

Bi-Ca-Sr-Cu-O SUPERCONDUCTORS OF (2122) COMPOSITION BY MELT PROCESSING

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ABSTRACT

A Bi-Ca-Sr-Cu-O composition having the cation ratio (2122) was melted in an Al_2O_3 crucible and cast in a graphite mold. Glassy samples as large as 1 cm in thickness were obtained. Crystallization of this glass at 865 C yielded a pumice-like material containing at least two crystalline phases, one of which was the tetragonal (2122) phase. The material exhibited a sharp drop in resistances over the range 133-91 K, but zero resistance was not obtained at temperatures above 91 K. Remelting of the as-cast glass followed by crystallization at 865 C yielded a monolithic sample, free of extensive gas bubbles, which contained the phase(s) seen in crystallized (2223) and (4334) compositions but not the tetragonal (2122) phase. The resistance vs. temperature relation for this material again indicated a sharp drop in resistance beginning about 103 K; but zero resistance was not achieved at temperatures above 87 K.

INTRODUCTION

In recent months, considerable attention has been directed to superconductors in the Bi-Ca-Sr-Cu-O system. Several compositions in this system have been explored using a variety of synthesis

methods (see references in companion paper). In general, two phases are observed in samples, with a plate-like phase having the cation composition $\text{Bi}_2\text{Ca}_1\text{Sr}_2\text{Cu}_2$ being associated with the high temperature superconductivity. Attempts to fabricate samples consisting entirely of this phase have not been completely successful; and most activity has been directed to compositions such as (2223) and (4334) in which the (2122) phase is a major constituent in the microstructure.

Besides synthesizing ceramic superconductors by wet chemical methods, attention in our laboratory has been directed to melt processing of such superconductors. A companion paper in these proceedings describes results obtained by melt processing three Bi-Ca-Sr-Cu-O compositions having the cation compositions (2223), (4334), and (4223). For each, glass formation and crystallization behavior as well as resistivity vs. temperature relations are described. The present paper focusses attention on melt processing of the (2122) composition. The work was undertaken to explore whether melt processing could avoid problems encountered in other approaches to processing the (2122) material.

EXPERIMENTAL PROCEDURE

Bi-Ca-Sr-Cu-O in the cation ratio (2122) was prepared by melting at 1060 C in an impervious Al_2O_3 crucible for 15 minutes. The batch materials were Bi_2O_3 , CaCO_3 , SrCO_3 , and CuO . The melt was quite fluid and corrosive; and some dissolution of the crucible material was noted. Based on experience with other Ba-Ca-Sr-Cu-O compositions, a few percent Al_2O_3 should have been incorporated in the melt and should have promoted glass formation. The melt was cast into a graphite mold. The material near the mold surface was glassy in appearance; while that near the surface had crystallized to a considerable extent. The thickness of the glassy-appearing layer was about 1 cm. Since this layer was found to contain a number of small crystals but was substantially amorphous, it is termed "glassy".

Heat treatments of the "glassy" material were carried out at 865 C in an oxygen atmosphere for various times using a muffle furnace. Also used to heat treat the "glassy" material was an optical microscope provided with a hot stage. In a third set of experiments,

previously melted and cast samples were remelted in a Pt crucible at 900 C for fifteen minutes and the crucible subsequently transferred to 860 C where it was maintained for 10 minutes. The microstructures obtained by the various heat treatments were characterized by optical microscopy; and the crystallization products were further characterized by X-ray diffraction. Four probe d.c. electrical measurements were performed using the linear 4 point and Van de Pauw configurations. A current of 1mA was used during the measurement. Dry helium gas was flowed through the cryostat to improve heat transfer.

RESULTS

The as-cast material, having a thickness of about 1 cm., was all glassy in appearance (no evidence was found for internal crystals visible at magnifications of 100-200X), save for a thin skin on the top surface (the melt-vapor interface). This surface skin had crystalline material, was typically less than 0.1mm in thickness, and was also observed on much thinner samples (samples whose thickness was in the range of 1 mm). No such crystalline skin was found on the surfaces which had been in contact with the graphite mold. X-ray diffraction of the bulk of the cast material indicated only a broad diffraction maximum typical of an amorphous material.

When placed in a furnace provided with an oxygen atmosphere and maintained at 865 C, the samples were observed to have crystallized completely in periods of less than 1 hour. During such times, pronounced slumping of the samples was observed. In addition, marked evolution of gas took place during such crystallization treatments, presumably from the raw materials used in preparing the original melts. This evolution of gas produced a pumice-like appearance of the samples.

X-ray diffraction analysis of the crystallized samples indicated that an important crystallization product was the second phase(s) seen previously in crystallized samples of the (2223) and (4334) compositions, rather than the expected dominance of the tetragonal (2122) phase. There was, however, a significant fraction of the tetragonal (2122) phase included in the body. A representative X-ray diffraction pattern of the pumice-like crystallized material is shown in Figure 1, for a sample treated at 865 C for 6 hours.

The resistance vs. temperature relation for material crystallized at 865 C for 1 hour is shown in Figure 2. As seen there, a sharp drop

in resistance is observed over the temperature range 133-91K; but the condition of zero resistance is not achieved at temperatures above 91K.

When the as-cast material was remelted in a Pt crucible at 900 C, gas evolution was complete within 15 minutes. When the temperature was lowered to 865 C and maintained at that temperature for 10 minutes, complete crystallization of the sample was observed. In this case, however, the sample had a monolithic character, without the presence of large numbers of gas bubbles. X-ray diffraction of this body indicated the presence of only the other phase(s) seen in crystallized samples of (2223) or (4334) composition. No diffraction peaks were seen which corresponded to the (2122) phase.

The resistance vs. temperature relation for this remelted and crystallized material is presented in Figure 3. As shown there, a sharp drop in resistance with decreasing temperature, beginning at about 103 K, is observed. The state of zero resistance is, however, not observed at temperatures above 87 K.

DISCUSSION

The glass-forming ability of the (2122) composition as melted in Al_2O_3 is remarkable. The melt has a viscosity like that of water at temperatures in the range of 1050 C; yet it can readily be formed as a glass with a thickness of 1 cm. This implies a rapid increase in viscosity with falling temperature below the liquidus and a low temperature of equilibrium between the melt and the phase which crystallizes-and perhaps a high crystal-liquid surface energy for this phase as well. Once nucleated, crystal growth of this phase is rapid; and the condition for glass formation is similar to that of familiar metallic materials-i.e., glass formation is dominated by crystal nucleation.

The evolution of gas observed on reheating the glass to the temperature range of crystallization rendered difficult the detailed determination of crystallization behavior. At a temperature of 865 C, the material did not have a very high viscosity; and the sample displayed slumping as well as rapid crystallization. The crystallization product was not simply the tetragonal (2122) phase, but was a mixture of phases seen previously in the crystallization of Bi-Ca-Sr-Cu-O compositions having the compositions (2223) and (4334). This similarity may be seen by comparing the diffraction

pattern in Figure 1 for the (2122) material crystallized at 865 C with the pattern shown in Figure 4 for a (2223) material crystallized at the same temperature. In both cases, the original melts had been prepared in Al_2O_3 .

Microstructural observations of crystallized bodies of both compositions indicated the absence of a glass phase occupying any significant volume fraction. Hence it is curious, and remains unexplained, how two very different compositions could yield such similar diffraction patterns-particularly since each composition has been identified with a specific superconducting phase. The tetragonal (2122) phase is clearly identifiable in the microstructures by its plate-like appearance.

The resistance vs. temperature relation for the (2122) material shows a drop in resistance beginning at an exceptionally high temperature-in the range of 130 K. At the lowest temperature of measurement (91 K), the state of zero resistance had not been reached; but extrapolation of the data to lower temperatures suggests that the fully superconducting state would have been reached by a temperature of about 80 K or higher. This value compares well with the critical temperature suggested for the tetragonal (2122) phase, 85 K.

Reheating the as-cast glass to 900 C made it possible to eliminate the gas bubbles from the melt. Subsequent cooling of this melt to 865 C led to complete crystallization in times less than 10 minutes. The thermal history of this sample (cooled from the melt) is quite different from that of the sample cast at room temperature and reheated to the crystallization temperature. In detail, the resistance vs. temperature relations are different for the two samples (compare Figures 2 and 3). The extrapolated temperature of zero resistance is, however, quite similar in the two cases-as are the diffraction patterns for the two samples.

The role of Al_2O_3 , picked up in the melt by its reaction with the crucible, in affecting the resistance vs. temperature relations is unclear from the present data on the (2122) composition. Results on the (2223) composition prepared with different amounts of Al_2O_3 incorporation suggest the absence of a significant effect in this regard (see companion paper at this symposium). The presence of Al_2O_3 could, however, affect the critical current density-a quantity not explored in the work to date.

Taken in toto, the results of the present study, those of our companion paper, and those of other authors on the Y-Ba-Cu-O system, seem encouraging for the use of melt processing to form high temperature superconductors. The compositions-particularly those in the Bi-Ca-Sr-Cu-O system-are surprisingly good glass formers; so they can readily be prepared as glasses on cooling the melt. On subsequent reheating, they crystallize rapidly. This implies that the overall processing can be carried out with rapidity and efficiency.

ACKNOWLEDGEMENTS

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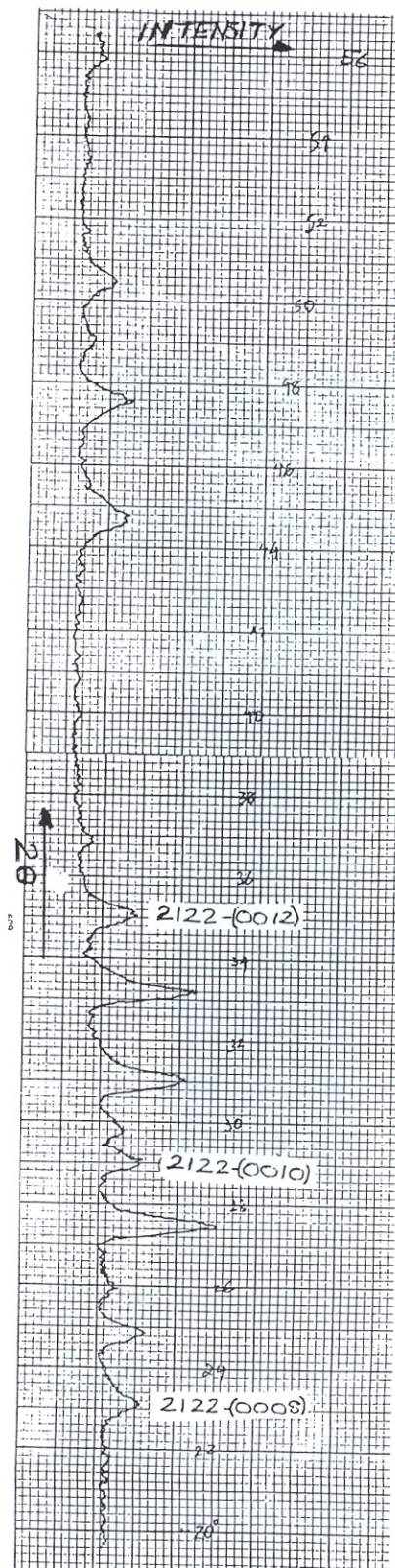


Figure 1: X-ray diffraction pattern of composition (2122) cast from the melt and crystallized at 865 C for 6 hours

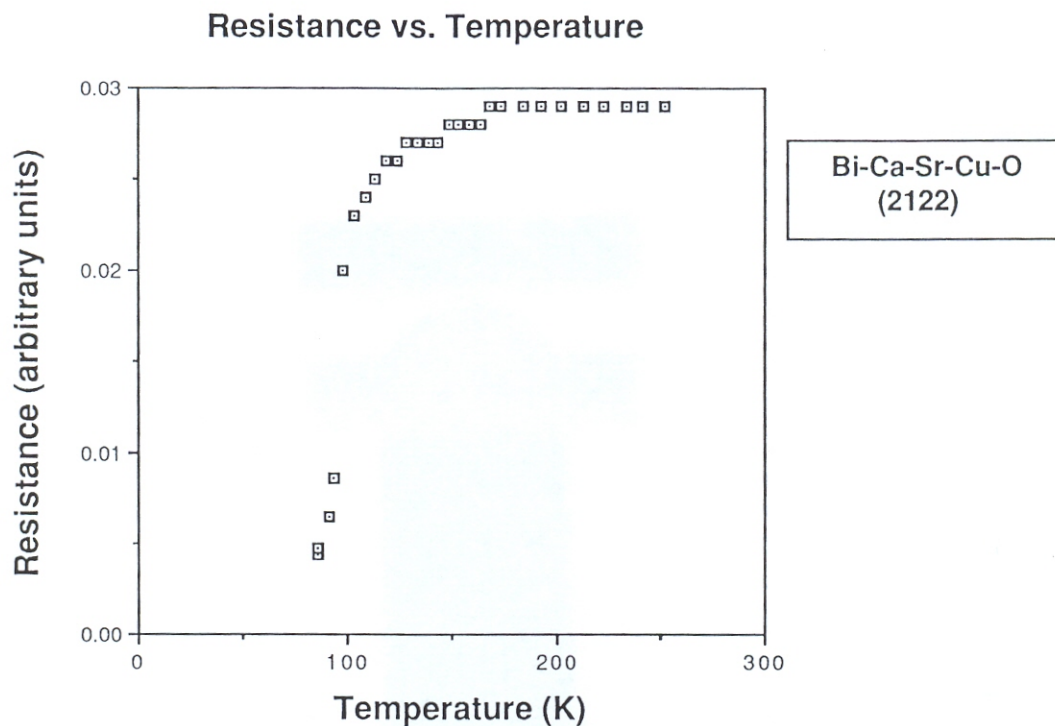


Figure 2: Resistance vs. temperature relation for composition (2122) cast from the melt and crystallized at 865 C for 1 hour

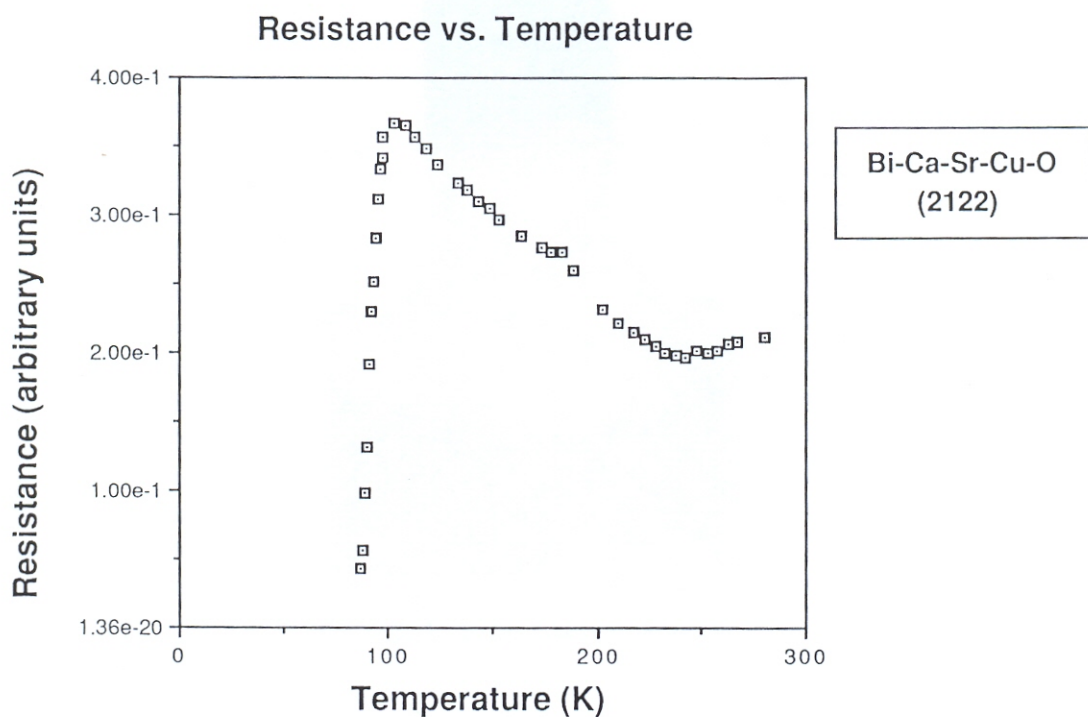


Figure 3: Resistance vs. temperature relation for composition (2122) cast from the melt, remelted at 900 C, and crystallized at 865 C for 10 minutes

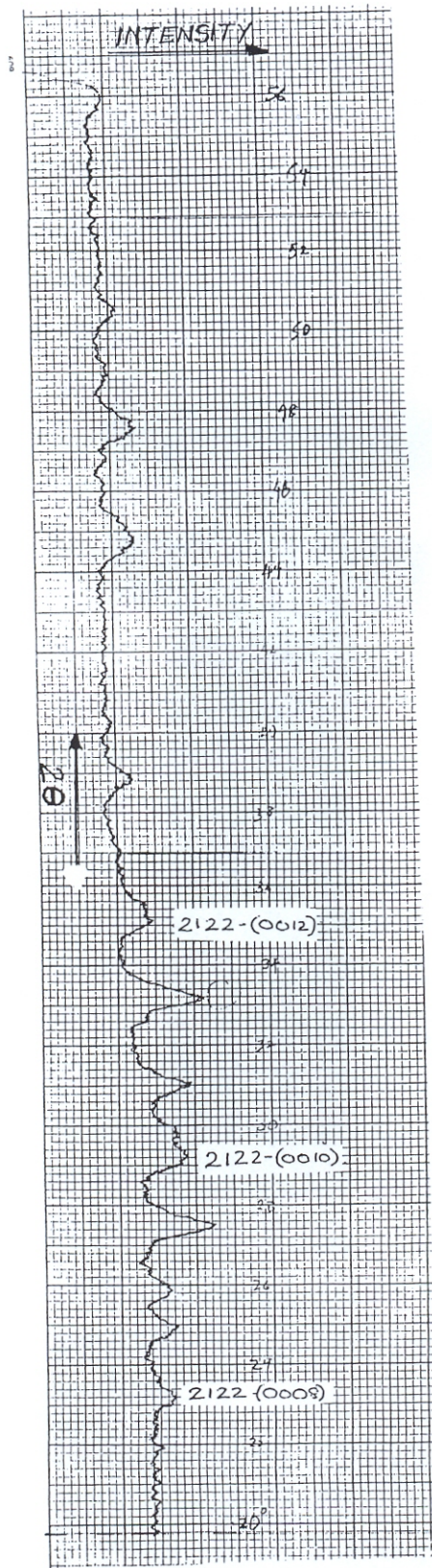


Figure 4: X-ray diffraction pattern of composition (2223) cast from the melt and crystallized at 865 C for 20 minutes