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Interplay of low and high T_c phases in Bi–Sr–Ca–Cu–O superconductor

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Abstract. In the Bi–Sr–Ca–Cu–O system stringent conditions of heat-treatment lead to the formation of a mixture of both the low and high T_c phases and obtaining a single-phase material becomes extremely difficult. This study reports preparation of samples with single superconducting transitions at ~ 75 K and ~ 108 K; the compositions of which correspond to $n = 2, 3$ in the series $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$. X-ray diffraction studies show that the lower T_c material is a relatively pure phase while the higher T_c phase only co-exists with the lower T_c phase. The most obvious effect of doping the system with lead is to make the reaction take place faster and thereby increase the volume fraction of the 110 K phase.

Keywords. Low T_c phase; high T_c phase; Bi-superconductor.

1. Introduction

In general, superconductivity at temperatures greater than 100 K becomes a possibility in Bi- and Tl-based materials when additional Ca–CuO_2 layers are intercalated into a lower T_c structure. The Bi-superconductor belongs to the structural family $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ (Tarascon *et al* 1988) in which the phases corresponding to $n = 1$ to 3 have so far been found to be superconducting. The Ca-free material ($n = 1$) has a very low T_c of 7 K (Michel *et al* 1987) and much interest in this series began with the increase in T_c to 80 K (for $n = 2$) and 110 K (for $n = 3$) rendered by the inclusion of additional Ca–CuO_2 layers (Maeda *et al* 1988). While it is speculated that the 80 K phase is the most stable phase in this system, the solid-state diffusion method invariably leads to a mixture of all the above phases and even the 80 K material is not obtained as a single phase unless the processing conditions are carefully controlled. As of today, obtaining the 110 K structure as a single phase in the pure Bi–Sr–Ca–Cu–O system has not been possible at all. However, this has been achieved with the help of several dopants. Pb-doping, first attempted by Sunshine *et al* (1989) has been effective in stabilizing the 110 K phase and thereby increasing its volume fraction in the sintered material even though the uncertainty regarding the role of Pb still exists. The interplay of these low and high T_c phases during fabrication leads to interesting superconducting properties and it is the aim of this paper to point out some of these.

2. Experimental

The starting materials used for the preparation of the Bi-based copper oxide superconductors were high purity (> 99.9%) Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO and PbO. These materials were mixed in various proportions (the details of all the compositions tried are reported elsewhere) (Upadhyay *et al* 1990) and calcinated at temperatures between 810 and 820°C for about 20 h. The calcinated powders were ground, pelletized, and sintered in air and oxygen at different temperatures. The pure Bi–Sr–Ca–Cu–O system was sintered at 850, 860 and 875°C while the Pb-doped materials were heat-treated at 820, 830, 835 and 845°C. The four-probe a.c. resistivity method was used to determine the transition temperatures. X-ray diffraction was studied on Siemens D-500 diffractometer using the standard CuK_α radiation. Scanning electron micrograph was taken on the JEOL-JSM 35CX unit operating at 25 kV.

3. Results

3.1 *Undoped Bi–Sr–Ca–Cu–O system*

Figure 1 shows the resistance versus temperature curves for the samples prepared from the 1112 starting composition of the undoped material. Curve A represents the sample sintered at 850°C for 10 days. The gradual decrease in resistance before the sharp drop to zero at 75 K suggests that the formation of the 110 K phase has not taken place. The same composition when sintered at 860°C, however, does show onset of superconductivity at 110 K and zero resistance at 80 K. The increase in $T_c(0)$ also indicates that when the conditions are favourable for obtaining an ordered 80 K structure they also promote formation of the 110 K phase. This makes isolation of either phase very difficult. The other starting compositions (2212, 2223, 4334 etc.—details reported elsewhere) also show similar two transitions and only the relative fractions and sharpness of the curves vary with the sintering conditions.

XRD patterns of most samples show strong peaks corresponding to reflections due to the elongated c-axis. Figure 3 shows the typical pattern observed for the low T_c (2212) phase. In the low angle region only one peak at 2θ value of 5.6°; corresponding to the (002) reflection, suggests that only the 2212 phase is dominant in the sample. Most lines in the spectra can be identified with the b.c.t structure with lattice

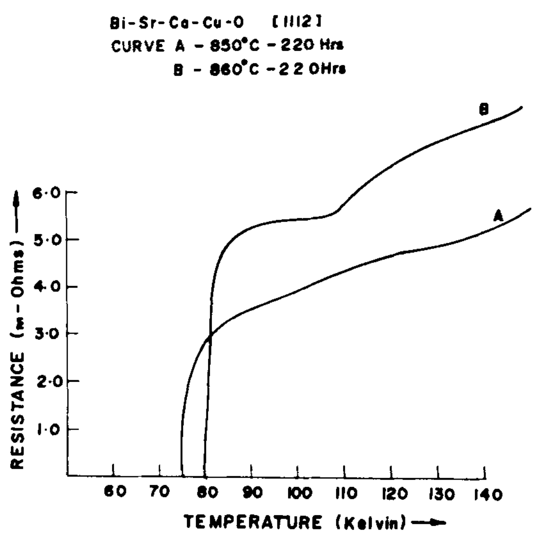

Figure 1. Resistance vs temperature curve for pure Bi–Sr–Ca–Cu–O samples. Sintering at lower temperature (A) prevented the formation of high T_c phase which is indicated by the drop in resistivity at 115 K (B).

parameters $a = b = 3{\cdot}894$ Å and $c = 30{\cdot}588$ Å. The remaining lines (not marked in the figure) either correspond to the un-reacted material such as CuO ($2\theta = 37{\cdot}4°$) or they are due to reflections from planes other than $(00l)$ where $l = 2, 6, 8$ etc. as indicated in the figure.

3.2 *Pb-doped system*

R-T curves for Pb-doped samples $Bi_{1\cdot8}Pb_{0\cdot2}Sr_2Ca_2Cu_3O_x$ and $Bi_{1\cdot4}Pb_{0\cdot6}Sr_2Ca_2Cu_3O_x$ are shown in figure 2a,b. The samples of both compositions when sintered at 835°C for only 65 h show sharp transitions with onset at 110 K and $T_c(0)$ at 104 K for Pb = 0·2 (curve A figure 2a) and T_c onset at 112 K and $T_c(0)$ at 108 K for Pb = 0·6 (curve A figure 2b). Figure 2a also shows the effect of prolonged annealing on the $Bi_{1\cdot8}Pb_{0\cdot2}Sr_2Ca_2Cu_3O_x$ composition. It is seen that while the onset of transition remains around 110 K the $T_c(0)$ begins to shift to a lower value as the duration of sintering is increased (curves B and C figure 2a). $T_c(0)$ shifts from 104 K to 80 K when the sintering time is increased from 65 to 220 for this composition. The same effect is observed in the $Bi_{1\cdot4}Pb_{0\cdot6}Sr_2Ca_2Cu_3O_x$ composition when the sintering temperature is raised to 845°C (figure 2b). The stability of the 110 K phase is more sensitive to duration of sintering in samples having low Pb-content as indicated by the broad transitions observed in figure 2a. It is also sensitive to temperatures of sintering as zero resistance above 77 K was not readily obtained when sintering is done at 845°C, which was not the case for the $Bi_{1\cdot4}Pb_{0\cdot6}Sr_2Ca_2Cu_3O_x$ samples.

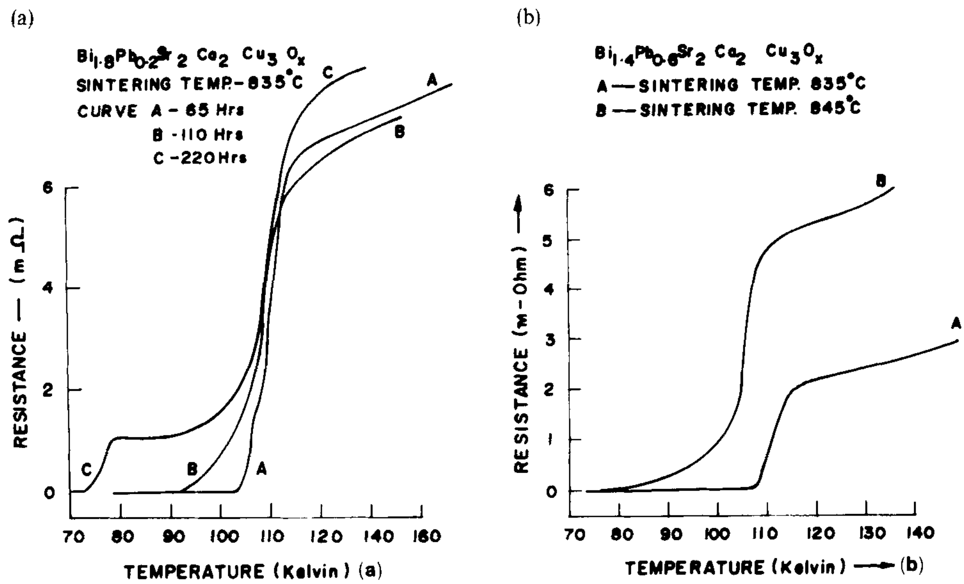

Figure 2. **a.** Resistance vs temperature curve for Pb-doped $Bi_{1\cdot8}Pb_{0\cdot2}Sr_2Ca_2Cu_3O_x$ samples. The shift in resistance zero towards lower T_c increases with longer sintering time indicating the disintegration of the 110 K phase. **b.** Resistance vs temperature curve for Pb-doped $Bi_{1\cdot4}Pb_{0\cdot6}Sr_2Ca_2Cu_3O_x$ samples. Higher sintering temperature also has the same effect of shifting the T_c (zero) to a lower value.

4. Discussion

The above results show that to obtain reproducible zero resistance in the un-doped Bi–Sr–Ca–Cu–O material (at 80 K) sintering time of about 10 days is required whereas the Pb-doped samples easily show this behaviour (zero *R* at temperatures greater than 100 K) when sintered for only 65 h. In fact, doping with Pb so much enhances the formation of superconducting phases that the 80 K material gets formed during calcination of fresh oxides (Bi, Cu and Pb) and carbonates (Sr and Ca). This can be seen from the XRD pattern of the $Bi_{1\cdot4}Pb_{0\cdot6}Sr_2Ca_2Cu_3O_x$ sample taken just after calcination at 810°C for 20 h (figure 4). The strong (002) peak at 2θ value of 5.6° (and other lines also as indicated in the figure) corresponds to the 2212 structure. Of course, there is plenty of un-reacted material—as evidenced from the unidentified peaks in the figure because sufficient time of heat-treatment has not been allowed. Figure 5 shows the XRD pattern of the same sample as of figure 4 after it was pelletized

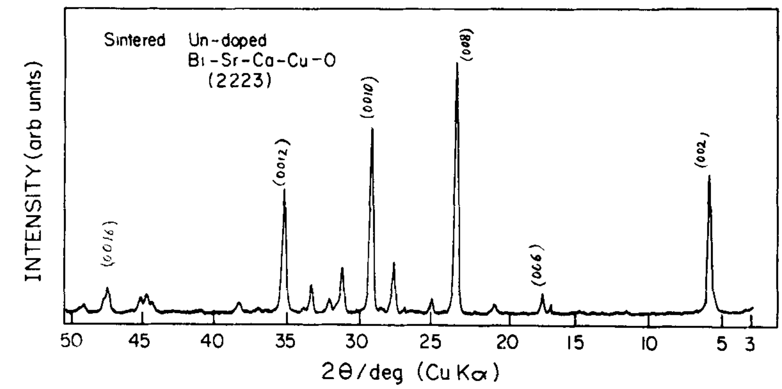

Figure 3. XRD pattern of an un-doped Bi–Sr–Ca–Cu–O sample showing strong peaks of the low T_c 2212 phase confirming the long periodicity of the *c*-axis (as indicated by the (00*l*) lines).

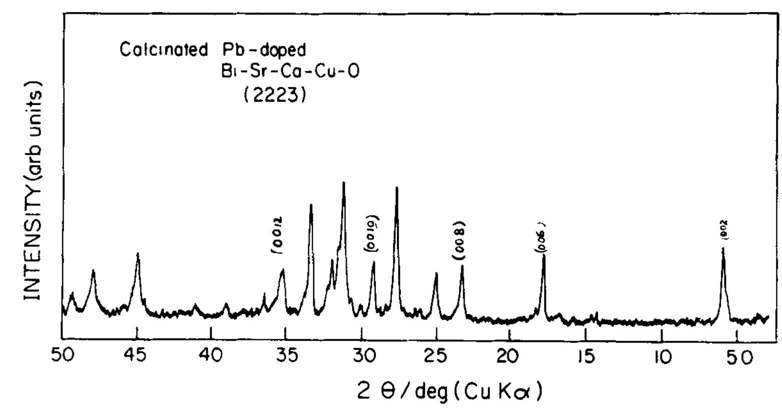

Figure 4. XRD pattern of the Pb-doped $Bi_{1\cdot4}Pb_{0\cdot6}Sr_2Ca_2Cu_3O_x$ sample calcinated for only 20 h at 810°C. The strong peaks characteristic of the low T_c phase are clearly identified. The pattern also shows peaks due to unreacted material.

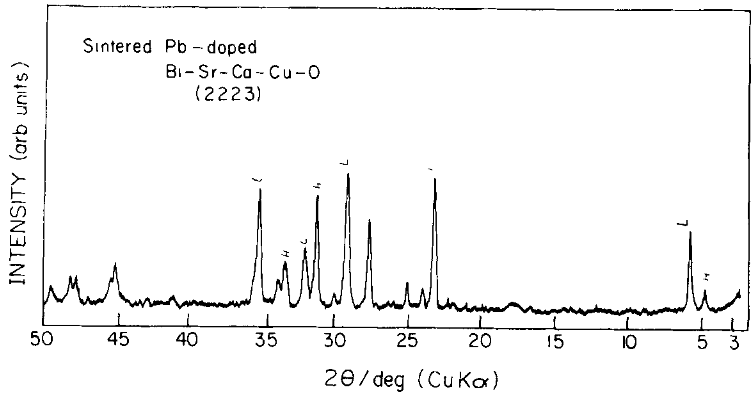

Figure 5. XRD pattern of the Pb-doped $Bi_{1\cdot4}Pb_{0\cdot6}Sr_2Ca_2Cu_3$ sample sintered at 835°C for 65 h. Peaks corresponding to both low (L) and high (H) T_c phases are present.

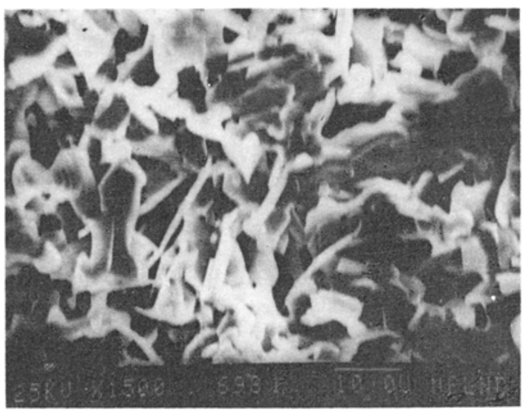

Figure 6. Scanning electron micrograph of the undoped 2223 superconductor sintered at 875°C. Plate-like microcrystals can be seen which are formed because of sintering at temperature close to melting point.

and sintered for 65 h at 835°C. One can see that the unidentified peaks have now been replaced by the reflections due to the high T_c phase. The low-angle peaks at 2θ values of 4·8 and 5·6°—corresponding to (002) reflections of the high T_c (2223) and low T_c (2212), confirm the long periodicity of both these structures. The peaks marked (H) can be comfortably matched with the (c-axis) parameters = 37·7 Å and those marked with (L) correspond to the low T_c structure having c-parameter = 30·7 Å. The presence of both these phases is not indicated by the sharp transition at 108 K (figure 2b) for this sample.

The co-existence of both low and high T_c phases, which is more like an inter-growth of two structures rather than two macroscopic phases is likely to cause ambiguity in defining the important superconducting parameters like H_{c2}, and particularly, have a detrimental effect on the critical current property of the material. An immediate consequence of this effect could be the extreme field sensitivity of J_c. Materials in which high values of J_c have been achieved following special techniques (Kumakura *et al* 1989; Togano *et al* 1989) do not show these values as soon as magnetic field is applied to it.

In addition to the correlated structures, another feature of the Bi–Sr–Ca–Cu–O superconductor affecting the critical current property is the inter-growth of two different microstructures resulting due to the heat-treatment at temperatures close to the melting point of these materials. Figure 6, the SEM of the un-doped 2223 superconductor sintered at 875°C, shows formation of plate-like micro-crystals in the bulk material. Such a microstructure is common to almost all samples containing a sufficient amount of the 110 K phase. In high T_c oxide superconductors, when it is strongly believed that the weak-links at the grain-boundaries play a major role in limiting J_cs of these materials and grain-aligned samples or single-crystals show higher J_c values than the bulk sintered samples; it is unreasonable to expect a multiphase superconductor such as the Bi-system to show reproducible high values of J_c. Detailed experiments are in progress to confirm the above findings.

5. Conclusion

The main conclusion of the above study is that despite sharp superconducting transitions the sintered Bi–Sr–Ca–Cu–O material consists of more than one superconducting phase. Pb-doping makes the reaction faster and zero resistance at 80 K or 110 K is obtained in a relatively short time. This also stabilizes the higher T_c 110 K phase but prolonged annealing causes breaking up of the phase instead of ordering the atoms in the lattice.

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