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Oxide glass filaments and their superconducting phase by annealing

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Abstract. $Bi_4Ca_3Sr_3Cu_xO_y$ (4334) oxide glasses with different concentrations of the transition metal copper have been prepared by rapid quenching technique from respective melts. These glasses have been characterized from electrical, magnetic, dielectric and other properties. The semiconducting glasses are not superconducting even down to 4·2 K. However, by properly annealing the glasses in air or in oxygen atmosphere they can be converted into the corresponding superconducting phases with superconducting transition temperatures between 70 and 110 K depending on the Cu ion concentrations. The dc conductivity of the glasses could be explained with small polaron adiabatic hopping mechanism. Analysis shows that the correlated barrier hopping (CBH) mechanism is the most appropriate model for explaining the a.c. conductivities of these glasses. Addition of a small amount (about 2 wt%) of B_2O_3 makes it possible to draw glass filaments which could also be converted into the superconducting phase with T_c values lower than those obtained from the respective pure glasses.

Keywords. Glass-ceramic route; high temperature superconducting filaments; oxide glass filaments.

1. Introduction

First report on the novel method of making superconducting oxide (HITSO) like $Y_1Ba_2Cu_3O_x$ (123) using glass to ceramic route (GCR) was made by Komatsu *et al* (1987) and subsequently several reports have been made (Chaudhuri *et al* 1989a; Som and Chaudhuri 1990) describing the preparation and characterization of many other HITSO materials prepared by the GCR technique. Since the HITSO thus prepared are very dense, and since it is convenient to make HITSO wires or tapes from the glass phase, the GCR technique is popular (Som and Chaudhuri 1990). The microstructures of these glasses could be well controlled and the crystallites in a particular orientation can be aligned when one starts making HITSO using GCR method. Recently we prepared Y–Ba–Cu–O, Y–Ba–Sr–Cu–O, Bi–Sr–Ca–Cu–O and (Bi, Pb)–Ca–Sr–Cu–O type HITSO materials using the GCR technique. In the present paper, however, we report the electrical, magnetic, dielectric and other properties of the $Bi_4Sr_3Ca_3Cu_yO_x$ (4334) system for different values of transition metal (Cu) ion (TMI) concentrations (for $y = 3$–5). Attempt has also been made to make glass filaments and then convert them to the corresponding superconducting phase by properly annealing the glass filaments. A major problem for the preparation of Bi–Sr–Ca–Cu–O oxide glass fibres is the devitrification of the melts before drawing fibres from the melt. This problem was partially solved by adding B_2O_3 as glass former and varying the concentration of bismuth oxide in the glass. Since addition of B_2O_3 (~ 2 wt%) reduces the T_c values (for instance for the 4334 glasses) to about 75 K, we report in this paper the properties of the samples without B_2O_3.

2. Experimental

For making the (4334), (2223) etc. glasses Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO oxides were mixed well in suitable proportion. The mixed oxides were melted at 1200°C for 2 h, the melt quickly quenched as discussed earlier (Som and Chaudhuri 1990) and thin glass plates were made. The amorphous character of the glasses with different copper concentrations were tested by X-ray diffraction and SEM studies. The amorphous nature of one of the samples is shown in figure 1. The CuO concentration dependences of density of the glasses are shown in figure 2. The glass transition temperatures (ranging from 400–450°C) and the crystallization temperatures were obtained by differential thermal analysis.

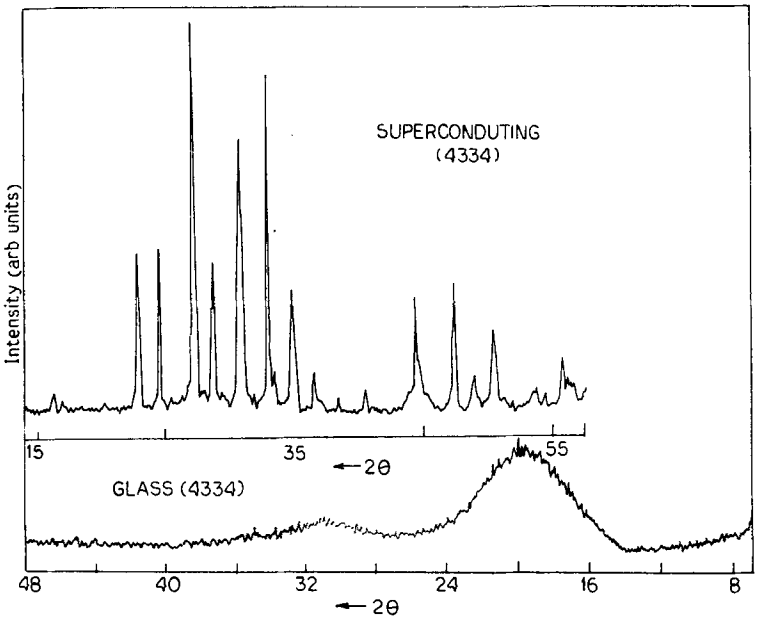

Figure 1. X-ray diffractograms of amorphous and crystalline phases of a particular sample.

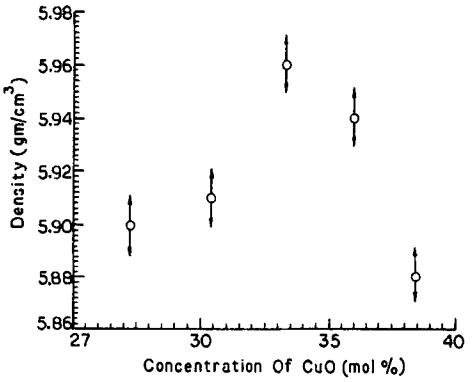

Figure 2. Variation of density with concentration of CuO.

2.1 *Preparation of glass filaments*

The oxide glass filaments were made by two techniques: (i) by pouring the melt through capillary tubes of silver and ceramics and removing the silver tubes or breaking the ceramic (or fused silica) tubes; (ii) by melting the (4334)-type glasses with appropriate quantity of B_2O_3 and drawing small fibres or tapes by melt-spinning technique. For a proper choice of B_2O_3 and Bi concentrations in the glass it is necessary to draw filaments of the glass and then annealing the filaments into the superconducting phase. This technique, though convenient, reduces the superconducting transition temperature T_c and increases the resistivity of the samples.

3. Properties of glasses

The electrical conductivity (σ_{dc}) of the glasses at a fixed temperature (300 K) for different CuO concentrations is shown in figure 3. It is seen that d.c. conductivity increases with increase of transition metal ion concentrations. The thermal variations of electrical conductivities of different glasses (figure 4) are consistent with the d.c. conductivity derived on the basis of the hopping of polarons in the adiabatic

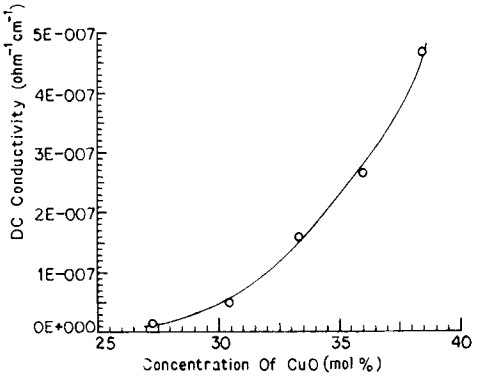

Figure 3. Variation of d.c. conductivity of the glasses with CuO concentration.

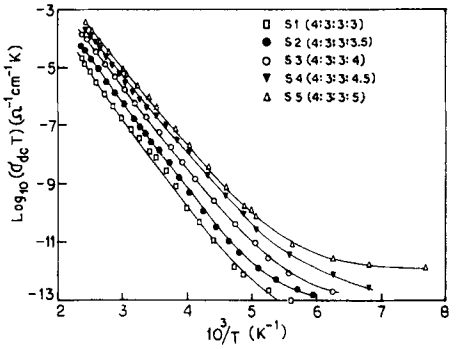

Figure 4. Thermal variation of d.c. conductivity of the glasses.

Table 1. Different physical parameters of the Bi–Sr–Ca–Cu–O glass.

Samples	S1	S2	S3	S4	S5
Composition (Bi:Sr:Ca:Cu)	(4:3:3:3)	(4:3:3:3·5)	(4:3:3:4)	(4:3:3:4·5)	(4:3:3:5)
Starting Cu content (wt%)	11·55	13·16	14.70	16·16	17·56
Final Cu content (wt%)	11·64	—	15·90	—	18·08
$N(10^{21}\,eV^{-1}\,cm^{-3})$	6·52	7·48	8·44	9·24	9·92
$\rho(g\,cm^{-3})$	5·90	5·91	5·96	5·94	5·88
$\beta = Cu^{+}/Cu_{tot}$	0·84	0·81	0·87	0·86	0·85
R(Å)	5·35	5·11	4·91	4·77	4·66
r_p(Å)	2·16	2·06	1·98	1·92	1·88
W at 250 K	0·566	0·542	0·521	0·503	0·480
W at 400 K	0·698	0·674	0·646	0·627	0·615
$\nu_0(10^{12}Hz)$	9·16	8·54	8·12	8·00	7·75
$\alpha(Å^{-1})$	1·23	1·03	0·97	0·75	0·87
∞(at 300 K)*	13·5	—	13·6	14·2	14·5

*Estimated from the Cole-Cole plot of dielectric constant data (Chaudhuri and Som, unpublished).

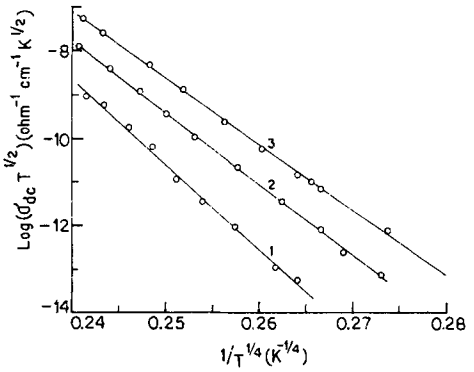

Figure 5. $T^{-1/4}$ versus $\log(\sigma_{d.c}T^{1/2})$ plot for three glass samples.

approximation (Austin and Mott 1969) and given by

$$\sigma_{dc} = \frac{\nu_{ph}Ne^2}{k_BT}C(1-C)\exp(-2\alpha R)\exp(-W/k_BT), \tag{1}$$

where ν_{ph} is the phonon frequency, N the number of TMI sites per unit volume, R the average TMI site spacing, C and α are, respectively, the ratio of TMI concentration in the low valency state to the total TMI concentration and the wave vector decay constant. The different parameters of the model obtained by fitting with the experimental data are shown in table 1. Mott's $T^{-1/4}$ analysis for the variable range hopping (VRH) in the low-temperature regime was found to be not suitable for the glasses. On the other hand, Greaves' expression (Greaves 1973) for variable range hopping in the intermediate temperature regime which gives $\sigma_{dc}T^{1/2} = A\exp(-B/T^{1/4})$ with $B = 2{\cdot}1[\alpha^3/k_BN(E_F)]^{1/4}$ seems to be applicable for the glasses. The

$T^{-1/4}$ versus $\log(\sigma_{dc}T^{1/2})$ plot is shown in figure 5. The variation of activation energy W with TMI (Cu) concentration is shown in figure 6.

The a.c. conductivity (figure 7) of the glasses can be written as

$$\sigma_{ac} = \sigma_{total}(\omega) - \sigma_{dc}. \tag{2}$$

The frequency dependence of a.c. conductivity obeys the general behaviour of the amorphous glasses viz.

$$\sigma_{ac}(\omega) = A\,\omega^{s}. \tag{3}$$

However, the correlated barrier hopping (CBH) model for a.c. conductivity of amorphous glasses proposed by Pike (1972) and Elliott (1977) was best suited for the present semiconducting glass system. The most general formula for the conductivity obtained from the CBH model is given by

$$\sigma_{ac} = \frac{1}{24}\pi^3 N^2 \varepsilon_0 \varepsilon R_{\omega}^6, \tag{4}$$

where ε_0 and ε are the permittivity of the free space and the dielectric constant of the

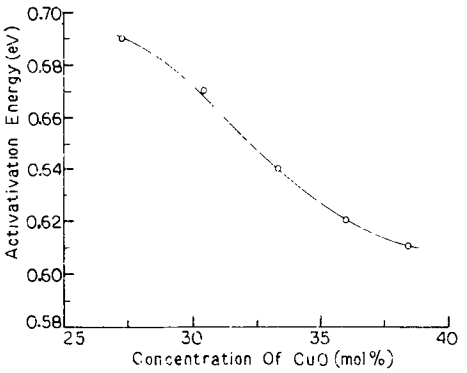

Figure 6. Concentration (CuO) dependences of activation energy.

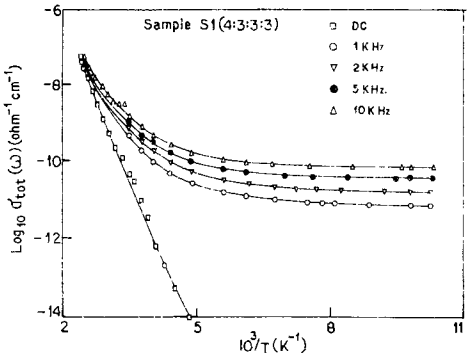

Figure 7. Thermal variation of a.c. conductivity of a typical glass sample at different frequencies

sample respectively. The average hopping distance R_ω is given by

$$R_\omega = (2e^2/\pi\varepsilon_0\varepsilon)[W_M + k_B T \ln(1/\omega\tau_0)], \tag{5}$$

where W_M is the barrier height. The model parameters calculated with this equation are shown in table 1.

3.1 *Electrical conductivity and magnetic susceptibility of the superconducting phase*

The d.c. electrical conductivity of the heat-treated (at 850°C for 24 h in air) superconducting samples (both pellets or filaments) was measured by the standard

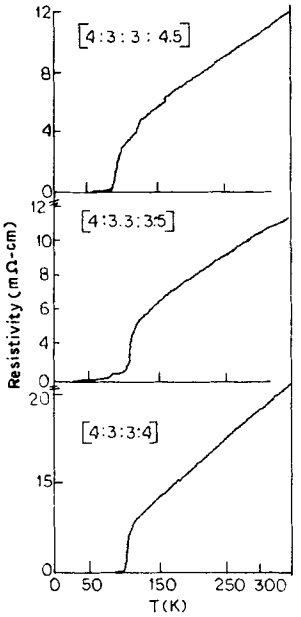

Figure 8. Thermal variation of resistivity of the superconducting phase obtained by annealing the glass.

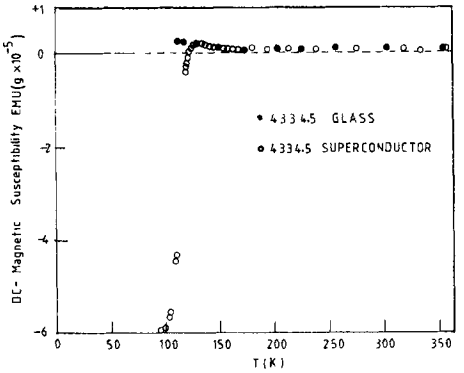

Figure 9. Magnetic susceptibility of glass and its corresponding superconducting phase.

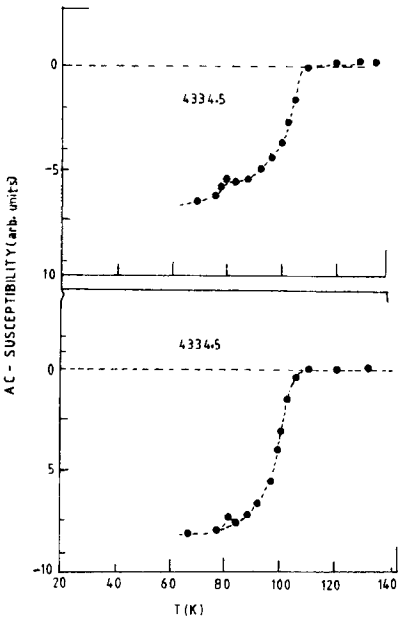

Figure 10. Thermal variations of the a.c. magnetic susceptibility of some superconductors obtained from the glass phases.

four-probe method in the temperature range of 77 to 300 K. The X-ray diffraction pattern of one of the samples after being annealed is shown in figure 1. The plot of electrical resistivity as a function of temperature is shown in figure 8 showing T_c around 85 K. The corresponding d.c. magnetic susceptibilities of the glass and superconducting sample are shown in figure 9. Both from the thermal variations of electrical resistivity and magnetic susceptibility the superconducting behaviour of the samples can be well visualized (figure 10).

4. Conclusion

The transition metal oxide glasses like $Bi_4Sr_3Ca_3Cu_xO_y$ ($x = 3$–5) behave almost similarly with other transition metal oxide glasses as V_2O_5–P_2O_5 (Sayer and Mansingh 1972), V_2O_5–Bi_2O_3 (Ghosh and Chaudhuri 1986), Bi_2O_3–Fe_2O_3 (Chaudhuri *et al* 1989b) etc which do not become superconducting unlike (4334) glasses. The addition of B_2O_3 glass-forming oxides appears to be suitable for various technological applications.

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