

Both  $[M_2(\text{form})_4]^+$  ( $M = \text{Ni}, \text{Pd}$ ) solutions have strong absorptions in the near-infrared. The spectra are reported in supplementary Figure 4 and contrasted with those of the corresponding neutral species. An assignment of such bands will be presented following a molecular orbital study under way.

A bulk electrolysis was attempted for the palladium species at +1.35 V in order to electrogenerate the  $[\text{Pd}_2(\text{form})_4]^{2+}$  species, but more than two electrons per molecule were consumed in the process and a following cyclic voltammetric experiment showed that most of the electroactive species had been destroyed. We attribute this instability to a slow process that follows the generation of the  $[\text{Pd}_2(\text{form})_4]^{2+}$  species, since the peak separation and the peak currents in the process centered at  $E_{1/2} = +1.19$  V in the cyclic voltammogram of  $\text{Pd}_2(\text{form})_4$  (see Figure 2b) do not show any significant deviation from reversibility. Such a slow process may involve either the solvent or the formamidinato ligand.

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**Supplementary Material Available:** Tables of crystallographic data, atomic fractional coordinates, bond distances and angles, and temperature factors for  $\text{Ni}_2(\text{form})_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Pd}_2(\text{form})_4 \cdot 2\text{H}_2\text{O}$  and figures showing EPR spectra of  $M_2(\text{form})_4^+ \text{PF}_6^-$  (Figure 3) and visible spectra of  $[M_2(\text{form})_4]^{n+}$  (Figure 4) (10 pages). Ordering information is given on any current masthead page.

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### Comparison of Carbonate, Citrate, and Oxalate Chemical Routes to the High- $T_c$ Metal Oxide Superconductors $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

Sir:

It has been well over a decade since superconducting transition temperatures ( $T_c$ ) reached a maximum of 23.7 K in the metal-alloy A-15 compounds such as  $\text{Nb}_3\text{Ge}$ .<sup>1</sup> Recently, Bednorz and Müller<sup>2</sup> observed superconductivity in oxygen-deficient compounds in the La-Ba-Cu-O (LBCO) system with overall composition  $\text{La}_{5-x}\text{Ba}_x\text{Cu}_5\text{O}_{5(3-y)}$ . For various values of  $x$ , a three-phase mixture was present with an onset  $T_c$  of  $\sim 35$  K and with zero resistance achieved at  $T \sim 13$  K. Uchida et al.<sup>3</sup> and Takagi et al.<sup>4</sup> subsequently identified the superconducting phase in the LBCO system as having the composition  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$  ( $y$  unspecified) with the  $\text{K}_2\text{NiF}_4$  layered-perovskite structure (tetragonal, space group  $I4/mmm$ ). Onset  $T_c$ 's in the 30 K range with zero-resistance temperatures of  $\sim 22$  K were reported.<sup>3,4</sup> Simultaneously, Chu et al.<sup>5</sup> observed in samples with overall compositions of

**Table I.** Stoichiometric Ratios for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  Compounds Prepared from Different Chemical Routes

|                        | La/Sr/Cu ratio for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4^a$ |                |                |
|------------------------|---|----------------|----------------|
|                        | $x = 0.10$  | $x = 0.15$     | $x = 0.20$     |
| carbonate <sup>b</sup> | 1.90/0.10/1.00  | 1.85/0.14/0.96 | 1.80/0.19/1.03 |
| citrate                | 1.90/0.11/1.00  | 1.85/0.13/1.00 | 1.80/0.21/1.01 |
| carbonate <sup>c</sup> | 1.90/0.04/0.96  | 1.85/0.07/0.95 | 1.80/0.09/0.94 |
| oxalate <sup>c</sup>   | 1.90/0.01/0.93  |                | 1.80/0.03/0.84 |

<sup>a</sup> Analysis accuracy is approximately 5% of each number. <sup>b</sup> With adjustment to pH 7-8. <sup>c</sup> Without pH adjustment.

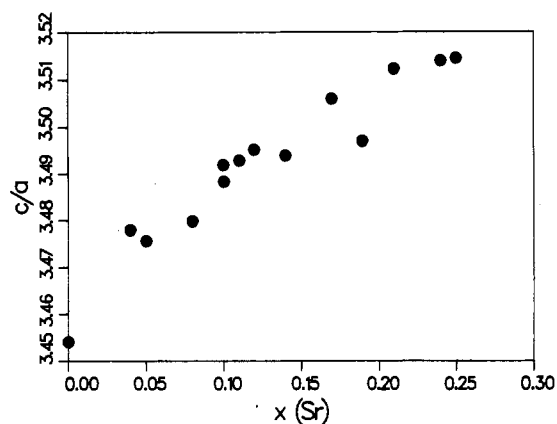
$\text{La}_{1-x}\text{Ba}_x\text{CuO}_{3-y}$  ( $x = 0.15-0.20$ ,  $y$  unknown) onset  $T_c$ 's of 32 K, which could be increased to 40.2 K and later to 52.5 K<sup>5b</sup> at a pressure of  $\sim 12$  kbar. Shortly thereafter, Jorgensen et al.<sup>6</sup> reported the crystal structure of  $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$  (confirmed  $\text{K}_2\text{NiF}_4$  layered-perovskite, derived from powder neutron diffraction studies) with  $T_c \approx 33$  K. Cava et al.<sup>7</sup> and Capone et al.<sup>8</sup> then demonstrated that with the use of strontium in place of barium, materials of composition  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  attained zero resistance at much higher temperatures, for example near 36 K for  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ .<sup>7</sup> Finally, reports<sup>9</sup> of large resistance decreases at  $T \sim 49$  K and higher in LBCO materials suggested the possibility of much higher transition temperatures. A very recent report<sup>10</sup> shows that a  $T_c$  of 93 K occurs at ambient pressure in the Y-Ba-Cu-O system. In many of the cited studies bulk superconductivity was confirmed by Meissner effect measurements. Clearly, superconductivity at  $T_c$ 's approximately quadruple that achieved previously has been observed, thereby opening a new frontier in research on superconducting materials.

The wide range of sample compositions reported thus far suggests that (i) considerable optimization of preparative conditions is required, and (ii)  $T_c$  varies with change in the alkaline-earth metal and its concentration. All reports (vide supra) suffer from the same major difficulties: incomplete synthesis conditions have been given and the reported compositions have been based only on initial reactant concentrations. As yet, no chemical analyses of the final products have been reported. Generally, the materials are prepared by repeated grinding and sintering of the parent oxides,<sup>3-5,7</sup> by co-precipitation reactions with oxalate<sup>2,6,9</sup> and carbonate,<sup>8</sup> or by a complexing reaction with citrate,<sup>3</sup> again followed by sample firing, grinding, and annealing. The main advantage of the solution techniques is that the final oxide products are more uniformly mixed than those prepared from binary oxides. In this communication we compare the carbonate, citrate, and oxalate solution techniques for the synthesis of the high- $T_c$  compounds  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ .

**Synthesis. Carbonate Route.** A detailed procedure for the preparation of  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  is given below. Samples of different metal compositions may be prepared by obvious changes in stoichiometry. Powdered samples (reagent grade) of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (8.25 g, 19.1 mmol),  $\text{Sr}(\text{NO}_3)_2$  (0.33 g, 1.6 mmol), and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (2.50 g, 10.3 mmol) are dissolved together in 100 mL of distilled water. The nitrate solution is vigorously stirred and neutralized to pH 7-8, in order to suppress bicarbonate formation, by titration with a KOH solution ( $\sim 19$  mmol). A solution of  $\text{K}_2\text{CO}_3$  (5.69 g, 41.2 mmol) in 60 mL of water is slowly added with stirring to the above mixture to give a thick, light blue precipitate. The precipitate is repeatedly washed and centrifuged

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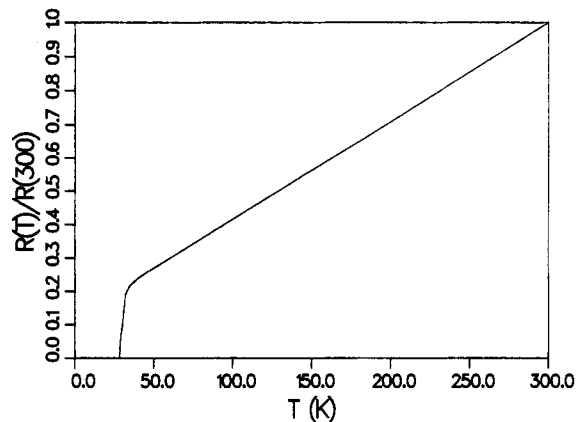
**Figure 1.** Values of the  $c/a$  ratio, which correlates<sup>18</sup> with  $T_c$ , as a function of composition  $x$  in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  samples. The value of  $a$  at  $x = 0$  was calculated from the corresponding orthorhombic parameters.

until the filtrate gives a pH of less than 8.8. The resulting blue powder is dried at 140 °C overnight and calcined at 820 °C for 2 h. The black powder is ground and pressed into pellets and sintered at ~1100 °C in air for 4 h. Sections of the pellets are then annealed at 500 °C in an  $\text{Ar}/\text{O}_2$  gas mixture.

**Citrate Route.**<sup>11,12</sup> The same proportions of powdered metal nitrates dissolved in distilled water are employed to synthesize  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  by the citrate route. A 1.3-g sample of powdered citric acid and 1.1 mL of ethylene glycol are added per gram of expected final sample. The resulting blue solution is stirred and heated to 90 °C, at which temperature a vigorous reaction occurs and copious amounts of  $\text{NO}_x$  gas are evolved. The heat is turned off while the stirring is continued. The reaction is complete within about 2 h, and the solution begins to set into a gel. The gel is subsequently decomposed to a solid by heating it in a Pyrex beaker on a hot plate. The resulting black solid is ground into a powder finer than 20 mesh. This powder is pressed into pellets, sintered, and annealed according to the previously described methods.

**Oxalate Route.**<sup>13</sup> This procedure generally follows the steps employed in the carbonate method but with the use of potassium oxalate for the precipitation. Although this route is the first reported wet chemical procedure<sup>2a</sup> for these materials, it is not a recommended one. It is surprising that the oxalate method has been used instead of the carbonate or citrate methods because of the relative solubilities ( $\text{SrC}_2\text{O}_4$  is approximately four times more soluble than  $\text{SrCO}_3$ ). In addition, the oxalate route appears to require finer control of pH to completely precipitate all components.<sup>13,14</sup> Finally, another complication is that  $\text{La}^{3+}$  in the presence of alkali-metal oxalate reacts first to yield the desired precipitate and then reacts with any excess reagent to form a double salt.<sup>14</sup> Thus, when precipitating lanthanum with alkali-metal oxalate,  $\text{La}_2\text{Ox}_3 \cdot \text{H}_2\text{O}$  first precipitates, but upon further addition of oxalate, the formation of the double salt competes with the precipitation of strontium and copper oxalates.<sup>15</sup> The control of compound stoichiometry by the oxalate method, therefore, appears to be more difficult than by the carbonate or citrate methods. This partially explains the mixed phases reported earlier.<sup>2,6</sup>

**Analysis.** We have synthesized, by the three routes outlined above, a variety of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  samples with  $x = 0.05$ – $0.30$ .



**Figure 2.** Relative resistivity as a function of temperature for an unannealed sample of polycrystalline  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ .

Chemical analyses of the products by each route for initial stoichiometries of  $x = 0.10$ ,  $0.15$ , and  $0.20$ , respectively, are summarized in Table I. These analyses pertain to the metal constituents only (La, Sr, Cu) and were carried out by the method of inductively coupled plasma/atomic emission spectroscopy (ICP/AES). The analyzed products are the samples obtained after sintering but before  $\text{O}_2$  annealing. Only insignificant changes in stoichiometry occur in the annealing step. The major discrepancies, if any, occur in the wet chemical procedures. Analyses of the products after precipitation (blue powders), but prior to heat treatments, give variable results because the products are either hydrated or partially decarboxylated. An examination of the table shows that the pH-adjusted carbonate route and the citrate route give final products close to the initial stoichiometric ratios. Samples prepared by the oxalate or carbonate routes without pH adjustment incorporate only a small fraction of the original Sr. The pH-adjusted carbonate route results in essentially complete precipitation. A disadvantage in this procedure is that the final washing is time consuming for large amounts of material. The citrate route is much more efficient. These wet chemical procedures work well for  $x < 0.3$ . Above this composition, additional phases of the La–Sr–Cu–O system are formed.<sup>16</sup>

X-ray powder diffraction analyses of the sintered black pellets showed that the synthesized materials consisted of the superconducting phase having the layered-perovskite structure<sup>16</sup> (tetragonal, space group  $I4/mmm$ ). A plot of the unit cell  $c/a$  ratio as a function of composition for  $x = 0.05$  to  $\sim 0.25$ , as derived from the chemical analyses, is illustrated in Figure 1. This curve shows a monotonic increase in  $c/a$  with increasing  $x$ , similar to that reported by Kanbe et al.<sup>17</sup>

The superconducting properties are determined as much by the oxygen stoichiometry<sup>7</sup> as by the metal stoichiometry, and therefore, the sintering and annealing temperatures and  $\text{O}_2$  partial pressures all influence the conductive properties of the materials. Figure 2 illustrates the resistivity (four-probe technique) as a function of temperature for one of our samples of composition  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  prior to  $\text{O}_2$  annealing. The room-temperature resistivity was estimated to be  $\rho(300 \text{ K}) \approx 1000 \mu\Omega \text{ cm}$ . The resistivity curve shows metallic behavior from 300 to below 50 K and then a drop in resistance to the superconducting state. The onset of the resistance drop is 40 K, the midpoint of the transition is 30.5 K, and zero resistance below instrument resolution occurs at 28.3 K. The 10–90% transition width is  $\sim 4$  K. These parameters compare favorably with the data reported by Cava et al.<sup>7</sup> for an  $\text{O}_2$ -annealed sample of the same composition prepared from

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sintered mixtures of the oxides. In several samples, we have observed resistivities indicative of mixtures of metallic and semiconducting regions that lead to broad superconducting transitions with zero resistance occurring in the region of 10–20 K depending on  $x$ . Annealing with  $O_2$  can often improve the conductive properties of such samples.<sup>18</sup>

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## Articles

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### Preparation and Crystal Structures of $(Te_2Se_8)(AsF_6)_2$ , $(Te_{4.5}Se_{5.5})(AsF_6)_2$ , and $(Te_2Se_6)(Te_2Se_8)(AsF_6)_4(SO_2)_2$

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The preparation of the compounds  $(Te_2Se_8)(MF_6)_2$  (**1a**, M = As; **1b**, M = Sb),  $(Te_{4.5}Se_{5.5})(AsF_6)_2$  (**2**), and  $(Te_2Se_6)(Te_2Se_8)(AsF_6)_4(SO_2)_2$  (**3**) and the crystal structures of **1a**, **2**, and **3** are reported. Compound **3** contains the cations  $Te_2Se_6^{2+}$  and  $Te_2Se_8^{2+}$ , hexafluoroarsenate anions, and  $SO_2$  solvent molecules. The novel  $Te_2Se_6^{2+}$  cation is not isostructural with the previously known cations  $Se_8^{2+}$  and  $S_8^{2+}$  but instead adopts a bicyclo[2.2.2]octane structure with tellurium atoms in the three-coordinate positions. In both **1a** and **3** the  $Te_2Se_8^{2+}$  cations have slightly different dimensions from those observed for the cation in the previously reported compound  $(Te_2Se_8)(AsF_6)_2(SO_2)$ . Compounds **1a** and **1b** are isomorphous. In **2** the  $Te_{4.5}Se_{5.5}^{2+}$  cation is a disordered mixture of  $Te_2Se_{10-x}^{2+}$  cations. Some structural relationships between these and related cations are discussed. Crystal data for each compound are as follows: **1a** [**1b**], orthorhombic,  $Pbcn$ ,  $a = 16.118$  (3) Å [16.489 (3) Å],  $b = 13.098$  (3) Å [13.251 (4) Å],  $c = 18.951$  (4) Å [19.422 (6) Å],  $V = 4001$  (1) Å<sup>3</sup> [4244 (2) Å<sup>3</sup>]; **2**, orthorhombic,  $Pbcn$ ,  $a = 14.790$  (3) Å,  $b = 10.783$  (2) Å,  $c = 13.304$  (2) Å,  $V = 2121.7$  (7) Å<sup>3</sup>; **3**, monoclinic,  $P2_1/c$ ,  $a = 12.432$  (4) Å,  $b = 15.956$  (6) Å,  $c = 23.053$  (10) Å,  $\beta = 96.61$  (3)°,  $V = 4542$  (3) Å<sup>3</sup>.

#### Introduction

It has been well-established that the pentafluorides  $AsF_5$  and  $SbF_5$  react with sulfur, selenium, or tellurium in  $SO_2$  solution to produce crystalline, ionic compounds such as  $(S_8)(AsF_6)_2$ ,<sup>1</sup>  $(Se_{10})(SbF_6)_2$ ,<sup>2</sup> and  $(Te_6)(AsF_6)_4(SO_2)_2$ .<sup>3</sup> Mixtures of chalcogens have been oxidized to give salts containing mixtures of homopolyatomic cations such as  $(Te_6)(Se_8)(AsF_6)_6(SO_2)_4$  or heteropolyatomic cations such as  $(Te_3S_3)(AsF_6)_2$ ,<sup>5</sup>  $(Te_2Se_2)(Sb_3F_{14})(SbF_6)_6$ ,<sup>6</sup> and  $(Te_2Se_8)(AsF_6)_2(SO_2)$ .<sup>7</sup> In the present work we carried out reactions with stoichiometries that might have led to cations such as  $Te_2Se_{10}^{2+}$ ,  $Te_2Se_{14}^{2+}$ , and  $Te_2S_2Se_2^{2+}$ , but instead we obtained new salts of the  $Te_2Se_8^{2+}$  cation and a salt containing

the new  $Te_2Se_6^{2+}$  cation. Although the  $Te_2Se_8^{2+}$  cation is isostructural with the  $Se_{10}^{2+}$  cation,<sup>2,8</sup> the  $Te_2Se_6^{2+}$  cation is not isostructural with the  $Se_8^{2+}$  cation<sup>4,9</sup> but has a novel cubelike structure unlike that of any of the previously known polyatomic cations of the chalcogens.

#### Experimental Section

**Materials.** Elemental sulfur (BDH), selenium (Koch-Light Laboratories Ltd., 99.95%), and tellurium (Koch-Light Laboratories Ltd., 99.7%) were dried under vacuum at room temperature overnight before use. Antimony pentafluoride (Ozark-Mahoning) was distilled under vacuum and stored in an FEP bottle. Arsenic pentafluoride was prepared from the elements in a nickel can on a Monel vacuum line and stored in a nickel cylinder. Sulfur dioxide (Canadian Liquid Air) was stored over  $P_4O_{10}$  for at least 24 h before use. All reactions were carried out under vacuum in flame-sealed, double-bulb vessels fitted with medium porosity glass frits. Solid transfers were done in nitrogen-filled dryboxes.

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