Effect of CuO addition in Bi–Sr–Ca–Cu–O and Y–Ba–Cu–O ceramics

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Abstract. The effect of adding CuO matrix to $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ and $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductors was investigated through resistivity, XRD, SEM, thermoelectric power (TEP), and ac magnetization studies. Samples with as low as 20% (by weight) of the superconducting phase showed superconducting transition in resistivity-temperature (R - T), with the superconducting zero around 77 K in thermoelectric power, critical current (J_c) values were evaluated by applying Bean's critical state model. CuO could be added to the superconducting material without any significant deterioration in the quality of the samples, up to a concentration of as low as 40% (by weight) of the superconducting material.

Keywords. Superconductivity; crystal growth; X-ray diffraction; magnetic properties.

1. Introduction

Large anisotropies observed in resistivity, thermoelectric power (TEP), critical field (H_c) and critical current value (J_c) in a - b plane and along the c -axis (Dinger *et al* 1987; Hagen *et al* 1988; Martin *et al* 1988; Wang and Ong 1988) make high- T_c superconductors a class of their own. The granular nature of these polycrystalline materials limits the maximum transport critical current J_c , that can conduct through these superconductors. It therefore becomes a necessity to analyse the percolation between these grains of various types of crystal structures to further enhance the transport critical current. Various workers in this field believe that percolation threshold, i.e. the minimum volume percentage of superconductor in a non-superconducting matrix that shows a zero in the transport property, varies. A zero in TEP could be obtained without getting zero resistance for the electrical conduction (Jha *et al* 1989; Mammou *et al* 1994). We pursued this work further, and analysed two series of samples with CuO added respectively to $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ and $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, for various studies like resistivity, TEP, XRD and SEM.

2. Experimental

Powdered samples of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ and $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, were prepared using standard solid state-ceramic technique. Bi-2223 samples, after repeated grinding and calcination, were sintered at 830°C for 72 h in air. $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ samples were calcined at 850°C for 24 h, crushed, ground and then recalcined at 875°C for 24 h, mixed and ground again. The powders, thus obtained,

were pressed into pellets and rectangular bars ($35 \times 3 \times 4 \text{ mm}^3$). The bars were sintered at 920°C for 24 h under flowing oxygen. We used CuO as the insulating matrix and, by weight, we mixed it with the two superconducting powders to make two series of composites, i.e. BCu with $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_8 + x\%$ CuO series ($x = 0, 20, 40, 60$, and 80), and YCu with $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} + y\%$ CuO series ($y = 0, 0.2, 0.4, 0.7, 0.75, 0.80, 0.85, 0.90$, and 0.95).

The resistivity-temperature (R - T) measurements were carried out using standard four-probe method. A calibrated Si-diode sensor, of type DT-500 (Lake Shore), was used for measuring the specimen temperature. The accuracy in temperature measurement was 0.1 K. The crystal structures of these specimens were studied by obtaining room temperature X-ray diffraction pattern of all the specimens on a Sieman's D-500 powder X-ray diffractometer using CuK_α radiation. The lattice parameters were evaluated for some of the specimens. The grain morphology of most of the specimens was studied using SEM technique. Zero-field-cooled a.c. magnetization measurements were carried out at 77 K on some of the specimens, 4 mm in width and approximately $16 \times 1.8 \text{ mm}^2$ in cross-section, at a frequency of 317 Hz at fixed applied fields in the range of 1–10 Oe. Hysteresis loops observed on the oscilloscope screen were plotted using the attached plotter.

3. Results and discussion

3.1 Samples with CuO added to $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_8$: BCu series

The results of XRD studies and the R - T studies for the pure and other samples of the BCu series are given

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The SEM picture of these samples indicate platelet type of typical superconducting 2223 particles, which decrease in number with the enhanced CuO concentration. Specimen with 20% of superconducting phase (figure 3) shows good amount of 2223 grains. Pure specimen, and the specimen with 80% of the superconducting phase, show

3.2 Samples with CuO added to $Y_1Ba_2Cu_3O_{7-\delta}$: YCu series

Table 1 describes the T_{c0} ($\rho = 0$) values for these samples for various concentrations. Specimens up to 85% of insulator show a superconducting transition, however, T_{c0} above 77 K is obtained only for specimens with 70% concentration. For specimens with 10% or less concen-

Figure 2. Resistance versus temperature curves for **a.** $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_8 + x\%$ CuO for $x = 0, 20, 40$ and 60 ; and **b.** $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_8 + 80\%$ CuO.

tration of superconducting material, there is absence of superconducting transition. The behaviour of the resistivity curves is metallic at higher concentrations of the superconducting phase, but the slope decreases rapidly and curves in the normal region become increasingly flat, indicating the insulating trend in the normal state resistivity. However, at very low concentrations of the superconducting phase, the behaviour tends to be purely insulating. Specimen with 80% of the insulator was zero in the TEP. The noise for low superconductor concentrations was dominant enough to observe zero in thermoelectric power. This noise seems to be an inherent behaviour of these low concentration samples ($y \geq 85\%$).

All the specimens ($y \leq 80\%$) show a characteristic superconducting hump. Furthermore, the positive TEP values, obtained in all the specimens, indicate that the conduction in these materials is via holes. This result had been earlier proven by Hall coefficient measurements (Wang and Ong 1988), and also is in agreement with reports on TEP (Mitra *et al* 1987; Srinivasan *et al* 1987; Trodahl and Mawdsley 1987; Crommie *et al* 1988; Ma *et al* 1989). The superconducting hump or the peak, just above T_c , as shown in figures 6 and 7, is a peculiar feature of the TEP of these superconductors, which has widely been reported for both in bulk and single-crystal specimens. Several reasons and theories to explain this peak have been put forth. While Ma *et al* (1989), and Trodahl and Mawdsley (1987) attributed it to an enhanced phonon drag effect that truncated at the onset of superconductivity; Jha *et al* (1989) attributed the anomaly

to the pair fluctuation effect. They modified the free-electron expression for TEP, given by MacDonald *et al* (1962). The modified expression is given below:

$$S = \frac{\pi^2 k_B^2 T}{3e E_F} \left[\frac{\partial \ln \rho(E)}{\partial \ln E} + \frac{\partial \ln v^2(E)}{\partial \ln E} + \frac{\partial \ln \tau(E)}{\partial \ln E} \right]_{E=E_F} \quad (1)$$

While modifying, they took into account the strong temperature dependence of $\rho(E)$ and $v(E)$ due to pair fluctuation in the normal state. After considering two peculiar features of these superconductors, viz. the short coherence length and the 2D nature, the modified expression given by Kumar (1989) is:

$$S = \frac{\pi^2 k_B}{3e} \left(\frac{T}{T_f} \right) = \frac{1}{1 + T_\xi |\ln \mu| / 4T} \left[\frac{1 + (T_\xi T_f / 2T^2) |\ln \mu|}{1 + T_\xi |\ln \mu| / 4T} \right], \quad (2)$$

Figure 3. SEM micrograph of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_8 + 80\% \text{CuO}$.

Figure 4. XRD patterns of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} + y\% \text{CuO}$ ($y = 0, 40$ and 80).

where $k_B T_f = E_f$, $k_B T_\xi = \hbar^2 / (2m\xi^2)$ and $m = (1 - T_c/T)$. The above expression does explain the anomalous temperature variation of the TEP, but gives an exaggerated value for the TEP peak. As suggested by Kang *et al* (1989), the effect of disorder, phonon drag, or a possible magnon drag on TEP needs consideration. In our specimens, with the increasing CuO concentration, the height of the peak continuously increases, thereby indicating some possible effects due to the influence of the CuO matrix on phonon drag.

3.3 Mechanism of percolation; in resistivity and in thermoelectric power

High- T_c superconductors consist of isolated grains with good superconducting characteristics, separated by regions which are weakly superconducting or could be even insulating (Mishra *et al* 1996). The conduction through the grains is governed by the strength of the intergrain coupling (weak links) that is usually assumed to be of Josephson type (Deutscher *et al* 1980).

The grains get coupled when the Josephson coupling energy exceeds the thermal energy ($k_B T_c$). As the temperature is lowered, more and more grains get coupled until the specimen reaches a temperature where the coupling probability becomes equal to the percolation threshold. This temperature marks the transition temperature T_{c0} , that shows the presence of an infinite cluster of coupled superconducting grains. It is quite expected if pure HTSC phases be isolated and no low T_c phase be formed, percolation is possible much below 20%, the observed threshold value for these systems.

However, the theoretical limit for this percolation threshold value, suggested by Zallen and Scher (1971), for superconductors, is either when the superconducting volume fraction (SVF) is above the percolation threshold (17 V%) or if the interparticle separation is smaller or comparable to the coherence length. In the latter situation the cooper pair will tunnel through from one superconducting particle to another via the proximity effect and superconductivity will be observed. In TEP specimens, the proximity-effect mechanism does not appear to operate, since the coherence length is only 10–20 Å. Moreover, in TEP, lower value of threshold is expected, based on the mode of transition suggested by Jha *et al* (see figure 8). Thus in TEP, cooper pair tunnelling is expected to occur through the grains in perpendicular paths or isotherms, so that no voltage-drop contribution arises towards the TEP as a result of this kind of tunnelling, and thus the voltage developed remains zero. This explains the observation of zero in the thermoelectric power for a lower concentration of the superconducting phase, i.e. 20% that does not show a zero in its R - T behaviour (figure 7).

Table 1. T_c ($\rho = 0$) and the magnetic critical current density values (J_c) for different percentages of the superconducting phase.

x % CuO	T_{c0} (K)	J_c (A/m ²)	Y % CuO	T_{c0} (K)	J_c (A/m ²)
0	102.6	118.5	0	90.0	845
20	100.2	190.0	20	87.0	1666
40	98.0	142.3	40	86.0	1109
60	96.0	85.5	70	84.5	—
80	< 77 K	41.3	75	76*	—
100	**	—	80	75*	—
—	—	—	90	**	—

*Extrapolated values

**No transition down to 77 K

Figure 5. Resistance vs temperature curves for $Y_1Ba_2Cu_3O_{7-\delta} + x\%$ CuO ($x = 70, 75$ and 80).

Figure 6. Thermoelectric power vs temperature of $Y_1Ba_2Cu_3O_{7-\delta}$ (pure).

3.4 Estimation of critical current density, J_c : low field magnetization studies

Generally, HTSC materials show low value of the critical field, H_{c1} . Consequently, these materials easily acquire the mixed state. For an approximate estimation of J_c , and also for investigation of the low-field magnetic effects on these superconductors, we carried out low-field hysteresis measurements. Opening up of loops by our specimens, indicate low value of H_{c1} for these specimens. In general, the loops are elliptical. However, for the higher fields a distortion in shape, to near rectangular or parallelogram-like, occurred (figure 9). We tried to explain the shape of the loop in our specimen, assigning different parameters a and H/H^* , in the following equations derived by Ji *et al* (1989). The equations are:

$$4\pi M = 4\pi M_{\text{Bean}} - aH, \quad (3)$$

Figure 7. Thermoelectric power vs temperature of $Y_1Ba_2Cu_3O_{7-\delta} + 80\% CuO$.

Figure 8. A percolation mechanism for zero thermoelectric power in a composite consisting of superconducting grains in a non-superconducting matrix. The grains widely separated in transverse direction do have overlapping along the longitudinal direction.

$$4\pi M_{\text{Bean}} = B - H, \text{ where } \frac{\int H(x)dx}{\int dx}. \quad (4)$$

The near-rectangular loops obtained for higher values agree well with the theoretically predicted hysteresis loops based on the formulae:

$$4\pi M = 4\pi M_{\text{Bean}} - (0.02)H \text{ (figure 10a),}$$

and

$$4\pi M = 4\pi M_{\text{Bean}} \text{ (figure 10b).}$$

Furthermore, the loops were giving a very low values of 0 to 0.2 in the above equations. This implies that the proportion of the grains in the Meissner state is quite low, below 2%. Perhaps, the field had penetrated all the grains (beside the intergranular regions), which is quite expected at the higher fields. While the loops were observed to be elliptical, in case grain contribution was there and 'a' was well above zero; the loops tended to acquire a rectangular shape with 'a' approaching the zero value.

Figure 9. A.C. magnetization hysteresis loops of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_8$.

Figure 10. Hysteresis loops predicted by the formulae: a. $4\pi M = 4\pi M_{\text{Bean}} - (0.02) H$; and b. $4\pi M = 4\pi M_{\text{Bean}}$.

Therefore the Bean's model appears to be sufficient to explain shape of the experimental loops obtained, and it can be applied to evaluate the J_c (magnetization) using the formula $J_c = 2\Delta M/d$; $\Delta M (= M^+ - M^-)$, d being respectively the magnitude of the remnant magnetization and the thickness of the sample. The J_c values at $H_{ac} = 9.7$ Oe (table 1). The critical current values have shown wide variations. In general, J_c showed an increase with the applied magnetic field. For YCu sample with no CuO concentration, the value is maximum, and varies from 297.6 A/m^2 to 845 A/m^2 . This is in contrast to the J_c values we obtained for pure Bi-specimens, that seems to be limited below 150 A/m^2 . For the specimen of YCu series with 20% of CuO, though we obtained low values of J_c , the values were only for the higher fields of 6.15 Oe and 9.7 Oe. The obtained values roughly approached and even exceeded the values of the pure sample. For other concentrations however, this value has been found to decrease because of the decreasing concentration of the superconductor in the specimen. The similar trend was followed by BCu samples as well (see table 1). The area of the loops increased with the field, indicating that loss

due to the viscous drag was operating and that this drag increased in high- T_c materials for very low fields. One interesting observation on these loops was the small asymmetry in their shapes after their distortion from the ellipse. The flatness in the loops, especially in YCu samples, could be either owing to the Bean-Livingston effect (Bean and Livingston 1964) or the various viscous effects, discussed earlier, present in these superconductors.

4. Conclusion

Based on our work, we can conclude that CuO can be mixed with the superconducting material without any significant deterioration in the transition temperature, and the transport current of the specimens. Percolation values, of as low as 20%, indicate that superconducting materials can be mixed with CuO without losing their quality as a superconductor. Zero in thermoelectric power was shown by the specimens with higher CuO concentrations compared to our results on resistivity studies. A peak, generally attributed to phonon drag effect, appears just before the superconducting transition in thermoelectric power. The height of this peak increases with increasing CuO concentration. This indicates an increase in the phonon drag in these specimens owing to an increase in the CuO concentration. Thus, it appears that mixing of these superconducting materials with a suitable non-superconducting material, could further facilitate maximum transport critical current, J_c , in the long-drawn superconducting wires, which could be commercially used in high- T_c superconducting materials.

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