JOURNAL OF MATERIALS SCIENCE 27 (1992) 2363–2366

Role of Pb substitution and a study of synthesizing procedure for Bi-based superconductors

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Bulk superconductors of the $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O_y$ system have been synthesized by changing the Bi/Pb ratio. The effect of Pb substitution on T_c has been studied by standard d.c. resistivity measurements. An appropriate thermal procedure and time for the preparation of the 110 K phase has also been studied at length. The experiments indicate that the best results are obtained for $x = 0.2$ and that a slow cooling process is necessary for a better control of the thermal process. Indexed X-ray diffraction patterns indicate the lattice parameters of low- and high-T_c phases as $a_L = 0.54004$ nm, $b_L = 0.5445$ nm, $c_L = 3.084$ nm and $a_H = 0.5483$ nm, $b_H = 0.5339$ nm, $c_H = 3.772$ nm, respectively. The observed superconducting behaviour is stable on thermal cycling between 77 and 300 K.

1. Introduction

The discovery of 30 K superconductivity in the La–Ba–Cu–O system [1] and 90 K superconductivity in the R–Ba–Cu–O (R = Y, rare earth) system [2] stimulated a world-wide search for even higher-temperature superconductors. In the Bi–Sr–Ca–Cu–O system Maeda *et al.* [3] reported bulk superconductivity at 75 K and evidence of superconductivity at 120 K (onset). We now know that there are three superconducting phases having the general formula $Bi_2Sr_2Ca_{z-1}Cu_zO_y$ where $z = 1, 2$ and 3 and these phases have transition temperatures of 10, 80 and 110 K, respectively.

By substitution of Bi with Tl, and Sr with Ba, a new series of phases is formed with the general formula $Tl_2Ba_2Ca_{z-1}Cu_zO_y$ where $z = 1, 2, 3$ and $T_c = 80$, 100, 120 K, respectively [4]. The phases with Tl can be easily prepared for every z. The preparation of the 110 K phase of $Bi_2Sr_2Ca_2Cu_3O_y$ has some difficulties compared to the 75 K phase. Many studies dealing with element substitution have been made to separate the high-T_c phase from the low-T_c phase.

In order to make samples having a large percentage of 110 K phase with respect to the 75 K phase, the material should be heat-treated for a prolonged time close to its melting point ($\approx 880\,^\circ$C). Partial substitution of Pb for Bi has been reported to be effective in preparing the high-T_c phase [5–9]. This improved behaviour has been observed in this system with Pb substitution in mixtures with starting cation proportions ranging from 1112 to 4457. It is also reported [10, 11] that the partial replacement of Bi with Pb and Sb is capable of giving the 110 K phase when annealed for three days at 850–865 °C, compared to the 10-day annealing time needed to prepare samples of the same quality when substituting Bi by Pb only.

A detailed study was conducted in order to identify the optimum starting composition and heating programme for obtaining the best bulk superconductive properties in the $(Bi_{1-x}Pb_x)_2Ca_2Sr_2Cu_3O_y$ system. This paper describes our observations resulting from the progressive increase of Pb/Bi ratio in batches with cation proportions of 2223, and the thermal treatment which must be followed to obtain the pure phase with $T_c(R_{zero}) = 103$ K. Although many papers have dealt with the preparation of pure 110 K phase, we believe that our work, through a systematic study of d.c. resistivity measurement and X-ray diffraction, indicates the optimum amount of Pb and an appropriate thermal treatment required for the preparation of pure 110 K phase.

2. Experimental procedure

A series of samples with starting composition $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O_y$, $x = 0, 0.1, 0.2, 0.25$ and 0.3, were prepared by the solid-state reaction technique under a normal atmosphere. Starting materials Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO of at least 99.9% purity were mixed thoroughly in appropriate proportions using an agate mortar and pestle. The mixture was calcined at 800 °C in a porcelain boat for 24 h. A tube furnace was used for the heat treatment. Both ends of the tube furnace were closed with high-temperature wool during the heat-treatment. The temperature was measured with the help of a Pt/Pt–13% Rd thermocouple. Pellets of diameter 14 mm and thickness 1–2 mm were pressed at a pressure of 4–6 tonne cm^{-2}. At least two pellets of each composition were made and the pellets were sintered in a normal atmosphere at $850 \pm 10\,^\circ$C for 160 h. This particular temperature and time were found to be most suitable for these experiments. The suitability of these two parameters was determined by some

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preliminary experiments. Samples were either air-quenched or slowly cooled. For slow cooling, the furnace was switched off at 850 ± 10 °C and both ends of the furnace were opened. The furnace took about 12 h to return to room temperature.

3. Results and discussion

A true superconductor not only shows zero resistance but also excludes a magnetic field completely (the Meissner effect). Two tests were performed on. the pellets to check whether the material was a superconductor or not. First, the resistance of the pellets was checked with the help of an Avometer. It was observed that if the resistance of the pellets at room temperature was less than 20 Ω, the material was often a superconductor. The second and positive test for superconductive behaviour of our samples was the observation of the Meissner effect. The visual demonstration [12] of the Meissner effect was carried out by placing a small magnet on a pellet of the sample and cooling the system to liquid nitrogen temperature. The results of this test are given in Table I.

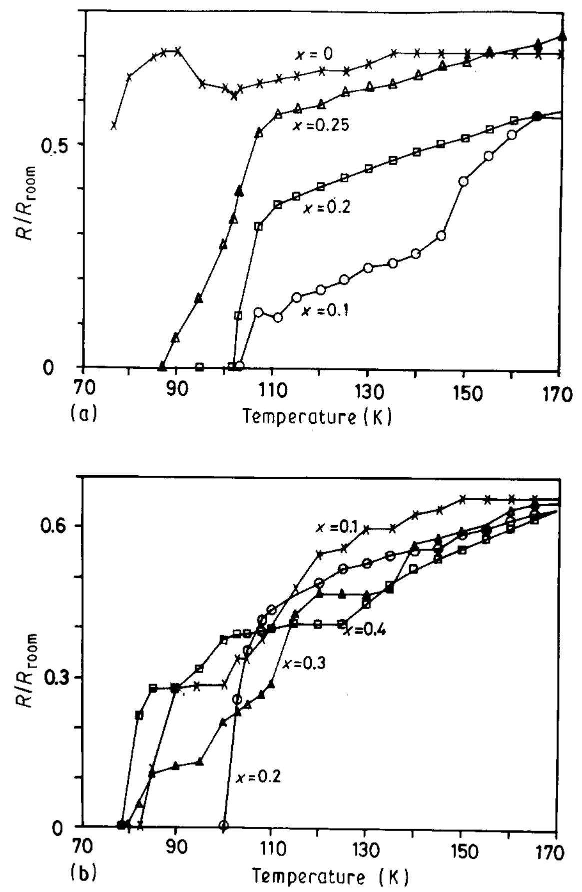

Figure 1 Normalized resistance, R/R_{room}, of $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O_y$ as a function of temperature after heating for 160 h: (a) slowly cooled, (b) quenched in air.

The d.c. electrical resistivity was measured by the standard four-probe technique. Resistivity versus temperature for all samples was measured at a current of 10 mA. Ag paste was used for electrical contacts. Fig. 1 shows the resistance versus temperature plots for the samples with $x = 0, 0.1, 0.2, 0.25$ and 0.3. The data are normalized to 300 K. Two different thermal treatments show that for pure $Bi_2Sr_2Ca_2Cu_3O_y$, the behaviour of the sample is complicated. Many mixed phases are formed. For slowly cooled samples not even the zero-resistance transition temperature is achieved above the boiling point of the liquid nitrogen, although $T_c(R_{zero})$ for the air-quenched samples is achieved at 78 K. For $x = 0.1$, again the results depend upon the method of cooling the samples. For slow-cooled material only the high-T_c phase was obtained, but it appears from the data that there was also a phase at about 150 K. On the other hand, when the sample with $x = 0.1$ was air-quenched, the low-temperature phase was more prominent. The situation is, however, different for the samples with $x = 0.2$. The samples prepared under two different conditions show resistivity behaviour that is almost identical. Here, the full superconducting transition occurs in a single stage beginning at 110 K with zero resistance being attained at 103 ± 1 K. The behaviour suggests that due to the addition of Pb, considerable enrichment of high-T_c phase has occurred in these specimens. The results are identical whether the sample is air-quenched or cooled slowly. However, when the Pb level is increased to $x = 0.25$ and the sample was cooled slowly a minute first resistive transition was observed. The resistivity as a function of temperature for $x = 0.25$ is shown in Fig. 2.

For $x = 0.3$, the behaviour of the samples again depends on the method of cooling the samples. For

TABLE I Nominal stoichiometry, the thermal process and transition temperatures for $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O_y$, where $x = 0, 0.1, 0.2, 0.25$, and 0.3 (maximum heating temperature 850 ± 10 °C, held for 160 h)

Treatment	Nominal initial composition					Critical temperature (K) (± 1K)		Meissner effect at 77 K
	Bi	Pb	Sr	Ca	Cu	T_c(onset)	T_c(zero)	
Air-quenched	0.2	0.0	2.0	2.0	3.0	85	78	Nil
	1.8	0.2	2.0	2.0	3.0	90	83	Minute
	1.6	0.4	2.0	2.0	3.0	110	100	Strong
	1.5	0.5	2.0	2.0	3.0	Semiconducting		Nil
	1.4	0.6	2.0	2.0	3.0	90	80	Nil
Slow-cooled	2.0	0.0	2.0	2.0	3.0	87	< 77	Nil
	1.8	0.2	2.0	2.0	3.0	150	104	Strong
	1.6	0.4	2.0	2.0	3.0	110	103	Strong
	1.5	0.5	2.0	2.0	3.0	125	87	Minute
	1.4	0.6	2.0	2.0	3.0	82	< 77	Nil

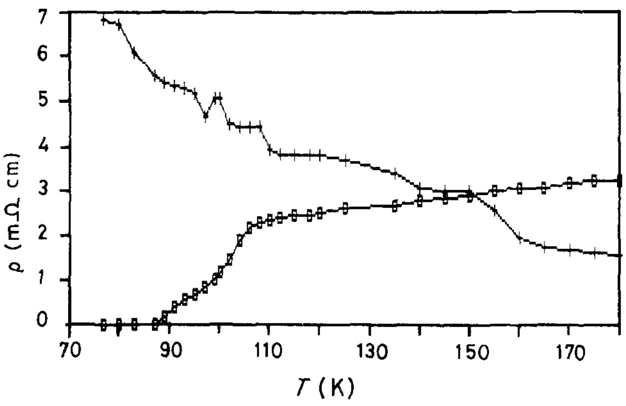

Figure 2 Resistivity as a function of temperature for $(Bi_{0.75}Pb_{0.25})_2Sr_2Ca_2Cu_3O_y$ after heating for 160 h: (□) slowly cooled, (+) quenched in air.

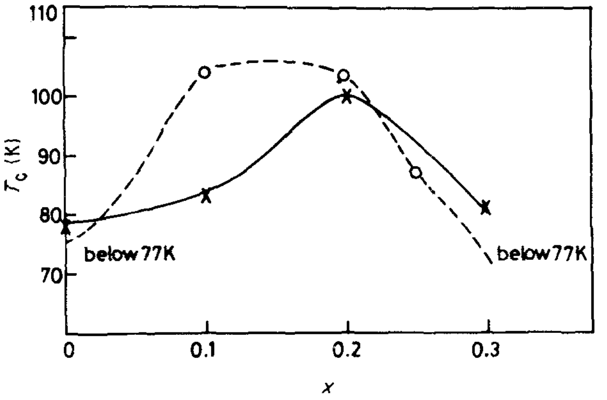

Figure 3 Concentration of Pb versus $T_c(R_{zero})$ for $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O_y$ by two thermal processes: (○) slowly cooled, (×) quenched in air.

air-quenched samples, the material showed mixed phases and the transition of the lowest phase was 81 K. Similarly, for slow-cooled specimens it was not possible to achieve the superconducting phase above 77 K. Fig. 3 shows a plot of $T_c(R_{zero})$ versus the concentration of x. It is evident from the graph that $x = 0.1$–0.2 is the best concentration of Pb for the preparation of 110 K phase. Also the "slow cooling" thermal procedure gives better results. As is evident from Table I, only those samples which showed a Meissner effect had transition temperatures above the boiling point of liquid nitrogen. Table I also shows that the transition temperature also depends upon the method of preparation of the sample except for $x = 0.2$. For that the results are almost identical. The samples were also cycled between 77 and 300 K, and the observed superconducting behaviour was stable.

X-ray diffraction patterns for samples with $x = 0.2$ and 0.25 are shown in Fig. 4. The high- and low-T_c phases are characterized by a (0 0 2) reflection of $2\theta = 4.7$ and 5.7°, respectively. It is evident from the X-ray pattern that for $x = 0.25$ the low-T_c phase is dominant while for $x = 0.2$ almost pure high-T_c phase is present. The lattice constants for the low-T_c phase $x = 0.25$) are calculated to be $a_L = 0.5004(4)$ nm, $b_L = 0.5445(5)$ nm and $c_L = 3.084(2)$ nm, while those calculated for the high-temperature phase

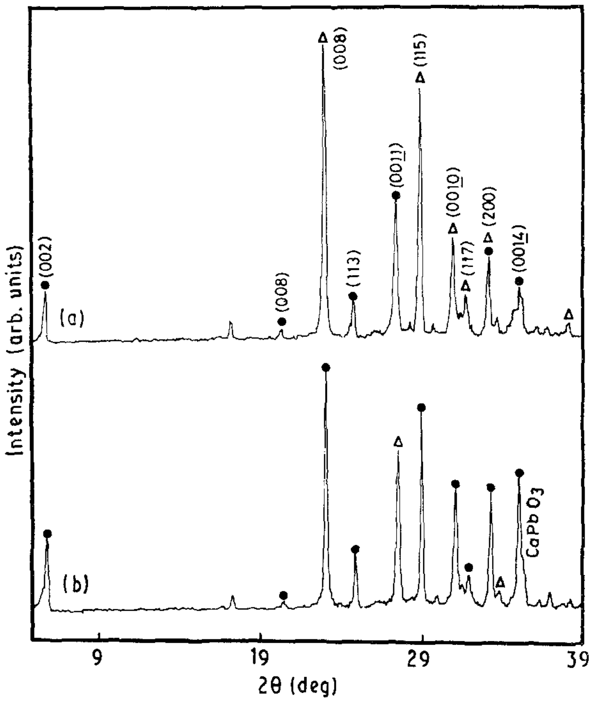

Figure 4 X-ray diffraction patterns recorded at room temperature for slowly cooled $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O_y$. Cu$K_\alpha$ radiation (40 kV, 30 mA) was used. (a) $x = 0.25$, (b) $x = 0.2$; (●) high-T_c phase, (△) low-T_c phase.

are $a_H = 0.5483(4)$ nm, $b_H = 0.5339(2)$ nm and $c_H = 3.772(2)$ nm. This confirms that the high and low phases differ mainly in the length of the c-axis, i.e. in the number of layers stacked in a unit cell. It is also worth mentioning that the X-ray diffractogram obtained for $x = 0.2$ for air-quenched material was identical to that of the slow-cooled specimen. It is difficult to determine the exact space group at this stage. Our lattice constants are also in an agreement with a recent report [13].

4. Conclusions

The present investigations show the beneficial effects of Pb addition to the Bi–Sr–Ca–Cu–O system with a nominal composition of $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O_y$ where $x = 0.1, 0.2, 0.25$ and 0.3, and include investigation of the thermal procedure for the growth of the high-T_c phase. A single high-temperature phase was obtained for $x = 0.2$ using either the "slow cooling" or the "air-quenched" thermal technique. It is interesting to note that we obtained the 110 K phase at a sintering temperature of 850 ± 10 °C and an annealing time of 160 h, while Pissas *et al.* [14] reported 360 h to get the 110 K phase. The growth rate of the 2223 phase in the samples with Pb in the place of Bi is faster than the rate in samples with Bi only. It is worth noticing that below or above $x = 0.2$, mixed phases are always formed. This phenomenon points to the formation of a boundary, perhaps due to the incorporation of impurities into the lattice.

Fig. 3 also shows evidence that the "slow cooling" technique gives a high $T_c(R_{zero})$. Finally, the crystallographic constants of the low- and high-T_c phases are determined from the X-ray diffractograms. The observed superconducting behaviour is also stable upon thermal cycling between 77 and 300 K.

Acknowledgement

This work is supported by the National Scientific Research and Development Board, Pakistan. One of us (A.M.) wishes to thank Hania and Punoo for their friendly cooperation during the course of this research period.

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Received 10 December 1990
and accepted 1 May 1991