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Preparation and characterization of Ag-added $Bi_{1\cdot 84}Pb_{0\cdot 4}Sr_2Ca_{2\cdot 2}Cu_3O_{10+x}$ bulk tube conductors for cryogen free superconducting magnet

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Abstract. **Bulk tube conductors of $Bi_{1\cdot 84}Pb_{0\cdot 4}Sr_2Ca_{2\cdot 2}Cu_3O_{10+x}$ with addition of silver varying from 0 to 25 wt% (not reported earlier) were systematically studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), electrical transport and a.c. susceptibility techniques. The tube conductors formed by cold isostatic pressing (CIP) of the powders obtained from spray drying method have been made successfully. It was found that Ag addition has not only affected the formation of the desired Bi-2223 phase and the microstructure of these large bulk tube samples thereby influencing on the critical current (I_c), it also reduces the contact resistance to minimize the cryogen losses. These variations have been found to be Ag content dependent. An optimized value of 10 wt% Ag has been found to produce the best quality tubes showing reproducible I_c value > 120 Amp at 77 K which is in general a requirement to energies of the cryogen free conventional/HTSC superconducting magnets below 20 K.**

Keywords. **Superconductivity; Bi-2223 tube conductor; spray drying; cold isostatic pressing.**

1. Introduction

High temperature superconductors (HTS) are expected to be used in many electrical power fields among which a bulk high current lead is one of the most promising application as it can reduce much of the power losses as well as heat leakage due to their low thermal conductivity as compared with a conventional metallic Cu lead (Dorri *et al* 1991; Grivon *et al* 1991; Wu *et al* 1991; Yamada *et al* 1993). Among all the HTS having T_c above 77 K (LNT), the Bi-2223 phase having the highest $T_c \sim 110$–120 K is known to yield higher critical current (I_c) and is now the most potential candidate for its use as current leads in newly developed cryogen free superconducting magnets. However, in the existing literature, there are only few reports on the bulk sintered Bi-2223 tube conductors.

Critical requirement for the bulk high current conductor is high J_c. However, non-textured, porous structure with random arrangement of superconducting grains generally obtained in the bulk sintered intrinsically brittle oxide ceramic superconducting samples lead to lower J_c, which makes their technological applications limited. In order to overcome these drawbacks, many processes like melt texturing (Jin *et al* 1988), mechanical texturing (Ohkura *et al* 1994; Satou *et al* 1994) and floating zone (Michishita *et al* 1996) etc have been developed. Since Bi-2223 compound melts incongruently (Dou *et al* 1990), melt process will not be that suitable for tube fabrication. Also, the mechanical texturing (pressing and/or rolling) for these large bulk tube samples will not be that practicable as is easily done in the case of small pellets/tapes (Satou *et al* 1994) and long tapes (Ohkura *et al* 1994; Okada *et al* 1996). Thus, we have to seek some other alternative method like impurity incorporation etc. Among all the impurities, only Ag has non-poisonous effects on the superconductivity of Bi-2223. Besides this, it has numerous technical advantages too, which include decreasing of melting temperature and facilitating the formation of Bi-2223 phase (Dou *et al* 1990; Jones *et al* 1990; Grivel *et al* 1994), development of strong texture with *c*-axis (Comert *et al* 1994), counter balancing the intrinsic brittle nature (Michishita *et al* 1996), decrease of normal state resistance (Dzhafarov *et al* 1995), increase of J_c (Matsushita *et al* 1994) etc. It is to be pointed out here that most of these studies on Ag addition to Bi-2223 compound have been done on bulk samples in the form of pellets, small/long tapes etc. However, similar reports on large bulk tube samples are scarce.

Although Ag addition is expected to increase thermal conductivity marginally, at the same time, it lowers the contact resistance (R_c), which decreases Joule healing at the contact and contributes to the reduction of the heat

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leak from a current lead also. The use of tube conductors especially generated a fresh interest in cryogen free superconducting magnets. As only these current leads can reduce the heat load to an extent (1/10 of the conventional leads), a superconducting magnet: conventional Cu/Nb:Ti or HTSC can be used at temperatures around 4·2 K conveniently and economically. The present study deals with HTS (Bi-2223) tube conductors which are useful in operation of cryogen free superconducting magnet system requiring I_c ~ 100 Amp for 5 T field production. Results of phase detection, superconducting, microstructural and contact resistance studies on Ag added (0–25 wt%) Bi-2223 bulk tubes fabricated from cold isostatic pressing of calcined BPSCCO spray dried powder, which is expected to have uniform distribution of the constituent elements including Ag at atomic level have been reported.

2. Experimental

To fabricate the bulk Bi-2223 tube samples, the pure and silver added powders having nominal composition of $Bi_{1·84}Pb_{0·4}Sr_2Ca_{2·2}Cu_3O_{10+x}$: Ag (0–25 wt%) were prepared by spray drying technique. High purity nitrates of Bi, Pb, Sr, Ca and Cu were taken in appropriate amount in order to get the above mentioned composition and then dissolved in double distilled water separately. The individual solution was stirred continuously with mild heating. A few drops of dilute nitric acid were also added to fasten the process. Silver nitrate solutions with different amounts varying from 0 to 25 wt% were made separately and then added to each of the above solution with continuous mixing and stirring. By using Armfield SD-04 spray dryer, these mixed solutions having different Ag content were then spray dried separately and the resulting powder was collected by a cyclone. The outlet and inlet temperatures were kept at around 110°C (to prevent hydration of the complex salt) and 260°C respectively. This process produced spray dried powder without and with Ag ensuring uniform and homogeneous mixing of all the constituent elements at atomic level. These resulting powders were calcined for an hour first at 600°C, then at 780°C and finally at 800°C for 6 h with two intermediate grindings and ball milling. The final calcined powder was ball milled for 48 h and the average grain size of the powder was of the order of 0·8 μm.

These ball milled calcined powders were then packed into a rubber mold and formed into bulk tubes by cold isostatic pressing (CIP) at 30 MPa. The tubes made are of length, 20 cm; OD ~ 3 cm and ID ~ 2·8 cm, the size which is most suitable and convertable for the cryogen free superconducting magnet systems. These tubes were sintered at around 825°C in air for 40 h in a programmable tube furnace with a constant zone of 30·5 cm. These were crushed, ball milled for 72 h and the CIP process was performed again before sintering for another 60 h. The heating and cooling rates were 200°C/h. These were then investigated for X-ray diffraction (XRD), scanning electron microscopy (SEM), energy disperse analysis for X-ray (EDAX), critical temperature (T_c) and critical current (I_c) analysis.

For phase identification analysis, various portions of the calcined powder were taken and the sample tube pieces in a rectangular shape (15 mm × 5 mm) were cut from the sintered tubes. A Siemens D-500 diffractometer with CuK_a radiation was used for the above studies. For microstructural and elemental compositional analyses, a JEOL: JSM 840 scanning electron microscope and Oxford Link ISIS 300 (Co Standard), respectively were used. The resistance vs temperature measurements were carried out in the temperature range 77–300 K by the standard four-probe method using a nanovolt meter (Keithley model 196) and a current source (Keithley, programmable current source 224). The temperature of the sample was recorded by a calibrated platinum resistance thermometer. The changes in a.c. susceptibility ($c_{a.c.}$) with temperature were also measured by using a close cycle refrigerator [Sumitomo model: SRD 204]. The temperature was monitored by a gold/iron chrome thermocouple within an accuracy of ± 0·1 K. The transport critical current (I_c) of all these bulk tubes were measured with a criteria of 1 μV/cm along the longest dimension parallel to the growth direction by a d.c. four-probe method at 77 K under self magnetic field by using Keithley 196 nano-voltmeter, Aplab d.c. power supply (current range: 1 mA to 120 A with a resolution of 1 mA and accuracy of ± 0·5 mA) Keithley 197 autorange DMM and Keithley 224 programmable current source. Air drying Ag-paste was used for electrical contacts. In order to improve the contacts, metallic silver sheets were fixed to the tubes in the form of rings with Ag paste. The whole assembly was then dried in oven. The overall contact resistance including the silver layer/silver sheet and the soldered portion on both sides of each tube at 77 K in the zero magnetic field was measured by the three-terminal method.

3. Results

Bulk sintered Bi-2223 tubes fabricated by the sintering process are shown in figure 1. The X-ray diffraction analysis of different portions of the calcined powder showed identical patterns, this indicated that the calcined powder used for making tubes is homogeneous and it consists essentially of the Bi-2212 phase with Ca_2PbO_4 as the secondary phase and Bi-2223 as the minor phase. Presence of secondary phases is essential to accelerate the formation of the desired Bi-2223 phase during long sintering. A typical XRD pattern is shown in figure 2 for the 5 wt% Ag added sample. XRD patterns of all the BPSCCO samples with 0–25 wt% Ag were also performed on both the outer as well as inner surfaces of the tube pieces and the comparison is depicted in figure 3 for the sample containing 20 wt% Ag. It was found that for the outer surface (figure 3a) most of the peaks could be indexed for the Bi-2212 phase. It also shows that the *ab* planes of the nearly single Bi-2223 phase crystals are aligned along the tube longitudinal direction (i.e. along the current flow direction). Whereas, on the other hand, for the inner surface (figure 3b), additional peaks due to the Bi-2212 phase along with the Bi-2223 phase also appeared. This may be because the outer surface is relatively more exposed to oxygen as compared to the inner surface during sintering in air and thereby may lead to the enhanced volume fraction of the Bi-2223 phase.

Volume fraction (m) of the high-T_c Bi-2223 phase present in all the tube samples was also calculated by the following relation given by Matsushita *et al* (1994)

$$m = \Sigma H/(\Sigma H + \Sigma L + \Sigma I),$$

where, H, L and I correspond to 2223, 2212 and the minor impurity phases, respectively. It is to be mentioned here that, in all the sintered samples, no trace of any other impurity phase like Ca_2PbO_4 or Ca_2CuO_3 was observed. However, peaks due to Ag which is added intentionally starts appearing at and above 10 wt% and their intensity increases with increasing Ag content which suggested that silver existed in a metallic state.

Variation of Bi-2223 fraction (m) with Ag content is depicted in figure 4. It is clear that the high T_c fraction (m) increases with Ag content resulting into nearly single phase (Bi-2223) for the 10 wt% added sample and then followed by a decrease for higher Ag amount except for 20 wt% Ag. Interestingly, for 20 wt% Ag, the volume fraction of the Bi-2223 phase was found to be more than that in the 15 and 25 wt% Ag added samples.

SEM photographs of the fractured surface cross-sections of longitudinal as well as transverse of the Bi-2223 bulk tubes were taken. The longitudinal cross-section showed a comparatively more dense packing of the aligned grains with plate like crystals as compared to that of the transverse cross-section as evident from figure 5 for the 5 wt% Ag added sample. Changes in the morphology with Ag content (0–25 wt%) were also investigated and are shown in figure 6. In pure sample, a broad distribution of grain size was observed. On addition of Ag, a uniform grain size distribution with better oriented well connected plate like grains was observed. However, higher Ag contents with exception of 20 wt% Ag, lead to more random distribution and reduction in the grain size etc. It is to be noted that the 20 wt% Ag added sample showed the best microstructure

Figure 1. Bi-2223 bulk tubes fabricated by the sintering process.

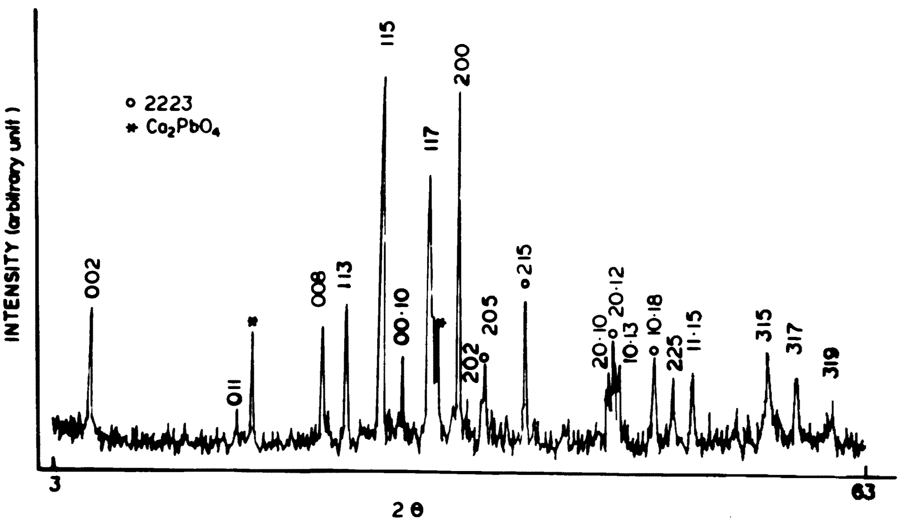

Figure 2. XRD pattern of calcined Bi-2223: 5 wt% Ag powder.

with highly dense packed aligned and much large Bi-2223 grains.

Further with regard to the presence of Ag, it was observed that although the Ag particles within the grain and/or grain boundaries are not so apparent in SEM, however, their presence both inside the grain as well as within the grains was detected by EDAX analyses. Compositions of the area as well as inside the grain for the two 5 and 20 wt% Ag samples are given below:

		Bi	Pb	Ag	Sr	Ca	Cu	O
For 5 wt% Ag: (at%)	Area	8·54	0·98	1·73	8·13	8·35	10·07	62·02
	Grain	9·64	0·43	0·97	9·33	9·89	14·68	56·06
For 20 wt% Ag: (at%)	Area	8·22	1·04	2·61	7·56	8·30	12·94	59·32
	Grain	9·11	0·95	1·82	9·45	9·57	14·09	55·01

The overall contact resistance including the silver layer/silver sheet and the soldered portion on both sides of each tube was also determined and found to decrease monotonically with the silver content. In the 10 wt% Ag added sample at 77 K in the zero magnetic field, it is as low as $3·5 \times 10^{-5}$ $2·1 \times 10^{-6}$ Ω which is about two to three orders of magnitude less than that in the sample without Ag and it follows ohmic relation up to 120 Amp (an upper limit desired to energies of the cryogen free superconducting magnet for the production of 5 T field).

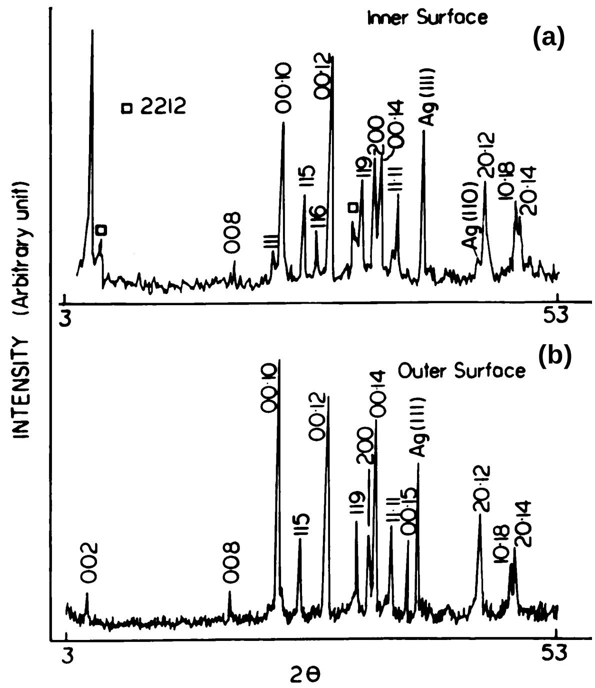

Figure 3. XRD patterns of Bi-2223 : 20 wt% Ag sintered samples showing a comparison of inner and outer surface.

Reduction in the contact resistance with Ag addition helps in minimizing the cryogen losses.

Figure 7 depicts the temperature dependences of resistance (a) and a.c. susceptibility (b) for 0–25 wt% Ag added samples. It is found from both the studies that T_c increases initially with increasing Ag content and reaches highest value around 120 K for 10 wt% Ag, beyond which it decreases.

From the R vs T behaviour (figure 7a), it is also observed that all the samples showed metallic behaviour in the normal state and the normal state resistance decreases from 0 to 10 wt% Ag addition. For 15 wt% Ag added sample, it increases to the highest value and finally, it decreases again for further Ag addition. It is to be mentioned here that in the case of 10 wt% Ag added sample, normal state resistance is lowest and T_c is highest with sharp transition (figure 7a).

Further, in the a.c. susceptibility curves (figure 7b), the signal intensity at the transition per unit weight of the Ag-added samples is several times as large as that of the non-Ag added samples and is largest for the 10 wt% Ag added sample. This may be attributed to an advanced formation of the high-T_c 2223 phase due to Ag addition and these results are in accordance with the XRD results (figure 4).

Values of I_c for different Ag contents are given in table 1. It was seen that the I_c values were found to increase initially with the increasing Ag content up to 10 wt% then decreased for higher Ag contents. For 10 wt% Ag added sample, I_c is more than 120 Amp in which a superconducting state of the tube conductor was still not broken. Interestingly, 20 wt% Ag added sample, again showed I_c to be > 120 Amps. However, at 25 wt% Ag, it decreased to the lowest value. It is to be pointed out here that both the samples with 10 wt% and 20 wt% Ag addition showed $I_c > 120$ Amp, therefore, these were subjected to thermal cycles. It was found that in the

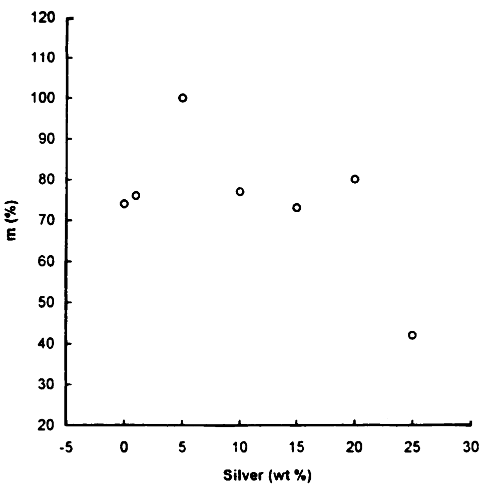

Figure 4. Variation of Bi-2223 phase volume fraction (m) with Ag content.

former sample, I_c value remained the same whereas that in the latter sample it decreased after two/three thermal cycles. This may be due to a better quality of the sample with 10 wt% Ag addition. To see its reproducibility, five more Bi-2223 tubes with 10 wt% Ag addition were made and tested for I_c values when subjected to thermal cycles. Nearly no change in I_c was found.

4. Discussion

The above measurements have suggested the beneficial role of Ag in low content region of Bi(Pb)-2223 bulk tube conductors with respect to the enhanced formation of 2223 phase, improvement in the microstructure and reduction in the contact resistance (R_c) as compared for high Ag content region with the exception of the 20 wt%. For lower Ag additions, presence of Ag along the grain boundaries although not so apparent in SEM was detected from the EDAX analysis and also can be evident from the reducing trend in the normal state resistance on increasing the Ag content. In 10 wt% Ag added sample, it appears that most of the silver goes to the grain boundaries and hence is available for conduction. Therefore, normal state resistance is minimum. However, for higher Ag additions,

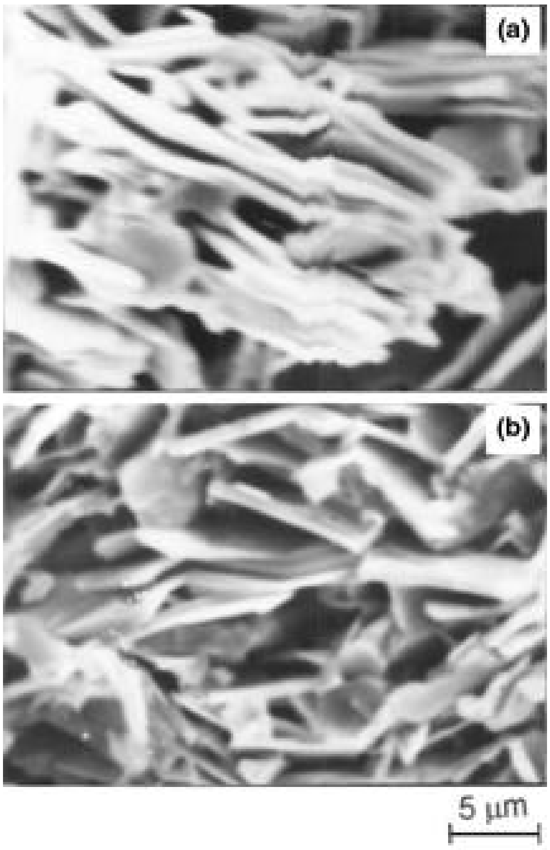

Figure 5. Scanning electron micrographs of fractured surfaces of the 5 wt% Ag added sample showing a comparison of longitudinal (**a**) and transverse (**b**) cross-sections.

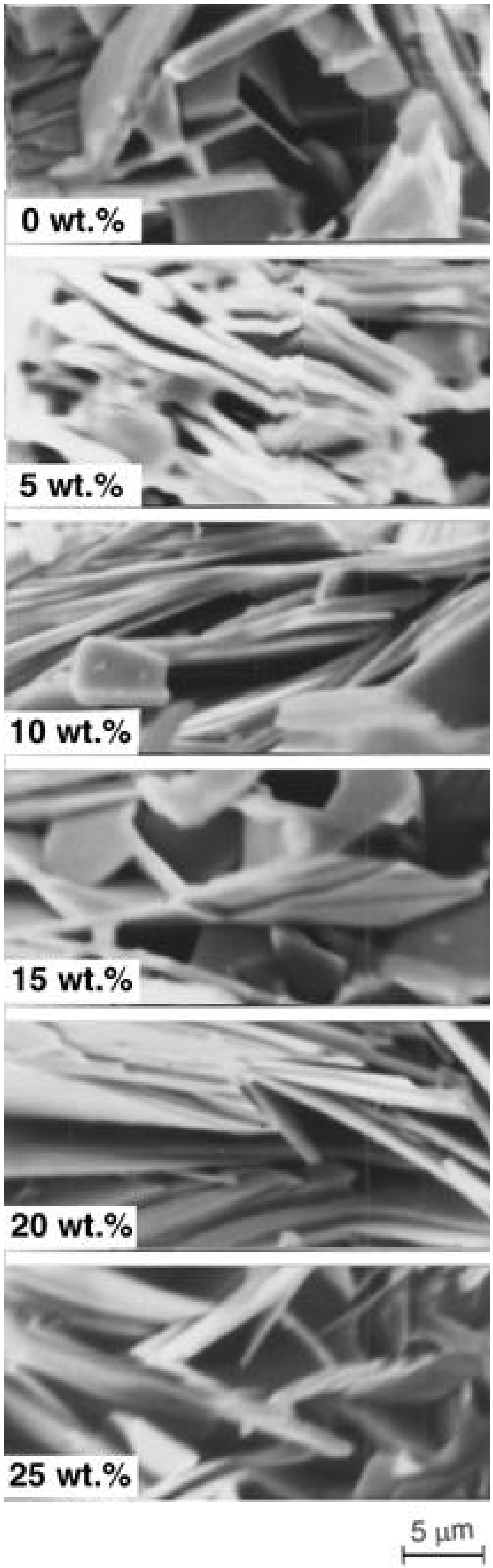

Figure 6. Scanning electron micrographs of fractured cross-section of the sintered Bi-2223 samples for 0, 5, 10, 15, 20 and 25 wt% Ag.

silver in metal form is detected in XRD patterns. Although the majority of silver in BPSCCO samples exist in metallic silver grain probably filling the grain boundaries, voids etc but a part of the Ag has also gone inside the grain as suggested by the EDAX analysis, therefore, less silver is available for normal electrical conductions thereby increasing the normal state resistance of the samples containing Ag > 10 wt%. A detailed investigation about diffusion of Ag in BSCCO system has been done by Comert *et al* (1994) who suggested that Ag can diffuse simultaneously into the voids, cracks, intergrain/intragrain regions etc. This improves the grain orientation and intergrain connectivity in the samples (as evident from figure 6) which causes the reduced contact resistance in the intergrain regions and as a result, the normal state resistance is considerably reduced (e.g. for 10 wt% Ag added sample, figure 7a), thus it could increase I_c via improved intergranular weak links through proximity effect.

Further, the fact that the presence of intergranular silver affects the process by which oxidation of bulk samples occurs during sintering is well known and found in the present studies also. All the XRD, SEM, resistivity, a.c. susceptibility and I_c studies implied that lower amount of Ag (up to 10 wt%) promotes the formation of 2223 phase to achieve higher T_c and larger I_c values. This may be attributed to the capability of Ag to facilitate oxygenation of the samples (Weinberger *et al* 1989) and could be responsible for nucleating more of the 2223 grains with the desired stoichiometry. Thus, the sample with 10 wt% Ag addition, which is nearly a single phase with improved microstructure has highest T_c and high I_c value.

Higher Ag content (except 20 wt%) leads to reduction in the grain size and discontinuities in the superconducting matrix as too large amount of metallic silver which does not superconduct gets diffused in the grain boundary region. All this effectively led to larger grain boundary area (figures 6c, e). This larger grain boundary area and the lower fraction of the 2223 phase (figures 7b and 4) probably reduced the overall I_c values. However, the reason for the exceptional case i.e. 20 wt% Ag added sample, showing I_c >120 Amp equivalent to 10 wt% Ag sample may be explained as follows.

For 0 to 10 wt% Ag addition, it appears that most of the Ag goes to grain boundaries and hence is available for conduction to reduce the normal state resistance. Similar results are reported by Savvides (1990). Further addition, say 15 wt%, probably lead to discontinuities in the superconducting matrix and is also indicated

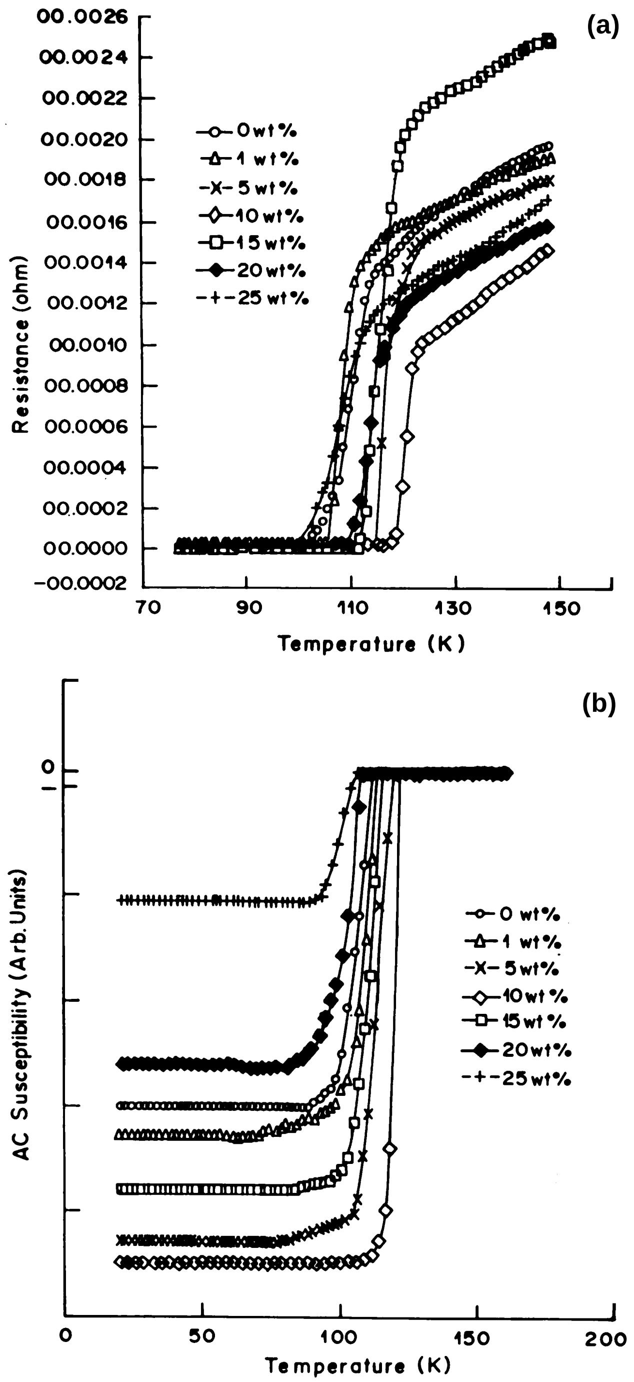

Figure 7. The temperature dependence of resistance (**a**) and a.c. susceptibility $c_{a.c.}$ (**b**) with temperature for 0–25 wt% Ag-added Bi-2223 sintered samples.

Table 1. Critical current (I_c) values at 77 K, self field for different Ag contents.

Ag (wt%)	Critical current (I_c) (Amp)
0	33
1	75
5	66
10	> 120
15	22
20	> 120
25	20

from the highest normal state resistance value as mentioned earlier (figure 7a). It appears that in this case, less silver is available for normal electrical conduction. However, for 20 wt% Ag addition it is most likely that the excessive Ag may leave the grain boundaries and start forming a separate phase and allowing relatively better intergranular contact/alignment in comparison to the rest of the sample (figure 6). All these factors combined and probably reduced R_c and increased I_c for 20 wt% Ag addition. However, still higher i.e. 25 wt% Ag addition, results in the removal of most of the intergranular Ag from the grain boundaries which was beneficial for the improved intergranular contacts and thus reduced I_c drastically.

5. Conclusions

To conclude, sintered Bi-2223 bulk tubes which are primarily designed to energies of the cryogen free superconducting magnet having $I_c > 120$ Amp at 77 K with addition of Ag (0–25 wt%) have been synthesized successfully from CIP of the homogeneous calcined spray dried powder. It is found that lower content of Ag addition to these large bulk tube conductors, significantly affects the properties of the weak links connecting superconducting grains within the sample and reduces the contact resistance and hence influencing I_c. Finally, under the present fabrication conditions, best results have been obtained for 10 wt% Ag addition producing $I_c > 120$ Amp which is desired to energies of the cryogen free superconducting magnet.

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