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Effect of oxide additives on T_c behaviour of $Bi_{2\cdot 1}Sr_{1\cdot 93}Ca_{0\cdot 97}Cu_2O_8$ system*

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Abstract. We have carried out studies on the effect of oxide additives ($Ca_{0\cdot 85}Sr_{0\cdot 15}CuO_2$, $BaBiO_3$ and $BaPbO_3$) on Bi-2212. Compositions up to 6 mole% of all the additives have been prepared and characterized by XRD, resistivity and ac susceptibility techniques. XRD studies indicate that all the materials are single phase. Resistivity and ac susceptibility studies indicate enhanced granular behaviour with the oxide additives. Low temperature (400°) sintering results in degradation of the Bi-2212 phase in the presence of the additives.

Keywords. Oxide additives; T_c behaviour; BiSrCaCuO.

1. Introduction

The high T_c materials are generally granular in nature with poor connectivity between the grains (Camps *et al* 1987). This is one of the limiting factors in achieving high J_c (Ekin *et al* 1987; Ciszek *et al* 1988; Kwak *et al* 1988). AC susceptibility technique has proved to be very useful in studying the weakly coupled granular nature of these materials. In the Bi-2212 system, the χ'–T plot clearly indicates the contributions from the individual grains (intragranular) and the weak links (intergranular) to the diamagnetic signal. The weak links arise due to various reasons such as compositional non-stoichiometry, intergrowth of related phases, impurities etc. It is interesting to study the effect of additives on the superconductivity as well as the microstructure of these materials. The additives preferentially segregate at the grain boundaries and affect the granular behaviour. The present work deals with the study of the effect of adding three additives viz. $Ca_{0\cdot 85}Sr_{0\cdot 15}CuO_2$, $BaBiO_3$ and $BaPbO_3$ on the superconductor $Bi_{2\cdot 1}Sr_{1\cdot 93}Ca_{0\cdot 97}Cu_2O_8$ (Bi-2212). All the three additives chosen are insulating (metallic in the case of $BaPbO_3$) parent compounds of superconductors and it would be interesting to study whether the additive phases themselves can be made superconducting by proximity effect. The granular behaviour is enhanced with the additives.

2. Experimental

About 15 g of $Bi_{2\cdot 1}Sr_{1\cdot 93}Ca_{0\cdot 97}Cu_2O_8$ (Bi-2212) was prepared using the solid state reaction method. This off-stoichiometric composition was chosen since an excess Bi at the SrO and Ca planes is known to stabilize the Bi-2212 phase (Ono *et al* 1989). The starting materials, Bi_2O_3 (99·999%), CuO (99·999%), $SrCO_3$ (99·999%)

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and $CaCO_3$ (99·98%; all Cerac, UK), were taken in the above mole ratios, ground and calcined in air at 810°C for 16 h. The subsequent heat treatments were also carried out in air at 840°C for 5–6 h and 875°C for 10 h with intermediate grinding. The material was then pressed into pellets (dia : 8 mm and 12 mm; thickness : 1–2 mm) and sintered at 870°C for 10 h in air and furnace cooled to room temperature. In order to enhance the T_c, the samples were introduced into a preheated furnace at 805°C for 1–2 h and then quenched in air. The additives $Ca_{0.85}Sr_{0.15}CuO_2$, $BaBiO_3$ and $BaPbO_3$ were added in steps of 2, 4 and 6 mole% to a known amount of Bi-2212. The mixture was ground thoroughly and heated at 875°C for 24 h. The resulting powder was pressed into pellets and sintered at the same temperature for 24 h.

The samples were characterized by powder X-ray diffraction (SEIFERT, Germany). Resistivity measurements were carried out by the four-probe van der Pauw method in the temperature range 300–13 K using a closed cycle He refrigerator (Leybold Hareas, Germany). AC susceptibility measurements were done on the samples at a field of 0·1 Oe and frequency of 300 Hz in the temperature range 300–13 K using the Sumitomo superconducting properties measurement equipment (Model SCR 204-T, Japan). The microstructure was determined using a scanning electron microscope (SEM; JEOL unit).

3. Results

XRD studies indicate that all the compositions up to 6 mole% of the additives are single phase (figure 1). Sharp peaks are observed indicative of well crystalline nature of the phases. The XRD patterns have been indexed on the basis of the orthorhombic Bi-2212 structure and no additional reflections have been observed. Lattice parameters have been calculated using the least square fit of the high angle reflections (table 1). The *a* and *b* lattice parameters do not show any significant change while the *c*-lattice parameter is found to increase slightly for higher concentration of $BaBiO_3$ and $BaPbO_3$ additives. Resistivity (ρ–T) measurements on Bi-2212 showed metallic behaviour in all the compositions, obeying the expression $\rho = \rho_0 + \alpha T$. The ρ_0 and α values along with ρ_{300K} values are listed in table 2.

Table 1. Orthorhombic lattice parameters for various concentrations of oxide additives in Bi–2212.

Additive	Conc. (mole%)	Lattice parameters *a* (Å)	*b* (Å)	*c* (Å)
$Ca_{0.85}Sr_{0.15}CuO_2$	0	5·392	5·392	30·718
	2	5·388	5·387	30·710
	4	5·389	5·386	30·716
	6	5·396	5·381	30·719
$BaBiO_3$	2	5·395	5·375	30·702
	4	5·395	5·382	30·761
	6	5·397	5·384	30·763
$BaPbO_3$	2	5·393	5·383	30·761
	4	5·395	5·395	30·753
	6	5·393	5·393	30·796

Table 2. Resistivity and ac susceptibility data on the additive containing phases of Bi-2212.

Additive	Resistivity data							Susceptibility data				
								χ'			χ''	
	Conc. (mole%)	$T_{c,\,onset}$ (K)	$T_{c,\,zero}$ (K)	ΔT_c (K)	ρ_{300} mΩcm	ρ_0 mΩcm	α μΩcm/°C	$T_{c,\,gran}$ (K)	$T_{c,\,bulk}$ (K)	δT_c[a] (K)	$T_{c,\,peak}$ (K)	FWHM[b] (K)
$Ca_{0.85}Sr_{0.15}CuO_2$	0·0	93	75	14	2·7	1·4	4·3	90	82	8	80	6
	2·0	90	68	18	2·8	1·7	4·3	80	69	11	68	8
	4·0	82	70	11	1·6	0·5	3·6	77·5	66	11·5	62	6·4
	6·0	44	–	–	4·0	3·2	3·2	76·6	58·5	18	50	15
$BaBiO_3$	2·0	81	73	10	1·0	0·2	2·6	75	69	6	68	6
	4·0	86	67	17	1·2	0·3	2·6	82·5	70·5	12	66	8·5
	6·0	95	56	30	3·7	3·2	2·4	82	49	33	38·5	16
$BaPbO_3$	2·0	86	72	13	1·5	0·5	3·3	79	69	10	67	6·4
	4·0	–	–	–	–	–	–	79	68	11	65·5	6·5
	6·0	81·5	65	12	1·7	0·75	3·2	79	68·5	10·5	65	6·4

[a] Transition width $\delta T_c = T_{c,\,gran} - T_{c,\,bulk}$; [b] Full width at half maximum.

Consistent $T_{c,\,zero}$ values in the range 74–76 K were obtained for the pure Bi-2212 phase. AC susceptibility studies on the pure Bi-2212 compound indicate a two-slope behaviour which reflects the transition from the regime where the grains are decoupled ($T_{c,\,gran}$) to the regime where the intergrain current circulates around the whole sample ($T_{c,\,bulk}$). In the compounds containing additives the following interesting observations have been made. (i) Resistivity studies indicate that with increase in additive concentration, the superconducting transition temperature ($T_{c,\,zero}$) systematically decreases and the ΔT_c ($T_c(90\%) - T_c(10\%)$) values progressively increase as can be seen from table 2 and figure 2 (a,b,c). However, for the phases containing $BaPbO_3$, although $T_{c,\,zero}$ decreases with concentration, no change in ΔT_c is seen, (ii) from the plot of the real part (χ'–T) of the ac susceptibility, we observe that both $T_{c,\,gran}$ and $T_{c,\,bulk}$ register a decrease in the additive compositions compared to

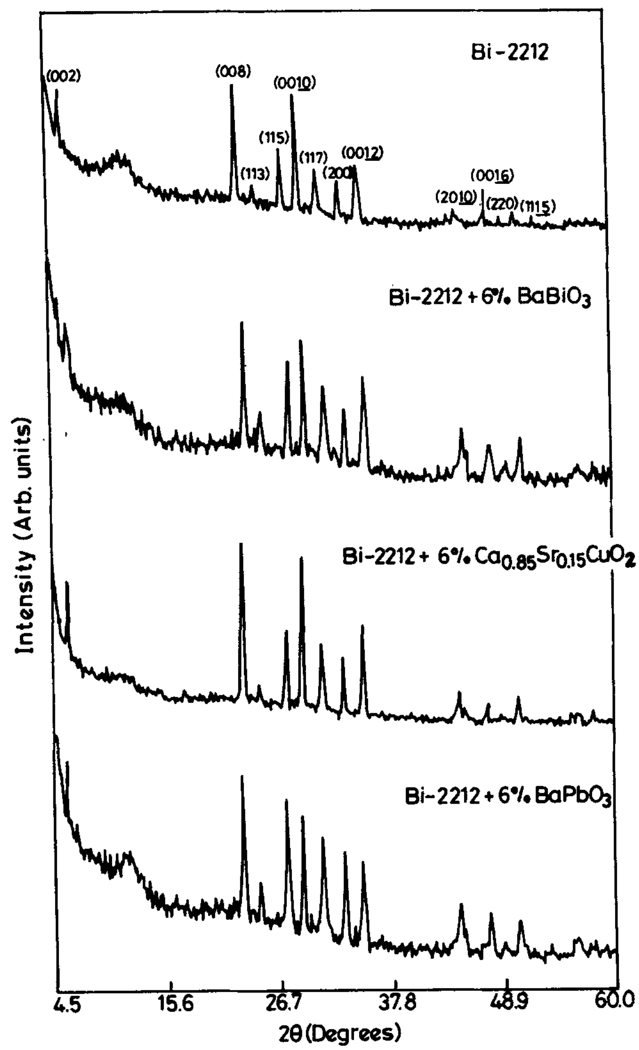


Figure 1. XRD patterns of Bi-2212 and the compositions containing additives.

the pure Bi-2212. However, variation in $T_{c,gran}$ is not significant when the additive concentration increases from 2 to 6 mole%. On the other hand, $T_{c,bulk}$ decreases systematically with increasing additive concentration from 2 to 6 mole% (except for compositions containing $BaPbO_3$). Effectively, the transition width ($T_{c,gran}-T_{c,bulk}$, denoted by δT_c) increases (table 2) from 10 K for Bi-2212 to about 15–20 K for the samples containing additives. For the samples containing $BaPbO_3$, a decrease in both $T_{c,gran}$ and $T_{c,bulk}$ are observed and the δT_c values are

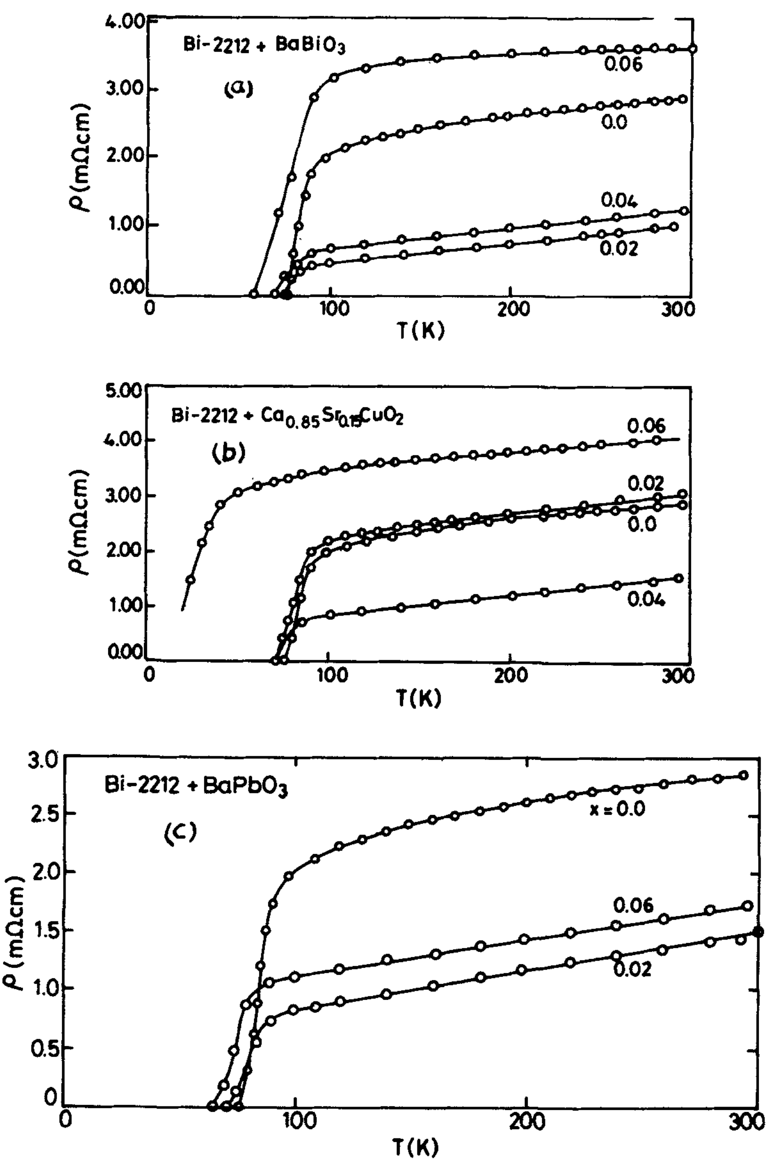
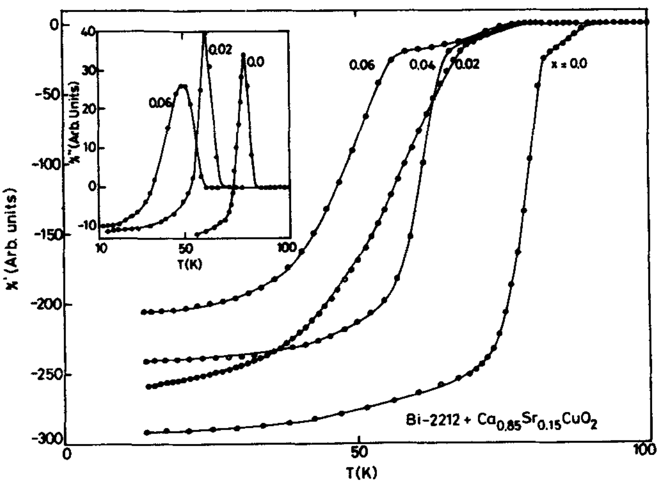
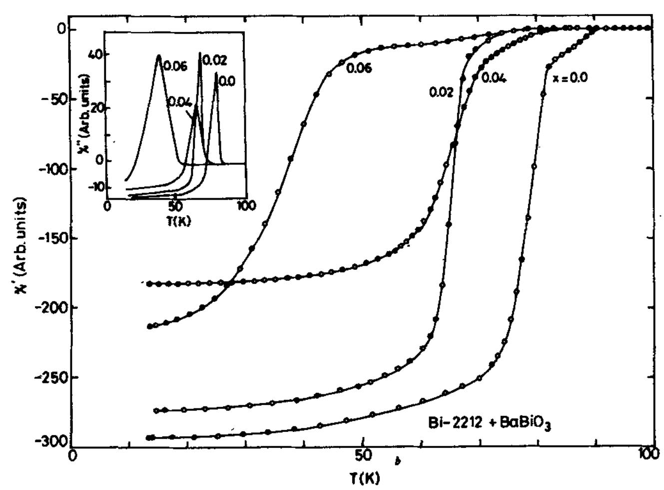
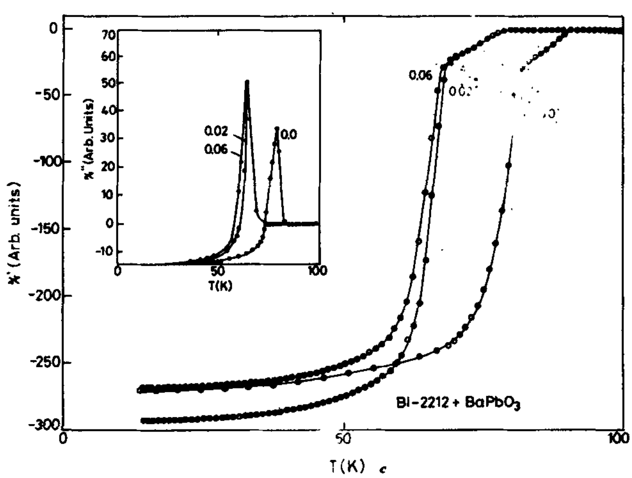


Figure 2. Resistivity ($\rho - T$) data on compositions with (a) $BaBiO_3$, (b) $Ca_{0.85}Sr_{0.15}CuO_2$ and (c) $BaPbO_3$.


χ' (Arb. units)
T(K)
0.06
0.04
0.02
x = 0.0
χ'' (Arb. Units)
Bi-2212 + $Ca_{0.85}Sr_{0.15}CuO_2$


χ' (Arb. units)
T(K)
0.06
0.02
0.04
x = 0.0
χ'' (Arb. units)
Bi-2212 + $BaBiO_3$
b


χ' (Arb. units)
T(K)
0.06
χ'' (Arb. Units)
0.02
0.06
0.0
Bi-2212 + $BaPbO_3$
c

same for all concentrations of the additives and (iii) the χ''–T plots for various concentrations of additives (insets of figures 3a, b and c) indicate that the width of the χ''–T peak increases with increasing concentration of the additives except in the case of $BaPbO_3$.

4. Discussion

The difference $T_{c,\text{gran}} - T_{c,\text{bulk}}$ (δT_c) represents the extent of granularity in the sample. The material can be thought of as consisting of a large number of grains embedded in a matrix of inhomogenous phase (grain boundary) which acts as a weak link between the grains. For very low ac fields, the nature and surface area of the weak link network relative to that of the grains determines the value of δT_c. The high value of δT_c observed for the compounds containing $BaBiO_3$ and $Ca_{0.85}Sr_{0.15}CuO_2$, indicates that the added oxide phases segregate between the grains leading to an increase in the transition width. In other words, the interconnectivity between the grains decreases and bulk superconductivity ($T_{c,\text{bulk}}$) occurs at a lower temperature. In the compound with 6 mole% of $Ca_{0.85}Sr_{0.15}CuO_2$, the diamagnetic signal does not saturate down to the lowest temperature. This is clearly in agreement with the $\rho - T$ data where a drop in the resistivity is observed but no superconductivity is detected down to 13 K. The materials containing $BaPbO_3$ (figure 3c) do not show any increase in δT_c in the χ'–T plot. This is in agreement with the results obtained from resistivity measurements (figure 2c) where ΔT_c remains almost a constant. The additives do not become superconducting on account of proximity effect. In case the additives were to become superconducting, δT_c would have decreased which is not so in the present case.

A single sharp peak in the χ''–T plots indicates the excellent quality of the material with good coupling between the grains. If r_g is the average radius of the grains and λ the London penetration depth, then for $r_g \gg \lambda$, the peak in χ'' is very sharp for low values of h_0 (Senoussi *et al* 1991). For very large grains, the area covered by the weak link network is negligible. This is valid for $T \ll T_c$. As T approaches T_c (or $h_0 \rightarrow H_{c2}$), λ tends to diverge and consequently, the whole surface of the sample will be covered by the weak link network. This leads to a sharp change (sharp peak) in χ''–T plot. On the other hand, when the number of weak links is very large as in the case of the additive containing compositions presently studied, the relative change in the total area covered by the weak link network will be very small when T approaches T_c and as a consequence, the peak in $\chi''(T)$ which reflects this change would not be very sharp.

In the present study, in the cases of materials containing $BaBiO_3$ and $Ca_{0.85}Sr_{0.15}CuO_2$, we observe that the width of the χ'' peak increases with increasing concentration of the additives. This clearly indicates that the weak link network is enhanced with the addition of oxide additives. However, for the samples containing

Figure 3. a–c. Real part of the ac susceptibility (χ'–T) data on Bi-2212 with $Ca_{0.85}Sr_{0.15}CuO_2$, $BaBiO_3$ and $BaPbO_3$ additives. As can be seen, δT_c ($T_{c,\text{gran}} - T_{c,\text{bulk}}$) increases with additive concentration. However, with $BaPbO_3$ addition, δT_c remains a constant. Insets show variation of imaginary part χ'' as a function of temperature. Peak width systematically increases with concentration for the compositions containing $Ca_{0.85}Sr_{0.15}CuO_2$ and $BaBiO_3$.

$BaPbO_3$, the width of χ'' is almost a constant indicating that there is no significant change in the microstructure which is clearly in agreement with the results obtained from resistivity data.

Scanning electron microscopy (SEM) photographs show qualitative changes in the microstructure of the pure and additive compositions. However, unequivocal correlations were not possible with the observed superconducting behaviour.

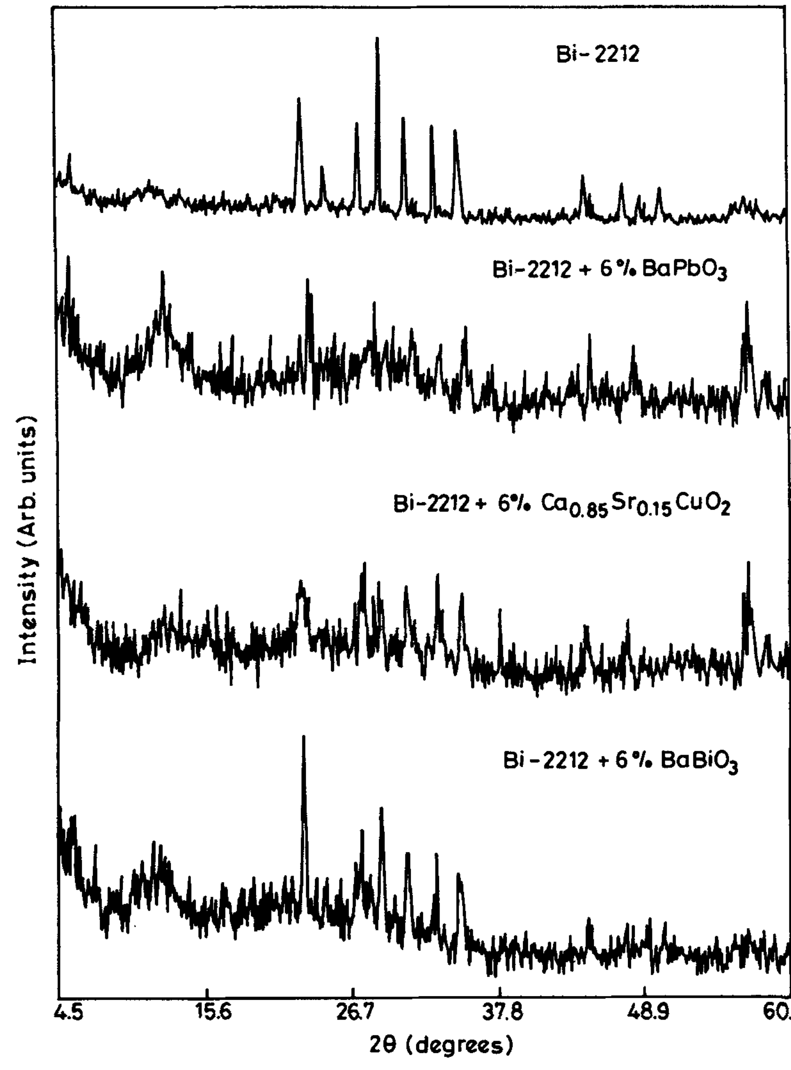


Figure 4. XRD patterns of Bi-2212 and the compositions containing 6 mole% of additives, sintered at 400°C. The Bi-2212 phase remains unchanged whereas the additive phases show a degradation of the Bi-2212 phase.

5. Effect of low temperature sintering

To explain the enhanced granular behaviour in the above phases, we have considered two possibilities: (i) the added oxides are non-interactive and concentrate only in the grain boundary region, as described earlier, since XRD patterns clearly show that the materials are all single phase and no impurities due to the additives are observed and (ii) since the sintering temperature is as high as 875°C, the possible interaction of the added oxide material with Bi-2212 cannot be ruled out which may be within the limits of detection by XRD. This could lead to a partial decomposition of the Bi-2212 superconductor and hence bulk superconductivity is observed at much lower temperatures. It was thought that by sintering at much lower temperatures (say 400°C) the interaction of the additive with the Bi-2212 phase would be minimal. We therefore prepared the end compositions with 6 mole% each of $BaBiO_3$, $BaPbO_3$ and $Ca_{0.85}Sr_{0.15}CuO_2$. The heat treatment was done on the powder at 400°C for 3 days; pelletized and sintered at 400°C for 3 days. The pure Bi-2212 pellet was also heated at the same temperature. XRD of the pure compound was found to be single phase and remained unchanged whereas the compounds containing additives showed very broad and less intense peaks (figure 4) indicating that the material has degraded in the presence of the oxide additive at 400°C. To check its reproducibility, we repeated the experiment and obtained identical results. AC susceptibility studies on these phases are shown in figure 5. For the compositions containing $BaBiO_3$ and $BaPbO_3$, the χ'–T plot shows a drop around 105 K indicating the presence of a small amount of high T_c (Bi-2223) phase and a second drop

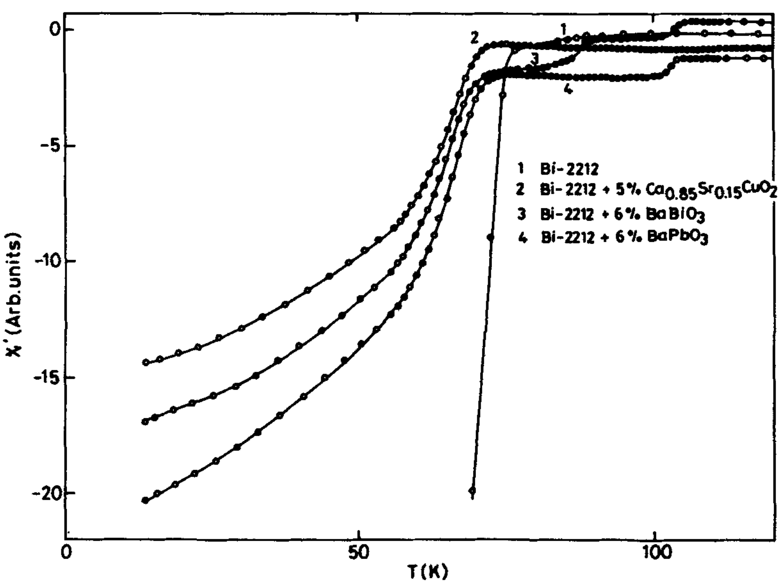


Figure 5. Real part of the ac susceptibility (χ'–T) data on Bi-2212 with 6 mole% of additives $Ca_{0.85}Sr_{0.15}CuO_2$, $BaBiO_3$ and $BaPbO_3$ sintered at 400°C. The Y-axis is very much expanded to show the details with regard to the additive compositions. Bi-2212 shows a signal at 250 μV with good saturation.

occurs at a much lower temperature. For the composition containing $Ca_{0.85}Sr_{0.15}CuO_2$, the high T_c phase is not seen. As can be seen, the signal strength in all the three cases has considerably decreased and the transition width is extremely broad. This indicates that the additive essentially degrades the 2212 phase and favours the formation of the high T_c phase at 400°C. However, no discernible peaks due to Bi-2223 could be seen in the XRD patterns since the phase would not have been well-crystallized when heated at such low temperatures. The formation temperature of Bi-2223 is 858°C which is lower than that of Bi-2212 (875°C) and hence it appears that in the presence of additives, the Bi-2212 phase is destroyed when heated at low temperatures leading to the slow formation of Bi-2223. SEM photographs taken on all these materials indicate qualitative changes in microstructure of the compounds with additives.

6. Conclusions

Studies on the effect of oxide additives on $Bi_{2.1}Sr_{1.93}Ca_{0.97}Cu_2O_8$ have indicated a change in the granular nature. Single phase materials have been obtained up to 6 mole% of the additives showing that the additives are non-interactive. Resistivity (ρ–T) and ac susceptibility (χ–T) studies indicate that the insulating oxide materials viz. $BaBiO_3$ and $Ca_{0.85}Sr_{0.15}CuO_2$ progressively increase the transition width δT_c ($T_{c,\,gran} - T_{c,\,bulk}$) with increasing concentration. SEM studies have indicated qualitative changes in the microstructure. No significant changes in δT_c are observed for the compositions with $BaPbO_3$.

Low temperature sintering of the compounds containing 6 mole% of the additives indicate that the materials are almost amorphous with no significant peaks of Bi-2212. AC susceptibility studies show that Bi-2212 is unstable in the presence of the additives when heated at low temperatures (400°C) and forms the Bi-2223 phase.

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References

Camps R A, Evetts J E, Glowacki B A, Newcomb S B, Somekh R E and Stobbs W M 1987 *Nature (London)* **329** 229

Ciszek M, Olejniczak J, Trojnar E, Zaleski A J, Roover A J M and Van de Klundert L J M 1988 *Physica* **C152** 247

Ekin J W 1987 *Adv. Ceram. Mater.* **2** 586

Kwak J F, Venturini E L, Nigrey P J and Ginley D S 1988 *Phys. Rev.* **B37** 9749

Ono A 1989 *Jpn J. Appl. Phys.* **28** L1372

Senoussi S, Aguillon C and Herasonds S 1991 *Physica* **C175** 215