic unit cells of about 4.3 Å, depending slightly on the ionic radii of M.

For the investigations and experiments herein disclosed for preparing the preferred class of bismuth-containing or bismuth- and lanthanum-containing precursors, a mixture may be formed containing barium nitrate and bismuth nitrate pentahydrate and, if a is greater than 0, also containing lanthanum oxide. In this tech-

ique the nitrates (and oxide, if applicable) in the appropriate amounts are oxidatively decomposed in air at about 800° C for 2-3 hours in a Linberg furnace followed by successive regrening and refining to 800° C. For a period of 3 to 70 hours until no unreacted nitrate can be detected in either the x-ray powder diffraction patterns or the infrared spectra of the oxygenated precursor compound product.

For the lanthanum-containing materials with a greater than zero, a smooth and essentially linear increase in lattice parameter with increasing lanthanum content is observed. Thus, as a is increased from zero to one, the lattice parameter of the fully oxidized precursor compounds increases smoothly from $a_0=8.711$ Å $(a=0)$ to $a_0=8.771$ Å $(a=1)$, Ba$_3$La$_2$Bi$_2$O$_{17+y}$. Because the two end members, Ba$_3$Bi$_2$O$_{17+y}$ and Ba$_2$La$_2$Bi$_2$O$_{17+y}$, are known to have $y=1$ in the above formulae as discussed by G. Thornton and A. J. Jacobson, Acta. Cryst. B34, 351–354 (1978) and V. R. Schofield, et al., Zeitschrift fuer Anorganische und Allgemeine Chemie, 319, 375–386 (1963), it follows that each of the oxidized precursor compounds with values of a intermediate between zero and one have $y=1$, and their compositions may be written as Ba$_3$La$_2$Bi$_2$O$_{17+y}$.

Once the precursor compound is obtained it is heated in a suitable reactor, preferably a Linberg tube furnace, in the presence of an amount of oxygen effective for a particular temperature to obtain an oxygen-deficient compound. The amount of oxygen which is effective will depend mainly on the type of precursor compound employed, the temperature at which the precursor is being heated, and the length of time for which the precursor is heated. Typically the heating will take place under a flow of a mixture of oxygen gas and an inert gas such as helium or argon at a flow rate of about 100 to 500 cm$^3$/minute. Higher or lower flow rates may be employed depending mainly on the amount of precursor sample and the size of the reactor tube.

The temperature at which the precursor compound is heated is likewise dependent on many factors such as the type or precursor compound and the amount of oxygen present. At minimum, the temperature should be about 600° C, but preferably the temperature is higher, and more preferably is 600° to 1000° C. The time for heating will similarly depend on several factors such as the precursor, temperature and oxygen partial pressure. When the class of compounds is Ba$_3$M$_3$Bi$_7$O$_{17+y}$, where M is trivalent, the interrelationships among the amount of oxygen, the temperature and the time employed can be expressed as follows, as demonstrated by the preferred class of compounds where M is lanthanum: When the temperature is decreased, a lower oxygen pressure is required to obtain the product. As the value of a in the compound is increased, the temperature must be increased and/or the oxygen partial pressure must be decreased and the time for heating must be increased to obtain the reduced product. Even when these parameters are adjusted, however, if a in the formula is increased beyond about 0.7 the product obtained on cooling will generally not be a single-phase material but rather will comprise two phases which may be a mixture of the fully oxidized material ($y=1$) and the fully reduced material ($y=0$). If the precursor compound is such that $a$ is 0.5, when the compound is heated at about 600° to 1000° C, the oxygen partial pressure will be between about 0.001 and 0.000002 atm, depending on the temperature. The preferred temperature range of
heating for a = 0.5 is 800° to 1000° C. and most preferred is 950° to 1000° C. When a temperature of 1000° C. is employed for a = 0.5 the oxygen partial pressure must be about 0.001 atm to obtain the product, whereas if the temperature is 950° C., the oxygen partial pressure is 5 about 0.0001 atm and the time is at least 8 hours, preferably 10 to 12 hours. When a is increased to about 0.65 or greater, the preferred temperature is 900° to 1000° C. and the preferred oxygen partial pressure is from 0.001 to 0.000002 atm, and the reaction must be carried out for a longer period of time.

The composition range for the class of bismuth-containing compounds of the formula Ba$_3$Bi$_2$O$_5$$_x$ (where $x$ is in the general formula of 0) and the conditions for the synthesis of these compounds are summarized in the 15 phase diagram depicted in FIG. 1. In this figure the temperature of heating is plotted against the $y$ value in Ba$_3$Bi$_2$O$_5$$_x$ for nine fixed oxygen partial pressures in the range from 0.0001 to 1.0 atm. Each of the nine families of points, designated a through i, represents 20 measurements at a fixed oxygen partial pressure. Thus, for plot a, represented by upright triangles (pointing upward), the oxygen partial pressure was 1.0 atm; for plot b, represented by squares, the oxygen partial pressure was 0.35 atm; for plot c, represented by plus signs, the oxygen partial pressure was 0.10 atm; for plot d, represented by triangles pointing to the right, the oxygen partial pressure was 0.03 atm; for plot e, represented by circles, the oxygen partial pressure was 0.01 atm; for plot f, represented by circles, the oxygen partial pressure was 0.0032 atm; for plot g, represented by triangles pointing downward, the oxygen partial pressure was 0.0010 atm; for plot h, represented by circles, the oxygen partial pressure was 0.00032 atm; and for plot i, represented by triangles pointing to the left, the oxygen partial pressure was 0.00010 atm. The lines connecting the points in the plots are drawn to aid the eye.

Phase boundaries are dashed in regions where there is some uncertainty.

This diagram (FIG. 1) shows that for a fixed oxygen partial pressure of 0.0032 atm, three single-phase regions (designated I to III), each with variable oxygen stoichiometry, are encountered as the temperature is raised from 750° to 850° C. In phase region I where $y$ is from 1.0 to 0.94, there is a narrow range of variable oxygen stoichiometry. In the single-phase regions II and III the oxygen stoichiometry ranges are: $y$ from 0.77 to 0.47 and 0.16 to 0.10, respectively.

The oxygen-deficient compounds herein can be easily reoxidized in the presence of oxygen or air. This reoxidation is very rapid in air at temperatures as low as 300° C. The thermogravimetric record of Ba$_3$La$_2$Bi$_2$O$_{5.1}$<sub>2+</sub> (where $y$ is about 0.14) in oxygen given in FIG. 2 shows that oxidation begins at temperatures above 200° C. and is very rapid at 300° C.

Table I-VIII list all of the observed x-ray diffraction data for several compounds from the preferred class of compounds (Ba$_3$La$_2$Bi$_2$O$_{5+x}$) over the angular range 10° < 2$\theta$ < 85°. For the oxidized precursors, the x-ray diffraction patterns can be roughly indexed on the basis of a pseudo-cubic lattice parameter $a_0$ = 2a. Here $a_0$ is the simple cubic distance characteristic of the Bi-O-Bi, Bi-O-La, or La-O-La arrays and varies from $a_0$ = 4.355(5) Å for Ba$_3$Bi$_2$O$_5$, with $a_0$ = 0 to $a_0$ = 4.385(5) Å for the lanthanum-containing material with $a_0$ = 1. With 65 the exception of certain of the materials for which $a_0$ = 0, all of the oxygen-deficient materials can be indexed on the basis of similar distortions of the simple cubic distance $a_0$. The cell volume expands as oxygen is lost from the lattice so that for the lanthanum-containing oxygen-deficient materials with $a_0$ = 1 and $y$ = 0, $a_0$ = 4.36 Å and the pseudocubic lattice parameter $a_0$ = 2a. For the material containing no lanthanum with $a_0$ = 0 and $y$ = 0, there is a pronounced tetragonal distortion so that ($a_0$ + $b_0$)/2 = 2a, where $a_0$ = 4.44 Å and $a_0$ and $b_0$ are the new tetragonal lattice parameters.

The invention is further explicated by the examples which follow. In all examples, the parts and percentages by weight and the temperatures are in degrees Celsius unless otherwise noted.

**EXAMPLE 1**

Preparation of Ba$_3$Bi$_2$O$_5$$_0$

Ba$_3$Bi$_2$O$_5$ was prepared by heating a mixture of 12.000 g Ba(NO$_3$)$_2$ and 22.269 g Bi(NO$_3$)$_3$·5H$_2$O in air at 400° C. for 2 hours followed by regaining and refining at 800° C. for 1 hr. and finally regaining and refiring at 800° C. for 1 day. About 2 g of this material was heated to 800° C. in a Lindberg tube furnace in an oxygen-argon mixture containing 100 ppm oxygen (0.001 atm oxygen) flowing at 300 cm$^3$/min. The furnace was maintained at 800° C. for 2.5 hours after which the heating was discontinued and the sample was cooled in the same gas mixture. The sample was magenta in color when removed from the furnace at ambient temperature. It was necessary to store the sample in a moisture-free, inert gas atmosphere to maintain its integrity. An x-ray powder diffraction pattern of this single-phase material was recorded with a diffractometer using CuKa radiation and the data is recorded in Table I. The pseudo-cubic lattice parameter of this perovskite-related structure is $a_0$ = 8.89(2)Å. Thermogravimetric oxidation in pure oxygen to 600° C. of the sample revealed its oxide stoichiometry as Ba$_3$Bi$_2$O$_{5.0}$.

<p>| TABLE I |
| X-Ray Powder Diffraction Data For Ba$_3$Bi$_2$O$<em>5$ |
|-----------|-------|-----------|
| peak      | d$</em>{cal}$ | intensity  |</p>
<table>
<thead>
<tr>
<th>number</th>
<th>(Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
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<td>5.41</td>
<td>w−</td>
</tr>
<tr>
<td>2</td>
<td>5.12</td>
<td>w−</td>
</tr>
<tr>
<td>3</td>
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</tr>
<tr>
<td>4</td>
<td>4.27</td>
<td>w+</td>
</tr>
<tr>
<td>5</td>
<td>3.92</td>
<td>w</td>
</tr>
<tr>
<td>6</td>
<td>3.54</td>
<td>w−</td>
</tr>
<tr>
<td>7</td>
<td>3.46</td>
<td>w−</td>
</tr>
<tr>
<td>8</td>
<td>3.39</td>
<td>w−</td>
</tr>
<tr>
<td>9</td>
<td>3.15</td>
<td>s+ +</td>
</tr>
<tr>
<td>10</td>
<td>3.11</td>
<td>m+</td>
</tr>
<tr>
<td>11</td>
<td>3.75</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>w−</td>
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<tr>
<td>14</td>
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<tr>
<td>15</td>
<td>2.236</td>
<td>m+</td>
</tr>
<tr>
<td>16</td>
<td>2.03</td>
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</tr>
<tr>
<td>17</td>
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<td>1.570</td>
<td>m</td>
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<tr>
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<td>1.554</td>
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<td>24</td>
<td>1.407</td>
<td>m−</td>
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<tr>
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<td>w+</td>
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<td>26</td>
<td>1.283</td>
<td>w−</td>
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</table>

RLM1502
TABLE II

4,482,644

x-Ray Powder Diffraction Pattern for Ba₂B₄O₉·₁.₅H₂O

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>d-value (observed) (Å)</th>
<th>d-value (calc.) (Å)</th>
<th>Intensity</th>
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<tr>
<td>1a</td>
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<td>5.521</td>
<td>5.108 w</td>
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<td>1b</td>
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<td>5.051</td>
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<td>4.372 w</td>
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<td>3</td>
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<td>300</td>
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<tr>
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<td>2.979 s-</td>
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<td>2.616 s-</td>
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<tr>
<td>50</td>
<td>200</td>
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<td>1.064 w-</td>
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</table>

*Calculated d-values were determined using $d = \sqrt{a^2 + b^2 + c^2}$, $a = 8.784 \AA$, $c = 8.977 \AA$.

EXAMPLE 3

Preparation of Ba₂B₄O₉·₁.₅H₂O (low symmetry form)

A 2 g sample of Ba₂B₄O₉·₁.₅H₂O prepared as described in Example 2 was heated for three hours at 770 °C. This sample contained 1000 ppm oxygen (0.001 atm oxygen). The product was cooled in a stream of pure argon. The resulting material was bright yellow and showed an x-ray diffraction pattern which could not be indexed on the basis of the pseudocubic perovskite. The observed d-values for this "low symmetry" Ba₂B₄O₉·₁.₅H₂O are given in Table III. However, a crystal of this material contained no BaO or B₂O₃. Thermogravimetric analysis of this material showed an oxygen stoichiometry of Ba₂B₄O₉·₆O₂±₀.₅O. The product of this reaction was Ba₂B₄O₉.

EXAMPLE 4

Preparation of Ba₂B₄O₉·₆

A 2 g sample of Ba₂B₄O₉·₁.₅H₂O prepared as described in Example 1 was heated for 5 hours at 715 °C in a stream of oxygen and argon containing 1000 ppm O₂ (0.001 atm O₂). The sample was cooled in the same atmosphere. The resulting material was brown and showed a perovskite-related x-ray diffraction pattern. The observed d-values and intensities are given in Table IV. Theweak line at 3.15 Å is at the position of the strongest line of Ba₂B₄O₉·₁.₅H₂O, and may indicate the presence of a trace amount of this phase. Thermogravimetric analysis of this material showed an oxygen stoichiometry of Ba₂B₄O₉·₁.₅H₂O. The product of this reaction was Ba₂B₄O₉.
TABLE IV-continued

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>d-value (observed) (Å)</th>
<th>Intensitya</th>
<th>Peak No.</th>
<th>d-value (observed) (Å)</th>
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</table>

Explanations:
- w = weak, m = medium, s = strong

EXAMPLE 5
Preparation of Ba$_2$La$_{0.5}$Bi$_3$O$_{12.5}$

A mixture of 12,000 g of Ba(NO$_3$)$_2$, 16,701 g of Bi(NO$_3$)$_3$, 5H$_2$O, and 1,870 g of La$_2$O$_3$ was heated in air for 400°C for two hours. The sample was reground and fired at 900°C in air for 1 hour followed by refining and refining at 800°C for 60 to 70 hours. The resulting material was determined by X-ray diffraction to be a pseudocubic perovskite material which could be roughly indexed using a lattice parameter a$_0$=8.74(1) Å. Comparison with the lattice parameters for Ba$_2$Bi$_2$O$_5$ and Ba$_2$LaBi$_2$O$_5$, shows that the correct oxygen composition for this material is specified by Ba$_2$La$_{0.5}$Bi$_3$O$_{12.5}$.

About 2 g of this composition was placed in an alumina boat in a Lindberg tube furnace under a gas stream of oxygen and argon containing 100 ppm oxygen (0.0001 atm partial pressure oxygen) flowing at 300 cm$^3$/min. Separate thermogravimetric measurements showed that this material began to lose oxygen at 730°C under these conditions and reached an approximate composition of Ba$_2$La$_{0.5}$Bi$_3$O$_{12.5}$ after being heated at 950°C for 12 to 24 hours. The reduced material obtained after heating for 14 hours at 950°C under the conditions described above in this example was bright yellow. Thermogravimetric reoxidation of this material in pure oxygen to 600°C showed that the oxygen stoichiometry of the reduced material was Ba$_2$La$_{0.5}$Bi$_3$O$_{12.5}$. X-ray diffraction analysis indicated that the product of this reoxidation was the starting material previously identified as Ba$_2$La$_{0.5}$Bi$_3$O$_{12.5}$.

The X-ray diffraction pattern of the oxygen-deficient material, indicated in Table V, shows its structure to be a pseudocubic perovskite with a$_0$ (reduced) = 8.94(1) Å. Additional investigations revealed that the diffraction pattern for the intermediate compositions where x is between 0 and 1 showed a two-phase mixture of Ba$_2$La$_{0.5}$Bi$_3$O$_{12.5}$ and Ba$_2$La$_{0.5}$Bi$_3$O$_{12.5}$.

TABLE V

<p>| X-ray Powder Diffraction Data for Ba$<em>2$La$</em>{0.5}$Bi$<em>3$O$</em>{12.5}$ |
|--------------------------|--------|------------------------|--------|</p>
<table>
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<th>Peak No.</th>
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<th>d$_{calculated}$ (Å)</th>
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<tr>
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<tr>
<td>11</td>
<td>2.24</td>
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</table>

EXAMPLE 6
Preparation of Ba$_2$La$_{0.75}$Bi$_3$O$_{12.75}$

A mixture of 3.0 g Ba(NO$_3$)$_2$, 3.340 g Bi(NO$_3$)$_3$, 5H$_2$O and 0.748 g La$_2$O$_3$ was heated and ground as described in Example 5 above. The product was found to be a pseudocubic perovskite material with a lattice parameter consistent with the composition Ba$_2$La$_{0.75}$Bi$_3$O$_{12.75}$. Thermogravimetric measurements in 0.0001 atm partial pressure oxygen showed that this material began to lose oxygen at 850°C. These investigations further showed that, at a temperature of 930°C, y=0.74 upon achieving equilibrium after about 20 hours. The material obtained was found to be rust colored.

EXAMPLE 7
Preparation of Ba$_2$La$_{0.75}$Bi$_3$O$_{12.75}$

A mixture of 6.0 g Ba(NO$_3$)$_2$, 6.959 g Bi(NO$_3$)$_3$, 5H$_2$O and 1.403 g La$_2$O$_3$ was heated as described in Example 5 to give a pseudocubic perovskite with a$_0$ = 8.75(1) Å. Again comparison with the lattice parameters for Ba$_2$Bi$_2$O$_5$ (a$_0$=8.71 Å) and Ba$_2$BiLa$_{0.75}$Bi$_3$O$_{12.75}$ (a$_0$=8.77 Å) shows that the correct oxygen composition for this fully oxidized material is specified by Ba$_2$La$_{0.75}$Bi$_3$O$_{12.75}$. This composition was heated as described in Example 5 to a temperature of 950°C in 0.0001 atm oxygen partial pressure for 16 hours. The X-ray diffraction pattern for the material, represented in Table VI, indicated that the material was composed of approximately two-thirds of Ba$_2$La$_{0.75}$Bi$_3$O$_{12.75}$ (pseudocubic perovskite lines at higher angles corresponding to this product at y=8.75(1) Å) and one-third of Ba$_2$La$_{0.75}$Bi$_3$O$_{12.75}$ (pseudocubic perovskite lines at lower angles corresponding to this product at y=8.95(1) Å).

TABLE VI

<p>| X-Ray Powder Diffraction Data for Ba$<em>2$La$</em>{0.75}$Bi$<em>3$O$</em>{12.75}$ |
|--------------------------|--------|------------------------|--------|</p>
<table>
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<tr>
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TABLE VI-continued

<table>
<thead>
<tr>
<th>X-Ray Powder Diffraction Data for Ba$_2$La$_2$Bi$<em>2$O$</em>{12+y}$</th>
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<tr>
<td>y = 0</td>
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<tr>
<td>Intensity$^b$</td>
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<tr>
<td>642              1.172</td>
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</table>

$^a$Indexing was done using a cubic cell with a$_0$ = 8.771(1) Å for y = 1 (oxidized) and a$_0$ = 8.951(1) Å for y = 0 (reduced) phases, respectively.

$^b$w = weak, m = medium, s = strong

EXAMPLE 8
Preparation of Ba$_2$LaBiO$_{5+y}$

A mixture of 13.068 g Ba(NO$_3$)$_2$, 12.125 g Bi(NO$_3$)$_3$, and 4.973 g La$_2$O$_3$ was heated as described in Example 5 to yield a pseudo-cubic perovskite with a$_0$ = 8.771(1) Å and with composition Ba$_2$LaBiO$_6$. This composition was found to be stable to reduction at a temperature of 950°C. 0.0001 atm partial oxygen pressure. On reducing the oxygen pressure to 0.00002 atm (a purified argon stream), heating the Ba$_2$LaBiO$_{5+y}$ for 2.5 days at 900°C resulted in an orange-yellow colored material whose stoichiometry was shown by thermogravimetric oxidation to be Ba$_2$Bi$_3$O$_{12+y}$. The X-ray diffraction pattern of the material, indicated in Table VII, showed predominantly Ba$_2$LaBiO$_6$ plus an additional pseudo-cubic perovskite material which could be indexed using a$_0$ = 8.951(3) Å. The latter minor phase was assumed to be Ba$_2$Bi$_3$O$_{12+y}$ materials constitute single phases under conditions of their synthesis at high temperature and low oxygen partial pressure. Phase separation occurred on cooling. Each of the lanthanum-containing compounds showed about a 7% increase in cell volume from the oxidized (y = 1) to the reduced (y = 0) phase comparable to the approximately 5% volume expansion when BaBiO$_2$ was reduced to BaB$_2$O$_4$. The fact that these materials are readily recrystallized in air or oxygen at relatively low temperatures (see Fig. 2) and that the Ba$_2$La$_2$Bi$_2$O$_{12+y}$, was observed as a reaction product upon reduction by propylene at 475—500°C. indicates that the class of compounds herein described are useful in oxidative dehydrogenation reactions.

TABLE VII

<table>
<thead>
<tr>
<th>X-Ray Powder Diffraction Data for Ba$<em>2$LaBiO$</em>{5+y}$</th>
<th>12</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>y = 1</td>
<td></td>
</tr>
<tr>
<td>y = 0</td>
<td></td>
</tr>
<tr>
<td>Intensity$^b$</td>
<td></td>
</tr>
<tr>
<td>1                4.72</td>
<td>w</td>
</tr>
<tr>
<td>2                2.20</td>
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</tr>
<tr>
<td>3                4.00</td>
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<td>4                4.22</td>
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</tr>
<tr>
<td>5                4.40</td>
<td>1.584</td>
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<tr>
<td>6                6.20</td>
<td>1.416</td>
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<tr>
<td>7                4.44</td>
<td>1.294</td>
</tr>
<tr>
<td>8                6.42</td>
<td>1.198</td>
</tr>
</tbody>
</table>

$^a$Indexing was done using a cubic cell with a$_0$ = 8.951(1) Å.

$^b$w = weak, m = medium, s = strong

All of the oxygen-deficient, bismuth-containing materials of Examples 1—9, which represent the preferred class of compounds herein, were found to be extremely hygroscopic and showed significant hydration in a matter of minutes under ambient conditions. The X-ray patterns are for the anhydrous materials, although there are indications that some hydration occurred during the measurement. It appears that substitution of lanthanum for a portion of the bismuth in Ba$_2$Bi$_3$O$_6$ suppressed the intermediate phase (Region II) in the phase diagram of Fig. 1. Long-term thermogravimetric studies indicated that the Ba$_2$La$_2$Bi$_2$O$_{12+y}$, materials constitute single phases under conditions of their synthesis at high temperature and low oxygen partial pressure. Phase separation occurred on cooling. Each of the lanthanum-containing compounds showed about a 7% increase in cell volume from the oxidized (y = 1) to the reduced (y = 0) phase comparable to the approximately 5% volume expansion when BaBiO$_2$ was reduced to BaB$_2$O$_4$. The fact that these materials are readily recrystallized in air or oxygen at relatively low temperatures (see Fig. 2) and that the Ba$_2$La$_2$Bi$_2$O$_{12+y}$, was observed as a reaction product upon reduction by propylene at 475—500°C. indicates that the class of compounds herein described are useful in oxidative dehydrogenation reactions.

EXAMPLE 9
Preparation of Ba$_2$Sc$_3$Bi$_2$O$_{12+y}$

A mixture of 10.454 g of Ba(NO$_3$)$_2$, 2.183 g of La$_2$O$_3$ and 12.9 g of Bi(NO$_3$)$_3$·5H$_2$O was heated as described in Example 5 to yield a pseudo-cubic perovskite with a$_0$ = 8.751(1) Å and 8.973(1) Å. Comparison with the lattice parameters for Ba$_2$BiO$_3$ (a$_0$ = 8.71 Å) and Ba$_2$Bi$_2$O$_3$ (a$_0$ = 8.77 Å) shows that the correct oxygen composition for this fully oxidized material is specified by Ba$_2$La$_2$Bi$_2$O$_{12+y}$. Thermogravimetric analysis of a 0.1 g sample of the resulting oxidized material showed that this material began to lose oxygen at a temperature of 905°C when exposed to an oxygen pressure of 0.001 atm and that upon increasing the temperature to 1000°C and reducing the oxygen pressure to 0.00002 atm (purified argon stream), the material was reduced to a composition Ba$_2$La$_2$Bi$_2$O$_{12+y}$ after a period of 12 to 24 hours. The x-ray diffraction spectrum of the resulting material, which was yellow in color, was that of a single phase pseudo-cubic perovskite material with a lattice parameter a$_0$ = 8.96(1) Å as indicated in Table VIII.

TABLE VIII

<table>
<thead>
<tr>
<th>X-Ray Powder Diffraction Data for Ba$_2$La$_2$Bi$<em>2$O$</em>{12+y}$</th>
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</thead>
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<tr>
<td>y = 1</td>
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</tr>
<tr>
<td>Intensity$^b$</td>
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</tr>
<tr>
<td>1                4.72</td>
<td>w</td>
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<td>2                2.20</td>
<td>3.16</td>
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<td>6                6.20</td>
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<td>7                4.44</td>
<td>1.294</td>
</tr>
<tr>
<td>8                6.42</td>
<td>1.198</td>
</tr>
</tbody>
</table>

$^a$Indexing was done using a cubic cell with a$_0$ = 8.96(1) Å.

$^b$w = weak, m = medium, s = strong

This example illustrates the preparation of a scandium-containing oxygen-deficient perovskite. A mixture of 15.680 g of Ba(NO$_3$)$_2$, 2.069 g of Sc(NO$_3$)$_3$ and 14.549 g of Bi(NO$_3$)$_3$·5H$_2$O was heated in air to 400°C for 1 hour, followed by regrinding and retreating at 400°C for an additional hour followed by several regrindings and refirings at 800°C in air for a total of 170 hours. Thermogravimetric analysis of a 0.1 g sample of the resulting oxidized material showed that this material began to lose oxygen at a temperature of 905°C when exposed to an oxygen pressure of 0.001 atm and that upon increasing the temperature to 925°C and holding at that temperature for a period of 1 hour, the material was reduced to the extent that the value of y in the composition Ba$_2$Sc$_3$Bi$_2$O$_{12+y}$, was decreased from its initial value by 0.30±0.04. Following cooling, the resulting oxygen-
deficient material was reoxidized by heating in oxygen to 600° C, with reoxidation being very rapid as the temperature was increased above 300° C.

EXAMPLE 11

Preparation of Ba₂Sc₂B₁₁O₅₃·½H₂O

This example illustrates the preparation of a scandium-containing oxygen-deficient perovskite for which the value of a in Ba₂Sc₂B₁₁O₅₃·½H₂O is intermediate between 0 and 1. A mixture of 10.454 g of Ba(NO₃)₂, 0.690 g of Sc₂O₃, and 14.550 g of Bi(NO₃)₃·5H₂O was heated as described in Example 10. Thermogravimetric analysis of a 0.1 g sample of the resulting fully oxidized material showed that this material began to lose oxygen at a temperature of 500° C when exposed to an oxygen pressure of 0.0001 atm. Upon increasing the temperature to 925° C and holding at 925° C for a period of 1 hour, the material was reduced to the extent that the value of y in the composition Ba₂Sc₂B₁₁O₅₃·½H₂O was decreased from its initial value of 0.84±0.04. Following cooling, the resulting oxygen-deficient material was reoxidized by heating in oxygen to 600° C, with reoxidation being very rapid as the temperature was increased above 300° C.

Examples 12-15 below, which illustrate the use of the reoxidizable compositions herein and/or their fully oxidized precursors as oxidizing agents, constitute the examples of U.S. patent application Ser. Nos. 485,708 and 485,707, respectively, filed of even date with this application, both now abandoned both having the applicants K. Poppiger and J. Longo. Wherever the word “moles” is used in the tables, it will be understood to mean moles per mole bismuth.

EXAMPLE 12

Catalyst mixtures were prepared either by mixing two moles of bismuth oxide with one mole of the post-transition metal oxide and one mole of the trivalent metal oxide, or by mixing three moles of bismuth oxide with two moles of the post-transition metal oxide and one mole of the divalent metal oxide catalyst, as indicated in Table IX. The mixtures were ground, heated to 400° C in air, and then cooled and ground in air, and reheated to 800° C in air or oxygen for 6 hours. This last step effectively increases the amount of oxygen.

4,482,644

available for reaction when contacted with a hydrocarbon to its maximum amount. Formation of catalyst was detected by X-ray diffraction analysis.

Each catalyst so prepared, in an amount of 3 grams, was supported on a glass frit in the isothermal zone of a 20 mm outer diameter glass reactor. The reactor was heated in a conventional resistance-heated furnace.

A feedstream consisting of about 5% isobutylene and 9% helium was introduced through each reactor at a rate of 30 cc per minute after heating the reactor and its contents to a temperature of 475° C. Helium. During the first two to three hours of reaction, samples of the reaction mixture were injected at 15 minute intervals using a gas sample valve into a gas chromatograph and the identity and quantity of each product were determined. The molar amounts of 2,5-dimethyl-1,5-hexadiene dimer and aromatic products per mole bismuth were calculated from the integrations of the chromatographic peaks so as to determine the total yield of all hydrocarbon products for each catalyst and the relative yield of para-xylene for each catalyst.

The types and yields of products as well as the relative yields of aromatic product for each catalyst is indicated in Table IX. The molar yields of each product are all expressed in units of moles per mole bismuth and are all normalized to the molar yield of p-xylene using Ba₂ScBiO₅₃·½H₂O as catalyst. (In the formulae, for catalysts containing Oₓ⁺, y has a maximum value of 2, whereas for the catalysts containing Oₓ⁺, y has a maximum value of 1.)

After sampling the reaction mixture for subsequent analysis (about 23 hours of reaction) each catalyst was regenerated by stopping the flow of feedstream and injecting oxygen gas into the reaction chamber for about 60 minutes. The feedstream was then reinitiated for subsequent conversion of isobutylene to products.

The results show that no broad generalization can be made as to which groups of the Periodic Table can be utilized effectively for production of para-xylene. It can be seen, however, that trivalent metal cations are preferred over divalent cations in the majority of catalysts for increasing the relative yield of aromatic product. For those materials which exhibit a good relative yield of para-xylene (e.g., greater than 70%), Ba₂ScBiO₅₃·½H₂O is by far the best catalyst under the conditions employed herein in terms of total yield of product.

---

**TABLE IX**

<table>
<thead>
<tr>
<th>Group of Periodic Table</th>
<th>Metal Oxide Catalyst</th>
<th>Yield of para-Xylene (A)</th>
<th>Yield of 2,5-Dimethyl-1,5-hexadiene Dimer (B)</th>
<th>Yield of Other Products* (C)</th>
<th>Relative Yield ø</th>
<th>Total Yield ø</th>
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<td>0.61</td>
</tr>
<tr>
<td></td>
<td>Ba₂LaBiO₅₃·½H₂O</td>
<td>0.43</td>
<td>0.12</td>
<td>trace</td>
<td>78</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>Ba₂PrBiO₅₃·½H₂O</td>
<td>0.03</td>
<td>0.30</td>
<td>N.D.</td>
<td>9</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>Ba₂NdBiO₅₃·½H₂O</td>
<td>0.54</td>
<td>0.12</td>
<td>trace</td>
<td>82</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>Ba₂DyBiO₅₃·½H₂O</td>
<td>0.39</td>
<td>0.10</td>
<td>trace</td>
<td>80</td>
<td>0.49</td>
</tr>
<tr>
<td>Group IIB</td>
<td>Ba₂AlBiO₅₃·½H₂O</td>
<td>0.03</td>
<td>0.30</td>
<td>N.D.</td>
<td>9</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>Ba₂GaBiO₅₃·½H₂O</td>
<td>0.32</td>
<td>0.22</td>
<td>trace</td>
<td>59</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>Ba₂InBiO₅₃·½H₂O</td>
<td>0.69</td>
<td>0.05</td>
<td>less than 0.05</td>
<td>92</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Ba₂TlBiO₅₃·½H₂O</td>
<td>0.65</td>
<td>0.40</td>
<td>less than 0.05</td>
<td>62</td>
<td>1.05</td>
</tr>
</tbody>
</table>

* Relative to p-xylene (100).

**RLM1506**
TABLE IX-continued

<table>
<thead>
<tr>
<th>Group of Periodic Table</th>
<th>Metal Oxide Catalyst</th>
<th>Yield of 2,5-Dimethyl-1,5-Hexadiene Dimmer (B)</th>
<th>Yield of Other Products A B C</th>
<th>Relative Yield A + B + C</th>
<th>Total Yield A B C</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIA</td>
<td>Ba₂MgBi₂O₅⁺⁺</td>
<td>0.23</td>
<td>0.34</td>
<td>0.09</td>
<td>35</td>
</tr>
</tbody>
</table>

*Comparable examples.

**This number is normalized to the moles of p-xylene produced using Ba₂MgBi₂O₅⁺⁺ as catalyst, which was arbitrarily assigned a value of 1.0.

**Other products detected (excluding combustion products, e.g., CO and CO₂) were benzene, cineole, 2,5-dimethyl-1,5-hexadiene, and two unidentified products (resinolene and α-macroxylenol were not detected).

**This number represents the total of the yields of p-xylene divided by the sum of the yields of p-xylene, 2,5-dimethyl-1,5-hexadiene dimmer, and other hydrocarbon products, multiplied by 100.

**This number represents the sum of the yields of p-xylene, 2,5-dimethyl-1,5-hexadiene dimmer, and other hydrocarbon products.

N.D. = not detectable

EXAMPLE 13

The procedure of Example 12 was repeated except that propylene gas was substituted for isobutylene gas. The catalyst employed and the results obtained are indicated in Table X. All nomenclature used in the table follows from Example 12.

For those catalysts which exhibit a good relative yield of benzene (e.g., greater than 50%), the results show that Ba₂ScBi₂O₅⁺⁺ is the best catalyst in terms of total yield of products.

TABLE X

<table>
<thead>
<tr>
<th>Group of Periodic Table</th>
<th>Metal Oxide Catalyst</th>
<th>Yield of Benzene (A)</th>
<th>Yield of 1,5-Hexadiene Dimmer (B)</th>
<th>Yield of Other Products A B C</th>
<th>Relative Yield A + B + C</th>
<th>Total Yield A B C</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIA</td>
<td>Ba₂MgBi₂O₅⁺⁺</td>
<td>0.21</td>
<td>0.17</td>
<td>N.D.</td>
<td>64</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>Ba₂Bi₂O₅⁺⁺</td>
<td>0.14</td>
<td>0.11</td>
<td>N.D.</td>
<td>56</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Ba₂ScBi₂O₅⁺⁺</td>
<td>1.00</td>
<td>0.02</td>
<td>trace</td>
<td>98</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>Ba₂YBi₂O₅⁺⁺</td>
<td>0.18</td>
<td>0.01</td>
<td>trace</td>
<td>95</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>Ba₂La₂Bi₂O₅⁺⁺</td>
<td>0.18</td>
<td>0.02</td>
<td>trace</td>
<td>90</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>Ba₂PrBi₂O₅⁺⁺</td>
<td>0.02</td>
<td>0.18</td>
<td>trace</td>
<td>70</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>Ba₂NdBi₂O₅⁺⁺</td>
<td>0.06</td>
<td>0.01</td>
<td>trace</td>
<td>86</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>Ba₂DyBi₂O₅⁺⁺</td>
<td>0.10</td>
<td>0.02</td>
<td>trace</td>
<td>83</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Ba₂HoBi₂O₅⁺⁺</td>
<td>0.03</td>
<td>0.01</td>
<td>N.D.</td>
<td>75</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Ba₂ErBi₂O₅⁺⁺</td>
<td>0.17</td>
<td>0.13</td>
<td>trace</td>
<td>57</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Ba₂TbBi₂O₅⁺⁺</td>
<td>0.65</td>
<td>0.18</td>
<td>N.D.</td>
<td>78</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>Ba₂YbBi₂O₅⁺⁺</td>
<td>0.60</td>
<td>0.60</td>
<td>N.D.</td>
<td>90</td>
<td>1.20</td>
</tr>
</tbody>
</table>

*This number is normalized to the moles of benzene produced using Ba₂ScBi₂O₅⁺⁺ as catalyst, which was arbitrarily assigned a value of 1.0.

**Other products detected (excluding combustion products, e.g., CO and CO₂) were 1,4-hexadiene isomers (mixture).

**This number (mole fraction) represents the sum of the yields of benzene, 1,5-hexadiene dimmer, and other products, multiplied by 100.

**This number represents the summation of the yields of benzene, 1,5-hexadiene dimmer, and other hydrocarbon products.

N.D. = not detectable

EXAMPLE 14

Catalyst mixtures were prepared either by mixing two moles of barium oxide with one mole of the post-transition metal oxide and one mole of the trivalent metal oxide, or by mixing three moles of barium oxide with two moles of the post-transition metal oxide and one mole of the divalent metal oxide catalyst, as indicated in Table XI. The mixtures were ground, heated to 400°C in air, and then cooled and ground in air, and reheated to 800°C in air or oxygen for 6 hours. This last step effectively increases the amount of oxygen available for reaction when contacted with a hydrocarbon to its maximum amount. Formation of catalyst was detected by X-ray diffraction analysis.

Each catalyst so prepared, in an amount of 3 grams, was supported on a glass frit in the isothermal zone of a 20 mm outer diameter glass reactor. The reactor was heated in a conventional resistance-heated furnace.

A feedstream consisting of about 5% isobutylene and 95% helium was introduced through each reactor at a rate of 30 cc per minute after heating the reactor and its contents to a temperature of 475°C in helium. During the first two to three hours of reaction, samples of the reaction mixture were injected at 15 minute intervals using a gas sampling valve into a gas chromatograph and the identity and quantity of each product were determined. The molar amounts of 1,5-dimethyl-1,5-hexadiene dimer and other products per mole bismuth were calculated from the integrations of the chromatographic peaks so as to determine the total yield of all hydrocarbon products for each catalyst and the relative

yield of dimer for each catalyst.

The types and yields of products as well as the relative yields of aromatic product for each catalyst are indicated in Table XI. The molar yields of each product are all expressed in units of moles per mole bismuth and are all normalized to the molar yield of p-xylene using Ba₂ScBi₂O₅⁺⁺ as catalyst. In the formulae, for catalysts containing O₅⁺⁺ y has a maximum value of 2, whereas for the catalysts containing O₅⁺⁺ y has a maximum value of 1.

After sampling the reaction mixture for subsequent analysis (about 2-3 hours of reaction) each catalyst was regenerated by stopping the flow of feedstream and injecting oxygen gas into the reaction chamber for about 60 minutes. The feedstream was then reinitiated for subsequent conversion of isobutylene to products.

For those catalysts which exhibit a good relative yield of 2,5-dimethyl-1,5-hexadiene dimer (e.g., at least 50%), the results show that Ba₂ScBi₂O₅⁺⁺ is clearly the best of all catalysts tested in terms of total yield of products.
### TABLE XI

<table>
<thead>
<tr>
<th>Group of Periodic Table</th>
<th>Metal Oxide Catalyst</th>
<th>Yield of 2,5-Dimethyl-1,5-hexadiene (A)</th>
<th>Yield of para-Xylene (B)</th>
<th>Yield of Other Products(^2) (C)</th>
<th>Relative Yield of 2,5-Dimethyl-1,5-hexadiene Dimer(^3) A + B + C</th>
<th>Total Yield(^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIA</td>
<td>Ba(\text{MgBiO}_3)</td>
<td>0.22</td>
<td>0.05</td>
<td>trace</td>
<td>87</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>BaCa(\text{MgBiO}_3)</td>
<td>0.14</td>
<td>0.17</td>
<td>trace</td>
<td>67</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>BaSr(\text{BiO}_2)</td>
<td>0.13</td>
<td>0.01</td>
<td>N.D.</td>
<td>93</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{BiO}_2)</td>
<td>0.13</td>
<td>0.01</td>
<td>N.D.</td>
<td>93</td>
<td>0.14</td>
</tr>
<tr>
<td>IIB</td>
<td>Ba(\text{SrBiO}_2)</td>
<td>0.01</td>
<td>1.00</td>
<td>trace</td>
<td>1</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{CaBiO}_2)</td>
<td>0.12</td>
<td>0.04</td>
<td>N.D.</td>
<td>88</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{MgBiO}_3)</td>
<td>0.07</td>
<td>0.03</td>
<td>N.D.</td>
<td>91</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{BiO}_2)</td>
<td>0.12</td>
<td>0.02</td>
<td>trace</td>
<td>17</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.11</td>
<td>trace</td>
<td>58</td>
<td>0.36</td>
</tr>
<tr>
<td>III</td>
<td>Ba(\text{CaBiO}_2)</td>
<td>0.29</td>
<td>0.01</td>
<td>N.D.</td>
<td>100</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{SrBiO}_2)</td>
<td>0.29</td>
<td>0.01</td>
<td>N.D.</td>
<td>97</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{MgBiO}_3)</td>
<td>0.35</td>
<td>0.04</td>
<td>trace</td>
<td>90</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{BiO}_2)</td>
<td>0.37</td>
<td>0.03</td>
<td>N.D.</td>
<td>91</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.03</td>
<td>trace</td>
<td>52</td>
<td>0.66</td>
</tr>
</tbody>
</table>

\(^1\) Comparative example.

\(^2\) Other products detected (excluding combination products, e.g., CO and CO\(_2\)) were benzene, toluene, 2,3-dimethyl-1,3-hexadiene, and 2,3-dimethyl-1,3-hexadiene-1,4-oxide (a different isomer of 2,3-dimethyl-1,3-hexadiene was not detected).

\(^3\) Number ( mole fraction) represents the yield of 2,5-dimethyl-1,5-hexadiene dimer divided by the sum of the yields of 2,5-dimethyl-1,5-hexadiene dimer, para-xylene, and other products, multiplied by 100%.

\(^4\) Number represents the sum of the yields of 2,5-dimethyl-1,5-hexadiene dimer, para-xylene, and other hydrocarbon products.

N.D. = not detectable.

### EXAMPLE 15

The procedure of Example 14 was repeated except that propylene gas was substituted for isobutylene gas.

The catalysts employed and the results obtained are indicated in Table XII. All nomenclature used in the table follows from Example 14.

The results show that Ba\(\text{SrBiO}_2\) is a superior catalyst in terms of relative yield of dimer.

### TABLE XII

<table>
<thead>
<tr>
<th>Group of Periodic Table</th>
<th>Metal Oxide Catalyst</th>
<th>Yield of 1,5-Hexadiene Dimer(^5) (A)</th>
<th>Yield of Benzen(^6) (B)</th>
<th>Yield of Other Products(^7) (C)</th>
<th>Relative Yield of 1,5-Hexadiene Dimer(^5) A + B + C</th>
<th>Total Yield(^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIA</td>
<td>Ba(\text{MgBiO}_3)</td>
<td>0.12</td>
<td>0.21</td>
<td>N.D.</td>
<td>36</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{CaBiO}_2)</td>
<td>0.06</td>
<td>0.03</td>
<td>trace</td>
<td>100</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{SrBiO}_2)</td>
<td>0.11</td>
<td>0.14</td>
<td>trace</td>
<td>69</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{MgBiO}_3)</td>
<td>0.02</td>
<td>1.00</td>
<td>trace</td>
<td>44</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{BiO}_2)</td>
<td>0.11</td>
<td>0.14</td>
<td>trace</td>
<td>2</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.03</td>
<td>trace</td>
<td>66</td>
<td>0.23</td>
</tr>
<tr>
<td>IIB</td>
<td>Ba(\text{SrBiO}_2)</td>
<td>0.23</td>
<td>0.12</td>
<td>N.D.</td>
<td>66</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{MgBiO}_3)</td>
<td>0.18</td>
<td>0.06</td>
<td>trace</td>
<td>30</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{BiO}_2)</td>
<td>0.01</td>
<td>0.01</td>
<td>trace</td>
<td>14</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.03</td>
<td>trace</td>
<td>83</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.08</td>
<td>trace</td>
<td>73</td>
<td>0.90</td>
</tr>
<tr>
<td>III</td>
<td>Ba(\text{CaBiO}_2)</td>
<td>0.05</td>
<td>0.00</td>
<td>trace</td>
<td>100</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{SrBiO}_2)</td>
<td>0.09</td>
<td>0.01</td>
<td>trace</td>
<td>100</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{MgBiO}_3)</td>
<td>0.12</td>
<td>0.03</td>
<td>trace</td>
<td>71</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Ba(\text{BiO}_2)</td>
<td>0.08</td>
<td>0.03</td>
<td>trace</td>
<td>100</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
<td>trace</td>
<td>25</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.18</td>
<td>trace</td>
<td>22</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.65</td>
<td>trace</td>
<td>22</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.11</td>
<td>trace</td>
<td>100</td>
<td>0.11</td>
</tr>
</tbody>
</table>

\(^5\) This number is normalized to the mole of benzene obtained using Ba\(\text{SrBiO}_3\) as catalyst, which was arbitrarily assigned a value of 1.00.

\(^6\) Other products detected (excluding combination products, e.g., CO and CO\(_2\)) were benzene, toluene, 2,3-dimethyl-1,3-hexadiene, and 2,3-dimethyl-1,3-hexadiene-1,4-oxide (a different isomer of 2,3-dimethyl-1,3-hexadiene was not detected).

\(^7\) This number (mole fraction) represents the yield of 1,5-hexadiene dimer divided by the sum of the yields of 1,5-hexadiene dimer, benzene, and other products, multiplied by 100%.

\(^4\) This number represents the sum of the yields of 1,5-hexadiene dimer, benzene, and other hydrocarbon products.

N.D. = not detectable.

What is claimed is:

1. An oxygen-deficient, barium-containing compound having a perovskite-type structure of the formula:

\[
\text{Ba}_M\text{M}^2\text{O}_{3+y}
\]
if M is a trivalent cation, or

\[ \text{Ba}_2\text{M}_2\text{O}_3 \cdot \text{O}_{1+y} \]

if M is a divalent cation, wherein M is selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, La, lanthanides of atomic number 58 or greater, Ni, Fe, Cu, Al, Ga, In, Zn, Cd, Hg, Bi, Tl and a mixture thereof, M' is selected from the group consisting of Sb or Bi, a is equal to or greater than 0 but less than or equal to 1, and if M is a trivalent cation, y is equal to or greater than 0 but less than 1, and if M is a divalent cation, y is equal to or greater than 0 but less than \((3+a)/2\).

2. An oxygen-deficient, bismuth-containing compound having a perovskite-type structure of the formula:

\[ \text{Ba}_2\text{M}_2\text{Bi}_2 \cdot \text{O}_{1+y} \]

wherein M is La or Sc, a is equal to or greater than 0 but less than or equal to 1 and y is equal to or greater than 0 but less than 1.

3. A compound according to claim 1 of the formula:

\[ \text{Ba}_2\text{Bi}_2 \cdot \text{O}_{1+y} \]

wherein y is equal to or greater than 0 but less than 1.

4. A compound according to claim 3 wherein y is from 0 to 0.6.

5. A compound according to claim 3 wherein y is about 0 or about 0.6.

6. A compound according to claim 2 of the formula:

\[ \text{Ba}_2\text{Ln}_2\text{Bi}_2 \cdot \text{O}_{1+y} \]

wherein a is greater than 0 but no greater than 1.

7. A compound according to claim 6 wherein y is less than or equal to 0.1.

8. A compound according to claim 6 wherein y is 0.

9. A process for preparing the oxygen-deficient, bismuth-containing compound of claim 1 which comprises heating a precursor compound of the formula:

\[ \text{Ba}_2\text{M}_2\text{O}_3 \cdot \text{O}_{1+y} \]

if M is a trivalent cation, or

\[ \text{Ba}_2\text{M}_2\text{O}_3 \cdot \text{O}_{1+y} \]

if M is a divalent cation, wherein M, M', and a are defined in claim 1, y is about 1 but not greater than 1 if M is trivalent, and y is about \((3+a)/2\) but not greater than \((3+a)/2\) if M is divalent, in the presence of an effective amount of oxygen at a temperature of at least about 600° C, depending on the particular precursor compound and the amount of oxygen present, for a sufficient period of time to produce the oxygen-deficient compound.

10. A process according to claim 9 wherein M is Sc or La and M' is Bi.

11. A process according to claim 9 wherein the precursor compound is of the formula:

\[ \text{Ba}_2\text{M}_2\text{Bi}_2 \cdot \text{O}_{1+y} \]

where M is La or Sc.

12. A process according to claim 11 wherein a is 0 and the precursor compound is prepared from a mixture of barium carbonate or nitrate with a salt or oxide of bismuth.

13. A process according to claim 11 wherein a is greater than 0 and the precursor compound is prepared from a mixture of barium carbonate or nitrate with a salt or oxide of bismuth and a salt or oxide of M.

14. A process according to claim 9 wherein the precursor compound is heated at from about 600° to 1000° C, depending on the particular precursor compound and the amount of oxygen present.

15. A process according to claim 11 wherein the precursor compound is heated at from about 800° to 1000° C, depending on the particular precursor compound and the amount of oxygen present.

16. A process according to claim 11 wherein the amount of oxygen present is sufficient to yield an oxygen partial pressure of between about 0.001 and 0.000002 atm.

17. A process according to claim 14 wherein the amount of oxygen present is sufficient to yield an oxygen partial pressure of between about 0.001 and 0.000002 atm.

18. A process for preparing an oxygen-deficient, bismuth-containing compound having a perovskite-type structure of the formula:

\[ \text{Ba}_2\text{Ln}_2\text{Bi}_2 \cdot \text{O}_{1+y} \]

wherein y is equal to or greater than 0 but less than 1, which process comprises (a) heating a mixture of \( \text{Ba}(\text{NO}_3)_2\), \( \text{Bi}(\text{NO}_3)_3\cdot5\text{H}_2\text{O} \) and \( \text{La}_2\text{O}_3 \) in air to 800° C in relative proportions so as to produce a precursor compound of the formula:

\[ \text{Ba}_2\text{M}_2\text{Bi}_2 \cdot \text{O}_{1+y} \]

and (b) heating the precursor compound at an oxygen partial pressure of between about 0.001 and 0.0001 atm and at a temperature of 950° to 1000° C, depending on the oxygen partial pressure, for a sufficient period of time to produce the oxygen-deficient compound.

19. A process according to claim 18 wherein y is 0.

20. A process according to claim 19 wherein the precursor compound is heated at 950° C at an oxygen partial pressure of 0.0001 atm for at least 8 hours.
CATION-REORDERED, BISMUTH-CONTAINING PEROVSKITES

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Field of Search ......................... 585/415, 417, 418, 520, 585/530, 533; 502/303, 525

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ABSTRACT
A class of cation-reordered, bismuth-containing compounds having a perovskite-type structure of the formula

$$\text{Ba}_2\text{La}_3\text{Bi}_2\text{O}_9$$

wherein y is greater than 0 but less than 1, is provided. Preferably, y is from 0.25 to 0.75, and most preferably y is 0.5.

The compositions herein are found to be particularly advantageous in the selective production of aromatic compounds from acyclic olefins, particularly in the production of benzene from propylene.

16 Claims, 4 Drawing Figures
CATION-REORDERED, BISMUTH-CONTAINING PEROVSKITES

BACKGROUND OF THE INVENTION

This invention relates to a class of cation-reordered, bismuth-containing compounds having a perovskite-type structure useful in oxidative dehydrogenation reactions and a process for their preparation. In addition, the invention relates to a process for selectively producing aromatic compounds from acyclic olefins, preferably propylene and styrene.

During a typical petroleum refining operation large quantities of low molecular weight paraffins and olefins are produced. Unlike paraffins which may be sold for fuels, olefins have undesirable combustion properties which hamper their potential use as fuels. Thus, much research effort has been directed to upgrading the olefins, either for use as fuel or as chemical intermediates in the chemical industry. For those olefins containing three and four carbon atoms much research has been directed toward obtaining reaction products such as dimer and aromatic products having greater potential commercial value, with bismuth oxide representing a conventional oxidation catalyst, particularly for producing dimers.

Oxidative conversions of unsaturated hydrocarbons have recently been conducted using various catalyst combinations. A recently published comprehensive review article on oxidative dehydrogenation of olefins is E. A. Mamedov, Russ. Chem. Review, 50, 291 (1981), which lists numerous references disclosing use of catalysts containing bismuth oxide in combination with other elements to convert olefins to dienes and aromatic products in the presence or absence of molecular oxygen.

SUMMARY OF THE INVENTION

In accordance with this invention a novel class of cation-reordered, bismuth-containing compounds having a perovskite-type structure of the formula:

$$\text{Ba}_2\text{La}_3\text{Bi}_2\text{O}_9$$

wherein \( y \) is greater than 0 but less than 1 is provided. These compounds are further characterized by having the x-ray powder diffraction pattern as set forth in Table 1 hereof. Preferably, \( y \) is from 0.2 to 0.75, most preferably 0.5.

The above class of compounds may be prepared by heating a first precursor compound represented by the formula:

$$\text{Ba}_2\text{La}_3\text{Bi}_2\text{O}_9$$

where \( y \) is defined above and which is characterized by having the x-ray diffraction pattern as set forth in Table 1 hereof, in the presence of an effective amount of oxygen at a temperature from about 600°C to its melting temperature, for a sufficient period of time to produce a second precursor compound which is oxygen deficient and which has a perovskite-type structure and which is represented by the formula:

$$\text{Ba}_2\text{La}_3\text{Bi}_2\text{O}_{9-y}$$

where \( y \) is as defined above and \( x \) is from about 0 to 1; and heating the second precursor compound to a temperature from about 400°C to about 650°C in an oxidizing environment.

The class of compounds herein, which are stable in air to at least 600°C, may be used in oxidative dehydrogenation reactions or in similar processes requiring solid oxidizing agents. In particular, the compounds herein are especially effective as catalysts in selectively producing aromatic products from C3 and C4 acyclic olefins, preferably benzene and xylene from propylene and styrene, respectively.

Specifically, most of the cation-reordered materials of this invention show nearly 100% selectivity for converting propylene to benzene at 510°C, as compared to a much lower selectivity observed when the first precursor compound described above, or the first precursor compound treated at high temperatures in flowing oxygen, is employed under identical conditions. Furthermore, the oxygen-deficient catalyst obtained after the propylene has been converted in accordance with the present invention can be regenerated by oxidation to yield a catalyst showing further improved performance in the conversion reaction.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical representation showing the relative amounts of 1.5 hexadiene and benzene produced from propylene (5% in helium) as a function of time at two different temperatures, 475°C and 510°C, by use of two materials, (A and B) both of which are represented by the formula Ba2La3Bi2O9. Both are re-ordered but one (B) was obtained by treating (A) in flowing oxygen at 900°C for 2.5 days prior to use.

FIG. 2 is a graphical representation showing the relative amounts of 1.5 hexadiene and benzene produced from propylene (5% in helium) as a function of time at two different temperatures, 475°C and 510°C, by use of two conventional cation ordered materials (C and D) both of which are represented by the formula Ba2La3Bi2O9 wherein material C is a first precursor compound as herein described and material D is the product of heating a sample of material C in flowing oxygen at 950°C for one day followed by heating at 900°C for 3.5 days.

FIG. 3 is a graphical representation showing the relative amounts of 1.5 hexadiene and benzene produced from propylene (5% in helium) as a function of time at temperatures of 475°C and 500°C by use of two materials (E and F), both of which are represented by the formula Ba2La3Bi2O9 wherein material E is cation re-ordered and F is conventionally cation ordered.

FIG. 4 is a graphical representation showing the relative amounts of 1.5 hexadiene and benzene produced from propylene (5% in helium) as a function of time at temperatures of 475°C and 500°C by use of two materials (G and H), both of which are represented by the formula Ba2La3Bi2O9 wherein material G is cation-reordered and H is conventionally cation ordered.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The class of cation-reordered bismuth-containing compounds of the present invention are found by x-ray diffraction analysis to have the perovskite-type structure as described in A. F. Wells, Structural Inorganic

The first precursor compounds, $\text{Ba}_2\text{La}_2\text{Bi}_2\ldots\text{O}_x$, where $x$ is greater than or equal to 3, were prepared by the following procedure: 5

1. A mixture of barium nitrate, bismuth nitrate, and lanthanum oxide was heated in a tube at $800^\circ\text{C}$ for 10 hours.
2. The mixture was then ground and heated in a tube at $1000^\circ\text{C}$ for another 10 hours.

The mixture was then heated in a tube at $1300^\circ\text{C}$ for 10 hours. The resulting product was a mixture of the fully oxidized material and the fully reduced material. If the first precursor compound is such that $y$ is 0.5, then the product is a mixture of the fully oxidized material and the fully reduced material.

The x-ray powder diffraction pattern of the novel composition of the present invention is shown in Table II, indicating that the cation reordering has occurred. The x-ray pattern of the cation reordering is a reflection of the novel composition of the present invention.

The cation-reordered compounds of the present invention are prepared by heating the first (fully oxidized) precursor compound, which is conventionally ordered, and which can be prepared by any of the convenient methods previously described in the presence of an amount of oxygen effective for a particular temperature to obtain a second precursor compound which is an oxygen-deficient perovskite structure of the formula $\text{Ba}_2\text{La}_2\text{Bi}_2\ldots\text{O}_{x-y}$, where $y$ is defined above and $x$ is greater than or equal to 3, but less than 8.

The temperature at which the first precursor compound is heated is dependent on many factors such as the type of first precursor compound and the amount of oxygen present. At minimum, the temperature should be about $600^\circ\text{C}$, but the temperature is preferably higher, for example about $700^\circ\text{C}$ to $1000^\circ\text{C}$.

The time of heating will similarly depend on several factors such as the type of first precursor compound and the amount of oxygen present. At minimum, the temperature should be about $600^\circ\text{C}$, but the temperature is preferably higher, for example about $700^\circ\text{C}$ to $1000^\circ\text{C}$.

The time of heating will similarly depend on several factors such as the type of first precursor compound, temperature, and oxygen partial pressure. The interrelationships among the amount of oxygen employed, the temperature, and the type of first precursor compound can be expressed as follows: When the temperature is decreased, a lower oxygen pressure is required to obtain the product. As the content of lanthanum in the first precursor compound is increased, either the temperature must be increased or the oxygen partial pressure decreased and the time for heating must be increased to obtain the reduced product. Even when these parameters are adjusted, however, if $y$ in the formula is increased beyond about 0.7 the second precursor obtained on cooling will generally not be a single-phase material but rather will comprise two phases which may be a mixture of the fully oxidized material ($x=0$) and the fully reduced material ($x=1$). If the first precursor compound is such that $y$ is 0.5, then the compound is heated at about $600^\circ\text{C}$ and $1000^\circ\text{C}$, the oxygen partial pressure will be between about 0.001 and 0.00001 atm, depending on the temperature. The preferred temperature range for heating is about $800^\circ\text{C}$ to $1000^\circ\text{C}$, and most preferred is about $900^\circ\text{C}$ to $1000^\circ\text{C}$.

When a temperature of about $1000^\circ\text{C}$ is employed when $y$ is 0.5, the oxygen partial pressure must be about 0.001 atm to obtain the second precursor compound, whereas if the temperature is about $950^\circ\text{C}$, the oxygen partial pressure is generally about 0.001 atm and the time required is at least 8 hours, preferably 10 to 12 hours.

When $y$ is increased to 1, no oxygen-deficient precursor will be obtained unless the oxygen partial pressure is reduced or the temperature is increased.

The second precursor compound thus obtained is then oxidized to form the cation-reordered product by heating the compound at a temperature no greater than about $650^\circ\text{C}$ in an oxidizing environment, preferably at about $400^\circ\text{C}$ to $600^\circ\text{C}$, and more preferably $600^\circ\text{C}$.

The time required for this oxidation will depend on the type of precursor employed, the temperature, the oxygen partial pressure, and the rate of gas flow, but is generally from about 1 to 4 hours, more preferably from about 1 to 3 hours.

The cation-reordered compound of this invention can be converted to an ordering similar to that of the conventionally ordered, fully oxidized compound by heating in flowing oxygen at a temperature of at least about $600^\circ\text{C}$, preferably about $900^\circ\text{C}$ to $1000^\circ\text{C}$ for at least one day, depending on the temperature.

The x-ray powder diffraction pattern of the compound which resulted when the cation-reordered material with $y=0.5$ was heated at $900^\circ\text{C}$ in flowing oxygen for 2.5 days, shown in Table III hereof, displays a clear (111) and a weak (333) reflection as does the diffraction pattern for the first precursor compound.
butene, 2-butene, isobutylene or mixtures of the same. The preferred olefins herein are propylene, which is selectively converted to butene, and isobutylene, which is selectively converted to para-xylene.

Although the catalysis reaction hereof can be conducted in the presence of oxygen, it is desirable to keep the amount of oxygen at a minimum. It is preferred that less than about 5 volume %, more preferably less than about 1 volume % of oxygen be present. It is most preferred to carry out the catalysis reaction under substantially anaerobic conditions. The volume percents are based on the total volume of gases. In the typical process herein a feedstock containing the olefin substrate is passed through a bed containing the catalyst (the cation-reordered compound of this invention), which is preferably unapportioned. An inert diluent gas such as nitrogen, methane, helium, argon, or the like is preferably added to the feedstock containing the olefinic hydrocarbon to minimize risk of explosion and complete oxidation of the olefin. Typically, the feedstock contains at most 5% olefin with the remainder being helium gas.

A temperature of about 425°C to 600°C is generally required to achieve significant conversion of the olefins to aromatic products. If the temperature is increased much above 600°C, decomposition may occur so as to form by-products or degradation products and problems may arise with respect to any regeneration of catalyst. The preferred temperature range for the process herein is about 450°C to 520°C.

The duration of the reaction is governed by such factors as, for example, the temperature, the amount and type of catalyst, and the rate at which the feedstock passes through the catalyst bed, which is preferably about 10 cc/min to 50 cc/min for a bed diameter of about 2 cm, but may be varied in accordance with the specific conditions employed. If the rate is too fast, of course, there will be a significant decrease in conversion of the feed, whereas if the rate is too slow, undesirable by-reactions may begin to occur.

After the reaction has proceeded for such a period of time that the catalyst has lost a significant amount of its lattice oxygen but prior to any destruction of the complex (for example, at about 450°C to 500°C at 30 cc/min for about 4 to 6 hours), the catalyst is preferably regenerated by reoxidation thereof with an oxidizing gas such as oxygen or air. The regeneration may take place at the reaction temperature or higher, preferably at 550°C to 600°C. The reaction can thus be conducted in a cyclic operation so that reaction occurs in one cycle and regeneration in a second cycle, or in a continuous operation wherein preferably two reactors are employed and a continuous stream of olefin flows through one reactor while the catalyst is regenerated in the second reactor. These cycles may be periodically reversed.

The aromatic product may be recovered by any suitable manner known in the art.

The invention is further described in the examples which follow. In the examples, all parts and percentages are by weight, and all temperatures are in °C, unless otherwise noted.

**EXAMPLE 2**

Preparation of BaLaO₅Bi₂O₇

A mixture of 12.000 g Ba(NO₃)₂, 16.701 g Bi(NO₃)₃·5H₂O and 1.870 g La₂O₃ was heated in air to 400°C for two hours. The sample was reground and fired at 800°C in air for one hour followed by grinding and refining at 800°C for 60 hours. The resulting first product precursor was determined by x-ray diffraction to be a pseudo cubic perovskite material which could be indexed using a lattice parameter a₀ = 8.74(1) Å, also written as a₀ = 8.74 ± 0.01 Å. Comparison with the lattice parameters for Ba₂Bi₂O₇ and Ba₂La₂Bi₂O₇ shows that the oxygen composition for this material is specified by Ba₂La₂Bi₂O₇. This material was placed in an alumina boat in a Lindberg tube furnace and heated in flowing oxygen to 950°C for 18 hours to ensure a fully oxidized starting material, which was then cooled without removal from the furnace. The gas stream was changed to a stream consisting of oxygen and air containing 100 ppm oxygen (0.0001 atm partial pressure of oxygen) flowing at 300 cm³/min. The temperature was then raised to 950°C and maintained for 16 hours before cooling in the same atmosphere to produce a light-brown oxygen-deficient material representing the second precursor. Without removal of the material from the furnace, the atmosphere was changed to pure oxygen flowing at 300 cm³/min and the temperature was raised to 600°C and maintained there for 2.5 hours before cooling in flowing oxygen to room temperature. Ancillary TGA experiments showed that the conditions were sufficient to re-oxidize fully the oxygen-deficient material formed during the treatment with 100 ppm oxygen to yield the compound of this invention.

The x-ray diffraction data for the first precursor and for the cation-reordered material obtained by re-oxidation at 600°C of the second precursor are shown in Tables I and II respectively. The data were recorded with a Philips diffractometer using CuKα radiation. The x-ray diffraction data of the material obtained by heating the cation-reordered material at 900°C in flowing oxygen for two days is shown in Table III. It can be seen from this data that the compounds represented in Tables I and III are conventionally cation-ordered materials having a (111) and (333) reflection whereas the compounds represented in Table II are cation-reordered, and do not exhibit reflections of the type (111) and (333).

**TABLE I**

<table>
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<td></td>
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**NOTE:**

w = weak; m = medium; s = strong. N.O. = not observed.
before cooling in the same atmosphere to produce an oxygen-deficient material, light brown in color, representing the second precursor. Ancillary TGA experiments showed that these conditions were sufficient to form Ba$_2$La$_2$Zn$_2$O$_{8-4y}$. Without removal of the material from the furnace, the atmosphere was changed to pure oxygen flowing at 300 cm$^3$/min. and the temperature was raised to 600°C and maintained there for 2 hours before cooling in flowing oxygen to room temperature. Ancillary TGA experiments showed that these conditions were sufficient to fully reoxidize the oxygen-deficient material formed during the treatment with 1000 ppm oxygen to yield the compound of the invention.

The X-ray diffraction data for the first precursor and for the cation-reordered material obtained by re-oxidation at 600°C of the second precursor are shown in Tables I and II, respectively. It can be seen that the (111) and (333) reflections are absent for the compound of composition Ba$_2$La$_2$Zn$_2$O$_{8-4y}$ in Table II, indicating that this compound has been cation-reordered.

**EXAMPLE 3**

Preparation of Ba$_2$La$_2$Zn$_2$O$_{8-4y}$

A mixture of 10.454 g of Ba(NO$_3$)$_2$, 2.183 g of La$_2$O$_3$ and 12.9 g of Ba(NO$_3$)$_2$.5H$_2$O was heated as described in Example 1 except that the final heating was done at 900°C instead of 800°C. The resulting first precursor product was determined by X-ray diffraction to be a pseudo-cubic perovskite material which could be indexed with a lattice parameter $a_0=8.75(1)$ Å. Comparison with the lattice parameters for Ba$_2$Bi$_2$O$_6$ ($a_0=8.71(1)$ Å) and Ba$_2$BiLaO$_6$ ($a_0=8.77(1)$ Å) shows that the oxygen composition of this material is given by Ba$_2$La$_2$Zn$_2$O$_{8-4y}$. This material was placed in an alumina boat in a Lindberg tube furnace and heated in flowing oxygen to 900°C for 2 hours to ensure a fully oxidized starting material which was cooled without removal from the furnace. The gas stream was changed to a stream of purified argon (0.000002 atm partial pressure of oxygen) flowing at 300 cm$^3$/min. The temperature was raised to 950°C and maintained there for 16 hours and then increased to 1000°C for an additional 24 hours before cooling in the same atmosphere to obtain a bright yellow oxygen-deficient material representing the second precursor. Ancillary TGA experiments showed that these conditions were sufficient to form Ba$_2$La$_2$Zn$_2$O$_{8-4y}$. Without removal of the sample from the furnace the atmosphere was changed to pure oxygen flowing at 300 cm$^3$/min. and the temperature was raised to 600°C and maintained for 2 hours before cooling in the same atmosphere to room temperature. Ancillary TGA experiments showed that these conditions were sufficient to fully reoxidize the oxygen deficient material formed in the previous step to yield the compound of the invention.

The X-ray diffraction pattern for the first precursor and for the cation-reordered material obtained by reoxidation at 600°C of the second precursor are shown in Tables I and II. It can be seen that the (111) and (333) reflections are absent for the compound of composition Ba$_2$La$_2$Zn$_2$O$_{8-4y}$ in Table II indicating that this compound has been cation-reordered.

**TABLE II**

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**EXAMPLE 2**

Preparation of Ba$_2$La$_2$Zn$_2$O$_{8-4y}$

A mixture of 10.454 g of Ba(NO$_3$)$_2$, 16.974 g of Ba(NO$_3$)$_2$.5H$_2$O and 3.815 g of La$_2$O$_3$ was heated as described in Example 1 except that the final firing in air was done at 900°C instead of 800°C. The resulting first precursor product was determined by X-ray diffraction to be a pseudo-cubic perovskite material which could be indexed with a lattice parameter $a_0=8.72(1)$ Å. Comparison with the lattice parameters for Ba$_2$Bi$_2$O$_6$ ($a_0=8.71(1)$ Å) and Ba$_2$BiLaO$_6$ ($a_0=8.77(1)$ Å) shows that the oxygen composition of this material is given by Ba$_2$La$_2$Zn$_2$O$_{8-4y}$. This material was placed in an alumina boat in a Lindberg tube furnace and heated at 920°C for 14 hours in a gas stream consisting of oxygen and argon containing 1000 ppm oxygen (0.000 atm partial pressure of oxygen) flowing at 300 cm$^3$/min.
Example 4

Selective Production of Benzene

In four separate experiments, each of the four materials A-D, having the composition $\text{Ba}_2\text{La}_2\text{Si}_5\text{O}_{16}$, was singly deposited in an amount of 3 grams in a quartz upflow reactor with a 0.75 inch (1.9 cm) diameter. Material A was the final product of Example 1. Material B was the material resulting when Material A was heated in flowing oxygen at 900°C for 2.5 days. Material C was the first product of Example 1, i.e., the material obtained on successive regrindings and refirings to 800°C of a mixture of $\text{Ba}({\text{NO}_3})_2$, $\text{Bi}({\text{NO}_3})_3$, $\text{H}_2\text{O}$ and $\text{La}_2\text{O}_3$ heated in air. Material D was obtained by heating Material C in flowing oxygen at 950°C for one day followed by 3.5 days at 900°C. Thus, Material A is a cation-reordered material of this invention and Material B is obtained by high temperature treatment of Material A. Materials C and D represent conventionally ordered materials as a comparison.

A feedstream consisting of about 5% propylene and 95% helium flowing at a rate of 30 cc min$^{-1}$ was passed through the reactor which was heated to a temperature of 475°C. After about 24 hours of reaction at 475°C, the temperature was increased to 510°C and the reactions proceeded at the higher temperature to yield a total reaction time of six hours. Each reaction was monitored by injecting, at regular intervals, a sample of each product reaction mixture into a gas chromatograph. The identity and relative amounts of each product were thereby determined.

The results obtained for Materials A and B, on the one hand, and Materials C and D, on the other hand, are shown in FIGS. 1 and 2, respectively, which represent plots of the relative amounts of 1,5-hexadiene and benzene formed as a function of time. All four materials showed low production of carbon oxides, low benzene make, and comparable production of the 1,5-hexadiene dimer which was the dominant product during the initial reaction at 475°C. Materials A and B did, however, show a small early build-up of benzene which was much less pronounced with Materials C and D at 475°C. The most dramatic differences among the four materials occurred upon increasing the reaction temperature from 475°C to 510°C. Both Materials A and B, representing the cation-reordered material and its high temperature oxygen treated counterpart, respectively, showed a substantial build-up of benzene production with an accompanying rapid decrease in the production of the dimer. Thus, the selectivity for conversion of propylene to benzene at 510°C was nearly 100% after an initial induction period of about 1.5 hours and 3 hours for Materials A and B, respectively. On comparing the results in FIG. 1 with those in FIG. 2, it can be seen that the steady-state production of benzene by the materials which have undergone cation reordering (of FIG. 1) is greater by a factor of six to eight than the production of benzene by the conventionally ordered materials (of FIG. 2), which were tested under identical conditions. Moreover, when a perovskite of the composition $\text{Ba}_2\text{LaBiO}_4$, prepared by mixing appropriate molar amounts of barium nitrate, bismuth nitrate pentahydrate, and lanthanum oxide, heating the mixture to 400°C for 2 to 3 hours then cooling and grinding in air and reheating to 800°C in air for 60 hours in a furnace with an intermediate regird, was tested under identical conditions for conversion of propylene to benzene, it was found to have a lower conversion rate than Materials A and B by about a factor of one-half, even though the latter materials have a lower La to Bi ratio.

A X-ray diffraction analysis of the solid reaction products obtained after the catalytic reactions were completed showed that for Materials A and B significant quantities of the oxygen-deficient material $\text{Ba}_2\text{LaO}_2\text{Bi}_5\text{O}_{16}$ were present, while for comparative Materials C and D, which exhibited much lower conversion rates, the dominant phase was the fully oxidized material $\text{Ba}_2\text{La}_2\text{Si}_5\text{O}_{16}$ and little if any $\text{Ba}_2\text{LaO}_2\text{Bi}_5\text{O}_{16}$ was present.

In an additional experiment, the solid product material produced by reacting Material A with propylene was removed from the reactor and was regenerated by oxidation at 600°C in flowing oxygen. Using a mixture of 5% propylene in helium and conditions identical to those described above, the results showed that the regenerated material produced approximately equal amounts of the 1,5-hexadiene and benzene at 475°C at a level very comparable to that obtained using Material A. When the temperature was increased to 500°C, the benzene production rapidly increased to about 150% of the maximum level shown in FIG. 1. As observed with Material A the production of 1,5-hexadiene rapidly decreased, so that after two hours at 510°C the regenerated material effected essentially 100% conversion of propylene to benzene with a slow decrease in benzene production as time progressed. The results thus show that the loss in activity due to depletion of lattice oxygen may be avoided by treatment of the oxygen-deficient cation-reordered material with oxygen.

Example 5

Selective Production of Benzene from $\text{Ba}_2\text{La}_2\text{Bi}_5\text{O}_{16}$

In two separate experiments, each of two materials E and F, having the composition $\text{Ba}_2\text{LaO}_2\text{Bi}_5\text{O}_{16}$, was separately deposited in the amount of 3 grams in a quartz upflow reactor with a 0.75 inch (1.9 cm) diameter. Material E was cation reordered while Material F was conventionally ordered, each having each prepared as described in Example 2 where Material E is the final product and Material F is the first precursor product of Example 2.

A feedstream consisting of about 5% propylene and 95% helium flowing at a rate of 30 cc min$^{-1}$ was passed through the reactor which was heated to a temperature of 475°C. After about 24 hours of reaction at 475°C, the temperature was increased to 500°C, and the reactions proceeded at the higher temperature to yield a total reaction time of seven hours. Each reaction was monitored by injecting, at regular intervals, a sample of each product reaction mixture into a gas chromatograph. The identity and relative amounts of each product were thereby determined.

The results obtained for Materials E and F are shown in FIG. 3 which represents plots of the relative amounts of 1,5-hexadiene and benzene formed as a function of time. Both materials showed low production of carbon oxides, low benzene make, and comparable production of the 1,5-hexadiene dimer which was the dominant product during the initial reaction at 475°C. At 475°C, material E did show a small early build-up of benzene which was absent for Material F. A dramatic difference between these two materials occurred upon increasing the reaction temperature from 475°C to 500°C. Material E, representing the cation-reordered material, showed a
substantial build-up of benzene production with an accompanying rapid decrease in the production of the dimer, while Material F, representing the conventionally ordered material, continued to produce the dimer as the dominant product. For the cation-reordered Material E, the selectivity for conversion of propylene to benzene at 500°C was nearly 100% after an initial induction period of about four hours. Comparing the results for Materials E and F given in FIG. 3, it is clear that the cation reordered process increases the overall propylene conversion rate and dramatically improves selectivity toward the aromatic product as the reaction temperature is increased from 475°C to 500°C.

EXAMPLE 6
Selective Production of Benzene from B2L60.6(Bi1.3)O6

In two separate experiments, each of two Materials G and H, having the composition B2L60.6(Bi1.3)O6, was separately deposited in the amount of 3 grams in a quartz upflow reactor with a 0.75 inch (1.9 cm) diameter. Material G was cation reordered, while Material H was conventionally ordered each having been prepared as described in Example 3 where Material G is the final product and Material H is the first precursor product of Example 3. A feedstream consisting of about 5% propylene and 95% helium flowing at a rate of 30 cm min⁻¹ was passed through the reactor which was heated to a temperature of 475°C. After about 1 hour of reaction at 475°C, the temperature was increased to 500°C and the reactions proceeded at the higher temperature to yield a total reaction time of 44 hours. Each reaction was monitored by injecting, at regular intervals, a sample of each product reaction mixture into a gas chromatograph. The identity and relative amounts of each product were thereby determined.

The results obtained for Materials G and H are shown in FIG. 4 which represents plots of the relative amounts of 1,5-hexadiene and benzene formed as a function of time. Both materials showed low production of carbon oxides, low benzene make, and comparable production of the 1,5-hexadiene dimer which was essentially the only product during the initial reaction at 475°C. Material G showed a slight buildup of benzene as the temperature was increased to 500°C, while Material H showed essentially no benzene yield even at 500°C. Both materials showed a gradual decline over several hours in production of the dimer as the reactor temperature was held at 500°C.

In summary, the present invention is seen to provide a class of fully oxidized, cation-reordered, bismuth- and lanthanum-containing compounds having a perovskite-type structure and a process for the preparation thereof. Also provided is a process for selectively producing aromatic products from C6-C10 acyclic olefins using the class of compounds herein.

What is claimed is:
1. A cation-reordered, bismuth-containing compound having a perovskite-type structure of the formula:

\[ \text{Ba}_2\text{La}_{0.6}\text{Bi}_{2.0}\text{O}_6 \]

wherein y is greater than 0 but less than 1, the compound being further characterized by having the x-ray powder diffraction pattern indicated in Table II.

2. A compound according to claim 1 which is prepared by heating a compound having a perovskite-type structure of the formula:

\[ \text{Ba}_2\text{La}_{0.6}\text{Bi}_{2.0-x}\text{O}_6 \]

wherein y and x are greater than 0 but less than 1, at a temperature no greater than about 600°C in flowing oxygen.

3. A compound according to claim 1 wherein y is from 0.25 to 0.75.

4. A compound according to claim 1 wherein y is 0.5.

5. A process for preparing a cation-reordered, bismuth-containing compound having a perovskite-type structure of the formula:

\[ \text{Ba}_2\text{La}_{0.6}\text{Bi}_{2.0-x}\text{O}_6 \]

wherein y is greater than 0 but less than 1, the compound having the x-ray powder diffraction pattern indicated in Table II, which process comprises:
(a) heating a first precursor compound of the formula:

\[ \text{Ba}_2\text{La}_{0.6}\text{Bi}_{2.0-x}\text{O}_6 \]

wherein y is defined above and the x-ray diffraction pattern given in Table I, in the presence of an effective amount of oxygen at a temperature of at least about 600°C, depending on the particular precursor compound and the amount of oxygen present, for a sufficient period of time to produce a second precursor compound which is oxygen deficient and has a perovskite-type structure of the formula:

\[ \text{Ba}_2\text{La}_{0.6}\text{Bi}_{2.0-x}\text{O}_6 \]

where y is defined above and x is greater than 0 but no greater than 1; and
(b) heating the second precursor compound at a temperature no greater than about 650°C in flowing oxygen for a sufficient period of time to reoxidize the second precursor compound.

6. A process according to claim 5 wherein y is 0.25 to 0.75.

7. A process according to claim 5 wherein y is 0.5.

8. A process according to claim 5 wherein the first precursor compound is prepared from a mixture of \( \text{B}_{12}\text{N} \), \( \text{B}_{12}\text{N}_2\text{O}_5\), \( \text{B}_{12}\text{N}_3\text{H}_2\text{O}_6 \) and \( \text{La}_2\text{O}_3 \).

9. A process according to claim 5 wherein the mixture is heated in air to about 800°C.

10. A process according to claim 5 wherein the first precursor compound is heated at from about 600°C to 1000°C, depending on the particular precursor compound and the amount of oxygen present.

11. A process according to claim 5 wherein the first precursor compound is heated at from about 800°C to 1000°C, depending on the particular precursor compound.

12. A process according to claim 5 wherein the amount of oxygen present is sufficient to yield an oxygen partial pressure of between about 0.001 and 0.000001 atm.

13. A process according to claim 5 wherein the first precursor compound is heated at an oxygen partial pressure of between about 0.001 and 0.000001 atm and at a temperature of 900°C to 1000°C, depending on the oxygen partial pressure.
13. A process according to claim 5 wherein the first precursor compound is heated at 950° C. at an oxygen partial pressure of 0.0001 atm for at least 8 hours and y is 0.5.

14. A process according to claim 14 wherein the second precursor compound is heated at a temperature of about 250° to 650° C.

15. A process according to claim 5 wherein the second precursor compound is heated at a temperature of about 600° C. for at least 2.5 hours.
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## Notes

- January 3 - Trip to St. Louis, Mo.
- January 10 - Trip to Chicago, Ill.
- January 20 - Meeting with Mr. Brown
- January 31 - Birthday Party

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