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Effect of silver on the formation of $Bi_2Sr_2Ca_2Cu_3O_{10}$ (Bi-2 2 2 3) superconductors by sol–gel process

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Bi-2 2 2 3 superconductors with silver additions are synthesized by sol–gel process. The effect of silver on the formation of Bi-2 2 2 3 phase is studied. The addition of silver brings down the reaction temperature as well as annealing time for the formation of Bi-2 2 2 3 phase. The presence of silver affects the T_c of the Bi-2 2 1 2 phase. The heat treatment of silver added Bi-2 2 2 3 samples above 1113 K show poor superconducting properties due to partial melting of Bi-2 2 2 3 phase. © *1998 Chapman & Hall*

1. Introduction

Bi-2 2 2 3 superconductor is a potential material for practical applications. The material being a ceramic and due to its brittle nature, it is difficult to fabricate Bi-2 2 2 3 into different shapes and forms. Silver is being widely used as sheathing material for drawing tapes and wires [1, 2]. Since silver is extensively used as a sheathing material, several reports are available on the effect of silver on the superconducting properties of Bi-2 2 2 3 with respect to process parameters namely, heat treatment temperatures, environment, composition etc. [2–7]. There are conflicting reports in the literature with regard to the role of silver on the superconducting properties of Bi-2 2 2 3 compound. Dou *et al.* find that silver addition depresses the superconducting transition temperature (T_c) and the critical current density (J_c) and the lattice parameters decrease when the samples are heat treated in air or oxygen [3, 4]. However, several groups have found the absence of any chemical reaction between silver and Bi-2 2 2 3 compound either in oxygen or in air [3–5]. It was found that the addition of silver enhances the formation of Bi-2 2 2 3 phase and improves the kinetics of the sintering process [5, 8].

It is believed that fine and homogeneous powders are required to obtain dense and uniformly sintered bodies, because dense, sintered polycrystalline materials with a minimum of weak links have good superconducting and mechanical properties. In most of the cases discussed above, silver is added to Bi-2 2 2 3 either in the form of silver powder or silver oxide or its peroxide. Very few groups have introduced silver at precursor stage during the synthesis of the superconducting compound by the conventional solid state route [7, 9]. There are no reports on the synthesis of Bi-2 2 2 3–Ag composites by wet chemical routes. However, a few reports are available for Y–1 2 3–Ag composites synthesized by nitrate precursor solution route and sol–gel route [10]. In fact, Huang *et al.* found that the physical properties and microstructure of 1 2 3–Ag composites depend largely on the preparative conditions than on the amount of silver [11].

In the present study the synthesis of Bi-2 2 2 3–Ag composites through the sol–gel process is investigated. Since silver is introduced at the molecular level, its effect on the formation of Bi-2 2 2 3 compound is studied. The optimum silver content, and temperature of formation are identified for obtaining high density Bi-2 2 2 3–Ag composites.

2. Experimental procedure

The composition $Bi_{1.68}Pb_{0.32}Sr_{1.75}Ca_{1.8}Cu_{2.8}O_{10}$ which results in the formation of a phase pure compound [12] is chosen for studying the effect of silver on the formation of the Bi-2 2 2 3 compound. Nitrates of bismuth, strontium, silver and acetates of copper, calcium and lead are used as starting materials. The procedure adopted for the preparation of the gel is described elsewhere [12]. Silver nitrate is added in such a way that the amount of silver in the Bi-2 2 2 3 compound is 5, 10, 20, 30 and 40 wt %. The gels are characterised by TG and DTA (Polymer STA-1500). The gels are decomposed in air at 723 K and are heat treated at 1103, 1113 and 1123 K for 60 h in air. Samples obtained after heat treatment are characterized by X-ray diffraction (XRD) (Seifert P 3000). Resistivity measurements are conducted on sintered pellets using van der Pauw four probe method. a.c. susceptibility measurements are carried out using Sumitomo (Japan model SCR 204 T) superconducting materials property measurement unit in the temperature range

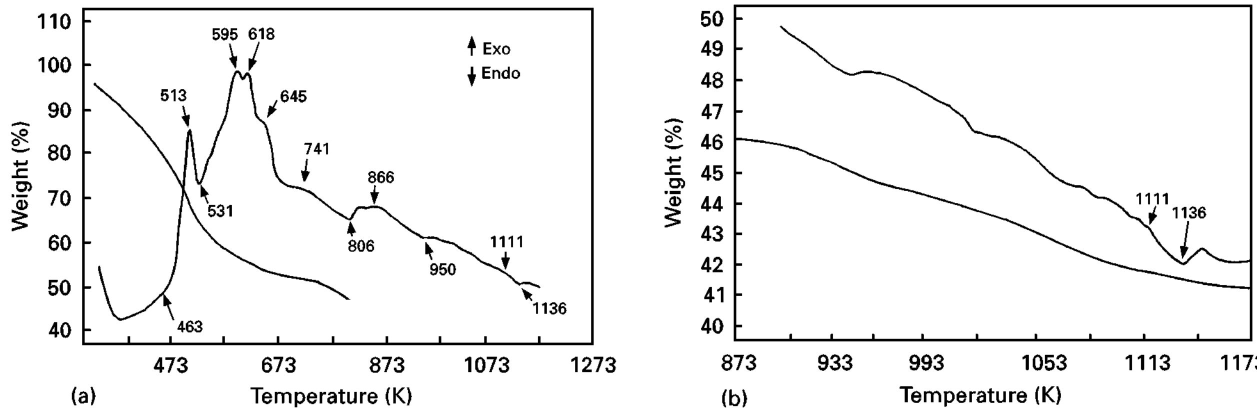

Figure 1 (a) TG and DTA patterns of Bi-2 2 2 3 precursor gels with Ag addition. (b) Expanded region of TG and DTA.

300–13 K in a field of the order of 7.95 A m^{-1} and frequency 330 Hz. Scanning electron microscopy (SEM) (Jeol model No. JSM 5300) studies are conducted on the sintered pellets to study the morphology of the samples.

3. Results and discussion

Fig. 1 shows the thermogravimetric (TG) and differential thermal analysis (DTA) patterns of a typical silver added gel sample. There are three stages of weight loss 300–673 K, 728–823 K and 830–1170 K. The weight loss in the first stage is caused by decomposition of the gel and is confirmed by three exothermic peaks (inception temperature = 463, 531 and 610 K) in this region. The weight loss in the second stage is caused by the formation of Bi-2 2 0 1 phase; corresponding to this an endotherm is observed at 741 K. The weight loss in the last stage is caused by the formation of various other phases oxygen loss etc. The endothermic peak at 866 K is caused by the eutectic melting of Ag_2O–PbO–CuO system [3]. The large endotherm at 1111 K is caused by the melting of the phases.

Figs 2 and 3 show the XRD patterns of silver added samples heat treated at 1113 and 1123 K, respectively. The various phases formed at these temperatures are

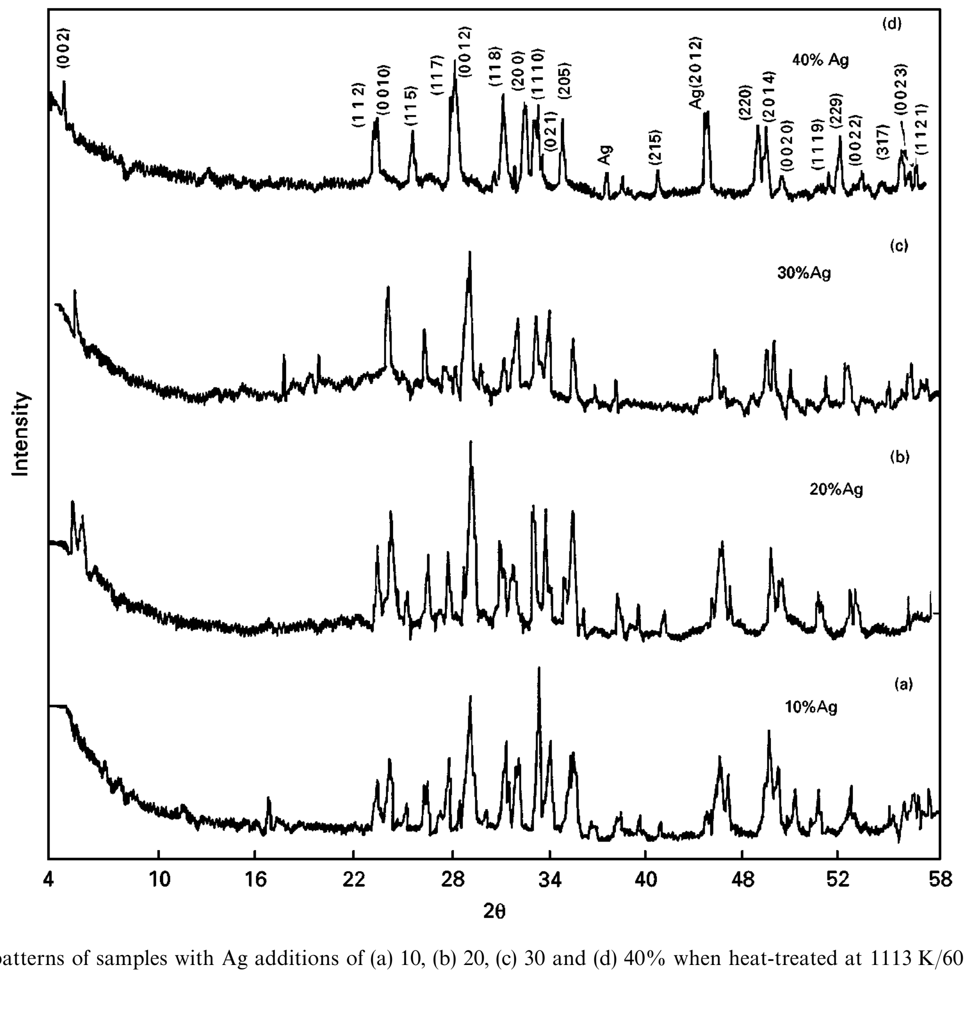

Figure 2 XRD patterns of samples with Ag additions of (a) 10, (b) 20, (c) 30 and (d) 40% when heat-treated at 1113 K/60 h.

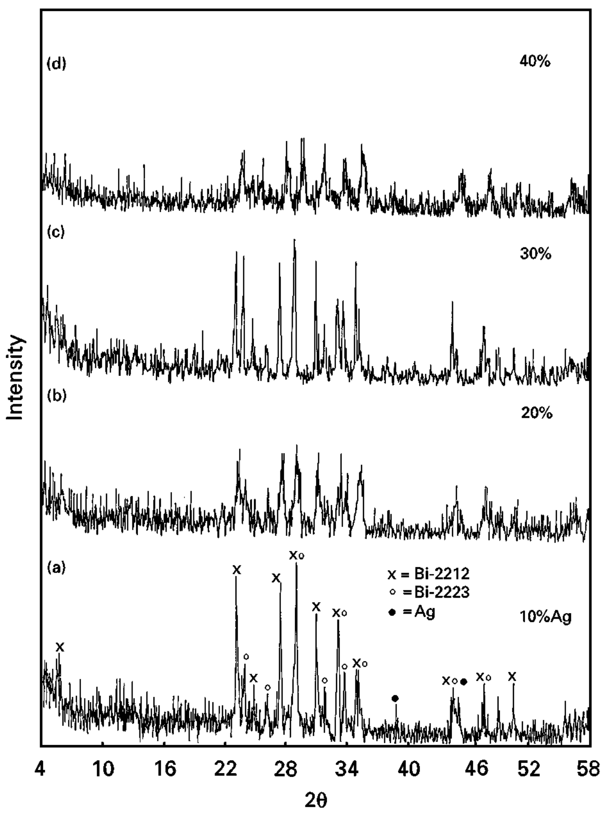

Figure 3 XRD patterns of samples with Ag additions of (a) 10, (b) 20, (c) 30 and (d) 40% when heat-treated at 1123 K/60 h.

given in Table I. Samples heat-treated at 1103 K show the formation of the Bi-2212 compound. However, the 5 wt % silver added sample shows several impurity phases along with the Bi-2212 compound whereas the sample without silver contains only Bi-2212 phase. The Bi-2223 phase formation occurs in the samples heat treated at 1113 K (Fig. 2). Nevertheless, the low T_c phase (Bi-2212) is found to be a major phase in 5, 10 and 20 wt % Ag added samples, whereas, phase pure Bi-2223 compound formation is observed in 30 and 40 wt % Ag added samples. It is evident that addition of silver brings down the formation temperature of Bi-2223 to 1113 K compared to 1123 K for samples without silver. Similar behaviour is also observed by the other workers and they explain that the compound formation occurs because of the liquid phase formation through the interaction of silver and the Bi-2212 phase [8]. The exact details of the liquid phase and its composition are not reported in the literature. The endotherm observed in the DTA patterns (Fig. 1) at 1111 K may be due to the formation of the liquid phase. Further, the heat treatment of the samples without Ag at 1113 K do not show the single phase formation of Bi-2223. Thus, it is concluded that silver enhances the kinetics of formation of the Bi-2223 phase. This may be because of the liquid phase formation by the interaction of silver with Bi-2212 phase.

Surprisingly, the samples heat-treated at 1123 K for 60 h do not show any improvement over those heat-treated at 1113 K. Further, a deterioration is observed in the 30 and 40 wt % silver added samples as evidenced by the presence of lines due to Bi-2212 phase in the XRD patterns (Fig. 3). The XRD patterns contain broad peaks and high noise level indicating the amorphous nature of the sample. The amorphous nature may be caused by the partial melting of the phase. The DTA pattern of the 40 wt % silver added sample (Fig. 4) shows a strong endotherm at 1123 K confirming the melting of the phase. The Bi-2223 sample without silver has an incongruent melting temperature of 1135 K [12]. The presence of silver shifts this temperature to 1123 K. The formation of Bi-2212 occurs by the decomposition of Bi-2223 phase during melting. Similar behaviour is also observed by Guo *et al.* [13] and the results obtained in the present study match well with their results.

To confirm the results obtained from XRD studies, a.c. magnetic susceptibility χ–T measurements are carried out on the pellets sintered at 1103, 1113 and 1123 K. Table II shows the $T_{c,onset}$ temperatures derived from χ–T plots for all the samples. The samples heat-treated at 1103 K show sharp diamagnetic transitions ranging from 40 to 60 K depending on the silver content whereas the samples without silver shows a sharp drop at 70 K. The presence of an eutectic between Ag_2O–PbO–CuO may deplete the cations in superconducting material leading to non-stoichiometric Bi-2212 phase having a lower transition. Fig. 5 shows the χ–T plots for the 1113 K heat-treated samples. The 30 and 40 wt % silver added samples show very sharp diamagnetic transitions at 107 K and other samples show a two-step behaviour indicating the presence of both Bi-2212 and 2223 phases. These results corroborate well with the XRD results. The susceptibility measurements on samples heat treated at 1123 K/60 h show the appearance of the Bi-2212 phase in 30 and 40 wt % silver doped samples (Table II).

Fig. 6 shows the electrical resistivity ρ–T plots of 1113 K heat-treated samples. The 40 and 30 wt % silver-doped samples show zero resistance above

TABLE I Formation of various phases in silver added samples when heat-treated at various temperatures

Sample no.	wt % Ag	1103 K/60 h	1113 K/60 h	1123 K/60 h
1	0	2212, Ca_2PbO_4 and CuO	2212	2212 and 2223
2	5	2212, 2201, Ca_2PbO_4 and CuO	2212	2212 and 2223
3	10	2212	2212 and 2223	2212 and 2223
4	20	2212	2212 and 2223	2212 and 2223
5	30	2212	2223	2212 and 2223
6	40	2212	2223	2212 and 2223

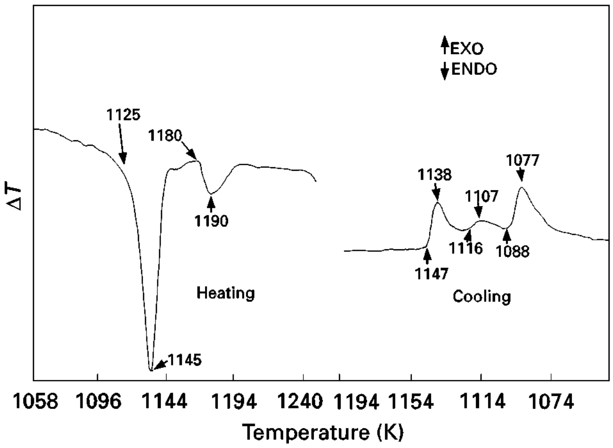

Figure 4 DTA patterns of Bi-2223 samples with 40 wt % Ag. The endotherm corresponds to the melting of the phase.

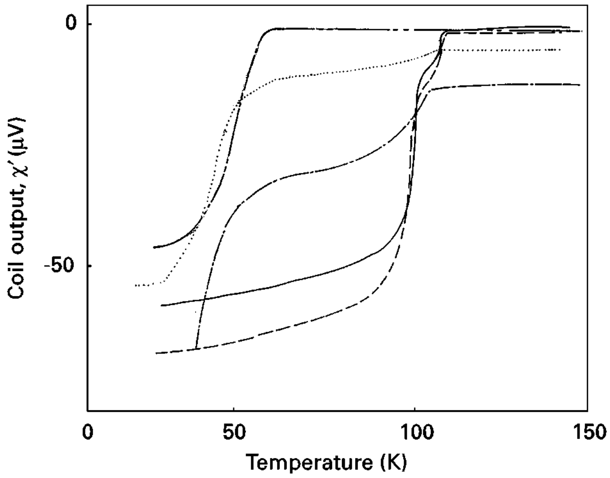

Figure 5 χ–T of samples with Ag addition heat-treated at 1113 K/60 h. Sharp transitions in 30 and 40 wt % Ag samples correspond to Bi-2223 phase. (——) 40% Ag; (– – –) 30% Ag; (- - - - -) 20% Ag; (–·–) 10% Ag; (–··–) 5% Ag.

105 K whereas other samples show $T_{c,zero}$ around 55–95 K. $\rho_{300\,K}$ is not very different from that of sample without silver, indicating the silver thus added is not coating the grain boundaries. The effect of silver content on $T_{c,zero}$, T_c and normal state resistivity of the samples are given in Table III. The T_c increases with silver concentrations. It can be concluded that not only temperature but also the amount of silver plays a role in the formation of Bi-2223 phase.

Similar behaviour is also reported in the literature with respect to silver content. Sarkar *et al.* [14]

TABLE II $T_{c,\,onset}$ values from χ–T plots of silver added samples

Sample no.	wt % Ag	$T_{c,\,onset}$ values from χ–T plots (K) 1103 K/60 h	1113 K/60 h	1113 K/120 h	1223 K/60 h
1	0	70	72	106, 83	106, 87
2	5	52.6	55	102.3	10052
3	10	92.7, 54.3	100, 67	105, 76	91, 46
4	20	54.3	106, 57	105, 76	91, 46
5	30	56.5	106, 97	–	100, 90, 60
6	40	54.75	106, 97	–	103, 90, 63

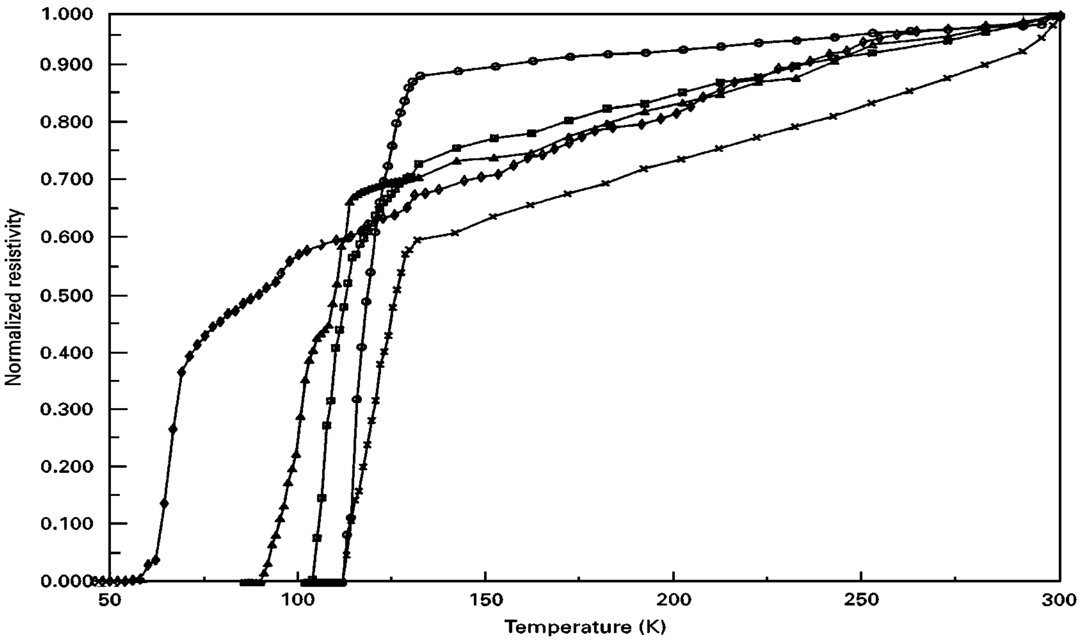

Figure 6 ρ–T plots of Ag added samples heat-treated at 1113 K/60 h showing the superconducting transitions. (◇) 5% Ag; (△) 10% Ag; (□) 20% Ag; (○) 30% Ag; (×) 40% Ag.

TABLE III Superconducting and normal state properties obtained from the ρ–T plots of silver added Bi-2 2 2 3 samples

Sample no.	wt % Ag	$T_{c,\,onset}$ (K)	$T_{c,\,zero}$ (K)	ΔT_c (90–10%) (K)	ρ_{300K} (mΩcm)	ρ_{150K} (mΩcm)
1	5	97	58	25	15	10.8
2	10	115	90	18	13.4	10
3	20	127	103	14	6.55	4.98
4	30	127	112	12	2.04	1.81
5	40	128	111	13	0.156	0.1

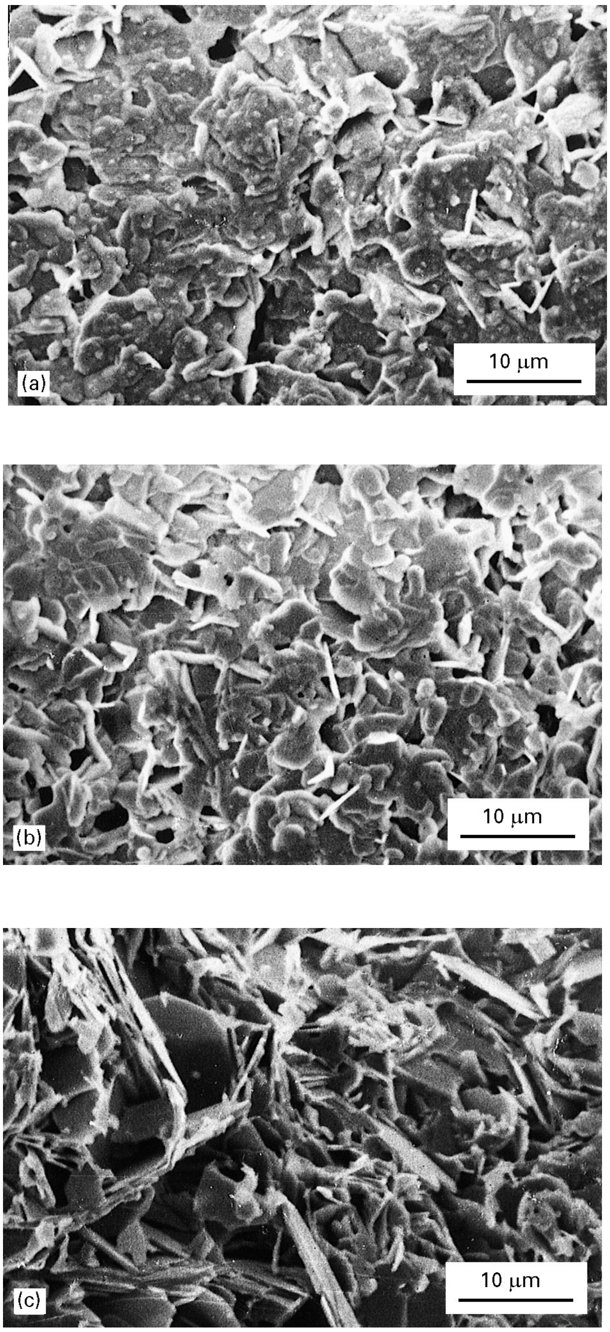

Figure 7 SEM micrographs of Bi-2 2 2 3 samples with (a) 20, (b) 30 and (d) 40 wt % of Ag additions.

observed that for silver contents between 0 to 25 wt %, T_c is depressed by as much as 40 K, but they are not able to explain the reason for this. However, from 19 to 70 wt % of silver, T_c increases and better transport

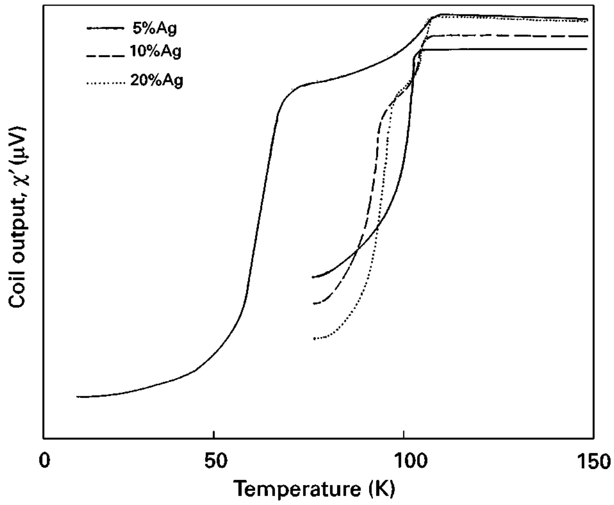

Figure 8 χ–T plots of Ag added samples heat-treated at 1103 K for 120 h. (——) 5% Ag; (– – –) 10% Ag; (· · ·) 20% Ag.

and diamagnetic properties are observed. In the present study depression in T_c is observed to be because of the formation of Bi-2 2 1 2 phase for low concentration of silver, as explained above.

At a relatively high temperature of 1113 K the composition of the liquid phase is apparently dominated by the oxide fraction of the composite and insufficient silver is present for forming a solvent system with the appropriate ionic composition needed for the proper nucleation and growth of the Bi-2 2 2 3 phase [14]. The presence of CuO in the XRD patterns for samples with low silver contents is an evidence of the excessive melting within the oxide system thereby deteriorating the superconducting properties. For samples with higher silver content, there is enough silver to form an extended solvent matrix and proper regrowth of 2 2 2 3 phase can occur even when there is large-scale melting. Plate-like morphology is required to obtain better superconducting properties and this morphology is absent in low silver content samples as observed in SEM micrographs (Fig. 7) whereas plate-type morphology is observed in 30 and 40 wt % silver added samples. The improvement in the densification of samples with increase in silver content are observed in SEM micrographs of silver added samples.

In order to improve T_c in low silver content samples, longer hours (60 + 60 h) of heat treatment are carried out at 1113 K. Very sharp diamagnetic transitions are observed at 106 K for 10 and 20 wt % and 103 K for 5 wt % silver samples (Fig. 8). Longer annealing facilitates growth of the Bi-2 2 2 3 phase. A similar effect is not observed in samples without silver. The samples without silver heat treated at 1113 K for 120 h show the presence of Bi-2 2 1 2 as major phase and Bi-2 2 2 3 as a minor phase. The phase formation is just initiated at high temperature and the susceptibility results showed to drops corresponding to both Bi-2 2 2 3 and Bi-2 2 1 2 phase.

4. Conclusions

The presence of silver brings down the reaction temperature as well as annealing time for the formation of

Bi-2 2 2 3 phase. The presence of silver affects the T_c of 2 2 1 2 phase. The heat treatment of Bi-2 2 2 3 samples above 1113 K in presence of silver leads to poor superconducting properties because of the partial melting of the Bi-2 2 2 3 phase.

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References

1. S. X. DOU and H. K. LI, *Super. Cond. Sci. Technol.* **6** (1993) 297.
2. G. V. RAMA RAO, C. RAVISHANKAR, U. V. VARADARAJU, S. VENUGOPAL, R. NAGARAJAN, S. VENKADESAN and S. L. MANNAN, presented at AGM of Materials Research Society of India at Bangalore, Feb. 1–3, 1996.
3. S. X. DOU, K. H. SONG, H. K. LIU, C. C. SORRELL, M. H. APPERLEY, A. J. GOUCH, N. SAVVIDES and D. W. HENSLEY, *Physica C* **160** (1989) 533.
4. S. X. DOU, K. H. SONG, C. C. SORRELL, M. H. APPERLEY and N. SAVVIDER, *Appl. Phys. Lett.* **56** (1990) 493.
5. T. MATSUSHITA, A. SUZUKI, T. KISHIDA, M. OKUDA and H. NAITO, *Super. Cond. Sci. Technol.* **7** (1994) 222.
6. J. C. GRIVEL and R. FLUKIGER, *Physica C* **165** (1994) 177.
7. P. S. MUKHERJEE, A. SIMON, P. KOSHY, P. GURUSWAMY and A. D. DAMODARAN, *Solid State Commun.* **76** (1990) 659.
8. H. G. LEE, G.W. HONG, J. J. KIM and M. Y. SONG, *Mater. Lett.* **23** (1995) 65.
9. R. YUFANG, Z. ZUOKAO, M. JAIN and H. PING, *Solid State Commun.* **75** (1990) 625.
10. T. W. LIU, D. H. CHEN, C. H. CHANG, C. T. CHANG, S. R. SHEEN, J. C. HUANG and M. K. WU, *Mater. Lett.* **19** (1994) 301.
11. C. Y. HUANG, H. H. TAI and M. K. WU, *Mod. Phys. Lett.* **83** (1989) 525.
12. G. V. RAMA RAO, U. V. VARADARAJU, S. VENKADESAN and S. L. MANNAN, *J. Solid State Chem.* **126** (1996) 55.
13. H. G. GUO, H. K. LIU and S. X. DOU, *J. Mater. Res.* **8** (1993) 2187.
14. A. K. SARKAR, Z. MAARTENSE and T. L. PETERSON, *ibid.* **7** (1992) 1672.

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