

## Superconductivity in Na-doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ system

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**Abstract.** Samples with the nominal composition  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Na}_x\text{Cu}_2\text{O}_y$  ( $x = 0, 0.1, 0.2$  and  $0.3$ ) were prepared by solid-state reaction of the individual compounds. X-ray diffraction patterns indicate that the samples have a majority 2212 phase with 2223 also being present. From the DC four-probe resistance data, we have observed that the furnace-cooled samples show metallic behaviour while the quenched samples show superconductivity up to 97 K.

**Keywords.** Na doping; quenching;  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ .

### 1. Introduction

The Bi-Sr-Ca-Cu-O system shows varying superconducting transition temperatures depending on the preparation techniques and also the dopants at different sites. It was recently reported (Koike *et al* 1989) that the  $T_c$  of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  (2212) system is strongly affected by the hole concentration in the  $\text{CuO}_2$  sheets. Similar observations were made in the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  system (Torrance *et al* 1988), in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system (Tokura *et al* 1988) and in the 2212 system (Groen *et al* 1989). The hole concentration in the Bi-Sr-Ca-Cu-O system is altered by substituting for Ca and Sr with other cations of similar ionic radii but differing valencies. It was reported (Kanai *et al* 1989) that the effect of substituting alkali metal dopants (like Li, Na, K, Rb) at the calcium site have a strong tendency to decompose the superconducting phase. They have reported that due to this decomposition, the volume fraction of the high  $T_c$  phase decreases and the transition temperature of the low  $T_c$  phase shows an increase by 8–10 K. Recent investigations in the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  system show that  $T_c$  varies with oxygen content (Buckley *et al* 1988). It was reported that the highest  $T_c$  of 95 K (Agarwal *et al* 1989) was obtained in this system with varying heat treatments.

The present investigation attempts to clarify whether the substitution of a monovalent alkali metal at the calcium site affects the  $T_c$  of the 2212 phase of the bismuth system. Two batches of samples were prepared with Na doping, one by furnace cooling and the other by quenching. The results of preparation, X-ray diffraction, resistivity and EDS are reported.

### 2. Experimental

Samples with nominal composition  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Na}_x\text{Cu}_2\text{O}_y$  with  $x = 0$  (sample A),  $x = 0.1$  (sample B),  $x = 0.2$  (sample C) and  $x = 0.3$  (sample D) were prepared by taking appropriate quantities of  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{NaNO}_3$  and  $\text{CuO}$ . These powders were ground together and the mixture presintered at 840°C for 24 h. This mixture was again reground and heated at 860°C for 24 h. These powders were then pressed into

pellets and annealed for 64 h at 860°C and furnace-cooled to room temperature. Another batch of samples was reannealed at 800°C for 40 h and quenched to liquid nitrogen temperature. Room temperature X-ray diffraction data were obtained with a Philips powder diffractometer using  $\text{CuK}\alpha$  radiation. A  $2\theta$  scan of  $1^\circ/\text{min}$  was adopted maintaining a chart speed of 1 cm/min. The D.C. electrical resistivity data on the samples were obtained by the standard four-probe method. The superconducting transition temperature ( $T_c$ ) was confirmed for the quenched samples with  $x = 0, 0.2$  and  $0.3$ . EDS spectra were recorded using a Jeol scanning electron microscope (model JSM 840).

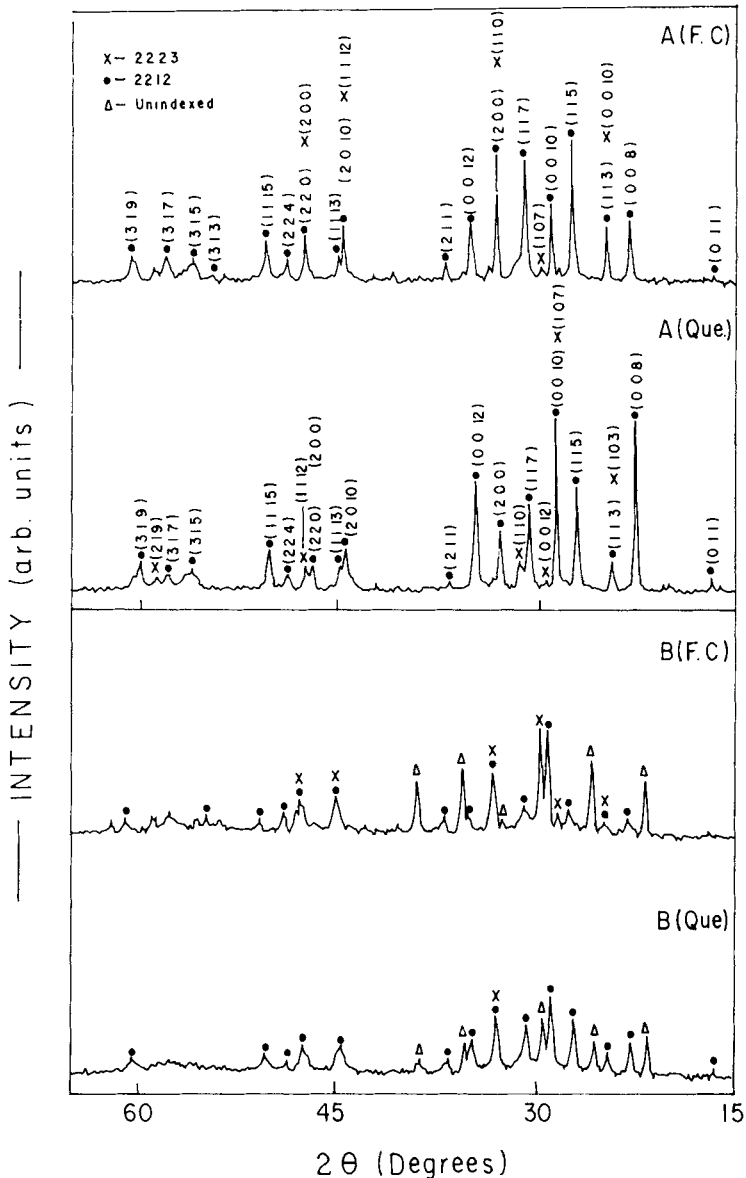


Figure 1. X-ray diffractograms of samples A and B (annealed and quenched).

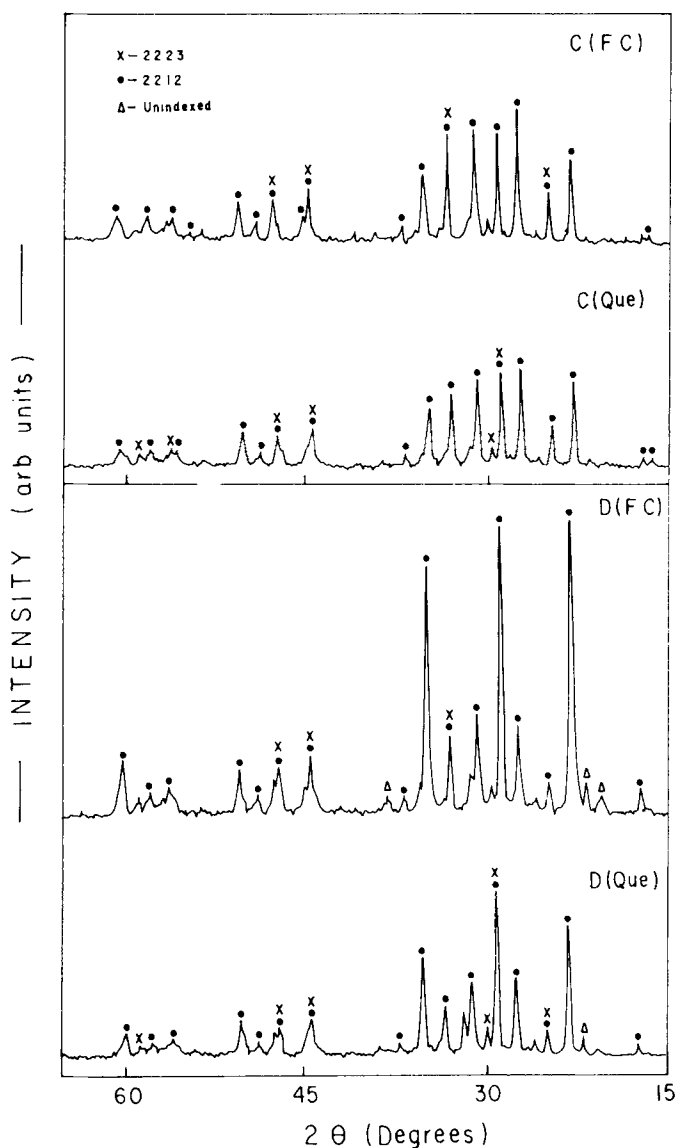


Figure 2. X-ray diffractograms of samples C and D (annealed and quenched).

### 3. Results and discussion

X-ray diffractograms of the two batches of samples, i.e. furnace-cooled (f.c.) and quenched (que) are given in figures 1 and 2. The patterns could be indexed and the values of  $(hkl)$  reflections are shown in the figures. Though the nominal starting composition was 2212, a systematic analysis of the XRD patterns indicates that both the 2212 and the 2223 phases appear to coexist in the samples, the former being the major phase. For the sample with  $x = 0$ , (sample-A) the characteristic peaks of the high  $T_c$  phase overlap with those of the low  $T_c$  phase in the furnace-cooled sample, while a

few of them separate out in the quenched sample. In the latter, XRD peaks shift to the low Bragg side, indicating an increase in the  $c$ -parameter. The intensities of the (001) reflections in the quenched sample show a three-fold increase compared to the furnace-cooled sample. From the additional XRD patterns shown in figure 3 for both the samples, it was observed that the characteristic (002) reflection occurs at  $2\theta = 4.9^\circ$  and pertains to the high  $T_c$  phase. In the sample with  $x = 0.1$ , apart from the 2212 and 2223 phases, there are also strong peaks at  $2\theta = 21.90, 25.90, 29.85, 40.20, 53.70$  and  $55.25$  which correspond to the 2201 phase. In the quenched sample with  $x = 0.1$ , the number of peaks corresponding to 2223 have reduced. Figure 2 shows the XRD patterns of samples C and D, both furnace-cooled and quenched. In both samples, we have observed the coexistence of the 2212 and 2223 phases as in sample A.

Resistivity data obtained from the four-probe technique for the furnace-cooled samples and the quenched samples are shown in figures 4 and 5. All the furnace-

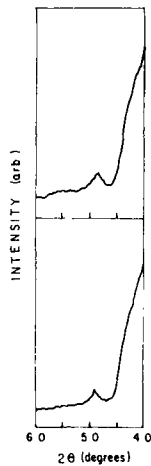


Figure 3. X-ray diffractograms of sample A (annealed and quenched) taken at  $2\theta = 4$  to  $6^\circ$ .

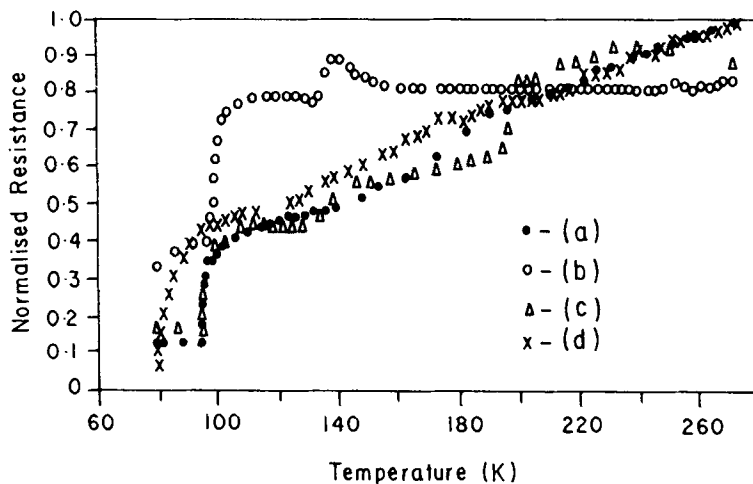


Figure 4. Normalized resistance vs temperature of samples A, B, C and D (furnace-cooled).

cooled samples show metallic behaviour while the quenched samples exhibit superconductivity above the liquid nitrogen temperature. Sample B (que) exhibit semiconducting behaviour up to 77 K. In sample A (que),  $T_c(0)$  is observed at 97 K which is greater than the value reported by others. In sample C (que),  $T_c(0)$  has been observed at 80 K while in sample D (que),  $T_c(0)$  is observed at 92 K.

The result in respect of sample A (que) showing a high  $T_c$  of 97 K is surprising to us,

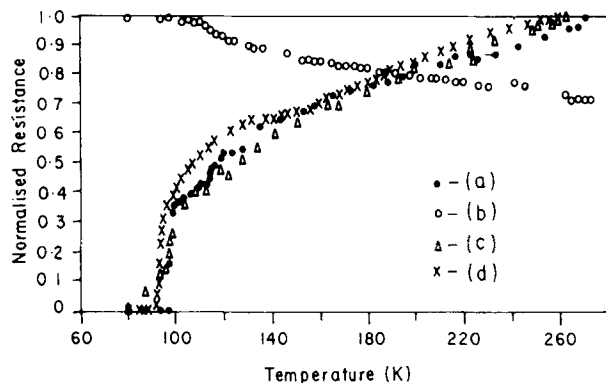


Figure 5. Normalized resistance vs temperature of samples A, B, C and D (quenched).

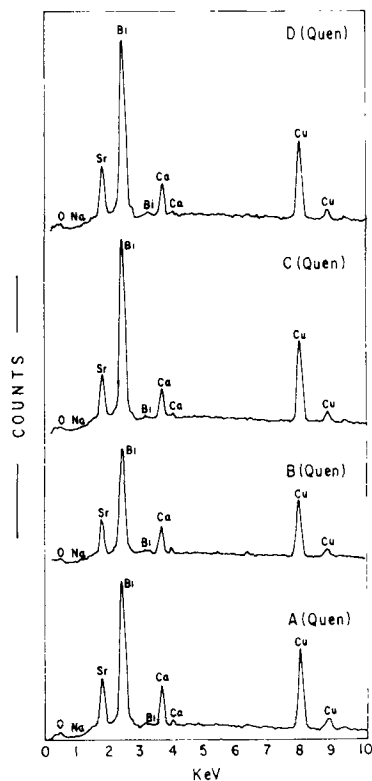


Figure 6. EDS spectra of samples A, B, C and D (quenched).

though there are reports claiming as high a  $T_c$  as 92 K (Buckley *et al* 1988) and 95 K (Agarwal *et al* 1989). This observation can be understood in the light of the fact that the sample is not a pure single-phase 2212, though it is one mimicking a single phase. The presence of the 2223 phase in some proportion might be responsible for the higher  $T_c$ .

Koike *et al* (1989) doped Na in the 2212 system and studied the  $T_c$  and the Hall effect. There was no mention whether Na entered the lattice or got evaporated during the process of heating cycles. There was no significant increase in the  $T_c$  values that they have reported with sodium doping. We have obtained EDS data from which it is seen that no appreciable traces of Na are found in our samples (figure 6). This leads one to feel that Na would not have entered the lattice. In such a case, the high  $T_c$  observed in the samples may be attributed to the non-stoichiometry introduced into the phases in having deficient calcium content, or that Na would have induced compensating oxygen vacancies. In addition, there is the presence of the high  $T_c$  phase. Further, the temperature cycles to which the samples of nominal compositions of 2212 were subjected to might also be responsible for the observation of high  $T_c$  in the present work. None of the furnace-cooled samples had shown  $T_c(0)$  up to 77 K, while the quenched samples showing superconductivity above 77 K confirms this viewpoint.

Notwithstanding the arguments put forward by earlier investigators (see for instance Koike *et al* 1989) that Na doping would increase the hole concentration, thereby showing an increase in transition temperature, we feel that the peculiar behaviour of addition of Na and its loss due to evaporation are to be carefully analysed before any conclusions can be drawn.

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