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Effect of annealing and quenching on superconductivity in Pb and Sb-doped $Bi_2Sr_2Ca_2Cu_3O_x$

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Abstract. Samples of the series $Bi_{1.9-x}Pb_xSb_{0.1}Sr_2Ca_2Cu_3O_y$ with $x = 0$, 0·1, 0·2, 0·3 and 0·4 were prepared by the solid-state route. The X-ray and d.c. electrical resistivity data on furnace-cooled and quenched samples are presented. Though the starting composition is 2223, the end products were multiphase with 4334 as the major phase. A superconducting transition with $T_c = 100$ K was observed in the pure 2223 sample after quenching. The furnace-cooled samples were metallic, while samples with $x = 0{\cdot}1$, 0·2 and 0·3 were superconducting after quenching. The amount of the 4334 phase decreases with increasing Pb content. Quenching seems to be favourable for the formation of the 4334 phase.

Keywords. High temperature superconductivity; quenching; lead and antimony doping.

1. Introduction

Since the discovery of superconductivity above 100 K (Maeda *et al* 1988; Chu *et al* 1988) in the Bi–Sr–Ca–Cu–O system, there has been intense research activity to identify the different phases in this system. It has been shown by various workers that this system is rich in superconducting phases. At least four different phases with the compositions $Bi_1Sr_1Ca_1Cu_2O_x$ (1112), $Bi_4Sr_3Ca_3Cu_4O_x$ (4334), $Bi_2Sr_2Ca_1Cu_2O_x$ (2212) and $Bi_2Sr_2Ca_2Cu_3O_x$ (2223) with transition temperatures in the range 77–110 K have been reported. Of these the 2223 phase has been reported (Tallon *et al* 1988a) to be responsible for a T_c of 107 K. It was shown (Cava *et al* 1988) that the substitution of Pb for Bi stabilizes the 107 K transition. Zero resistance at 132 K was reported (Liu *et al* 1989) in the multiphase system of $Bi_{1.9-x}Pb_xSb_{0.1}Sr_2Ca_2Cu_3O_y$.

Despite numerous reports in literature on the bismuth compounds, there are differences in the composition, values of the transition temperature and the lattice parameters. For example, it was reported (Torrance *et al* 1988) that the 2212 composition is tetragonal with lattice parameters $a = b = 0{\cdot}3821$ nm and $c = 3{\cdot}066$ nm, whereas the same sample has been reported (Pierre *et al* 1989) to be orthorhombic with $a \approx b \approx 0{\cdot}54$ nm and $c \approx 3{\cdot}08$ nm. Similarly, the 110 K phase was reported to be orthorhombic (Chen *et al* 1988) with $a = 0{\cdot}5420$ nm, $b = 0{\cdot}5447$ nm and $c = 3{\cdot}6804$ nm, while it was reported to possess the tetragonal structure (Pissas *et al* preprint) having $a = 0{\cdot}3821$ nm and $c = 3{\cdot}7034$ nm. In the lead-containing samples, it has been shown (Tallon *et al* 1988b) that Pb substitutes for Bi as well as Ca. At the same time, volatility of lead has also been reported to pose problems. In the present study, we report the synthesis and results on resistivity and X-ray diffraction studies on 2223 doped with Pb and Sb at the bismuth site.

2. Experimental

Samples of the series $Bi_{1.9-x}Pb_xSb_{0.1}Sr_2Ca_2Cu_3O_y$ with $x = 0$, 0·1, 0·2, 0·3 and 0·4 were synthesized by the solid-state route. Stoichiometric amounts of Bi_2O_3, $SrCO_3$,

$CaCO_3$ and CuO powders were taken and ground thoroughly. They were presintered at 820°C for 36 h and furnace-cooled to room temperature. The resulting mixture was reground and subjected to a second heat treatment at 840°C for 24 h. Finally, the powder was finely ground and pressed into pellets. These pellets were subjected to a long anneal at 870°C for 62 h and furnace-cooled to room temperature. For quenching studies, the pellets were reheated at 840°C for an additional duration of 20 h and quenched to liquid nitrogen temperature.

Resistivity was measured by the standard four-probe technique. The electrical contacts onto the sample were provided using thin copper wires and silver paint. X-ray data were obtained with CuK_α radiation using a Philips 1050 X-ray diffractometer. The scan rate was set at 1°/min and the chart speed was 1 cm/min.

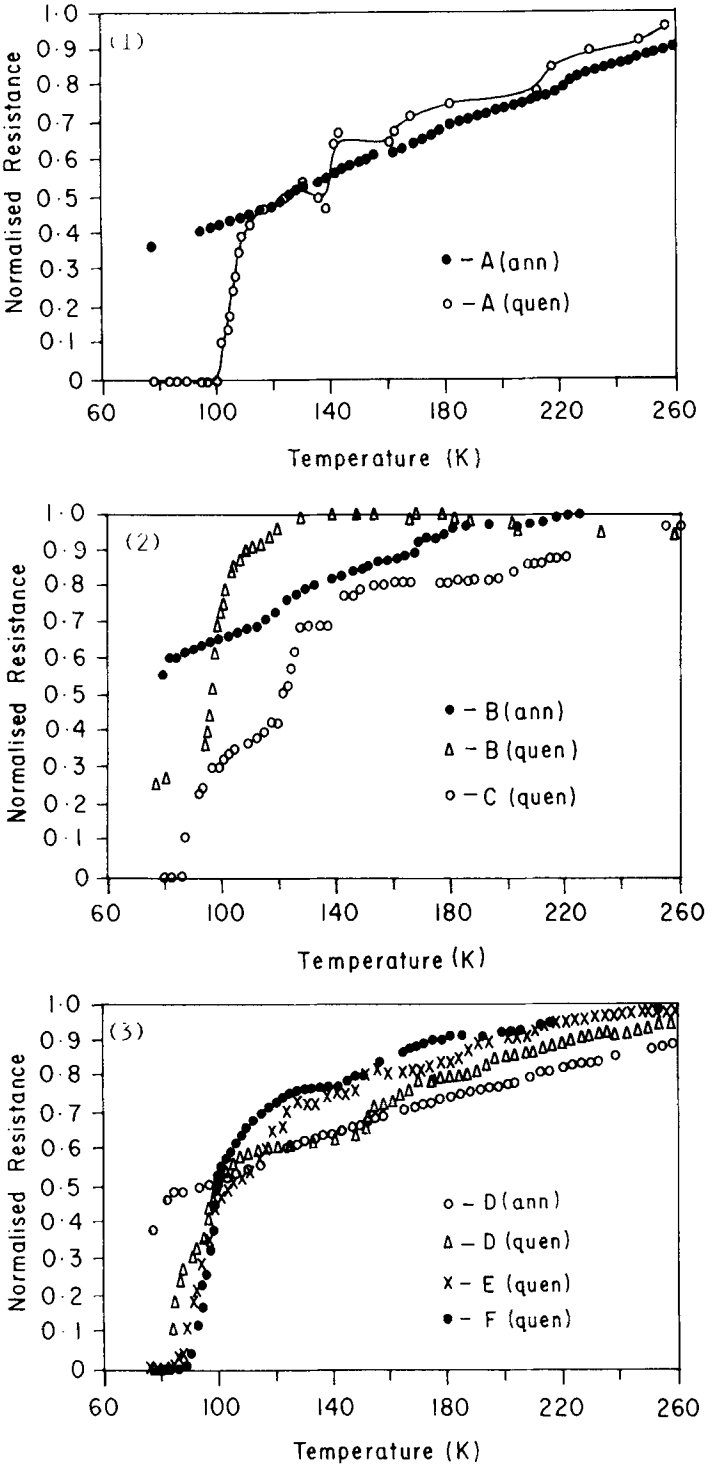
3. Results and discussion

Figures 1, 2 and 3 show the plots of the normalized resistance versus temperature of some of the samples under study. To facilitate comparison and discussion, the sample with nominal composition 2223 is denoted as sample A and the samples with $x = 0$, 0·1, 0·2, 0·3 and 0·4 are denoted with B, C, D, E and F respectively. From these plots, it can be seen that all the furnace-cooled samples show metallic behaviour up to liquid nitrogen temperature. The quenched samples except samples B and F show superconductivity above liquid nitrogen temperature. The sample B on quenching shows a peculiar behaviour. The resistance first increases with decreasing temperature up to about 140 K, after which it falls steeply to less than one fifth of its room temperature value of 19.8 milli ohm.

The multiphase nature of the samples can be seen from the plots of resistance versus temperature. On quenching, sample A shows two steps around 210 K and 160 K, and a pronounced drop around 140 K. The plots of all the quenched samples show anomalous behaviour in the region 150–120 K. From this, it may be inferred that small amounts of other phases with possibly higher T_c values could be present in these samples. Samples E and F on quenching display the resistivity 'toe' as reported (Tallon *et al* preprint b). Table 1 shows the T_c versus sample composition for the samples which have shown T_c.

Although the starting composition of our samples was 2223, a systematic analysis of the X-ray diffractograms shows that the samples contain 4334 as the major phase. A similar observation has been made in the literature (Chen *et al* 1988). A few peaks of the 2201 phase (as also reported by Torrance *et al* 1988) have also been identified in addition to the 2223 phase, indicating that apart from the dominating 4334 phase, these two are present in the samples as the minor phases. In each pattern, a few peaks could not be indexed on the basis of the above phases, indicating the presence of a small amount of additional phases.

Table 2 summarized the '2θ' and (hkl) values of sample A, both annealed and quenched. Figure 4 shows the X-ray diffractograms of these samples, as also those of sample F (annealed and quenched). The indices marked with an asterisk correspond to the 2223 phase and those marked with a plus correspond to the 2201 phase. In the annealed sample, the major phase is 4334, with 2201 present as the minor phase. In the quenched sample, the major phase is still 4334, but eight peaks could be indexed on the basis of the 2223 phase. The indexing of the peaks corresponding to the 4334



Figures 1–3. Plot of normalized resistance vs temperature of samples A to F. 1. Sample A (furnace-cooled and quenched). 2. Sample B (furnace-cooled and quenched) and sample C (quenched). 3. Sample D (furnace-cooled and quenched) and samples E and F (quenched).

Table 1. Transition temperature versus composition (see text).

Composition	T_c(K)
A (quenched)	100
C (quenched)	85
D (quenched)	83
E (quenched)	84

Table 2. X-ray data for sample A (see text for composition), annealed and quenched.

Annealed								Quenched							
2θ	h	k	l					2θ	h	k	l				
17·40	0	0	6					17·50	0	0	6				
23·10	0	0	8					23·25	0	0	8	|	1	0	1*
24·80	1	0	3					25·05	1	0	3				
27·60	1	0	5					27·60	1	0	5				
29·10	0	0	10	|	0	0	8+	29·20	0	0	10				
29·80				|	1	0	5+	31·00	1	0	7				
31·15	1	0	7					32·00				|	1	0	9*
33·20	1	1	0	|	1	1	0+	33·25	1	1	0	|	1	1	0*
33·70	1	1	2					33·80	1	1	2	|	0	0	14*
35·15	0	0	12					35·00	0	0	12				
or	1	1	4					36·4				|	1	1	6*
40·90	1	1	8					41·00	1	1	8				
44·60				|	1	1	8+	44·75	1	1	10				
45·20	1	0	13					45·10	1	0	13				
47·80	2	0	0	|	2	0	0+	47·30	0	0	16				
49·20	2	0	4					47·70	2	0	0	|	2	0	0*
50·65	1	0	15					48·20				|	1	1	14*
53·70	2	0	8					53·70	2	0	8	|	2	1	1*
54·50	2	1	3					56·00	2	1	5				
56·00	2	1	5					58·05	2	1	7				
58·10	2	1	7												
60·75	2	1	9												

phase shows that this phase has an I lattice. It has been reported (Tarascon *et al* 1988) that the 4334 phase has a T_c of about 85 K, and the 2223 phase has a T_c of about 100 K. We have obtained a T_c of 100 K for the quenched specimen of sample A, which, according to our X-ray analysis, contains the 4334 and 2223 phases.

Figure 5 shows the X-ray diffractograms of sample B (annealed and quenched) and sample C (quenched). Figure 6 shows the patterns of samples D and E (annealed and quenched) where the indices corresponding to the 4334 phase are marked with a solid circle. The peaks corresponding to the 2223 phase are indicated by a solid triangle and those of the 2201 phase, by 'X'. From the patterns, the following conclusions can be drawn. In all the patterns, the major phase is 4334. In the case of annealed samples,

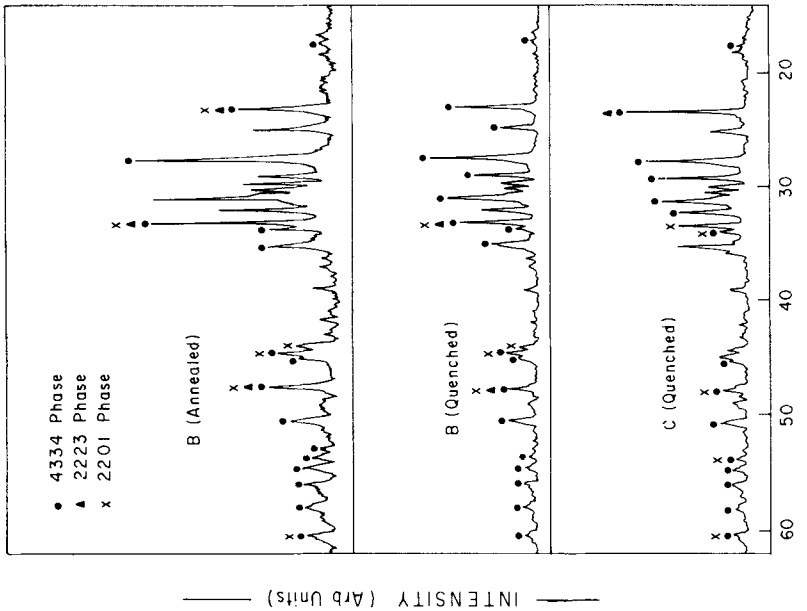


Figure 5. X-ray diffractograms of sample B (annealed and quenched) and sample C (quenched).

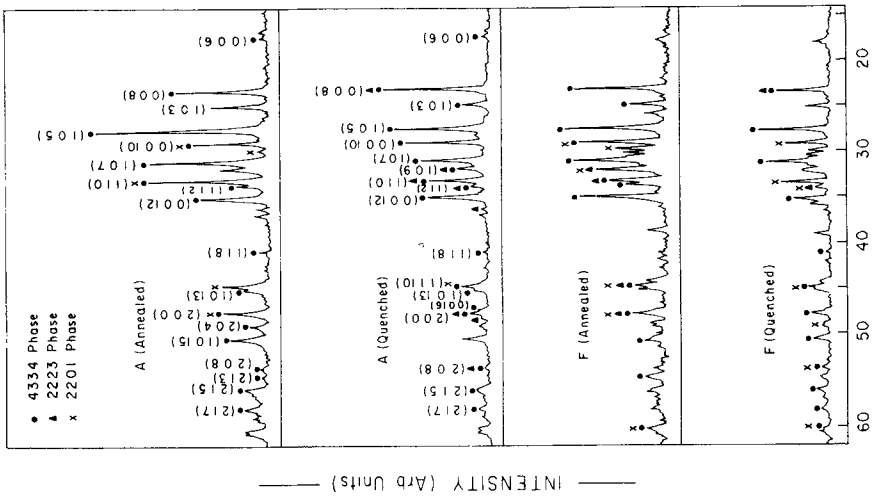


Figure 4. X-ray diffractograms of samples A and F (annealed and quenched).

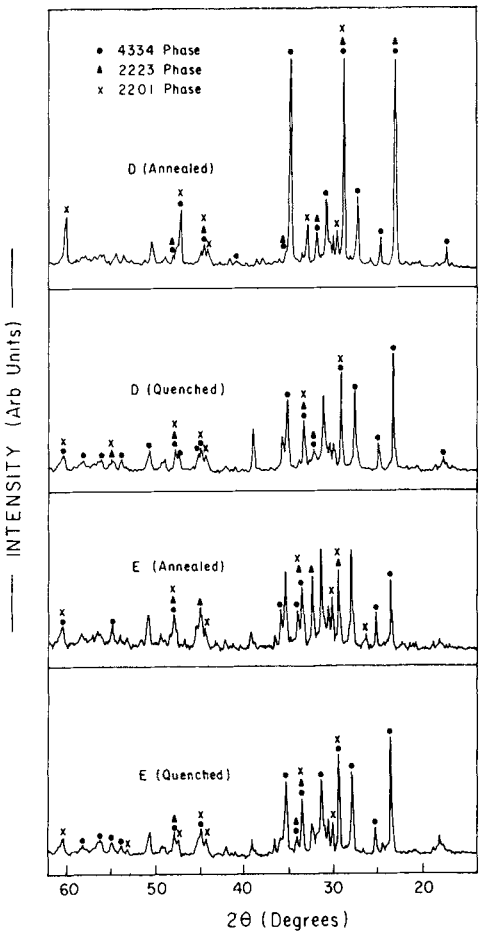


Figure 6. X-ray diffractograms of samples D and E (annealed and quenched).

the amount of the 4334 phase decreases with increasing lead content. However, quenching causes formation of 4334 as the major phase in the sample. This is clear from the number of lines indexed on the basis of the 4334 unit cell. Probably because of this, the quenched samples (except B and F) show superconductivity. It has been reported (Pierre *et al* 1989) that Pb enters the lattice. From the shifting of the peaks in the X-ray diffractograms and also the observation of smoothening of the plots of resistivity versus temperature, we believe that Pb has entered the lattice. However, additional studies are required to unequivocally establish the distribution of Pb and Sb at the different atomic sites in the Bi–Sr–Ca–Cu–O system.

The annealed samples do not show superconductivity but the quenched samples show superconductivity. This suggests that quenching favours the formation of the superconducting phase. In a different report (Suryanarayana *et al* 1990), we report that samples which have been quenched show superconductivity even after about four months' exposure to normal atmospheric conditions. It thus seems possible that stable and reproducible superconductivity can be achieved with quenching instead

of long annealing. Work in this direction and also to subject the samples to various heat treatments to obtain a majority single phase is in progress in our laboratory.

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