

Effect of Antimony Addition in Bi(Pb)-Sr-Ca-Cu-O on Superconductivity

S.A. Siddiqi, B. Akhtar, and A. Maqsood

A Pb + Sb doped material with nominal composition $Bi_{1.5}Pb_{0.1}Sb_{0.4}Sr_2Ca_2Cu_3O_y$ was prepared by the solid state reaction technique. The resistance of the specimen prepared at 860 °C gradually decreased by increasing the annealing time. The material was characterized by x-ray diffraction (XRD), electrical resistance, alternating current susceptibility, and magnetization measurements. Results confirm the formation of a newly discovered 4441 phase (having monoclinic symmetry with lattice constants a = 22.1523 Å, b = 5.9057 Å, c = 19.9598 Å, and with β = 99°) along with two minor phases, 2223 and 2212. The formation of this new phase appears to reduce the superconducting properties.

Keywords
superconductivity

1. Introduction

THE discovery of high temperature superconductivity in the Bi-Sr-Ca-Cu-O system (Ref 1, 2) attracted considerable attention due to relatively high T_c values and their rare earth free compositions. In this system, three distinct superconducting phases having the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_y$, where n = 1, 2, 3, exist and have T_c values of 10, 80, and 110 K, respectively. One of the major problems faced in this system is to prepare the high T_c phase ($Bi_2Sr_2Ca_2Cu_3O_{10}$ or 2223) in pure form, i.e. free from other low T_c phases.

Many attempts were made to achieve this goal and to raise further the T_c value. This includes annealing at different temperatures for different periods of time and doping or substituting with other elements. It was found that partial replacement of Bi by Pb promotes the formation of the 2223 phase (Ref 3). Later it was shown that addition of some silver in the Bi(Pb)-Sr-Ca-Cu-O system led to the sharpening of the transition temperature (Ref 4). However, the most interesting results were published by Hongbao et al. (Ref 5), who claimed to raise the T_c value to ~164 K by incorporating a small amount of Sb in the Bi(Pb)-Sr-Ca-Cu-O system. Some other authors (Ref 6, 7) also showed that the transition temperature can be increased substantially from 110 K by doping Sb in the Bi(Pb)-based system. However for Pb + Sb doped materials, there are also some contradicting results about improving the T_c values and the stability of the high T_c phases (Ref 8).

The literature survey indicates that with Pb + Sb doping in Bi-Sr-Ca-Cu-O samples, the quality of the samples becomes very much dependent upon their synthesizing conditions. The specimens have been prepared by many different techniques, such as solid state reaction (Ref 6, 9, 10), matrix reaction (Ref 8), and melt quenching (Ref 7). The addition of Sb in the Bi(Pb)-based system seems to enhance the formation of the 2223 phase and/or the formation of a new phase (Ref 6). The role of the new phase on superconductivity needs further investigation. Another interesting observation in this system is that the diamagnetic signal obtained by various authors does not always correlate with the resistance-temperature characteristics (Ref 8, 10-12). With this background, a composition was prepared relatively rich in Sb in the $(Bi,Pb)_2$-Sr_2-Ca_2-Cu_3-O_y system, and was expected to contain a large proportion of the new 4441 phase in order to assess its effect on superconductivity. The samples were prepared by conventional solid state reaction and were characterized by XRD, electrical resistance, alternating current susceptibility, and magnetic measurements.

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2. Experimental Procedure

The samples with a starting composition of $Bi_{1.5}Pb_{0.1}Sb_{0.4}Sr_2Ca_2Cu_3O_y$ were prepared by the solid state reaction method. Powders of 99.99% purity Bi_2O_3, PbO, Sb_2O_3, $SrCO_3$, $CaCO_3$, and CuO were mixed thoroughly in appropriate proportion using an agate mortar and pestle. The mixed material was then pressed into pellets 15 mm diam and 1.5 to 2.5 mm thick under 4 to 6 tons pressure. The samples were heated in a tube furnace in an open atmosphere at 800 to 860 °C. The temperature was measured with the help of a Pt/Pt 13% Rd thermocouple. The pellets were heated for ≤600 h following different cycles of time and temperature. In each cycle, the samples were furnace cooled, which normally took ~8 h.

The room temperature XRD patterns were recorded in the 2θ range of 5° to 60° using a RIGAKU XRD-II, Rigaku-USA, Inc., Danvers, MA, diffractometer with Cu Kα radiation. Two XRD patterns of the sample were taken, one after first heating for 158 h and the second after the final heating for 600 h. The electrical resistance of the sample after each heating was measured by a conventional four probe method within the range of 77 to 300 K. Electrical contacts were made by using silver conducting paint. Alternating current susceptibility measurements of the sample were taken using a sensitive ac set up employing the mutual inductance method. The magnetization versus magnetic field M-H loop measurements were performed with a commercial vibrating sample magnetometer at 77 K in a uniform magnetic field of 2.5 KOe. The magnetic field was applied perpendicular to the length of the sample.

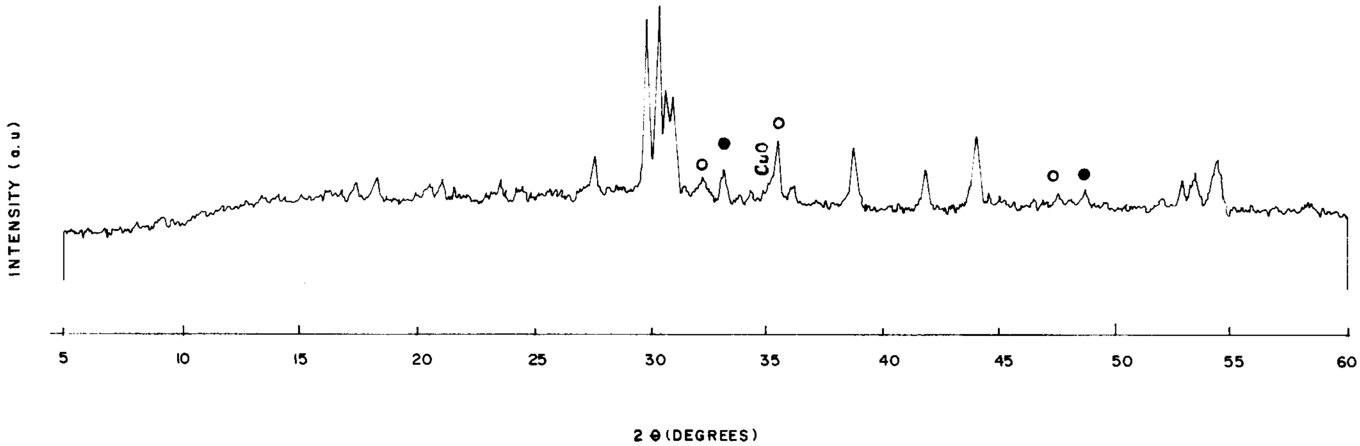

Fig. 1 XRD pattern from $Bi_{1.5}Pb_{0.1}Sb_{0.4}Sr_2Ca_2Cu_3O_y$ after heating for 158 h up to 825 °C

Table 1 Effect of sintering on superconductivity

Total sintering time, h	Sintering temperature(a), °C	Symbol	Critical temperature(b), K 1	2	3	Meissner effect at 77 K
158	825	❑	132	92	<77	Weak
268	845	+	132	102	<77	Weak
375	860	◊	137	107	<77	Weak
468	860	Δ	145	108	<77	Weak
600	860	×	124	85	<77	Weak

(**a**) Sintering temperature is ±5 °C. (**b**) Critical temperature is ±1 K. 1 and 2 indicate first and second significant deviations in the resistance versus temperature curves as shown in Fig. 3. 3 indicates T_c zero temperature

3. Results and Discussion

A true superconductor not only shows zero resistance but also excludes magnetic flux completely (the Meissner effect). The visual demonstration of the Meissner effect was carried out by cooling the pellets to liquid nitrogen temperature and bringing them near to a magnet. The tests (given in Table 1) show that the samples annealed for various periods of time exhibit a weak Meissner effect. Almost no significant change in the Meissner effect is observed with increases in annealing time.

XRD patterns for $Bi_{1.5}Pb_{0.1}Sb_{0.4}Sr_2Ca_2Cu_3O_y$ after the first (158 h) and the final (600 h) heatings are shown in Fig. 1 and 2, respectively. The patterns reveal the formation of a new phase (4441) along with two minor phases: a high T_c phase (2223) with orthorhombic symmetry (closed circles) and another low T_c phase (2212) with tetragonal symmetry (open circles). An indexed list of the new phase, 4441, is given in Table 2 by adopting the monoclinic structure symmetry as used in Ref 10. These patterns show that due to Sb, phase 4441 forms even after first heating and coexists with the 2212 and 2223 phases. The pattern also indicates the presence of CuO. The proportion of high and low T_c phases improves slightly with long term heating. The lattice constants of the 4441 phase are a = 22.1523 Å, b = 5.9057 Å, and c = 19.9598 Å; β = 99°. These cell parameters are comparable with values reported by various other authors (Ref 6, 10).

Resistance ratio versus temperature measurements on the specimens after each heat treatment were carried out using a current of 10 mA. Figure 3 shows the resistance versus temperature measurements on the samples with different heat treatment histories. The data are normalized to room temperature. The different symbols used for the specimen heated for various periods of time and temperatures are also given in Table 1 and Fig. 3. Observe that the resistance of the sample decreases by annealing for longer periods of time but not to zero at 77 K even after heating for 600 h. The T_c onset of the samples determined by resistance-temperature measurements after each heat treatment are given in Table 1. All the samples show metallic behavior on cooling below room temperature, but zero resistance is not attained down to 77 K, the limit of these measurements. In most of the samples, the resistance drops sharply at 120 K or below. The fact that they do not show superconducting behavior at 77 K indicates that the grains of the higher T_c phase are poorly connected and do not find percolating paths for zero resistance. Another reason for not observing zero resistance at 77 K may be the use of high measuring current (10 mA). The T_c values of the Sb doped BPSCCO samples exhibit strong dependence on the measuring current. Agnihotry et al. (Ref 6) used various measuring currents for 20% Sb doped BSCCO samples and found that the T_c values decreased on increasing the current from 100 μA to 2 mA in five different values of current. High T_c (zero) values were observed only at low measur-

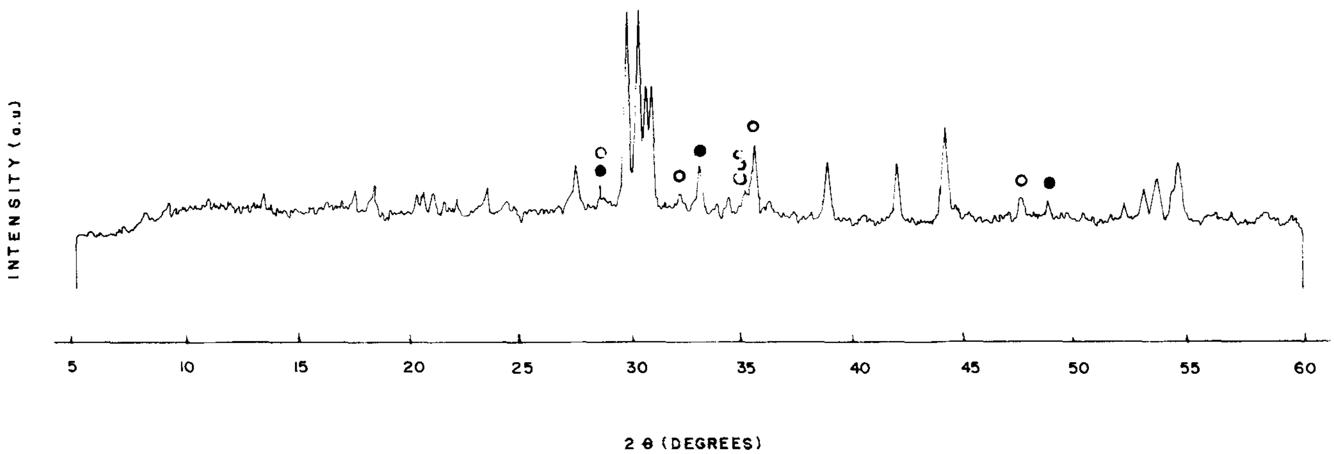

Fig. 2 XRD pattern of $Bi_{1.5}Pb_{0.1}Sb_{0.4}Sr_2Ca_2Cu_3O_y$ after final heating for 600 h at 860 °C

Table 2 X-ray diffraction data for the New 4441 phase

Peak No.	Angle 2θ, degrees	d value, Ångstrom	h k l
1	8.00	11.0512	200
2	9.40	9.4081	−102
3	13.50	6.5587	−103
4	17.60	5.0389	012
5	18.50	4.7958	112
6	20.20	4.3959	311
7	20.50	4.3322	−312
8	20.75	4.2806	204
9	21.30	4.1713	501
10	22.00	4.0401	410
11	23.50	3.7855	014
12	24.50	3.6332	600
13	27.30	3.2666	512
14	29.80	2.9980	206
15	30.25	2.9544	020
16	30.75	2.9075	120
17	31.20	2.8666	−116
18	36.50	2.4616	117
19	41.80	2.1609	218
20	43.65	2.0735	1002
21	52.00	1.7585	029
22	52.80	1.7337	916
23	53.30	1.7186	631
24	54.20	1.6922	4110

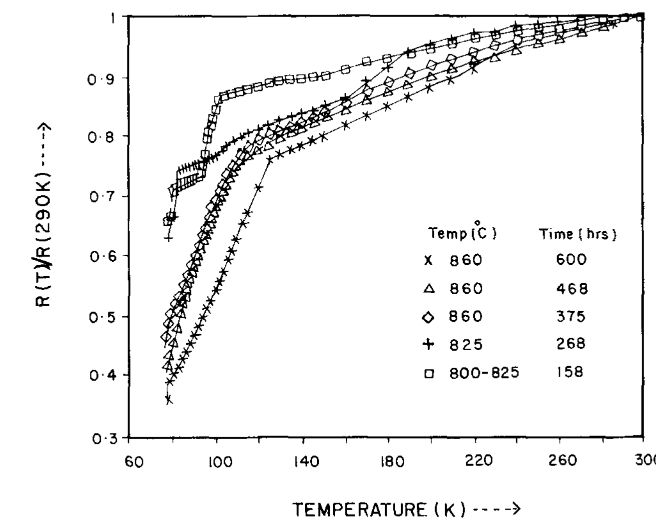

Fig. 3 Normalized resistance versus temperature curves of $Bi_{1.5}Pb_{0.1}Sb_{0.4}Sr_2Ca_2Cu_3O_y$ heated for various time periods

ing values of current. Our value for the current is five times higher than the maximum value they have used. The presence of a Meissner effect in the sample and the observation of a characteristic magnetization *M-H* loop as shown in Fig. 4 clearly indicate that the material contains some fraction of a superconducting phase.

Table 1 and Fig. 5 show that the T_c (onset) has a dependence on the heating time. The highest value for the first onset of high T_c phase is 145 K, and the second major deviation is at 108 K for probably the low T_c phase present after heating for 468 h. These values decrease to 124 and 85 K, respectively, by heating further for a total of 600 h. The ac susceptibility (χ) measurements made on the sample after final heating are shown in Fig. 6. The curve shows the diamagnetic transition of the material. Figure 6 shows that two phases (108 + 1 K and 87 + 1 K) are present in the material. The inconsistency in the resistance and the ac susceptibility measurements are expected due to the presence of a large grain boundary area, which separates the superconducting phases. The grain boundary region is probably rich in Sb, which gives rise to the formation of some insulating or semiconducting phase, which does not allow percolation. Similar results are also observed in another system reported by Khan et al. (Ref 11) and Zuya et al. (Ref 12).

Measurements to determine the magnetization of the sample as a function of the applied field at 77 K yielded the *M-H* loop shown in Fig. 4. It is evident that the critical field H_{c1} corresponding to the point, at which the *M-H* characteristic first shows linearity, is not more than 75 Oe. Almost complete reversibility of the *M-H* loop for $H > 1.6$ KOe indicates low pinning of the vortices and consequently low critical currents. Our

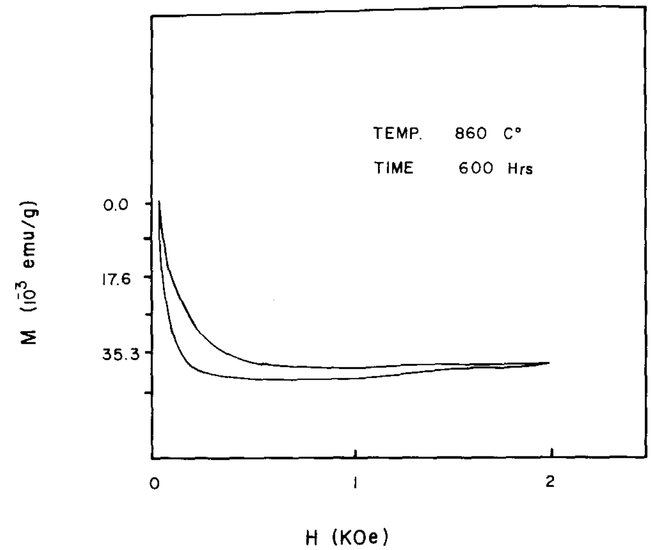

Fig. 4 *M-H* loop at 77 K of the specimen heated for 600 h at 860 °C

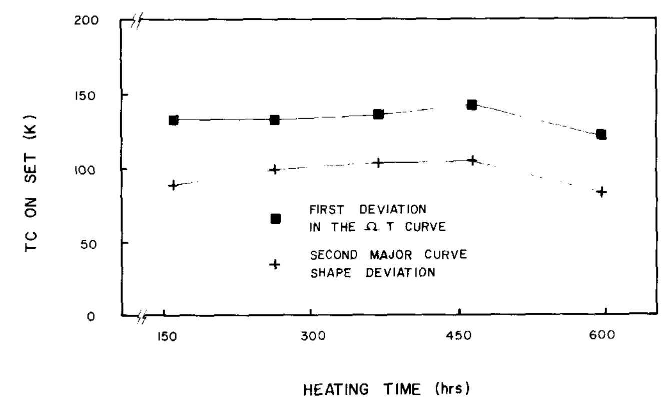

Fig. 5 T_C versus annealing time curves. (■) indicates first significant deviation in the resistance versus temperature curves. (+) indicates second major shape deviation in the resistance versus temperature curve

results with those of another system reported by Khan et al. (Ref 11).

4. Conclusion

The results indicate that high level doping by Sb (20%) in the Bi(Pb)-Sr-Ca-Cu-O system does not have a beneficial effect for improving the superconducting properties of the material. By comparing these results with those reported by previous workers (Ref 7, 13), it can be concluded that the incorporation of Sb of more than $x = 0.1$ seems to assist the formation of a new phase (4441), already reported by Tingzu et al. (Ref 10) and confirmed by Agnihotry et al. (Ref 6). The earlier investigations on this phase indicate that it has a broad transition region (T_c^{on} = 140 K, T_c^0 = 52 K). The formation of this phase not only hampers the formation of the 2223 phase but appears to remain in the grain boundary areas. The superconducting 2223 or 2212 phases, which are present, do no percolate and show a broad transition. The addition of Sb in such a large proportion (20%) gives rise to a new phase, 4441, which is nonsuperconducting between room temperature and 77 K. The new phase hampers the formation of 2212 and 2223 phases and, hence, deteriorates the superconducting properties of the material.

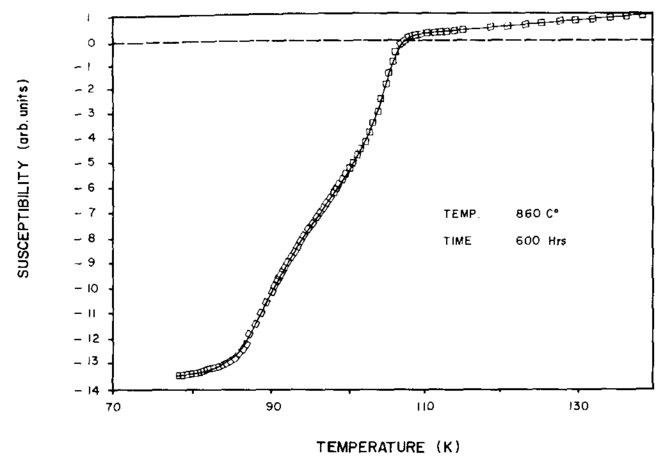

Fig. 6 Alternating current susceptibility curve for the sample after 600 h heating at 860 °C

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