COPRECIPITATION PROCESS FOR THE PREPARATION OF SUPERCONDUCTIVE Bi-Sr-Ca-Cu OXIDES

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Bi-Sr-Ca-Cu superconducting oxide powders were prepared from an aqueous solution containing Bi, Sr, Ca, and Cu salts and oxalic acid via coprecipitation using triethyl amine as a base. The dried precipitate was found to have a satisfactory stoichiometry and a particle size of 0.3 μm. Subsequent calcination at 800 °C for 10 h and sintering at 870 °C for 12 h yielded a superconducting phase with \( T_c \) above 80 K. This process can be employed for large-scale preparation of Bi-Sr-Ca-Cu-O superconducting powder.

1. Introduction

Since Maeda et al. \cite{1} discovered a new superconducting material in the Bi–Sr–Ca–Cu–O system having two phases with \( T_c \) values of 80 and 110 K, this work has attracted much attention. Nearly all subsequent studies conclude that only the 80 K phase could be prepared in a single phase. A multiphase material was obtained when preparing the 110 K phase.

The conventional method for preparation of the Bi–Sr–Ca–Cu–O compound by means of solid-state reaction \cite{2-4} has many inherent problems, e.g., less homogeneity, larger particle size, less reproducibility and longer heat-treatment time. Coprecipitation is a better process because it can produce powders of smaller particle size and higher homogeneity. Two most common coprecipitation methods \cite{5,6} were employed. One is to use oxalic acid as a precipitating agent and adjusting the \( pH \) by NaOH or KOH. The other is using ammonium oxalate directly as the precipitant. However, the former has drawbacks such as possible contamination of the product with Na\(^+\) and K\(^+\) ions, while the latter results in non-stoichiometry. In this paper we report a new Bi–Sr–Ca–Cu–O preparation process from aqueous solution using oxalic acid as precipitant and triethyl amine for \( pH \) adjustment. The resulting Bi–Sr–Ca–Cu–O superconducting powder is of high homogeneity and possesses the desired stoichiometry.

2. Experimental procedures

All the chemicals were high-purity grade purchased from Merck AG and used without further treatment. Deionized water was used throughout all chemical procedures.

The Bi(NO\(_3\))\(_3\)·5H\(_2\)O, Sr(NO\(_3\))\(_2\), Ca(NO\(_3\))\(_2\)·2H\(_2\)O and Cu(NO\(_3\))\(_2\)·3H\(_2\)O were weighed for the molar ratio 2:2:1:2 [Bi(NO\(_3\))\(_3\)·5H\(_2\)O = 0.005 mole], and dissolved in 10 ml 2M nitric acid solution with constant stirring. The aqueous Et\(_3\)N/H\(_2\)C\(_2\)O\(_4\) solution was prepared by dissolving an excess amount (20%) of oxalic acid required for the precipitation of the total metal ions into 50 ml H\(_2\)O, whereas different amounts of Et\(_3\)N were added to adjust the Et\(_3\)N/H\(_2\)C\(_2\)O\(_4\) ratio which varies from 0 to 3. The mixture was vigorously stirred for 10 min to ensure complete dissolution. The nitrate salts of the metals were added dropwise into Et\(_3\)N/H\(_2\)C\(_2\)O\(_4\) while stirring vigorously. During mixing, a pale blue powder gradually formed. The solution was quenched by use of an ice-water bath while stirring. About one-half hour later, it was filtered and the precipitate dried at 140 °C for 6 h. The dehydrated powders were subjected to cal-

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cination at 800°C in air for 10 h, and then pressed into a cylindrical pellet 2 mm thick and 10 mm in diameter under a pressure of 2 ton cm⁻². Sintering was performed at 850°C in air for 12 h.

The amount of metal residue in the filtrate solution were analyzed by inductively coupled plasmaatomic emission spectrometry. Particle size of the precipitate was measured by laser scattering using a Coulter model N4 particle analyzer. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the dried powders were obtained by use of a TGD 7000 (Ulvac Co.). The ac electrical resistivity measurements were made by using a standard four-probe technique. Fine copper wire, which served as the voltage and current leads, was attached to the sample by using air-drying silver paste. A personal computer interface, which is capable of fully automated data acquisition, was employed for the resistance measurements. Magnetization data were obtained by use of a SQUID magnetometer (Quantum design) in which the sample was moved slowly through the pick-up coil. The structure was determined by use of a Philips X-ray diffractometer (XRD) using Cu Ka radiation.

3. Results and discussion

Usually the adjustment of pH is a crucial factor in the quantitative precipitation of metal ions from aqueous solution. In order to circumvent possible contamination from non-volatile metal ions such as K⁺ and Na⁺ through the form of KOH and NaOH, a base such as ammonia and/or organic amine are commonly employed. In this study a mixture of triethyl amine and oxalic acid was used. Triethyl amine, being a liquid with reasonably high solubility in water, can be easily handled and because of lower volatility its concentration can be kept virtually constant during chemical processing. Furthermore, a high basicity and less complexing ability toward the Cu(II) ion, as compared with ammonia, renders it easier to control the solution at higher pH. A lower dielectric constant as compared with ammonia and water is also helpful for quantitative precipitation of the metal ions.

As the nitrate solution was added to Et₃N/H₂C₂O₄ solutions with ratios varying from 0 to 3, the pH values increased gradually up to a ratio of 2 and increased abruptly beyond 2, as shown in fig. 1. The color of the filtrate was observed to change from colorless to pale blue and finally to deep blue in accordance with the pH increase, indicating the dissolution of the Cu(II) from the precipitate into the solution at higher pH. The elemental analyses of the filtrates using atomic emission spectroscopy, as shown in fig. 2, indicates that all the metal ions can be stoichiometrically precipitated for Et₃N/H₂C₂O₄ ratios around 2.2. At lower ratios, losses of Ca²⁺ and Sr²⁺ are apparent and at higher ratios considerable loss of Bi³⁺ and Cu²⁺ was observed. A dry pale blue precipitate with a particle size of 0.3 μm was obtained under optimum conditions.

The DTA/TGA thermograms (fig. 3) show a gradual weight loss from 100 to 220°C. A sharp weight loss accompanied by two exothermic peaks between 220 and 350°C was observed, which is indicative of the loss of organic moieties. Subsequent heating up to 800°C results in weight loss due to the
decomposition of SrCO₃ and CaCO₃ into SrO and CaO. Above 800°C, a Bi–Sr–Ca–Cu–O compound will be formed.

Table 1 summarizes the zero-resistance temperatures \( T_0 \) of the superconducting powders prepared under various conditions. For the bulk of A10, A13 and A14, obtained from \( r=2.2 \) precursor powders of different batches and sintered at 870°C, the \( T_0 \) values were about 80 K. The temperature dependence of the resistance for A10, shown in fig. 4, exhibits a

<table>
<thead>
<tr>
<th>No.</th>
<th>Ratio (( v )) ( (\text{Et}_3\text{N}/\text{H}_2\text{C}_2\text{O}_4) )</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>( T_0 ) (K)</th>
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</thead>
<tbody>
<tr>
<td>A1</td>
<td>0</td>
<td>850</td>
<td>12</td>
<td>SC*</td>
</tr>
<tr>
<td>A2</td>
<td>0.3</td>
<td>850</td>
<td>12</td>
<td>&lt;40</td>
</tr>
<tr>
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<td>0.8</td>
<td>850</td>
<td>12</td>
<td>\sim40</td>
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<tr>
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<td>850</td>
<td>12</td>
<td>64</td>
</tr>
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<td>63</td>
</tr>
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<td>50</td>
</tr>
<tr>
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<td>850</td>
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</tr>
<tr>
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<td>850</td>
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</table>

* SC stands for semiconductor.
sharp transition around 85 K and $T_0$ of 82 K. The narrow optimum range is also consistent with the prediction of the analytical data (fig. 2).

Fig. 5 displays the temperature dependence of the field-cooled (FC) Meissner effect and zero-field-cooled (ZFC) shielding effect SQUID magnetization data for sample A10 measured in a field of 100 Oe between 5 and 130 K. As shown in fig. 5, the superconducting transition at the temperature of 80 K was observed and it is consistent with the results of resistance measurements.

Fig. 6 shows the XRD pattern of A10. The major peak belong to $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ ($T_c = 80$ K) as obtained by others. However, there are three peaks due to unknown minor phases (denoted by solid triangles).

4. Conclusion

A new coprecipitation process using oxalic acid and triethyl amine can provide uniform and small particle size of a Bi–Sr–Ca–Cu–O precursor powder. After calcining and sintering, the 80 K superconductor is obtained as shown by resistance, XRD and susceptibility measurements. This process has the potential for large-scale preparation.

Acknowledgement

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References