X-ray diffraction analysis and occurrence of multiple phases in Bi-Sr-Ca-Cu-O superconductors

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Abstract. Starting composition 1112 for Bi-Sr-Ca-Cu-oxide yields multiphase superconductors with the proportion of constituent phases depending sensitively on the annealing temperature. The R-T curves show zero resistivity and the transition corresponding to $T_c = 80$ K phase prominently. However, indexing of X-ray diffraction peaks reveals presence of $80$ K (low $T_c$) as well as $108$ K (high $T_c$) phase. The low $T_c$ phase thus corresponds to the orthorhombic structure with a unit cell of $a = 5.4 \text{Å}$, $b = 27 \text{Å}$ and $c = 30.56 \text{Å}$. This is further understood to be composed of a pseudotetragonal cell of $a = b = 5.41 \text{Å}$. The high $T_c$ phase similarly pertains to the orthorhombic structure with $c = 36 \text{Å}$.

Keywords. High temperature superconductivity; Bi-Sr-Ca-Cu-O; X-ray diffraction; multiple phase.

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1. Introduction

Bismuth-based high temperature superconductors are very attractive due to their rare earth free composition, inertness to moisture and possibility of incorporation of additional copper oxide layers (Bok 1988) in order to study effects on superconducting transition temperatures. Earlier work (Michel et al 1987; Akimitsu et al 1987) on BiSrCuO$_x$ could find $T_c$ in the range of 7–22 K. However, Maeda through his famous work (Maeda et al 1988) could attain $T_c$ up to 110 K with zero resistivity observable at 80 K by merely adding calcium to the earlier system. This system with composition BiSrCaCu$_2$O$_x$ (1112 hereafter) led to hectic research activity in this and other compositions. Some other groups (Hazen et al 1988; Subramanian et al 1988; Sunshine et al 1988; Tarascon et al 1988) not only confirmed the results but could even determine compositions and assign structures to the members of this exotic series.

Studies on Bi-Sr-Ca-Cu-O show superconducting properties to depend strongly on starting composition (Kajitani et al 1988), Sr/Ca ratio (Itoh et al 1988), processing (annealing/quenching) temperature (Yavari and Lejay 1988) and temperatures for oxygen treatment (Iguchi and Sugishita 1988).

In the present work we have synthesized Bi-Sr-Ca-Cu-O superconductor with starting composition 1112. Effects of annealing temperatures on structure of final compositions have been studied in a wide temperature range through R-T, X-ray diffraction (XRD) and microstructure studies.
2. Experimental procedure

The samples were prepared by the usual solid state reaction of well-mixed powders of Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$, CuO in the molar ratio of Bi:Sr:Ca:Cu:: 1:1:1:2. Calcination was done at 750–820°C for about 16 hours. Grinding, pelletization and calcination were done repeatedly for homogenization. The pellets (12 mm dia, thickness 2–3 mm) were annealed (sintered) at a fixed temperature within the range 700–900°C and furnace-cooled subsequently. Individual pellets were cut in rectangular bar shape to attach four probes using air drying silver paint for resistivity measurements. The temperature was monitored below and above the liquid nitrogen temperatures with calibrated platinum resistance and germanium thermometers respectively. A suitable program was developed to record R-T plots using all Keithley-224 programmable current source, 181 nanovoltmeter and 195 A digital multimeter linked to an HP computer (model 9126) through IEEE 488 bus. It was programmed to null thermo emf for each observation, besides averaging for forward and reverse biasings.

XRD studies were carried out on Siemen's diffractometer (model D-500) using CuK$_\alpha$ radiations. Microstructures were studied with a scanning electron microscope (JEOL JSM model 35 CF) and composition determined through EDX (model Kevex 7000–77) attachment.

3. Results and discussion

A large number of samples were prepared. The zero resistivity for these varied between 40 and 80 K depending on the magnitude of the annealing temperature. A few

![Figure 1. Representative R-T curves for Bi-Sr-Ca-Cu-O samples. The curves (a) to (c) are for those annealed for 16 h at 800, 820 and 840°C respectively, whereas curves (d) and (e) are for samples first premelted for four minutes at 880 and 900°C respectively before annealing them for 16 h at 860°C in each case.](image)