

THE INFLUENCE OF SAMARIUM DOPING IN $\text{Bi}_{1.6}(\text{Pb}_{0.4})\text{Sr}_{2-x}\text{Sm}_x\text{Ca}_2\text{Cu}_3\text{O}_y$ PREPARED BY COPRECIPITATION METHOD

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ABSTRACT

The influence of Sm doping on the phase formation, normal state properties and microstructure development of Bi-2223 superconductors was systematically investigated. Samarium was incorporated in the strontium site with x ranging from 0.00 to 0.30 prepared via coprecipitation technique. The four point probe measurements showed the loss in metallic behaviour for the samples with Sm doped above x=0.2. XRD results showed the decrease of the volume percentage of the 2223 phase followed by increasing in the density of the lattice. The SEM micrographs showed the decrease in the grain size for all samples containing samarium. The temperature dependence of ac susceptibility data shows the shifting towards lower temperature as the Sm concentration increases presence of low T_{conset} phase. The imaginary component, χ'' , shows a decrease in the intergranular coupling peak, T_p , towards lower temperature as the Sm concentration increases. Samarium did not enhance the $T_{c(R=0)}$ but gradually decreases its value from 102. K to 52 K for x=0.00 to x=0.20 respectively.

Key words: High Temperature Superconductors; Oxalic precursor; Coprecipitation.

INTRODUCTION

Bi(Pb)-Sr-Ca-Cu-O system has been investigated by many research groups concerning the preparation, superconducting properties, effect of doping as well as the structure of these compounds [1-5]. Studying the effect of doping on BSCCO system provides an opportunity to vary functional and mechanical properties of the material [6]. The dopant can influence kinetics and mechanism of HTSC phase formation, thus changing the final microstructure of the superconductor. In addition the dopant can form fine inclusions of stable phases serving as effective pinning centers. This method seems attractive for further improvement of critical current density in Bi(Pb)-2223 tapes [7,8]. The chemical routes such as oxalic acid coprecipitation, sol-gel [9] and micro-emulsion-based techniques [10] are given priority to fabricate Bi(Pb)SrCaCuO powder in order to get high compositional homogeneity in such multi-component powder.

In this paper we describe the preparation of oxalate precursor which is used to produce $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{2-x}\text{Sm}_x\text{Ca}_2\text{Cu}_3\text{O}_8$ superconductor with x = 0.00, 0.02, 0.06, 0.10, 0.20, and 0.30. We carried out a systematic investigation of oxalate coprecipitation processes, using metal acetates and oxalic acid starting materials with 2-propanol and deionized water as solvents. Results of DC electrical resistance-temperature measurements, XRD, ac susceptibility measurements and SEM are presented.

EXPERIMENTAL

The superconducting material was prepared via coprecipitation technique where stoichiometric amounts of each Bi^{+3} , Pb^{+2} , Sr^{+2} , Ca^{+2} , Cu^{+2} and Sm^{+3} compounds were weighed and dissolved separately in optimum amount of glacial acetic acid and droplets of water at 80°C . The solutions were mixed to form solution (A). The oxalic acid was dissolved in water: isopropanol (1:1.5) to have a concentration of 0.5M (solution B). Solution (A) was added to the stirred solution (B) in an ice bath and a uniform, stable, blue suspension was obtained. The slurry was filtered after 5 minutes of reaction. The drying stage was carried out in the temperature range of $80\text{--}85^\circ\text{C}$ for 4 hours. The blue powder was slightly aggregated with particle size of $0.1\text{--}0.6\ \mu\text{m}$. The powder precursor was heated to 730°C in air for 12 hours to remove the remaining volatile materials. The calcined powder was reground in a marble mortar for 10 minutes and heat up again at 845°C in air for 24 hours followed by cooling at $2^\circ\text{C}/\text{minute}$. The powders was reground and then pressed into pellets of $\sim 12.5\text{-mm}$ diameter and $\sim 2\ \text{mm}$ thickness. The pellets were sintered at 850°C for 24 hours and slowly cooled to room temperature at 120°C per hour. Resistivity measurements of the samples were carried out using the four-point probe technique with silver paint contacts. Ac susceptibility measurements were carried out using Lakeshore AC susceptometer model 7000. The amplitudes of the ac fields were varied between 0.1 Oe to 10 Oe at a fixed frequency of 125 Hz. The cryogenic system used was a Closed Cycle Helium Cryostat. The samples were also examined by X-ray powder diffraction with Cu K_α radiation using Phillips PW1830. Scanning electron microscope (SEM) micrographs were recorded using a JEOL 6400.

RESULTS AND DISCUSSION

X-ray diffraction patterns for Sm doped samples (Fig.1) show that the peak (002 H) at $2\theta \sim 4.7^\circ$ does not exist in any doped samples but was replaced with (002 L) at $2\theta = 5.8^\circ$, (013 H) peak decreased in intensity as Sm concentration increased. However, this peak disappeared at concentrations above $x=0.20$. (0010 H) and (113 H) peaks belonging to 2223 phase did not appear in any doped samples but were replaced with an unknown peak at 23.25° and (113 L) for all concentrations. The peaks corresponding to (0012 H) and (119 H) diminished as the concentration of Sm increased. The peaks that belonged to the 2212 phase (119 L), (115 L) and (113L) increased in intensity as Sm doping increased. In addition, the intensity of the peak (0111H) and (2012 H) was found to increase gradually as Sm concentration increased followed by some shifting in (0012 H) to the higher angle. An unknown peak was observed at $2\theta = 32.2^\circ$ replacing the peak belonging to (119 H). The (115 LL) peak which belongs to the 2201 phase was observed at $x \geq 0.10$. The volume fraction of the 2223 phase (V_{2223}) in the sample was determined using the equation

$$V_{2223} \% = \frac{\sum I_{2223}}{\sum I_{2223} + \sum I_{2212} + \sum I_{others}} \times 100\%$$

where the I_{2223} is the XRD peak intensity of the 2223 phase, I_{2212} is the XRD peak intensity of the 2212 phase and I_{others} is the peak intensity of other phases. The volume fraction of the 2223 phase for samples with $x=0.0, 0.02, 0.06, 0.10, 0.20$ and 0.30 were 93, 68, 61, 59, 59 and 56 %, respectively.

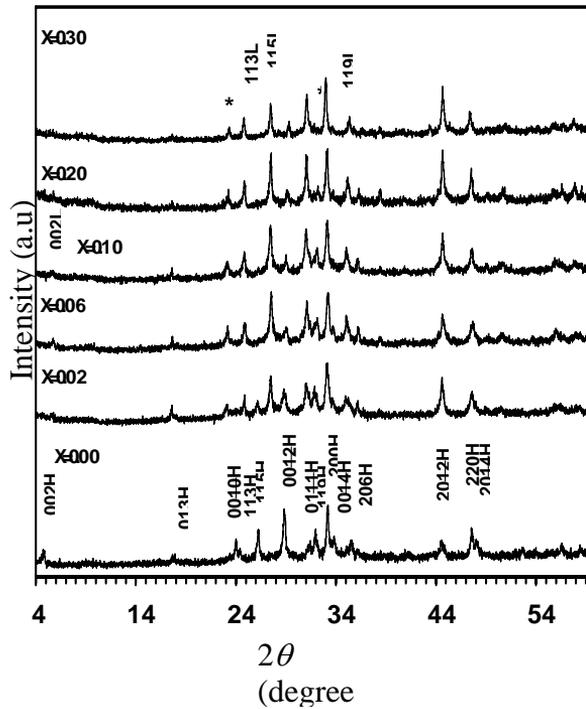


Figure 1: X-ray diffraction patterns for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{2-x}\text{Sm}_x\text{Ca}_2\text{Cu}_3\text{O}_8$ sintered for 24 hours

The temperature dependence of the normalized resistance to room temperature of the samples is presented in Figure 2. The samples displayed a metallic normal state behaviour for Sm concentration below $x \leq 0.2$ followed by shift in T_C towards low temperature. Meanwhile, the sample lost its superconductivity at Sm concentration $x > 0.2$. As observed in the $x=0.02$ sample, zero resistance temperature, $T_{C(R=0)}$ and onset temperature, $T_{C\text{-onset}}$ are 94 K and 110 K, respectively. The widening of the transition width $\Delta T=16$ K implies that this sample has small traces of 2212 the low T_C phase but it is still dominated by the 2223 phase.

Sample with $x=0.06$ shows $T_{C(R=0)}$ and $T_{C\text{-onset}}$ at 66 K and 104 K, respectively. The two step feature of the R-T curve for this sample can be observed clearly. Comparing to the sample with $x=0.10$ where the T_C remained 54 K and 80 K for $T_{C(R=0)}$ and $T_{C\text{-onset}}$ respectively, for $x=0.2$ the $T_{C(R=0)}$ and $T_{C\text{-onset}}$ was found to be 52 and 74 respectively. The samples with $x \leq 0.2$ were dominated by the 2212 phase and non-superconducting phase which suppresses the T_C and finally led to a metal to insulator transition for higher Sm concentration.

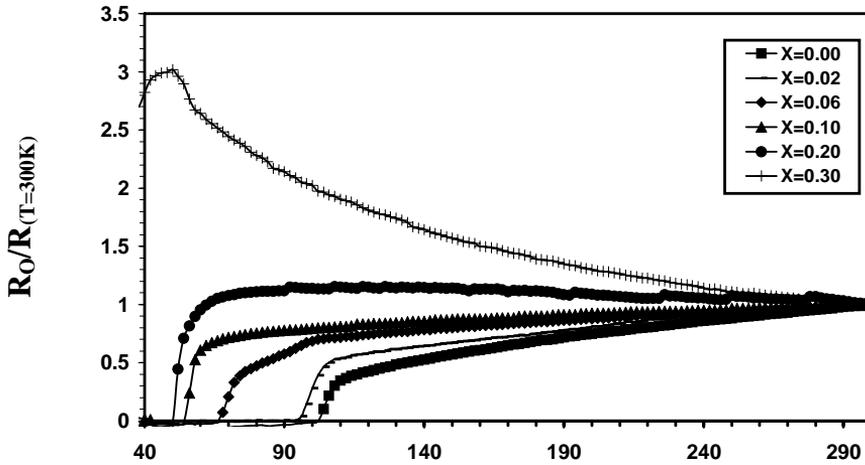


Figure 2: Normalized resistance ($R/R_{(T=300K)}$) as a function of temperature for samples with various concentrations of Sm in $Bi_{1.6}Pb_{0.4}Sr_{2-x}Sm_xCa_2Cu_3O_{\delta}$.

The temperature variation of the complex magnetic susceptibility, $\chi = \chi' + i\chi''$, in various ac fields H_{ac} . The applied fields, H_{ac} (0.1 Oe, 0.5 Oe, 1 Oe, 5 Oe and 10 Oe) were varied at constant frequency of 125 Hz. The measurements were performed on rectangular samples at different temperature ranging from 30 K up to 120 K. The onset temperature, $T_{C-onset}$ for the samples doped with Sm were observed at 106.9, 97.0, 84.2 and 72.9 K for samples $x = 0.02, 0.06, 0.10$ and 0.20 , respectively, however, there was no signals observed for sample above concentration $x=0.20$ indicating that they have lost their superconducting properties. This could be due to the influence of non-superconducting phases. It was also observed that all samples at different concentrations did not show any intrinsic peaks associated with the intragranular loss near $T_{C-onset}$. Only intergranular loss was observed associated with shifting of $T_{C-onset}$ towards the lower temperature as Sm concentration increased.

Fig.3 (a) showed the temperature variation of the real component, χ' curves at an applied magnetic field of 0.10 Oe. The graph displayed two-step feature indicating the weak coupling behaviour of the samples. The decreasing of shielded volume associated with shift of the $T_{C-onset}^{2nd}$ towards lower temperature as the Sm concentration increased. From the graph it could be concluded that the grains connectivity in doped samples decrease as Sm composition increased because of the phase transition occurred at $x=0.06$. That cause a change in the chemical compositions for the samples above that concentration so the rest of the elements react together to form an insulating phase suppressing the superconductivity.

Imaginary component, χ'' , shows a bigger shift of the intergranular coupling peak, T_p , towards lower temperature as the Sm concentration increased when the applied magnetic field is 0.10 Oe as shown in Fig.3 (b). The coupling peak, T_p for the Sm-free is resolved at 102.0 K but shifted to 92.8 K in 0.02 sample confirming that $x=0.02$ has

lower intergranular critical current density J_{cm} than the pure one. However, the coupling peak, T_p for samples with Sm concentrations of $x= 0.10$ observed at 75.0 K which is higher than sample with $x= 0.06$ which obtained ~ 73 K which is due to the phase transition as mentioned above. The coupling peak, T_p , of the sample $x= 0.20$ was found to be 47.4 K. T_p for sample with $x=0.3$ was not observed indicating the increase of weak links between the grains. The surface of the grains in this sample is probably layered with low T_c -phases and an unknown phase corresponding to non-superconducting phase and hence weakened the Josephson current, I_0 passing through the layers.

By determining the phase locking temperature, T_{cj} associated with the onset of the lower transition temperature and using the Ambegaokar-Baratoff [11] equation, $I_0 = 1.57 \times 10^{-8} T_c^2 / (T_c - T_{cj})$, the Josephson's current I_0 passing through the grains boundaries for all the samples are summarized in Table 1

Sm composition	$T_{C-onset}$	T_{Cj}	$I_0(\mu A)$
0	108.0	105.5	73.84
0.02	106.6	97.9	20.61
0.06	97.0	77.8	7.68
0.1	84.2	79.2	22.43
0.2	72.9	52.4	4.07

Table1. The calculated values of Josephson current (I_0) for BSCCO at different doping ratios.

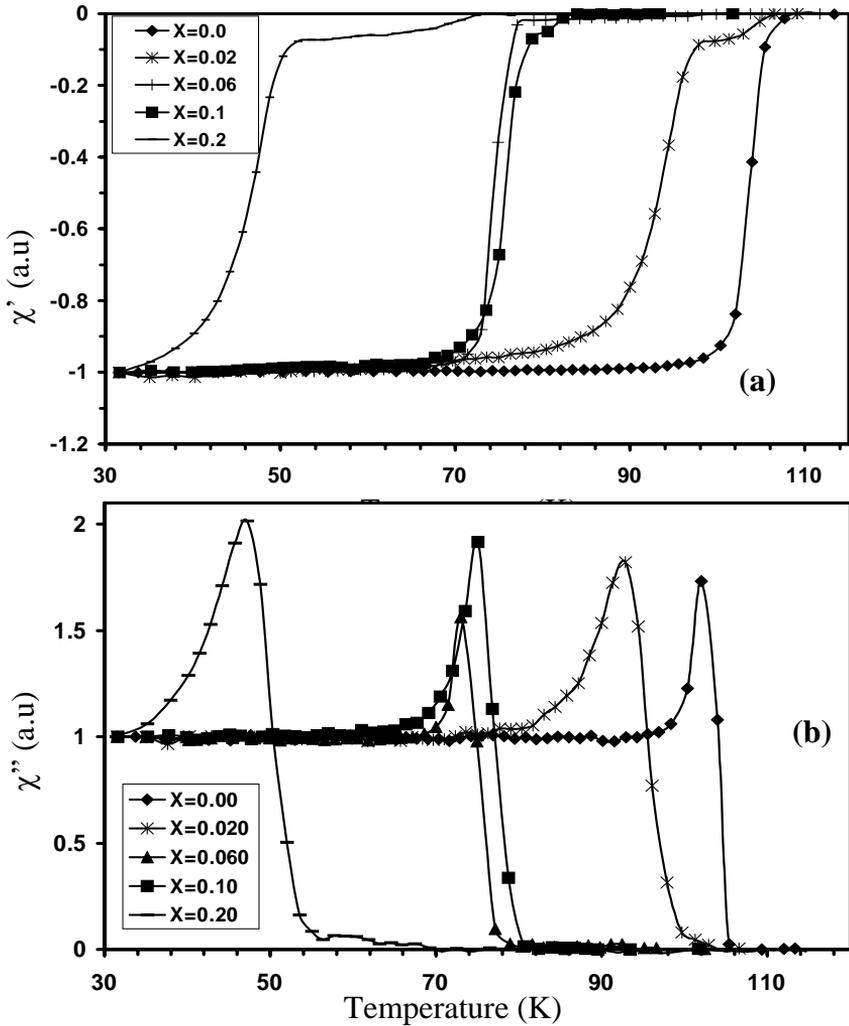


Figure 3: The AC susceptibility as a function of temperature for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{2-x}\text{Sm}_x\text{Ca}_2\text{Cu}_3\text{O}_8$ at applied magnetic field 0.1 Oe. (a) Real part, (b) Imaginary part.

SEM micrographs for the doped samples with magnification 2300X displayed compacted layers of thin flaky plate-like grains with random distribution. In addition, grains of large size due to 2223 phase appeared with grain size $\sim 10\mu\text{A}$ in the pure sample as shown in Figure. 5a. The grain size decreased by 1/4 for the samples containing samarium dopant as compared to the undoped samples. Addition of Sm at Bi sites enhanced the growth of 2212 phase.

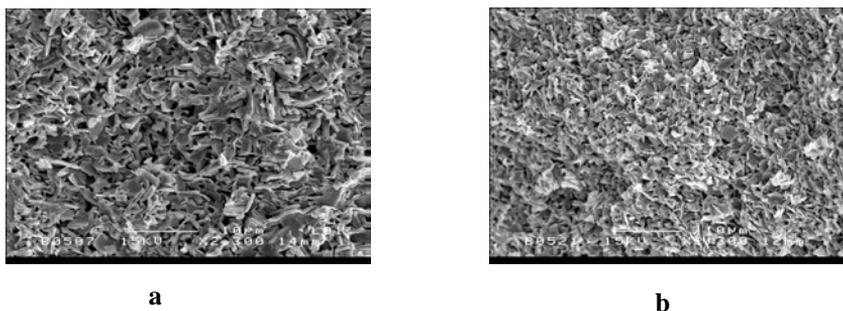


Figure 4: SEM micrograph at 2300X magnification for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{2-x}\text{Sm}_x\text{Ca}_2\text{Cu}_3\text{O}_8$ samples with (a) $x=0.06$, and (b) $x=0.20$

CONCLUSION

In conclusion, Bi-2223: Sm systems have been successfully prepared via coprecipitation method with Sm doping at different composition ($X=0.02, 0.06, 0.10, 0.20$ and 0.3). The system showed that the 2223 phase is converted to 2212 phase for very dilute concentrations of Sm with consequent decrease in T_C and finally leads to a metal to insulator transition for higher x . It has also been observed that the T_C suppression rate is more in Sm-substituted system indicating that the magnetic nature of the ion also may contribute to the lowering of T_C . Ac magnetic susceptibility measurements showed a decrease in the grain connectivity followed by decrease in the grain size as the Sm concentration increases which also proved through the SEM micrographs.

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