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Sintering effect on Bi(Pb)–Sr–Ca–Cu–O high-T_c superconductors

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D.c. electrical resistivity, a.c. magnetic susceptibility and X-ray diffraction techniques have been used to investigate the superconductive and structural properties in the systems $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{4.5}O_Y$ and $Bi_{1.6}Pb_{0.2}Sr_2Ca_2Cu_4O_y$. It is observed that the preparation method and heating methodology affect the properties of materials. Step sintering is of greater value for magnetic properties of the samples whereas prolonged sintering makes the systems more metallic and a smooth variation in resistivity with temperature is observed. The superconducting phase identified by X-ray diffraction analysis is mainly the high-T_c phase in all the samples. Resistivity and susceptibility measurements also indicate primarily the high-T_c phase.

1. Introduction

High-temperature superconductors are very interesting and also challenging. One of the most widely studied systems is the Bi–Sr–Ca–Cu–O system, owing to its chemical stability against aggressive environmental contaminations (for example, water vapour and CO_2) compared to the La–Sr–Cu–O or Y–Ba–Cu–O systems [1], which has made it attractive for potential applications. Widely studied phases in this system, which are often referred to by their superconductivity transition temperature, T_c, or by their Bi:Sr:Ca:Cu atomic ratio, are 110 K or $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ (2223) phase for $n = 3$, and the 85 K or (2212) phase for $n = 2$.

It has been reported that partial substitution of bismuth by lead not only enhances the formation of high-T_c phase [2,3] but also stabilizes it [4, 5] in bulk ceramic samples. High-T_c phase proportion is sensitive to lead composition and the thermal procedure adopted for the material preparation [6]. Zero resistance was achieved at 117 K in the $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{2+z}O_y$ system for $z = 1.6$, and an a.c. susceptibility step at around 150 K was also observed [7]. Ali *et al.* [8] carried out further work on this system and obtained zero resistance at 130 K for $z = 2$, but non-reproducibility of the recipe was reported. A sample with $z = 2.0$ was again prepared for an enumerated study and similar results were reproduced. The $T_{c,0}$ obtained in our case was 127 ± 1 K. The system was found to be sensitive to copper composition [8], and lead is also supposed to stabilize the high-T_c phase, so the present work describes the superconductive characteristics of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{4.5}O_y$ and $Bi_{1.6}Pb_{0.2}Sr_2Ca_2Cu_4O_y$ systems. The effect of sintering on $T_{c,0}$ and the magnetic behaviour of these two systems, have been discussed.

2. Experimental procedure

Samples composed of nearly single high-T_c phase were synthesized by the solid-state reaction in air. Stoichiometric mixtures of high-purity Bi_2O_3, CuO, $SrCO_3$, $CaCO_3$ and PbO gave the starting nominal compositions of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{4.5}O_y$ and $Bi_{1.6}Pb_{0.2}Sr_2Ca_2Cu_4O_y$. Finely ground powders were then calcined for 15 h in air at 820 °C. After regrinding, the mixtures were pressed into disc-shaped pellets at a pressure of 20 kN. Rectangular bars were cut from the pellets and sintered in air for various times. Subsequently, all the samples were furnace cooled to room temperature at a moderate rate, because it was reported that the T_c value was strongly dependent on the cooling rate [9]. Nomenclature for the samples prepared is given in Table I. The d.c. electrical resistivity of the samples was measured by the standard four-probe method. Electrodes were made by using a silver paint. The mutual inductance bridge method was used for a.c. susceptibility measurements. For these measurements, a very low a.c. field (about 0.6 Oe and $f = 270$ Hz) was applied parallel to the axis of the rectangular bar-shaped specimens. The formation of phases was also checked by X-ray diffraction (XRD). XRD patterns were taken using monochromatic high-intensity $CoK_{\alpha1}$ radiation ($\lambda = 0.1789$ nm) at room temperature.

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TABLE I Nomenclature for the samples

Sample	Nominal composition	Sintering method
1	C1	Step (24 h interval)
2	C1	Continuous (144 h)
3	C2	Step (24 h interval)
4	C2	Continuous (144 h)
5	C2	Continuous (192 h)

[a] C1 = $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{4.5}O_y$, 222(4.5); C2 = $Bi_{1.6}Pb_{0.2}Sr_2Ca_2Cu_4O_y$, (1.8)224.

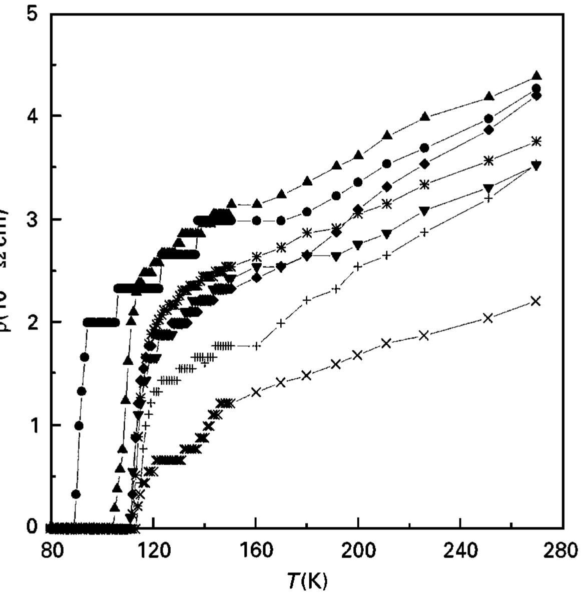

Figure 1 Temperature dependence of resistivity of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{4.5}O_y$ (samples 1 and 2). Sintering time (h): (●) 24, (▲) 48, (▼) 72, (◆) 96, (+) 120, (×) 144, (*) 144 (sample 2).

3. Results and discussion

3.1. Resistivity measurements

3.1.1. $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{4.5}O_y$

The resistivity behaviour of sample 1 for different sintering times is given in Fig. 1. It is observed that an increase in sintering time reduced the multiple phases in the sample, showing the completion of solid-state reaction. With increasing sintering time, $T_{c,0}$ increased and attained its maximum value (113 ± 1 K) after 120 h sintering. Also, the resistivity decreased with increasing sintering time. Although sample 1 has about 11% less $T_{c,0}$ as compared to a sample with composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_4O_y$ this is more stable and the results are reproducible. The value of $T_{c,0}$ at different sintering times is given in Table II. Another sample (sample 2) having the same calcining history was sintered continuously for 144 h and its $T_{c,0}$ was nearly the same as that of the sample 1. The resistivity of sample 2 shows very good metallic behaviour for $T > T_{c,0}$ and no rough transition phase was observed. This shows that continuous sintering is more favourable towards resistivity behaviour of the superconducting material.

3.1.2. $Bi_{1.6}Pb_{0.2}Sr_2Ca_2Cu_4O_y$

The resistivity behaviour of sample 3 for different sintering times is given in Fig. 2. It is observed that an increase in sintering time smoothed out the multiple phases initially present in the sample showing the completion of solid-state reaction. With increasing sintering time, $T_{c,0}$ increased and attained its maximum value (112 ± 1 K) after 144 h sintering. Also, the resistivity decreased with an increase in sintering time. The value of $T_{c,0}$ at different sintering times is given in Table II. Two other samples (samples 4 and 5), having the same calcining history, were sintered continuously for 144 and 192 h, respectively, when their $T_{c,0}$ values were nearly the same as that of sample 3. Resistivity of samples 4 and 5 shows very good metallic behaviour for $T > T_{c,0}$ and no rough transition phase was observed. Thus continuous sintering is more beneficial towards the resistivity behaviour of the superconducting materials.

3.2. A.c. susceptibility measurements

3.2.1. $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{4.5}O_y$

For the superconducting samples, the real part $\chi'(T)$ of the a.c. susceptibility was measured after each sintering step. $\chi'(T)$ of a.c. susceptibility versus temperature variation for samples 1 and 2 is shown in Fig. 3. The curves show that two phases are present in each case and these shift towards the right of the temperature scale after each sintering step. The diamagnetic transition in $\chi'(T)$ occurs sharply in the first phase and this diamagnetic transition increases with an increase of sintering steps. However, the transition did not appear to be completed which resulted in further transition. The slow transition in the case of the second phase, reflected the granular structure of the material with weak links in the intergrain regions. Similar behaviour has been reported for granular superconductors [10], where it has been observed that, in

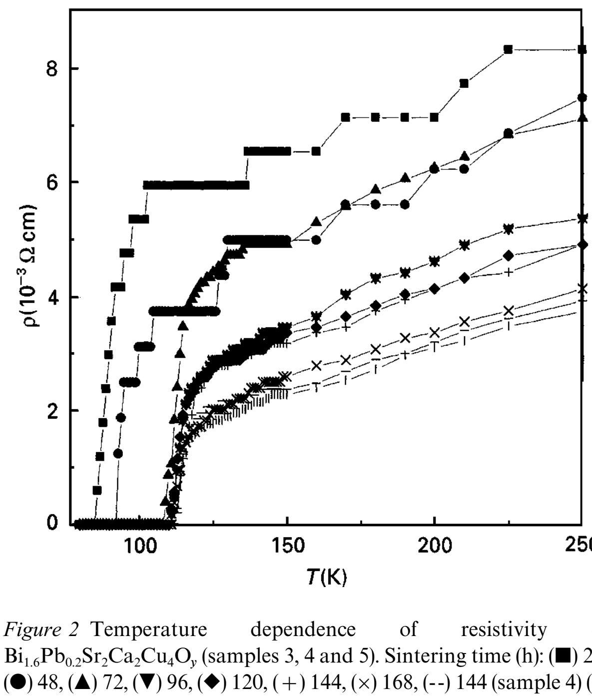

Figure 2 Temperature dependence of resistivity of $Bi_{1.6}Pb_{0.2}Sr_2Ca_2Cu_4O_y$ (samples 3, 4 and 5). Sintering time (h): (■) 24, (●) 48, (▲) 72, (▼) 96, (◆) 120, (+) 144, (×) 168, (--) 144 (sample 4) (1) 192 (sample 5).

TABLE II Critical transition temperatures for the samples at different sintering times

Sr. no.	Sintering time (h)	$T_{c,0}(\pm 1\ K)$				
		Composition C1		Composition C2		
		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
1	24	88	—	85	—	—
2	48	104	—	92	—	—
3	72	110	—	108	—	—
4	96	111	—	110	—	—
5	120	113	—	110	—	—
6	144	113	111	112	112	—
7	168	—	—	111	—	—
8	192	—	—	—	—	110

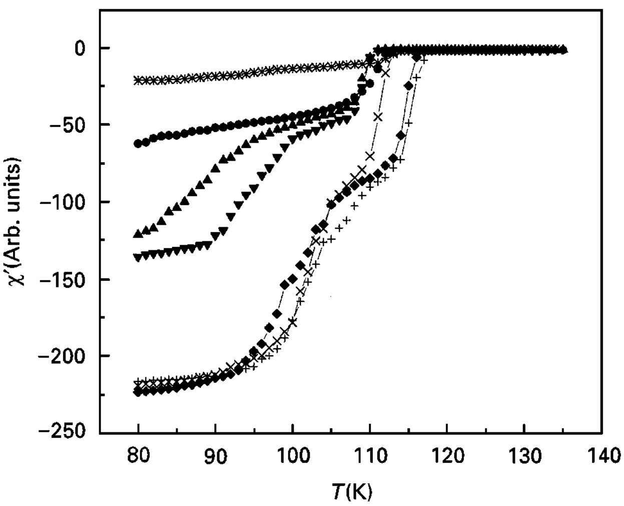

Figure 3 Temperature dependence of a.c. susceptibility (χ', real part) of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{4.5}O_y$ (samples 1 and 2). Sintering time (h): (●) 24, (▲) 48, (▼) 72, (◆) 96, (+) 120, (×) 144-, (∗) 144 (sample 2).

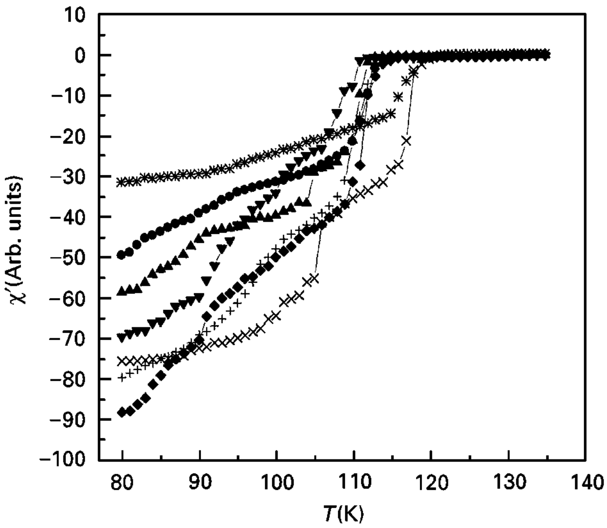

Figure 4 Temperature dependence of a.c. susceptibility (χ', real part) of $Bi_{1.6}Pb_{0.2}Sr_2Ca_2Cu_4O_y$ (samples 3, 4 and 5). and sintering time (h): (●) 48, (▲) 72, (▼) 96, (◆) 120, (+) 144, (×) 144, (sample 4) (∗) 192 (sample 5).

addition to the common problems (such as impurity, low density, etc.) from which a sample in this system may suffer, overall bulk properties are influenced by the granular T_c values of the two superconducting phases. These phases can increase the extent of T_c variations. The first phase is referred to as 2223 phase. The second drop in $\chi'(T)$ observed after two sintering steps, fell in the 2212 phase region. Subsequently, the second phase was far from the expected critical temperature of the 2212 phase, so it can be safely stated that this second drop in $\chi'(T)$ is due to intergrain coupling transition. The magnitude of the maximum diamagnetic signal increased with increasing sintering time, showing an increase in superconducting fraction, but an actual estimate of the superconducting fraction is not possible [11].

3.2.2. $Bi_{1.6}Pb_{0.2}Sr_2Ca_2Cu_4O_y$

$\chi'(T)$ of the a.c. susceptibility versus temperature variation for samples 3, 4 and 5, after each sintering step, is shown in Fig. 4. The curves show the presence of two phases. The diamagnetic transition in $\chi'(T)$ occurs sharply in the first phase and this diamagnetic transition increases with an increase of sintering steps. The slow transition in the case of the second phase, reflected the granular structure of the material with weak links in the intergrain regions. The first phase is referred to as a high-T_c phase or 2223 phase, but the second phase has no match in the literature. The magnitude of the maximum diamagnetic signal increased with increasing sintering time, showing an increase in superconducting fraction.

Samples 4 and 5 showed similar behaviour (Fig. 4) but the magnitude of the maximum diamagnetic signal for sample 5 is the weakest of all. This implies that step-wise sintering (as for sample 3) is more favourable for magnetic properties of the superconductor.

3.3. X-ray diffraction analysis

X-ray diffraction patterns of all the samples, after the final sintering were taken and are shown in Fig. 5. Comparing the data in the literature [6, 12–14], for the superconducting phases, the major phases obtained could be referred to the 2223 with partially substituted Bi^{3+} by Pb^{2+} with orthorhombic structure, as is clear from the lattice parameters [15] given in Table III. The experimental errors are indicated in parentheses.

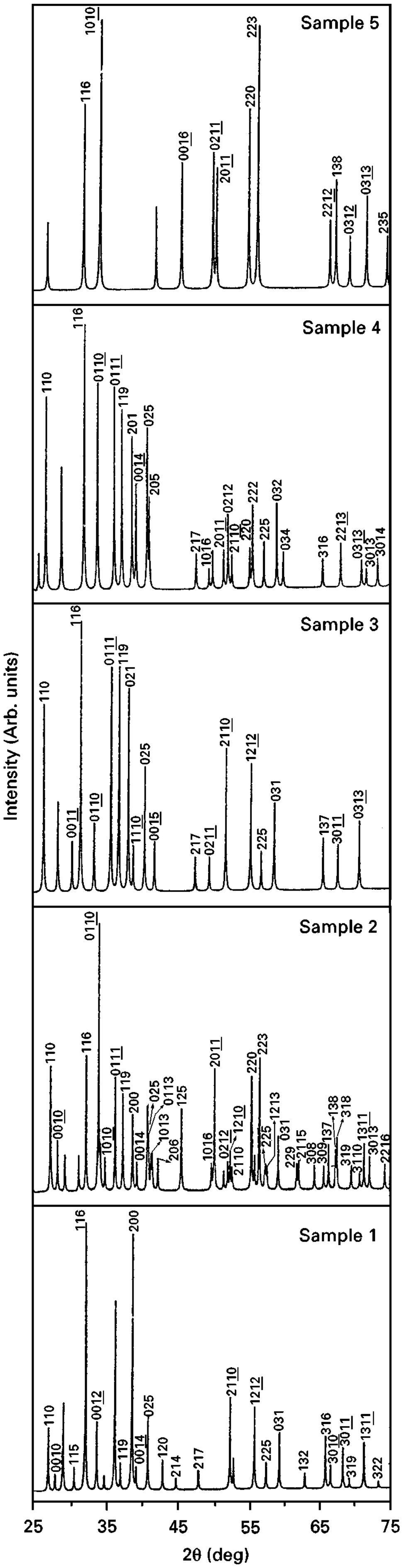

Figure 5 X-ray diffraction patterns of the five samples.

TABLE III Lattice parameters for the five samples

Sample	Lattice parameters (nm)		
	a	*b*	*c*
1	0.5405(6)	0.5448(7)	3.730(1)
2	0.5400(6)	0.5452(7)	3.726(8)
3	0.5419(7)	0.5449(4)	3.725(6)
4	0.5406(4)	0.5453(4)	3.722(5)
5	0.5410(1)	0.5460(1)	3.700(1)

A few lines could not be indexed; these may indicate some low-T_c phase.

4. Conclusion

Samples were prepared by the solid-state reaction method and assuming identical thermal histories. The nominal starting compositions were $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{4.5}O_y$ and $Bi_{1.6}Pb_{0.2}Sr_2Ca_2Cu_4O_y$. Step sintering was found to be more favourable towards magnetic properties of the samples. Sustained sintering made the systems more metallic like and a smooth variation in resistivity with temperature was observed. It is observed that a long sintering period enhances the amount of high-T_c phase, as had been reported earlier [16]. Lattice parameters obtained for the phases by XRD are comparable to those reported in the literature for 2223 high-T_c phase. It can be stated that 222(4.5) and (1.8)224 compositions are very similar to 2223 compositions. Also an increase in copper or a decrease in lead showed similar results. In order to improve high-T_c phase, it is necessary to evaluate the exact ratio of all the stoichiometric components. Further work on compositional variation in barium, copper and strontium is in progress.

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