

Lead-doped bismuth ceramics; superconducting properties and effect of particle size

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The optimum lead concentration for maximum critical current density has been determined. Variations of superconducting transition temperature and critical current density with sintering duration are reported. Density variation with lead concentration was also measured. The effects of different starting particle sizes on the values of the superconducting transition temperature and critical current density were also studied.

1. Introduction

Since the discovery of multiphase $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ superconducting systems ($n = 1, 2, \text{ and } 3$), there have been many attempts [1–4] to stabilize the high- T_c phase and to increase its volume fraction in the system. A number of reports have been published [5–10] on such systems doped with lead (i.e. $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$), showing that the addition of lead helps to grow and stabilize the high- T_c phase. The variation of transition temperature, T_c , with lead concentration in this system has been widely studied [5–10]. However, insufficient systematic work has been reported on the study of critical current density, J_c , and its variation with lead concentration.

Because of its superior superconducting properties, the $n = 3$ phase of $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ (or 2223 phase) [5–13] provides good impetus for further investigations. In this paper we report a systematic investigation of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ system with x varying from 0.0–0.8, to determine (i) the optimum lead concentration to obtain maximum critical current density, and (ii) the effect of time of sintering on the critical current density. To study the effects of starting particle size on the values of T_c and J_c , samples with $x = 0.3$, which exhibit the highest T_c and J_c values, of different particle size, were prepared and studied.

2. Experimental procedure

$\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ceramics were prepared using high-purity oxides and carbonates. The starting materials, taken in appropriate amounts, were thoroughly mixed and ground until the entire material passed through a 75 μm sieve. To study the effects of the particle size, samples of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ with four different starting particle sizes (i. e. ≤ 125 , 75, 53, and 40 μm) were prepared. Appropriate weights of the starting chemicals were mixed. The resulting powder was passed through appropriate sieves to select materials of the desired particle size. These samples are denoted 125, 75, 53 and 40, respectively. The filtered product was presintered at 800 °C for

24 h. The presintered samples were reground and passed through respective sieves and then pelletized. Final sintering of the pellets was done at 850 °C for varying durations and they were subsequently quenched in air. This sintering temperature and the subsequent rapid quenching in air are reported to be the most favourable conditions for the formation of high- T_c phase [11, 14]. Resistance measurements from 77 K to room temperature were carried out by a four-probe technique at 30 Hz using a lock-in-amplifier. Electrical contacts were made using silver epoxy resin. Critical current density measurements were made by the four-probe d.c. method employing the 1 $\mu\text{V cm}^{-1}$ criterion. Scanning electron micrographs were taken using a Philips SEM model 525M. Density measurements were carried out at room temperature using the displacement method. The samples were weighed using a balance with 0.1 mg accuracy.

3. Results

Fig. 1 shows the observed critical current density of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (x from 0.2–0.6) sintered for 70 and 140 h. Samples for $x = 0.0$ and 0.1 did not show $T_{c,\text{zero}}$ up to 77 K [10], and hence their J_c values could not be measured. It was observed that for both these sintering durations, the value of J_c increased sharply for the sample with $x = 0.2$ to that for the sample corresponding to $x = 0.3$, and as x increased further, J_c decreased continuously. It may be pointed out that similar variation in the value of $T_{c,\text{zero}}$ with x was observed [10]. Samples with $x = 0.7$ and 0.8 showed a very small critical current density ($\approx \text{mA cm}^{-2}$). As can be seen from Fig. 1, the J_c values for 140 h sintered samples are much higher than those of samples sintered for 70 h. The duration of sintering thus plays a crucial role. The difference in the two J_c values is maximum for $x = 0.3$. To examine further the effect of sintering duration on J_c , samples which showed maximum J_c , i. e. $x = 0.3$, were prepared again and sintered for 35 and 210 h. The critical current density values observed for samples sintered for 35 and 210 h, as well as those of samples sintered

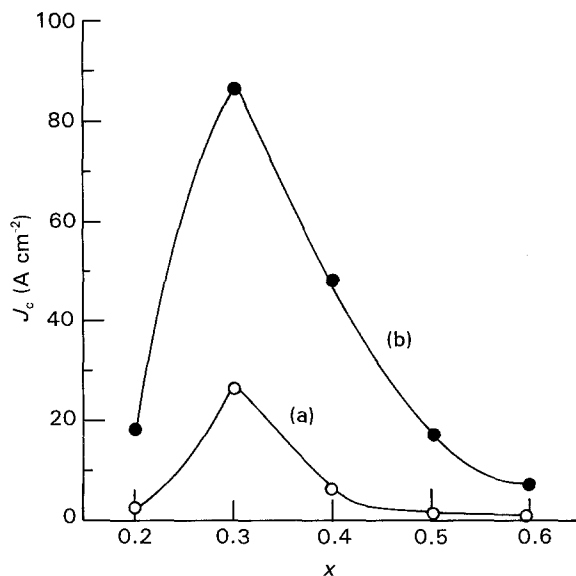


Figure 1 Variation of critical current density with x in the system $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ sintered for (a) 70 h and (b) 140 h.

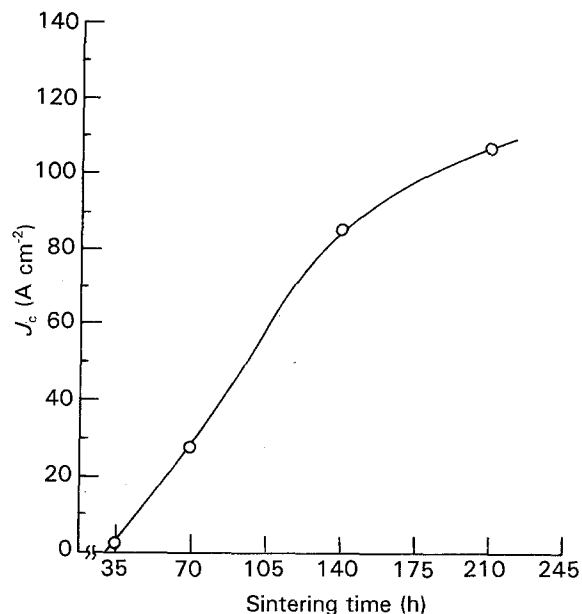


Figure 2 Variation of J_c with sintering time of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$.

for 70 and 140 h, are shown in Fig. 2. As can be seen, the J_c values are fairly sensitive to the sintering time. The observed $T_{c,\text{zero}}$ values of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ samples of different particle sizes and sintered for different durations are given in Table I. Fig. 3 shows a few typical R - T curves. It is observed that longer sintering times result in a slight increase in the value of $T_{c,\text{zero}}$. From the data presented in Table I, it follows that the 75 μm sample has the highest value of $T_{c,\text{zero}}$, and that samples of larger particle size require longer sintering times in order to exhibit superconducting transition in the temperature range studied in the present work.

Fig. 4 shows the observed variation of critical current density with particle size for samples sintered for 210 h. It is observed that of the samples studied, those with a particle size of 53 μm have the highest values of J_c .

Fig. 5a and b show scanning electron micrographs of two samples, 75 and 40, respectively. A careful observation of the micrographs reveals that both samples have randomly oriented grains and that sample 40 has grains smaller than those of sample 75. It is expected that any electric current through sample 40 will encounter a larger number of grain boundaries than that passing through sample 75.

Fig. 6 shows the density variation of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ with x . The density decreases from 5.05 g cm^{-3} to 3.48 g cm^{-3} as x increases from 0.0–0.4. Beyond $x = 0.4$, the density shows an increase up to $x = 0.8$, almost regaining its initial value corresponding to $x = 0.0$.

4. Discussion

Improvement in the values of $T_{c,\text{zero}}$ and J_c with longer sintering times can be explained on the basis of the fact that impurity phases, such as Ca_2PbO_4 and low- T_c phase, are expected to transform into high- T_c phase on prolonged sintering, thereby increasing the

TABLE I $T_{c,\text{zero}}$ of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ samples of different particle sizes sintered for different durations.

Sintering time (h)	$T_{c,\text{zero}}$ (K)			
	125 μm	75 μm	53 μm	40 μm
35	a	a	90	84
70	a	111	109	107
140	84	111	111	111
210	104	113	111	111

^a $T_{c,\text{zero}}$ not obtained.

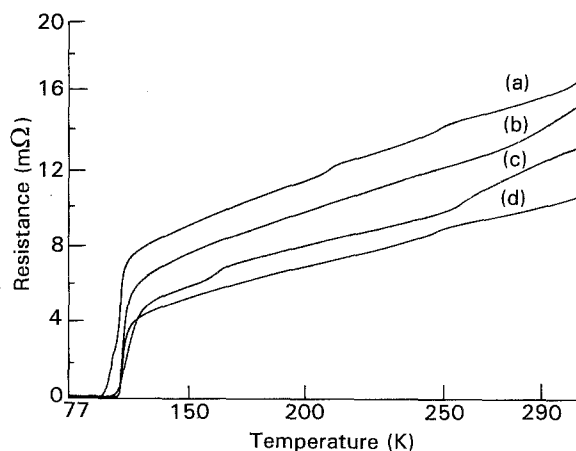


Figure 3 Typical resistance-temperature curves of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ of particle size (a) 125 μm (b) 75 μm , (c) 53 μm , and (d) 40 μm ; all sintered for 210 h.

volume fraction of the high- T_c phase [10, 12]. In addition, a remarkable increase in the value of J_c with increasing sintering time suggests an improved coupling between the superconducting grains. The initial increase in the value of $T_{c,\text{zero}}$ up to $x = 0.3$, and a subsequent decrease with increasing x , was reported in an earlier work [10]. A similar behaviour is observed

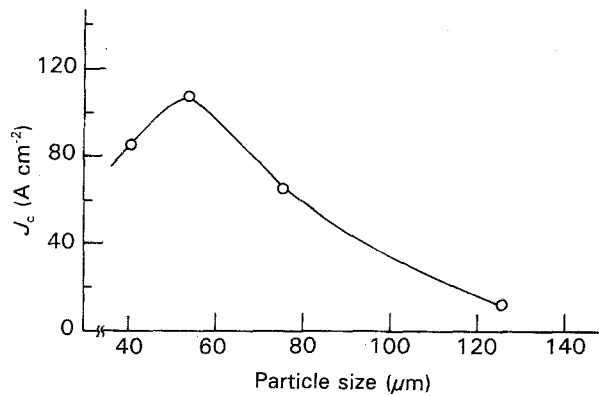


Figure 4 Variation of J_c with particle size of a sample with $x = 0.3$.

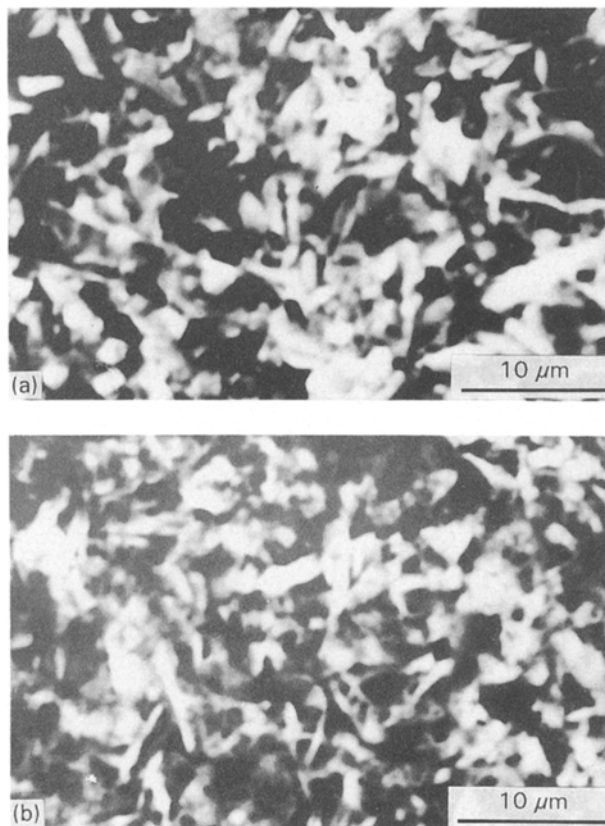


Figure 5 Scanning electron micrographs of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ samples (a) 75 and (b) 40, both sintered for 70 h.

for J_c , as shown in Fig. 1. For low concentrations ($x \leq 0.3$) almost all of the added lead exists as Pb^{2+} [10]. The replacement of Bi^{3+} ions by Pb^{2+} ions generates additional holes in the CuO planes in order to conserve electrical charge and this results in an increase in the values of $T_{c,\text{zero}}$ and J_c . For $x \geq 0.4$, some of the added lead exists as Pb^{4+} , and charge conservation considerations suggest suppression of superconductivity [10]. Lead going into the system as Pb^{2+} and Pb^{4+} for lower and higher values, respectively, of x , also explains the observed density variation, Fig. 6.

Density variation could be due to changes in mass and/or volume of the unit cell. In a large unit cell of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, replacement of a small quantity of bismuth (atomic mass 208.98 a.m.u) by its

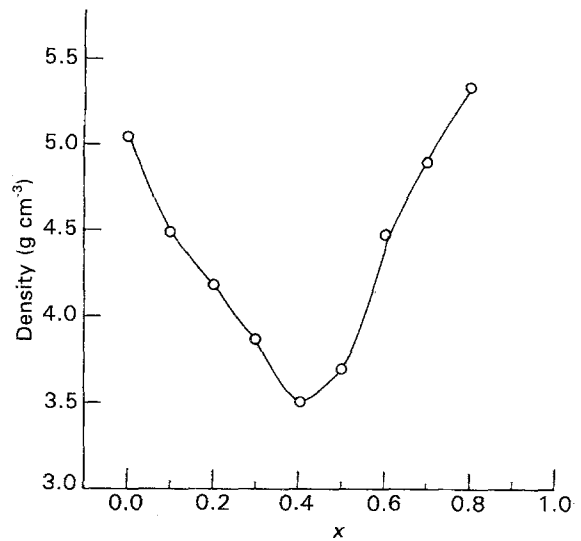


Figure 6 Density variation of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ with x , of samples sintered for 70 h.

neighbouring atom, lead (atomic mass 207.19 a.m.u), in the periodic table, cannot account for sufficient change in mass needed to explain the observed variation in density. The changes in density are, therefore, due primarily to the changes in the volume of the unit cell. It was concluded in earlier reports [10, 12] that lead predominantly occupies bismuth sites. The radii of Bi^{3+} and Pb^{2+} being 0.096 and 0.12 nm, respectively, replacement of Bi^{3+} by Pb^{2+} will increase the volume of the unit cell. For $x \geq 0.4$, however, as stated earlier, lead enters as Pb^{4+} (radius 0.084 nm), resulting in a reduction in the lattice parameters; a reduction in the value of the c -parameter has been reported in the past [10, 15]. Density increase with x for $x > 0.4$ is thus unstable. From the difference in the radii of Pb^{2+} and Pb^{4+} from that of Bi^{3+} , the initial decrease in the value of density with x is expected to be faster than the subsequent increase. This is indeed observed in the present investigations.

There are reports that low density is one of the causes of low J_c value [16, 17]. However, the value of J_c is also sensitive to the number of holes, the absence of low- T_c and impurity phases, good intergrain coupling and high volume fraction of the 2223 phase present. The effect of all these factors, which are influenced by the amount of lead present in the system, is to increase the value of J_c . As indicated earlier, when x increases above 0.3, the hole concentration decreases, impurity phases such as Ca_2PbO_4 are increasingly formed [13], which deteriorate intergrain coupling. The observed values of J_c suggest that these effects become important in samples with higher x values and overtake the opposing effects due to density variation.

It is known that partial melting during sintering helps to grow the high- T_c phase [11, 18] probably by enhancing proper diffusion and improving connectivity of grains. Partial melting of the starting powder is expected to be related to the particle size. Larger particles require a longer sintering time and probably higher sintering temperature to undergo partial melting and hence proper diffusion. Larger particles

therefore do not show superconducting transition when sintered for short times. Insufficient diffusion is also the cause of poor coupling between the grains which results in lower values of J_c . However, when the particle size is made very small, the number of grain boundaries increases causing a degradation of superconducting properties. It thus follows that whereas large particle size is not suitable for better superconducting properties, very small particle size does not favour it either. The present work suggests that the best starting particle size is around 53 μm .

5. Conclusions

The sample with $x = 0.3$ exhibits the highest value of J_c . A longer sintering time is very effective in increasing the value of J_c . The effect of density on the value of J_c is significant at lower x values; at higher x values the opposite effect dominates. Samples with a starting particle size of 53 μm give the best superconducting properties.

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