Superconducting properties of the Bi–Ca–Sr–Cu–O system

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Abstract. The electrical properties of unquenched and rapidly quenched bulk samples of granular $\text{Bi}_2\text{Ca}_1\text{Sr}_2\text{Cu}_2\text{O}_x$ system have been studied. Electrical resistivity measurements show superconductivity transition temperature ($R = 0$) at 72 K, 80 K and 90.5 K. X-ray crystallographic studies show that most samples were of single-phase.

Keywords. Electrical resistivity; superconducting transition; X-ray crystallography.

1. Introduction

High temperature superconductivity in Bi–Ca–Sr–Cu–O has attracted considerable attention (Maeda *et al* 1988; Rao 1988; Hazen *et al* 1988; Tarascon *et al* 1988; Rao *et al* 1988). X-ray diffraction studies have also been carried out by many research groups (Bordet *et al* 1988; Takayama *et al* 1988; Syono *et al* 1988) to identify and characterize the superconducting phase. The 80 K superconductivity phase has been reported to have a composition of $\text{Bi}_2\text{Ca}_1\text{Sr}_2\text{Cu}_2\text{O}_x$ while the 110 K phase has a possible composition of $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ (Zandbergen *et al* 1988). It is clear that this class of materials encompasses several distinct superconducting phases and that the physical properties measured greatly depend not only on the elemental composition but on the preparation details. The present paper reports the preparation of two batches of superconducting samples (quenched and unquenched) and the measurement of their electrical resistivity and X-ray diffraction studies to understand the basic feature of the Bi–Ca–Sr–Cu–O system.

2. Experiment

Bulk sample of 2:1:2:2 composition was prepared by the solid-state reaction of Bi_2O_3 , CuO, SrCO_3 and CaCO_3 powders. The method of synthesis consisted of reacting together Bi_2O_3 and a base matrix of $\text{CaSr}_2\text{Cu}_2\text{O}_5$. The matrix was prepared by thoroughly mixing appropriate quantities of CaCO_3 , SrCO_3 and CuO by heating in an alumina boat at 800–900°C with intermittent grindings. The reacted powder was cooled, ground and pelletized 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 removed from the furnace and quenched by immersing in liquid nitrogen. The pellets were cut in parallelepiped shape to measure the electrical resistivity. Contacts were made using silver paste in the sample surface. Resistivity was measured by the conventional four-probe method. An XY plotter was used to measure voltage and temperature. The temperature was measured using a copper-constantan thermocouple.

Figures 1 and 2. Resistivity vs temperature of $\text{Bi}_2\text{Ca}_1\text{Sr}_2\text{Cu}_2\text{O}_x$ at current density of 15 mA/mm^2 . Curve 1. Unquenched sample. Curve 2. Quenched sample. Curve 3. For quenched sample, taken 15 days after that in curve 2.

The experimental details of the measuring technique were reported earlier (Naqvi *et al* 1989).

3. Results and discussion

R - T curves for typical unquenched and rapidly quenched specimens are shown in figures 1 and 2. The resistivity of the unquenched sample from batch (I) shows metallic temperature behaviour down to the superconducting onset at 90 K, while zero resistance T_c is observed at 72 K. From batch (I) most of the unquenched samples showed a zero resistance around 72–75 K. Figure 1 shows the typical behaviour of one of the representative samples belonging to batch (I). The measurements have been done at a current density of 15 mA/mm^2 . The T_c of the sample did not degrade with increase of current density. This indicates that the sample can endure current density variations. The transition width in the sample is around 18 K.

The resistivity of the rapid quenched sample from batch (II) in figure 2 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 literature (Shi *et al* 1988) for samples deviating from the 2:1:2:2 composition. Some of our rapidly-quenched samples were found to attain the behaviour of unquenched material over a few days when exposed to the atmosphere at ambient temperatures. The resistivity curve shows T_c onset around 94 K and zero resistance at 80 K. The changes in T_c and electrical resistivity are attributed to the uptake of atmospheric oxygen as pointed out earlier (Tallon *et al* 1988; King *et al* 1989).

The specimen samples of batches (I) and (II) were examined by 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

By using a matrix method it is possible to prepare pure superconductivity phase in the Bi–Ca–Sr–Cu–O system starting from stoichiometric ratios (2122) of the constituent oxides. Also superconducting phase (2122) can be prepared from quenching and slow cooling (unquenched).

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