EPR and optical absorption spectral investigations of Cu$^{2+}$ ions in alkaline earth alumino borate glasses
1. Introduction

Borate and phosphate glasses are excellent matrices to realise various optical functions of transition and rare-earth ions [1,2]. Borate glasses are used as electro-optic switches, electro-optic modulators, solid state laser materials and non-linear optical parametric converters [3,4].

Recently, there has been a lot of interest in aluminates due to their potential as materials with useful optical properties [5]. Hosono et al. [6] reported photochromism in calcium aluminate glasses which find applications in glass-window curtains, visible intensity wind shields as well as ophthalmic and space devices [7]. Alkaline earth alumino borates are of some technical interest because of their electrical insulating properties [8]. Qui and Hirao [9] reported, for the first time, long lasting phosphorescence in calcium alumino borate glasses doped with Eu$^{2+}$ ions.

The EPR and the optical absorption studies of the transition metal ions in glasses give much information on their structure. By changing the composition of the glass, the local environment of the transition metal ion can be changed [10] and can be studied by EPR and optical absorption spectra. Nicklin et al. [8] reported EPR spectra of BaO-B$_2$O$_3$-Al$_2$O$_3$ and CaO-B$_2$O$_3$-Al$_2$O$_3$ glasses containing Mn$^{2+}$, Fe$^{3+}$ and Cu$^{2+}$ ions at room temperature and discussed the results in terms of the glassy regions of the phase diagram.

In this chapter, the author presents the results of EPR and optical absorption studies on calcium alumino borate (CaAB) glasses doped with different mol % of Cu$^{2+}$ ions at various temperatures. By correlating the EPR and the optical absorption data, the nature of the bonding between Cu$^{2+}$ ion and ligands in the glasses is estimated.
2. Experimental

The starting materials, CaCO$_3$, Al$_2$O$_3$, H$_3$BO$_3$, MgCO$_3$, SrCO$_3$ and CuO, used in the preparation of the glasses were of analar grade. The batch compositions of the glasses, studied in the present work, are listed in Table 1. The chemicals were weighed accurately, mixed thoroughly and ground to fine powder. The batches were melted, in air, in an electrical furnace at 1473 K for half an hour. The melt was then quenched by pouring onto a polished brass plate and pressing it with another brass plate. The glasses thus obtained were pale green in colour with high transparency.

A powdered glass sample of 100 mg was taken in a quartz tube for the EPR measurements. The EPR spectra of all the glass samples were recorded on a JEOL FE1X ESR spectrometer, operating in the X-band frequencies, with a field modulation of 100 kHz. The microwave frequency was kept at 9.205 GHz. The magnetic field was scanned from 220 mT to 420 mT at a scan rate of 25 mT-min$^{-1}$. The EPR spectrum of CuSO$_4$.5H$_2$O powdered substance was also recorded as a reference to calculate number of spins.

The EPR spectra of 0.1 mol % of CuO doped CaAB glass were recorded at different temperatures (123 – 423 K) using JES-VT-3A2 variable temperature controller.

The optical absorption spectra of all the glasses were recorded at room temperature on a JASCO V-570 UV-VIS-NIR spectrophotometer in the wavelength range 200 nm to 900 nm. The glass samples of thickness 1.5 mm were used for optical measurements.
<table>
<thead>
<tr>
<th>S.No</th>
<th>Glass system</th>
<th>Glass code</th>
<th>CaCO$_3$</th>
<th>Al$_2$O$_3$</th>
<th>H$_3$BO$_3$</th>
<th>MgCO$_3$</th>
<th>SrCO$_3$</th>
<th>CuO</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>Calcium alumino borate</td>
<td>CaAB</td>
<td>25</td>
<td>15</td>
<td>60</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>Calcium alumino borate: 0.05CuO</td>
<td>CaAB 0.05</td>
<td>24.95</td>
<td>15</td>
<td>60</td>
<td>–</td>
<td>–</td>
<td>0.05</td>
</tr>
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<td>CaAB 0.1</td>
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<td>15</td>
<td>60</td>
<td>–</td>
<td>–</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>Calcium alumino borate: 0.25 CuO</td>
<td>CaAB 0.25</td>
<td>24.75</td>
<td>15</td>
<td>60</td>
<td>–</td>
<td>–</td>
<td>0.25</td>
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<td>CaAB 0.5</td>
<td>24.5</td>
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<td>–</td>
<td>–</td>
<td>0.5</td>
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<td>6</td>
<td>Calcium alumino borate: 0.75 CuO</td>
<td>CaAB 0.75</td>
<td>24.25</td>
<td>15</td>
<td>60</td>
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<td>0.75</td>
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<td>CaAB 1</td>
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<td>60</td>
<td>–</td>
<td>–</td>
<td>1</td>
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<td>8</td>
<td>Calcium alumino borate: 1.25 CuO</td>
<td>CaAB 1.25</td>
<td>23.75</td>
<td>15</td>
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<td>–</td>
<td>1.25</td>
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<td>9</td>
<td>Calcium alumino borate: 1.5 CuO</td>
<td>CaAB 1.5</td>
<td>23.5</td>
<td>15</td>
<td>60</td>
<td>–</td>
<td>–</td>
<td>1.5</td>
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<td>Magnesium alumino borate: 0.1 CuO</td>
<td>MgAB 0.1</td>
<td>–</td>
<td>15</td>
<td>60</td>
<td>24.9</td>
<td>–</td>
<td>0.1</td>
</tr>
<tr>
<td>11</td>
<td>Strontium alumino borate: 0.1 CuO</td>
<td>SrAB 0.1</td>
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<td>15</td>
<td>60</td>
<td>–</td>
<td>24.9</td>
<td>0.1</td>
</tr>
</tbody>
</table>
3. Theory

3.1 EPR studies

Copper (Z = 29) has an electronic configuration [Ar] 3d^{10}4s^{1} where [Ar] is the electronic configuration of Argon atom. In its +2 oxidation state, copper ion will have an electronic configuration [Ar] 3d^{9}. Thus Cu^{2+} ion possesses an effective spin 1/2 associated with magnetic spin angular momentum, \( M_s = \pm 1/2 \), leading to a doubly degenerate spin energy state in the absence of magnetic field. In the presence of magnetic field, the degeneracy is removed and the transitions occur between two energy levels, given by the resonance condition, \( \nu = g \beta H \). As the nuclear spin (I) of the Cu^{2+} ion is 3/2, the interaction between the nuclear magnetic moment and the electronic magnetic moment (both spin and orbital) result in the hyperfine structure in the EPR spectrum. Thus each fine structure line splits into \((2I+1)\) components, as illustrated in Fig. 7 of Chapter I, for the case of \( S = 1/2 \) and \( I = 3/2 \). The allowed transitions, corresponding to the selection rules \( \Delta M_s = \pm 1 \) and \( \Delta M_I = 0 \), result in four lines which are equally spaced.

EPR spectrum of transition metal ions depends on the ion, the symmetry and the strength of the crystal field, the spin-orbit coupling and the effects such as the hyperfine interaction between electrons and nucleus. All these interactions can be analysed by using a general spin-Hamiltonian of the form [11]

\[
\mathcal{H} = \beta \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}
\]  

(1)

The first term on the right hand side of the equation (1) corresponds to the Zeeman term and the second term indicates the hyperfine interaction. ‘\( g \)’ is the Lande’s g-factor and ‘\( A \)’ is the hyperfine splitting constant. \( \mathbf{g} \) and \( \mathbf{A} \) are tensor quantities.
3.2 Optical absorption studies

In octahedral symmetry, the ground state electron configuration of \(t_{2g}^6e_g^3\) gives rise to \(^2E_g\) as the ground state. When one of the electrons of \(t_{2g}\) orbital is promoted to \(e_g\) orbital, the excited electronic configuration, \(t_{2g}^5e_g^4\) gives rise to \(^2T_{2g}\) as the upper state. Thus only one absorption band corresponding to the transition \(^2E_g \rightarrow ^2T_{2g}\) is expected for \(Cu^{2+}\) ions in an octahedral symmetry. Since the ground state, \(^2E_g\) splits under the effect of Jahn-Teller distortion, it is difficult to have a regular octahedrally coordinated \(Cu^{2+}\) ion complexes [12]. Since the \(^2E_g\) state can split only in tetragonal field but not in the trigonal field, the \(Cu^{2+}\) ion doped glasses, normally, exhibit tetragonal or lower symmetries.

In a tetragonal field, the ground state \(^2E_g\) will split into \(^2B_{1g}\) and \(^2A_{1g}\) while the upper state \(^2T_{2g}\) will split into \(^2B_{2g}\) and \(^2T_{1g}\) levels. The splitting of the energy levels in octahedral (\(O_h\)) and tetragonal (\(D_{4h}\)) symmetries is shown in Fig. 1.

4. Results and analysis

4.1 EPR studies

No EPR signal was observed in the undoped glasses, confirming that the starting materials were free from the paramagnetic impurities. The EPR spectra of CaAB glasses, doped with different concentrations (mol %) of \(Cu^{2+}\) ions, are shown in Fig. 2. The \(Cu^{2+}\) ion, with \(S = 1/2\), has a nuclear spin \(I = 3/2\) for both \(^{63}Cu\) (natural abundance 69%) and \(^{65}Cu\) (natural abundance 31%). Hence, \((2I+1)\) i.e., four parallel and four perpendicular hyperfine (hf) components would be expected. In the present work, three weak parallel components are observed in the lower field region and the fourth parallel component is overlapped with the perpendicular component. The perpendicular components, in the high field.
Fig. 1 Schematic energy level diagram of Cu$^{2+}$ ion in octahedral, tetragonal and rhombic fields.
Fig. 2 The EPR spectra of CaAB glasses doped with different Cu²⁺ ion concentrations.
region, are well resolved and are more intense. The EPR spectra of all the glasses doped with Cu$^{2+}$ ions exhibit resonance signals similar to those reported for Cu$^{2+}$ ions in other glass systems [13-19].

The number of spins participating in the resonance can be calculated with the help of the reference sample [CuSO$_4$·5H$_2$O] using the formula given by Weil et al. [20]

\[
N = \frac{A_s (\text{scan}_s)^2 G_{\text{std}} (B_m)_{\text{std}} (g_{\text{std}})^2 [S (S+1)]_{\text{std}} (P_{\text{std}})^{1/2}}{A_{\text{std}} (\text{scan}_{\text{std}})^2 G_s (B_m)_s (g_s)^2 [S (S+1)]_s (P_s)^{1/2}}
\]

where the symbols have their usual meaning (see Chapter III).

The number of spins participating in the resonance was calculated for different concentrations of Cu$^{2+}$ ions and listed in Table 2.

**Table 2**: Number of spins, susceptibility, optical band gap and Urbach energy of the glasses studied in the present work.

<table>
<thead>
<tr>
<th>Glass code</th>
<th>Number of spins (N) ($10^{22}$ kg$^{-1}$)</th>
<th>Susceptibility ($\chi$, $10^3$ m$^3$ / kg)</th>
<th>Optical band gap ($E_{\text{opt}}$, eV)</th>
<th>Urbach energy ($\Delta E$, eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaAB 0.05</td>
<td>-</td>
<td>-</td>
<td>3.142</td>
<td>0.212</td>
</tr>
<tr>
<td>CaAB 0.1</td>
<td>1.02</td>
<td>2.63</td>
<td>3.111</td>
<td>0.247</td>
</tr>
<tr>
<td>CaAB 0.25</td>
<td>2.94</td>
<td>8.23</td>
<td>3.096</td>
<td>0.287</td>
</tr>
<tr>
<td>CaAB 0.5</td>
<td>4.45</td>
<td>12.44</td>
<td>3.060</td>
<td>0.287</td>
</tr>
<tr>
<td>CaAB 0.75</td>
<td>5.58</td>
<td>15.62</td>
<td>2.985</td>
<td>0.290</td>
</tr>
<tr>
<td>CaAB 1</td>
<td>9.98</td>
<td>27.96</td>
<td>2.948</td>
<td>0.307</td>
</tr>
<tr>
<td>CaAB 1.25</td>
<td>10.60</td>
<td>29.73</td>
<td>2.885</td>
<td>0.311</td>
</tr>
<tr>
<td>CaAB 1.5</td>
<td>11.76</td>
<td>32.97</td>
<td>2.845</td>
<td>0.324</td>
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</table>
Fig. 3 shows a plot of the number of spins participating in the resonance as a function of the concentration of Cu$^{2+}$ ions in the CaAB glasses.

Fig. 4 shows the EPR spectra of CaAB glass, doped with 0.1 mol % of Cu$^{2+}$ ions, recorded at different temperatures. The number of spins (N) participating in the resonance was calculated at different temperatures (T). Fig. 5 shows a plot of Log N as a function of 1/T.

4.2 Calculation of paramagnetic susceptibility from EPR data

The paramagnetic susceptibility ($\chi$) was calculated at room temperature, for CaAB glass doped with different concentrations of Cu$^{2+}$ ions, using the formula

$$\chi = N g^2 \beta^2 J (J + 1) / 3 k_B T$$

here, 'N' is the number of spins per kg; 'J' is the total angular momentum; '\beta' is the Bohr magneton; 'k_B' is the Boltzmann constant; 'T' is the absolute temperature and 'g' is the g factor. N and g [= (g_\parallel + 2g_\perp) / 3] are taken from the EPR data. The values of paramagnetic susceptibility for various glasses are listed in Table 2. The paramagnetic susceptibility was also calculated at different temperatures for CaAB glass doped with 0.1 mol % of Cu$^{2+}$ ions. A plot of reciprocal of susceptibility (1/$\chi$) as a function of absolute temperature of the glass is shown in Fig. 6.

4.3 Optical absorption studies

The optical absorption spectra of all the CaAB glasses doped with different concentrations of Cu$^{2+}$ ions are recorded at room temperature. All the spectra show a single broad band centered at 12750 cm$^{-1}$ (784 nm). This band is
Fig. 3 A plot of number of spins as a function of Cu$^{2+}$ ion concentration in the CaAB glasses.
Fig. 4(a) The EPR spectra of CaAB glass doped with 0.1 mol % of Cu$^{2+}$ ions recorded at different temperatures (123 to 273 K).
Fig. 4(b) The EPR spectra of CaAB glass doped with 0.1 mol % of Cu$^{2+}$ ions recorded at different temperatures (296 to 423 K).
Fig. 5 A plot of Log N as a function of 1/T of CaAB glass doped with 0.1 mol % Cu$^{2+}$ ions.
Fig. 6 A plot of reciprocal of susceptibility ($1/\chi$) as a function of absolute temperature for CaAB glass doped with 0.1 mol % of Cu$^{2+}$ ions.
attributed to the $^{2}B_{1g} \rightarrow ^{2}B_{2g}$ transition of Cu$^{2+}$ ions in the distorted octahedral sites. The observed band positions of this transition are similar to those reported in the literature [21-24].

Fig. 7 shows the optical absorption spectra of XAB glasses (X = Mg, Ca, Sr) doped with 0.1 mol % of Cu$^{2+}$ ions. The observed bands were centered at 13440 cm$^{-1}$ (744 nm), 12750 cm$^{-1}$ (784 nm) and 12885 cm$^{-1}$ (776 nm) corresponding to MgAB, CaAB and SrAB glasses respectively. The oscillator strengths ($f$) of the band maxima of these glasses have been calculated by assuming Gaussian distribution using the formula [25]

$$f = 4.32 \times 10^{-9} \times \epsilon \Delta \nu$$

where $\Delta \nu$ is the full width at half maximum (FWHM) of the absorption band in cm$^{-1}$ and $\epsilon = A/bc$, where $A$ is the absorbance at band maxima, $b$ is the thickness of the glass and $c$ is the concentration Cu$^{2+}$ in the glass. It is observed that the oscillator strength increases with the increase of ionic radius of the alkaline earth ion (Mg < Ca < Sr) in the glasses. The band maxima and their oscillator strengths of these glasses are listed in Table 3.

4.4 Optical band gap ($E_{opt}$) and Urbach energy ($\Delta E$)

For amorphous substances, particularly at lower values of absorption coefficient, the absorption coefficient, $\alpha(\nu)$ increases exponentially with photon energy ($h\nu$) in accordance with the empirical relation [26]

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

here, $\alpha_0$ is a constant, $\Delta E$ is the Urbach energy which indicates the width of the band tails of the localized states. The broadening of the exciton levels at the
Fig. 7 Optical absorption spectra of the XAB glass (X= Mg, Ca, Sr) doped with 0.1 mol % of Cu$^{2+}$ ions, recorded at room temperature.
**Table 3:** The spin-Hamiltonian parameters, Optical band maximum, Oscillator strength, molecular orbital coefficient, and theoretical optical basicity of XAB 0.1 glasses studied in the present work.

<table>
<thead>
<tr>
<th>Glass System</th>
<th>$g_\parallel$</th>
<th>$g_\perp$</th>
<th>$A_\parallel$ $\times 10^4$ cm$^{-1}$</th>
<th>$A_\perp$ $\times 10^4$ cm$^{-1}$</th>
<th>Transition</th>
<th>Oscillator strength $\times 10^4$</th>
<th>$\alpha^2$</th>
<th>Theoretical optical basicity($\Lambda_{ab}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAB 0.1</td>
<td>2.318</td>
<td>2.045</td>
<td>114</td>
<td>22</td>
<td>$^{2}B_{1g} \rightarrow ^{2}B_{2g}$ cm$^{-1}$</td>
<td>13440</td>
<td>4.64</td>
<td>0.65</td>
</tr>
<tr>
<td>CaAB 0.1</td>
<td>2.296</td>
<td>2.045</td>
<td>131</td>
<td>23</td>
<td>$^{2}B_{1g} \rightarrow ^{2}B_{2g}$ cm$^{-1}$</td>
<td>12750</td>
<td>6.04</td>
<td>0.71</td>
</tr>
<tr>
<td>SrAB 0.1</td>
<td>2.307</td>
<td>2.047</td>
<td>129</td>
<td>23</td>
<td>$^{2}B_{1g} \rightarrow ^{2}B_{2g}$ cm$^{-1}$</td>
<td>12885</td>
<td>6.30</td>
<td>0.68</td>
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</table>

(The errors in $g$ and $A$ values are $\pm 0.001$ and $\pm 2 \times 10^{-4}$ cm$^{-1}$ respectively)
absorption edge is dominated by the random electric fields due to either the lack of long range order or the presence of defects [27,28].

For an absorption by indirect transition, the equation takes the form

\[ E_{\text{opt}} = h\nu - (\alpha h\nu/B)^{1/2} \]  

here, 'B' is a constant and 'E_{opt}' is the optical band gap. This relation can be applied to many oxide glasses [26].

Fig. 8(a) shows a plot between \((\alpha h\nu)^{1/2}\) and \(h\nu\) corresponding to ultraviolet absorption edges of CaAB glasses doped with different concentrations of Cu\(^{2+}\) ions (0.05, 0.5, 1.0, 1.5 mol %). From this plot, the optical band gap \((E_{\text{opt}})\) can be obtained by extrapolating the linear region of the curve to the \(h\nu\) - axis. Fig. 8(b) shows a plot of \(\ln \alpha(\nu)\) and \(h\nu\) of the glasses. The reciprocal of the slope of the linear region of the curve gives the Urbach energy of the corresponding glass. The values of optical band gap and Urbach energy of the glasses are listed in Table 2.

Similarly, Fig. 9(a) shows a plot between \((\alpha h\nu)^{1/2}\) and \(h\nu\) corresponding to ultraviolet absorption edges for XAB glasses (X = Mg, Ca, Sr) doped with 0.1 mol % of Cu\(^{2+}\) ions. Fig 9(b) shows a plot between \(\ln \alpha(\nu)\) and \(h\nu\) for XAB glasses (X = Mg, Ca, Sr) doped with 0.1 mol % of Cu\(^{2+}\) ions.

4.5 Optical basicity \((\Lambda_{ak})\)

The optical basicity of an oxide glass measures the ability of the glass to donate negative charge to the probe ion [29]. It can be predicted from the composition of the glass and the basicity moderating parameters of various cations present [30].
Fig. 8(a) A plot of $(\alpha h \nu)^{1/2}$ as a function of $h \nu$ and (b) A plot of $\ln \alpha(\nu)$ as a function of $h \nu$ for CaAB glasses.
Fig. 9(a) A plot between $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ and
(b) A plot between $\ln \alpha(\nu)$ as a function of $h\nu$ for XAB glasses ($X = $ Mg, Ca, Sr) doped with 0.1 mol % of Cu$^{2+}$ ions.
The theoretical optical basicity ($\Lambda_{th}$) of a glass can be calculated using the formula

$$\Lambda_{th} = \sum_{i=1}^{n} \frac{Z_i r_i}{|Z_0| \gamma_i}$$

where the symbols have their usual meaning (see Chapter III). The basicity moderating parameter $\gamma_i$ can be calculated using the formula [30]

$$\gamma_i = 1.36 (x_i - 0.26)$$

here, $x_i$ is the Pauling electronegativity of the $i^{th}$ cation. The values of the theoretical optical basicity ($\Lambda_{th}$) of all the glasses were calculated and it is observed that the optical basicity of the glasses decreases with the increase of the Cu$^{2+}$ ion concentration, but it increases with the increase of ionic radius of alkaline earth metal in the glass. The values of the theoretical optical basicity ($\Lambda_{th}$) of XAB0.1 ($X = \text{Mg, Ca, Sr}$) glasses are presented in Table 3.

5. Discussion

5.1 EPR studies

It is well known that Cu$^{2+}$ ion in glasses and aqueous complexes may not exist in a regular octahedral coordination. The cubic symmetry of Cu$^{2+}$ ion is disturbed due to the presence of the electronic hole in the degenerate $dx^2-y^2$ orbital exhibiting tetragonal distortion. Hence, Cu$^{2+}$ ions in glasses will be predominantly in axially elongated octahedral sites.
The EPR spectra of Cu$^{2+}$ ions can be analysed by using an axial spin-Hamiltonian of the form [11]:

$$\mathcal{H} = \beta \left( g_\parallel B_2 S_z + g_\perp \left( B_x S_x + B_y S_y \right) \right) + A_\parallel S_z I_z + A_\perp (S_x I_x + S_y I_y)$$ ------(9)

in this equation, the symbols have their usual meaning. The nuclear quadrupole and the nuclear Zeeman interaction terms are ignored.

The solution of the spin-Hamiltonian gives the expressions for the peak positions related to the principal 'g' and 'A' tensors [31]. The spin-Hamiltonian parameters of all the glasses have been evaluated. It is observed that there is no significant change in these parameters with the change in Cu$^{2+}$ ion concentration. However, the values of $g_\parallel$ and $g_\perp$ suggest that the Cu$^{2+}$ ions in the glasses are coordinated by six ligands that form an octahedron elongated along the z-axis [18,19,32,33]. Moreover, it is observed that, in the glasses, $g_\parallel > g_\perp > g_e$ (free electron g value, $g_e = 2.0023$). This suggests that the ground state of Cu$^{2+}$ ions is $d_{x^2-y^2}$ orbital ($^2B_1g$ state). The spin-Hamiltonian parameters of $XAB$ 0.1 ($X = \text{Mg, Ca, Sr}$) glasses are also listed in Table 3.

From Fig.3, it is clear that the number of spins increases monotonically with the increase of Cu$^{2+}$ ion concentration in the glasses. At higher Cu$^{2+}$ ion concentration, the hf structure of perpendicular components diminished as a result of the individual line broadening which is due to the increased dipolar interactions with the ligand field fluctuations around the paramagnetic ion [18,19].

Fig. 5 shows a plot of Log N as a function of $1/T$, which suggests a linear relationship between Log N and $1/T$, a phenomenon that can be expected from
the Boltzmann law. From this plot, the activation energy (0.02 eV) has been calculated.

Fig. 6 shows a plot of $1/\chi$ as function of $T$, which is a straight line in accordance with the Curie’s law. From the plot, the Curie temperature (101 K) has been evaluated. This value was found to be in good agreement with the value reported for Cu$^{2+}$ ion in the literature [34].

5.2 Optical absorption studies

The observed optical absorption band positions of XAB 0.1 (X= Mg, Ca, Sr) glasses, in the present study, are listed in Table 3. The observed broad band has been assigned to the $^2B_{1g} \rightarrow ^2B_{2g}$ transition of Cu$^{2+}$ ions present in axially elongated octahedral sites. The intensity of absorption increases with the increase of ionic radius of the alkaline earth ion in the glass. The values of the calculated oscillator strengths of the absorption bands of the glasses are found to be in good agreement with those reported for Cu$^{2+}$ ions in the literature [25, 35, 36].

It is known that the Coulombic force between alkaline earth ion and O$^{2-}$ ion decreases with the increase of the ionic radius of the alkaline earth ion. Thus the strength of the bond between the alkaline earth ion and the O$^{2-}$ ion decreases which increases the basicity of the glass. But when the basicity of a glass increases, the formation of the oxidised states of the metal ion is favoured more. Therefore the proportion of Cu$^{2+}$ ions in the glass increases with the increase of the ionic radius of the alkaline earth ion and hence the intensity of the absorption increases.
The in-plane $\sigma$ bonding coefficient, $\alpha^2$ can be calculated from the EPR data using the formula given by Kuska et al. [37].

$$\alpha^2 = \frac{7}{4} \left[ \frac{A_{||}}{P} - \frac{A}{P} + \frac{2}{3} g_0 - \frac{5}{21} g_\perp - \frac{6}{7} \right]$$

here, $P = 0.036 \text{ cm}^{-1}$ and $A = (A_{||} + 2A_\perp)/3$.

If $\alpha^2 = 1$, the in-plane $\sigma$ bonding would be completely ionic. If the overlapping integral were vanishingly small and $\alpha^2 = 0.5$, the bonding could be completely covalent. However, because the overlapping integral is sizeable ($S_{\text{oxygen}} = 0.076$), we cannot speak strictly of covalent versus ionic bonds but we can say that smaller the value of $\alpha^2$, greater the covalent nature of the bond.

The calculated values of $\alpha^2$ for XAB 0.1 (X= Mg, Ca, Sr) glasses are listed in Table 3. These values suggest that the in-plane $\sigma$ bonding in the glasses is moderately covalent in nature.

5.3 Optical energy gap and Urbach energy

The values of the optical energy gap and the Urbach energy of the glasses, in the present work, are of the same order as those reported in the literature for borate glasses [38]. The optical band gap was found to decrease with the increase of Cu$^{2+}$ ion concentration. This is because the addition of Cu$^{2+}$ ions introduces additional defect states e.g. colour centers in the glass matrix [39]. The density of the localised states was found to be proportional to the concentration of these defects [40]. Hence with the increase of CuO content in the glass, the localized states of the colour centers may overlap and extend into the mobility gap resulting in the decrease of the optical band gap. The optical
band gap of the CaAB glass doped with 0.1 mol % of Cu$^{2+}$ ions (3.11 eV) is found to be far greater than the activation energy (0.02 eV) calculated from the EPR data. Hassan and Hogarth [26] observed similar results from the DC conductivity measurements at different temperatures. This suggests that the activation is not across the whole gap, but it may be possibly from one or more trapping levels to the conduction band or from bonding states to a trapping level.

The Urbach energy is found to increase with the increase of Cu$^{2+}$ ion concentration in the CaAB glasses. An increase in the Urbach energy could be considered as due to increased number of defects in the glass [41]. Thus the values of the Urbach energy of CaAB glasses suggest that the number of defects increase with the increase of Cu$^{2+}$ ion concentration.

6. Conclusions

(a) From the EPR and optical absorption data, it is found that the Cu$^{2+}$ ions in the calcium alumino borate glasses, occupy tetragonally distorted octahedral sites elongated along z-axis with d$_{x^2-y^2}$ as the ground state.

(b) The paramagnetic susceptibilities of calcium alumino borate glass, doped with 0.1 mol % of Cu$^{2+}$ ions, are calculated at different temperatures. The plot of $1/\chi$ and $T$ is found to be in accordance with the Curie's law. From the plot, Curie temperature (101 K) was evaluated.

(c) The optical absorption spectra of the glasses show a single broad band due to $^2B_{1g} \rightarrow ^2B_{2g}$ transition of Cu$^{2+}$ ions in axially elongated octahedral sites. The increase in the intensity of absorption of XAB 0.1 (X= Mg, Ca, Sr) glasses, with the increase of the ionic radius of the alkaline earth ion is explained based on Coulombic forces.
(d) By correlating EPR and optical data, the molecular orbital bonding coefficient is evaluated. This value suggests that the in-plane \( \sigma \) bonding in the glasses is moderately covalent in nature.

(e) The optical energy gap and the Urbach energies of the glasses are found to depend on \( \text{Cu}^{2+} \) ion concentration. This is attributed to the increase in defects with the increase of \( \text{Cu}^{2+} \) ion concentration in the glasses.
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