

Investigations on Bi-Sr-Ca-Cu-O Glasses: Thermal, Magnetic, and Transport Properties¹

K. J. Rao² and S. Lakshmi Raghavan³

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

Received November 17, 1993; in revised form March 10, 1994; accepted March 17, 1994

IN HONOR OF C. N. R. RAO ON HIS 60TH BIRTHDAY

Glasses of composition $\text{Bi}_2\text{Sr}_2\text{CaCu}_n\text{O}_{6+n}$ ($n = 2$ to 5) have been prepared by the melt quenching technique. Thermal, electrical, and magnetic properties of these glasses have been examined. Electrical conductivities suggest the validity of the multiphonon assisted hopping model. Susceptibilities indicate weak antiferromagnetic coupling. However, the electron spin resonance (ESR) studies suggest a large proportion of spins to be ESR inactive. A structural model of the glasses has been proposed that considers both Bi_2O_3 and CuO as glass formers. It is shown that the properties of the glasses investigated in this work are consistent with the model. © 1994 Academic Press, Inc.

INTRODUCTION

Several Bi-Sr-Ca-Cu-O compositions easily form glasses over a wide range of compositions (1-7). They have been of significant interest since the compounds $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ for $n = 1-3$ exhibit high-temperature superconductivity (8-10). But the glasses are not known to exhibit superconductivity. We are interested in the possibility of introducing large amounts (up to 50 mol%) of CuO into these glasses and examining their transport and magnetic properties. Cu^{2+} ions tend to occupy positions with four-coordination to oxygen in a planar geometry in ionic glasses. Structures of glasses, particularly of complex systems containing a glass-forming oxide, can be modeled using structural units which are metal-oxygen polyhedra. In the Bi-Sr-Ca-Cu-O glasses, both Bi_2O_3 and CuO can act as glass formers since the covalencies in the two are equal. In this paper, we have examined the thermal, electrical, and magnetic properties of glasses with composition $\text{Bi}_2\text{Sr}_2\text{CaCu}_n\text{O}_{6+n}$ from $n = 2$ to 5 . We have proposed a structural model for these glasses that considers Bi_2O_3 and CuO as glass form-

ing oxides. We have discussed electrical and magnetic properties of the glasses in the light of the structural model.

EXPERIMENTAL

$\text{Bi}_2\text{Sr}_2\text{CaCu}_n\text{O}_{6+n}$ glasses ($n = 2-5$) were prepared starting from Analar Grade Bi_2O_3 , SrCO_3 , CaO , and CuO . Stoichiometric amounts of the above materials were thoroughly mixed and calcined in a platinum crucible at 1073 K in an electrically heated muffle furnace. After calcination, the samples were melted in a Thermolyne-1700 high-temperature furnace at 1473 K and held at that temperature for about 15 min. Melts were then quenched between two stainless steel plates. All glasses were prepared in the form of platelets. Samples were quite stable and no weight increases were observed after they were kept in air for a long time. Being kept in oxygen ambient for several days did not also alter their physical properties (DSC, XRD, and conductivity) to any measurable extent.

The glass transition temperatures (T_g) and the heat capacities (C_p) of the glasses were measured using a Perkin-Elmer DSC-2 differential scanning calorimeter. Glass samples weighing about 30-40 mg were hermetically sealed in gold pans. C_p measurements were made in a limited temperature range from about 100 K below T_g to a temperature limited on the higher side by the crystallization of the samples (about 50°C above T_g). A uniform heating rate of 10°C/min was maintained in all the measurements. Sapphire was used as the calibration standard for calculating the heat capacity. The glass transition temperature was determined as the intersection of the extrapolated linear portions around the glass transition in the C_p vs temperature plot.

The electron spin resonance spectra were recorded using a Varian ESR spectrometer in the X-band at a frequency of 9.05 GHz in the range 0-5000 G both at room temperature and at 77 K. The spin concentrations of the

¹ Contribution No. 994 from the Solid State and Structural Chemistry Unit.

² To whom correspondence should be addressed.

³ At the Materials Research Centre.

Cu^{2+} ions were determined by comparing the area under the integrated spectra of the glass and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The details are given in the text. Magnetic susceptibility measurements were performed on the glass samples using a George Associates Lewis coil force magnetometer in the temperature range 10–300 K at a constant field of 5000 G. The magnetic moment of the Cu^{2+} ions were found from the Curie constant.

The conductivity measurements were carried out by the two probe method by applying a constant voltage to the sample and measuring the current. The samples for the conductivity measurements were annealed at 300°C to remove thermal stresses present in the glass. Gold electrodes were deposited by vacuum evaporation on both sides. A calibrated Cr–Al thermocouple was used to measure the temperature. The ohmic nature of the contacts was confirmed by checking the linearity of the I – V characteristics up to 20 V. The measurements were done from room temperature to 150°C. Voltages were applied using a Keithley model 221A voltage/current source and the current was measured with a 610C electrometer (having a sensitivity of 10^{-14} A).

The FT infrared transmission spectra were recorded using a Bruker FTIR spectrometer in the range 700–100 cm^{-1} . The spectra were recorded on samples in the form of pellets made with polyacetylene.

RESULTS AND DISCUSSION

Thermal Properties

The amorphous nature of the samples were confirmed by X-ray diffraction which showed a very broad peak around $2\theta = 30^\circ$ (Fig. 1). Glasses exhibited clear identifiable glass transition temperatures (T_g) in the DSC measurements (Fig. 2). T_g values of the glasses are listed in Table 1. T_g decreases from 684 to 665 K as the CuO content increases from $n = 2$ –5 but the decrease is not significant. It has earlier been reported that, over a wide

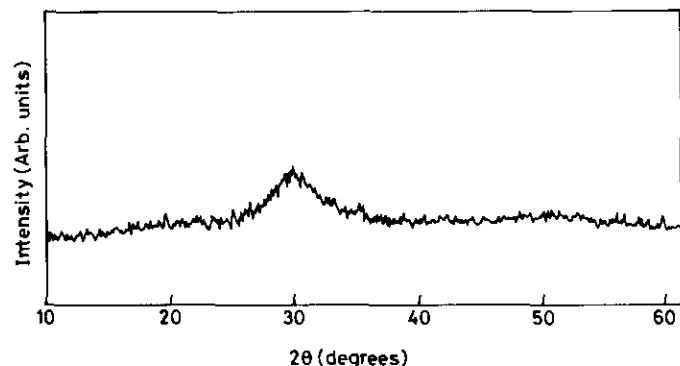


FIG. 1. X-ray diffraction pattern of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{6+n}$ glass showing the amorphous nature of the sample.

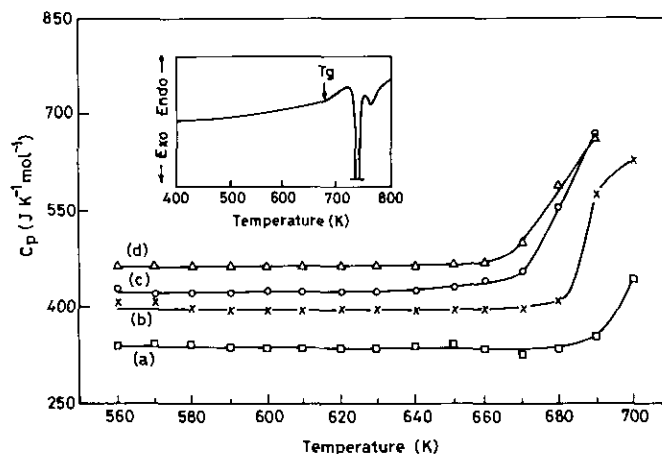


FIG. 2. Temperature dependence of the heat capacity (C_p) of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_n\text{O}_{6+n}$ glasses (a) $n = 2$, (b) $n = 3$, (c) $n = 4$ and (d) $n = 5$. The inset shows a DSC curve for the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{6+n}$ in which the glass transition is indicated.

range of compositions (up to $n = 6$), similar melting temperatures (~ 1170 K) are exhibited in DTA measurements (4). Thus T_g/T_m ratio is approximately $673/1123 \approx 0.55$ which indicates reasonable stability of the glasses. The observed decrease in T_g can be attributed to a slight increase in covalency of bonding as the CuO concentration is increased. The first crystallization temperature (T_x) also decreases as a function of CuO. The value of $(T_x - T_g)$ is an approximate indicator of the thermal stability of the glasses and it decreases as the CuO content increases.

The glass transition temperatures are known to scale with the cohesive energy of the system. But due to the absence of detailed thermodynamic data, cohesive energies could not be evaluated. Alternately, trends of cohesive energy density variations can be examined using approximate methods (11). For example, the cohesive energies can be considered as roughly proportional to the cation charge per unit volume because only one type of anions (O^{2-}) are present in the system. Since the molar volumes are known (Table 1) we can evaluate this quantity as units of e (electronic charge) per cm^3 . These values vary from 0.107 to 0.116 for a variation of n from 2 to 5. This suggests very little change in cohesive energy densities. Correspondingly, the T_g values do not vary much in the composition range of n values.

The heat capacities below T_g for all the glasses are shown in Table 1. These values may be compared with the Dulong–Petit heat capacities (also given in Table 1) for all the compositions. Values of ΔC_p at T_g could not be measured accurately since the glasses tended to crystallize within about 40 K above T_g . The experimental heat capacities are generally lower than the Dulong–Petit heat capacities. This suggests that the vibrational modes are not fully excited at these temperatures. The electronega-

TABLE I
The Experimental Parameters Determined for $\text{Bi}_2\text{Sr}_2\text{CaCu}_n\text{O}_{6+n}$ Glasses

Comp. (n)	T_g (K)	Density (g/cm ³)	Molar volume (cm ³)	C_p (J/K/mol)		Spin conc. 10 ¹⁸ /cm ³	Magnetic moment /Cu ion (BM)	Activation energy (eV)
				DSC	(3nR)			
2	684	5.942	150.18	328.56	374.13	7.71	0.55	0.34
3	680	5.963	162.99	402.83	424.01	4.2	0.39	0.33
4	670	5.908	177.97	417.93	473.98	3.2	0.37	0.32
5	665	5.953	189.99	473.21	523.78	0.93	0.35	0.27

tivities of Cu (1.90) and Bi (2.02) are quite similar and the Pauling ionicities of Cu–O (0.31) and Bi–O (0.3) bonds are also very similar, while those of SrO (0.46) and CaO (0.46) are higher. Thus Bi_2O_3 and CuO may be considered to form a covalent random network which is modified by SrO and CaO in the same manner as that in which a SiO_2 network is modified by alkaline earth oxides. Since Cu–O and Bi–O bonds are significantly covalent, tightly bound structural entities such as $[\text{BiO}_{6/2}]^{3-}$ and $[\text{CuO}_{4/2}]^{2-}$ can be visualized as constituting the building blocks of the glass structure. Other units such as $[\text{BiO}_{3/2}\text{O}]^{2-}$, $[\text{BiO}_{2/2}\text{O}_2]^{3-}$, or $[\text{CuO}_{2/2}\text{O}_2]^{4-}$ are formed when enough O^{2-} ions are available from added modifier oxides. Since T_g , T_m , etc., are similar, the structures of the glasses can be considered to be similar and we suggest that only a few types of building blocks are present in all the glasses. On this assumption, a tentative structural model is proposed below for the Bi–Sr–Ca–Cu–O glasses and experimental observations are discussed in the light of this model.

Structural Model of Bi–Sr–Ca–Cu–O Glasses

Hypothetical glass of composition $\text{Bi}_2\text{Sr}_2\text{CaCu}_0\text{O}_{6+0}$ is assumed to consist of only $[\text{BiO}_{6/2}]$ units which act as the building blocks. All oxygens are two-coordinated, as in other oxide glasses, so that the proper representation of the octahedral units is $[\text{BiO}_{6/2}]^{3-}$. All the glasses presently investigated can be considered as a dilution of the above $\text{Bi}_2\text{O}_3 \cdot 2\text{SrO} \cdot \text{CaO}$ glass by addition of CuO. Thus the simplest possibility is a permeation of $-\text{Cu}-\text{O}-\text{Cu}-\text{O}-$ chains through the structure in such a way that some of the oxygens coordinating to Bi in $[\text{BiO}_6]$ units further coordinate to Cu. This will result in the formation of $[\text{CuO}_4]$ units and the additional coordination is provided by a dative bond from oxygens in $[\text{BiO}_6]$ units. The oxygen from Cu–O–Cu–O chains also participate similarly in a reciprocal manner to other nearby copper atoms in the structure. This ensures that the oxygens in the glass structure are all chemically similar. The total number of oxygen atoms present in $\text{Bi}_2\text{O}_3 \cdot 2\text{SrO} \cdot \text{CaO} \cdot n\text{CuO}$ is $(6+n)$, which can in principle form $(18+3n)$ bonds, two normal and one dative each. Two Bi atoms account for

the 12 bonds and the balance of $(6+3n)$ bonds can provide coordination to n Cu atoms ($4n$ bonds). If all oxygens are three-bonded, then $n=6$. Thus up to $n=6$ (6 CuO in the glass composition) oxygen atoms have to bond to only three metal atoms (Bi or Cu). Thus, the glasses in this investigation ($n \leq 5$) consist of only two- and three-bonded oxygens. $[\text{BiO}_6]$ octahedra are connected to $[\text{CuO}_4]$ units with appropriate number of three-connected oxygens. The effective (formal) charges on the $[\text{BiO}_6]$ units will depend on the number of three-connected oxygens present in them. Some of the units will be like $[\text{BiO}_{6/2}]^{3-}$, $[\text{CuO}_{4/3}]^{0.66-}$, $[\text{BiO}_{6/3}]^-$ etc.

The FTIR spectra of the glasses are shown in Fig. 3 for the two compositions $n=2$ and $n=5$. There is hardly any change in the peak positions. In the other compositions, also, the peak positions were identical and the intensities were different but interpolatable. Thus, it appears that the nature of the building blocks remains essentially unaltered in all the glass compositions. This supports the basic assumption in the structural model.

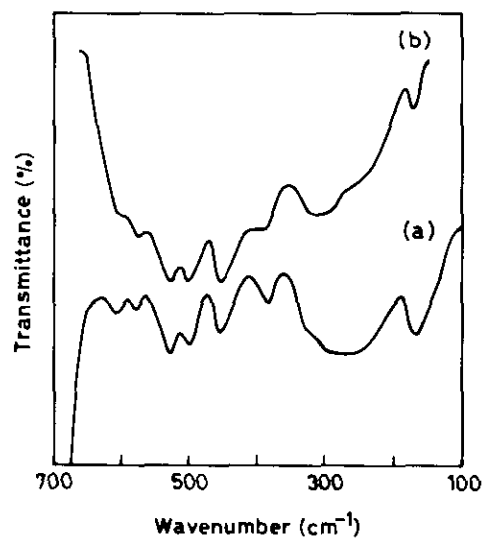


FIG. 3. FTIR spectra for the compositions $n=2$ and $n=5$ of $\text{Bi}_2\text{Sr}_2\text{CaCu}_n\text{O}_{6+n}$ glasses showing no change in the peak positions.

Since the formation of dative bonds by oxygens in $[\text{BiO}_6]$ and $[\text{CuO}_4]$ units increases systematically by the addition of CuO , systematic increase in the molar volume of the glasses is observed as n increases from 2 to 5. The bond angle $M\text{-O-M}$ in glasses such as SiO_2 is known to be quite flexible (12). Similarly, the Bi-O-Bi , Bi-O-Cu , and Cu-O-Cu angles may be considered quite flexible. Therefore, the hybridization character of the lone pair (a pure p or sp^n) on oxygen involved in the formation of dative bonds also varies. This has implications for the observed variations in the conductivity of the glasses, which will be discussed later.

DC Conductivity

The semilogarithmic plots of the conductivity as a function of temperature are shown in Fig. 4. Evidently, the glasses are all semiconducting with rather low values of the dc conductivity (σ) compared to the metallic behavior of the crystalline phases of the same composition. Present studies are confined to a small range of high temperatures and the transport is phonon assisted (13). Activation energies obtained from Fig. 4 are listed in Table 1. The top of the valence band in oxide glasses is constituted of oxygen $2p$ lone pairs. Indeed, in the proposed structure, oxygens are required to exhibit a coordination number greater than 2 through dative bond formation using lone pairs. Thus, the lone pairs involved in the dative bond formation are stabilized due to σ -type bonding to Cu atoms. As a consequence, the density of σ states are

increased at the expense of lone pair states. Both σ and σ^* levels spread in width as CuO concentration is increased and the lone pair band is narrowed to some extent. Due to the spread in antibonding σ^* levels, there is a net reduction in the gap between the top of the valence band (which is populated by the uncoordinated lone pair) and the conduction band in spite of the narrowing of the lone pair bands. This is reflected in a decrease of the experimental activation barriers.

We have also examined the electron transport in these glasses using a thermally assisted hopping mechanism involving $\text{Cu}^+/\text{Cu}^{2+}$ ion sites involved in conduction ($\text{Bi}^{3+}/\text{Bi}^{5+}$ states are not invoked since they are strongly binding states). A hopping transport mechanism may not be inconsistent with the band structure description if we assume that the electron jump from Cu^+ to Cu^{2+} occurs via excitation of the electron to the antibonding σ^* levels. The activation barriers, W , are rather low. The low values of both σ and W in

$$\sigma = \sigma_0 \exp(-W/kT) \quad (1)$$

suggest that σ_0 should be very low. High-temperature conductivities have been discussed by Triberis and Friedman (14) using a multiphonon-assisted small polaron hopping model. The conductivity is given by

$$\sigma = \sigma'_0 \exp[-T'_0/T]^{2/5}, \quad (2)$$

where σ'_0 and T'_0 are constants and T'_0 is given by

$$T'_0 = 8.5n_0^{1/2}\alpha^{3/2}/kN_0, \quad (3)$$

where α is a constant which describes the extent of the localized state wavefunction and n_0 and N_0 are the densities of hopping sites and localized states respectively. This model has been successfully applied to a variety of chalcogenide and oxide glasses (15-17). Plots of $\ln \sigma$ as a function of $T^{-2/5}$ are shown in Fig. 5. They are quite linear, suggesting the applicability of this approach. The values of T'_0 are obtained from the slopes of these curves and are given in Table 2. In order to examine the validity of this model further, we consider the critical percolation parameter (ξ) in this model, which is given by

$$\xi = [T'_0/T]^{2/5} = 2\alpha R_{ij} + 3(E_i + E_j)/kT, \quad (4)$$

where R_{ij} is the site spacing and E_i and E_j are the polaron binding energies of the sites i and j . The value of E_i (or E_j) can be taken to be twice the hopping energy W (15). Hence $(2\alpha R_{ij})$ can be obtained for a particular temperature. These values calculated at a temperature of 400 K are shown in Table 2. We have assumed a plausible value of α ($=1.2 \text{ \AA}^{-1}$) and calculated R_{ij} values, which are also

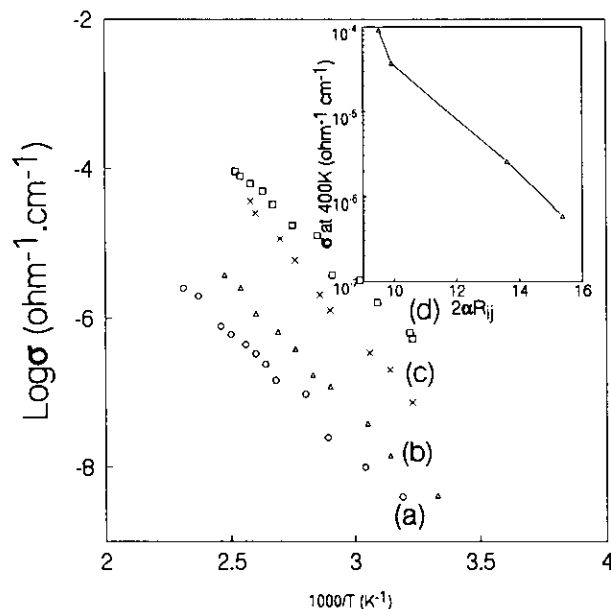


FIG. 4. $\text{Log } \sigma$ as a function of $1/T$ for the $\text{Bi}_2\text{Sr}_2\text{CaCu}_n\text{O}_{6+n}$ glasses (a) $n = 2$, (b) $n = 3$, (c) $n = 4$, and (d) $n = 5$.

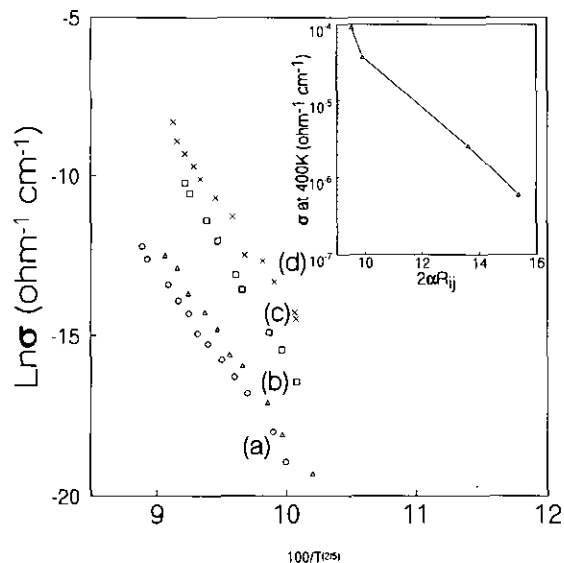


FIG. 5. $\text{Ln } \sigma$ as a function of temperature for the $\text{Bi}_2\text{Sr}_2\text{CaCu}_n\text{O}_{6+n}$ glasses (a) $n = 2$, (b) $n = 3$, (c) $n = 4$, and (d) $n = 5$. The inset shows the conductivity (σ) as a function ($2\alpha R_{ij}$) for these glasses. (The values are at 400 K.)

tabulated in Table 2. These are compared with the inter-site spacing, R , calculated from the composition and molar volume data as $R = (4\pi N/3)^{1/3}$, in which N is the concentration of the TM ions. The calculated values of R are also listed in Table 2. R_{ij} and R compare reasonably well. R_{ij} values decrease when CuO concentration increases in these glasses much as the R values do. We realize the importance of $(2\alpha R_{ij})$ values even better by plotting conductivities as a function of $(2\alpha R_{ij})$ (inset of Fig. 5). $2\alpha R_{ij}$ decreases with increasing conductivity, which shows that the value of R_{ij} is significant to the conductivity mechanism (14), contrary to the assumption by Sayer and Mansingh (18), who treated it as a constant.

The fact that these glasses are simply semiconducting almost precludes the possibility of superconductivity. This is indeed confirmed by the absence of any tendency toward the onset of diamagnetism in the susceptibility

TABLE 2

The Parameters Obtained from the Resistivity Data of $\text{Bi}_2\text{Sr}_2\text{CaCu}_n\text{O}_n$ Glasses using the Tribiris and Friedman Formulation (Calculations Refer to 400 K)

Comp. (n)	T_0 (K) 10^6	$2\alpha R_{ij}$	R_{ij} from Eq. 6 (\AA)	$R(4\pi N/3)^{1/3}$ (\AA)
2	1.667	15.38	5.7	3.1
3	1.112	13.61	5.4	2.78
4	0.834	9.92	4.2	2.66
5	0.822	9.51	3.9	2.47

measurements at temperatures down to 20 K. The present studies have demonstrated that the concentration of CuO in glasses does not change the nature of conduction. Since only the crystalline phases of these compositions (up to $n = 3$) exhibit a superconducting transition, it is evident that the crystalline order is of seminal importance to superconductivity. That the coherence lengths in the crystalline superconducting phases of the same materials are of the order of a few \AA makes it appear that glasses could also exhibit superconductivity in view of the preponderance of intermediate range order (up to 20 \AA or more in some cases (19)) in many of them. Evidently this is not so.

Transport is considered as arising from holes in the valence band in the corresponding crystalline phases. But these hole states are fully localized in glasses, due to disorder, and hence do not give rise to metallicity as they do in crystalline materials.

Magnetic Studies: Susceptibilities

The dc magnetization studies performed on these samples show that they are paramagnetic at room temperature. As a function of temperature, the susceptibility followed the Curie behavior characteristic of a paramagnetic material (Fig. 6). Upon extrapolation toward low temperatures, it is observed that the intersection of the magnetization curve occurs at negative values of temperature (see inset Fig. 6), suggesting an antiferromagnetic ordering, although the suggested value of the Néel temperature, T_N , ($= -\theta$) is rather low (~ 10 K). The

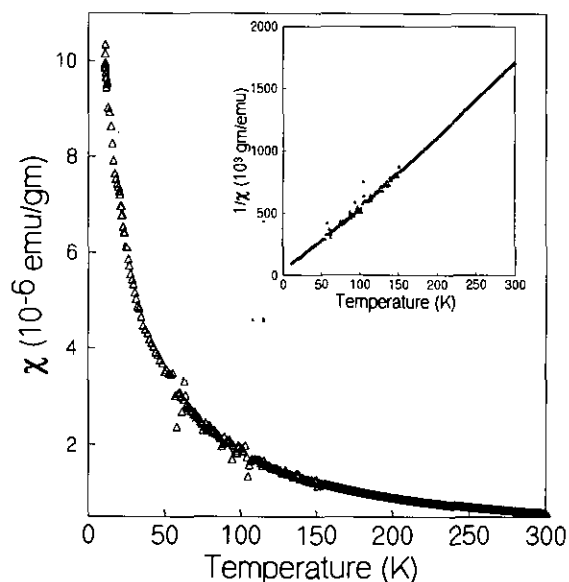


FIG. 6. Temperature dependence of magnetic susceptibility (χ) for the $\text{Bi}_2\text{Sr}_2\text{CaCu}_n\text{O}_{6+n}$ glass. The inset shows inverse susceptibility ($1/\chi$) as a function of temperature for the same sample.

effective magnetic moments per Cu ion were estimated from the slopes of the susceptibility curves for all the samples and are given in Table 1. It can be seen that the magnetic moment decreases as a function of increasing CuO content. This value is significantly lower than the spin only moment of Cu^{2+} (1.73 BM). This is suggestive of significant covalency of bonding in the measured moments. Further, in the glass compositions $\text{Bi}_2\text{O}_3 \cdot 2\text{SrO} \cdot \text{CaO} \cdot n\text{CuO}$, Cu atoms have to compete more and more in order to allow the formation of $[\text{CuO}_4]$ units as n is increased via dative bond formation. It is easily visualized that this requires adjustable orientation of the Cu-O bonds. Hence O-Cu-O bond angles have to vary in magnitude, which in turn requires different degrees of participation of the d orbitals of copper in forming hybridized orbitals. This manifests as increasing covalency as n is increased and results in decreased magnetic moment values. The magnitudes of the moments reported here are similar to those reported earlier for one of the glass compositions (7). The estimated Néel temperature is rather low and the coupling of the Cu^{2+} spins is weak. The weak coupling suggests the absence of any significant intermediate range positional order of Cu^{2+} ions in glass consistent with the variations in nature of hybridization of both copper and oxygen orbitals.

ESR Spectra

The ESR spectra recorded for the various samples are shown in Fig. 7. The spectra are generally very broad and no hyperfine splitting is observed for any of the samples, as observed in the spectra of several other glasses (20–22). What is rather surprising is the intensity of the spectra. The spin concentrations of the Cu^{2+} ions determined by comparing the area of the integrated ESR spectrum of the sample with that of a standard, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, is

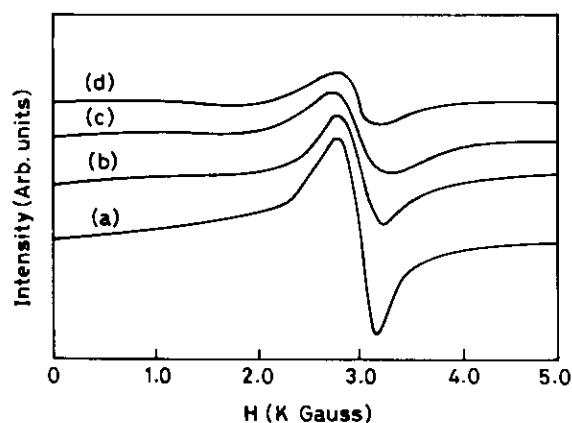


FIG. 7. EPR spectra for $\text{Bi}_2\text{Sr}_2\text{CaCu}_n\text{O}_{6+n}$ glasses (a) $n = 2$, (b) $n = 3$, (c) $n = 4$, and (d) $n = 5$.

found to be very low. Specifically, if A and B are the areas of the integrated spectrum for the glass and the standard, respectively, then the spin concentrations of the Cu^{2+} ions are estimated from $X = (A/B)y$, where y is the spins of the standard and is given by $y = (\text{Wt. of } \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \times N_A)/(\text{mol wt of } \text{CuSO}_4 \cdot 5\text{H}_2\text{O})$, where N_A is Avogadro's number. If the weight of the glass is W and the density ρ , then $X/(W/\rho)$ gives the number of spins/cm³ of the glass, which is shown in Table 1.

The spin concentrations are of the order of $10^{18}/\text{cm}^3$ though the total Cu ion concentration/cm³ as indicated from the composition and molar volume is of the order of $10^{21}/\text{cm}^3$. Oxygen is unlikely to have been lost to any significant degree because reheating the samples in air or keeping them for long durations did not result in any increase in weight. Susceptibility, ESR signals, and conductivity exhibit no changes under such treatment. Further, the susceptibilities are consistent with the Cu being present as Cu^{2+} . However, the observation of the ESR activity in these glasses is itself significant because crystalline compounds of the formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ ($n = 1, 2, 3$) do not exhibit ESR absorption at all (23–26) while the glasses do. It is well known that Cu^{2+} ions (spin $\frac{1}{2}$) are extremely easy to detect in ESR spectra. The absence of the EPR signal in crystalline materials is not understood satisfactorily, although some plausible explanations have been proposed. One such explanation is possible Cu^{2+} - Cu^{2+} pair formation with spin singlet ground state, where such pairs are involved in forming resonating valence bonds (23, 24). Such an explanation is appropriate to account for the absence of ESR activity in glasses also. But the disadvantage of this explanation is that no ESR signal has been observed at 1000 K from the possible triplet states ($S = 1$) in crystalline solids, though spins should decouple when heated to about 1000 K (the pairing energies of the spins rarely exceed 1000 K). The ESR active spins in the glasses however are very low in concentration and are of the order of 10^{-3} times the total number of spins. The ESR line shape and the intensity do not change (Fig. 8) when cooled to liquid nitrogen temperature, which indicates that the ESR response is not associated with simple relaxation phenomena. We have also irradiated the samples kept in the ESR spectrometer cavity at 77 K with ultraviolet light (for 20 min) and examined the effect on ESR absorption. We expected spin decoupling to occur by irradiation and ESR active triplets to form, which would increase the ESR intensity. But we found no change in the ESR spectra (Fig. 8), indicating that it is not associated with any antiferromagnetic coupling. It may be noted that the energy of the UV photons is an order of magnitude greater than the thermal energy at 1000 K. The latter is considered as a reasonable magnitude of any ground state spin coupling energy.

It could also be argued that the decrease in the number

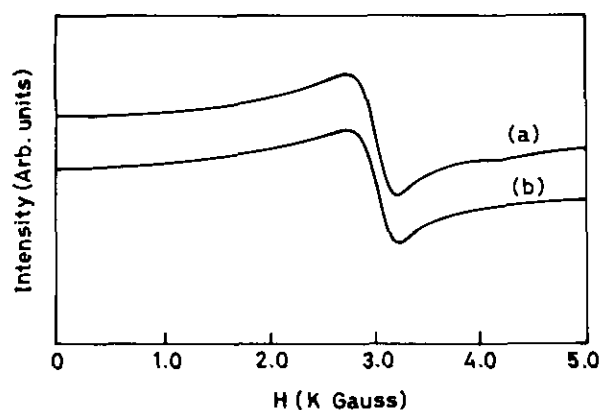


FIG. 8. EPR spectra of $\text{Bi}_7\text{Sr}_2\text{CaCu}_2\text{O}_{6+n}$ glasses at 77 K (a) before irradiation and (b) after UV irradiation for 20 min.

of spins in the ESR is due to the disproportionation reaction, $2\text{Cu}^{2+} \rightleftharpoons \text{Cu}^+ + \text{Cu}^{3+}$. This disproportionation reaction is, however, endothermic. In addition, since Cu^+ and Cu^{3+} do not carry spin moments, their formation entails a corresponding decrease in the measured χ values also. Even if one were to assume that the moments of Cu^{2+} ions in the present glasses are close to the free ion moment (two to three times greater than those measured in the present experiments, see Table I), it would be impossible to account for the reduction of Cu^{2+} spins through a disproportionation reaction alone to the level observed in the ESR experiments and simultaneously to account for the observed χ values. It may be recalled here that annealing in oxygen below T_g registered no effect either on χ or on ESR values. Further, the absence of hyperfine splitting is suggestive of a reasonably large number of interacting Cu^{2+} spins, which is contrary to the expectation of a high degree of disproportionation reaction. Therefore, at this time, we have no explanation for this unusual ESR behaviour of Bi-Sr-Ca-Cu-O glasses.

CONCLUSIONS

The present studies of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_n\text{O}_{6+n}$ glasses have borne out a few results of importance in the context of magnetic and electron transport behavior in these glasses. They are all semiconducting and are unlikely to exhibit superconductivity, since disorder localizes the carriers at the top of the valence band. The studies have also shown that a large percentage of spin-bearing ions contribute only to magnetic susceptibilities but not to ESR resonance. We are not aware of whether this phenomenon is present in any other glasses. More impor-

tantly for glass structures, these studies have shown that the observed properties are consistent with the existence of structural motifs. Bi and Cu form structural units of $[\text{BiO}_6]$ and $[\text{CuO}_4]$, respectively. The inherent flexibility of $M\text{-O-M}$ bond angles not only allows glass formation but also influences the thermal, electrical, and magnetic properties.

The authors dedicate this article to Professor C. N. R. Rao, F. R. S., who is a great teacher. One of the authors (K. J. R.) has been a Ph.D. student and a long time associate of Professor Rao.

REFERENCES

1. H. Zheng and J. D. MacKenzie, *Phys. Rev. B* **38**, 7166 (1988).
2. V. Skumreyev, R. Puznik, N. Karpe, H. Zhang-He, M. Pont, H. Medelius, D.-X. Chen, and K. V. Rao, *Physica C* **152**, 315 (1989).
3. D. Shi, M. Tang, M. S. Boley, M. Hash, K. Vandervoort, H. Claus, and Y. N. Lwin, *Phys. Rev. B* **40**, 2247 (1989).
4. Y. Dimitryev, B. Samuneva, Y. Ivanova, E. Gattef, V. Mihailova, and A. Staneva, *Supercond. Sci. Technol.* **3**, 606 (1990).
5. K. B. R. Varma, K. J. Rao, and C. N. R. Rao, *Appl. Phys. Lett.* **54**, 69 (1989).
6. T. Komatsu, T. Ohki, C. Hirose, and K. Matusita, *J. Non-Cryst. Solids* **113**, 274 (1989).
7. P. Somasundaram and A. M. Umarji, *Physica C* **209**, 393 (1989).
8. C. Michel, M. Herrien, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, *Z. Phys. B* **68**, 421 (1987).
9. H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, *Jpn. J. Appl. Phys. Part 2* **27**, L209 (1988).
10. M. A. Subramanian, C. C. Torardi, J. C. Calabrese, J. Gopalakrishnan, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdry, and A. W. Sleight, *Science* **239**, 1015 (1988).
11. P. S. L. Narasimham and K. J. Rao, *J. Non-Cryst. Solids* **27**, 225 (1978).
12. I. Farnan, P. J. Grandinetti, J. H. Baltisberger, J. C. Stebbins, U. Werner, M. A. Eastman, and A. Pines, *Nature* **358**, 31 (1992).
13. N. F. Mott, *J. Non-Cryst. Solids* **1**, 1 (1968).
14. G. P. Triberis and L. R. Friedman, *J. Phys. C* **14**, 4631 (1981).
15. U. Selvaraj and K. J. Rao, *Philos. Mag. B*, **58**, 203 (1988).
16. R. Mohan and K. J. Rao, *Mater. Res. Bull.* **18**, 195 (1983).
17. G. P. Triberis, *J. Non-Cryst. Solids* **81**, 86 (1986).
18. M. Sayer and A. Mansingh, *Phys. Rev. B* **6**, 4629 (1972).
19. K. J. Rao, *Proc. Ind. Acad. Sci.* **93**, 389 (1984).
20. H. G. K. Sundar and K. J. Rao, *J. Non-Cryst. Solids* **50**, 137 (1982).
21. B. Sreedhar, J. Lakshmana Rao, and S. V. J. Lakshman, *J. Non-Cryst. Solids* **124**, 216 (1990).
22. M. A. Hassan, C. A. Hogarth, and K. A. K. Lott, *J. Mater. Sci. Lett.* **24**, 1645 (1989).
23. F. Mehran, S. E. Barnes, and G. V. Chandrasekar, *Solid State Commun.* **67**, 1187 (1988).
24. F. Mehran, and P. W. Anderson, *Solid State Commun.* **71**, 29 (1989).
25. E. W. Ong, B. L. Ramakrishna, and Z. Iqbal, *Solid State Commun.* **66**, 171 (1988).
26. W. R. McKinnon, J. R. Morton, and G. Pleizier, *Solid State Commun.* **66**, 1093 (1988).