Superconducting Ceramics in the Bi_{1.5}SrCaCu_{2}O_{x} System by Melt Quenching Technique

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SUPERCONDUCTING CERAMICS IN THE $\text{Bi}_{1.5}\text{SrCaCu}_2\text{O}_x$ SYSTEM BY MELT QUENCHING TECHNIQUE

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SUMMARY

$\text{Bi}_{1.5}\text{SrCaCu}_2\text{O}_x$ has been prepared in the glassy state by rapid quenching of the melt. The kinetics of crystallization of various phases in the glass have been evaluated by a variable heating rate differential scanning calorimetry method. The formation of various phases on thermal treatments of the glass has been investigated by powder x-ray diffraction and electrical resistivity measurements. Heating at 450°C formed $\text{Bi}_2\text{Sr}_2\text{CuO}_6$, which disappeared on further heating at 765°C, where $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ formed. Prolonged heating at 845°C resulted in the formation of a small amount of a phase with $T_c$ onset of ~108K, believed to be $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$. This specimen showed zero resistivity at 54K. The glass ceramic approach could offer several advantages in the fabrication of the high-$T_c$ superconductors in desired practical shapes such as continuous fibers, wires, tapes, etc.

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INTRODUCTION

The formation of superconducting ceramics via the melt quenching and glass-ceramic route would allow well established glass manufacturing techniques to be used for commercial oxide superconductor fabrication. Precipitation of Y-Ba-Cu-O superconductors from oxide glasses containing B2O3 and other glass formers has been tried without much success1. Since Bi2O3 is known2 to be a reasonably good glass former, the discovery of superconductivity in the Bi-Sr-Ca-Cu-O system by Maeda et al.3 makes it a promising choice for fabrication of superconducting materials by the glass ceramic route. Several groups4-7 have characterized and studied the formation of superconducting phases in glasses of this system. The present work focuses on the kinetics of crystallization of both superconducting and non-superconducting compounds in the Bi-Sr-Ca-Cu-O glass, and the thermal treatments needed to increase the fraction of the high-Tc superconducting phase.

EXPERIMENTAL METHODS

Reagent grade Bi2O3, CaCO3, SrCO3, and CuO were mixed in stoichiometric amounts to yield ~15g of Bi1.5SrCaCu2Ox. The mixture was heated in a covered Pt crucible to 830°C for 1h to decompose the carbonates and then melted and kept at 1300°C for 2h for homogeneization of the melt. The melt was rapidly quenched by pouring onto a steel plate and covering with another similar steel
plate. This resulted into opaque sheets of glass <1mm thick. Regions of black and bronze colored crystals were evident on the top and bottom surfaces of the glass sheets. The crystallite regions did not extend appreciably into the bulk. Powder x-ray diffraction (XRD) pattern of these sheets was characteristic of glass. XRD patterns were recorded at room temperature with Cu Kα radiation in the 2θ range 10 - 80° using a Philips ADP 3600 automated diffractometer equipped with a crystal monochromator. Chemical analysis of the glass was carried out using atomic absorption technique. The batch and analyzed weight % of various elements in the as-quenched glass were Bi(46.9, 47.3), Sr(13.1, 13.7), Ca(6.0, 6.2), and Cu(19.0, 18.3) indicating no material loss during the glass melting.

Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer TGS-2 system. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were performed to determine the glass transition and crystallization temperatures, using the Perkin-Elmer DTA 1500 and DSC-4 interfaced with computerized data acquisition and analysis systems. Using a kinetic model of Bansal et al.\(^8\), the kinetics of crystallization of various phases formed during thermal treatment were determined via a variable heating rate DSC method employing scan rates of 2 - 40°C/min. Several heat treatments were conducted based on the thermal events observed in the DTA and DSC, and the crystalline phases present after each treatment were identified by powder XRD.
The superconducting transition temperature ($T_c$) of some of these devitrified specimens was determined using four-point electrical resistivity measurements. Microstructures of the crystallized samples were observed in a scanning electron microscope (SEM).

**RESULTS AND DISCUSSION**

**Thermal Analyses**

The DTA thermogram of the fast quenched $\text{Bi}_1.5\text{SrCaCu}_2\text{O}_x$ glass recorded at a heating rate of 10°C/min in air is shown in Fig. 1. A number of peaks are present. The glass transition is observed at 390°C, a sharp crystallization exotherm at ~453°C followed by a broad peak between 540 and 585°C. A strong melting endotherm is present between 840 - 890°C followed by weak peaks at 899 and 94°C which may be assigned to the melting of minor crystalline phases.

The DSC trace of a $\text{BiSrCaCu}_2\text{O}_x$ glass is very similar to the low-temperature region of Fig. 1. On a glass of the same nominal composition as reported here, Komatsu et al. observed crystallization peaks of similar magnitude, but at 40 - 50°C higher temperature. There are several possible reasons for this discrepancy: (1) Their glasses may have contained some alumina from the crucibles in which they were melted, which could reduce the tendency to devitrification; (2) The present glass samples
showed some surface crystallization after quenching as well as after brief heating suggesting that surface nucleation may have lowered the crystallization temperatures in the present work.

Komatsu et al.⁴ also observed a broad endotherm at 768°C that is absent in Fig. 1. These workers concluded that the 768°C transformation was crucial to the formation of a high-temperature superconducting phase. Although this transition was not observed in the present work, Bi₂Sr₂CaCu₂O₈ phase was present in samples heated in this range, as discussed below.

The DSC trace of the glass recorded at a scan rate of 10°C/min in air is presented in Fig. 2. The exotherms which appeared as single peaks in the DTA (Fig. 1) have split up into double peaks in the DSC. This probably indicates simultaneous crystallization of multiple phases on heat treatment of the glass. A variable heating rate DSC method was used to evaluate the kinetics of crystallization of various phases in the glass. DSC scans were recorded at heating rates of 2, 5, 10, 20, 30, and 40°C/min. The positions of various peaks at various scan rates are listed in Table I. The peak positions are seen to shift to higher temperatures with increase in heating rate. The kinetic parameters were evaluated using a kinetic model of Bansal et al.⁸ which is expressed as:

\[
\ln\left(\frac{T_p^2}{\alpha}\right) = \ln\left(\frac{E}{R}\right) - \ln\nu + \frac{E}{RT_p} \quad (1)
\]
where $T_p$ is the peak maximum temperature, $\alpha$ is the heating rate, $E$ the activation energy, $R$ the gas constant, and $\nu$ the frequency factor. Eq. (1) is an extension of the Johnson-Mehl-Avrami isothermal kinetic model for use in non-isothermal methods. In the derivation of eq.(1) it has been assumed that the rate of reaction is maximum at the peak, which is valid for a power-compensated DSC. It has been demonstrated in earlier studies$^9,10$ that the kinetic parameters determined from non-isothermal DSC using eq.(1) are in excellent agreement with those derived from the isothermal method. Plots of $\ln[T_p^2/\alpha]$ vs. $1/T_p$ for the four DSC peaks are shown in Fig. 3. The lines are from linear least-squares fitting. All the plots are linear indicating applicability of the kinetic model of Bansal et al.$^8$. Values of the kinetic parameters for the processes corresponding to the four DSC peaks were evaluated from linear least-squares fitting of the data of Table I and the results are listed in Table II. The values of activation energy for three of the processes are about the same. The reason for this is not clear at this point.

TGA of a glass sample heated at 5°C/min to 850°C followed by cooling at the same rate is shown in Fig. 4. The entire cycle of heating and cooling was carried out in flowing oxygen. The sample weight remains unaltered up to ~500°C followed by a slow and continuous weight gain to ~800°C. The maximum gain in sample weight is ~1.7%. This probably results from oxidation of Cu and/or Bi. On cooling, almost no change in sample weight is observed.
indicating an irreversible oxidation step during heating. A high Cu oxidation state is a common feature of the high-T$_c$ compounds. The evidence of oxidation in Fig. 4 indicates that an oxidation step may be necessary for forming high-T$_c$ phases from melt-processed Bi-Sr-Ca-Cu-O materials.

**XRD Analysis of Crystallization Events**

The quenched glass samples were subjected to various thermal treatments as shown in Table III. The heat treatment temperatures were chosen from the positions of various peaks in the DTA thermogram. The various phases formed in these heat treated specimens were identified from powder XRD. Typical powder XRD patterns are shown in Fig. 5 and 6 and the results are summarized in Table III. Bi$_2$Sr$_2$CuO$_6^{11}$ was the predominant crystalline phase observed in samples A, D, and B with intensities increasing from A to B to D. In addition, three samples contained diffraction peaks at 0.290, 0.246, and 0.240 nm. These peaks approximately doubled in intensity from sample A to samples B and D, but maintained constant intensities relative to each other in all these three samples. These observations suggest that these peaks arise from a single unidentified phase, which first crystallized near 450°C. It was not possible to determine whether this phase formed before or after Bi$_2$Sr$_2$CuO$_6$, but the appearance of two closely spaced exothermic events near 450°C in the DSC is consistent with the formation of two distinct phases. The exothermic peaks near 560°C
appear to be related to the disappearance of a phase with an XRD reflection at 0.175 nm and/or the appearance of a phase with reflections at 0.219 and 0.177 nm.

Heating at 765°C (samples C and E, Table III) resulted in the diminishment of Bi$_2$Sr$_2$CuO$_6$ and the appearance of Bi$_2$Sr$_2$CaCu$_2$O$_8$ and CuO as major phases. The Bi$_2$Sr$_2$CaCu$_2$O$_8$ lattice was a few percent larger compared to the XRD data of Torrance et al. In addition, a moderately strong peak at 0.388 nm was observed in these samples, as well as a very weak 0.244 nm peak which is characteristic of an unidentified phase.

Heating for a few days at 845°C (samples F and G, Table III) yielded Bi$_2$Sr$_2$CaCu$_2$O$_8$ as a major phase, Bi$_2$Sr$_2$CuO$_6$ as a minor phase, the 0.244 nm phase (weakly), and CuO as a trace phase. The Bi$_2$Sr$_2$CuO$_6$ peaks were noticeably stronger in the fast-cooled sample, suggesting that upon slow cooling from 845°C the Bi$_2$Sr$_2$CuO$_6$ reacts with residual glass, CuO, and/or the unidentified crystalline phases to form more Bi$_2$Sr$_2$CaCu$_2$O$_8$. This is consistent with early reports that the higher-$T_C$ phases in this system become unstable with respect to the lower-$T_C$ phases as the temperature increases toward the melting point. The weak presence of CuO in these samples contrasts with the 765°C samples, but it is not clear what role the CuO formation around 765°C may play in the crystallization of Bi$_2$Sr$_2$CaCu$_2$O$_8$, such as nucleating the superconducting phase or perhaps being consumed during its formation. Reflections at 0.369 and 0.262 nm, which have been
associated with the 110K Bi-Sr-Ca-Cu-O superconducting phase, were not observed, although a small resistance drop near 110K was observed in the slow-cooled sample (vide infra).

**SEM Microstructures**

The SEM micrograph of the fracture surface of the specimen heated at 450°C for 2h is presented in Fig. 7. The crystals appear to nucleate at the surface and grow into the bulk of the sample. Fig. 8 shows the SEM micrographs from two different regions of the same sample annealed for 2h each at 450 and 560°C and slow cooled. Crystallization is not yet complete as seen from the presence of glassy regions in the sample.

**Electrical Resistivity Measurements**

The plots of electrical resistivity as a function of temperature for the samples annealed at 765°C and above are presented in Figs. 9 and 10 and the results for all the specimens are summarized in Table IV. All four samples exhibited a sharp drop in resistance between 82 and 88K, consistent with the XRD results showing the presence of Bi$_2$Sr$_2$CaCu$_2$O$_8$, which has been previously identified as the 80K superconducting phase. In most other respects, however, the resistivity behavior of these specimens differs appreciably. The 2h heated samples (C and E, Table IV) showed broad superconducting transitions, reaching zero resistance at 47 and 38K respectively. Sample E (765°C, 2h)
displayed semiconducting behavior in the normal state, whereas sample C, which was brought to the annealing temperature in stages, showed nearly flat behavior from 90 to 300K. The XRD traces of these specimens were virtually identical, however. The high-$T_c$ oxides typically exhibit metallic normal state behavior when single phase, indicating that the above-transition resistivity of these samples is strongly influenced by the non-superconducting crystalline and glassy phases that are still major components after 2 - 6h of annealing.

Samples heated at 845°C for 88h (F and G, Table IV) consisted mostly of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, but their resistivity behavior differed strongly with their post-annealing cooling schedules. The fast-cooled sample showed strong semiconducting behavior in the normal state. After a sharp drop in resistance at 88K, its resistivity leveled off, dropped again around 50K, and did not reach zero until 11K. The slow-cooled specimen, in contrast, showed metallic normal state behavior, a small drop in resistivity at $\sim$108K, a major drop at 87K, and the highest zero-resistivity $T_c$ in this work (55K). In conjunction with the XRD findings that the slow-cooled sample contained less $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ than the fast-cooled, these results qualitatively support reports that the higher-$T_c$ phases ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$) form from and on the surface of grains of the lower-$T_c$ phases$^{14}$. It should be repeated,
however, that no Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ was detected in the XRD traces of these samples, despite the 108K resistivity drop in the slow-cooled sample.

Shi et al.\textsuperscript{6} have shown that zero resistivity can be obtained at 105K in a glass sample of nominal composition Bi$_2$Sr$_2$Ca$_3$Cu$_4$O$_x$ after heating at 870°C for a week. Bansal and Farrell\textsuperscript{15} have also observed $T_c(R = 0)$ of 107.2K in a glass ceramic of starting composition Bi$_{1.5}$Pb$_{0.5}$Sr$_2$Ca$_2$Cu$_3$O$_x$ which had been annealed at 840°C for more than 10 days. These results indicate very slow reaction kinetics for the formation of the 108K phase, probably due to the long range diffusive ordering involved.

**SUMMARY AND CONCLUSIONS**

Bi$_{1.5}$SrCaCu$_2$O$_x$ glass, prepared by rapid quenching of the melt, had a $T_g$ of 390°C, crystallization temperature of $\sim$450°C, and melting temperature of $\sim$878°C. On heating in air, a slow and irreversible gain in weight ($\sim$1.7%) is observed probably due to oxidation of the material. Kinetic parameters for the crystallization of various phases in the parent glass have been evaluated from a variable heating rate DSC method. On thermal annealing a number of phases crystallized out from the glass. All glass-ceramic samples were multiphase. Bi$_2$Sr$_2$CuO$_6$ was the main crystalline phase in samples heated at $\geq$560°C. Bi$_2$Sr$_2$CaCu$_2$O$_8$ appeared in specimens annealed at $\geq$765°C. High-$T_c$ phase, probably Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$, was formed on extended heating at 845°C.
indicating slow kinetics. Furnace cooled samples showed higher $T_C$ than those air-quenched after annealing under identical conditions. Obtaining practical superconducting materials via the glass precursor route will require tailoring the starting composition and thermal treatments to eliminate or minimize the effects of the non-superconducting phases and devising approaches with more favorable rapid crystallization kinetics.

ACKNOWLEDGMENTS

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### TABLE III. - CRYSTALLINE PHASES IDENTIFIED FROM POWDER X-RAY DIFFRACTION IN B11.5SrCaCu20x GLASS SAMPLES ANNEALED AT VARIOUS TEMPERATURES IN AIR

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature, °C</th>
<th>Heat treatment</th>
<th>Phases; d(nm) of unidentified lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>450</td>
<td>Slow</td>
<td>B12Sr2CuO6: 0.29, 0.246, 0.240, 0.214, 0.175</td>
</tr>
<tr>
<td>B</td>
<td>450</td>
<td>Slow</td>
<td>B12Sr2CuO6: 0.291, 0.279, 0.247, 0.241, 0.219, 0.213, 0.177</td>
</tr>
<tr>
<td>C</td>
<td>450</td>
<td>Slow</td>
<td>B12Sr2CaCu2O8; CuO; B12Sr2CuO6 (trace); 0.387</td>
</tr>
<tr>
<td></td>
<td>560</td>
<td>Slow</td>
<td>B12Sr2CuO6: 0.290, 0.283, 0.246, 0.241, 0.213, 0.177</td>
</tr>
<tr>
<td>D</td>
<td>560</td>
<td>Slow</td>
<td>B12Sr2CaCu2O8; CuO; B12Sr2CuO6: 0.389</td>
</tr>
<tr>
<td>E</td>
<td>765</td>
<td>Slow</td>
<td>B12Sr2CaCu2O8; B12Sr2CuO6; CuO (trace); 0.244, 0.213</td>
</tr>
<tr>
<td>F</td>
<td>845</td>
<td>Quenched</td>
<td>B12Sr2CaCu2O8; B12Sr2CuO6; CuO (trace); 0.244</td>
</tr>
<tr>
<td>G</td>
<td>845</td>
<td>Slow</td>
<td>B12Sr2CaCu2O8; B12Sr2CuO6; CuO (trace); 0.244</td>
</tr>
</tbody>
</table>

### TABLE IV. - SUPERCONDUCTING TRANSITION TEMPERATURES FROM ELECTRICAL RESISTANCE MEASUREMENTS FOR B11.5SrCaCu20x GLASS SPECIMENS SUBJECTED TO VARIOUS THERMAL TREATMENTS IN AIR

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat treatment</th>
<th>Resistive Tc Onset</th>
<th>R = 0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature, °C</td>
<td>Time, h</td>
<td>Cooling</td>
</tr>
<tr>
<td>A</td>
<td>450</td>
<td>2</td>
<td>Slow</td>
</tr>
<tr>
<td>B</td>
<td>450</td>
<td>2</td>
<td>Slow</td>
</tr>
<tr>
<td></td>
<td>560</td>
<td>2</td>
<td>Slow</td>
</tr>
<tr>
<td>C</td>
<td>450</td>
<td>2</td>
<td>Slow</td>
</tr>
<tr>
<td></td>
<td>560</td>
<td>2</td>
<td>Slow</td>
</tr>
<tr>
<td></td>
<td>765</td>
<td>2</td>
<td>Slow</td>
</tr>
<tr>
<td>D</td>
<td>560</td>
<td>2</td>
<td>Slow</td>
</tr>
<tr>
<td>E</td>
<td>765</td>
<td>2</td>
<td>Slow</td>
</tr>
<tr>
<td>F</td>
<td>845</td>
<td>88</td>
<td>Quenched</td>
</tr>
<tr>
<td>G</td>
<td>845</td>
<td>88</td>
<td>Slow</td>
</tr>
</tbody>
</table>

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Figure 1. - DTA thermogram of $\text{Bi}_2\text{SrCaCu}_2\text{O}_8$ glass in air at a heating rate of 10 °C/min.

Figure 2. - Typical DSC scan of $\text{Bi}_2\text{SrCaCu}_2\text{O}_8$ glass in inert atmosphere at a heating rate of 10 °C/min.

Figure 3. - Plots of $\ln\left(\frac{T_P^2}{\alpha}\right)$ against reciprocal of peak temperature, $1/T_P$, for the various exotherms observed in the DSC scans of $\text{Bi}_2\text{SrCaCu}_2\text{O}_8$ glass.

Figure 4. - TGA thermogram of $\text{Bi}_2\text{SrCaCu}_2\text{O}_8$ glass recorded at the heating and cooling rates of 5 °C/min under flowing oxygen.
FIGURE 5. - POWDER X-RAY DIFFRACTION SPECTRA OF Bi$_{1.5}$Sr$_2$CaCu$_2$O$_x$ GLASS SAMPLES ANNEALED AT VARIOUS TEMPERATURES AND SLOW COOLED IN AIR.

FIGURE 6. - POWDER X-RAY DIFFRACTION PATTERNS OF Bi$_{1.5}$Sr$_2$CaCu$_2$O$_x$ GLASS SPECIMENS ANNEALED AT 845 °C FOR 88 HR AND FAST QUENCHED OR SLOW COOLED IN AIR.
FIGURE 7. - SEM MICROGRAPH OF FRACTURE SURFACE OF A Bi$_{1.5}$SrCaCu$_2$O$_x$ GLASS SPECIMEN ANNEALED AT 450 °C FOR 2 HR IN AIR AND SLOW COOLED.

(a) CRYSTALLINE.

(b) GLASSY REGION.

FIGURE 8. - SEM MICROGRAPHS FROM TWO DIFFERENT REGIONS OF THE FRACTURE SURFACE OF A Bi$_{1.5}$SrCaCu$_2$O$_x$ GLASS SAMPLE HEATED FOR 2 HR EACH AT 450 AND 560 °C IN AIR.
FIGURE 9. - TEMPERATURE DEPENDENCE OF RESISTANCE OF Bi$_2$SrCaCuO$_x$ GLASS SAMPLES ANNEALED AT VARIOUS TEMPERATURES AND SLOW COOLED IN AIR.

FIGURE 10. - TEMPERATURE DEPENDENCE OF RESISTANCE, NORMALIZED TO ITS VALUE AT 296 K, OF Bi$_2$SrCaCuO$_x$ GLASS SAMPLES ANNEALED AT 845 °C FOR 88 HR AND FURNACE COOLED OR FAST QUENCHED IN AIR.
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