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EPR and Optical Absorption Studies of Cu^{2+} in Boro-Arsenate Glasses

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Electron paramagnetic resonance (EPR) and optical absorption studies of xMgO- (25-x) Li_2O-$50B_2O_3$-$25As_2O_3$ glasses were made by introducing Cu^{2+} as a spin probe. The EPR spectra of all the glass samples recorded at X-band frequencies have similar spectral features. The Cu^{2+} ions are in well-defined axial sites, but subjected to small distortion leading to the broadening of the spectra. The spin-Hamiltonian parameter values indicate that the ground state of Cu^{2+} is d_{x2-y2} and the site symmetry around Cu^{2+} ions is tetragonal distorted octahedral. The optical absorption spectra exhibited a broadband corresponding to the d-d transition bands of Cu^{2+} ion. By correlating EPR and optical data, the bond parameters were evaluated and the values show purely ionic nature for the in-plane σ bonding and in-plane π bonding. The out-of-plane π bonding is moderately covalent.

Keywords: *Glass, spin-Hamiltonian, Optical Absorption, Electron Spin Resonance*

1. Introduction

Heavy metal oxide based glasses containing As_2O_3 has received significant attention owing to their interesting optical applications. These glasses have large non-linear optical susceptibility coefficient[1-4] that makes them suitable for potential applications in non-linear optical devices (such as ultra-fast optical switches and power limiters), broad band optical amplifiers operating around 1.5 μm and in a number of solid state ionic devices.

Electron paramagnetic resonance (EPR) spectroscopy is an experimental technique sometimes capable of determining the co-ordination and environment of paramagnetic ions in glasses[5,6]. EPR behaviors of oxide glasses doped with transition metal (TM) ions have been extensively studied to obtain information on the glassy network and to identify the site symmetry around the TM ions[7-10]. Glasses containing TM ions exhibit memory and photo conducting properties[11]. Recently, Sumalatha et al.[12], Hayder Khudhair Obayes et al.[13], Edukondalu et al.[14] studied the local structure around Cu^{2+} ion in oxide glasses by EPR spectra. Copper (II) is the most amenable ion for EPR studies. The main advantage of using Cu^{2+} as the spin probe is that it EPR spectra can easily be recorded at room temperature, the spectrum is simple and the spread of the spectrum is large enough to detect minute changes in the coordination sphere[15].

Optical absorption of transition metal ions in glasses is influenced by the host structure into which the transition metal ions are incorporated. In oxide glasses, the TM ions mostly form coordination complexes with doubly charged oxygen as the ligands. The actual structure will depend on the composition of the glass system[16]. By correlating the EPR and optical spectra, one can obtain information regarding the bond parameters which determine the metal-ligand bond in the glasses. The properties of a glass can often be altered by the addition of a network modifier to the basic constituents. The commonly used network modifiers are the alkali and alkaline earth oxides[17]. It was observed that the properties of an alkali oxide glass show a non-linear behavior when one kind of alkali is gradually replaced by another. This departure from linearity is called the mixed alkali effect[18]. Similar observations were made in the case of mixed alkali-alkaline earth oxide glasses[19]. This phenomenon is called mixed oxide effect. In this paper, we report EPR and optical absorption studies of Cu^{2+} spin probe in the quaternary glass system xMgO-(25-x)Li_2O-$50B_2O_3$-$25As_2O_3$. The influence of varying the concentrations of Li_2O and MgO, which acts as network modifiers on the spin-Hamiltonian parameters, is discussed.

2. Experimental

Pure and copper (1 mole %) doped glass, samples of composition (table 1) xMgO-(25-x)Li_2O-$50B_2O_3$-$25As_2O_3$ ($0 \leq x \leq 25$) were prepared using the conventional melt-quench technique. Glasses were prepared by mixing the required proportions of the reagent grade Li_2CO_3, H_3BO_3, As_2O_3 (May and Baker), MgO (Fluka) and CuO in an electrical furnace using silica crucibles. The furnace temperature is varied from 1000- 1150 °C depending on the glass composition. For samples taken from different regions of the bulk specimen, the absence of any Bragg peaks in the X-ray diffraction pattern confirmed that the glasses are amorphous and homogeneous.

The room temperature EPR spectra of powdered glass samples were recorded using a JOEL PE-3X EPR spectrometer

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operating in the X-band and employing a field modulation of 100 kHz. DPPH was used as the standard *g* marker for the determination of magnetic field. The optical absorption spectra of the present glasses in 200 – 800 nm region was recorded by using a Shimadzu spectrometer (model UV-3100) at room temperature.

3. Results and Discussion

3.1. EPR spectra

The room temperature Cu^{2+} ion doped EPR spectra of the present glasses were shown in Figure 1. The EPR spectra of Cu^{2+} ions in the remaining glasses exhibited the same spectral features. In all the EPR spectra recorded in the present investigation three parallel components were observed in the low field region. However, the perpendicular components are not resolved, leading to an intense line in the high field region.

Spectroscopic splitting (g) and hyperfine (A) tensors with axial symmetry have been assumed in the analysis of EPR spectra of oxide glasses[20,21]. The Jahn-Teller effect causes predominantly an elongated octahedral coordination with four short in-plane bond lengths. Therefore an axial spin–Hamiltonian can be employed in the analysis of the EPR spectra which is given below:

$$H = g_{||}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{||} I_z S_z + A_{\perp}(I_x S_x + I_y S_y) \quad (1)$$

where the symbols have their usual meanings[22]. The nuclear quadrupole contribution is neglected. The calculated spin-Hamiltonian parameters are given in Table 1.

The observed g values are characteristic of Cu^{2+} coordinated by six ligands, which form an octahedron elongated along the z-axis. The general nature of the ligand coordination can be obtained[23] from the fact that $g_{||}, g_{\perp}, A_{||}$ and $A_{\perp}$ $g|| > g_{\perp} > 2.0023$. Only an environment elongated along one of the cube axis can yield this result. In the present investigation, it is observed that $g|| > g_{\perp} > g_e$. Therefore from the *g* values and shape of the EPR spectra, it can be concluded that the ground state of the Cu^{2+} is $d_{x^2-y^2}$ orbital, the Cu^{2+} ions being located in tetragonally distorted octahedral sites[12,20,23,24].

The $g_{||}$ and $A_{||}$ values are found to be dependent on the glass composition while $g_{\perp}$ and $A_{\perp}$ values are essentially constant. The variation of $g_{||}$ and $A_{||}$ with MgO content is illustrated in Figure 2. $g_{||}$ and $A_{||}$ varies non-linearly as the MgO content increases: $g_{||}$ decreases and then increases whereas $A_{||}$ increases and then decreases indicating the change in the tetragonal distortion of Cu^{2+} ions[25]. The variation in $g_{||}$ and $A_{||}$ values may be associated with the change in the environment of Cu^{2+}. In the B_2O_3 glasses, the addition of network modifiers (MgO and Li_2O) leads to an increase in the coordination number of a certain portion of the boron atoms from 3 to 4. It is assumed that the resulting glass is composed of both triangular and tetrahedral units which form a relatively open network with holes between the oxygen atoms of sufficient size to accommodate the Li and Mg ions[15]. As a doubly charged cation, Mg^{2+} is sufficiently strong to split the network. Thus, sufficient non-bridging oxygen's are available for good coordination in the broken network. The alkali oxide Li_2O makes available additional weakly bonded O^{2-} for each Mg^{2+}, i.e. Mg^{2+}captures the O^{2-} from Li_2O and this happens at the expense of Li_2O coordination. Li^+ should remain in the neighborhood of the next stronger Mg^{2+} than that it should be incorporated separately into the rigid network. The configuration Li-O-Mg may energetically favored. The solubility of the Cu^{2+} increases with the addition of the network modifiers presumably due to the coordination of the metal ion by the extra oxygen ions. Thus, incorporation of MgO into the glass will influence the field at the site of Cu^{2+}, which in turn will reflect in the non-linear variation of the spin Hamiltonian parameters as observed in the present study.

The line width of the parallel hyperfine components was found to increase with increasing values of the nuclear spin quantum number (*ml*), which may be due to fluctuations in both the ligand fields and bond covalencies from one copper (II) complex to the next, giving rise to a narrow distribution in g[24]. The mobility of the paramagnetic species in the glass medium may also affect the EPR line shape.

3.2. Optical absorption spectra

In a regular octahedral field, the $3d^9$ configuration would result in the adegenrate ground state (^2E_g). In glasses, it is assumed that no site is perfect cubic due to the disordered vitreous state. Hence, the tetragonal distortion is endemic to the vitreous state that leads to splitting of energy levels. It is observed that the elongated structures are usually more energetically favored than the compressed ones. For Cu^{2+} in an elongated octahedral symmetry , more than one band is observed[1]. Figure 3 presents the optical absorption spectrum of Cu^{2+} ions in the present glasses.

The optical absorption co-efficient α(ν), near the fundamental absorption edge of the curve in the above figure was determined from the relation

$$\alpha(v) = (1/d)\log(I_t/I_0) \quad (2)$$

where I_0 and I_t are the intensities of the incident and transmitted beams, respectively, and d is thickness of the glass sample. The factor $\log(I_0/I_t)$ corresponds to absorbance. Davis and Mott[26] and Tauc and Menth[27] relate this data to the optical band gap, E_{opt} through the following general relation proposed for amorphous materials

$$\alpha(v) = B(hv - E_{opt})^n/hv \quad (3)$$

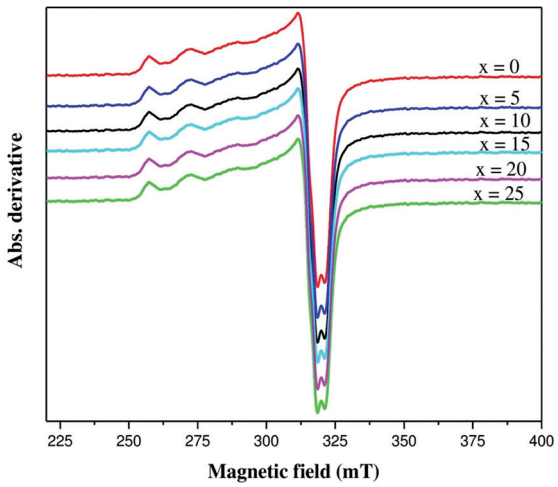

Figure 1: EPR spectra of Cu^{2+} in the present glass system.

where B is a constant related to the extent of the band tailing and hν is incident photon energy. The index n determines the type of electronic transitions causing the absorption, and takes the values 1/2, 2, 3/2 and 3 for direct allowed, indirect allowed, direct forbidden, and indirect forbidden transitions. By plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of photon energy hν, one can find the optical energy band gap E_{opt} for indirect and direct transitions, respectively. The respective values of E_{opt} are obtained by extrapolating to $(\alpha h\nu)^{1/2} = 0$ for indirect transition and $(\alpha h\nu)^2 = 0$ for direct transition. Figure 4 represents the Tauc plots $\{(\alpha h\nu)^{1/2}$ *vs* hν} for different glass samples. The values of the all optical energy gap, E_{opt}, thus obtained from the extrapolation of the linear region of Tauc plots are presented in Table 2. In the present glasses, the indirect band gap energy varies from 2.34 to 2.5 eV and dirct band gap energy vary between 2.55 to 2.68 eV respectively. In the present glasses, the compositional dependence of direct and indirect optical band gap energies is illustrated in Figure 5. It is observed that the band gap energies vary non-linearly with compositional parameter, indicating the existence of mixed alkali effect.

The main feature of the absorption edge of amorphous materials is an exponential increase of absorption coefficient α(ν) with photon energy hν, which is given by the Urbach rule[28]

$$\alpha(v) = C\exp(h\nu/\Delta E) \quad (4)$$

where C is a constant, and ΔE is the Urbach energy which is a measure of band tailing. The values of Urbach energy (ΔE) were determined by taking the reciprocals of slopes of the linear portion of ln(α) vs hν curves. The Urbach energy values of the present glass samples are presented in Table 2. The compositional dependence of Urbach energy ΔE is illustrated in Figure 6. Urbach energy is varying non-linearly with a compositional parameter indicating the existence of mixed alkali effect in present glasses.

The optical absorption spectra of all glasses studied reveal only a broad absorption band. The optical absorption peak position values are determined by peak pick facility of the spectrometer and are presented in Table 1 and shown in Figure 7.

The stable state of copper are Cu^+ and Cu^{2+}. The Cu^+ ion has $3d^{10}$ configuration and consequently is not expected to have any ligand field band. The Cu^{2+} ion has the $3d^9$ configuration and the spectra associated with the Cu^{2+} ion are *d–d* transitions which can be described in terms of the ligand field theory[29]. In a regular octahedral field, the $3d^9$ configuration would result in a degenerate ground state (^2E_g) and the Jahn-Teller effect gives a marked tetragonal distortion which leads to splitting of energy levels. 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 elongated structures are usually more energetically favored than the compressed

Table 1: Spin-Hamiltonian and optical absorption and bonding coefficients for Cu^{2+}ions in $xMgO-(25-x)Li_2O-50B_2O_3-25As_2O_3$ glasses.

Parameters	x=0	x=5	x=10	x=15	x=20	x=25
$g_{\parallel}$	2.455	2.442	2.430	2.434	2.439	2.446
$g_{\perp}$	2.057	2.057	2.057	2.058	2.058	2.058
$A_{\parallel}$	139	144	156	162	159	153
$A_{\perp}$	18	13	25	13	13	25
λ	722	740	758	730	769	770
G	8.276	8.038	7.819	7.751	7.840	7.966
ΔE_{xy}	12953	13513	13192	13698	13004	12987
α^2	0.901	0.906	0.928	0.970	0.964	0.933
β_1^2	0.981	0.989	0.916	0.919	0.887	0.931
β^2	0.657	0.653	0.638	0.610	0.614	0.634
Γ_{σ} (%)	21	20	16	6	18	15
Γ_{Π} (%)	4	2	17	16	23	14

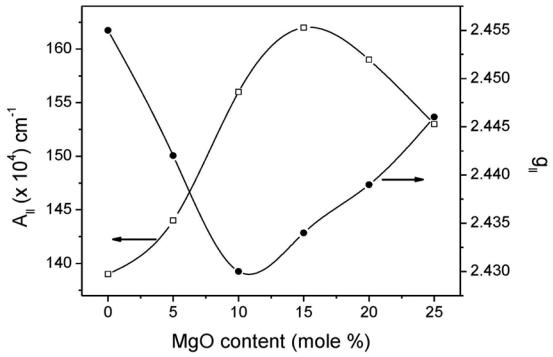

Figure 2: Variation of g|| and A|| with MgO content in the present study.

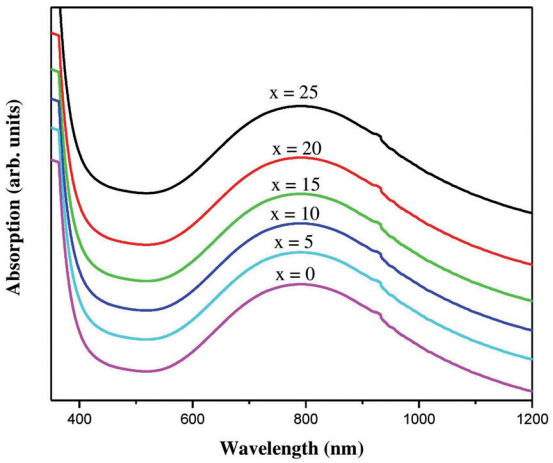

Figure 3: Optical absorption spectra of present glass system.

ones and the cupric ion exists in solution, solids and glasses in octahedral symmetry with a tetragonal distortion[30]. For Cu^{2+} in elongated octahedral symmetry more than one band will be observed[12]. But only a single optical absorption maximum was observed in most of the cases[31,32]. This single optical band was interpreted as the overlap of all the three transitions. Hence, in the present investigation the observed asymmetric band around 13,192 cm^{-1} is due to the overlap of $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions. Most of the authors[33,34] assigned the observed optical peak to the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition (ΔE_{xy}) and have used this value in the evaluation of the bond parameters.

3.3. Cu^{2+} ligand bond nature

The EPR and optical absorption data can be related to evaluate the bonding coefficients of Cu^{2+}. The bonding between the Cu^{2+} ion and its ligands can be described in terms of the covalency parameters α^2, β^2 and β_1^2 where α^2 describes the in-plane σ bonding with the copper $d_{x^2-y^2}$ orbital, β^2 describes the out-of-plane π bonding with the d_{xz} and d_{yz} orbital and the β_1^2 parameter is a measure of the in-plane π bonding with the d_{xy} orbital. The values of α^2 lie between 0.5 and 1, the limits of pure covalent and pure ionic bonding, respectively. The terms β^2 and β_1^2can be interpreted similarly.

EPR results give rise to a new parameter (G), which is defined as

$$G = (g_{ll} - g_e)/(g_\perp - g_e) \quad (5)$$

If the G value falls in between 3 and 5, the unit cell contains magnetically equivalent ions. If the G value is less than 3, the exchange coupling among the magnetically non-equivalent Cu(II) ions in the unit cell is not very strong. If G is greater than 5, a strong exchange coupling takes place among the magnetically non -equivalent Cu(II) ions in the unit cell. Truly compressed structures are relatively rare when compared to elongated structures[35].

The bonding parameters were evaluated using the equations given below[36]

$$\alpha^2 = -(A_{||}P) + (g_{||} - 2) + 3/7(g_\perp - 2) + 0.04 \quad (6)$$

$$\beta_1^2 = [(g_\perp/g_e) - 1]\Delta E_{xy}/3312\alpha^2 \quad (7)$$

$$\beta^2 = [(g_\perp/g_e) - 1]\Delta E_{xz,yz}/828\alpha^2 \quad (8)$$

where P is the dipolar hyperfine coupling parameter. ΔE_{xy} is the energy corresponding to the transition $^2B_{1g} \rightarrow {}^2B_{2g}$ and λ is the spin-orbit coupling constant (λ= -828 cm^{-1}).

The corresponding value of $\Delta E_{xz,yz}$ was calculated using the approximation[17]

$$\Delta E_{xz,yz} = 1656K^2/(g_\perp/g_e) \quad (9)$$

$$\Gamma_\sigma = 200(1 - S)(1 - \alpha^2)/(1 - 2S)\% \text{ and}$$

$$\Gamma_\pi = 200(1 - \beta_1^2)\% \quad (10)$$

where K^2 is the orbital reduction factor (= 0.77).

The normalized covalencies of Cu (II)-O in-plane bonds of σ and π symmetry are expressed[37] in terms of bonding coefficients α^2 and β_1^2 as follows. Where S is the overlap integral (S_{oxy} = 0.076). The calculated values of α^2, β_1^2, β^2, are presented in Table 1. are illustrated in Figure 8. The normalized covalency of Cu (II)-O in-plane bonding of π symmetry (Γ_π) indicates the basicity of the oxide ion. The values of α^2 andβ_1^2 indicate pure ionic for the in-plane σ bonding and in-plane π bonds, while β^2 out of the plane. Π bonding seems to be mostly covalent nature in all the glass systems.

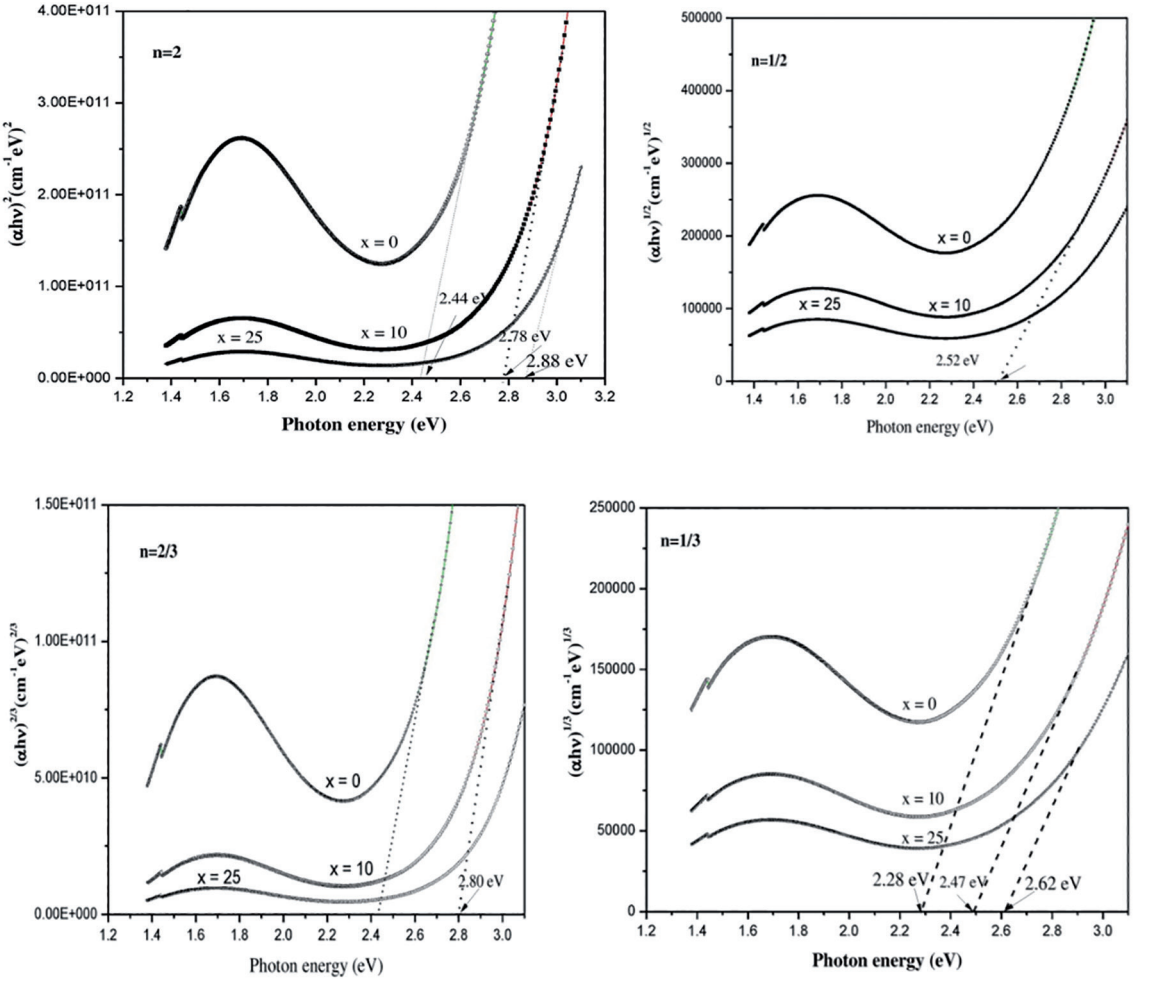

Figure 4: Tauc's plots (n=1/2, 2, 2/3 and 1/3) for the present glass system.

Table 2: Optical parameters of the present glass system.

Parameter	x = 0	x = 5	x = 10	x = 15	x = 20	x = 25
Optical band gap energies (E_{opt}) (eV) (± 0.05)						
Indirect allowed (n=1/2)	2.50	2.39	2.42	2.34	2.38	2.41
Indirect forbidden (n=1/3)	2.42	3.35	2.37	3.32	2.37	2.40
Direct allowed (n=2)	2.66	2.59	2.68	2.62	2.55	2.64
Direct forbidden (n=2/3)	2.65	2.61	2.70	2.64	2.66	2.67
Urbach energy ΔE (eV) (±0.001)	0.426	0.421	0.429	0.399	0.428	0.423

4. Conclusions

The quaternary glass system of $xMgO-(25-x)Li_2O-50B_2O_3-25As_2O_3$ ($0 \leq x \leq 25$) were prepared, and their optical and EPR measurements have been studied. The following conclusions were made: From EPR and optical measurements it is clear that Cu^{2+} ions are present in all the glasses investigated and they exist on tetragonally distorted octahedral sites with $d_{x^2-y^2}$. The spin-Hamiltonian parameters are influenced by the composition of glass which may be attributed to the change of ligand field strength around Cu^{2+}. With increasing MgO content the ligand field strength is reduced around the Cu^{2+} ion due to the modification of the boron-oxygen network. The bond parameter values show purely ionic nature of the in-plane σ bonding and in-plane π bonding. The out-of-plane π bonding is moderately covalent.

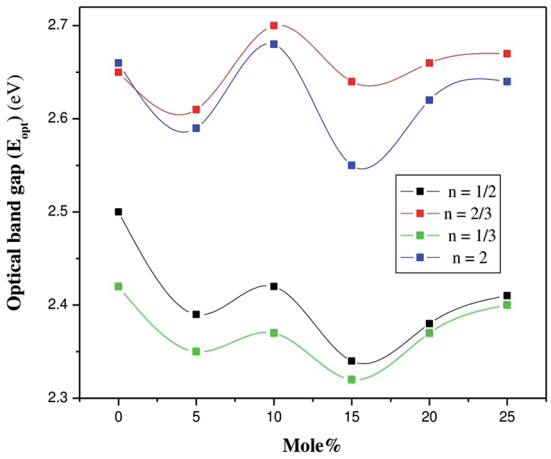

Figure 5: Optical band gap energy (for all transitions) as a function of composition (mol%) in present glasses.

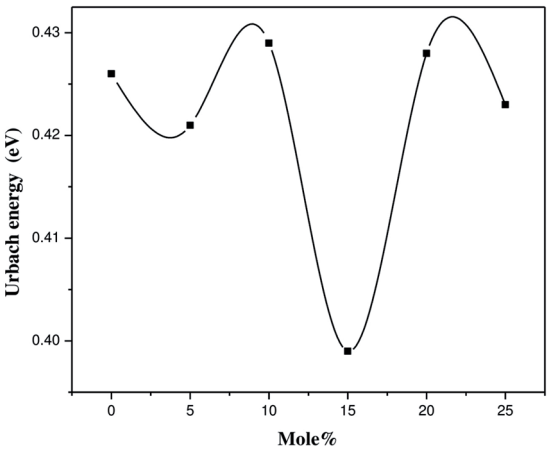

Figure 6: Compositional dependence of Urbach energy (ΔE) in the present glasses.

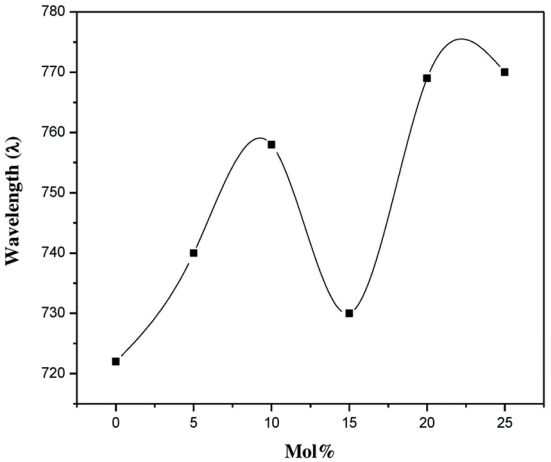

Figure 7: The compositional mole% as a function of peak position (λ).

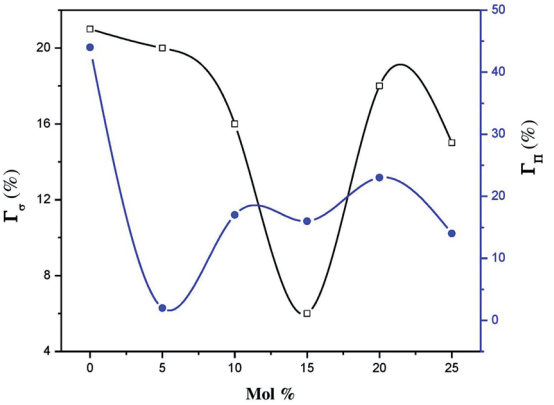

Figure 8: The mole% as a function of Γ_σ and Γ_π

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