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## Spectroscopic investigations on Cu(II) ions doped in alkali lead borotellurite glasses

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Received 6 April 1999, in final form 13 July 1999

**Abstract.** Electron paramagnetic resonance, optical absorption spectra, Raman spectra and physical properties of copper(II) ions in  $(85 - x/2)R_2B_4O_7 - xPbO - yCuO - (15 - x/2 - y)TeO_2$  ( $x = 0, 10$ ;  $y = 0.1 - 1.5$ ;  $R = Li, Na$  or  $K$ ) glasses were studied. EPR spectra of all the glasses show resonance peaks characteristic of  $Cu^{2+}$  ions. The number of spins participating in the resonance was measured as a function of temperature and the activation energy was calculated. From the EPR and density measurements, the ratio of number of copper ions in +2 state to the total copper ions (i.e.,  $N_2/N_T$ ) was calculated. The paramagnetic susceptibility was calculated from the EPR data at various temperatures and the Curie constant was calculated from the  $1/\chi - T$  graph. The optical absorption spectra of all the samples show a broad absorption band; the position of the band maxima varies from 14 500 to 12 700  $cm^{-1}$  for glasses with different alkali ions. The optical energy gap  $E_{opt}$  and Urbach energy  $\Delta E$  were calculated for all the glass samples from their ultraviolet edges. The optical energy gap varies between 3.4 and 2.7 eV and increases from Li to K glasses. Also, it was observed that as copper ion concentration is increased,  $E_{opt}$  decreases while  $\Delta E$  increases. This was explained as due to change in non-bridging oxygen content. Raman spectra of three samples were recorded at room temperature. The bands were assigned as due to various groups of boron.

### 1. Introduction

Tellurite glasses were considered to be important because of their optical and electrical properties and as potential optical CD memory devices. The distinguishing factor of the matrix of this glass is that the tellurium atoms have unshared pairs of electrons which do not take part in bonding. On the other hand, their relatively low temperature of crystallization and melting makes these types of glass active candidates for CD memory devices. Further, these glasses are characterized by low glass transition temperature, high refractive index and high transmittance from ultraviolet to near-infrared. Yet the knowledge of the structure of tellurite glasses is limited (Burger *et al* 1992).

It is known that  $TeO_2$  in combination with modifiers, like  $PbO$ , forms stable glasses at cooling rates typical of glass preparation ( $< 1 K min^{-1}$ ). Recently, the tellurite glasses have drawn the attention of many investigators for their optical (Hassan and Hogarth 1988, Sabry and El-Samanoudy 1995, Vithal *et al* 1997), electrical (Sunandana and Rao 1985, Hassan and Hogarth 1988, Vithal *et al* 1997, Sabry and El-Samanoudy 1995), Raman (Komatsu *et al* 1996, Pan and Morgan 1997), infrared (Sunandana and Rao 1985, Sabry and El-Samanoudy 1995), thermal and DTA (Sunandana and Rao 1985, Pan and Morgan 1997), XPS (Himei *et al* 1997) and EPR and magnetic susceptibility (Ardelean *et al* 1997) studies.

The electron paramagnetic resonance (EPR) spectrum of transition metal ions in glasses is an interesting research subject (Griscom 1990) and affords a method to investigate glass structure. The ability to characterize the local structure of a paramagnetic centre and sensitive detection of structural changes form the basis for the increasing number of applications of the EPR technique to glasses (Stoßer and Nofz 1994).

The spin-Hamiltonian parameters and optical absorption bands of  $\text{Cu}^{2+}$  ions in glasses are sensitive to the ligands present around them and the type of alkali ion present in the glass. The authors are interested to know how these parameters vary with the alkali and lead ions in alkali lead borotellurite glasses. Hence the authors have studied the electron paramagnetic resonance, optical and physical properties of  $\text{R}_2\text{B}_4\text{O}_7\text{-PbO-CuO-TeO}_2$  and  $\text{R}_2\text{B}_4\text{O}_7\text{-CuO-TeO}_2$  ( $\text{R} = \text{Li, Na or K}$ ) glasses.

## 2. Experimental techniques

The glass samples were prepared by the melt quenching method with the compositions given in table 1. The starting materials used in the present work were  $\text{Li}_2\text{B}_4\text{O}_7$ ,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ,  $\text{K}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ ,  $\text{TeO}_2$ ,  $\text{PbO}$ ,  $\text{CuO}$ . All chemicals were weighed accurately using an electrical balance, ground to fine powder and mixed thoroughly. The batches were melted in porcelain crucibles by placing them in an electrical furnace. The melting temperatures of the batches are given in table 1. The melts were, then, poured on a polished brass plate and pressed quickly with another brass plate. The glasses thus obtained were transparent and bluish in colour. Care was taken to obtain glasses of uniform thickness for recording optical absorption spectra. The glasses thus obtained were annealed at  $150^\circ\text{C}$  for 3 hours to remove the thermal strains. Good quality glasses obtained after polishing were used for optical measurements.

The densities of all the glasses were measured at room temperature using Archimedes' principle with toluene as the immersing liquid. The refractive index of the glass samples was measured using an Abbe refractometer at sodium yellow wavelength (589.3 nm).

Electron paramagnetic resonance spectra were recorded at room temperature on an EPR spectrometer (JEOL FE 1X) operating in the X-band frequencies with a modulation frequency of 100 kHz. The microwave frequency was 9.205 GHz. The magnetic field was scanned from 220 to 420 mT with a scan speed of  $25 \text{ mT min}^{-1}$ . A powdered glass specimen of 100 mg was taken in a quartz tube for EPR measurements. Polycrystalline DPPH with a  $g$  value of 2.0036 was used as a standard field marker. The EPR spectrum of the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  powdered substance was also recorded at 9.205 GHz as a reference to calculate the number of spins.

The EPR spectrum of a 1 mol%  $\text{CuO}$  doped potassium lead borotellurite (KPT1) glass sample was recorded at different temperatures (103–433 K) using a variable temperature controller (JES UCI 2AX). A temperature stability of  $\pm 1 \text{ K}$  was easily obtained by waiting approximately half an hour at the set temperature before recording a spectrum, at each temperature.

Optical absorption spectra of all the glass samples doped with copper ions were recorded at room temperature on a Hitachi U-3400 UV-VIS-NIR spectrophotometer from 200 to 900 nm. Glass samples of thickness 1.99 to 2.24 mm were taken for optical recordings.

Raman spectra of three glass samples (1 mol%  $\text{CuO}$  doped lithium borotellurite (LT1), 1 mol%  $\text{CuO}$  doped lithium lead borotellurite (LPT1) and 1 mol%  $\text{CuO}$  doped sodium lead borotellurite (NPT1)) were recorded in near-back-scattering geometry. The emission line at 488 nm of Ar ions at a power of 400 mW was used for excitation. The monochromator (SPEX 1404) equipped with a holographic grating ( $1800 \text{ grooves mm}^{-1}$ ) was used. The spectra were scanned for a Raman shift of  $0\text{--}2000 \text{ cm}^{-1}$ , recorded at room temperature and at a resolution of  $3.3 \text{ cm}^{-1}$ .

**Table 1.** Composition of the glasses studied in the present work.

Glass system	Glass code	Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	K <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	TeO <sub>2</sub>	PbO	CuO	Melting temperature (°C)
Lithium lead borotellurite glass	LPT	80	—	—	10	10	—	943
Lithium lead borotellurite glass:1 CuO	LPT1	80	—	—	9	10	1	943
Sodium lead borotellurite glass	NPT	—	80	—	10	10	—	852
Sodium lead borotellurite glass:1 CuO	NPT1	—	80	—	9	10	1	852
Potassium lead borotellurite glass	KPT	—	—	80	10	10	—	852
Potassium lead borotellurite glass:1 CuO	KPT1	—	—	80	9	10	1	852
Lithium borotellurite glass	LT	85	—	—	15	—	—	943
Lithium borotellurite glass:1 CuO	LT1	85	—	—	14	—	1	943
Sodium borotellurite glass	NT	—	85	—	15	—	—	852
Sodium borotellurite glass:1 CuO	NT1	—	85	—	14	—	1	852
Potassium borotellurite glass	KT	—	—	85	15	—	—	852
Potassium borotellurite glass:1 CuO	KT1	—	—	85	14	—	1	852
Sodium borotellurite glass:0.1 CuO	NPT0.1	—	80	—	9.9	10	0.1	852
Sodium borotellurite glass:0.5 CuO	NPT0.5	—	80	—	9.5	10	0.5	852
Sodium borotellurite glass:0.75 CuO	NPT0.75	—	80	—	9.25	10	0.75	852
Sodium borotellurite glass:1.5 CuO	NPT1.5	—	80	—	8.5	10	1.5	852

### 3. Results and analysis

#### 3.1. Electron paramagnetic resonance studies

No EPR signal is observed in the undoped glasses confirming that the starting materials used in the present work were free from transition metal impurities. The EPR spectra of  $\text{Cu}^{2+}$  ions doped in the present glasses exhibit three parallel components and four perpendicular components. These spectra are similar to  $\text{Cu}^{2+}$  ions doped in  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ ,  $\text{K}_2\text{SO}_4-\text{ZnSO}_4$  glasses (Kawazoe *et al* 1978), soda-borate glasses (Bandyopadhyay 1980), alkali cadmium borosulphate glasses (Rao *et al* 1992),  $\text{Bi}_2\text{O}_3-\text{GeO}_2$  glasses (Ardelean *et al* 1996) and alkali barium borate glasses (Sreekanth Chakradhar *et al* 1998). Figure 1 shows the EPR spectra of a KPT1 glass sample at different temperatures.

The number of spins can be calculated with the help of a reference ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) by using the formula (Weil *et al* 1994):

$$N = \frac{A_x (P_{std})^{1/2} (\text{scan}_x)^2 G_{std} (B_m)_{std} (g_{std})^2 [S(S+1)]_{std}}{A_{std} (P_x)^{1/2} (\text{scan}_{std})^2 G_x (B_m)_x (g_x)^2 [S(S+1)]_x} [\text{std}] \quad (1)$$

where  $A$  is the area under the absorption curve which can be obtained by double integrating the first derivative absorption curve; 'scan' is the magnetic field corresponding to the unit length of the chart;  $G$  is the gain;  $B_m$  is the modulation field width;  $g$  is the  $g$  factor;  $S$  is the spin of the system in its ground state;  $P$  is the power of the microwave. The subscripts 'x' and 'std' represent the corresponding quantities for the  $\text{Cu}^{2+}$ :glass sample and the reference ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) respectively.

The number of  $\text{Cu}^{2+}$  ions in KPT1 glass sample was calculated at various temperatures from the EPR spectra of the sample recorded at different temperatures. Figure 2 shows a plot of  $\log N$  against  $1/T$  for this glass sample. The number of  $\text{Cu}^{2+}$  ions in different glasses at room temperature studied in the present work was also calculated and is presented in table 5.

#### 3.2. Calculation of susceptibility from EPR data

The paramagnetic susceptibility can be calculated from the EPR data using the formula:

$$\chi = \frac{N g^2 \beta^2 J(J+1)}{3k_B T} \quad (2)$$

where  $N$  is the number of spins per  $\text{m}^3$ ; the rest of the symbols having their usual meanings.  $N$  can be calculated using equation (1) and  $g(=(g_{\parallel} + 2g_{\perp})/3)$  is taken from EPR data. Using the above equation, paramagnetic susceptibility was calculated at various temperatures. A plot of reciprocal of susceptibility ( $1/\chi$ ) as a function of absolute temperature ( $T$ ) is shown in figure 3.

#### 3.3. Physical properties

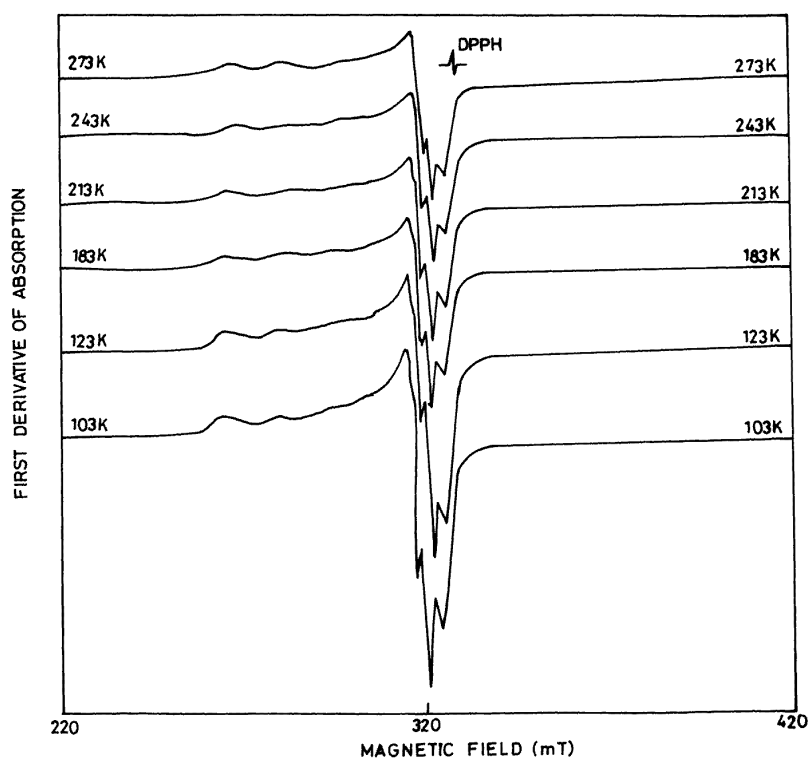
The molar volume can be calculated from the composition of the glass and its density. The optical dielectric constant  $p\delta\epsilon/\delta p$  can be calculated using the formula (Schroeder 1980):

$$p\delta\epsilon/\delta p = \epsilon - 1 = (n^2 - 1) \quad (3)$$

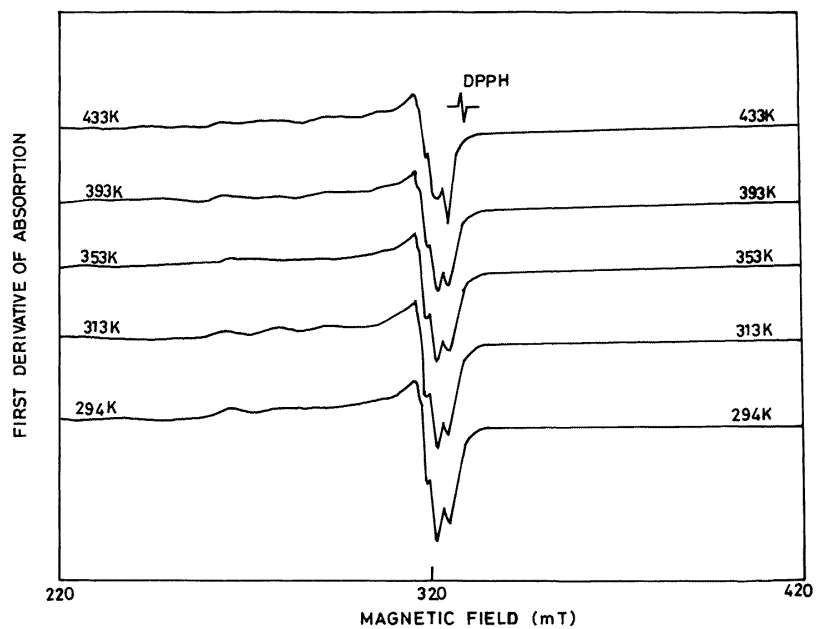
where  $n$  is the refractive index of the glass sample.

The polaron radius  $r_p$  can be calculated using the formula (Ahmed *et al* 1984):

$$r_p = \frac{1}{2}(\pi/6N)^{1/3} \quad (4)$$

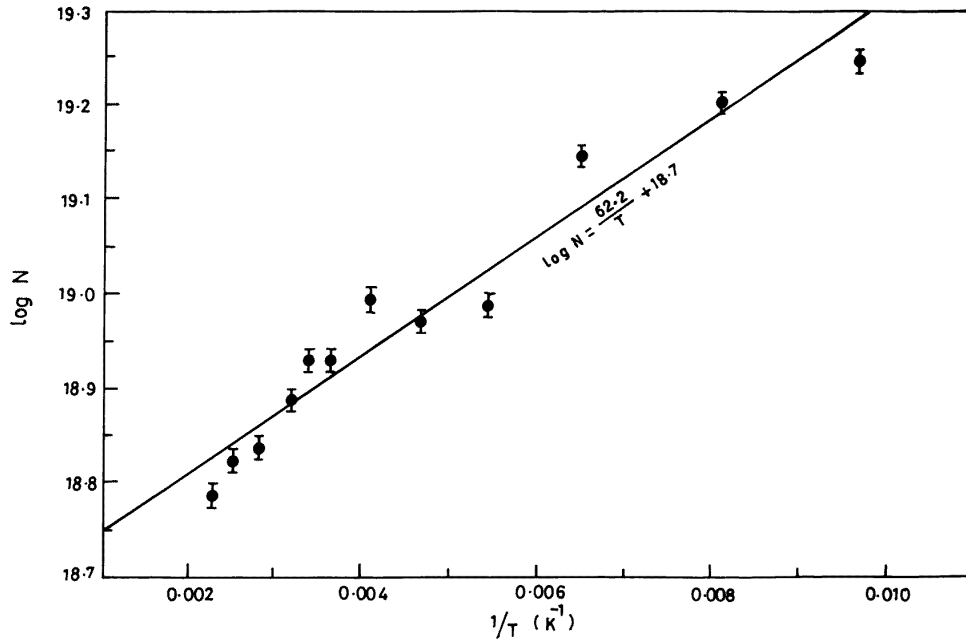


(a)



(b)

**Figure 1.** EPR spectra of potassium lead borotellurite glass sample containing 1 mol% of CuO (KPT1) at (a) low temperatures and (b) high temperatures.



**Figure 2.** A plot of  $\log N$  against  $1/T$  for a potassium lead borotellurite glass sample containing 1 mol% of CuO (KPT1).

where  $N$  is the number of copper ions per unit volume; and inter-ionic separation can be estimated using the equation (Ahmed *et al* 1984):

$$r_i = (1/N)^{1/3}. \quad (5)$$

The electronic polarizability  $\alpha_e$  can be calculated using the formula (Klonkowski 1985):

$$\alpha_e = \frac{3(n^2 - 1)}{4\pi N(n^2 + 2)}. \quad (6)$$

Table 2 lists the densities, molar volumes, refractive indices, number of copper ions per unit volume, the optical dielectric constants, polaron radii, inter-ionic distances and electronic polarizabilities calculated from the above relations for the glasses studied in the present work.

The optical basicity of an oxide glass will reflect the ability of glass to donate negative charge to the probe ion (Easteal and Marcom 1979). Duffy and Ingram (1975) proposed that the optical basicity can be predicted from the composition of the glass and basicity moderating parameters of various cations present.

The theoretical value of the optical basicity of the glass can be estimated using the formula:

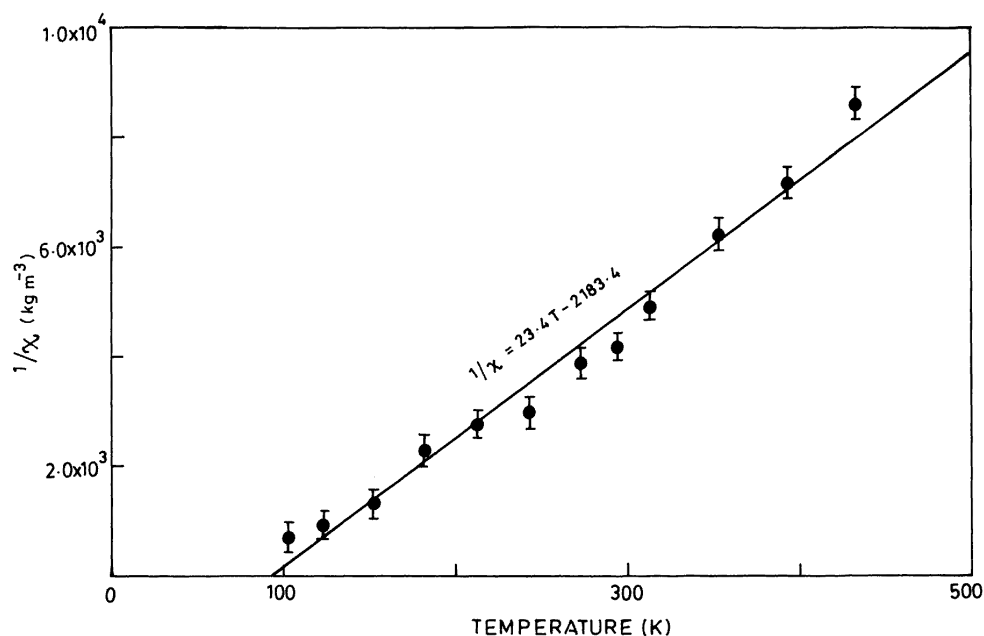
$$\Lambda_{th} = \sum_{i=1}^n \frac{z_i r_i}{|z_o| \gamma_i} \quad (7)$$

The symbols used in the above equation were explained in detail by Murali *et al* (1997). The theoretical values of optical basicity ( $\Lambda_{th}$ ) for all glass samples were calculated and are presented in table 2.

**Table 2.** Physical parameters for the glasses studied in the present work.

Glass sample	Density ( $\text{g cm}^{-3}$ )	Molar volume $V$ ( $\text{cm}^3$ )	Refractive index	Number of Cu ions ( $10^{20}$ ions $\text{cm}^{-3}$ )	Optical dielectric constant	Polaron radius $r_p$ ( $\text{\AA}$ )	Intertonic distance $r_i$ ( $\text{\AA}$ )	Electronic polarizability ( $10^{-22}$ $\text{cm}^3$ )	Optical basicity ( $\Lambda_{th}$ )
LPT1	3.4777	49.26	1.481	1.2227	1.1934	8.1	20.2	5.5565	0.5162
NPT1	3.2972	59.75	1.329	1.0081	0.7662	8.7	21.5	4.818	0.5380
KPT1	3.8287	58.18	1.489	1.0352	1.2171	8.6	21.3	6.6559	0.5678
LT1	3.8722	42.31	1.441	1.4236	1.0765	7.7	19.2	4.4284	0.5229
NT1	6.7405	28.35	1.332	2.1243	0.7742	6.8	16.8	2.3053	0.5450
KT1	4.3507	50.22	1.477	1.1993	1.1815	8.2	20.3	5.6246	0.5754





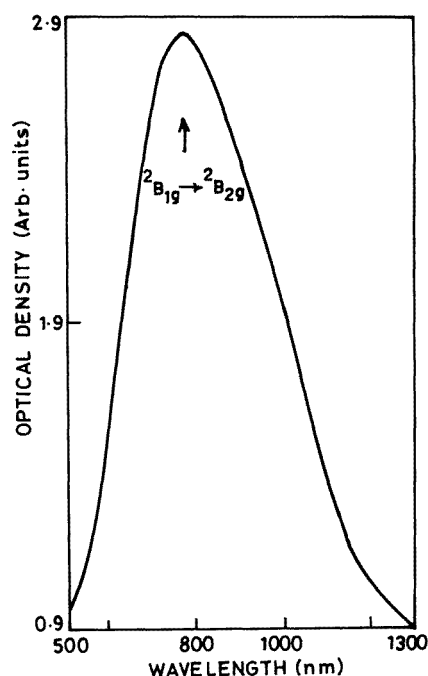
**Figure 3.** Graph of the reciprocal of susceptibility (calculated using equation (2)) against absolute temperature ( $T$ ) for a potassium lead borotellurite glass sample containing 1 mol% of CuO (KPT1).

**Table 3.** Optical band maxima, molecular orbital bond parameters and optical energy gaps and Urbach energies for the glasses studied in the present work.

Glass sample	Transition ${}^2B_{1g} \rightarrow {}^2B_{2g}$ ( $\text{cm}^{-1}$ )	$\beta_1^2$	$\alpha^2$	$\Gamma\pi$ (%)	$\Gamma\sigma$ (%)	Optical energy gap (eV)	Urbach energy $\Delta E$ (eV)
LPT1	13 045	0.9086	0.6944	18.28	66.60	2.875	0.3688
NPT1	14 480	0.8804	0.7210	23.92	60.80	2.900	0.2884
KPT1	12 915	0.8598	0.6540	28.04	75.40	3.320	0.2510
LT1	12 870	0.9445	0.6323	11.10	80.13	2.875	0.2783
NT1	12 710	0.8892	0.6480	22.16	76.71	3.000	0.2506
KT1	12 910	0.8646	0.6567	27.08	74.81	3.125	0.3033

### 3.4. Optical absorption spectra

Figure 4 shows the optical absorption spectrum of the LPT1 glass sample at room temperature observed between 500 nm and 1300 nm. From the figure, we can observe that there is only one broad absorption band centred at 766.3 nm ( $13\,045\text{ cm}^{-1}$ ). This band has been assigned to  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  transition of  $\text{Cu}^{2+}$  ions in a distorted octahedral site. The optical absorption spectra of all other samples are very similar to figure 4 showing one band corresponding to the transition  ${}^2B_{1g} \rightarrow {}^2B_{2g}$ . The exact band positions of individual glasses studied in the present work are listed in table 3.



**Figure 4.** Optical absorption spectrum of lithium lead borotellurite glass sample containing 1 mol% of CuO (LPT1) at room temperature.

### 3.5. Optical energy gap and Urbach energy

A main feature of the absorption edge of amorphous semiconductors is an exponential increase of the absorption coefficient  $\alpha(\nu)$  with photon energy ( $h\nu$ ) in accordance with an empirical relation (Hassan and Hogarth 1988):

$$\alpha = \alpha_0 \exp(h\nu/\Delta E) \quad (8)$$

where  $\alpha_0$  is a constant,  $\Delta E$  is the Urbach energy which indicates the width of the band tails of the localized states and  $\nu$  is the frequency of radiation. The broadening of the exciton levels at the absorption edge is dominated by the random electric fields due to either the lack of long range order or the presence of defects (Gan Fuxi 1992, Davis and Mott 1970).

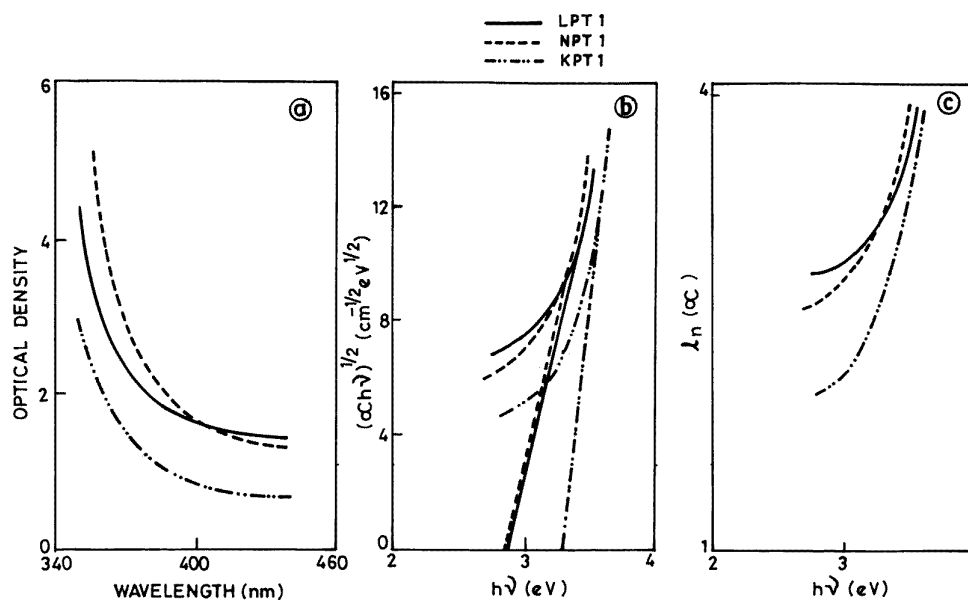
For an absorption by indirect transitions, the equation takes the form:

$$\alpha(\nu) = A(h\nu - E_{opt})^2/h\nu \quad (9)$$

where  $A$  is a constant and  $E_{opt}$  is the band gap. This relation applies to many oxide glasses (Hassan and Hogarth 1988). Plots were drawn between  $(\alpha h\nu)^{1/2}$  and  $h\nu$ . Figures 5(a) and (b) show the ultraviolet absorption edge and corresponding  $(\alpha h\nu)^{1/2}-h\nu$  graph for LPT1, NPT1 and KPT1 glass samples.

Plots were also drawn with  $\ln \alpha$  against  $h\nu$  (a typical plot for LPT1, NPT1 and KPT1 glass samples is shown in figure 5(c)). From these plots, the slopes and thereby the Urbach energy were calculated. The optical energy gaps and Urbach energies of the glasses studied in the present work are given in table 3.

Figure 6 shows a plot of optical energy gap and Urbach energy as a function of copper ion concentration for the NPTx series of glass samples.



**Figure 5.** (a) Ultraviolet absorption edge, (b) a plot between  $(\alpha h\nu)^{1/2}$  and  $h\nu$  and (c) a plot between  $\ln \alpha$  and  $h\nu$  for LPT1, NPT1 and KPT1 glass samples.

**Table 4.** Assignment and positions (in  $\text{cm}^{-1}$ ) of Raman bands of LT1, LPT1 and NPT1 glass samples at room temperature.

Assignment	LT1	LPT1	NPT1
Loose $\text{BO}_4$ units	492	496	488
Chain type metaborate groups		720	
Boroxol groups	792	808	768

### 3.6. Raman spectra

Figure 7 shows the Raman spectra of a glass (NPT1) sample at room temperature. The spectra of the remaining two (*viz.*, LT1 and LPT1) are similar and not shown. Table 4 lists the bands observed in the Raman spectra of these three glass samples at room temperature.

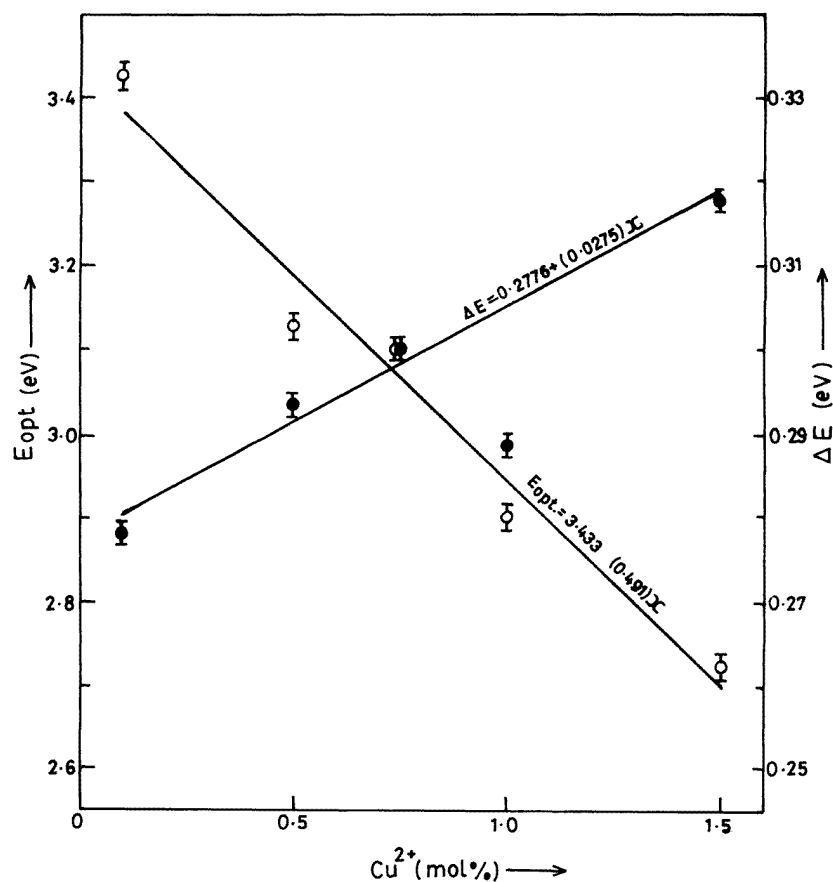
## 4. Discussion

### 4.1. EPR studies

For  $\text{Cu}^{2+}$  ions, a regular octahedral site may not exist; because the cubic symmetry is disturbed by electronic hole in the degenerate  $d_{x^2-y^2}$  orbital and this produces the tetragonal distortion. The EPR spectra of  $\text{Cu}^{2+}$  ions in the present glasses can be analysed by using an axial spin Hamiltonian of the form

$$\mathcal{H} = \beta g_{\parallel} H_z S_z + \beta g_{\perp} (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y). \quad (10)$$

The symbols in the above equations have their usual meanings; the nuclear quadrupole and nuclear Zeeman interaction terms are ignored.



**Figure 6.** Variation of  $E_{opt}$  and  $\Delta E$  with mol% of CuO in the sodium lead borotellurite NPTx series of glasses (where  $x$  indicates mol% of CuO).

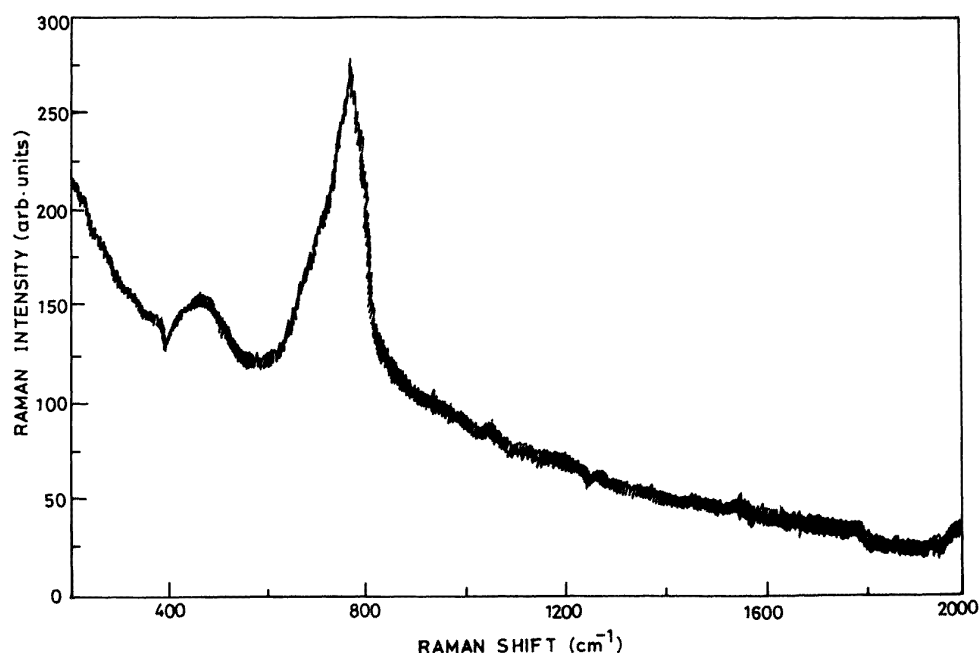
The solution of the spin Hamiltonian gives the expression for the peak position of the principal  $g$  and  $A$  tensors as (Bleaney *et al* 1955):

$$h\nu = g_{\parallel}\beta H + mA_{\parallel} + (15/4 - m^2)[A_{\perp}^2/(2g_{\parallel}\beta H)] \quad (11a)$$

$$h\nu = g_{\perp}\beta H + mA_{\perp} + (15/4 - m^2)[(A_{\parallel}^2 + A_{\perp}^2)/(4g_{\perp}\beta H)] \quad (11b)$$

for parallel and perpendicular peaks respectively. Here  $m$  is the nuclear magnetic quantum number of the copper nucleus with values  $3/2$ ,  $1/2$ ,  $-1/2$  and  $-3/2$  and  $\nu$  is the microwave frequency at resonance. Using equations (11a) and (b), the spin-Hamiltonian parameters were evaluated for all the glasses and are presented in table 5. From table 5, we observe that  $g_{\parallel}$  and  $g_{\perp}$  values decrease from Li to K glasses. This confirms that the copper ions are surrounded by oxygen ligands which are coordinated to different alkali ions. There is no significant change in the spin-Hamiltonian parameters as the copper concentration is increased.

Figure 2 shows a plot of  $\log N$  against  $1/T$ . From the graph the activation energy can be calculated. From the graph, we can observe that as temperature is lowered the number of spins increases and further we can observe a linear relationship between  $\log N$  and  $1/T$ , a phenomenon that can be expected from the Boltzmann law. The activation energy thus calculated was found to be  $1.978 \times 10^{-21}$  J (0.01235 eV).



**Figure 7.** Raman spectra of the sodium lead borotellurite glass sample containing 1 mol% of CuO (NPT1) at room temperature.

**Table 5.** Spin-Hamiltonian parameters, number of  $\text{Cu}^{2+}$  ions and susceptibilities for the glasses studied in the present work.

Glass sample	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ ( $10^{-4} \text{ cm}^{-1}$ )	$A_{\perp}$ ( $10^{-4} \text{ cm}^{-1}$ )	Number of spins per 100 mg (in $10^{16}$ )	$N_2/N_T$	Susceptibility ( $10^{-4} \text{ m}^3 \text{ kg}^{-1}$ )
LPT1	2.323	2.067	129	22	18.179	0.0517	5.099
NPT1	2.293	2.056	136	23	13.027	0.0426	3.595
KPT1	2.291	2.051	130	26	23.847	0.0882	6.557
LT1	2.310	2.063	117	26	17.017	0.0463	4.742
NT1	2.303	2.060	122	24	15.493	0.0492	4.300
KT1	2.294	2.056	129	25	24.415	0.0886	6.741

(The errors in  $g$  and  $A$  values are  $\pm 0.001$  and  $\pm 1 \times 10^{-4} \text{ cm}^{-1}$ , respectively.)

The number of copper ions (shown in table 2) calculated from density measurements will be the sum of copper ions in +2 oxidation state ( $N_2$ ) and +1 oxidation state ( $N_1$ ). Since the EPR technique is sensitive for copper ions in the +2 oxidation state ( $N_2$ ) only, the number of spins indicated in table 5 represents the number of copper ions in +2 oxidation state. From these two numbers, the ratio of number of copper ions in +2 state to total spins ( $N_T = N_1 + N_2$ ) is calculated (i.e.  $N_2/N_T$ ) and is presented in table 5.

Figure 3 shows a graph between reciprocal of susceptibility and absolute temperature. The graph is a straight line in accordance with the Curie's law. From the graph, the Curie constant ( $42.681 \times 10^{-3}$ ) and Curie temperature (93.2 K) have been calculated. The Curie constant calculated in the present work is in good agreement with the measured value ( $44.9 \times 10^{-3} \text{ emu mol}^{-1}$ ) reported for  $\text{Cu}^{2+}$  ions in  $\text{TeO}_2\text{-B}_2\text{O}_3\text{-PbO}$  glasses (Ardelean *et al* 1996).

The susceptibilities for all the samples at room temperature are listed in table 5. From the values it is observed that the susceptibilities are higher for potassium containing glasses than sodium glasses while that for lithium containing glasses is intermediate.

#### 4.2. Optical absorption spectrum

Table 3 lists the absorption bands observed for different glasses reported in the present work. Each of these bands was assigned to the transition  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  as given in table 3. From the table, we can observe that the band positions fall at higher energies for glasses with lead content than that for glasses without lead content for each alkali ion. This indicates that the crystal field around the central metal ion ( $\text{Cu}^{2+}$ ) is influenced by the lead ion in glasses. Table 3 also lists the molecular orbital coefficients  $\beta_1^2$ ,  $\alpha^2$ ,  $\Gamma\pi$  (%) and  $\Gamma\sigma$  (%) calculated from the formulae given in the literature (Kivelson and Neiman 1961, Kuska *et al* 1967). The parameters  $\beta_1^2$  and  $\alpha^2$  can be taken as a measure of the in-plane  $\sigma$  bonding and in-plane  $\pi$  bonding between the d orbital of the central metal ion ( $\text{Cu}^{2+}$ ) and p orbital of the ligand.  $\Gamma\sigma$  and  $\Gamma\pi$  represent the normalized covalency of the  $\text{Cu}^{2+}$ -O in-plane bondings of  $\sigma$  and  $\pi$  symmetry. From the table, it is observed that the  $\beta_1^2$  value decreases and the  $\alpha^2$  value increases from Li to K (for glasses with and without lead content). (However, there is an unusual decrease in the  $\alpha^2$  value from the NPT1 to the KPT1 glass sample, the reason for which is unclear.) This indicates that the in-plane  $\sigma$  bonding and the in-plane  $\pi$  bonding are dependent on the type of alkali ion present in the glass which are coordinated to the oxygen ligands. This in turn indicates that the central metal ion ( $\text{Cu}^{2+}$ ) is surrounded by oxygen ligands which are coordinated to different alkali ions. This supports the conclusion drawn from spin-Hamiltonian parameters.

#### 4.3. Optical energy gap and Urbach energy

The values of the optical energy gap observed in the present work for different glasses are listed in table 3. The values obtained in the present case were of the same order for those of copper tellurium oxide glasses (Hassan and Hogarth 1988),  $\text{PbO}-\text{TeO}_2$  glasses (Vithal *et al* 1997) and tellurium borate glasses (Sabry and El-Samanoudy 1995) reported in the literature. The optical energy gap for the KPT1 glass sample (3.32 eV) is far greater than the activation energy (0.01235 eV) calculated from EPR spectra at different temperatures (figure 2). Hassan and Hogarth (1988) also observed a similar phenomenon where they calculated the activation energy from the dc conductivity measurements at different temperatures. This can be explained by suggesting that the activation is not across the whole gap but is possibly from one or more trapping levels to the conduction band or from bonding states to a trapping level.

The widths ( $\Delta E$ ) of the tails of the localized states within the optical band gap for the present glasses lie in the same range as reported for copper tellurium oxide glasses (Hassan and Hogarth 1988),  $\text{PbO}-\text{TeO}_2$  glasses (Vithal *et al* 1997) and tellurium borate glasses (Sabry and El-Samanoudy 1995). The values of  $\Delta E$  observed for various glasses in the present work are given in table 3. From the table, we can observe that the least Urbach energy (0.251 eV) is observed for KPT1 and NT1 glass samples. This suggests that defects in these glass samples are minimum.

Figure 6 shows a plot of optical energy gap ( $E_{opt}$ ) and Urbach energy ( $\Delta E$ ) as a function of the copper ion content in the glass. From the figure we can observe that the energy gap increases with CuO content while Urbach energy decreases with increasing CuO content. Similar behaviour was observed by Hassan and Hogarth (1988). The decrease in optical energy gap can be attributed due to the increase in non-bridging oxygen ion content with increasing CuO content.

Further, from figure 6, we can observe that the Urbach energy increases with  $\text{Cu}^{2+}$  concentration. Generally, an increase in Urbach energy can be considered as due to increased defects (Vithal *et al* 1997). Hence, the increase in the Urbach energy with  $\text{Cu}^{2+}$  concentration confirms the increased number of defects with  $\text{Cu}^{2+}$  concentration.

#### 4.4. Raman spectra

Raman spectra of the three glass samples (LT1, LPT1 and NPT1) show two peaks at  $488\text{--}496\text{ cm}^{-1}$  and  $768\text{--}808\text{ cm}^{-1}$ . In addition, the LPT1 glass sample shows a peak at  $720\text{ cm}^{-1}$ . The band in the region of  $488\text{--}496\text{ cm}^{-1}$  was assigned as due to loose  $\text{BO}_4$  units (Kamitsos *et al* 1983); that in the region of  $768\text{--}808\text{ cm}^{-1}$  is due to boroxol groups (Konijnendijk 1975). The band in the region of  $720\text{ cm}^{-1}$  can be assigned to chain type metaborate groups (Culea *et al* 1994).

It can be noticed that the Raman spectra consists of bands due to boron groups only and those due to tellurite groups are absent. Since the mol% of tellurium oxide is less when compared to that of boric acid in the glasses, the bands due to tellurite groups will be of less intensity and hence could not be identified in the Raman spectra.

### 5. Conclusions

- (1) From the EPR and optical absorption spectra of  $\text{Cu}^{2+}$  ions in alkali lead borotellurite glasses, it was observed that the copper ions occupied octahedral sites with tetragonal distortion and that they were surrounded by oxygen ligands which are coordinated to alkali ions and lead ions in the glasses studied.
- (2) The EPR spectra of copper ions at different temperatures show a linear dependence between  $\log N$  and  $1/T$ . The activation energy was calculated and found to be  $1.978 \times 10^{-21}$  J.
- (3) From the number of spins calculated from the EPR spectra and density measurements, the ratio of copper ions in +2 oxidation state to total number of Cu ions (in +1 state and +2 state) was calculated and found to be of the order of 0.05.
- (4) The susceptibilities were calculated for  $\text{Cu}^{2+}$  ions at room and various temperatures from EPR data. The linear dependence between  $1/\chi$  and  $T$  was used to calculate the Curie constant and found to be in good agreement with the value reported in literature for copper ions in glasses.
- (5) The optical energy gap ( $E_{opt}$ ) and the Urbach energies ( $\Delta E$ ) were found to be dependent upon the type of alkali ion and the presence of lead ions.
- (6)  $E_{opt}$  and  $\Delta E$  were found to change with CuO content which was assigned to the increase in non-bridging oxygen content with increase in CuO.
- (7) By correlating the EPR and optical data, it was observed that the in-plane  $\sigma$  bonding decreases and in-plane  $\pi$  bonding increases from Li to K (for glasses with and without lead content).
- (8) The Raman spectra of the glasses show three bands and were assigned as due to the different groups of boron atoms.

### Acknowledgments

One of the authors (AM) is thankful to the Council of Scientific and Industrial Research (New Delhi) for the award of a senior research fellowship. The authors thank Professor Ivan Ivanov (Sweden) for recording the Raman spectra.

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