

Optical absorption and electron spin resonance studies of Cu^{2+} in $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{As}_2\text{O}_3$ glasses

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Abstract. The local structure around Cu^{2+} ion has been examined by means of electron spin resonance and optical absorption measurements in $x\text{Li}_2\text{O}-(40-x)\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-10\text{As}_2\text{O}_3$ glasses. The site symmetry around Cu^{2+} ions is tetragonally distorted octahedral. The ground state of Cu^{2+} is $d_{x^2-y^2}$. The glass exhibited broad absorption band near infrared region and small absorption band around 548 nm, which was assigned to the ${}^2B_{1g} \rightarrow {}^2E_g$ transition.

Keywords. Glass transition temperature; ESR; optical absorption; bonding parameters.

1. Introduction

Oxide glasses formed with heavy metal ions have received significant attention owing to their interesting optical applications. These glasses are better competitors for optical transmission studies due to their long infrared cut-off (Fu and Yatsuda 1995; Pan and Ghosh 2000).

Electron spin resonance (ESR) spectroscopy is an experimental technique sometimes capable of determining the coordination and environment of paramagnetic ions in glasses (Sands 1955; Castner Jr *et al* 1960). Several studies have been made on the ESR spectra of transition metal ions in various oxide glasses (Bogomolova 1979; Chand *et al* 1999). Recently, Murali and Rao (1999) and Karthikeyan and Mohan (2003) studied the ESR and optical absorption spectra of Cu^{2+} ions doped alkali lead borotellurite and sodium borobismuthate glasses. Ardelean *et al* (1997) investigated ESR and magnetic susceptibility studies of Fe^{3+} ions in lead based glasses. Chandrasekhar *et al* (2002) revealed distorted octahedral environment for the paramagnetic ion in ESR study of Cr^{3+} ions doped sodium phosphate glasses.

Optical absorption of transition metal ions in glasses is influenced by host structure into which the transition metal ions are incorporated. In oxide glasses, the transition metal ions mostly form coordination complexes with doubly charged oxygen as the ligands. The actual symmetry will depend on the composition of the glass system (France *et al* 1986). By correlating the ESR and optical spectra, one can obtain information regarding the bond parameters which determines the metal ligand bond in the glasses.

We investigated the differential scanning calorimeter studies in $x\text{Li}_2\text{O}-(40-x)\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-10\text{As}_2\text{O}_3$ glasses. In this paper, we report the ESR and optical absorption spectra of Cu^{2+} ions in $x\text{Li}_2\text{O}-(40-x)\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-10\text{As}_2\text{O}_3$ glasses. The values of x were adjusted so that the compositional parameter defined as $R = \text{Li}_2\text{O}/(\text{Li}_2\text{O} + \text{Na}_2\text{O})$ takes the values 0, 0.25, 0.5, 0.75 and 1.

2. Experimental

Pure and copper doped glass samples whose batch compositions are given in table 1, were prepared by melt quench technique at $1000^\circ-1150^\circ\text{C}$ depending on the glass composition. The melt was quickly cast in a stainless steel mould kept at 200°C , and then annealed at 200°C for a duration of about 14 h.

The thermal behaviour of the glass samples was investigated using a differential scanning calorimeter (TA Instruments DSC 2010) with a heating rate of $10^\circ\text{C}/\text{min}$. The glass transition temperatures are given in table 1.

The ESR spectra were recorded on powdered glass samples at room temperature using a Bruker ER200D SRC spectrometer operating in the X-band and employing a field modulation of 100 kHz. DPPH was used as g-marker for the determination of magnetic field. The room temperature optical absorption spectra in the 200–900 nm region was measured by using a Shimadzu, model UV 3100 spectrophotometer.

3. Results

3.1 ESR spectra

An ESR spectrum typical of Cu^{2+} in these glasses is shown in figure 1.

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The spectrum was analysed using the spin-Hamiltonian

$$\mathcal{H} = g_{\parallel} \mathbf{b} H_z S_z + g_{\perp} \mathbf{b} (H_x S_x + H_y S_y) + A_{\parallel} I_z S_z + A_{\perp} (I_x S_x + I_y S_y),$$

where the symbols have their usual meanings (Bleaney *et al* 1955). The hyperfine peak positions are related to the principal values of g and A tensors by the solutions of the spin-Hamiltonian. The parallel hyperfine peaks are resolved in the present glasses, and perpendicular hyperfine peaks are unresolved. Three hyperfine lines were observed on the parallel features of the spectrum. The resolution and linewidths of hyperfine lines increase with the increase in the compositional parameter, R . The changes in the hyperfine linewidths can be attributed to the fluctuations in the coordination sphere surrounding the probe Cu^{2+} ion (Kawazoe *et al* 1978). The spin-Hamiltonian parameters reported for various glasses are given in table 2.

3.2 Optical absorption spectra

The optical absorption spectra of Cu^{2+} ions in these

glasses are shown in figure 2. A single absorption band in the near infrared region was observed for all samples. In addition to this band, a second small absorption band was also observed around 548 nm in the spectra of G3, G4 and G5 samples. The near infrared band can be identified as the $d-d$ transition band due to Cu^{2+} ions (Siegel and Lorenc 1966). The optical absorption bands reported for Cu^{2+} ions in the glass system are given in table 2.

4. Discussion

4.1 Optical absorption

The spectra associated with the Cu^{2+} ion are $d-d$ transitions which can be described in terms of the ligand field theory (Bates 1962). In a regular octahedral field, the $3d^9$ configuration would result in a degenerate ground state (2E_g). In glasses it is assumed that due to disordered vitreous state no site is perfectly cubic. Therefore, tetragonal distortions are endemic to the vitreous state which leads to splitting of energy levels. It is observed that the elon-

Table 1. Glass composition in present study.

Glass no.	Glass composition	Compositional parameter (R)	Density (g/cc)	T_g ($^{\circ}\text{C}$)
G1	40 Na_2O -50 B_2O_3 -10 As_2O_3	0.00	2.40	447
G2	10 Li_2O -30 Na_2O -50 B_2O_3 -10 As_2O_3	0.25	3.33	461
G3	20 Li_2O -20 Na_2O -50 B_2O_3 -10 As_2O_3	0.50	3.41	480
G4	30 Li_2O -10 Na_2O -50 B_2O_3 -10 As_2O_3	0.75	2.92	482
G5	40 Li_2O -50 B_2O_3 -10 As_2O_3	1.00	2.62	490

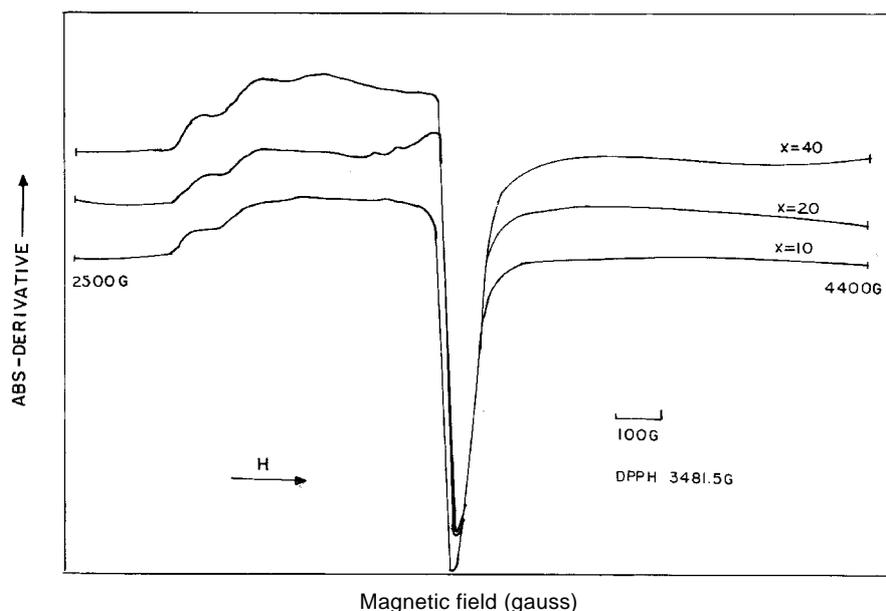
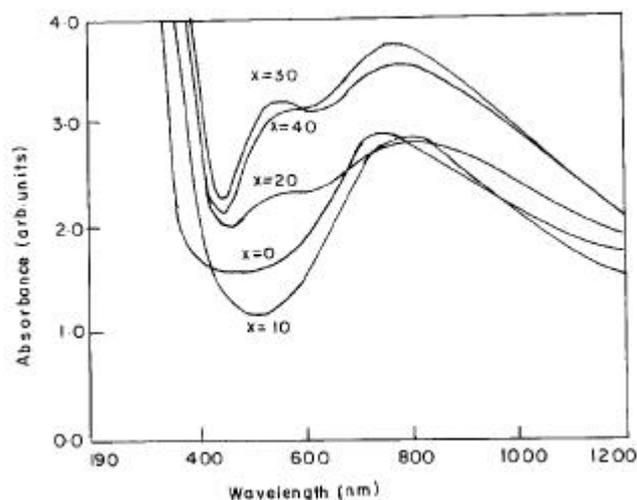


Figure 1. Electron spin resonance spectra of copper doped $x\text{Li}_2\text{O}$ -(40-x) Na_2O -50 B_2O_3 -10 As_2O_3 ($x = 10, 20$ and 40) glasses at room temperature.

Table 2. Spin-Hamiltonian parameters, optical absorption bands and bonding coefficients for Cu^{2+} ions in the present glasses.

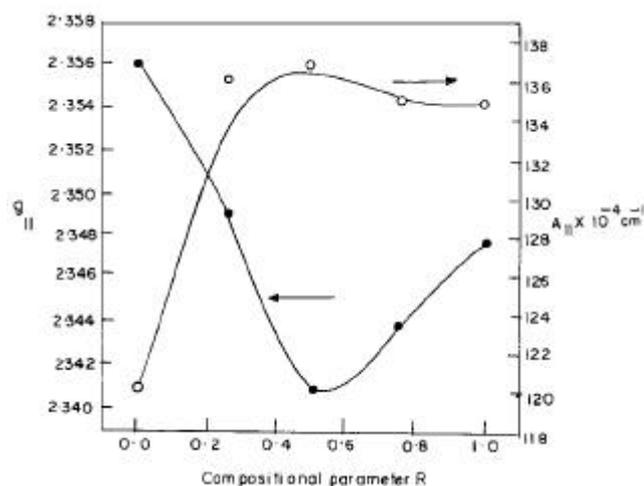
Glass system	g_{\parallel} (± 0.002)	g_{\perp} (± 0.001)	A_{\parallel} (10^{-4} cm^{-1}) (± 2)	ΔE_{xy} (cm^{-1})	$\Delta E_{xz, yz}$ (cm^{-1})	a^2	b_1^2	Γ_s (%)	Γ_p (%)
G1	2.356	2.064	120	13,236	—	0.75	0.93	52.9	13.4
G2	2.349	2.071	136	12,422	—	0.79	0.81	44.1	37.0
G3	2.341	2.068	137	13,054	18,248	0.79	0.84	45.6	31.3
G4	2.344	2.069	135	12,853	18,248	0.78	0.83	46.0	32.0
G5	2.348	2.071	135	12,828	18,248	0.79	0.84	45.0	31.4

**Figure 2.** Optical absorption spectra of Cu^{2+} ions in $x\text{Li}_2\text{O}-(40-x)\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-10\text{As}_2\text{O}_3$ glasses.

gated structures are usually more energetically favoured than the compressed ones (Jorgensen 1955). For Cu^{2+} in elongated octahedral symmetry more than one band will be observed. Hence in the present investigation the observed asymmetric band around $12,880 \text{ cm}^{-1}$ is due to the overlap of ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions. We attribute the observed small band at $18,248 \text{ cm}^{-1}$ (548 nm) to the ${}^2B_{1g} \rightarrow {}^2E_g$ transition in the tetragonal symmetry. Similar observation was reported by Ohishi *et al* (1983) in zirconium fluoride glasses around $23,529 \text{ cm}^{-1}$ (425 nm). The occurrence of the band around 548 nm signifies the distortion around the probe ion environment as the compositional parameter increases.

4.2 ESR spectra

The observed g_{\parallel} and g_{\perp} values show that $g_{\parallel} > g_{\perp} > 2.0023$. Therefore, we can conclude that Cu^{2+} has an octahedral environment elongated along one of the cube axis and the ground state of the Cu^{2+} is $d_{x^2-y^2}$ (Imagawa 1968). This configuration satisfies the condition for applying the analysis developed by Maki and McGarvey (1958) and modified by Kivelson and Neiman (1969). The observed A_{\perp} and g_{\perp} values remain invariant within the interval of

**Figure 3.** Compositional dependence of spin-Hamiltonian parameters, A_{\parallel} and g_{\parallel} , in mixed alkali boroarsenate glasses.

uncertainty. A_{\parallel} and g_{\parallel} of the samples change, but in opposite directions with the compositional parameter, R : g_{\parallel} decreases and A_{\parallel} increases as the ratio, R , increases to 0.5 but the situation is reversed as the ratio increases further. This is depicted in figure 3. These changes in the spin-Hamiltonian parameters can be attributed to the variation of ligand field around the probe ion. Similar observation was reported in lithium sodium borate glasses (Suresh Babu *et al* 1990).

4.3 Bonding parameters

To determine the bonding coefficients of Cu^{2+} , one need to know the frequencies from the optical absorption bands, which indicate the ΔE_{xy} and $\Delta E_{xz, yz}$. The ΔE_{xy} is the frequency of an intense absorption band in the optical spectrum of Cu^{2+} in a given glass. $\Delta E_{xz, yz}$ was calculated for compositions, $R = 0$ and 0.25 , with the help of an approximation formula (Klonkowski *et al* 1983)

$$\Delta E_{xz, yz} = 2k_{\perp}^2 \mathbf{I}_0 / (g_e - g_{\perp}),$$

where k_{\perp}^2 is the orbital reduction factor ($k_{\perp}^2 = 0.77$) and \mathbf{I}_0 the spin orbit coupling constant ($\mathbf{I}_0 = -828 \text{ cm}^{-1}$) (Kivelson and Neiman 1969).

The bonding coefficients, \mathbf{a}^2 , \mathbf{b}_1^2 and \mathbf{b}^2 describe respectively, the in-plane σ bonding, in-plane π bonding and out-of-plane π bonding of the Cu^{2+} complex in the glasses. The value \mathbf{a}^2 will lie between 0.5 and 1, the limits for pure covalent and ionic bonding, respectively. The terms, \mathbf{b}_1^2 and \mathbf{b}^2 , are interpreted similarly. The values of \mathbf{b}^2 may be expected to lie sufficiently close to unity in the bonding coefficient calculations (Klonkowski *et al* 1983). The \mathbf{a}^2 values were evaluated using the following equation (Kivelson and Neiman 1969).

$$\mathbf{a}^2 = |A_{||}/P| + (g_{||} - 2) + 3/7 (g_{\perp} - 2) + 0.04,$$

where P is the dipolar hyperfine coupling parameter.

From table 2, the \mathbf{a}^2 values indicate an intermediate ionic bond for the Cu(II)-O^- in-plane σ bonding. The glass becomes more ionic as the lithium content is increased. The in-plane π bonding has an ionic component and \mathbf{b}_1^2 varies as lithium content increases. However, the out-of-plane π bonding for the cupric ion has an invariant covalent component in all the samples within the experimental error.

The normalized covalency of $\text{Cu}^{2+}\text{-O}$ in-plane bonding of σ or π symmetry is expressed by (Kawazoe *et al* 1978)

$$\Gamma_{\sigma} = 200 (1 - S) (1 - \mathbf{a}^2)/(1 - 2S)\%$$

and

$$\Gamma_{\pi} = 200 (1 - \mathbf{b}_1^2)\%,$$

where S is the overlap integral ($S_{\text{oxy}} = 0.076$).

The normalized covalency (Γ_{π}) of $\text{Cu}^{2+}\text{-O}$ bonding of π symmetry indicates the basicity of the oxide ion. We observe that the covalency of the in-plane σ bonding (Γ_{σ}) decreases and the covalency of in-plane π bonding (Γ_{π}) increases.

5. Conclusions

From the ESR and optical absorption studies discussed above, the following conclusions may be drawn.

(I) An elongated octahedral coordination of Cu^{2+} is observed.

(II) The \mathbf{a}^2 indicates that σ bonding is ionic and remains so with the compositional parameter.

References

- Ardelean I, Peteanu M, Filip S, Simon V and Gyroffy G 1997 *Solid State Commun.* **102** 341
- Bates T 1962 in *Modern aspects of the vitreous state* (ed.) J D Mackenzie (London: Butterworths) **Vol. 2**, p. 195
- Bleaney B, Bowers K D and Pryce M H L 1955 *Proc. R. Soc.* **A228** 147
- Bogomolova L D 1979 *J. Non-Cryst. Solids* **30** 379
- Castner Jr T, Newell G S, Holton W C and Slichter C P 1960 *J. Chem. Phys.* **32** 668
- Chand I, Seth V P, Prakash D and Gupta S K 1999 *Phys. Chem. Glasses* **40** 153
- Chandrasekhar A V, Ravikumar R V S S N, Reddy B J, Reddy Y P and Rao P S 2002 *Glass Technol.* **43** 32
- France P W, Carter S F and Parker J M 1986 *Phys. Chem. Glasses* **27** 32
- Fu J and Yatsuda H 1995 *Phys. Chem. Glasses* **36** 211
- Imagawa H 1968 *Phys. Status Solidi* **B30** 469
- Jorgensen C K 1955 *Acta Chem. Scand.* **9** 1362
- Karthikeyan B and Mohan S 2003 *Mater. Letts* **57** 3789
- Kawazoe H, Hosono H and Kanazawa T 1978 *J. Non-Cryst. Solids* **29** 173
- Kivelson D and Neiman R 1969 *J. Chem. Phys.* **35** 149
- Klonkowski A, Frischat G H and Ritcher T 1983 *Phys. Chem. Glasses* **24** 47
- Maki A H and McGarvey B R 1958 *J. Chem. Phys.* **45** 31
- Murali A and Rao J L 1999 *J. Phys. Condens. Matter* **11** 7921
- Ohishi Y, Mitachi S, Kanamori T and Manabe T 1983 *Phys. Chem. Glasses* **24** 135
- Pan A and Ghosh A 2000 *J. Non-Cryst. Solids* **271** 157
- Sands R H 1955 *Phys. Rev.* **99** 1222
- Siegel J and Lorenc J A 1966 *J. Chem. Phys.* **45** 2315
- Suresh Babu D, Ramana M V, Sathyanarayan S G and Sastry G S 1990 *Phys. Chem. Glasses* **31** 80