STUDY OF THE SUPERCONDUCTING PROPERTIES OF THE Bi-Ca-Sr-Cu-O SYSTEM

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ABSTRACT

We have studied the electrical properties of unquenched and rapidly quenched bulk samples of granular Bi$_2$Ca$_{1-x}$Sr$_2$Cu$_{2-x}$O$_x$ system. Electrical resistivity measurements show the superconducting transition temperature (R=0) at 72 K, 80 K, and 90.5 K. X-ray crystallographic studies showed that most of the samples were of single phase.

1. INTRODUCTION

High-temperature superconductivity in the Bi-Ca-Sr-Cu-O system has been observed and has attracted considerable attention in the year 1988 (Maeda et al., 1988; Rao, 1988; Hazen et al., 1988; Tarascon et al., 1988; and Rao et al., 1988). Furthermore, the X-ray diffraction studies have also been carried out by many researchers (Bordet et al., 1988; Takayama et al., 1988, and Syono et al., 1988) with the objective of identifying and characterizing the superconducting phase.

The 80 K superconductivity phase has been identified to have a composition of Bi$_2$Ca$_{1-x}$Sr$_2$Cu$_{2-x}$O$_x$ while 110 K phase as reported in the literature has a possible composition of Bi$_2$Ca$_{1-x}$Sr$_2$Cu$_{2-x}$O$_y$ system (Zandenbergen et al., 1988). It has become clear that this class of materials encompasses several distinct superconducting phases and that the physical properties measured depend greatly not only on the elemental composition, but also on the details of the preparation method. Present work reports the preparation of two batches of superconducting samples (quenched and unquenched) and the measurement of their electrical resistivity and X-ray diffraction to understand the effect of oxygen stoichiometry on $T_c$ of the Bi-Ca-Sr-Cu-O system.

2. EXPERIMENT

Bulk samples with the 2:1:2:2 composition have been prepared by solid-state reaction of Bi$_2$O$_3$, CuO, SrCO$_3$ and CaCO$_3$ powders. The method of synthesis consisted of reacting together Bi$_2$O$_3$, and a base matrix of CaSr$_2$Cu$_{2-x}$O$_x$. The matrix was first made by thoroughly mixing appropriate amounts of CaCO$_3$, SrCO$_3$, and CuO by heating in an alumina boat at 800°C to 900°C with intermittent grinding. The reacted powder was cooled, ground well and made into pellets, and was heated for a couple of hours.

One batch of pellets was slowly removed from the furnace and cooled to room temperature (unquenched), while another batch was pulled out of the furnace and immediately quenched by immersion in liquid nitrogen. Pellets were cut in the shape of a parallelepiped for the electrical resistivity measurements. Contacts were made with the help of silver paste to the surface of the sample. Resistivity temperature and current-voltage data were measured by a conventional
four-probe method. The experimental parametric details of the measuring techniques have already been reported in our previous work (Naqvi et al., 1989a, 1989b).

3. RESULTS AND DISCUSSION

Resistivity-versus-temperature curves for typical unquenched and rapidly quenched specimens are shown in Figures A and B. The resistivity of the unquenched sample, curve C-I from Batch 1 shows metallic temperature behavior down to the superconducting onset which begins at 90 K, while zero resistance $T_c$ is observed at 72 K. It is worthwhile to mention here that from Batch 1, most of the unquenched samples showed a zero resistance around 72-75 K. Shown in curve C-I of Figure A is the typical behavior of one of the representative samples belonging to Batch 1. These measurements have been done at a current density of 15 mA/mm². It was observed that the $T_c$ of the sample did not degrade at all with the increase of current density. This is indicative of the fact that the sample can endure current density variations. The transition width in the sample is found to be around 18 K.

The resistivity of the rapidly quenched sample of Batch 2, shown in Figure B, curve II showed improved metallic behaviour above the superconducting onset around 105 K while zero resistance was found at 90.5 K. None of the samples showed any evidence of a second onset at 105-110 K as reported in the literature (Shi et al., 1988) for samples deviating from the 2:1:2:2 composition. Some of our rapidly quenched samples were found to slowly relax to the behaviour of unquenched material over a period of some days if exposed to the atmosphere at ambient temperatures. The resistivity curve for a sample similar to curve II but exposed to the atmosphere for 15 days is shown in curve III. It has been suggested that the improved behaviour of quenched material is caused by an oxygen deficiency (Tallon et al., 1988) and this decay could then result from the uptake of atmospheric oxygen. This behaviour is in fine agreement with the work reported by King et al., 1989. This behaviour is not clear but the technological implications of this decay clearly indicate the need for a detailed study of the quenching mechanism. The specimens of samples of Batches 1 and 2 were examined by an X-ray diffractometer after crushing. The crystal structure was found to be orthorhombic (Bordet et al., 1988). X-ray crystallographic studies showed that most of the samples were of single phase.

4. CONCLUSIONS

It is established that in using a matrix method it is possible to prepare the pure superconductivity phase in the Bi-Ca-Sr-Cu-O system starting from stoichiometric ratios (2122) of the constituent oxides. Besides this, superconducting phase (2122) can also be prepared from quenching and slow cooling (unquenched).

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Figure A. The temperature-dependent resistivity of the unquenched sample.

Figure B. The temperature-dependent resistivity of the quenched sample; curve II showing the $T_{co} = 90.5$ K.