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$Bi_4Sr_3Ca_3Cu_4O_{16}$ glass and superconducting glass ceramics

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A $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass has been successfully fabricated by the melting process. Glass transition temperature, crystallization temperature, and liquid temperature of the glass are 434, 478, and 833 °C, respectively. After the glass is heat treated at 800 °C, a glass ceramic is formed. A comparison of the x-ray-diffraction pattern of the superconducting $Bi_4Sr_3Ca_3Cu_4O_{16+x}$ ceramic to the $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass ceramic revealed preferred orientation in the glass-ceramic crystals. The superconducting transition temperatures $T_{c(\text{onset})}$ and $T_{c(\text{zero})}$ of the glass ceramics are 100 and 45 K, respectively.

I. INTRODUCTION

The discovery of the high-temperature superconducting La-Ba-Cu-O system[1] has led to the subsequent discovery of a series of other superconducting systems: Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O, and Tl-Ba-Ca-Cu-O.[2-4] The Bi-Sr-Ca-Cu-O system generally consists of a few superconducting phases with different T_c and the formation of these phases is process dependent.[5] One phase for superconductivity in the Bi-Sr-Ca-Cu-O system is considered to be $Bi_4Sr_3Ca_3Cu_4O_{16-x}$ with $T_c = 85$ K.

The practical applications of high-T_c superconducting materials require (a) the ability to be fabricated into specific shapes such as fibers, wires, tapes, or films, and (b) the ability to carry high current. Many ceramic processes have been applied to fabricate $YBa_2Cu_3O_{7-x}$ materials.[6,7] Here we report a new way of fabricating Bi-Sr-Ca-Cu-O materials: the glass-ceramics process.

II. EXPERIMENTAL RESULTS AND DISCUSSION

A. $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass

Bismuth oxide, strontium carbonate, calcium carbonate, and copper oxide were mixed with the ratio Bi:Sr:Ca:Cu=4:3:3:4. A 5-g batch was melted at 950 °C for 2 h in air in alumina crucibles, and then the melt was quenched by pressing the cast liquid between two brass plates. The 1-mm-thick glass formed was dark red. The glass was electrically insulating and its density was 5.73 g/cm^3.

Figure 1(a) is the x-ray-diffraction pattern (obtained using Cu $K\alpha$ radiation) of the resulting material. It shows that the material was glassy. The differential thermal analysis (DTA) curve (Fig. 2) of the material showed that the glass transition temperature was about 434 °C, and the crystallization temperature was 478 °C. The liquid temperature of the glass is about 833 °C. Table I lists the

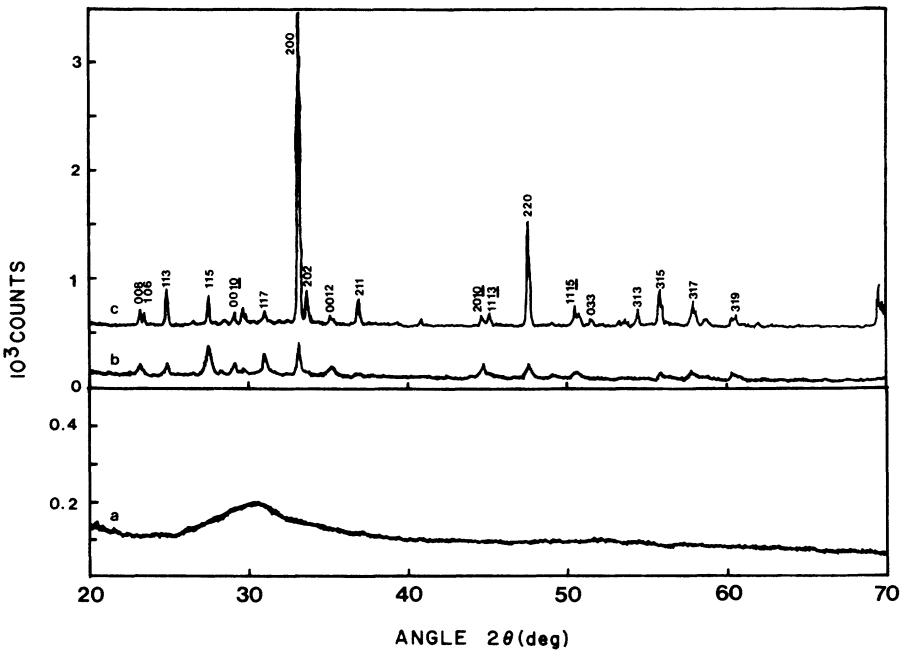

FIG. 1. X-ray-diffraction patterns of (a) $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass, (b) glass-ceramics powder, and (c) glass-ceramic bulk. The assignment of the Miller indices noted above each peak in (c) is based on Ref. 10.

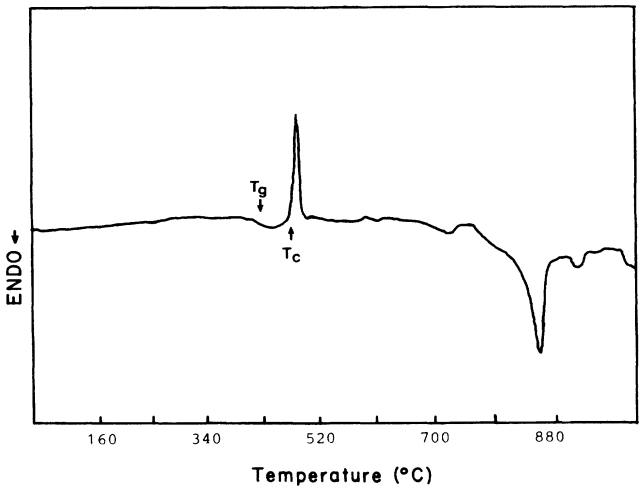

FIG. 2. Differential thermal analysis of $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass (heating rate: 10 °C/min).

properties of this glass.

Although Bi_2O_3 by itself does not form glass easily, it is known that when melted with mixture of other oxides, glass is formed.[8] Most known glasses containing a significantly high concentration of Bi_2O_3 have relatively low T_G of less than 350 °C.[9] The present glass has a T_G of 434 °C which is somewhat surprising.

B. $Bi_4Sr_3Ca_3Cu_4O_{16+x}$ glass ceramics

When the $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass was annealed at 800 °C in air, it crystallized [Figs. 1(b) and 1(c)]. X-ray diffraction of the bulk [Fig. 1(c)] and powder [Fig. 1(b)] (ground from the bulk) showed that the crystalline phase is superconducting $Bi_4Sr_3Ca_3Cu_4O_{16+x}$. As shown, the x-ray-diffraction peaks of the bulk solid at 2θ: 25°, 33°, 37°, 47°, 54°, 56°, 58°, and 70° were enhanced, especially for the 33° and 37° peaks since the $Bi_4Sr_3Ca_3Cu_4O_{16+x}$ crystals were strongly anisotopic ($a = 3.817$ Å, $c = 30.6$ Å).[5] All these enhanced peaks came from the atom planes nearly parallel and parallel to c axis.[10] Therefore, this enhancement of the diffraction peaks indicated c-axis preferred orientation of the $Bi_4Sr_3Ca_3Cu_4O_{16+x}$ crystals in the bulk sample. Figure 3 shows the scanning electronic micrograph (SEM) of the $Bi_4Sr_3Ca_3Cu_4O_{16+x}$ bulk glass ceramic. The crystals were platelike and had preferred orientation while the crystal size was uniform. SEM also showed that the glass ceramic was almost dense. This agrees with the density results. According to the calculation,[11] the density of the $Bi_2Sr_{2.5}Ca_{0.5}Cu_2O_{8+y}$ single crystal was 6.70 g/cm^3. So the calculated density of the $Bi_4Sr_3Ca_3Cu_4O_{16}$ crystal should be 6.35 g/cm^3 assuming the simple substitution of Ca for Sr. The observed density of the $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass ceramic was 6.25 g/cm^3. This indicated that the glass ceramic was about 98.5% (=6.25/6.35) dense.

TABLE I. $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass. Glass transition temperature, 434 °C. Crystallization temperature, 478 °C. Density, 5.73 g/cm^3. Infrared cutoff, 5.5 μm.

	mol%	wt.%
Bi_2O_3	16.7	54.0
SrO	25.0	18.0
CaO	25.0	9.7
CuO	33.3	18.3

FIG. 3. Scanning electronic micrograph of superconducting $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass ceramic (length of the bar: 2 μm).

The $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass ceramics are signficantly denser than the glass. The difference in density would imply large shrinkage during the crystallization of the $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass. The electrical resistivity of the glass and glass ceramic are about 10^7 Ω cm and 1 Ω cm, respectively.

C. Superconducting properties

Electrical resistivity was measured by the standard four-probe method for the bar shape of 0.5×1×6 mm^3,

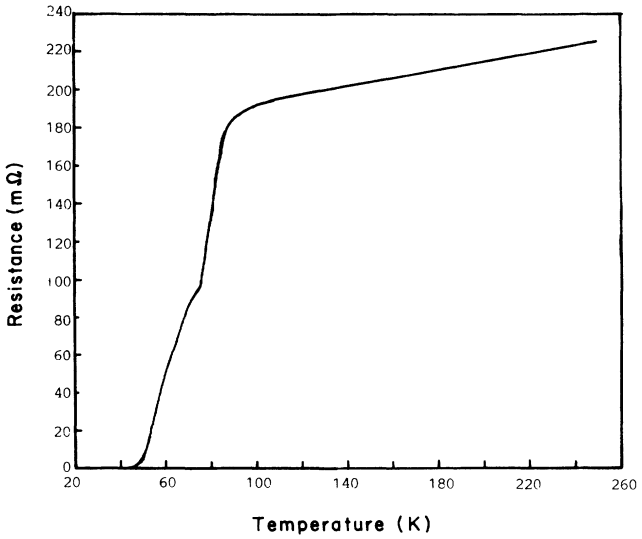

FIG. 4. Temperature dependence of resistance for $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass ceramic.

with silver paste electrical contacts. Figure 4 showed the resistivity of the $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass ceramic as a function of temperature. At room temperature, the resistance of the specimen was about 0.23 Ω. The resistivity decreases linearly from room temperature down to 105 K. Then it derived from linearity to the superconducting onset 100 K. The first sharp resistivity drop ended at 75 K. Then the second drop began, and reached zero resistance at 45 K.

The $T_{c(zero)}$ of the Bi-Sr-Ca-Cu-O system is dependent on the process conditions.[3,5] The annealing temperature is an important factor. The closer to the melting point of the annealing temperature, the higher the $T_{c(zero)}$ of the materials.[3,5] It also has been observed that the materials exhibiting a sharp resistance drop near 110 K possess $T_{c(zero)}$ lower than 80 K.[5] The lower $T_{c(zero)}$ of the $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass ceramic may be due to nonideal processing. Further investigation is being carried out to optimize the glass ceramics process to obtain higher $T_{c(zero)}$.

D. Summary and conclusions

It is well known that two main reasons for low-critical current density J_c of high-T_c superconducting ceramics are random distribution of the crystals and the relatively high porosity of these ceramics. The preferred orientation and almost pore-free structure of the present superconducting $Bi_4Sr_3Ca_3Cu_4O_{16+x}$ materials implies that the glass-ceramics process is a most promising technique for the fabrication of the high-T_c superconducting Bi-Sr-Ca-Cu-O materials. The glass route is also of practical importance in the fabrication of specific shapes (fibers, wires, and tapes).[12]

In conclusion, a $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass has been successfully fabricated. Glass transition, crystallization, and liquid temperatures of the glass are 434, 478, and 833 °C, respectively. After annealing at 800 °C, the glass crystallizes, and the resulting glass ceramic is superconducting with $T_{c(onset)} = 100$ K, and $T_{c(zero)} = 45$ K. Further efforts on optimizing the process, and the formation of glass fibers, are needed.

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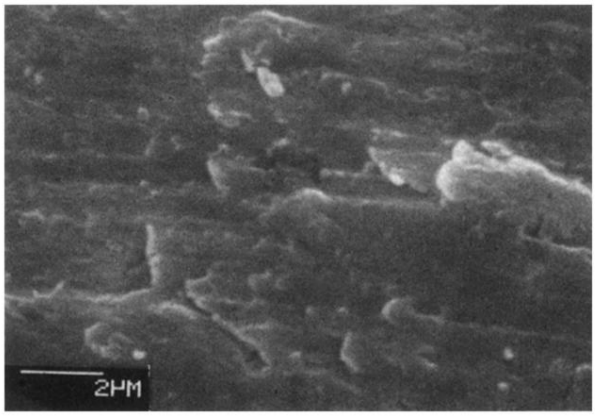
[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).
[2] M. K. Wu *et al.*, Phys. Rev. Lett. **58**, 908 (1987).
[3] H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. Lett. **27**, L129 (1988).
[4] Z. Z. Sheng and A. M. Hermann, Nature **332**, 138 (1988).
[5] J. M. Tarascon *et al.*, Phys. Rev. B **37**, 9382 (1988).
[6] Haixing Zheng, K. C. Chen, and J. D. Mackenzie, in *Extended Abstracts: High-Temperature Superconductors II,* edited by D. W. Capone II, W. H. Butler, B. Batlogg, and C. W.Chu (Materials Research Society, Pittsburgh, 1988), Vol. EA-14, p. 93.
[7] R. Pool, Science **240**, 25 (1988).
[8] H. Rawson, *Inorganic Glass-Forming Systems* (Academic, London, 1967).
[9] W. H. Dumbaugh, Phys. Chem. Glasses **19**, 121 (1978); **27**, 119 (1986).
[10] R. M. Hazen *et al.*, Phys. Rev. Lett. **60**, 1174 (1988).
[11] M. A. Subramanlan, *et al.*, Science **239**, 1015 (1988).
[12] P. W. McMillan, *Glass Ceramics*, 2nd ed. (Academic, London 1979).



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