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Effect of addition of barium, tin and silver on Bi–Sr–Ca–Cu–O ceramic superconductors

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The effect of addition of barium, tin and silver, at the expense of bismuth, on the transition temperature and structure of the Bi–Sr–Ca–Cu–O system has been studied. A comparison of the results with that of lead added samples indicates that ability of lead in enhancing the superconducting phase formation is unique. It is observed that none of the above additives replaces Bi^{3+} ions in the lattice structure.

1. Introduction

The Bi–Sr–Ca–Cu–O system having the structural formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ is characterized by three phases corresponding, respectively, to the value of n as 1 (2201 or the semiconducting phase, $T_c \approx 20$ K), 2 (2212 or the low-T_c phase, $T_c \approx 85$ K) and 3 (2223 or the high-T_c phase, $T_c \approx 110$ K) [1–5]. The high-T_c phase is usually small in volume fraction. Among many other methods, addition of lead has been used to enhance the volume fraction of the high-T_c phase [6–10]. It is believed that Pb^{2+} ions replace Bi^{3+} in the structure and improve the superconducting behaviour [9, 10]. To know whether the enhancement of superconducting properties is possible by adding only Pb^{2+} to the system or any other divalent cation can be used for this purpose, samples with the addition of a small amount of barium were prepared and studied. As discussed later in Section 3.1, the addition of barium did not improve the superconducting properties. It is to be noted that the electronic configuration of Ba^{2+} and Pb^{2+} are quite different. It was felt that it may be helpful to add a divalent ion which has its electronic structure close to that of Pb^{2+}. Since tin is just before lead in group IVA of the periodic table, the two have similar electronic structure (Pb: $[Xe]4f^{14}5d^{10}6s^26p^2$, Sn: $[Kr]4d^{10}5s^25p^2$). Samples with tin added were therefore prepared and studied.

It has been reported [8–10] that Pb^{2+} occupies Bi^{3+} sites in the structure, and in order to conserve electric charge, holes are generated which in turn improve the superconducting behaviour of the system. It is likely that introduction of monovalent ions may further enhance this process. To check this, samples with silver (Ag^+) added were prepared and investigated.

In the present work, the effect of addition of barium, tin and silver at the expense of bismuth on the superconducting properties and structure of the $Bi_2Sr_2Ca_2Cu_3O_{10}$ system were studied using resistance-temperature (R-T) and X-ray diffraction (XRD) measurements. Differential thermal analysis (DTA) of some of the samples were carried out to know their thermal profile.

2. Experimental procedure

$Bi_{2-x}M_xSr_2Ca_2Cu_3O_{10}$ ceramic samples (where $x = 0.1, 0.3, 0.5$ and M stands for Ba or Sn or Ag) were prepared from high purity oxides and carbonates. The starting materials, taken in appropriate amounts, were thoroughly mixed until the entire material passed through a 75 µm sieve. Calcination of the powdered samples was done at 800 °C for 24 h. The calcined samples were again ground, passed through the same sieve and then pelletized.

It is known [11, 12] that the sintering of pellets at a temperature just below the melting-onset temperature helps "grow" the high-T_c phase. For this purpose it was desirable to know the melting profile of the samples. Therefore DTA of some of the samples at a scan rate of 10 °C min^{-1} using a DuPont System 2000 was done. Based on the DTA analysis, the temperature at which samples are to be sintered was decided upon, details are given at the appropriate point in the next section. The sintering was carried out for 70 h as this duration of sintering is known to be sufficient for the growth of the superconducting phases [9, 10]. The sintered pellets were quenched in air, as this is reported to improve superconductivity in these materials. Resistance measurements from room temperature down to 77 K were carried out by an a.c. four-probe technique at 30 Hz using a lock-in-amplifier. Electrical contacts were made using silver epoxy resin. Using CuK_α X-rays, diffractographs of the powdered samples were recorded on a computer-controlled Rigaku Geigerflex D/Max-B system in the range $2° \leqslant 2\theta \leqslant 60°$ with a scan step of 0.05° at the rate of 10° min^{-1}. The diffraction peaks at $2\theta \approx 4.7°$ and 5.7°, corresponding to the (002) planes of the high-T_c and the low-T_c phase, respectively [8, 9, 13], are known to be quite clean, far apart form other peaks and can be seen distinctly, if present. The areas under these two peaks were therefore considered for accurate determination of the relative amounts of the two superconducting phases present in the samples. For this purpose, X-ray diffractographs were therefore re-recorded at the rate of 0.3° min^{-1} in the range $2° \leqslant 2\theta \leqslant 8°$.

3. Results and discussion

3.1. Barium added Bi–Sr–Ca–Cu–O system

The observed DTA thermograph of the sample $Bi_{1.7}Ba_{0.3}Sr_2Ca_2Cu_3O_{10}$ is shown in Fig. 1. The melting onset occurs at 857.33 °C and the melting process is complete at 912.43 °C. For reasons already explained, the final sintering of barium substituted samples was done at 850 °C, a few degrees below the melting onset temperature.

The R-T plot of the samples are shown in Fig. 2. The sample with $x = 0.1$ shows a metallic behaviour. Although transition sets in at 84 K, no $T_{c.zero}$ was obtained down until 77 K. The R-T plot of the sample with $x = 0.3$ initially shows a negative slope indicative of semiconducting behaviour. This character, however, changes at around 100 K and transition sets in at 95 K. This sample also does not attain zero resistance until 77 K. The sample with $x = 0.5$ shows a semiconducting behaviour from room temperature until 77 K without recording any superconducting transition. The slope of the R-T curve for this sample increases with decreasing temperature.

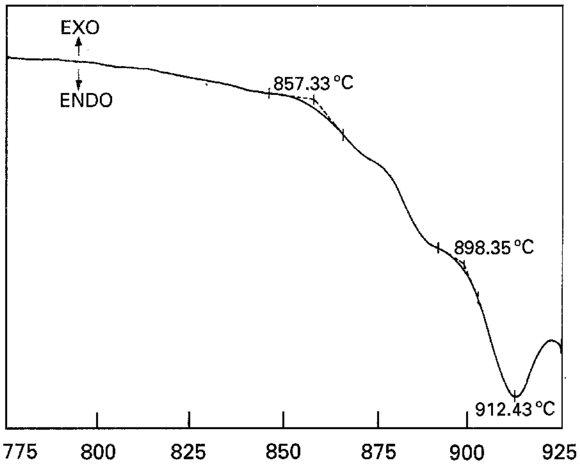

Figure 1 DTA thermograph of $Bi_{1.7}Ba_{0.3}Sr_2Ca_2Cu_3O_{10}$ sample.

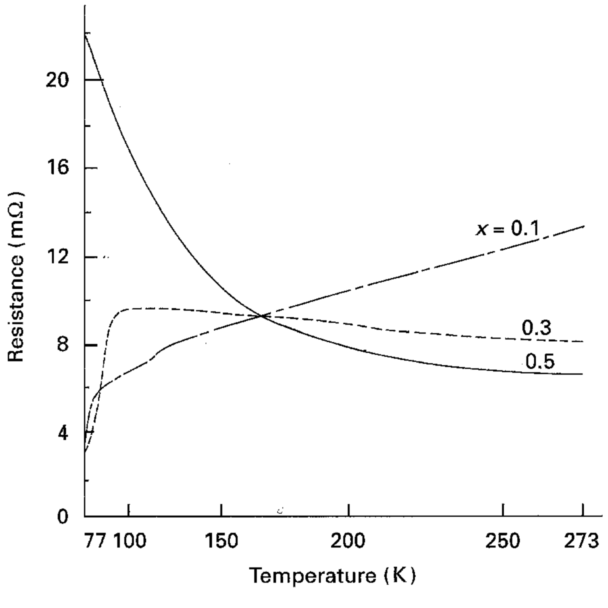

Figure 2 R-T plots of $Bi_{2-x}Ba_xSr_2Ca_2Cu_3O_{10}$ samples.

X-ray diffractographs recorded in the range $2° \leqslant 2\theta \leqslant 60°$ are shown in Fig. 3, while the diffractograph recorded in the range $2° \leqslant 2\theta \leqslant 8°$ are shown in Fig. 4. As seen in Fig. 4, there is no trace of the (0 0 2) peak at $2\theta \approx 4.7°$ corresponding to the high-T_c phase in any of the samples. In the sample with $x = 0.1$, the (0 0 2) peak of the low-T_c phase is present. The intensity of this low-T_c phase peak in the sample with $x = 0.3$ is very low and in the sample with $x = 0.5$ it does not appear at all.

In the observed X-ray diffractograph of the sample with $x = 0.1$ (Fig. 3) most of the peaks correspond to the low-T_c phase. A few peaks which correspond to none of the superconducting phases are also observed. These peaks probably correspond to impurity phases such as $BaCuO_3$ and $BaBiO_3$ [14]. This is further supported by the fact that as the barium concentration is increased, intensity of these peaks increases. Also, as observed in Fig. 3, the intensity of the peaks corresponding to the superconducting low-T_c phase decreases as barium concentration is increased. The c-parameters of the 2 2 1 2 phase, for the samples with $x = 0.1$ and 0.3, as calculated by the procedure detailed elsewhere [9] are 3.142 nm and 3.149 nm, respectively. The corresponding c-parameter of the 2 2 1 2 phase in the undoped sample is around 3.1 nm. Therefore, a small increase in the value of c-parameter is observed on the addition of barium.

In Bi–Sr–Ca–Cu–O superconducting structure, although SrO and CaO layers are not directly associated with superconductivity, nevertheless their presence is vital for superconductivity as they provide a

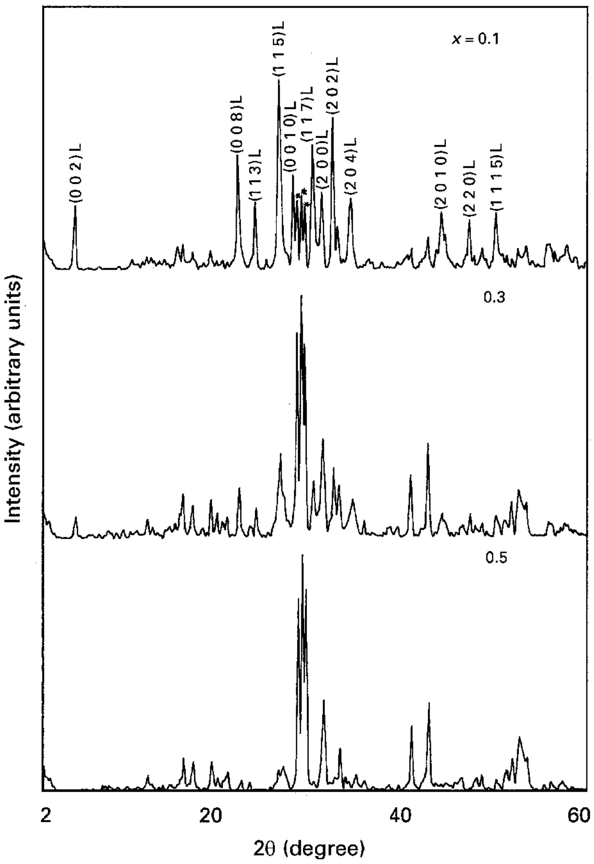

Figure 3 X-ray diffractographs of $Bi_{2-x}Ba_xSr_2Ca_2Cu_3O_{10}$ samples. L denotes the low-T_c phase and * the impurity phases.

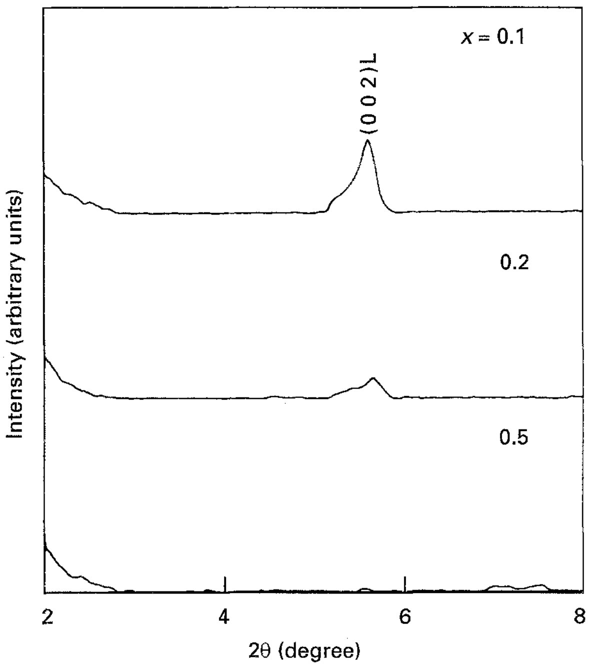

Figure 4 Low angle X-ray diffractographs of $Bi_{2-x}Ba_xSr_2Ca_2Cu_3O_{10}$ samples.

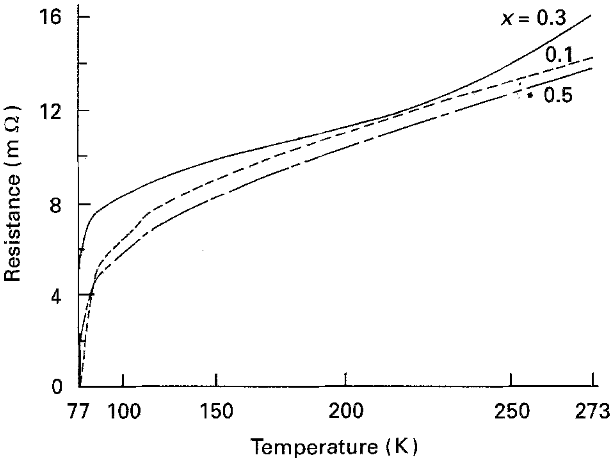

Figure 5 R-T plots of $Bi_{2-x}Sn_xSr_2Ca_2Cu_3O_{10}$ samples.

necessary lattice framework conducive to superconductivity in the $Cu-O_2$ planes [15]. In this superconducting material, Bi–O layers act as a charge reservoir [16]. If Ba^{2+} substitutes Bi^{3+}, an improved superconducting behaviour is expected as observed in Pb^{2+} substituted samples [8–10]. The observed deterioration of the superconducting behaviour suggests that barium goes to some cationic sites other than Bi^{3+} and/or it segregates as some impurity phase(s). As discussed earlier, impurity phase is indeed formed. Besides, a small increase in the value of the c-parameter indicates that in addition to segregating as impurity phase(s), barium partly enters the 2212 phase of the superconducting structure. From amongst $Bi^{3+}, Sr^{2+}, Ca^{2+}$ and Cu^{2+} ions, Sr^{2+} has the largest radius (0.112 nm). Therefore, it is not unreasonable to expect that Ba^{2+} (0.134 nm) will possibly occupy Sr^{2+}-sites instead of Bi^{3+}-sites (0.096 nm). As already mentioned, Sr is one of the necessary elements to provide a lattice framework conducive to superconductivity; lack of Sr in the structure makes this framework weaker and thus results in a poorer superconducting behaviour. A decrease in T_c on decreasing strontium content in the system has been observed earlier [17]. It is observed that as more and more Ba^{2+} occupies Sr^{2+} sites, specimens become increasingly less superconducting. Therefore, it is concluded that barium instead of going to Bi^{3+} sites, occupies Sr^{2+} sites in addition to its forming impurity phases and this deteriorates the superconducting behaviour.

3.2. Tin added Bi–Sr–Ca–Cu–O system

The melting onset temperature of the samples $Bi_{2-x}Sn_xSr_2Ca_2Cu_3O_{10}$ ($x = 0.1, 0.3$ and 0.5) as seen from the observed DTA thermograph was around 874 °C. The final sintering temperature of these samples was fixed at 870 °C.

The R-T plot of the samples are shown in Fig. 5. All these plots depict a positive slope indicating a metallic behaviour. The values of $T_{c.on}$ are observed to be 86, 89 and 89 K for $x = 0.1, 0.3$ and 0.5, respectively. The sample with $x = 0.3$ shows a $T_{c.zero}$ of 78 K; the other two samples did not attain zero resistance down to 77 K. It is important to point out that whereas all the samples with Pb doping (Pb = 0.1, 0.3 and 0.5) had shown [9] a $T_{c.on}$ of around 116 K, none of the tin doped samples have $T_{c.on}$ above 90 K, indicating total absence of the high-T_c phase.

The X-ray diffractographs recorded in the range $2° \leqslant 2\theta \leqslant 60°$ are shown in Fig. 6, while those recorded in the range $2° \leqslant 2\theta \leqslant 8°$ are shown in Fig. 7. As indicated earlier, the peaks at $2\theta \approx 4.7°$ and 5.7° correspond to the high-T_c and the low-T_c phase respectively [8–11]. As seen in Fig. 7, the peak at $2\theta \approx 5.7°$ corresponding to the low-T_c phase is present in all the three diffractographs and no peak at around 4.7° corresponding to the high-T_c phase is present in any of the diffractographs. Besides, all the peaks in the three diffractographs (Fig. 6) correspond to the low-T_c phase; none of the peaks could be indexed for the high-T_c phase. These observations indicate the absence of the high-T_c phase; a conclusion supported by the R-T measurements.

Tin exists in two oxidation states, Sn^{2+} and Sn^{4+}. In the present system, tin can either exist substitutionally at some suitable atomic sites and/or segregate as an impurity phase and not become a part of the structure. In case tin segregates as an impurity, one would expect in the diffractographs the appearance of peaks other than those attributable to the superconducting phases. The near total absence of unaccountable peaks rules out this possibility.

It had been concluded earlier [9, 10] that for low concentrations ($x \leqslant 0.3$), Pb primarily exists as Pb^{2+} and as the concentration is increased it also exists as Pb^{4+}. Chen *et al.* [18] had also reported tin existing as Sn^{4+} at higher concentrations in similar samples. As both lead and tin have similar electronic configurations, existence of tin in similar oxidation states is not unlikely. The ionic radii of $Bi^{3+}, Sr^{2+}, Ca^{2+}$ and Cu^{2+}

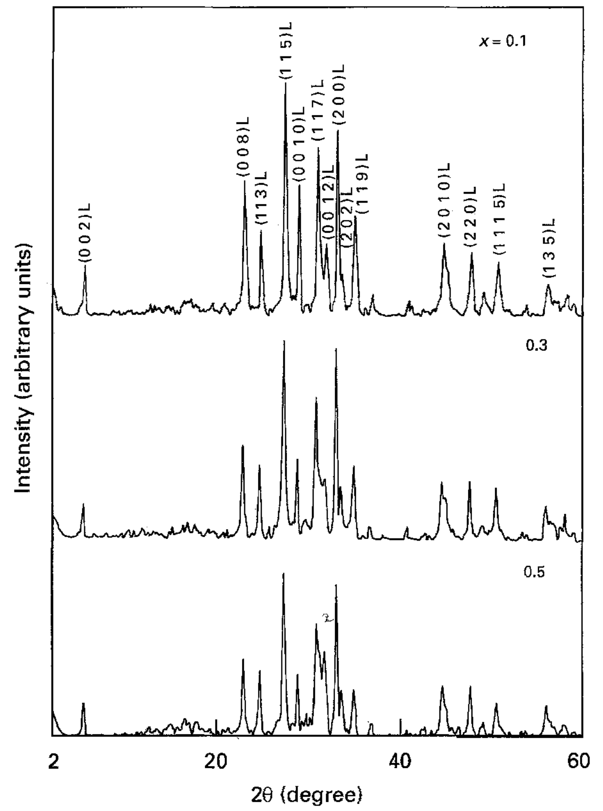

Figure 6 X-ray diffractographs of $Bi_{2-x}Sn_xSr_2Ca_2Cu_3O_{10}$ samples.

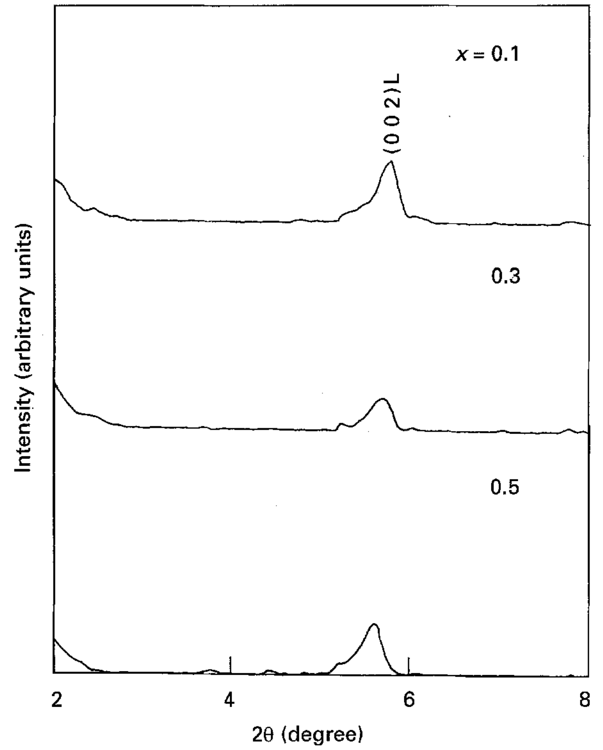

Figure 7 Low angle X-ray diffractographs of $Bi_{2-x}Sn_xSr_2Ca_2Cu_3O_{10}$ samples.

are 0.096, 0.112, 0.099 and 0.072 nm, respectively. From ionic size considerations, it seems that without disturbing the lattice appreciably, Sn^{2+} (0.093 nm) may go either to Bi^{3+} or to Ca^{2+} sites. If Sn^{2+} substitutes Sr^{2+} or Cu^{2+} sites, an appreciable change in the value of the c-parameter is expected which would result in a shift in the XRD peak positions. Since no shift of XRD peaks was observed, the possibility of Sn^{2+} replacing Sr^{2+} and Cu^{2+} is ruled out. If Sn^{2+} replaces Bi^{3+}, a superconducting behaviour similar to that of Pb^{2+} doped samples [8–10], i.e. improvement in superconducting behaviour, should have been observed. Since R-T measurements and XRD studies show the absence of the high-T_c phase, the possibility of Sn^{2+} going to Bi^{3+} sites is very small. It is, therefore, concluded that tin in Sn^{2+} oxidation state, goes primarily to the Ca^{2+} sites.

Ionic radii of Sn^{4+} and Cu^{2+} are 0.071 and 0.072 nm respectively. If Sn^{4+} substitutes some cationic sites other than Cu^{2+}, a change in c-parameter and hence a shift in the XRD peak positions is expected. This was, however, not observed. Therefore, it is reasonable to believe that Sn^{4+} occupies the Cu^{2+} sites.

It follows that tin in its oxidation states of Sn^{2+} and Sn^{4+} occupying Ca^{2+} and Cu^{2+} sites respectively, will result in the reduction of $CaCuO_2$ layers in the unit cell and retard the formation of $Bi_2Sr_2Ca_2Cu_3O_{10}$ structure. Also, Sn^{2+} and Sn^{4+} going to Ca^{2+} and Cu^{2+} sites respectively in the 2212 structure make it less superconducting, due to the reduction in the number of Cu–O_2 layers. Besides, superconductivity is also influenced by the presence of the Ca–O layers, the number of which decreases as a result of the above substitution. This is likely to lower the $T_{c.zero}$ to a temperature below the characteristic $T_{c.zero}$ (85 K) of the 2212 phase. This is indeed observed in the present work.

3.3. Silver added Bi–Sr–Ca–Cu–O system

The melting onset temperature of the samples $Bi_{2-x}Ag_xSr_2Ca_2Cu_3O_{10}$ ($x = 0.1$, 0.3 and 0.5) as seen from the observed DTA thermograph was around 861 °C. The final sintering temperature of the silver added samples was fixed at 855 °C.

The R-T plots of the samples are shown in Fig. 8. The values of $T_{c.on}$ for the three samples in increasing order of x are 89, 81 and 81 K, respectively. The sample with $x = 0.1$ was the only sample which exhibited a $T_{c.zero}$ of 78 K. All the three plots show a positive slope indicating a metallic behaviour.

The X-ray diffractographs of these samples are presented in Figs 9 and 10. No trace of the high-T_c (0 0 2) peak is visible in any of the diffractographs. The (0 0 2) peak of the low-T_c phase is present in all the three diffractographs and the intensity of this peak is the highest in the diffractograph of the sample with $x = 0.3$.

Most of the peaks in Fig. 9 correspond to the low-T_c phase. The presence of the peaks not corresponding to the superconducting phases may be due to some silver containing impurity phase. This is further supported by the fact that as the concentration of silver is increased, the intensity of these unidentified peaks increases. It is also observed that the c-parameter of the 2212 phase on silver addition does not show any significant change from that of the pure 2212 phase.

It seems that Ag^+ does not enter the structure of the low-T_c superconducting 2212 phase. This is further

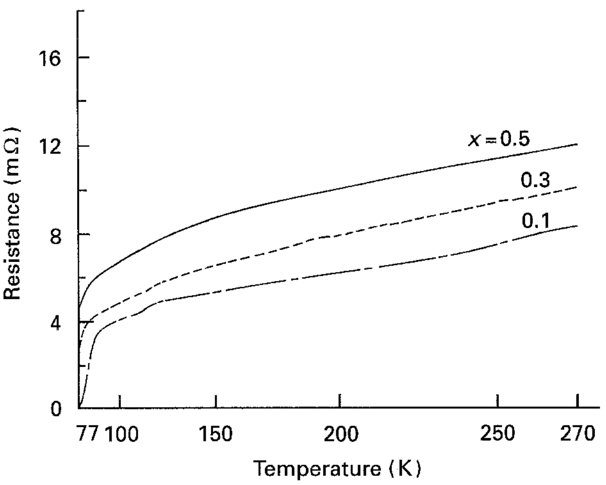

Figure 8 R-T plots of $Bi_{2-x}Ag_xSr_2Ca_2Cu_3O_{10}$ samples.

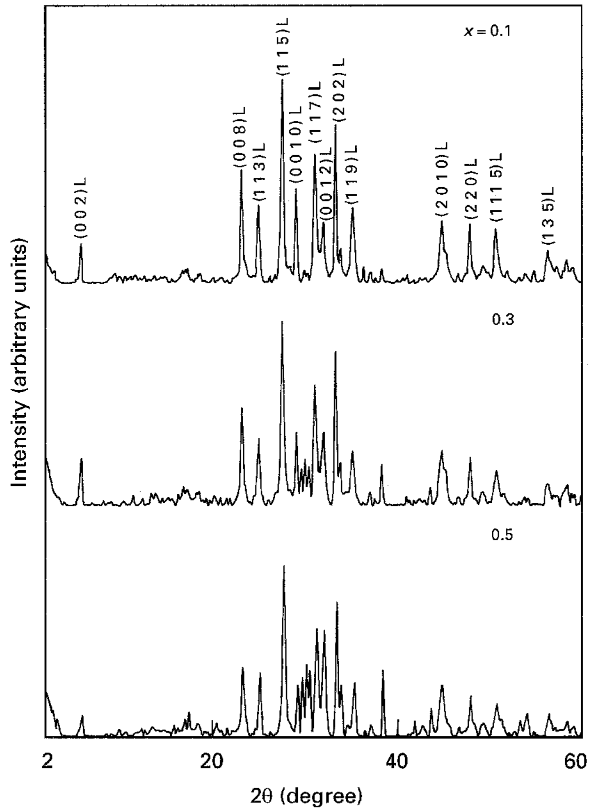

Figure 9 X-ray diffractographs of $Bi_{2-x}Ag_xSr_2Ca_2Cu_3O_{10}$ samples.

supported by the observation that on silver substitution, the c-parameter does not increase. Possibly, as in the case of $Y_1Ba_2Cu_3O_7$ [15, 19], silver sits at the intergrain boundaries and improves connectivity of superconducting grains and this accounts for a slight improvement in the volume fraction of the 2212 phase as x is increased from 0.1 to 0.3. On further increasing the silver concentration, the thickness of the grain boundary increases and becomes comparable to the coherence length and this limits the coupling between the grains. This may explain the slight decrease in the volume fraction of the 2212 phase as x increases from 0.3 to 0.5.

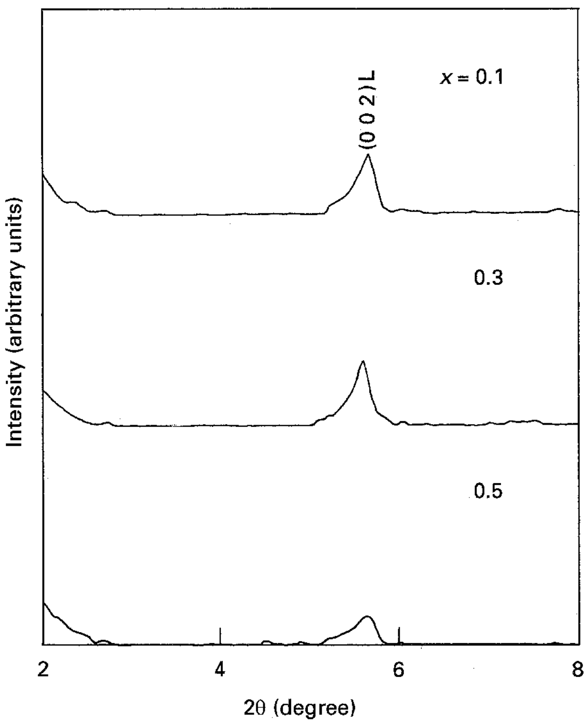

Figure 10 Low angle X-ray diffractographs of $Bi_{2-x}Ag_xSr_2Ca_2Cu_3O_{10}$ samples.

4. Conclusions

Addition of barium is not effective in improving the formation of superconducting phases as Ba^{2+} instead of occupying Bi^{3+} sites goes to Sr^{2+} sites. When tin is added to the system, Sn^{2+} and Sn^{4+} go to Ca and Cu sites respectively. This results in the reduction of $CaCuO_2$ layers in the unit cell and retard the formation of $Bi_2Sr_2Ca_2Cu_3O_{10}$ structure and also reduces the volume fraction of the $Bi_2Sr_2Ca_1Cu_2O_8$ phase. Ag^+ does not enter the superconducting unit cell structure and hence is not effective in improving the superconducting phase formation. The ability of lead in improving the superconducting behaviour is thus unique.

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