

Influence of sintering time and quenching on the formation of high T_c phase

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Abstract. Influence of sintering time and quenching in $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ ($x = 0.0, 0.1, 0.2, 0.25, 0.3$ and 0.4) samples have been studied by resistance and XRD measurements. In samples sintered at 850°C for 4 days, $T_c(0)$ increases with Pb concentration. $T_c(0)$ increased from 81 K for $x = 0.0$ to 109 K in $x = 0.30$ sample and then decreased. Increasing the sintering time to 10 days decreased the T_c . Quenching further decreased the $T_c(0)$. From X-ray diffraction patterns, the intensity peaks of low and high T_c phases have been measured. The addition of Pb promotes high T_c -phase. Sintering time, slow cooling and rapid quenching studies show that there is an optimum sintering time and cooling rate to produce a high T_c -phase.

Keywords. Sintering time; quenching; high T_c phase.

1. Introduction

A new family of high T_c superconductors, Bi–Ca–Sr–Cu–O, have been discovered by Maeda *et al* (1988) and Chu *et al* (1988) without the presence of any rare earth element. These compounds however showed two phases: one with the onset temperature of 70–80 K called the low T_c -phase and the other a high T_c -phase with onset temperatures between 110 and 120 K. This has led to a spurt of research activity in this system to obtain a single high T_c -phase. Earlier results showed that simply varying the composition and heat-treatment conditions were not sufficient for obtaining the high T_c -phase. Sunshine *et al* (1988) and Green *et al* (1988) showed that by addition of small amounts of lead in place of bismuth, $T_c(0)$ as high as 107 K could be obtained. The optimum concentration of lead and sintering conditions however differed very much from one another. Further the role played by lead in increasing the transition temperature is not understood clearly. We have therefore undertaken a systematic investigation of the effect of composition of lead, sintering time and quenching rate in the $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ system. The X-ray diffraction and resistivity results are presented. An attempt has been made to explain the role of lead in this system.

2. Experimental

The samples were prepared by solid-state reaction. Appropriate amounts of Bi_2O_3 , PbO , CaO , SrCO_3 and CuO were taken in molar ratios $2-x$; x ; 2; 2; 3 (where $x = 0.0, 0.10, 0.20, 0.25, 0.30$ and 0.40) and the powders were mixed and ground. The mixed powders (first batch) were heated at 750°C for 16 hr, at 800°C for 24 hr and 830°C for 50 hr, followed by intermediate grinding at each step. These were then pressed into pellets of 1 cm diameter by applying a load of 5 tons and sintered at 850°C for 4 days followed by slow cooling to room temperature. The second batch powders were heated at 750°C for 16 hr and at 800°C for 24 hr and pressed into

pellets. These samples were sintered for 10 days at 850°C. Among the second batch, the first set of samples was slowly cooled in the furnace to room temperature, the second set of samples were quenched to room temperature in air and the third set quenched in liquid nitrogen. The samples with $x = 0.0, 0.10, 0.20, 0.25, 0.30$ and 0.40 were designated as A, B, C, D, E and F respectively. D.C. resistance was measured with a standard Vander Paw technique using a Keithley nanovoltmeter and a constant current source. A current of 10 mA was sent through all the samples.

3. Results and discussion

Figure 1 shows the R_T/R_{\max} vs temperature graphs for samples A, B, D and E sintered at 850°C for 4 days and slowly cooled in the furnace to room temperature. As can be seen from the figure, $T_c(0)$ increases gradually from 81 K for sample A to 109 K for sample E. For sample F however $T_c(0)$ decreases to 89 K. As compared to samples A, B and D where the width of the transition is broad, the fall in resistance is steep in sample E. These results show that with increase in doping not only T_c increases but the volume fraction of high T_c -phase also increases and at higher concentrations T_c decreases.

Figure 2 shows the results of R_T/R_{\max} vs temperature for samples A, B, D and E sintered for 10 days at 850°C and slowly cooled in the furnace to room temperature.

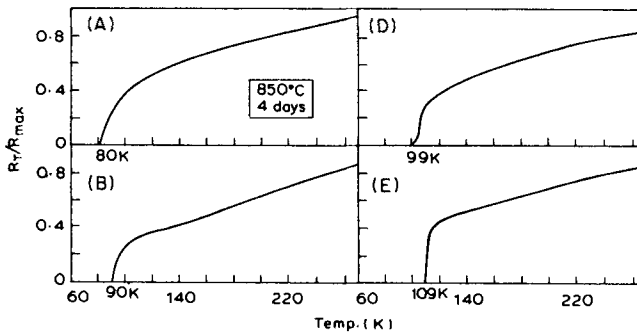


Figure 1. Resistance vs temperature curves for 4 days annealed samples A, B, D and E.

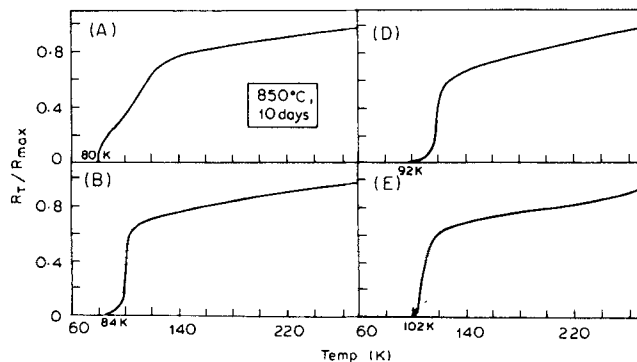


Figure 2. Resistance vs temperature curves for 10 days annealed samples A, B, D and E.

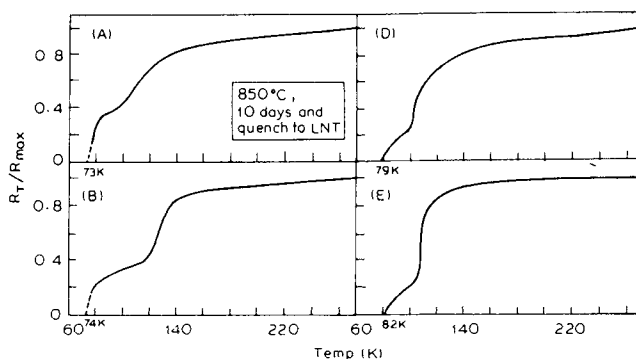


Figure 3. Resistance vs temperature curves for liquid nitrogen quenched samples A, B, D and E.

Table 1. Transition temperatures (in K)

Compound	First batch		Second batch	
	$T_c(0)$	1 set $T_c(0)$	2 set $T_c(0)$	3 set $T_c(0)$
$\text{Bi}_2\text{Co}_2\text{Sr}_2\text{Cu}_3\text{O}_y$	81	79	76*	73*
$\text{Bi}_{1.9}\text{Pb}_{0.1}\text{Co}_2\text{Sr}_2\text{Cu}_3\text{O}_y$	90	84	77	74*
$\text{Bi}_{1.80}\text{Pb}_{0.2}\text{Co}_2\text{Sr}_2\text{Cu}_3\text{O}_y$	98	88	82	78
$\text{Bi}_{1.75}\text{Pb}_{0.25}\text{Co}_2\text{Sr}_2\text{Cu}_3\text{O}_y$	99	92	86	79
$\text{Bi}_{1.70}\text{Pb}_{0.30}\text{Co}_2\text{Sr}_2\text{Cu}_3\text{O}_y$	109	102	92	82
$\text{Bi}_{1.60}\text{Pb}_{0.40}\text{Co}_2\text{Sr}_2\text{Cu}_3\text{O}_y$	89	—	—	—

*Obtained after extrapolation.

In these samples $T_c(0)$ increased from 79 K to 102 K with increase in Pb concentration. The width of the transition is very large for sample A as compared to D and the behaviour is the same as those sintered for 4 days. In samples B and D one can notice tails before T_c goes to zero. The same behaviour was observed by Tarascon *et al* (1988), Sastry *et al* (1989) and several others. This we attribute to the presence of a well-separated low T_c -phase from the high T_c -phase. To examine this further, the samples sintered at 850°C for 10 days were quenched in liquid nitrogen and the results obtained are shown in figure 3. In samples A and B the $T_c(0)$ are below LNT and those of D and E are 79 K and 82 K respectively. These results show that by quenching or rapidly cooling, the transition temperatures decreased considerably. Further one can notice long resistance tails in all the graphs indicating that the volume fraction of low T_c -phase increased due to quenching. Similar studies were made in samples sintered at 850°C for ten days and quenched to room temperature. The $T_c(0)$ are found to be intermediate to those of slowly-cooled and liquid nitrogen-quenched samples. The transition temperatures are given in table 1.

These results suggest longer sintering times than optimum, and rapid cooling decreases the volume fraction of the high T_c -phase and the transition temperature. To check these observations XRD studies were carried out and the results are presented in figures 4–6.

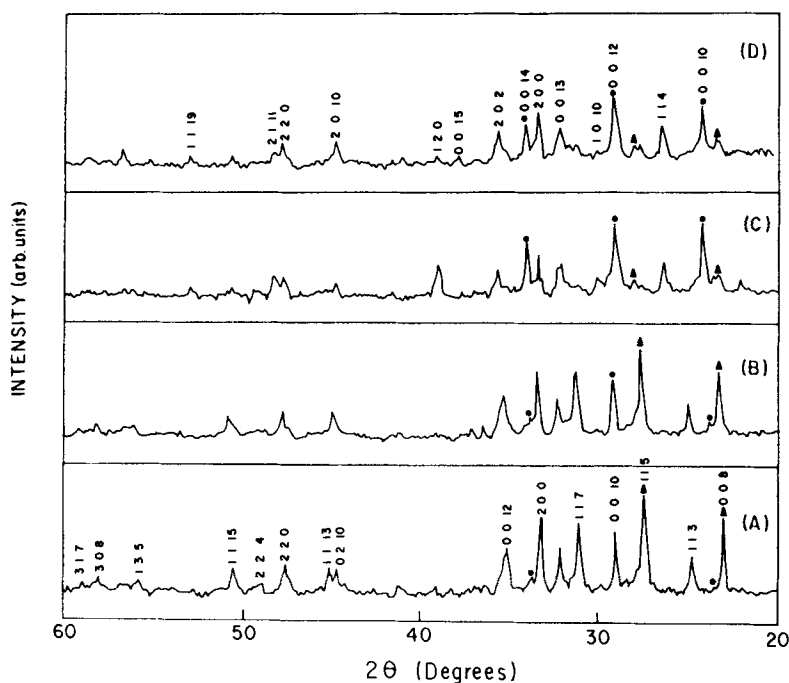


Figure 4. X-ray powder diffraction patterns of samples A, B, C and D (batch II, set 1) over the 2θ range from 20° and 60° obtained using a CuK_α radiation. The peaks denoted by (●) and (▲) correspond to the high and low T_c -phases respectively.

Figure 4 shows the X-ray diffraction patterns for samples A, B, C and D. The peaks for sample A have been indexed on the basis of Hazen *et al* (1988) and Chavira *et al* (1988) whereas those of B, C and D have been indexed following Jian *et al* (1988) and Chavira *et al* (1988). Accordingly peaks denoted by triangles correspond to the low T_c -phase whereas those shown by dots represent the high T_c -phase. It is clear from the figure that the reflections due to high T_c -phase significantly increase due to the addition of lead and those due to low T_c -phase decrease. These results show that the volume fraction of high T_c -phase increases with Pb concentration.

The X-ray diffraction for samples quenched in liquid nitrogen (figure 5) shows lower T_c compared to those cooled slowly to room temperature. A closer examination of the reflections and their intensities show that the high T_c -phase reflections increase in general while those of low T_c -phase decrease with increase in Pb concentration (figure 4).

Unlike in slowly-cooled samples, the intensities of reflections of low T_c -phase in sample B are greater as compared to sample A. Similarly in sample D, one can see both high and low T_c -phases. These results show that due to quenching the high T_c -phase probably dissociates partially into low T_c -phase and consequently T_c decreases. To examine this in more detail, the high T_c -phase and the low T_c -phase which are characterized by (002) reflections at $2\theta \simeq 4.85^\circ$ and $2\theta \simeq 5.78^\circ$ have been recorded on slowly cooled and liquid nitrogen quenched samples. These results are shown in figure 6 and their corresponding data presented in table 2. From table 2 one can

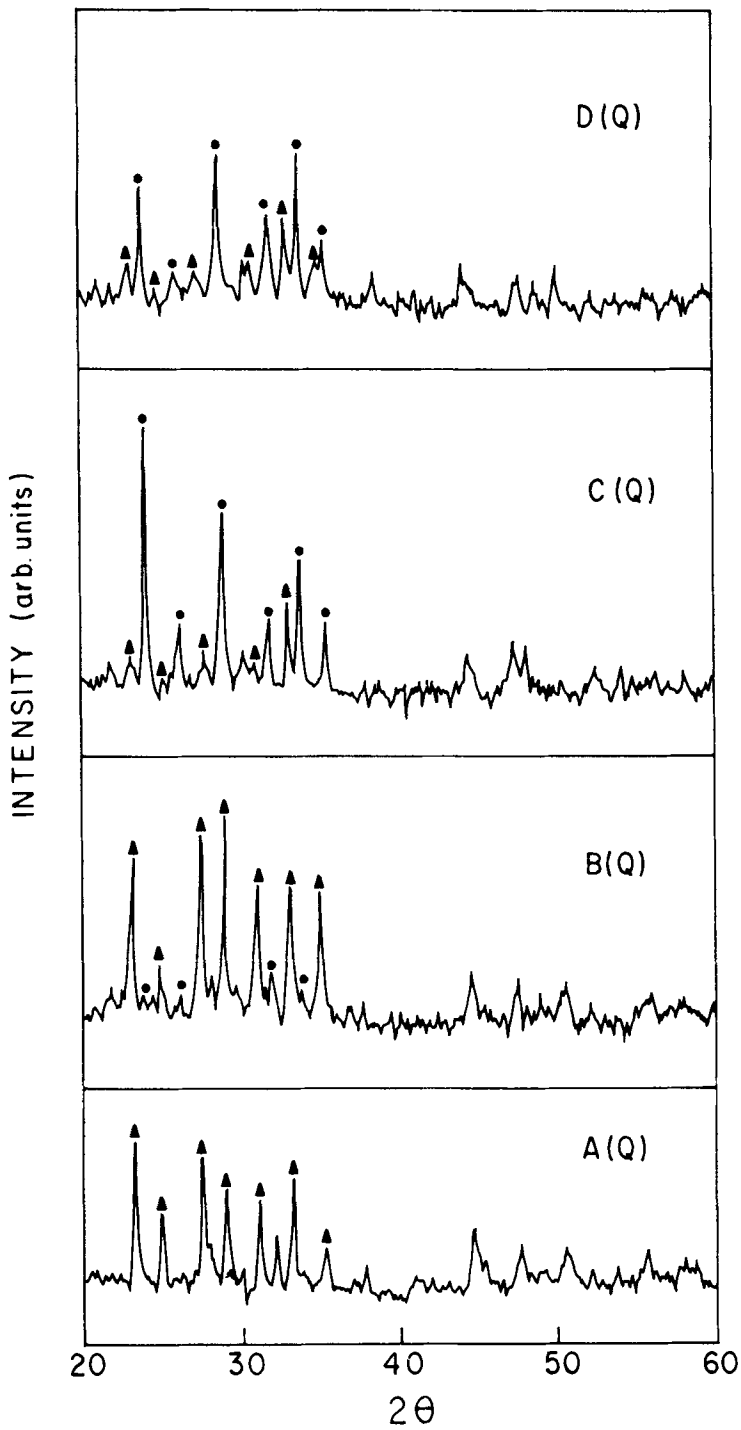


Figure 5. X-ray powder diffraction patterns of samples $A(Q)$, $B(Q)$, $C(Q)$ and $D(Q)$ (batch II, set 3) over the 2θ range from 20° and 60° obtained using a CuK_α radiation. The peaks denoted by (●) and (▲) correspond to the high and low T_c -phases respectively.

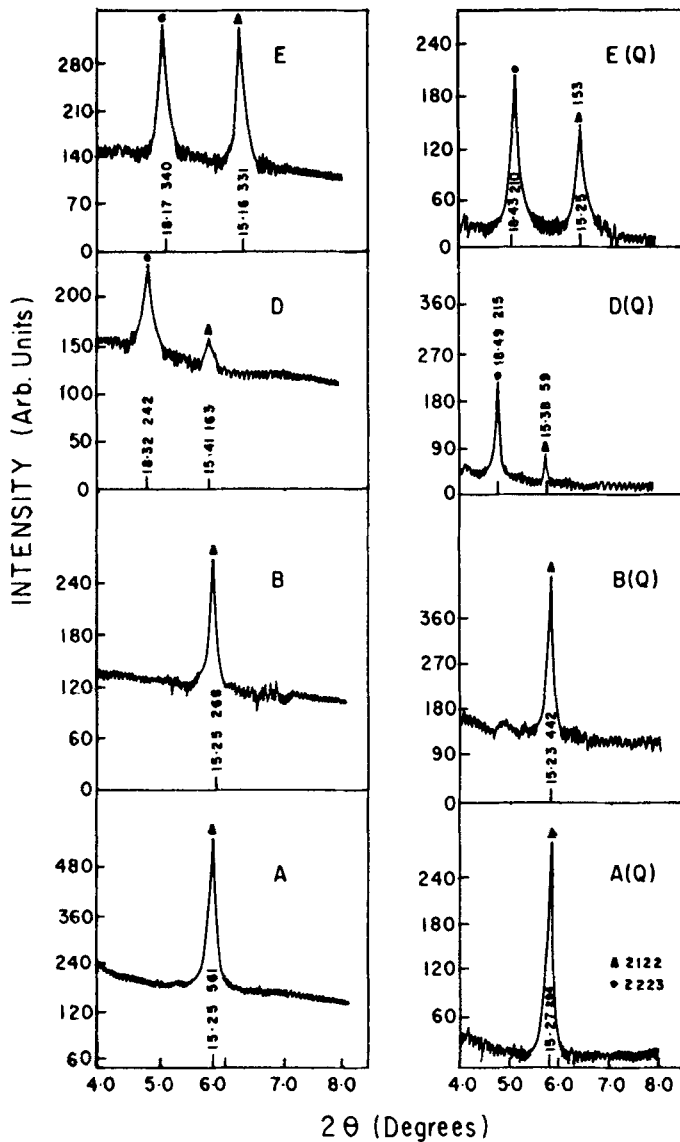


Figure 6. X-ray powder diffraction of (002) reflection for the samples A, B, D and E (batch II, set 1) and A(Q), B(Q), D(Q) and E(Q) (batch II, set 3). The peaks denoted by (●) and (▲) correspond to the 2223 and 2122 phases respectively.

notice that in $x = 0.10$ sample the intensity of 5.78 \AA low- T_c reflection peak is higher in quenched sample as compared to slowly-cooled ones. One can also notice that the intensity of high T_c -phase (4.81 \AA) decreased with quenching both in $x = 0.25$ and 0.30 samples. These results again confirm that the volume fraction of high T_c -phase decreases with quenching.

The results show that the concentration of Pb, sintering time, temperature and cooling rates appear to play an important role on the formation of high T_c -phase.

Table 2. Details of (002) reflection for slowly-cooled and quenched $\text{Bi}_{2-x}\text{Pb}_x\text{Co}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ samples

x	10 days at 850°C and slowly-cooled to room temperature						10 days at 850°C and quenched to liquid nitrogen temperature							
	Low T_c -phase			High T_c -phase			Low T_c -phase			High T_c -phase				
	$T_c(0)$	2	d	I_{\max}	2	d	I_{\max}	$T_c(0)$	2	d	I_{\max}	2	d	I_{\max}
0.0	79 K	5.79	15.253	561.5	—	—	—	73 K	5.782	15.272	284.1	—	—	—
0.10	84 K	5.789	15.255	268.0	—	—	—	74 K	5.797	15.234	442.0	—	—	—
0.25	92 K	5.72	15.41	163.0	4.81	18.325	242	79 K	5.74	15.38	59.4	4.79	18.409	215.4
0.30	102 K	5.82	15.16	331.0	4.859	18.173	340.0	82 K	5.787	15.25	153.2	4.79	18.43	210.4

4. Conclusions

- (i) The addition of Pb increases the volume fraction of high T_c -phase and also $T_c(0)$.
- (ii) There is an optimum concentration of Pb above which $T_c(0)$ decreases.
- (iii) There is optimum sintering time, above which $T_c(0)$ decreases.
- (iv) Quenching or rapidly cooling the samples decreases the volume fraction of high T_c -phase and lowers T_c .

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