Effect of rare-earth (Eu, Yb and Ag) substitutions on superconducting properties of the $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}R_X$(R = Eu, Yb, and Ag)$Cu_3O_Y$ system

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The superconducting properties of $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}R_x$(R = Eu, Yb and Ag)$Cu_3O_Y$ have been investigated by X-ray diffraction, electrical resistance and the peritectic transition of these superconductors was studied kinetically under different atmospheres and temperature gradients. X-ray diffraction results show that the volume fraction of the high-T_c (2 2 2 3) phase decreases and that of the low-T_c (2 2 1 2) phase increases as Eu, Yb and Ag concentrations increase. The resistivity measurements reveal that the T_c onset decreases down to 100 K for Eu, 85 K for Yb and 106 K for Ag concentrations. These results are explained on the basis of possible variations of hole concentration with trivalent rare earth ion substitutions. Activation energies and frequency factors for crystallisation were determined by non-isothermal differential thermal analysis (DTA), employing different models. It was found that both peritectic transition and reaction rate were dependent on the ambient atmosphere. Kinetic studies under different atmospheres revealed that the thermal stability of Bi-2 2 1 2 phase was greatly enhanced under oxygen atmosphere. © *1999 Kluwer Academic Publishers*

1. Introduction

In copper oxide superconductors it has now been well-established that superconducting properties are related to the hole concentration [1, 2]. Tarescon *et al.* [3] studied various substitutions of rare earth materials in the $Bi_4Sr_4Ca_{2-x}R_xCu_4O_Y$ system ($x > 1$) and reported that for $x = 1.5$ the compounds became semiconducting. They further found that the depression of T_c occurred no matter if the dopant was magnetic or nonmagnetic and that the superconducting properties were strongly affected by changes in the hole concentration, induced by the amount of doping. Awana *et al.* [4] found that the substitution of Dy and Tm in the bismuth based 2 2 1 2 system caused a superconductor-to-insulator transition.

Bornemann *et al.* [5] varied the hole density by partial replacement of Ca by Y (hole acceptor) in $Bi_2Sr_2CaCu_2O_8$ and Y by Ca (hole donor) in $YBa_2Cu_4O_8$. Kanai *et al.* [6] reported that the substitution of rare earth ions for Ca brings about a transition from the 2 2 2 3 to the 2 2 1 2 phase. As compared with the large amount of data for the 2 2 1 2 phase not much information exists about the 2 2 2 3 phase in terms of Eu and Yb substitutions. The critical current density of high-T_c superconductors is an important property that determines the practical applications of these materials in electronic devices, power transmission lines, generators, motors, and magnetic levitation applications. Polycrystalline bulk superconductors usually have a low critical current density J_c and this has been explained due to the so called weak coupling of the grains. It has been demonstrated that the addition of silver to YBCO and BISCCO superconductors improves theirs critical current densities without adversely affecting their superconducting properties.

Over the past few years, several synthesising techniques have been developed so that superconductors with desired properties can be obtained. These materials have been used to fabricate superconductors for practical applications. Yet two major issues, namely the kinetics and the stability of the phase seem to complicate the development of single phase 2 2 2 3 superconductors. Our systematic study has clarified the optimum heat treatment conditions for the formation of the 2 2 2 3 phase [7].

We report here the effects of Eu, Yb and Ag substitution for Ca in $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}R_x$(R = Eu, Yb and Ag)$Cu_3O_Y$ on structural, electrical and kinetic parameters.

2. Experiment

Samples of nominal compositions in $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}R_x$(R = Eu, Yb and Ag)$Cu_3O_Y$ with $x = 0.05$ were prepared by the glass precursor method described in our previous paper [8]. The phase formation was checked by X-ray diffraction (XRD pattern) which was recorded at room temperature with CuK_α radiation

in the 2θ range ($20°$ to $70°$) using an automated diffractometer. Differential thermal analysis was carried out in various atmospheres at different heating rates using Perkin-Elmer DSC-7. The kinetic of crystallisation of the glass was investigated from non-isothermal differential thermal analysis (DTA) using Perkin-Elmer (DTA-7) at the heating rate of 5 to $20°$/min. Glass samples were annealed in air for various length of time at temperatures selected from the DTA results. Electrical resistance was measured from 77 to 140 K by the standard four-probe configuration with $1.0~\mu$V/cm used as the criteria for J_c measurements.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the doped ($x = 0.05$) and undoped (with $x = 0$) samples annealed at $850°$C for 60 h in air, which revealed various phases present in the crystalline samples. A good agreement both in 'd' values and the intensity ratios of the high T_c and low T_c peaks was found with those reported in the literature [9, 10]. The pure sample A with no Ag showed a large percentage of the high-T_c 2 2 2 3 phase. It can be seen from Fig. 1a that number and intensities I of the high-T_c phase reflections are predominant compared to those of the low T_c 2 2 1 2 phase as shown in Fig. 1c and d. However with the addition of Ag, only those peaks corresponding to the low-T_c 2 2 1 2 phase was observed and their intensity increased as compared to those ob-

tained in sample 1(a). The peaks corresponding to the high-T_c 2 2 2 3 phase were absent. The volume fraction f_{2223} of the high-T_c 2 2 2 3 and low-T_c 2 2 1 2 phases have been determined using the following expressions.

$$f_{2223} = I_{2223(002)}/I_{2223(002)} + I_{2212(002)}$$

and

$$f_{2212} = I_{2212(002)}/I_{2212(002)} + I_{2223(002)}$$

respectively. We have also obtained reflections corresponding to the low-T_c phase annealed at $850°$C for 25 h (Fig. 2a) and high-T_c 2 2 2 3 phase annealed at $850°$C for 240 h in air (Fig. 2b) and the lattice constants for these samples. From the calculated values of the lattice constants we found that the high-T_c (2 2 2 3) $c = 308.8$ nm and low-T_c (2 2 1 2) phase $c = 378.0$ nm differ mainly in length of the c-axis.

From X-ray diffracation patterns we noticed that the volume fraction of the high-T_c phase increased with increase in sintering time (up to 240 h) while the low-T_c phase (2 2 1 2) decreased and these results are shown in Fig. 2. It is interesting to observe from Fig. 2 that the intensity of reflections corresponding to the high-T_c phase increased and those corresponding to the low-T_c phases decreased with increasing sintering time. In the samples sintered for 25 h no peaks appeared at $2\theta = 4.4°$ corresponding to (0 0 2) reflection. These results indicate that on heating the glass the $Bi_2Sr_2Ca_1Cu_2O_8$ (2 2 1 2) phase crystallises out first followed by the
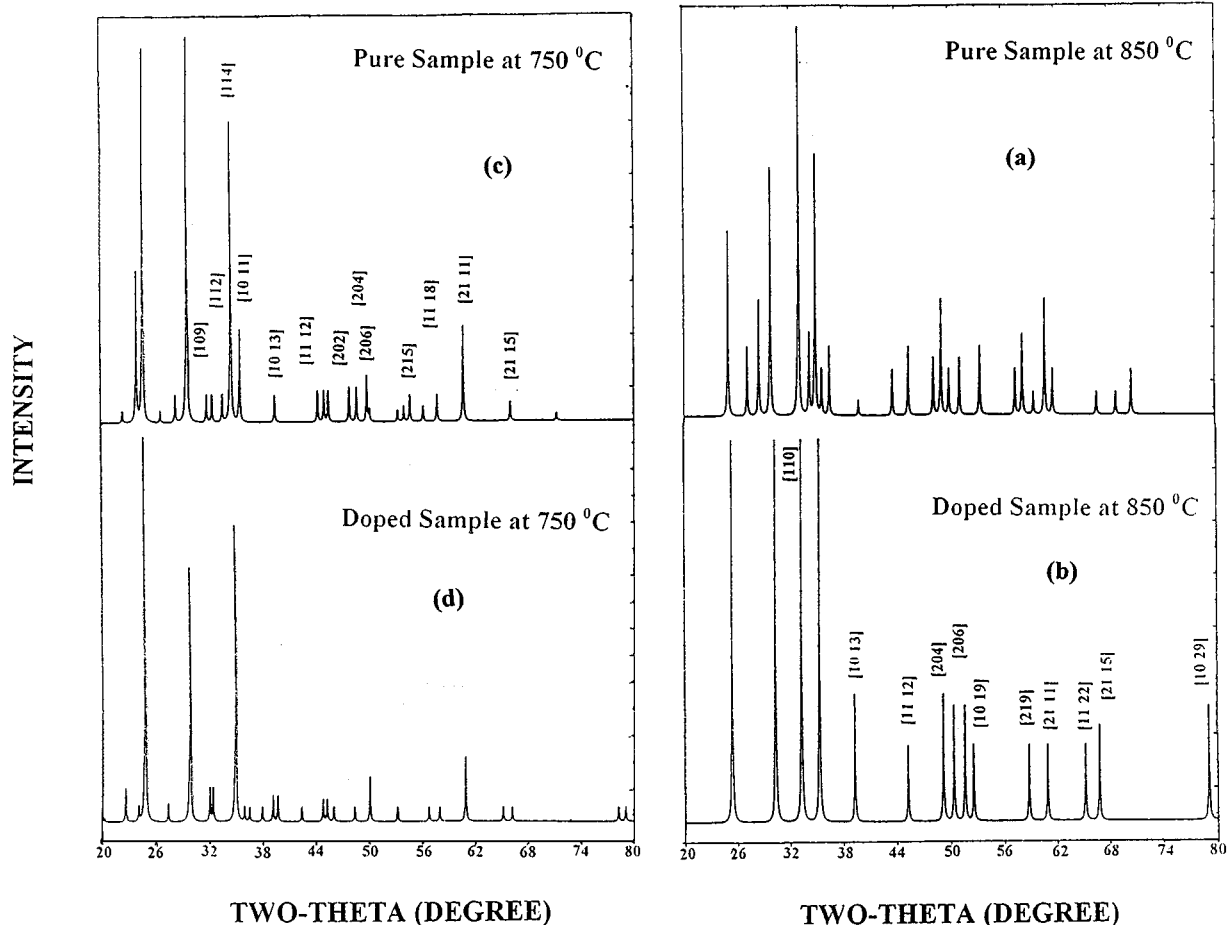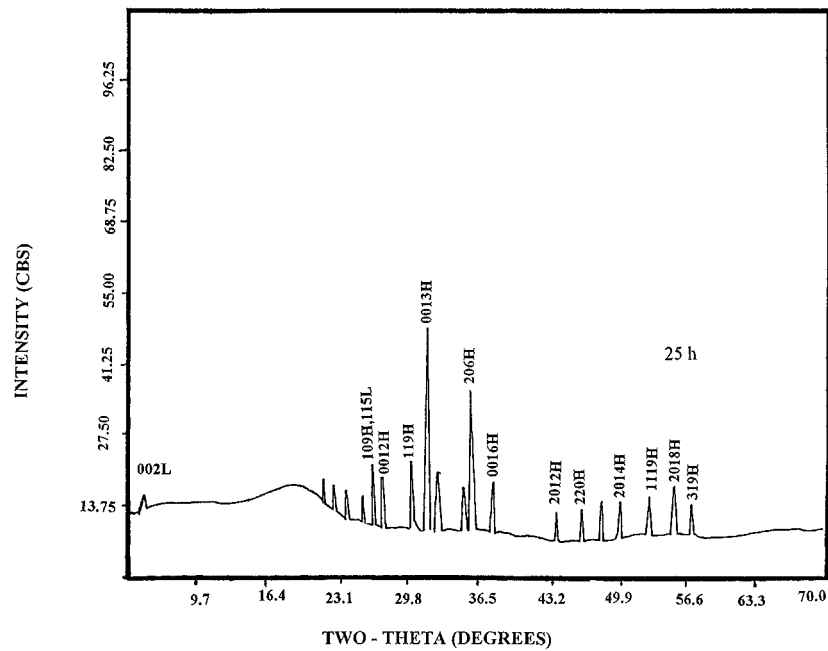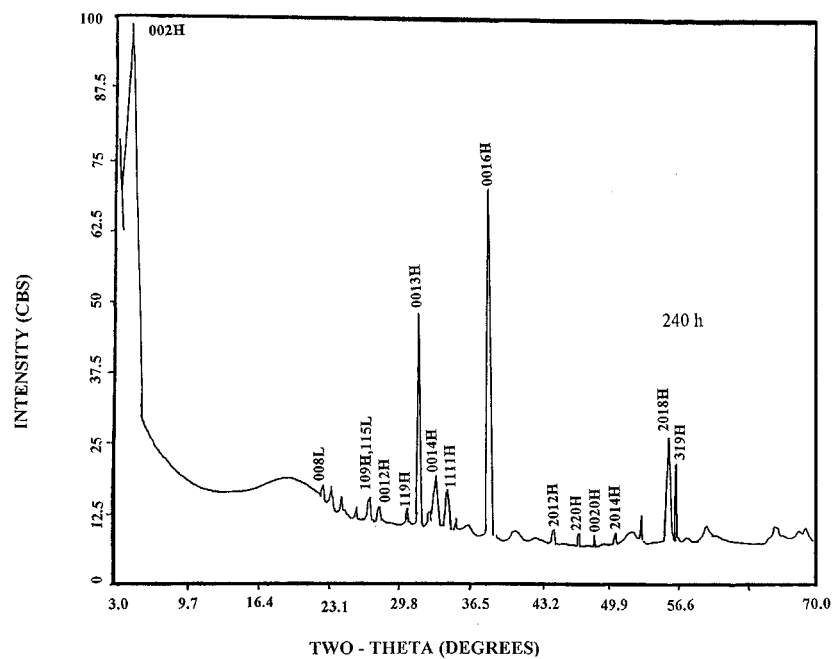

Figure 1 X-ray diffraction patterns of BPSCC pure and silver doped samples annealed at $750°$ and $850°$C for 60 h.

Figure 2 (a) X-ray diffraction patterns for $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Ag_xCu_3O_Y$ superconductor annealed at $850\,^\circ C$ for 25 h in air; (b) X-ray diffraction patterns for $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Ag_xCu_3O_Y$ superconductor annealed at $850\,^\circ C$ for 240 h in air. The peaks denoted by (H) and (L) correspond to the high-T_c (2 2 2 3) and low-T_c (2 2 1 2) peaks respectively.

formation of the 80 KBi_2 $Sr_2Ca_1Cu_2O_8$ (2 2 1 2) phase at higher temperature. The 110 K T_c phase, probably $Bi_2Sr_2Ca_2Cu_3O_{10}$ (2 2 2 3), starts appearing in this sample by reaction between the phases formed at lower temperatures and also that the volume fraction of high-T_c phase increases with sintering time. We reported earlier that the high-T_c phase started degrading after 250 h of sintering time and the T_c values also decreased. It can be observed from Fig. 2 that the percentage of the high T_c phase is around 96% and that of the low T_c phase approximately 4%.

Fig. 3 shows the $R(T)/R$ (300 K) plot as a function of temperature for all the samples down to liquid nitrogen. The transition temperature $T_c(0)$ at which the resistance

vanishes, decreases with increasing concentration of Eu, Yb and Ag. For sample A (undoped) $T_c(0)$ is equal to 109 K. Sample B (Ag doped) $T_c(0)$ decreases to 106 K, sample C (Yb doped) T_c is 100 K and sample D (Eu doped) $T_c(0)$ decreases to 85 K.

These results show that the substitution of $Ca^{2+} \rightarrow$ Eu^{3+} and $Ca^{2+} \rightarrow Yb^{3+}$ degrades the superconducting properties of 2 2 2 3 phase and confirm the hole carrier concentration is at an optimum value in the as-grown pure phase. The substitution of Ca^{2+} by the rare-earths Eu^{3+} and Yb^{3+} provides additional electrons which in turn decrease the hole carrier concentration leading to a decrease of T_c and of other superconducting properties. This observation is in agreement with earlier reports

TABLE I Activation energy and Avrami's exponent values for the $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}R_x(R = Eu, Yb)Cu_3O_Y$ system

S/no	Composition	Activation energy (KJ/mol) by Ozawa's Eq.	Kinetic parameters by Bansal's Eq			Avrami exponent 'n'
			Activation energy KJ/mol	Freq factor 'ν' (sec⁻¹)	K value	
1	$Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$	287	275.75	2×10^{17}	0.012	1.62
2	$Bi_{1.7}Pb_{0.3}Sr_2Ca_{1.95}Eu_{0.05}Cu_3O_7$	289	276.65	2.3×10^{20}	0.75	3.9
3	$Bi_{1.7}Pb_{0.3}Sr_2Ca_{1.95}Yb_{0.05}Cu_3O_y$	215	202.5	4.7×10^{21}	1.34	—

concerning Sm^{3+} and Dy^{3+} substitutions [11, 12]. DTA runs of sample containing Eu are recorded at different heating rates between 5 and 20 °C/min in nitrogen atmospheres and shown in Fig. 4. It is interesting to note from the DTA thermogram that the peak maximum (T_p) increases with increasing heating rates. The peak maximum corresponds to the temperature at which the rate of transformation of the viscous liquid in the crystal becomes a maximum. If the number of nucleation sites is increased e.g. by using slower heating rates, the peak maximum will occur at a temperature at which the melt viscosity is higher i.e. at a lower temperature. The variable heating rate DSC method was employed

to evaluate the kinetics of crystallisation. The values of the kinetic parameters were calculated from DTA data, presented in Table I using the kinetic models of Bansal and Doremus [13]. The equation used is:

$$\ln\left[\frac{T_p^2}{\alpha}\right] = \ln\left(\frac{E}{R}\right) - \ln(\nu) + \frac{E}{(RT_p)} \quad (1)$$

where T_p is the peak maximum temperature, α the heating rate, E the activation energy, R the gas constant and ν the frequency factor. The kinetic parameters (E and ν) are related to the reaction rate constant (K) by Arrhenius equation:

$$K = \nu e^{-(E/RT)} \quad (2)$$

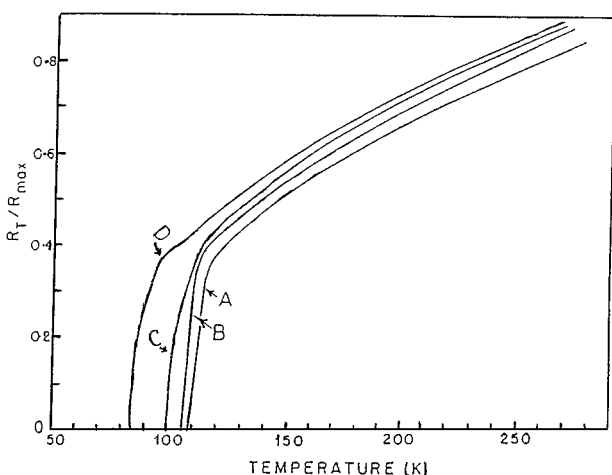*Figure 3* Plot of $R(T)/R$ (300 K) as a function of temperature down to liquid nitrogen temperature.
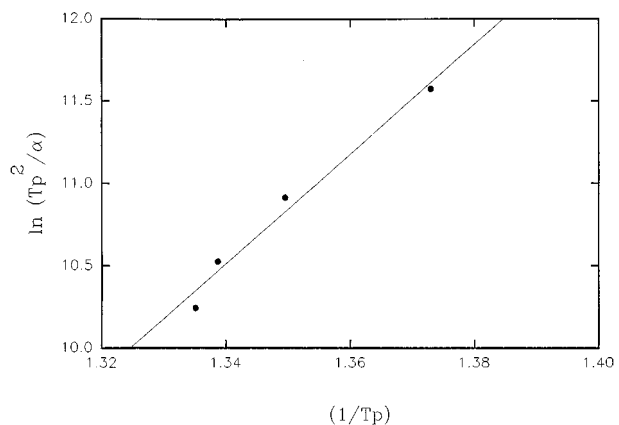

Figure 5 A plot of $\ln[T_p^2/\alpha]$ vs $[1/T_p]$ for a Eu doped sample.
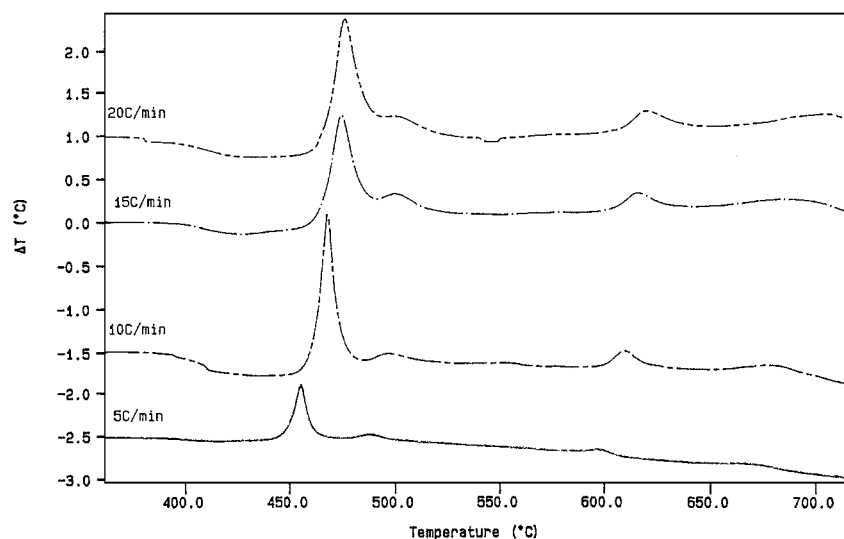

Figure 4 DTA curves in N atmosphere for Eu-doped samples recorded at heating rates of 5 to 20 °C/min.

In the derivation of Equation 1 it was assumed that the rate of reaction is a maximum at the peak and this is a valid assumption for the power compensated DSC. A plot of $[T_p/\alpha]$ vs. $[1/T_p]$ for the crystallisation of the glass was linear as shown in Fig. 5. From the earlier least-squares analysis fitting, values of the kinetic parameters were calculated (Table I). We also calculated the activation energy and Avrami's exponent values (Fig. 6) employing the technique of Ozawa and Chen (Fig. 7) and these are given in Table I.
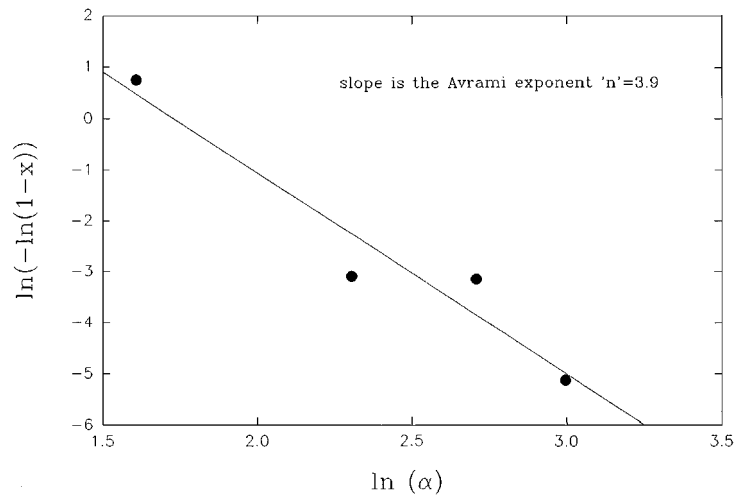

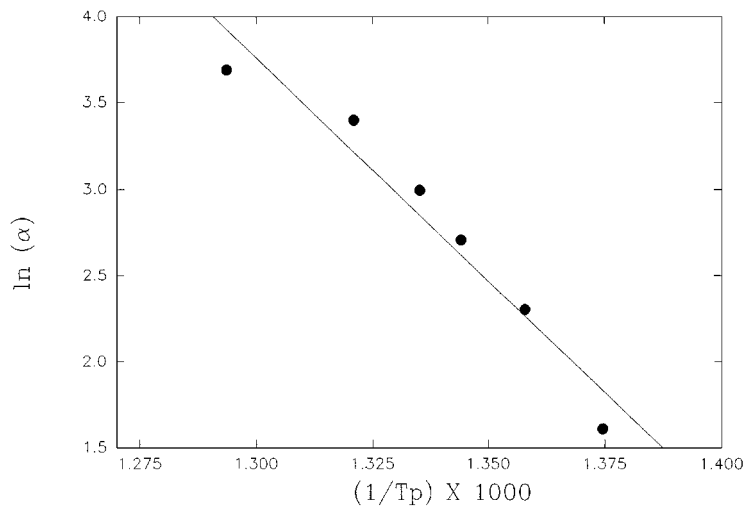*Figure 6* A plot of $\ln(\alpha)$ vs. $\ln(-\ln(1-x))$ (Avrami's exponent).

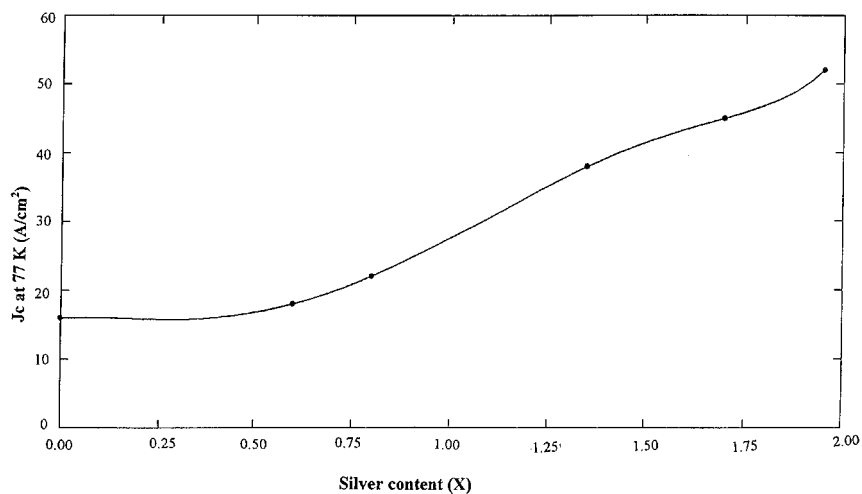*Figure 7* Plot of $1/T_p$ as a function of $\ln(\alpha)$ (Ozawa method).

Figure 8 Critical current density J_c (at 77 K) as a function of silver content for $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Ag_xCu_3O_Y$ at zero field.

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It is interesting to note that the values of E of a Eu doped sample as compared to undoped and Yb doped samples were greater. Thus it can be concluded that the thermal stability of Bi-2 2 2 3 doped with Eu was greatly increased. Fig. 8 shows the critical current density at 77 K as a function of silver concentration. It can be clearly seen that J_c increases with the concentration of silver. The maximum J_c was observed for $x = 3$ and remained constant thereafter. A plausible explanation for the increase in J_c with silver is given below. Jones *et al.* [14] and Jin *et al.* [15] have claimed that Ag atoms do not enter the lattice of BISCCO superconductors but appear to have partially filled up the voids between individual superconducting grains by preferential segregation. Savvides *et al.* [16] suggested that silver enhances the flux pinning in the intergranular regions, most probably by the development of oxygen point defects at the silver-superconductor interface and the stacking faults around silver grains. Therefore the transport critical current density (at 77 K is found to increase due to the improved link state between the grains. These results confirm the migration of metallic silver into the sites of grain boundaries and creation of superconductor-metal-superconductor regions. This observation is consistent with our earlier results [8, 17].

References
1. J. B. TORRANCE, Y. TOKURA, A. I. NAZZAL, A. BEZINGE, T. C. HUANG and S. S. P. PARKIN, *Phys. Rev. Letters* **61** (1988) 7156.
2. Y. TAKURA, J. B. TORRANCE, T. C. HUANG and A. I. NAZZAL, *Phys. Rev. B* **38** (1988) 7156.
3. J. M. TARASCON, P. BARBOUX, G. W. HULL, R. RAMESH, L. H. GREENE, M. GIROUND, M. S. HEDGE and W. R. MCKINNON, *ibid.* **39** (1989) 4316.
4. V. P. S. AWANA, S. K. AGARWAL, R. RAY, S. GUPTA and A. V. NARLIKAR, *Physica C* **191** (1992) 43.
5. H. J. BORNEMANN, D. E. MORRIS, H. B. LIU and P. K. NARWANKAR, *ibid.* **191** (1992) 211.
6. KANAI, T. KAMO and S. MATSUDA, *Japan J. Appl. Phys.* **28** (1989) L551.
7. M. N. KHAN and A. UL-HAQ, *ASM J. Materials Engineering and Performance* **5** (1996) 445.
8. M. N. KHAN, A. N. KAYANI and A. UL-HAQ, *J. Mater. Sci.* **33** (1998) 2365.
9. R. M. HAZEN, C. T. PREWITT, R. J. ANGEL, N. L. ROSS, L. W. FINGER (and others), *Phys. Rev. Letters* **60** (1998) 1174.
10. C. C. TORARDI, "Chemistry of Superconducting Materials," Vol. 1, (Nova, Commack, NY, 1991) p. 1.
11. K. N. KISHORE, M. MURALIDAR and H. BABU, *Physica C* **204** (1993) 299.
12. E. L. NASAIAH, U. V. SUBBA RAO, O. PENA and C. PERRIN, *Solid state Communication* **83** (1992) 689.
13. N. P. BANSAL and R. H. DOREMUS, *J. Thermal Anal* **29** (1984) 115.
14. T. E. JONES, J. W. SCHINDLER, R. D. BOSS, P. M. THIBADD and W. C. GINNIS, *Phys. Rev. B* **41** (1990) 7197.
15. S. JIN, R. C. SHERWOOD, T. H. TIEEL, G. W. KAMMLOTT and R. A. FASTNACHT (and others), *Appl. Phys. Letters.* **52** (1988) 1628.
16. N. SAVVIDES, A. KARSAROS and S. X. DOU, *Physica C* **179** (1991) 361.
17. M. N. KHAN and A. UL-HAQ, Proc. First Int. Conf. on Phase transformation, Islamabad, Pakistan, 1996 pp. 131.