

## Sol-Gel Preparations and Physical Properties of the Superconducting Phase $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$

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The system  $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$  with superconducting transition temperatures ( $T_c$ ) of 80 and 110 K has been obtained via a sol-gel process using oxalate as the complexing agent. The compound has metallic-like resistance and is formed by heating the precursor compound to temperatures near its melting point (885°C). The preparation is highly reproducible and leads to black-grained powders with excellent homogeneity and sinterability. The resulting material was examined by thermogravimetry (TG), X-ray diffraction, transmission electron microscopy (TEM), elemental analysis, surface area (BET), and resistivity measurements using a direct current source. Details involving the novel preparation and characterization of this material are discussed. © 1989 Academic Press, Inc.

Since Bednorz and Müller (1) reported the Ba-La-Cu-O system as a high- $T_c$  superconducting oxide much work has been carried out to find new types of materials with these properties. Recently, new  $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$  high- $T_c$  oxides with  $T_c = 80$  and 110 K have been reported (2-6). The recent discovery of this new family of high- $T_c$  superconductors involving orthorhombic unit cells has prompted us to apply the sol-gel process to obtain this substance instead of the commonly used solid-state reaction (2-7) between oxides. In this paper we describe the sol-gel preparation and subsequent characterization of the  $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$  superconductor phases.

The actual crystal structure of the 80 and 110 K phases is complex and not yet fully understood (3-8). It seems that the observed phases consist of alternating double perovskites and double Bi-O planes having a variable Bi-Sr-Ca composition in the solid solution. It has been suggested that the 110 K phase is similar to the 80 K phase with only a minor variation reflected in an improved atomic order (3-6).

Amorphous oxalate precursors were synthesized following the general principles of sol-gel procedures employed in the preparation of perovskite materials (9). Nitrates of constituent metals were dissolved in water in the desired proportions and mixed with an aqueous solution of oxalic acid. The molar ratio of oxalic acid to total ni-

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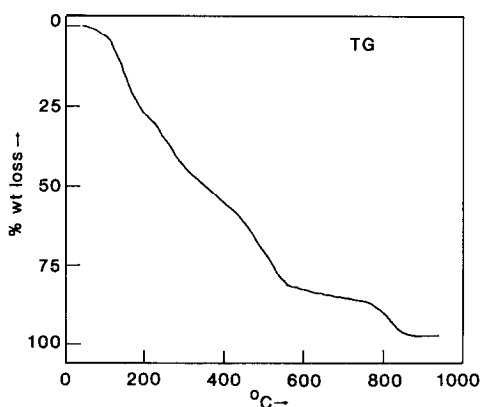


Fig. 1. Variation of weight loss with temperature for oxalate precursor of  $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$  in air. Heating rate was  $2^\circ\text{C}/\text{min}$ .

trate anions was fixed at two. This was the minimum amount of oxalic acid needed to bind all metal ions. Therefore the reactions start from an appropriate mixture of metal hydroxides and oxalic acid which acts as a buffer and a ligand inhibiting inhomogeneous precipitation (9). In 800 ml of  $\text{H}_2\text{O}$  were mixed 4.85 g ( $10^{-2}$  moles)  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , 2.12 g ( $10^{-2}$  moles)  $\text{Sr}(\text{NO}_3)_2$ , 2.36 g ( $10^{-2}$  moles)  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and 4.83 g ( $2 \cdot 10^{-2}$  moles)  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . In a separate flask 27.74 g ( $2.2 \cdot 10^{-1}$  moles) oxalic acid was dissolved. The mixture of nitrates and oxalates forms a cloudy solution. Water was slowly evaporated from the mixed solution at  $90^\circ\text{C}$  for 16 hr yielding a green-blue viscous gel. This gel was further dehydrated at  $120^\circ\text{C}$  for 5 hr. This material was then heated in  $\text{ZrO}_2$  crucibles at  $350^\circ\text{C}$  in air for 10 hr and subsequently for 6 hr at  $680^\circ\text{C}$  in flowing  $\text{O}_2$ . This last step eliminated residual carbon and oxalates as  $\text{CO}_2$ . We used a large furnace to avoid Sr, Ca-carbonate formation during oxalate elimination. During oxalate elimination—mainly as  $\text{CO}_2$ —there is a moment when the powder is surrounded by this gas. If a high local concentration of  $\text{O}_2$  is maintained there by using a large volume furnace, the possibil-

ity of carbonate formation during the elimination step is minimized. In this way, only 0.03% C was found in the resulting material via elemental analysis. Subsequently, the sample was heated for 16 hr at  $850^\circ\text{C}$ , 60 hr at  $880^\circ\text{C}$ , 0.4 hr at  $890^\circ\text{C}$ , and 9 hr at  $880^\circ\text{C}$ , cooling slowly at  $50^\circ\text{C}/\text{min}$  to form the orthorhombic structure. Since a large amount of metal carbonates was formed during the decomposition of the organics, very long annealing times were required close to, but not above, the melting point ( $885^\circ\text{C}$ ) reported for this material (2–6). Nevertheless, we found in the course of our work that even higher temperatures were needed ( $890^\circ\text{C}$ ) for complete formation of the superconducting perovskite.

Figure 1 shows a thermogravimetric analysis scan of the heat treatment in air. According to the thermogravimetry (TG) shown in Fig. 1, an 89% weight loss for oxalate precursor of  $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$  takes place up to  $1000^\circ\text{C}$ . These weight losses may occur in the following steps: (a)  $50$ – $130^\circ\text{C}$  superficial and structural water, (b)  $130$ – $300^\circ\text{C}$  decomposition of the nitrates, (c)  $300^\circ\text{C}$  decomposition of the organic constituents; (d)  $450$ – $500^\circ\text{C}$  intermediate species, e.g.,  $\text{CuO}$  and  $\text{Bi}_2\text{O}_3$ , formed during the chemical reaction decompose; (e)  $550$ – $700^\circ\text{C}$ ,  $\text{CaCO}_3$  and  $\text{SrCO}_3$  decompose (Fig. 1). As seen from Fig. 1, the reaction is complete at  $890^\circ\text{C}$ . At temperatures above  $890^\circ\text{C}$  a stable weight shows that the precursor is fully reacted to form the superconducting compound. The magnitude of the reported weight changes is consistent with what is expected based upon the starting materials and the oxalic acid addition. Thermogravimetry indicates that dehydration is completed by drying to  $120^\circ\text{C}$ . The subsequent pyrolysis products were  $\text{H}_2\text{O}$ ,  $\text{NO}_x$  (brown fumes), and  $\text{CO}_2$  and  $\text{CO}$  when the metals were introduced as nitrates, as in our case. Similar observations have been reported before for sol-gel ceramics (9).

Electron diffraction on the fine-grain

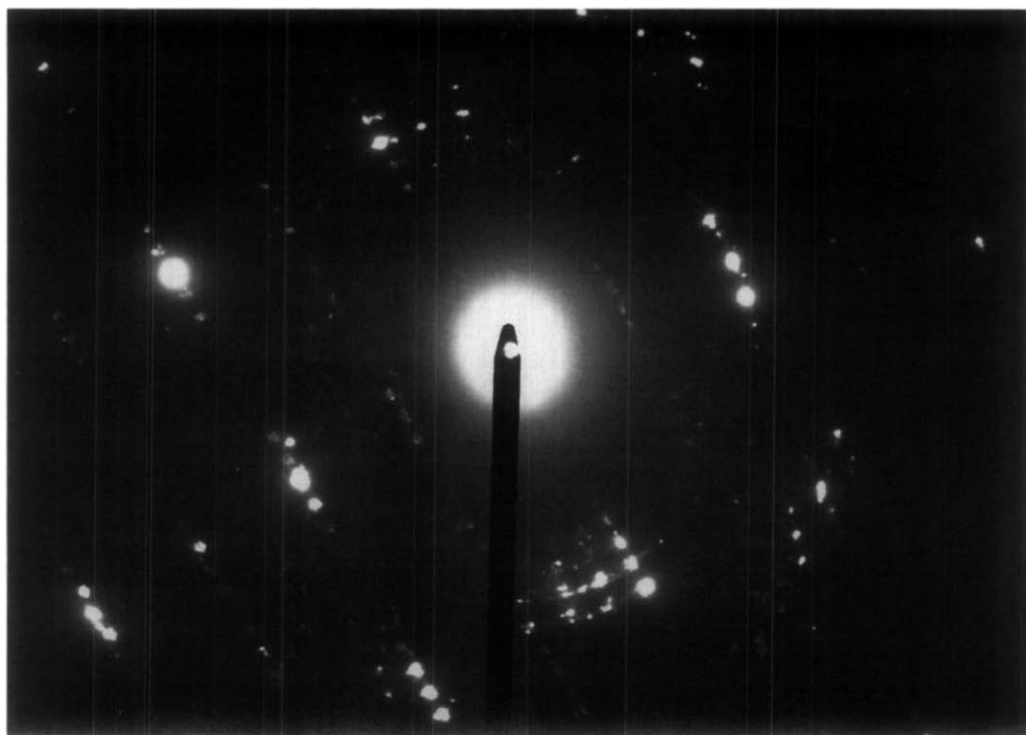


FIG. 2. Electron diffraction pattern for polycrystalline  $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$  prepared via sol-gel.

crystallites of black  $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$  was carried out using a Phillips 300 S instrument at 100 kV and the results are reported in Fig. 2. Until now only electron diffraction on single crystals has been reported (5–6). From Fig. 2, it is seen that numerous non-uniform electron diffraction patterns were obtained showing polycrystalline structure with numerous stacking faults and other defects (10). Many of these defects are probably associated with interfaces between alternating double-layer perovskite structure and Bi–O plane spacings (2–8).

Figure 3 presents the transmission electron microscopy (TEM) of oxalate based  $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$ . These particles show polycrystalline structure having sizes between 4900 and 7400 Å for 60% of the particles. The observed morphology reflects the layered structure of the light fine-grain material obtained. The powders have BET

surface areas from 1.2 to 1.9  $\text{m}^2/\text{g}$  corresponding to an effective particle size of 7400 to 4900 Å. It is interesting to note that BET surface areas for the powders heated to 800°C are substantially larger ( $>8 \text{ m}^2/\text{g}$ ), but these materials are not superconductive.

Resistivity measurements were carried out via the van der Pauw technique (11). The sample was prepared as a cylindrical disk 3 mm high. Gold leads were attached to the sample with silver paint contacts. For measuring the resistivity a temperature controller (Oxford Instr. C10 808) was used. The cooling rate was 5 K/min above 100 K and 1 K/min below 100 K. The temperature was measured with a CLTS temperature sensor (Oxford Instr. Cryogenic). Currents of 100  $\mu\text{A}$  to 1 mA were applied to the sample by a direct current source and the voltage was measured by a Keithley

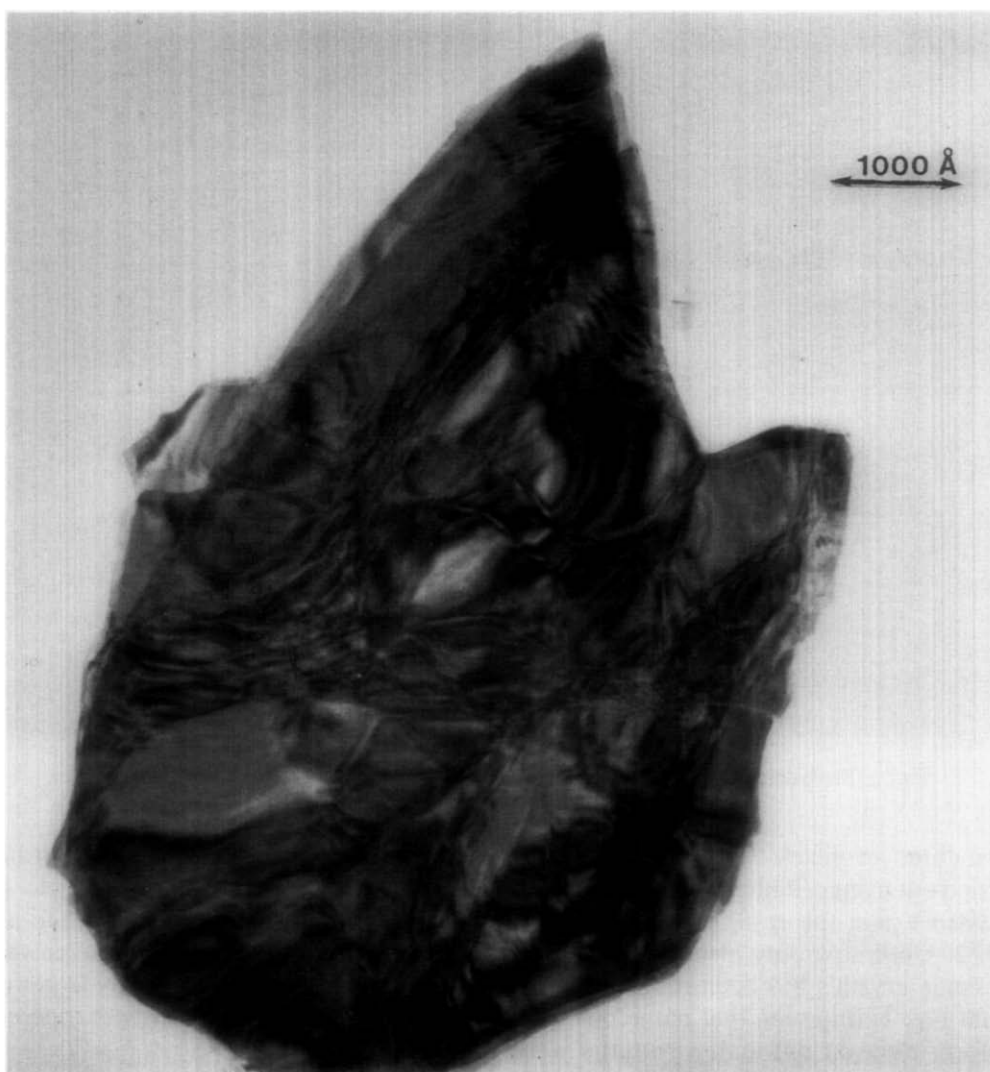


FIG. 3. Microstructure of  $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$ . Magnification 220,000.

A159 voltmeter. Each resistivity point was the average of 10 measurements in Fig. 4. Figure 4 shows the resistivity of  $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$  showing two superconducting transition temperatures at 80 and 110 K. The resistivity drops sharply at these two temperatures but zero resistance is not reached until 40 K for the second (80 K) phase.

Other resistivity measurements showed that when temperatures below 880°C were

used in the preparation of the superconductor, the  $T_c$  80 K phase formed to an even higher degree than reported in Fig. 4. High temperatures (800°C and above) and longer annealing times converted the 80 K material to 110 K indicating a slow kinetics step involving long-range diffusion of the cations. As previously reported (5–8), the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  formed at temperatures below 880°C reacts with Ca and Cu com-

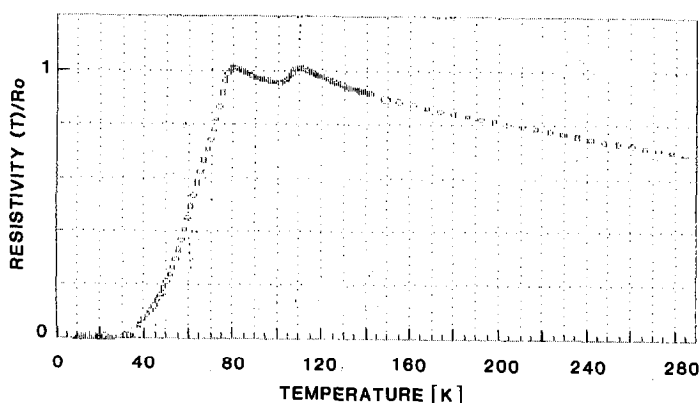


FIG. 4. Resistivity as a function of temperature for  $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$  oxalate-based material.

pounds over long periods of time to form the 110 K material, whose substructure is not entirely resolved (6).

In conclusion, we reported a novel sol-gel technique useful in the preparation of high- $T_c$   $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$  compound. Until now powder preparation methods which require solid-state diffusion have presented several problems when used as a synthetic route (2–5). This study shows the possibility of obtaining superconducting ceramics from carboxyl groups containing organic precursors via homogeneous chemical substitutions (12). These ceramic powders have a very low C content. By optimizing the annealing conditions the authors are confident that they will be able to form single-phase high- $T_c$  materials.

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