



## Effect of Sm addition on (Bi,Pb)-2212 superconductor

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### Abstract

The effect of Sm addition on the superconducting properties of (Bi,Pb)-2212 system in bulk polycrystalline form was studied. The Sm content was varied from  $x = 0.0$  (pure) to 0.5 on a general stoichiometry of  $\text{Bi}_{1.7}\text{Pb}_{0.4}\text{Sr}_{2.0}\text{Ca}_{1.1}\text{Cu}_{2.1}\text{Sm}_x\text{O}_y$ . Phase analysis by XRD, microstructural examination by SEM equipped with energy dispersive X-ray spectrometer (EDS), density measurements and superconductivity characterizations were done to evaluate the relative performance of the samples. Critical current density ( $J_c$ ) and superconductivity transition temperature ( $T_c$ ) of Sm added samples were found to be higher than that of the pure sample, i.e. without Sm added. A maximum  $J_c$  of  $719.4 \text{ A/cm}^2$  at 64 K was measured for the SM2 sample which is more than seven times higher than that of the pure sample ( $J_c = 94.1 \text{ A/cm}^2$ ). Also the  $T_c$  of the SM3 sample was the highest (94.1 K) compared to all other samples. Microstructural examination showed distinct variations in the grain morphology of the samples containing Sm. A Sr-rich oxide containing Pb(Bi) and Cu with square rectangular grains with rounded edges was observed in the microstructure of Sm added samples whose composition has been analysed through EDS. But such a secondary phase could not be distinguished from XRD analysis probably due to the peak overlapping with (Bi,Pb)-2212.

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### 1. Introduction

Since the discovery of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$  ( $n = 1$ ; Bi-2201,  $n = 2$ ; Bi-2212,  $n = 3$ ; Bi-2223)

by Maeda et al. [1], a compound without a rare earth element has generated great scientific interest among researchers both on fundamental issues concerning the mechanism of the origin of superconductivity and on technological aspects. For example, low temperature STM studies on BSCCO (2212) single crystals by substituting Zn atom in the Cu site of Cu–O layers, Pan et al. [2]

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made the first real space observation of d-wave symmetry in a HTS system. This throws light on the pairing mechanism of Cooper pairs which involves magnetic spin fluctuations of Cu atoms residing in Cu–O layers and is different from the pairing mechanism of low- $T_c$  superconductors, where electron–phonon coupling is involved. On the technological side, substitution of Pb for Bi, for improving the superconducting properties of both bulks and tapes [3–8] and the substitution of rare earth (RE) ions in place of Ca to stabilize the crystal structure of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{RE}_x\text{Cu}_2\text{O}_{8+\delta}$  [9] thin films and multilayers for rapid single flux quantum (RSFQ) device applications are subjects of special interest. Similarly there are many reports [10–22] on the substitution of rare earth elements in Bi-2212, in place of Ca or Sr in different forms such as melt textured polycrystalline or single crystalline samples, thin films and in bulk forms. Majority of such studies have concluded that even though RE substitution improves the structural stability of 2212, the superconducting properties such as  $T_c$  and  $J_c$  show a degrading tendency as the dopant concentration increases.

Recently we have reported an enhanced critical current density ( $J_c$ ) and  $T_c$  on (Bi,Pb)-2212 superconductor [23] by the addition of Pr. Interestingly a Sr rich secondary phase containing Pb(Bi) and Cu having an average composition of  $[\text{Pb}(\text{Bi})]_4\text{Sr}_6\text{Cu}_1\text{O}_5$ . As a continuation of the above work a systematic study on the effect of addition of Sm, a rare earth element having an ionic radii different from Pr has been conducted and the results are reported in this paper. There are only a very few studies on substitution of Sm in Bi-2212 [24,25] and the reported  $T_c$  values for Sm substituted Bi-2212 are lesser than the pure sample.

## 2. Experimental

Sm-added (Bi,Pb)-2212 superconductors were prepared by the traditional solid state synthesis. Sm was added to (Bi,Pb)-2212 system having an initial stoichiometry of  $\text{Bi}_{1.7}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{1.1}\text{Cu}_{2.1}\text{Sm}_x\text{O}_{8+\delta}$  (Sm = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5). Stoichiometric amounts of high purity raw materials such as  $\text{Bi}_2\text{O}_3$ , PbO,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Sm}_2\text{O}_3$  and CuO

(Aldrich 99.99%) were weighed using an electronic balance (Mettler AE 240) and mixed using a planetary ball mill (Frisch-Pulverisette 6) with agate bowl and balls in acetone medium for 1 h. After a three stage calcination process (800 °C/15 h + 820 °C/15 h + 830 °C/40 h) with intermediate grinding the samples were pelletized using a cylindrical die of 12 mm diameter under a force of 6 tons. All the calcinations were done in air with a heating rate of 3 °C/min. The average particle size of the precursor powders was estimated to be 5–6  $\mu\text{m}$  using a particle size analyzer (Micromeritics Sedigraph 5100). Heat treatment of the samples was done in two stages (850 °C/60 + 60 h) with one intermediate repeated pressing at the same force. The final thickness of the pellets was  $\sim 0.7$  mm.

Phase analysis of the samples were done using XRD (Philips X'pert Pro) equipped with monochromator at the diffracted beam side. Microstructural examination of the samples were done using SEM (JEOL JSM 5600LV). Compositional analysis of the samples were done using EDS attached to SEM. Density of the samples were determined by measuring the weight and dimensions. Critical current of the samples were measured at 64 K which was attained by applying vacuum to the cryogenic bath containing liquid nitrogen, using the four-probe method with a criterion of  $1 \mu\text{V cm}^{-1}$ . The transition temperature of the samples were determined by the four-probe dc electrical resistance method.

We label SM0, SM1, ..., SM5 for the samples with Sm content equal to 0.0, 0.1, ..., 0.5.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the samples after calcination at 830 °C for 40 h. The major phases detected are Bi-2212, Bi-2201, and  $\text{Ca}_2\text{PbO}_4$ . It is interesting to note that as the Sm content in the samples increases, the fraction of Bi-2201 reduces. This shows that Sm addition favours the formation of Bi-2212. It is also noted that as the Sm content increases very little fractions of  $\text{Ca}_2\text{CuO}_3$  is precipitated as a minor secondary phase. XRD patterns of the samples after

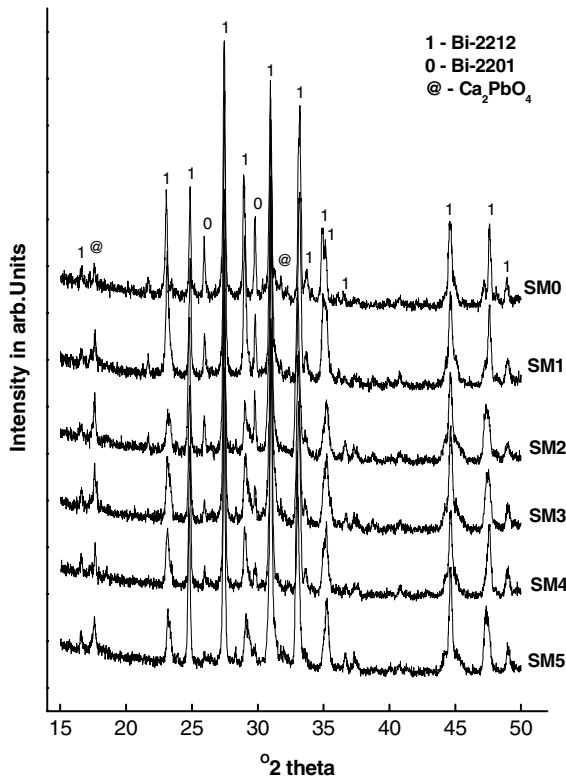


Fig. 1. XRD patterns of the samples after calcination at 830 °C/40 h.

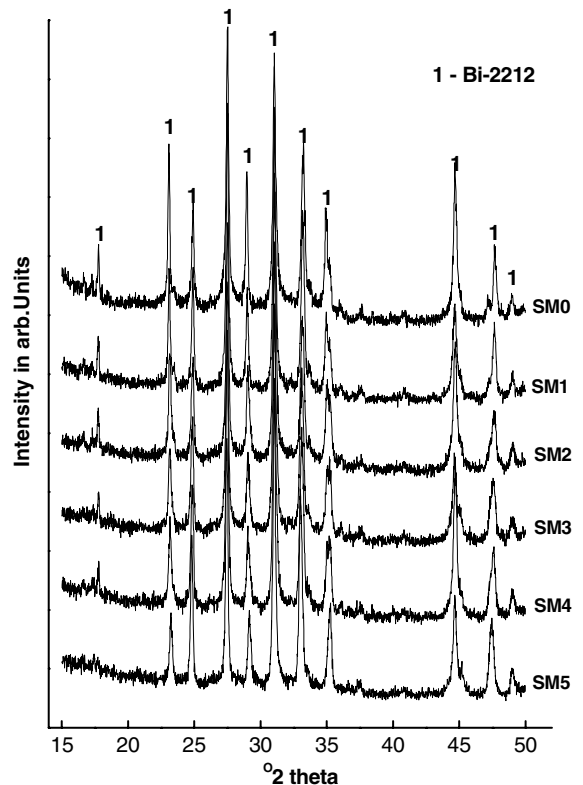


Fig. 2. XRD patterns of the samples after last stage heat treatment.

the final stage heat treatment are shown in Fig. 2. From the figure, it is clear that all the samples contain phase pure (Bi,Pb)-2212. No secondary phase containing Sm or any other cation is observed even though we have added Sm up to 0.5 in stoichiometric amount. This shows that Sm is entering into the crystal structure of (Bi,Pb)-2212.

The variation of density at different stages of processing as a function of Sm stoichiometry is shown in Fig. 3. The density values expressed as percentage of the theoretical density of Bi-2212 ( $6.6 \text{ g/cm}^3$ ) are shown on the right axis of the figure. After the first stage heat treatment the sintered density (density of the samples after heat treatment) of the samples are lesser than the green density (density of the samples before heat treatment). This reduction in density after sintering is a characteristic of the BSCCO system of superconductor. Repeated intermediate pressing can reduce the ret-

rograde densification and in the present case one such intermediate pressing has reduced the retrograde densification to a great extent as can be seen from Fig. 3. Also it is observed that Sm added samples show a lesser density than the pure sample. The decrease in density of Sm added samples is obvious when we observe the microstructure of the samples (Fig. 5). As the Sm content in the samples increases the porosity also increases and this reduces the apparent density of the samples. But irrespective of the increased porosity, the samples with Sm stoichiometry 0.4 and 0.5 shows an increase in density, but less than the pure sample.

Fig. 4 shows the variation of lattice parameters as a function of Sm doping percentage. The lattice parameter calculations were based on an orthorhombic symmetry assumed for (Bi,Pb)-2212. It is observed that there is a contraction along the 'c'-axis and a simultaneous expansion along  $a/b$ -

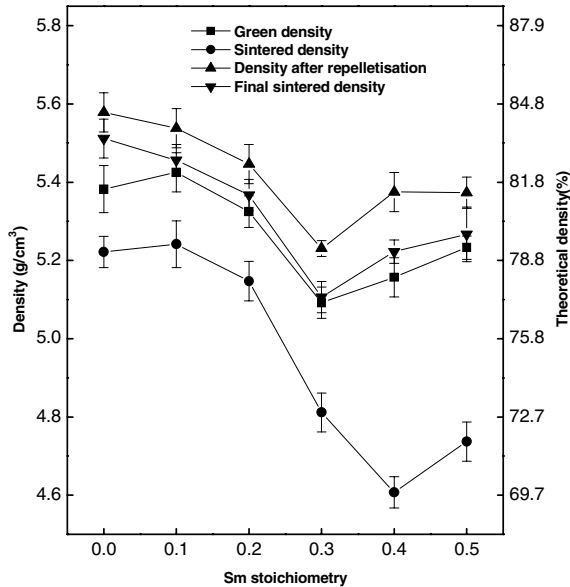


Fig. 3. Variation of density of the samples after different stages of heat treatment.

axis as the Sm content in the sample increases. This contraction along the  $c$ -axis is in consistent with earlier reports [13,16,26] wherein rare earth ions were substituted for calcium. This type of behaviour was also observed in our recent communication [23] where the Pr was added to (Bi,Pb)-2212. This also confirms the fact that Sm is entering into the crystal structure of (Bi,Pb)-2212. It is well established that high- $T_c$  copper oxides exhibit intergrowth structures consisting of superconducting layers of a fixed oxygen concentration and 'inactive' layers, like Bi–O layers of variable oxygen concentration which impart anisotropy, internal electric fields and a mismatch in the bond length [27]. Whenever a divalent cation such as  $\text{Ca}^{2+}$  or  $\text{Sr}^{2+}$  is being replaced by a trivalent rare earth ion the charge neutrality is established by incorporating additional oxygen ions in Bi–O planes of the crystal. As a result the net positive charge in the Bi–O planes reduces, so the repulsion between them is reduced. This induces a contraction of Bi–O layers and causes an increase in the covalency of Bi–O bonds. This results in the reduction of ' $c$ '-axis length and thereby improves the stability of 2212 phase. The elongation of  $a/b$ -axis is generally associated with the increase in the

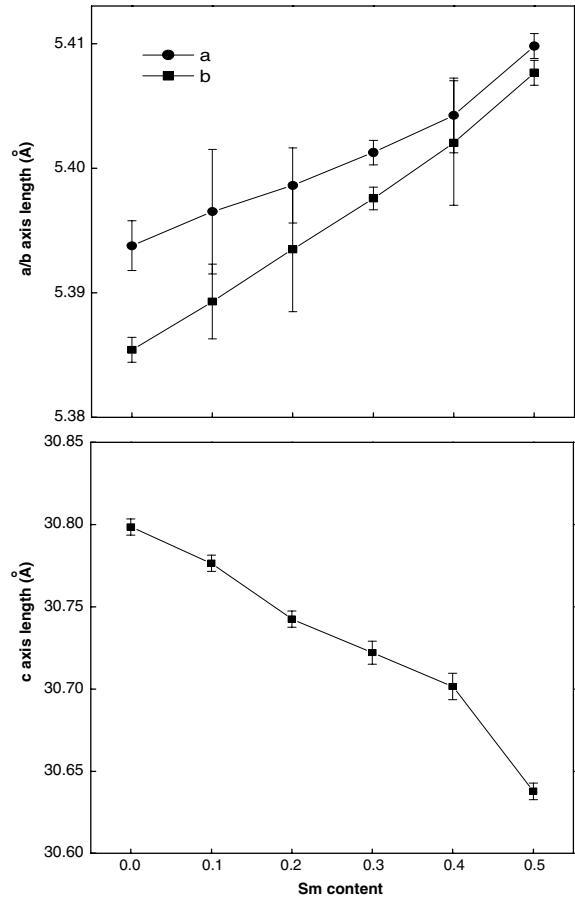


Fig. 4. Variation of lattice parameters as a function of Sm content.

Cu–O bond length in  $\text{CuO}_2$  planes, which controls the dimension in the basal planes [28].

Fig. 5 shows the SEM picture of the samples taken in the back scattered mode. The grain morphology of the sample show clear and distinct variations as the Sm content in the samples increases. For the SM0 and SM1 samples clean and flaky grains are observed which is the typical structure of BSCCO system. From SM2 onwards the grain morphology gradually changes with the edges of the grains becoming more and more rounded up. Moreover along with the main matrix a secondary phase having square or round shaped edges are observed. As the Sm content increases the percentage of such grains also increases and they are seen as colonies. Such second phase colonies are

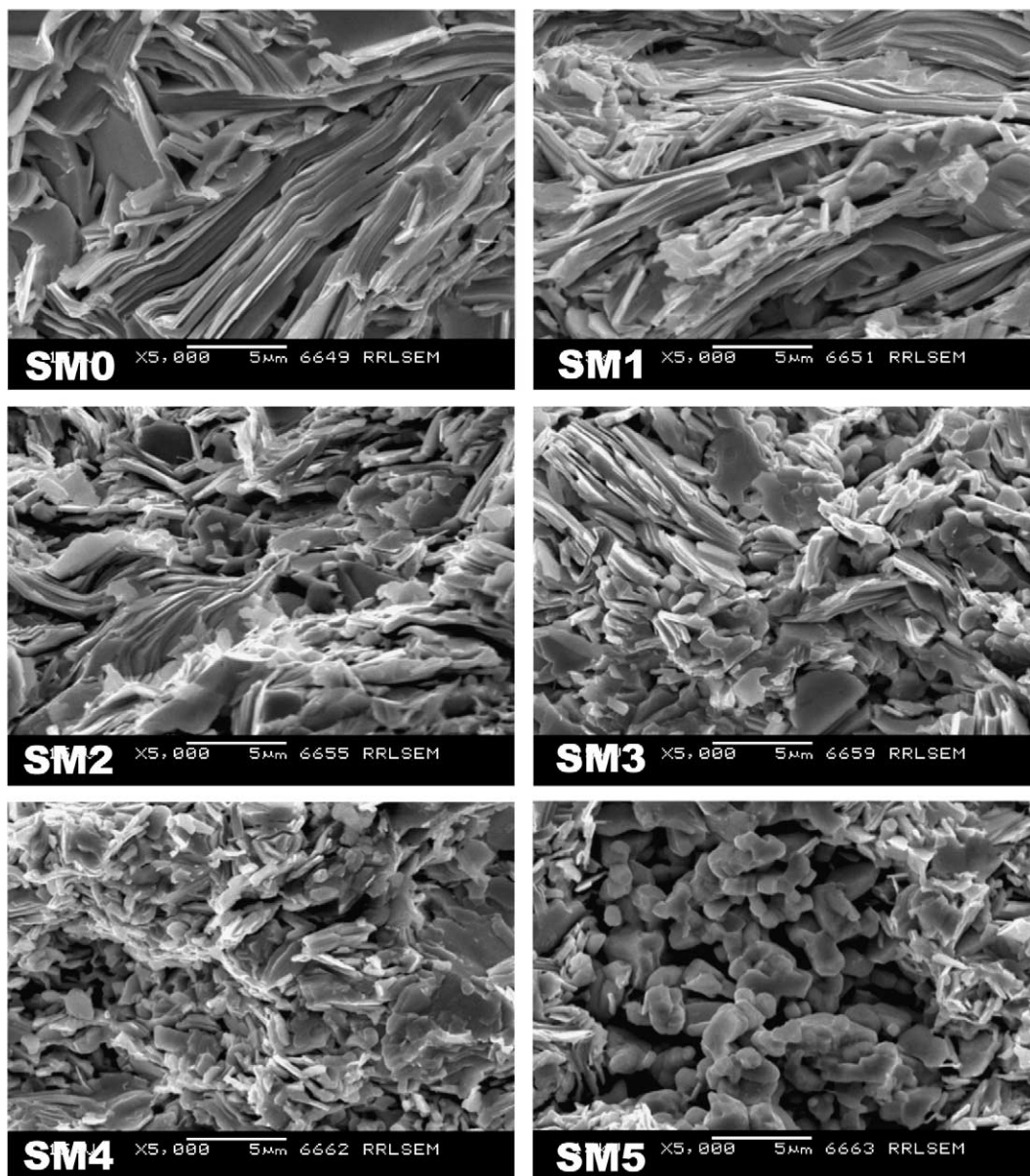


Fig. 5. SEM pictures of the samples taken in the back scattered mode.

observed in SM4 and SM5 samples. Such a secondary phase could not be identified as from the XRD analysis probably due to the peak overlapping with (Bi,Pb)-2212. But the composition of the secondary phase has been analyzed through EDS and the result is given in Fig. 6. The average composition of this phase is determined to be

$[\text{Pb}(\text{Bi})]_4\text{Sr}_6\text{Cu}_1\text{O}_x$ . The same type of secondary phase was also observed in our earlier work also [23]. So both these results confirm that if rare earth is added to (Bi,Pb)-2212 system while keeping the Ca stoichiometry intact, the added rare earth ions will be getting substituted at Sr site and the precipitated Sr ions form a secondary phase containing

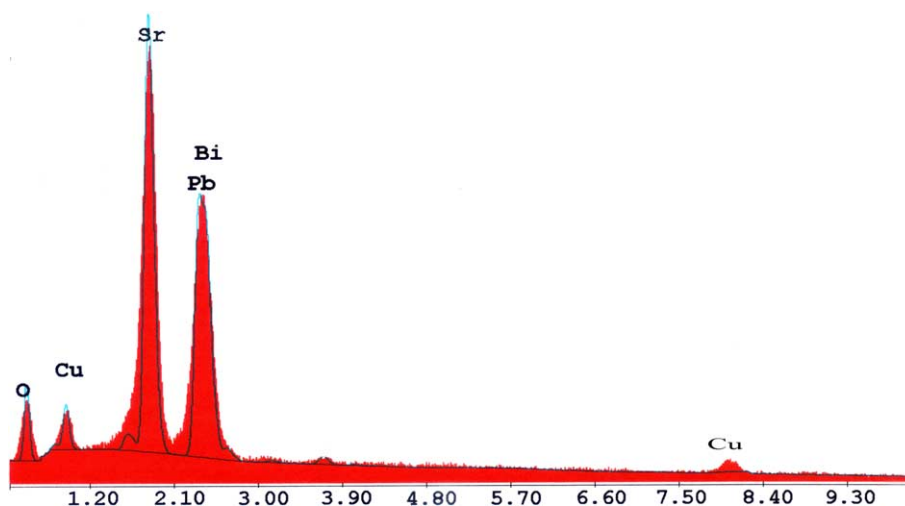


Fig. 6. EDS spectrum of the secondary phase observed in SM5.

Pb(Bi) and Cu. Work is in progress to isolate this secondary phase to have further characterization. Also detailed analysis such as electron probe microanalysis (EPMA), transmission electron microscopy (TEM), etc., are necessary to clarify and confirm these points.

The variation of normalized resistivity as a function of temperature for the pure and Sm added samples are shown in Fig. 7. All the samples show metallic behaviour up to the on-set temperature from where the transition to zero resistance occurs ( $T_{c-onset}$ ). The normal state resistivity of the samples are given in Table 1. The resistivity of the samples increases with increase in Sm content, but for the pure sample a pseudo transition is seen that precedes the actual on-set to zero resistance state at around 110 K. This may be due to the presence of small amount of 2223 or due to the structural defects formed by the intergrowth of additional Ca or Cu layers. The corresponding  $T_c$  values ( $T_{c-onset}$  and  $T_{c-zero}$ ) are shown in Table 1. The  $T_c$  values are defined as the temperature at which the deviation from normal state behaviour occurs ( $T_{c-onset}$ ). A maximum  $T_c$  of 94.1 K is shown by SM3 sample, while the  $T_c$  of pure sample is 78.7 K. Fig. 8(b) shows the  $J_c$  values as a function of Sm stoichiometry. It is noteworthy that, eventhough SM3 sample shows the highest  $T_c$ , the  $J_c$  of SM2 is the highest (719.4 A/cm<sup>2</sup>). SM5

shows the least  $J_c$  value (56.25 A/cm<sup>2</sup>) and pure sample has a  $J_c$  of 94.1 A/cm<sup>2</sup>.

The reasons for the enhancement of critical current density and  $T_c$  of Sm added samples cannot be correlated with phase purity or better microstructure observed for the samples. Phase analysis showed that phase pure Bi-2212 is formed for all the samples after the final stage of heat treatment. Microstructural examination revealed that pure sample has better microstructure with clean and flaky grains. Moreover SEM analysis showed the presence of a distinct secondary phase rich in Sr and containing Pb(Bi) and Cu. From this it can be understood that as Sm is added to (Bi,Pb)-2212, it replaces Sr ions from the crystal structure. The precipitated Sr ions react with Pb(Bi) and Cu to form a secondary phase rich in Sr. Another point to be noted is that no secondary phase containing Sm is observed even after the final stage heat treatment. So the substitution of Sr<sup>2+</sup> ions by Sm<sup>3+</sup> ions causes changes in carrier concentration or can lead to electronic or chemical inhomogeneity of charge reservoir layers (Bi–O/Sr–O) adjacent to the CuO<sub>2</sub> layers through which the actual supercurrent is believed to flow. Variation in charge concentration will lead to changes in  $T_c$  and thereby to  $J_c$ . As the dopant concentration increases the amount of secondary phase formed also increases. This will act as weak links

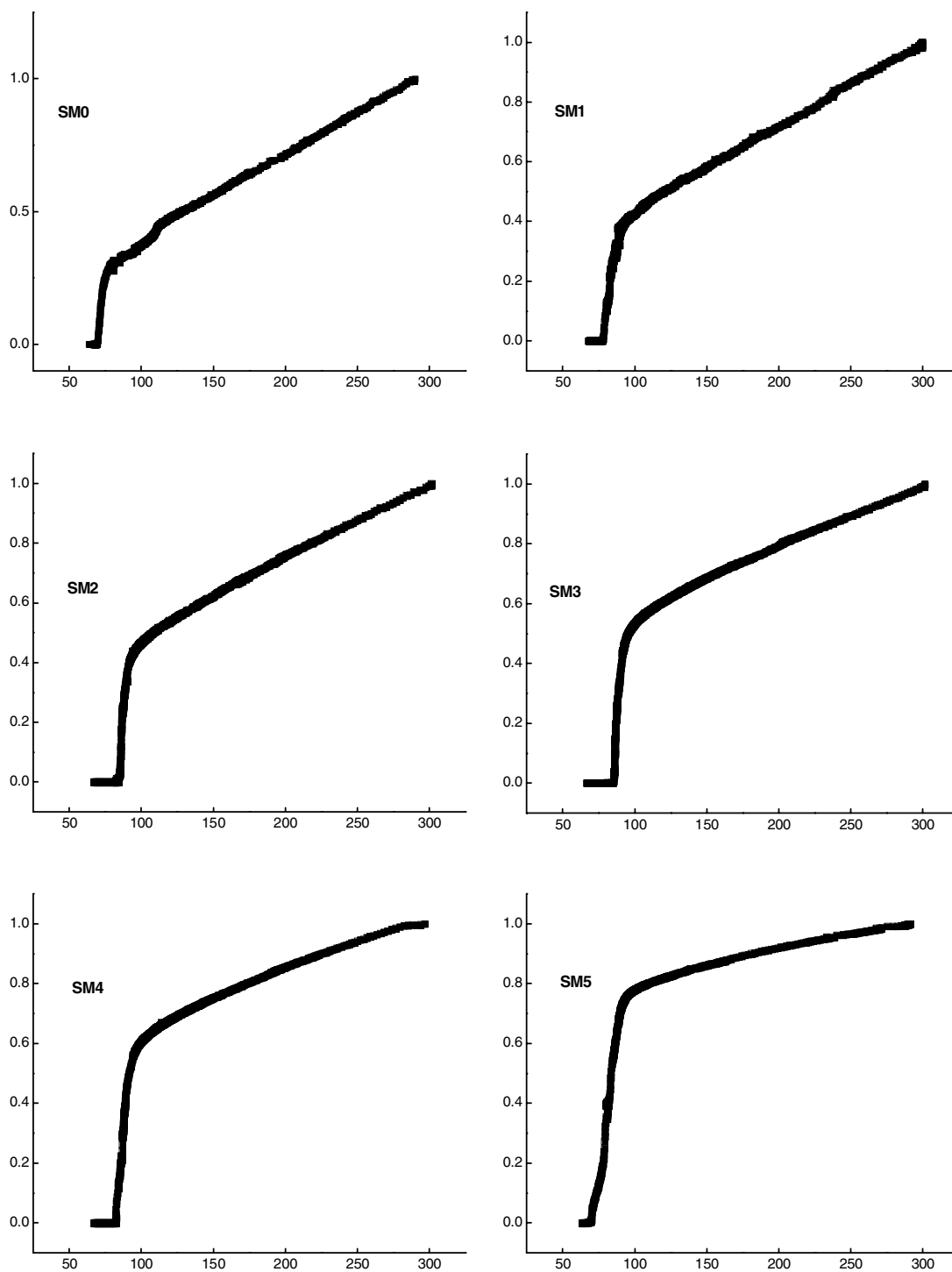


Fig. 7. Variation of normalised resistivity of the samples as a function of temperature. Horizontal axis: temperature (K), vertical axis: normalised resistivity.

Table 1  
 $T_{c\text{-onset}}$ ,  $T_{c\text{-zero}}$  and normal state resistivity of the samples

$X$	$T_{c\text{-onset}}$ (K)	$T_{c\text{-zero}}$ (K)	Normal state resistivity ( $\mu\Omega\text{ m}$ )
0	78.7	70	9.88
0.1	89.9	77.5	12.07
0.2	92.6	84.5	20.79
0.3	94.1	85.3	28.73
0.4	93.3	81.62	40.89
0.5	92	70	50.57

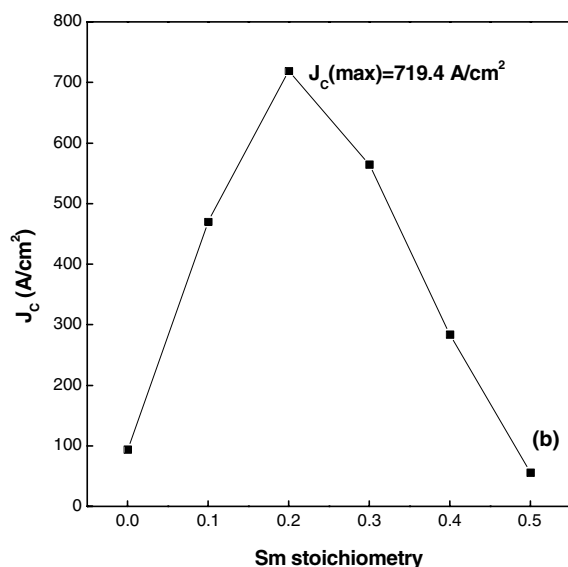
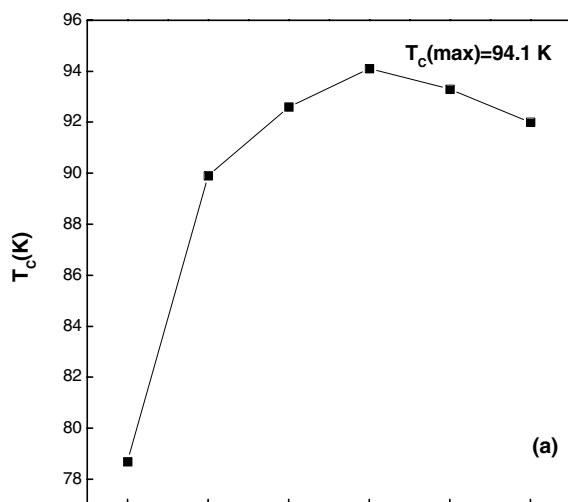


Fig. 8. Variations of  $T_c$  and  $J_c$  as a function of Sm stoichiometry.

inhibiting the flow of supercurrent. This can be reason for the reduction of  $J_c$  for the samples with Sm content  $>0.3$ . Another possibility is the formation of nanosize defects when Sr is being replaced by Sm ions and this will act as flux pinning centres enhancing the transport  $J_c$ .

It is worth comparing the results of Sm addition in (Bi,Pb)-2212 with that of Pr addition [23]. The maximum  $T_c$  value obtained by Sm addition is slightly higher than that observed for Pr addition. Moreover the highest  $T_c$  observed for Sm addition is at a stoichiometry of 0.3, whereas for Pr, it is observed for a stoichiometry of 0.2. But the  $J_c$  values show maximum at a stoichiometry 0.2 for both these samples. But the occurrence of maximum  $T_c$  for a higher doping percentage in the case of Sm can be thought of as due to the possibility of existence of multiple valency states for both Sm [[Xe]4f<sup>6</sup>6s<sup>2</sup>] and Pr [[Xe]4f<sup>3</sup>6s<sup>2</sup>]. Determining the variation of oxygen stoichiometry with respect to different concentration will give the valency state of substituted rare earth ions and the work is in progress. Also further analysis including dc magnetization measurements and structural investigations including TEM, STM/STS, etc., are needed to have a thorough understanding of the mechanism by which the critical current density ( $J_c$ ) and the transition temperature ( $T_c$ ) of Sm added samples enhances.

#### 4. Conclusions

The effect of Sm addition on the phase evolution, microstructure and superconducting properties of (Bi,Pb)-2212 system has been studied. It was found that the on-set of transition temperature increases from 79 K to 94 K for the sample having a Sm content of 0.3 in stoichiometric level compared to the pure sample. The sample with Sm content 0.2 shows the highest  $J_c$  value (719.4 A/cm<sup>2</sup>). A secondary phase rich in Sr and containing Pb(Bi) and Cu was observed in the microstructure for the Sm added samples. As the Sm content increases this phase grow in colonies and get isolated from the main matrix. Average composition of this phase is analyzed through EDS and is found to be [Pb(Bi)]<sub>4</sub>Sr<sub>6</sub>CuO<sub>x</sub>.



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