Synthesis and property evaluation of Y–Ba–Cu–O superconductors

A SRINIVASA RAO, O P ARORA and A PUROHIT*

David Taylor Research Center, Annapolis, Maryland 21402, USA

*Argonne National Laboratory, Argonne, Illinois 60439, USA

Abstract. Fine powders of yttrium, barium and copper oxide were synthesized by two different chemical precipitation methods using a spray atomizer. The average particle size in the sintered ceramic was in the range 1–2.5 microns and the superconducting transition temperature of different powders was in the range 60–90 K. With few exceptions, it was found that recalcination and annealing in oxygen will not improve the superconducting transition temperature.

Keywords. Synthesis; spray atomization; morphology; superconductivity.

1. Introduction

After the initial reports of Bednorz and Muller (1986), followed by other researchers (Wu *et al* 1987; Rao *et al* 1987), that certain ceramic oxides exhibit superconductivity, a surge of interest was shown to engineer these materials. Since the ceramic materials are very brittle, conventional mechanical forming techniques may be inadequate. In an attempt to engineer these materials into thin wires and tapes using the theory of superplastic deformation technology, this project was undertaken. In this paper, a new method for producing fine $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ powders, the as-synthesized powder characteristics, the morphology and the superconducting properties of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ in sintered ceramics are presented as a function of process methodology.

2. Experimental procedure

Yttrium, barium and copper oxide powders were prepared primarily using the chemical coprecipitation method. In this process, the nitrates of yttrium, barium and copper were dissolved in distilled water. Unlike the conventional coprecipitation method, the nitrate solution was sprayed into a pool of either ammonium oxalate or carbonate solution using a spray atomization unit whose details are given elsewhere (Srinivasa Rao *et al*, to be published). After coprecipitation, yttrium, barium and copper oxalate or carbonate were separated and dried at 80°C for 24 hr. The dry powder was then calcined at 920°C for 6 hr in air and annealed at 600°C for 6 hr in oxygen. During coprecipitation it was noticed that the precipitated copper oxalate or carbonate tend to redissolve in water. In order to overcome dissolution of copper salt, a new approach similar to the process one used for processing of zirconia/alumina composites was used (Srinivasa Rao and Cannon 1989). In this process, copper oxide was used instead of copper nitrate. Copper oxide/yttrium and barium nitrate suspensions were prepared and the suspensions sprayed into the pool of ammonium oxalate or carbonate solution. For convenience this process was referred to as copper oxide coating method. After complete precipitation of yttrium and barium oxalate or carbonate with copper oxide, the mixture was dried in an oven. Calcination and annealing were similar to that described above.

In order to compare powder characteristics of the chemical coprecipitation-derived powders with powders produced by conventional solid-state method, $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ powder was also synthesized using Y_2O_3 , BaCO_3 and CuO via solid-state reaction method. In this process, Y_2O_3 , BaCO_3 and CuO were ball-milled for 1 hr in distilled water. After drying, the powder was calcined at 940°C for 6 hr and annealed at 600°C for 6 hr in oxygen. It was pointed out that a higher calcination temperature was required for solid state reaction because it was noticed that when the calcination temperature was below 930°C , the reaction was incomplete. However, if the fine powders produced from the chemical precipitation method were calcined above 930°C , significant melting was noticed. For comparison of the powder properties, no additional corrections were made for the difference in the calcination temperature.

All calcined $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ samples except powders obtained via the solid-state reaction method crumbled into a fine powder upon gentle grinding. From the ground powder, 1 cm dia discs were dry-pressed and all the discs sintered at 920°C for 6 hr in air and annealed at 600°C for 6 hr in oxygen. The sintered discs were used for the electrical resistivity measurements, X-ray diffraction study and scanning electron microscopy analysis.

3. Results and discussion

The powder characteristics of yttrium, barium and copper oxalate or carbonate precursors and the pure $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ powders, as a function of process methodology is given in table 1. The results suggest that the grain size of yttrium, barium and copper oxide particles produced from the conventional solid-state reaction method is much larger (an order of magnitude larger) than the powders obtained from the chemical methods using spray atomization. The results also suggest that the solid-state reaction method produces much denser powder than the chemical process.

Figure 1 shows typical morphology of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ particles after sintering. The results suggest that the morphology of the superconducting ceramics can be classified into two categories viz. (i) long-elongated platelets (solid state reaction, copper oxide coated powder and coprecipitation via oxalate precursor methods) and (ii) square-shaped discs (coprecipitation via carbonate precursor). It has to be emphasized that the above conclusions were derived from the analysis of morphology of a number of samples produced from powders synthesized in different batches and not from micrographs shown above or obtained from a single sample.

Table 1(a). Yttrium, barium and copper oxide precursor powder characteristics.

Precursor powder characteristics	Coprecipitation method		Copper oxide coating method	
	Oxalate	Carbonate	Oxalate	Carbonate
Powder density (g/cc)	4.9	4.6	4.6	4.6
Surface area (m^2/g)	85	80	26	22
Mean crystallite size estimated from surface area of the powder (nm)	10	12	60	66

Table 1(b). Yttrium, barium and copper oxide powder characteristics. Powder calcination and annealing temperatures were 920 and 550°C respectively. Solid state reaction temperature and recalcination temperature was 940°C

Powder characteristics	Solid state reaction method	Coprecipitation method		Copper-oxide coating method	
		Oxalate	Carbonate	Oxalate	Carbonate
Powder density (g/cc)	6.2	6.0	5.6	5.8	5.7
Surface area (m ² /g)	0.2	1.6	1.8	1.2	1.3
Particle mean diameter (microns)	~ 10	~ 1.0	~ 1.6	~ 2.0	~ 2.6
Bulk density of the sintered material (% theoretical)	92	90	83	92	88

Figure 1. Scanning electron micrograph of the sintered $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ sample morphology. Powder preparation (A) solid state reaction, (B, C) chemical coprecipitation and (D) copper oxide coating with oxalate crystallites of yttrium and barium methods.

The structure of all $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ceramic samples was determined using a wide angle X-ray diffraction method. From a number of diffraction patterns, the superconducting orthorhombic and nonsuperconducting tetragonal phase ratio was estimated as a function of process methodology (figure 2). The results shown in figure 2 suggest that the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ powders synthesized from solid state and copper oxide coating methods retained the maximum orthorhombic crystal phase even after sintering at 920°C , while the powders produced via the coprecipitation method retained the minimum. The results also suggest that except for the carbonate precursor

Figure 2. Orthorhombic crystal phase vs the superconducting transition temperature (T_c) for samples that were calcined and annealed ($\circ$ $\bullet$ $\square$ $\triangle$ ∇) once and ($\bullet$ $\bullet$ $\blacksquare$ $\blacktriangle$ $\blacktriangledown$) two times. Powder preparation ($\square$ $\blacksquare$) solid state reaction, ($\triangle$ $\blacktriangle$ $\blacktriangledown$) chemical coprecipitation as ($\triangle$ $\blacktriangle$) oxalate and (∇ $\blacktriangledown$) carbonate of Y-Ba-Cu, and ($\circ$ $\bullet$ $\bullet$ $\bullet$) copper oxide coating as ($\circ$ $\bullet$) oxalate and ($\bullet$ $\bullet$) carbonate of Y-Ba method.

Table 2. Normal state electrical resistivity measured at 100 K of Y-Ba-Cu-O superconductor processed by solid state reaction, chemical coprecipitation and copper oxide coating methods.

Processing methodology	No. of calcination and annealing cycles	Superconducting transition temperature (K)	Normal state electrical resistivity (milli ohm-cm)
Solid-state reaction method	1	91	20
	2	93	12
Coprecipitation method (via oxalate route)	1	78	5
	2	80	4.5
Coprecipitation method (via carbonate route)	1	61	125
	2	69	25
Copper oxide coating method (via oxalate route)	1	89	3
	2	93	0.7
Copper oxide coating method (via carbonate route)	1	86	5
	2	90	1.5

derived powder, recalcination and annealing in oxygen has very little effect on increasing the orthorhombic crystal phase of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$.

The superconducting transition temperature and the normal state resistivity of these samples measured at 100 K are shown in table 2. Yttrium, barium and copper oxide produced from solid-state reaction and copper oxide coating methods show nearly the same superconducting transition temperature (T_c) of ~ 90 K, but their normal state resistivity varied considerably. The samples obtained via coprecipitation as oxalate or carbonate showed superconducting behaviour below $T_c \sim 80$ and 60 K respectively. However, T_c of carbonate-derived powder increased to ~ 70 K upon recalcination and annealing in oxygen.

In order to correlate the results obtained from electrical measurements and X-ray diffraction analysis, the orthorhombic and tetragonal phase ratio was plotted as a function of T_c (figure 2). From the results, it appears that T_c increases linearly with the degree of orthorhombic crystal phase. However, the increase tends to remain independent of the history of the powder synthesis method (i.e. the process methodology or the precursor history etc.).

It has been established that for maximum superplastic deformation it is important that the grain size is as small as possible; typically 100–500 nm. Although, our present process did not produce such fine-sintered particle sizes, it has demonstrated that a careful process control of fine crystallites produced from the spray atomization during sintering can produce fine-grained material.

4. Conclusion

From the present investigation the following conclusions can be derived:

- (i) Fine superconducting yttrium, barium and copper oxide powders can be produced either from chemical coprecipitation or copper oxide coating method using spray atomization process.
- (ii) While the copper oxide coating process produced the superconducting ceramic with T_c comparable to the powders produced from conventional solid state reaction ($T_c \sim 90$ K), T_c of the powders produced from coprecipitation process is in the range 60–80 K.
- (iii) The normal state resistivity of the powder produced from copper oxide coating method is the lowest amongst all the powders investigated.

References

- Bednorz J C and Muller K A 1986 *Z. Phys.* **B64** 189
- Rao C N R, Ganguly P, Gopalakrishnan J and Sharma D D 1987 *Mater. Res. Bull.* **22** 1159
- Srinivasa Rao A and Cannon W R 1989 *Ceram. Int.* **15** 179
- Srinivasa Rao A, Arora O P and Purohit A *Ceram. Int.* (to be published)
- Wu M K, Ashburn J R, Tong C T, Hor P T, Meng R L, Cao L, Huan Z J, Wang Y Q and Chu C W 1987 *Phys. Rev. Lett.* **58** 908