Preparation of $YBa_2Cu_3O_{7-x}$ superconductor by oxalate coprecipitation

P. KUMAR, V. PILLAI, D. O. SHAH
Center for Surface Science and Engineering, Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, USA

Since the discovery of a superconducting transition temperature (T_c) near 30 K in La–Ba–Cu-oxide by Bednorz and Müller [1], enormous efforts were made to study perovskite-like oxide superconductors. This led to the invention of new superconducting materials in the Y–Ba–Cu–O [2, 3] system with T_c above the boiling point of liquid nitrogen. Most recently, even higher-T_c ($\geq$110 K) phases were discovered in the Bi–Sr–Ca–Cu–O [4] and Tl–Ba–Ca–Cu–O [5] systems.

It is well known that the properties of oxide superconductors depend strongly on the synthesis technique and processing conditions. Therefore, the powder synthesis techniques are likely to play a crucial role in the preparation of bulk materials. The solid-state reaction is the most common process for preparing $YBa_2Cu_3O_{7-x}$ superconducting ceramics. This approach usually requires several heating and grinding cycles, and results in poor homogeneity, large particle size and irreproducibility. In order to achieve an acceptable level of homogeneity and better control of stoichiometry, chemical synthesis techniques such as coprecipitation [7–15], freeze drying [16], amorphous citrate processing [17–20] and chelation [21] have also been used. Homogeneous coprecipitation has been employed by various workers for precursor-powder synthesis with better homogeneity and stoichiometry, and is widely employed for the manufacture of high-quality ceramics [22]. Kini *et al.* [8] used K_2CO_3 as the precipitant in the presence of KOH to produce precursor carbonates with a possible contamination of potassium ion. Another effort, using the oxalate ion as precipitant, has been hindered by undesirable stoichiometry [9, 10] due to the different solubilities of individual oxalates. Because of the different solubilities of metal oxalates, it is necessary to optimize the experimental conditions carefully (e.g. pH and precipitating medium) to obtain the desired stoichiometric ratio in the precursor powder. The variation in stoichiometry with pH in aqueous media has been reported [17, 23, 24]. Most recent efforts have focused on the use of non-aqueous solvents to reduce the solubility of the oxalates [25, 26]. In this letter we report almost complete precipitation of oxalates (>99.9%) to obtain fine, homogeneous precursor powders in the required cationic ratio by utilizing acetic acid as a solvent.

The oxalate precursor powder for the fabrication of $YBa_2Cu_3O_{7-x}$ ceramic superconductor was prepared by homogeneous coprecipitation of the respective cations with the oxalate ion in acetic acid. Yttrium acetate [$Y(C_2H_3O_2)_3 \cdot 4H_2O$], barium carbonate ($BaCO_3$) and copper acetate [$Cu(C_2H_3O_2) \cdot H_2O$] were first dissolved in a 50:50 (by volume) acetic acid/water mixture in the cationic ratio of 1:2:3. The poor solubility of $BaCO_3$ in concentrated acetic acid necessitated this step. After evaporation to dryness, the residue was redissolved in 200 ml concentrated acetic acid to give 10 mmol Y^{3+}, 20 mmol Ba^{2+} and 30 mmol Cu^{2+} (a clear blue solution). In a typical experiment 200 ml of this solution was added dropwise into a solution of oxalic acid (a 10% excess over the required stoichiometric amount) in concentrated acetic acid. The mixture was stirred for 1 h and left undisturbed overnight. The precipitate was separated by ultracentrifugation and the remaining colourless supernatant was analysed for metal content. For inductively coupled plasma atomic emission spectroscopy (ICP/AES) analysis, the supernatant was evaporated to dryness and the residue was redissolved in dilute nitric acid. The analysis showed that more than 99.9% of each cation had precipitated as oxalate. The oxalate precipitate was washed with concentrated acetic acid twice, then dried at 100 °C for 12 h.

Thermogravimetric analysis (TEA) in air at a heating rate of 5 °C min^{-1} (Fig. 1) indicated the loss of water at a temperature below 200 °C, followed by the decomposition of CuC_2O_4 to CuO between 200 and 300 °C. The two-step decomposition of yttrium oxalate to Y_2O_3 via $Y_2(CO_3)_3$ occurred in the range between 300 and 550 °C, overlapped by the transformation of barium oxalate to barium carbonate. These decompositions agree with the weight changes observed for the individual oxalates and correspond

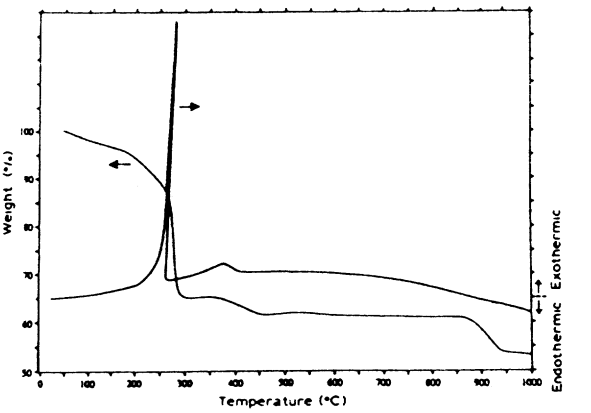

Figure 1 TGA/DTA thermograms for coprecipitated oxalates.

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with the exothermic peaks in the differential thermal analysis (DTA) curve. $BaCO_3$ starts to decompose to BaO at 870 °C and completes decomposition around 1000 °C. These results indicate that upon attaining a temperature of 650 °C for the coprecipitated oxalates, the oxalates are transformed into a mixture of Y_2O_3, $BaCO_3$ and CuO. The decomposition of $BaCO_3$ to BaO started at around 870 °C for the coprecipitated oxalates compared with at above 1000 °C for pure $BaCO_3$. These results are in agreement with those reported in the literature [27].

The oxalate precursor powder was calcined at 860 °C for 12 h in air, then cooled slowly (approximately 1 °C min^{-1}) to room temperature. The calcined powder was pressed into a pellet 6 mm in diameter under a static pressure of 120 MPa and the pellet was sintered at 940 °C for 6 h in air. The chemical composition of the calcined powder was determined by energy-dispersive X-ray analysis (EDAX). The structure and phase composition was determined with a Philips powder X-ray diffractometer using CuK_α radiation. The d.c. magnetic susceptibility measurements were done using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design). The surface morphology of the sintered specimen was examined by scanning electron microscopy (SEM).

The chemical composition of the calcined powder, as determined by EDAX, was in the required cationic ratio. The X-ray diffraction spectrum of the calcined powder revealed a negligible trace of Y_2BaCuO_5 (2 1 1 phase) along with a majority of the 123 phase. Prolonged heat treatment (12 h) at the same temperature (840 °C) resulted in pure orthorhombic $YBa_2Cu_3O_{7-x}$ (Fig. 2). For the sample sintered at 940 °C for 12 h the X-ray diffraction spectrum contained the lines for $YBa_2Cu_3O_{7-x}$ orthorhombic phase only.

The densities of sintered pellets were measured by the Archimedes method (immersion in iso-octane). The bulk density of the sintered pellet corresponded to 84.8% of the single-crystal density (6.37 g cm^{-3}) of $YBa_2Cu_3O_7$. The surface microstructure of the sintered pellets was observed under an SEM. Phase-pure grains as large as 10 μm in size were observed (Fig. 3).

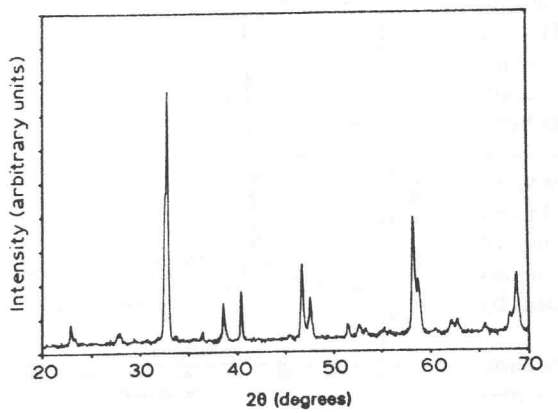

Figure 2 X-ray diffraction spectrum of $YBa_2Cu_3O_{7-x}$ prepared from oxalate precursor powder.

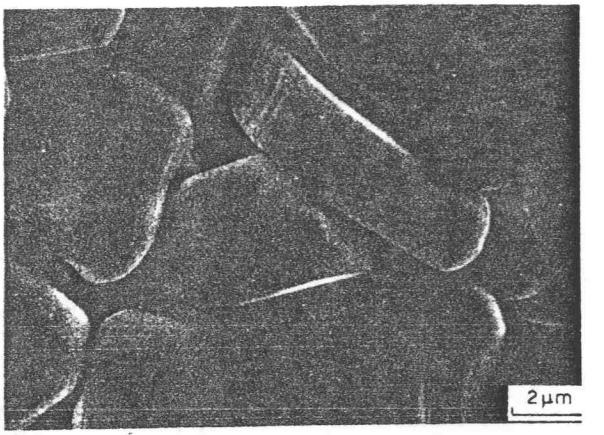

Figure 3 SEM micrograph of the sintered pellet prepared from coprecipitated oxalate precursor powder.

The temperature dependence of the d.c. susceptibility of the sintered pellet was measured by cooling the sample in zero field (diamagnetic shielding) and warming it in a field of 2.0 mT (flux expulsion). A T_c of 92 K was observed (Fig. 4). The diamagnetization-corrected value of the low-field zero-field-cooled signal (Meissner shielding) was 53% of that of an ideal sample ($-1/4\pi$). This does not represent the best value obtainable from the bulk precipitation and it may be further improved by the oxygenation and the optimization of sintering conditions.

It may be concluded that complete, stoichiometrically correct precipitation of yttrium, barium and copper as oxalates can be achieved by using acetic acid as a solvent. Furthermore, phase-pure $YBa_2Cu_3O_{7-x}$ superconductor with a T_c of 92 K can be prepared from the coprecipitated oxalate precursor powder after the proper heat treatment.

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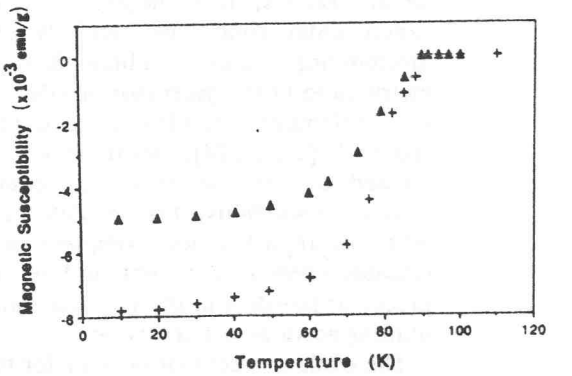

Figure 4 Temperature dependence of the d.c. susceptibility of the sintered pellet prepared from the coprecipitated oxalate precursor powder: (+) zero-field-cooled and (▲) field-cooled branch.

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