Abstract

A series of stable and transparent glasses with the composition 59B_2O_3–10Na_2O–(30 – x)CdO–xZnO–1CuO (0 ≤ x ≤ 30) were prepared by conventional melt-quenching technique. These glasses were characterized using X-ray diffraction (XRD), Fourier-transform infrared (FTIR) and Raman spectroscopes, differential scanning calorimetry (DSC), optical absorption, and electron paramagnetic resonance (EPR). XRD and DSC analysis confirmed the glassy nature of the prepared samples. The physical properties such as density (\(\rho\)), molar volume (\(V_m\)), oxygen packing density (OPD), and the molar volume of oxygen (\(V_o\)) were calculated and discussed. FTIR and Raman studies showed that the glass network consists of BO_3 and BO_4 units in various borate groups. From DSC, it was found that the glass transition temperature (\(T_g\)) varies nonlinearly with the addition of ZnO content in place of CdO. Both EPR and optical absorption results have confirmed that the Cu^{2+} ions are in octahedral coordination with a strong tetrahedral distortion. The changes in various spectroscopic properties of Cu^{2+} ions in the glasses such as spin-Hamiltonian parameters (\(g_{zz}, g_{zz},\) and \(A_0\)) and bonding coefficients (\(\alpha^2, \beta_1^2,\) and \(\beta^2\)) were understood with the help of FTIR and Raman studies.

Keywords: glasses, DSC, Raman, FTIR, EPR

1. Introduction

Alkali borate systems are attractive materials from a fundamental point of view as well as technological point of view [1]. From the literature, it has been observed that certain borate glasses are of greater interest and relevance because of their suitability in the progress of waveguides, electro-optic switches and modulators, magneto-optic materials, and solid-state...
laser materials [2]. B$_2$O$_3$–ZnO glass has a high transparent window in the region from 370 nm to 2.2 μm, and these glasses are attractive host materials to incorporate rare earth elements for optoelectronics and optical fibers [3, 4]. The properties of B$_2$O$_3$ glass can often be altered by the addition of network modifiers. The most commonly used network modifiers are the alkali (Li$_2$O, Na$_2$O, and K$_2$O) and alkaline earth oxides (MgO, CaO, SrO, and BaO) [5, 6]. When mixed with these glass modifiers, its internal structure is rearranged due to the formation of non-bridging oxygen [7]. In particular, the addition of alkali oxide to pure B$_2$O$_3$ causes a progressive change of the boron atom coordination number (CN), from 3 (BO$_3$) to 4 (BO$_4$), and results in the formation of various borate units (diborate, triborate, tetraborate groups, etc.) [1].

From the literature, it was found that with the presence of ZnO or CdO in B$_2$O$_3$ glass matrix, UV transmission ability could be enhanced [8]. Therefore the authors have selected Na$_2$O, CdO, and ZnO as network modifiers. The addition of Cd and Zn oxides also results in the large glass formation domain [9]. When zinc oxide is introduced to borate glasses, there are two ways in which zinc ion can get incorporated into the glass. Zinc oxide may act as a network modifier by disrupting the bonds connecting neighboring [BO$_3$] and [BO$_4$] groups. On the other hand, zinc oxide can be incorporated into the glass as [ZnO$_4$] structural units. Besides Cu$^{2+}$ ions have been chosen in the present study as an EPR probe due to its EPR spectrum being sensitive enough to detect minute changes in the structure of the glasses [10]. Therefore in this article, authors have been presented the structural changes of Cu$^{2+}$ ions-doped B$_2$O$_3$–Na$_2$O–CdO–ZnO glass induced by addition of ZnO into B$_2$O$_3$ glass matrix at 10 mol% Na$_2$O content. The various literature surveys show no evidences on structural study using FTIR, Raman spectroscopy, EPR, and optical absorption. Therefore the authors have planned to investigate the structural, optical, and physical changes in the Cu$^{2+}$ ions-doped B$_2$O$_3$–Na$_2$O–CdO–ZnO glass system. The authors have also studied the spin-Hamiltonian parameters and site symmetry around Cu$^{2+}$ ions in these glasses using EPR and optical absorption studies. The variations in the thermal properties and other physical properties in terms of structural changes of glasses have been discussed [6].

2. Experimental

2.1. Glass preparation

Glasses with compositional formula 59B$_2$O$_3$–10Na$_2$O–(30 − x)CdO–xZnO–1CuO (where x = 0, 7.5, 15, 22.5, and 30 mol%) were prepared using melt-quenching technique, and a series of glasses along with their codes are given in Table 1. All the chemicals used were of 99% purity from well-known companies (sd-fine, Merck, and Loba Chemie).

Appropriate amounts of H$_3$BO$_3$, Na$_2$CO$_3$, ZnO, and CdO were ground with a mortar and pestle and thoroughly mixed. About 1 mol% CuO was added as a spin probe and was melted in a platinum crucible at 1000°C for 30 min in an Autoset electric furnace; a similar technique was employed by Devde et al. [6].
During the melting the crucible with homogeneous mixture was covered with a lid to avoid the volatility of the powder compounds or contamination from the furnace. Melts were stirred frequently to promote homogeneity, and the liquids were rapidly poured into a mold made with a stainless steel which was maintained at 200°C and pressed with another stainless steel plate maintained at the same temperature. The prepared glass samples were then transferred to another furnace and annealed at 300°C for 6 h to relieve thermal stress and strains of the glass samples. The prepared samples were examined, and it was found that the samples are clear, bubble free, and transparent.

2.2. Physical properties

Archimedes’ method using xylene as immersion liquid was employed for the measurement of densities of the prepared glasses at room temperature. An average of three samples of each glass code was used. Obtained density values were used to calculate the molar volume using relation $V_m = M/\rho$, where $M$ and $\rho$ are the average molecular weight and density of the glasses, respectively. Oxygen packing density (OPD) was calculated using the relation $OPD = \Sigma x_i n_i / V_{mo}$, where $x_i$ is the molar fraction of an oxide $R_nO_m$ and $n_i$ is the number of oxygen atoms of this oxide [6]. The molar volume of oxygen ($V_{o}$) is the volume of glass in which 1 mole of oxygen is contained. These values were calculated using the relation $V_o = (V_m)(1/\Sigma x_i n_i)$.

Various spectroscopic techniques were employed for structure investigation of present glass system.

2.3. XRD

X-ray diffraction patterns of the glass samples were recorded from Philips diffractometer (PANalytical X-pert PRO model) with Cu K$_\alpha$ (1.54 Å) source at room temperature.

2.4. FTIR studies

The infrared transmission spectra of all glasses were recorded at room temperature in the wave number range 400–1800 cm$^{-1}$ by a Shimadzu FTIR-8001 Fourier-transform computerized infrared spectrometer. The IR transmission measurements were made using the KBr pellet technique.
2.5. Raman studies

Raman spectra of all prepared glasses were recorded at room temperature in the range 200–1800 cm\(^{-1}\) using a He–Ne excitation source (632.81 nm) coupled with Jobin Yvon Horiba (LABRAM HR-800) micro Raman spectrometer equipped with a 50× objective lens to focus the laser beam. The incident laser power was focused in a diameter of ~1–2 μm, and a notch filter was used to suppress Rayleigh light. Samples used for the measurement were of 1 mm thickness and 1 cm in diameter. Raman shifts are measured with a precision of ~0.3 cm\(^{-1}\), and the spectral resolution is of the order 1 cm\(^{-1}\); a similar characterization was studied by Upender et al. [11].

2.6. DSC studies

Differential scanning calorimetry of the prepared glass powders was carried out at temperatures up to 850°C at the rate of 10°C/min using a SETARAM instrument (Model LABSYS EVO DSC; SETARAM Instrumentation, Caluire, France) to determine the thermal properties of the glasses [6].

2.7. EPR studies

JEOL-JES FE 3X EPR spectrometer was employed for recording EPR spectra of the glass samples in the X-band at room temperature with 100 kHz field modulation. Polycrystalline diphenyl picryl hydrazyl (DPPH) was used as the standard “g” marker for the determination of magnetic field; a similar technique was employed by G. Upender et al. for invention of structure of WO\(_3\)–GeO\(_2\)–TeO\(_2\) glasses [12].

2.8. UV-Visible absorption studies

UV-Visible absorption spectra of prepared borate-based glasses were recorded by using LABINDIA Analytical UV-3092 spectrophotometer in the wavelength range 350–900 nm at room temperature. The precision of wavelength measurement is about ±1 nm [12].

3. Results and discussion

3.1. Basic glass properties

The physical parameters of the present glasses are presented in Table 2. It is observed that the density (ρ) decreases from 3.334 to 2.815 g/cm\(^3\) with the addition of ZnO content from 0 to 30 mol% at the expense of CdO content. This could be due to the lower molecular weight of ZnO (81.38 g/mol) in comparison with CdO (128.4 g/mol). This could also be due to the lower density of ZnO (ρ = 5.606 g/cm\(^3\)) than that of CdO (ρ = 6.95 g/cm\(^3\)). The molar volume (V\(_m\)) increases from 25.972 to 26.224 cm\(^3\)/mol with ZnO content up to 15 mol% then V\(_m\) starts decreasing from 26.224 to 25.995 and then to 25.749 with further
addition of ZnO up to 30 mol% at the expense of CdO. This could be due to the difference between cation radii of Cd$^{2+}$ ion (1.03 Å) and Zn$^{2+}$ ion (0.83 Å). The nonlinear variation in $V_m$ also suggests the dual role of ZnO content as in the present system ZnO up to 15 mol%, it plays a modifier role, and beyond it plays a glass former role. It is also observed that the oxygen packing density (OPD) decreases from 83.936 to 83.129 mol/l, while oxygen molar volume ($V_o$) increases from 11.914 to 12.029 cm$^3$/mol with ZnO content up to 15 mol%. But OPD increases from 83.129 to 84.663, while $V_o$ decreases from 12.029 to 11.812 with ZnO addition up to 30 mol%. The nonlinear variation in OPD and $V_o$ values with the increase in ZnO content from 0 to 30 mol% could be due to the variation in density ($\rho$) and the dual role of ZnO in the present glass system, while the number of oxygen atoms in the glass network remains the same according to the ratio 1:1.

3.2. XRD

The obtained XRD patterns of BNCZ glass system are shown in Figure 1. It is clear that a broad hump is repeatedly observed in all the samples and is the characteristic of glass, and there is no evidence of crystallization. Hence it is confirmed that the prepared samples possess glassy nature.

3.3. FTIR studies

The IR transmission spectra of all the glasses were recorded in the wave number range 1600–400 cm$^{-1}$ and are shown in Figure 2. The band positions and their assignments are given in Table 3.

In the BNCZ glass system, significant bands are observed at about ~474, 694, 970–1040, 1250–1260, and 1360–1375 cm$^{-1}$. These bands assigned to B$_2$O$_3$ and about 80% of the boron atoms are present in the boroxol rings, B$_2$O$_6$, that are interconnected by independent BO$_3$ groups. The vibrational modes of the vitreous borate network are mainly active in three infrared regions. The IR features located in the first region that ranges between 1200 and 1600 cm$^{-1}$ [13]. The second region ranges between 800 and 1200 cm$^{-1}$, and the third region ranges between 600 and 800 cm$^{-1}$. From Figure 2 it is evidently seen that the structure of the glass network formed

| Parameter | $x = 0$ | $x = 7.5$ | $x = 15$ | $x = 22.5$ | $x = 30$ |
|-----------|---------|-----------|----------|------------|----------|
| *AMW (g/mol) | 86.589 | 83.062 | 79.536 | 76.009 | 72.483 |
| $\rho$ (g/cc) | 3.334 | 3.181 | 3.033 | 2.924 | 2.815 |
| $V_m$ (cm$^3$/mol) | 25.972 | 26.112 | 26.224 | 25.995 | 25.749 |
| OPD (mol/l) | 83.936 | 83.487 | 83.129 | 83.862 | 84.663 |
| $V_o$ (cm$^3$/mol) | 11.914 | 11.978 | 12.029 | 11.924 | 11.812 |

*AMW: average molecular weight.
†Error in $V_m$ is ±0.005.

Table 2. Physical parameters of 59B$_2$O$_3$–10Na$_2$O–(30–$x$)CdO–xZnO–1CuO (0 ≤ $x$ ≤ 30 mol%) glass system.
by boron ions is significantly changed with the incorporation of ZnO at the expense of CdO content. The absence of IR band at ~806 cm\(^{-1}\) indicates that the boroxol rings are not formed in the present glass system, and hence the structure of the glasses consists of borate groups other than the boroxol rings. The weak band observed at ~474 cm\(^{-1}\) in all the glasses is attributed to the vibration of metal cations in their oxygen sites \(\text{RO}_4\) groups where \(R = \text{Cd, Zn}\) [16].
The bands observed around 694 cm\(^{-1}\) could be attributed to the bending vibration of B–O–B linkages of various borate groups [17]. The bands near 979 cm\(^{-1}\) are assigned to B–O asymmetric stretching of BO\(_4\) units of diborate groups [18]. This band shifts to higher wave number side, i.e., from 979 to 1040, while the intensity of this band significantly decreased with the increase of ZnO content up to 30 mol\%.

The bands observed at around 1040 cm\(^{-1}\) are due to B–O stretching vibrations of BO\(_4\) units in tri-, tetra-, and pentaborate groups [12, 19, 20]. The bands that appeared in the range of 1260 cm\(^{-1}\) are assigned to B–O symmetric stretching vibrations of (BO\(_3\))\(_3^-\) units in metaborate and orthoborates [21]. The intensity of this band is unaffected with the addition of ZnO content up to 30 mol\%. The bands at around 1363–1375 cm\(^{-1}\) could be attributed due to symmetric stretching vibrations of B–O bonds of trigonal (BO\(_3\))\(_3^-\) units in metaborate, pyroborate, and orthoborates [21]. The broadness of these bands was found to be more with the substitution of ZnO content up to 30 mol\%. The B\(_2\)O\(_3\) is built up of BO\(_3\) triangles, and upon adding ZnO, the coordination number of the boron changes from SP\(_3\) tetrahedral BO\(_4\) to form SP\(_2\) planar BO\(_3\), preserving the B–O bonding without the creation of non-bridging oxygen ions. It means that the introduction of ZnO causes a significant formation of the BO\(_3\) groups with a lower coordination number. Therefore, the progressive increase in ZnO content makes the IR bands observed at about 1040 and 1373 cm\(^{-1}\) more pronounced. This means that the BO\(_3\) groups and hence the bridging oxygen contents are increased with increasing of ZnO content on the expenses of CdO content.

### 3.4. Raman studies

Figure 3 shows the Raman spectra of the present glass system in the spectral range 200–1800 cm\(^{-1}\) consisting of sharp, broad peaks and shoulders.

The Raman peak positions are summarized in Table 4.

| Band positions | Assignment |
|----------------|------------|
| 1360–1375      | Symmetric stretching vibrations of B–O bonds of trigonal (BO\(_3\))\(_3^-\) units in Meta, Pyro and ortho borates |
| 1260           | Symmetric stretching vibrations of B–O of (BO\(_3\))\(_3^-\) units in meta and Ortho Borates |
| 1040           | B–O stretching vibrations of BO\(_4\) units in tri-, tetra- and pentaborate groups |
| 970            | B–O asymmetric stretching of BO\(_4\) units of diborate groups |
| 690            | Bending vibrations of B–O–B linkages in borate network |

Table 3. Band positions and assignments of IR bands of 59B\(_2\)O\(_3\)–10Na\(_2\)O–(30 – x)CdO–xZnO–1CuO (0 ≤ x ≤ 30 mol\%) glass system.
rings with both BO$_3$ triangles and BO$_4$ tetrahedra (tri-, tetra-, or pentaborate groups) [29, 30]. The intensity of this peak is significantly increased with the addition of ZnO content up to 30 mol%. This observation suggests more number of BO$_3$ units instead of BO$_4$ units in six-membered rings. No Raman peaks appeared at around ~834 cm$^{-1}$ in any of the glass, and it indicates that there are no pyroborate groups (B$_2$O$_5^{4-}$) present in these glasses. The pentaborate and tetraborate groups were assigned by the peaks observed in the range ~930–950 of Raman spectrum. The broad band around 1420 cm$^{-1}$ was assigned to the B–O$^-$ bonds attached to the large number of borate groups [31, 32]. The decrease in intensity of the peak at ~1420 cm$^{-1}$ is due to increase of ZnO content up to 30 mol%. This shows that significant formation of Zn$^{2+}$-B–O$^-$ bonds by reducing the number of non-bridging oxygen’s (NBO’s) similar finding was recorded by Upentre et al. for the glass system (90–x)TeO$_2$–10GeO$_2$–xWO$_3$ (7.5 ≤ x ≤ 30) doped with Cu$^{2+}$ ions [33]. The observed slight decrease in intensity and shift in the peak ~470 toward lower wave number (447 cm$^{-1}$) indicates the decrease of penta- or diborate groups in the glasses. The intensity of the peak at ~940 cm$^{-1}$ decreases while shifts to lower wave number.

Figure 3. Raman spectra of 59B$_2$O$_3$–10Na$_2$O–(30 − x)CdO–xZnO–1CuO (0 = x = 30 mol%) glass system.

| Sample code | Raman peaks (cm$^{-1}$) |
|-------------|-------------------------|
| BNCZ1       | 470 697 770 948 1420    |
| BNCZ2       | 464 697 770 943 1420    |
| BNCZ3       | 464 697 770 942 1420    |
| BNCZ4       | 457 697 770 935 1420    |
| BNCZ5       | 447 697 770 932 1420    |

Table 4. Raman peak positions of 59B$_2$O$_3$–10Na$_2$O–(30 − x)CdO–xZnO–1CuO (0 ≤ x ≤ 30 mol%) glass system, with error ±1 cm$^{-1}$. 

rings with both BO$_3$ triangles and BO$_4$ tetrahedra (tri-, tetra-, or pentaborate groups) [29, 30].
from 948 to 943, 942, 935, and then 932 with increase in ZnO content. This may indicate the presence of less number of pentaborate groups and bond lengths of B–O bonds of pentaborate groups could be increased. The above results suggest the presence of more BO$_3$ units in the glasses with the addition ZnO as Zn$^{2+}$ establishes the linkages of NBOs with BO$_4$ units.

3.5. Differential scanning calorimetry (DSC)

The DSC thermograms of the present glasses are shown in Figure 4. Glass transition temperature ($T_g$) is always visible, and this result is in agreement with the result of XRD data as both the techniques confirm the glassy nature of the samples.

The values of glass transition temperature ($T_g$) are given in Table 5.

From this table it is observed that $T_g$ decreases from 497 to 488°C with gradual increase in ZnO content up to 15 mol% at the expense of CdO, and thereafter $T_g$ increases from 488 to 492 and then to 496°C with further addition of ZnO up to 30 mol%. This behavior suggests that $T_g$ varies nonlinearly with the addition of ZnO content in place of CdO. It is well known that a higher cation radius of Cd$^{2+}$ (1.03 Å) replaced with a lower cation radius of Zn$^{2+}$ (0.83 Å) decreases the overall cation polarizability (polarizability is proportional to the cation size); as a result, $T_g$ should decrease linearly with ZnO content. On the contrary to this, the bond strength of Zn–O (151 kJ/mol) is more than that of Cd–O (101 kJ/mol) [33]; as a result, $T_g$ should increase linearly. But none of the reasons are suitable in this case. Therefore, the observed nonlinear variation in $T_g$ with ZnO content can be understood in the following way: As it was observed clearly from FTIR and Raman that more numbers of BO$_4$ units are present up to 15 mol% of ZnO, then with further addition of ZnO in place of CdO up to 30 mol%,
most of BO\textsubscript{4} units are converted to BO\textsubscript{3} units. The bond strength of BO\textsubscript{4} units (373 kJ/mol) is smaller than BO\textsubscript{3} units (498 (kJ/mol)) \cite{34}. Hence, T\textsubscript{g} decreases up to 15 mol\% of ZnO and then starts increasing with further addition of ZnO up to 30 mol\%. Besides this the higher field strength of Zn\textsuperscript{2+} ions (0.53 cm\textsuperscript{-2}) than that of Cd\textsuperscript{2+} ions (0.38 cm\textsuperscript{-2}) in the glass network also causes to increase the T\textsubscript{g} \cite{34}. However, the ionicities of both Zn–O (51\%) and Cd–O (51\%) are the same, and its role could be neglected. From Figure 4 it is clearly seen that except in BNCZ1 the onset crystallization temperature (T\textsubscript{o}) is not prominently observed with the incorporation of ZnO content. This indicates that the increase of ZnO in place of CdO has a tendency to prevent crystallization. Thus, the present glasses are more thermally stable against crystallization.

3.6. EPR studies

The electron paramagnetic resonance spectra of Cu\textsuperscript{2+}-doped BNCZ series are shown in Figure 5. It is essential to dope the glass samples with Cu\textsuperscript{2+} ions as this gives resonance signals; a similar work is reported in earlier literature \cite{35–37}. The copper ions with spin 1/2 gives a nuclear spin I = 3/2 for \textsuperscript{63}Cu and \textsuperscript{65}Cu and therefore results in (2I + 1) hyperfine components, i.e., four parallel and four perpendicular components.

The spectra recorded for prepared glass series exhibit three parallel components in the lower field region and one parallel component which is overlapped with the perpendicular component. The EPR spectra of copper ions in all the glass samples have been analyzed using an axial spin-Hamiltonian in which the quadrupole and nuclear Zeeman interaction terms are ignored.

\[
H = g_{||} \beta H_{z} S_{z} + g_{\perp} \beta (H_{x} S_{x} + H_{y} S_{y}) + A_{||} S_{z} I_{z} + A_{\perp} (S_{x} I_{x} + S_{y} I_{y})
\]  \hspace{1cm} (1)

The symbols have their usual meaning.

The solution to the spin-Hamiltonian gives the expressions for the peak positions related to the principal values of g and A tensor as follows \cite{35–37}.

For parallel hyperfine peaks,

\[
hv = g_{||} \beta H_{z} + mA_{||} + (15/4 - m^2) A_{\perp}^2 / 2g_{||} \beta H_{z} \]

\hspace{1cm} (2)

| Sample code | Glass Transigirían temperature T\textsubscript{g} (°C) |
|-------------|---------------------------------|
| BNCZ1       | 497                             |
| BNCZ2       | 494                             |
| BNCZ3       | 488                             |
| BNCZ4       | 492                             |
| BNCZ5       | 496                             |

Table 5. Glass Transigirían temperature T\textsubscript{g} (°C) for compositions of 59B\textsubscript{2}O\textsubscript{3}–10Na\textsubscript{2}O–(30 − x)CdO–xZnO–1CuO (0 ≤ x ≤ 30 mol\%) glass system.
For perpendicular hyperfine peaks, the symbols have the usual meaning. Using Eqs. (2) and (3), the spin-Hamiltonian parameters of all the glasses have been calculated and are tabulated as shown in Table 6 [12].

\[
\hbar = g_{\perp} \beta H_{\perp} + \mathbf{m} A_{\perp} + \left(\frac{15}{4} A_{\perp}^2 + A_{\parallel}^2\right) / 4 g_{\parallel} \beta H_{\perp}
\]

(3)

The symbols have the usual meaning. Using Eqs. (2) and (3), the spin-Hamiltonian parameters of all the glasses have been calculated and are tabulated as shown in Table 6 [12].

From Table 6, the \( g_{\parallel}, g_{\perp} \) and \( A_{\perp} \) values are found to be dependent on the glass composition. It is found that \( g_{\parallel} \geq g_{\perp} \geq g_{e} \) (where \( g_{e} = 2.0023 \) is free electron \( g \)-value). Therefore from the \( g_{\parallel} \) values and shape of the EPR spectra, it can be concluded that the ground state of the \( \text{Cu}^{2+} \) is \( d_{\perp}^{0} \) orbital \( ^2B_{g} \) state, the \( \text{Cu}^{2+} \) ions are located in tetragonally distorted octahedral sites [35–37]. The changes in the spin-Hamiltonian parameters with varying ZnO content in the place of CdO content are attributed to the change in electron cloud density around the \( \text{Cu}^{2+} \) ions in the glass network. The change in electron cloud density can be understood in the following way: From FTIR and Raman structural analysis, it was observed that the structure of the glasses changed with the incorporation of ZnO content from 0 to 30 mol%. The increasing ZnO content from 0 to 30 mol% to \( \text{B}_{2}\text{O}_{3} \) glass network leads to change the coordination number of certain boron atoms from 4 to 3. Thus it is understood that every glass composition of the glass system is composed of both triangular (BO\(_3\)) and tetrahedral (BO\(_4\)) units. Therefore, some of the \( \text{Cu}^{2+} \) ions are surrounded by these groups containing NBOs which may present varied electron cloud density around \( \text{Cu}^{2+} \) site in the form of \( \text{CuO}_6 \) and hence the variations in the spin-Hamiltonian parameters as observed in the present glass system. The variations in EPR parameters not only depend on the above said reasons but also depend on the differences in the field strengths of various cations (\( \text{B}^{3+} \) (1.39 cm\(^{-2}\)), \( \text{Na}^{+} \) (0.18 cm\(^{-2}\)), \( \text{Cd}^{2+} \) (0.38 cm\(^{-2}\), and \( \text{Zn}^{2+} \) (0.53 cm\(^{-2}\)) as well as the cation polarizabilities of \( \text{Na}^{+} \) ions.
(0.181 Å$^3$), Zn$^{2+}$ ions (0.283 Å$^3$), Cd$^{2+}$ ions (1.087 Å$^3$), and B$^{3+}$ ions (0.002 Å$^3$) [6] that cause the fluctuations in the ligand field around Cu$^{2+}$ ions, and this in turn varies the spin-Hamiltonian parameters as observed.

### 3.7. Optical absorption studies

The UV-Visible absorption spectra of prepared glass series were displaced in Figure 6.

The observed absorption band around ~765 nm in BNCZ1 is assigned to the $^3\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$ transition ($\Delta E_{xy}$) of Cu$^{2+}$ ion in octahedral coordination with a strong tetrahedral distortion, and the EPR results were found to be in agreement with this assumption [36]. From Figure 6, it was found that the absorption peak firstly blueshifted, i.e., from 764 to 760 and then to 756 nm with the addition of ZnO up to 15 mol%, and then redshifted, i.e., from 756 to 760 to 763 nm with the further addition of ZnO from 15 to 30 mol%. This result is consistent with the observations made in FTIR, Raman, and DSC. As pointed out by Raman and IR analysis, the major structural changes in the present glass take place with the addition of divalent ZnO. This consequence suggests that ZnO enters the glass system in the form of network modifier. Hence, all the observations are clearly from tetragonal (BO$_4$) to trigonal (BO$_3$) units with the incorporation of ZnO content at the expense of CdO content.

The variation in peak position with ZnO doping in glass system BNCZ (30 mol%) indicates the change in the ligand field around paramagnetic Cu$^{2+}$ ions. This could be due to higher field strength of Zn$^{2+}$ ions (0.53 cm$^{-2}$) than that of Cd$^{2+}$ ions (0.38 cm$^{-2}$) [33]. The change in polarizability of oxygen ions surrounding the Cu$^{2+}$ may also change the peak position [6]. This can be understood as follows. As ZnO content substitutes CdO content from 0 to 30 mol%, from IR and Raman structural analysis, it was observed that ZnO has played the dual role. Thus, during the modifier role of ZnO (up to 15 mol%), weak bonds Zn$^{2+}$–O–B were formed in the place of B–O–B or Cd–O–B, whereas during the former role of ZnO (from 15 to 30 mol%), strong Zn–O–B bonds were formed. Thus the oxygen ions in Zn$^{2+}$–O–B bonds are less tightly bound than in B–O–B or Cd–O–B bonds. Thus the oxygen ions can be treated as NBOs in which electrons are loosely bound to the nucleus, and hence these NBOs are more polarized than the oxygen ions in B–O–B or Cd–O–B. These NBOs are decreased during the conversion of BO$_4$ units into BO$_3$ units when ZnO started playing the former role above 15 mol%. Similar observations

| Glass code | $\mathcal{g}_1$ | $\mathcal{g}_2$ | $A_s(\times10^4 \text{ cm}^{-1})$ |
|------------|----------------|----------------|---------------------------------|
| BNCZ1      | 2.323          | 2.064          | 147                             |
| BNCZ2      | 2.322          | 2.068          | 147                             |
| BNCZ3      | 2.325          | 2.066          | 148                             |
| BNCZ4      | 2.327          | 2.069          | 146                             |
| BNCZ5      | 2.326          | 2.068          | 147                             |

Table 6. Spin-Hamiltonian parameters (SHP) of 59B$_2$O$_3$–10Na$_2$O–(30 − x)CdO–xZnO–1CuO (0 ≤ x ≤ 30 mol%) glass system.
were reported by other authors [37]. With the conversion of four coordination boron atoms [BO$_4$] into three coordination boron atoms [BO$_3$], the excess of oxygen converts some of Zn$^{2+}$ ions into tetrahedra [ZnO$_4$] where the structural modification in the glass network could be reason for the variation of the ligand field strength of Cu$^{2+}$ ions. This may be the reason why the optical absorption maximum has showed the nonlinear variation with ZnO content.

3.7.1. Cu$^{2+}$-ligand bonding nature

The data of EPR and optical absorption can be correlated to understand the environment around Cu$^{2+}$ ions in the present glass network; in connection to this, the bonding parameters were evaluated using EPR and optical data by the following equations [6].

\[
g_{\|} = 2.0023(1-4\lambda \alpha^2 \beta_1^2/\Delta E_{xy}) \quad (4)
\]

\[
g_{\perp} = 2.0023(1-\lambda \alpha^2 \beta^2/\Delta E_{xz,yz}) \quad (5)
\]

where $\Delta E_{xy}$ and $\Delta E_{xz,yz}$ are the energies corresponding to the transitions of $^2\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$ and $^3\text{B}_{1g} \rightarrow ^3\text{E}_{g}$ respectively, and $\lambda$ is the spin-orbit coupling constant ($\approx -828$ cm$^{-1}$) and the bonding coefficients $\alpha^2$, $\beta_1^2$, and $\beta^2$ ($=1.00$) characterize in-plane $\sigma$ bonding $16$ between the d orbital of Cu$^{2+}$ and the p orbital of ligand, in-plane $\pi$ bonding between the d orbital of Cu$^{2+}$ and p orbital of ligand and out-of-plane $\pi$ bonding between the d orbital of Cu$^{2+}$ and p orbital of ligand in the glasses respectively [6]. Besides the values of $\Delta E_{xy}$ and $\Delta E_{xz,yz}$ are also calculated and presented in Table 7. In the present glasses, the bonding parameters $\alpha^2$, $\beta_1^2$, and $\beta^2$ were evaluated using the following equations [38, 39] and are displayed in Table 7.
Here $P$ is dipolar hyperfine coupling parameter ($=0.036 \text{ cm}^{-1}$). From Eqs. (4) and (5), in order to determine $\text{Cu}^{2+}$ bonding coefficients, besides the EPR parameters, the energy positions of the absorption bands of $\text{Cu}^{2+}$ which indicate the values of $\Delta E_{xy}$ and $\Delta E_{xz,yz}$ are required. Since one absorption band corresponding to $2B_{1g} \rightarrow 2B_{2g}$ transition ($\Delta E_{xy}$, are presented in Table 7) was observed, the position of the second band can be estimated by using the following equation [39] and the values are presented in Table 7.

$$\alpha^2 = \left| \frac{A^\|}{P} \right| + \frac{3}{7}(g^\perp - 2) + 0.04$$  \hspace{1cm} (6)

$$\beta^2 = \left[ (g^\//g_e) - 1 \right] \Delta E_{xy}/4\lambda \alpha^2$$  \hspace{1cm} (7)

$$\beta_1^2 = \left[ (g^\perp/g_e) - 1 \right] \Delta E_{xz,yz}/\lambda \alpha^2$$  \hspace{1cm} (8)

Here $P$ is dipolar hyperfine coupling parameter ($=0.036 \text{ cm}^{-1}$). From Eqs. (4) and (5), in order to determine $\text{Cu}^{2+}$ bonding coefficients, besides the EPR parameters, the energy positions of the absorption bands of $\text{Cu}^{2+}$ which indicate the values of $\Delta E_{xy}$ and $\Delta E_{xz,yz}$ are required. Since one absorption band corresponding to $3B_{1g} \rightarrow 3B_{2g}$ transition ($\Delta E_{xy}$, are presented in Table 7) was observed, the position of the second band can be estimated by using the following equation [39] and the values are presented in Table 7.

$$\Delta E_{xz,yz}(2B_{1g} \rightarrow 2E_g) = 2K^2 \lambda/2.0023 \cdot g_\perp$$  \hspace{1cm} (9)

where $K^2$ is the orbital reduction factor ($K^2 = 0.77$) and $\lambda$ is the spin-orbit coupling constant.

The normalized covalency of the $\text{Cu}^{2+}$–O in-plane bonding of $\sigma$ and $\pi$ symmetry is expressed in terms of bonding coefficients $\alpha^2$ and $\beta_1^2$ as follows:

$$\Gamma_\sigma = 200(1-S) \left( 1-\alpha^2 \right)/(1-2S)\%$$  \hspace{1cm} (10)

$$\Gamma_\pi = 200(1-\beta_1^2)\%$$  \hspace{1cm} (11)

where $S$ is the overlapping integral ($S_{xy} = 0.076$). The values of $\Gamma_\sigma$ and $\Gamma_\pi$ are given in Table 6. It is clear from Table 7 that both of these values are varied with addition of ZnO content to $B_2O_3$ network. This could be due to variation of structural changes within the glasses. In

| Parameter | $x = 0$ | $x = 7.5$ | $x = 15$ | $x = 22.5$ | $x = 30$ |
|-----------|---------|----------|---------|----------|---------|
| $\lambda$ (nm) ($\pm 1$) | 764 | 760 | 756 | 760 | 763 |
| $\Delta E_{xy}$ (cm$^{-1}$) | 13,089 | 13,158 | 13,228 | 13,158 | 13,106 |
| $\Delta E_{xz,yz}$ (cm$^{-1}$) | 20,666 | 19,408 | 20,017 | 19,117 | 19,408 |
| $\alpha^2$ | 0.798 | 0.799 | 0.804 | 0.802 | 0.803 |
| $\beta^2$ | 0.964 | 0.963 | 0.957 | 0.959 | 0.958 |
| $\beta_1^2$ | 0.793 | 0.794 | 0.801 | 0.803 | 0.797 |
| $\Gamma_\sigma$ (%) | 41.4 | 41.2 | 39.8 | 39.4 | 40.6 |
| $\Gamma_\pi$ (%) | 37.33 | 37.15 | 36.22 | 36.59 | 36.41 |

Table 7. Bonding parameters of $59B_2O_3$–10Na$_2$O–(30 – $x$)CdO–xZnO–1CuO (0 ≤ $x$ ≤ 30 mol%) glass system.
general if \( \alpha^2 \) have smaller values, then the greater the covalent nature of the bonding. The calculated values of \( \alpha^2 \) for prepared glass series (the range 0.798–0.803) suggest that the in-plane \( \sigma \) bonding in the glasses is moderately covalent in nature, whereas the values of \( \beta^2 \) (0.793–0.803) obtained for various glasses indicate that the in-plane \( \pi \) bonding is significantly ionic in nature.

The changes in this parameter can be attributed to the changes in O–X bonds (where X = B, Cd, and Zn) because it reflects the competition in the Cu\(^{2+}\)–O–X bonds, between the cupric ion and its neighboring X cations for attracting the lone pairs of the intervening oxygen ions. In the present system, the values of \( \beta^2 \) were found to be close to unity, and it suggests that out-of-plane \( \pi \) bonding is more ionic in nature and the magnitudes of all bonding parameters are comparable to those found for Cu\(^{2+}\) in other glasses [6].

4. Conclusions

Transparent glasses with composition 59B\(_2\)O\(_3\)–10Na\(_2\)O–(30 – x)CdO–xZnO–1CuO (where \( x = 0, 7.5, 15, 22.5, \) and 30 mol\%) were prepared by melt-quenching technique. It was observed that the density (\( \rho \)) decreases, while OPD, molar volume (\( V_m \)), and oxygen molar volume (\( V_o \)) are nonlinearly varying with the addition of ZnO content from 0 to 30 mol\% at the expense of CdO content. From FTIR studies, it is found that the glasses are composed of [BO\(_4\)] and [BO\(_3\)] units in various borate groups. FTIR and Raman studies revealed that more numbers of BO\(_4\) units are present up to 15 mol\% of ZnO, and then with further addition of ZnO in place of CdO up to 30 mol\%, most of BO\(_4\) units are converted to BO\(_3\) units. The nonlinear variation in \( T_g \) is due to the dual role of ZnO. From EPR results, it was found that \( g_|| > g_\perp \) and the changes in spin-Hamiltonian parameters are primarily due to the ligand field variations around Cu\(^{2+}\) ions. It is found that \( g_|| > g_\perp \) for the present glass system. This suggests that the Cu\(^{2+}\) ions in the present glasses are coordinated by six ligands (CuO\(_6\) chromophore) which form an octahedron elongated along the z-axis and also suggests that the ground state of Cu\(^{2+}\) ions is the d\(_{x^2−y^2}\) orbital (\( ^3B_{1g} \) state). From the optical absorption studies, it was found that broad absorption maximum is due to \( ^3B_{1g} \rightarrow ^3B_{2g} \) transition of Cu\(^{2+}\) ion. The change in polarizability of oxygen ions surrounding the Cu\(^{2+}\) could be the reason for the variation of the peak position. The optical absorption results also suggested that there is covalency for the in-plane \( \sigma \)-bonding and that the in-plane \( \pi \)-bonding is significantly ionic in nature in Cu\(^{2+}\)–O bonds.

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