

Role of lead in the growth of the high T_c phase in the $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ systems

L S VAIDHYANATHAN, A M NIRAIMATHI, P MAJUMDAR, G RANGARAJAN, M MURALIDHAR*, D MANGAPATHI RAO*, M NAGABHUSHANAM* and V HARI BABU*

Department of Physics, Indian Institute of Technology, Madras 600 036, India.

*Department of Physics, Osmania University, Hyderabad 500 134, India.

Abstract. $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ superconducting samples with $0 < x < 0.3$ have been synthesized and characterized using X-ray powder diffraction. T_c and superconducting volume fraction have been measured using a.c. magnetic susceptibility, d.c. electrical resistivity as well as X-band microwave surface resistance in the normal state. The data indicate the growth of the high T_c (2223) phase with corresponding reduction of the low T_c (2122) phase with increasing x , up to 0.25. Beyond this value of x there is a slight deterioration of the superconducting behaviour.

Keywords. High T_c superconductors; X-ray diffraction; d.c. resistivity; a.c. susceptibility; microwave absorption.

1. Introduction

The Pb-substituted Bi-Sr-Ca-Cu-O system, in spite of its multiphase nature, has higher T_c than the 1-2-3 compounds and is non-toxic in nature. So far, no quantitative and correlated studies have been carried out on this system using a wide variety of techniques, which would have lead to better understanding of the physical processes. We have therefore undertaken a systematic investigation of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ system for various values of x . X-ray diffraction, d.c. resistivity, a.c. susceptibility and zero field microwave surface resistance measurements have been made and the results are presented here.

2. Experimental details

X-ray powder patterns were recorded using a Philips PW 1700 X-ray powder diffractometer with CuK_α ($\lambda = 1.5418 \text{ \AA}$) radiation.

The d.c. resistivity was measured using the Van der Pauw method. To automate this method, an IBM-compatible PC/XT was used with PREMA DMM model 6000/01 and a Keithley constant current source through IEEE 488 interface.

A.C. susceptibility apparatus has been described elsewhere (Vaidhyathan 1989). For microwave surface resistance measurements a standard X-band bridge with TE 108 cavity and a cold finger attachment to the sample were used. Details of the method have been described elsewhere (Majumdar 1989).

3. Results and discussion

The compound with $x = 0$ showed initially an almost linear decrease in resistance down to 135 K and reached zero resistance at 79 K. The large width of the transition indicated the probable multiphase nature of the compound. For $x = 0.1$ compound the decrease was linear down to 115 K and thereafter dropped steeply down to 102 K. The resistance finally reached zero value at 81 K. For $x = 0.2$ compound, the resistance was found to decrease linearly down to 125 K and reached zero value at 85 K. The behaviour of the compound with $x = 0.25$ was similar to that for $x = 0.2$ except that a tail could be noticed between 116 and 96 K. For $x = 0.3$, the decrease in resistance was linear down to 119 K and then there was a further decrease to zero value at 102 K. No tail was observed and the width of the transition was 17 K.

The computed values of the d.c. resistivity of all the samples after storage for a few months and where necessary subsequent heat-treatment under standard conditions, are shown in figure 1. It is clearly seen that ρ_{dc} in the normal state and the temperature corresponding to a maximum in $d\rho_{dc}/dT$ at the transition increase monotonically with the composition x of Pb. Almost all the samples showed zero resistivity around 72 K.

Figure 2A shows the X-ray diffraction pattern for $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ ($x = 0$) sample. A broad agreement both in the d values and the intensity ratios of prominent peaks viz. (1 1 3), (1 1 5), (1 1 7), (2 0 0) and (2 2 0) was found with the values reported by Hazen *et al* (1988), Chavira *et al* (1988) and Pierre *et al* (1989). These are shown in table 1 along with the data of Hazen *et al* (1988) who determined the lattice constants assuming the structure to be orthorhombic and obtained the cell parameter values, $a = 5.41$ Å, $b = 5.439$ Å and $c = 30.78$ Å. These parameters have been related to the simple cubic perovskite cell (a cube with $a = 3.85$ Å) by the ratios $\sqrt{2}:5:\sqrt{2}:8$. They identified this as the low T_c (80 K) 2122 phase. More precisely they represented it as $\text{Bi}_2\text{Ca}_2(\text{Ca}_{0.39}\text{Sr}_{0.56}\text{Bi}_{0.05})_3\text{O}_{8+y}$. Chavira *et al* (1988) obtained $a = 5.42$ Å, $b = 5.42$ Å and $c = 30.9$ Å. They have also done computer-stimulated spectra for this 2122 (80 K) phase by using *Fmmm*, *Cccm* and *Immm* space groups respectively and found that *Fmmm* was the best choice. Pierre *et al* (1989) obtained $a \simeq b \simeq 5.4$ Å and $c \simeq 30.8$ Å. It is thus clear that $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ predominantly contains the 2122 phase. A few small peaks denoted by dots which probably correspond to high T_c phase can also be seen from figure 2A. Figures 2 B, C, D show the X-ray diffraction patterns for the $x = 0.1$, 0.2 and 0.25 samples. The d values and intensity ratios observed are given in table 2 along with those of Jian *et al* (1988) for comparison. The results show good agreement. Jian *et al* (1988) assumed this to be a new structure and indexed it with an orthorhombic cell ($a = 5.09$ Å, $b = 5.18$ Å and $c = 36.98$ Å). Our d values and intensities of the peaks also coincided with those reported by Chavira *et al* (1988) for the $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ compound in which they have obtained a $T_c(0)$ at 106 K. Lattice parameters of these high T_c 2223 (110 K) phase have been determined by them and are $a = 5.41$, $b = 5.42$ Å and $c = 37.0$ Å. Pierre *et al* (1989) indexed the 2223 phase with reference to an orthorhombic cell having the lattice constants $a \simeq b \simeq 5.4$ Å and $c \simeq 37$ Å. Xianhui *et al* (1989) obtained $T_c(0)$ at 105 K in a $\text{Bi}_{2.5}\text{Pb}_{0.5}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ sample and obtained values of the predominant diffraction peaks at 3.708 Å, 3.089 Å and 2.652 Å. We have also obtained values of 3.707 Å, 3.089 Å and 2.648 Å corresponding to the (00 10), (00 12) and (00 14) reflections of the high T_c phase.

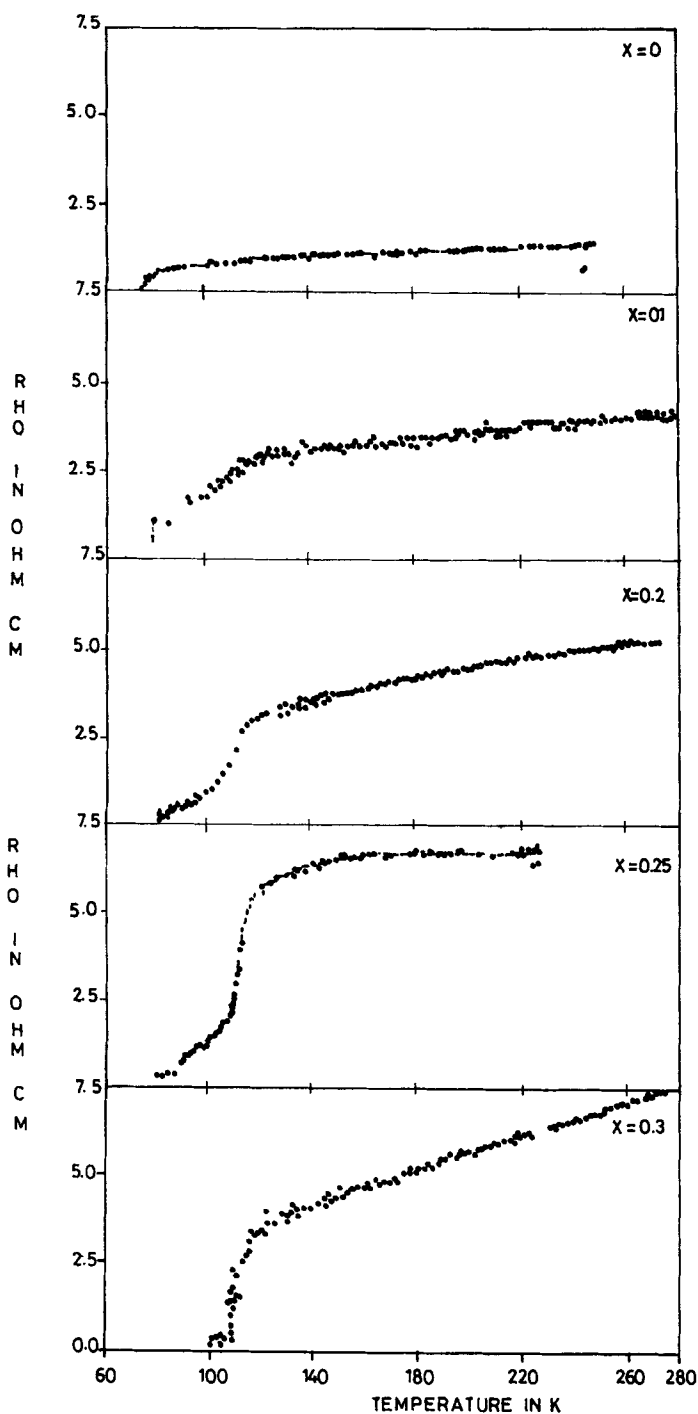
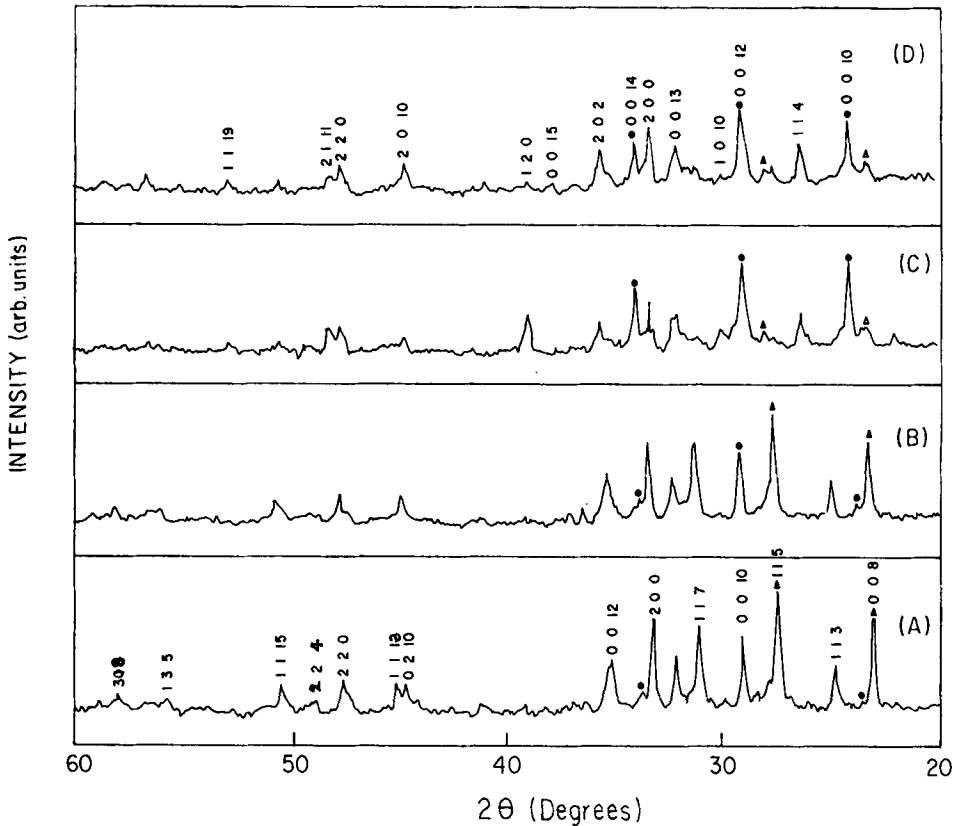


Figure 1. DC resistivity vs temperature of $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$.

Table 1. Powder diffraction data of $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$.

h	k	l	d_{obs} (present) A	d_{obs} /4/ A	d_{cal} A	I/I_0 (present)	I/I_0 /4/
1	1	3	3.586	3.593	3.594	41	41
1	1	5	3.243	3.257	2.256	100	100
1	1	7	3.889	3.890	2.891	73	62
2	0	0	2.706	2.709	2.705	76	91
2	0	10	2.029	2.033	2.032	26	26
2	2	0	1.910	1.915	1.918	29	31

**Figure 2.** X-ray diffraction pattern for $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$, where A is for $x=0$, B is for $x=0.1$, C is for $x=0.2$ and D is for $x=0.25$.

Toghe *et al* (1989) prepared superconducting thick film of $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$, and found $T_c(0)$ at 80 K in films sintered at 850°C for 30 min and $T_c(0)$ at 102 K in films sintered for 15 h. They have also observed that the 110 K phase (002), (008), (0010), (0014) and (0016) X-ray peaks which were absent in 30 min sintered films. Our results presented in table 2 show that the intensities of the (0010), (0012) and (0014) peaks which correspond to high T_c (110 K) phase increase considerably with lead doping.

The a.c. susceptibility data are displayed in figure 3, while the T_c (onset) and the corresponding volume fraction calculated using a Pb reference sample are shown in

Table 2. X-ray diffraction data of $\text{Bi}_{1.80}\text{Pb}_{0.20}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$

<i>h</i>	<i>k</i>	<i>l</i>	d_{obs}	d_{obs}	d_{cal}	I/I_0	I/I_0
			(present)	/5/			
0	0	10	3.705	3.704	3.699	99	88
1	1	4	3.388	3.394	3.381	46	39
0	0	12	3.089	3.087	3.082	100	100
0	0	18	2.823	2.844	2.845	42	36
0	0	14	2.648	2.644	2.642	70	87
2	1	11	1.889	1.889	1.890	29	30

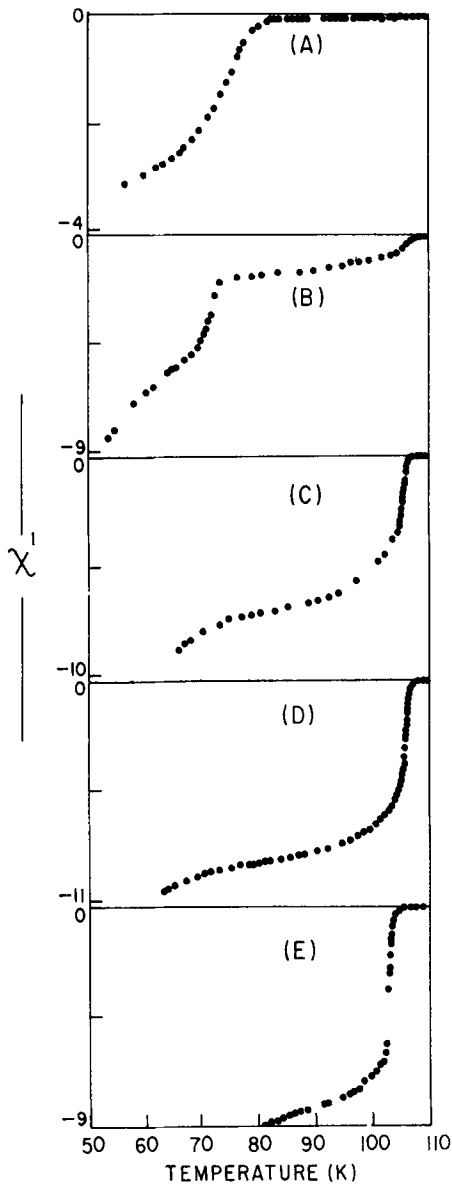


Figure 3. χ' vs temperature of $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$, where A is for $x=0$, B is for $x=0.1$, C is for $x=0.2$, D is for $x=0.25$ and E is for $x=0.30$.

Table 3. Experimental data of $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$.

x	ρ_{dc} m Ω cm	$d\rho/dT$ m Ω cm/K	T_c^{on} (on) K	vol.fra. (%)	$R_{\text{microwave}}$ Ω	$R_{\text{microwave cal}}$ Ω
0.00	1.083	0.003	108.4	14.68	9.6	0.63
0.05	1.92	0.0063	108.0	17.44	10.6	0.84
0.10	3.17	0.0083	109.2	41.23	11.4	1.08
0.20	3.83	0.0145	107.5	43.14	12.5	1.19
0.25	6.58	0.0104	107.7	48.81	14.9	1.56
0.30	4.41	0.0291	105.0	40.66	29.8	1.27

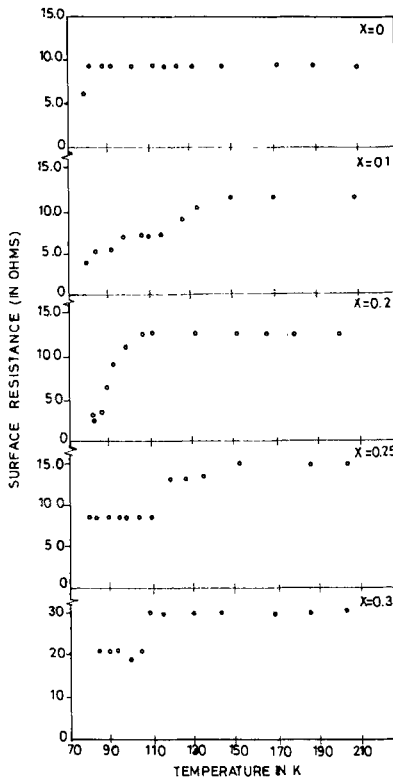
**Figure 4.** Microwave surface resistance vs temperature of $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$.

table 3. The T_c and corresponding volume fractions are found to be lower in the case of the $x = 0.30$ sample as compared to the one with $x = 0.25$, for which both have a maximum value. In the case of $x = 0.20, 0.25$ and 0.30 samples, a small but distinct maxima in χ'' were also detected close to T_c .

The microwave surface resistance obtained from bandwidth measurements (figure 4) in the normal state for different values of Pb are also given in table 3. This trend agrees with ρ_{dc} shown in figure 1. However the microwave values differ by about one order of magnitude from the values derived from ρ_{dc} . This may be because of surface

irregularities and granularity of the material. The multiphase nature of the undoped samples and the growth of the high T_c phase with Pb substitution are also clearly seen in the microwave data. The relatively small superconducting volume fractions are also reflected in the existence of large microwave absorption below T_c which is sometimes as high as 50% of that in the normal state. More work, preferably with single crystals, would be necessary to understand the origin of the absorption and its relationship to the penetration of the microwave magnetic field in the superconductor.

4. Remarks

The data discussed above clearly show that T_c and the volume fraction of the high T_c phase are enhanced with an increase in Pb concentration up to $x = 0.25$. Various mechanisms such as donation of carriers by Pb when it replaces Bi (Xianhai *et al* 1989) and increase of volume fraction of high T_c phase due to modification of high temperature reaction (Chavira *et al* 1988) have been suggested to explain the role of lead in increasing the high T_c phase. In the present studies we have added PbO rather than PbO₂ to enhance T_c and the arguments of Xianhai *et al* (1989) therefore may not apply in the present case. The results of Pierre *et al* (1989) showed that Pb actually enters in the structure of the 2122 phase. Since the radius of the Pb ion is smaller than that of the Bi ion, the structure of the 2122 phase can get modified if Pb occupies the position of Bi and result in a 2223 phase. The decrease in the volume fraction of high T_c phase for $x = 0.3$ may be due to the precipitation of excess Pb at the dislocations and grain boundaries. Further studies are in progress.

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References

- Chavira E, Escudero R, Rios-Jara D and Leon L M 1988 *Phys. Rev.* **B38** 9272
- Chu C W *et al* 1988 *Phys. Rev. Lett.* **60** 941
- Green S M, Jiong C, Mei Y, Lao H L and Politis C 1988 *Phys. Rev.* **B38** 5016
- Hazen M *et al* 1988 *Phys. Rev. Lett.* **60** 1174
- Jian C, Zuyao C, Yitae Q, Jian Sheng X, Zhenghui H, Shifeng S, Minhu F and Qirui Z 1988 *Solid State Commun.* **68** 327
- Maeda M, Tanaka Y, Fukutomi M and Anano T 1988 *Jpn. J. Appl. Phys. Lett.* **27** 4209
- Majumdar P and Rangarajan G 1989 *Proceedings of DAE symposium on Solid State Physics* **32C** 205
- Michel C, Hervieu M, Borel M M, Granolin A, Deslandes F, Provost J and Raveau B 1987 *Z. Phys.* **B68** 421
- Pierre L, Mörin D, Schneek J, Toledono J C, Primot J, Degmt C, Etrill J and Savary H 1989 *Solid State Commun.* **69** 499
- Sunshine S A *et al* 1988 *Mater. Res. Bull.* **14** 24
- Toghe N, Akamatsu Y, Tsuboi S, Tatsumisago M and Minami T 1989 *Jap. J. Appl. Phys.* **28** 1408
- Vaidhyanathan L S, Raju N P and Rangarajan G 1989 *Indian J. Pure Appl. Phys.* **27** 438
- Xianhui C, Xia J, Chen Z, Qian Y, Fan C, Yang L, Chu C, Xucheng and Zhang Q 1989 *Solid State Commun.* **71** 117