

RESEARCH ARTICLE



**DIELECTRIC AND SPECTROSCOPIC INVESTIGATIONS OF COPPER IONS IN
PbO-Bi₂O₃-B₂O₃ GLASS MATRIX**

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ABSTRACT

Lead bismuth borate glasses have been developed by varying the content of CuO in the chemical compositions $(20-x) \text{PbO}-40\text{Bi}_2\text{O}_3-40 \text{B}_2\text{O}_3-x \text{CuO}$, where $x = 0.2, 0.4, 0.6, 0.8,$ and 1mol. \% . The samples were characterized by x-ray diffraction and scanning electron microscopy techniques. Dielectric properties (viz., dielectric constant ϵ' , loss $\tan \delta$, ac conductivity σ_{ac}) over a wide range of frequency and temperature as a function of concentration of CuO have been carried out. Optical absorption, luminescence, ESR and IR spectral studies have also been investigated. The results of the dielectric properties have indicated that the glasses possess high insulating character when the concentration of CuO is $> 0.6 \text{ mol. \%}$. The analysis of results of dielectric and spectroscopic studies has revealed that as the concentration of CuO is increased beyond 0.6 mol. \% in the glass matrix, a part of Cu^{2+} ions has been reduced to Cu^+ ions that have influenced the physical properties of these glasses.

Key words: Amorphous materials, dielectric response, X-ray diffraction

INTRODUCTION

During recent years, there has been a great deal of interest in preparing and investigation of the structure of heavy metal oxide $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses due to high refractive index, high IR transparency and high third order non-linear optical susceptibility [1, 2]. These qualities attribute $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses have found prospective applications in optical and devices in optoelectronics such as ultrafast switches, infrared windows, optical isolators and waveguides in the infrared region [3-5]. But, heavy metal oxides like Bi_2O_3 unable to form

the glass by itself because of high polarizability and low field strength of the Bi^{3+} ions. Further, Bi_2O_3 may exist in the glass matrix in $[\text{BiO}_3]$ pyramidal and $[\text{BiO}_6]$ octahedral units [6-8] with the participation of the conventional glass former B_2O_3 and modifier PbO [9]. Furthermore, bismuth ion was found to be a great luminescent trigger with testing applications in lasers in the form of a good sensitizer for certain rare earth ions [10, 11]. Kityk et al. have done thorough work on Bi_2O_3 -based glasses recently [12-15].

Lead oxide is commonly used as a component in the low melting glasses and additionally these kinds of glasses possess extremely high radioactive resistance because of their high density as well as atomic number [16]. When the modifier oxide PbO added to bismuth borate glasses, the glasses are supposed to become highly stable as well as chemically inert; since PbO has a dual role: such as a modifier with PbO_6 structural units and as a glass network former with $\text{PbO}_{4/2}$ pyramidal units [17]. B_2O_3 is a well-known network former and is found in almost all essential commercially available glasses. All studies report that B_2O_3 is made substantially of BO_3 triangles which forms boroxol rings. Moreover, the addition of modifier oxides to B_2O_3 changes some BO_3 triangles to BO_4 tetrahedron, which exists in different structural borate groups [18-20] and this is confirmed from the study of the IR spectra of these glasses.

Copper is generally used in the preparation of some industrial colored glasses, as the red glass hematite, aventurine, and rubies. Copper may exist in glass forming oxide glasses as cupric (Cu^{2+}) and cuprous (Cu^+) ions. Glasses containing copper as the main component are of increasing interest due to their semi-conducting properties and many other potential applications [21, 22]. The electronic structure of the copper atom is $[\text{Ar}] 3d^{10} 4s^1$; five d orbital occupied for the cuprous ion and it does not produce the colouring [23], while Cu^{2+} ions create color centers and create blue and green glasses with an absorption band in the visible region [24, 25]. The Cu^{2+} content, its specific coordination, composition and basicity of the glass plays an important role in the colour of the glass. Colours produced by Cu^{2+} ions in various glasses have been explained [26] by means of ligand field theory. A large number of recent studies on the structure of copper ions in a variety of inorganic glass systems [21, 22, 27, 28] including bismuth borate glasses [29, 30] are available; but most of these are concentrated on structural investigations by means of IR and magnetic studies. The systematic literature analysis indicates yet still there are a great deal of opportunity to investigate on lead bismuth borate glasses mixed with CuO , particularly in terms of dielectric properties. The study of dielectric properties (dielectric constant ϵ' , loss $\tan \delta$ and ac conductivity σ_{ac}) of the glass materials assists to expect the insulating nature, understanding the conduction phenomenon and also provides the information on the structural point of views of the glasses to a wide area of extent [31-34]. The aim of this paper is to explore the valence states of copper ions and also to throw some light on ac conduction phenomenon in $\text{PbO}-\text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3$ glass system, by thorough investigation of dielectric properties in addition with spectroscopic studies (viz., optical absorption, luminescence emission, ESR and IR spectra).

2. Experimental

The composition $(20-x)\text{PbO}-40\text{Bi}_2\text{O}_3-40\text{B}_2\text{O}_3-x\text{CuO}$ with $0 \leq x \leq 1.0$ mol. % is chosen for the present study and the details of the samples are as follows:

C_0 : 20 $\text{PbO}-40\text{Bi}_2\text{O}_3-40\text{B}_2\text{O}_3$

C_2 : 19.8 $\text{PbO}-40\text{Bi}_2\text{O}_3-40\text{B}_2\text{O}_3$: 0.2 CuO

C_4 : 19.6 $\text{PbO}-40\text{Bi}_2\text{O}_3-40\text{B}_2\text{O}_3$: 0.4 CuO

C_6 : 19.4 $\text{PbO}-40\text{Bi}_2\text{O}_3-40\text{B}_2\text{O}_3$: 0.6 CuO

C_8 : 19.2 $\text{PbO}-40\text{Bi}_2\text{O}_3-40\text{B}_2\text{O}_3$: 0.8 CuO

C_{10} : 19.0 $\text{PbO}-40\text{Bi}_2\text{O}_3-40\text{B}_2\text{O}_3$: 1.0 CuO

Appropriate amounts (all in mol. %) of analytical grade of reagents of PbO , Bi_2O_3 , H_3BO_3 and CuO powders were thoroughly mixed in an agate mortar and melted in a thick-walled silica crucible in the temperature range 950-1000 °C in an automatic temperature controlled furnace for about one hour until a bubble free transparent liquid was formed. The resultant bubble free melt was then poured in a brass mould

and subsequently annealed from 300 °C with a cooling rate of 1 °C/min. x-ray diffraction and scanning electron microscopy studies confirmed the amorphous nature of the present study glass samples. The samples were then ground and optically polished. The final dimensions of the samples used for dielectric, optical absorption and luminescence studies were about 1 cm × of 1 cm × 0.2 cm. The density d of the glasses is determined to an accuracy of (± 0.001) by the Archimedes' principle using O-xylene (99.99 % pure) as the buoyant liquid with OHAUS balance (model AR 2140). The optical absorption spectra of the glasses were recorded at room temperature in the wavelength range 300-1200 nm up to a resolution of 0.1 nm using CARY 100 (Varian) Spectrometer. The luminescence spectra of these glasses were determined in the wavelength range 300-900 nm on FluroMax-3 (Jobin-Yvon, Horiba) using Xenon lamp of power 150 W as excitation source. The ESR spectra of the fine powders of the samples were noted at room temperature on E11Z Varian X- band ($\nu = 9.5$ GHz) ESR spectrometer. Infrared transmission spectra were recorded in a Bruker IFS 66V-IR spectrometer with a resolution of 0.1 cm^{-1} in the range 400-2000 cm^{-1} using potassium bromide pellets (300 mg) possessing pulverized glass (1.5 mg). A layer of the silver painting was applied (to the biggest faces of area) on both sides of the glasses to serve as electrodes for dielectric measurements. The painted samples were then dried up with a hot blower up to 10 minutes on both sides. The dielectric measurements were taken at various temperatures and frequencies using the HP 4263B LCR meter. The accuracy in measuring the dielectric constant is $\sim 10^{-3}$ and in dielectric loss is $\sim 10^{-4}$.

3. RESULTS

Our visual analysis, the absence of peaks in the x-ray diffraction patterns (Fig. 1) and the SEM photographs (Fig. 2) confirmed that the prepared samples were of amorphous state. From the measured values of density d and average molecular weight \bar{M} of the samples, various other physical parameters such as copper ion concentration N_i , mean copper ion separation r_i and Polaron radius r_p in $\text{PbO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3\text{:CuO}$ glass samples have been calculated and listed in Table1. The dielectric constant ϵ' and loss $\tan \delta$ at room temperature ($\approx 30^\circ\text{C}$) of pure $\text{PbO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses at 100 kHz are determined to be 7.46 and 0.006 respectively; the values of ϵ' and loss $\tan \delta$ of these glasses are observed to increase considerably with a decrease in frequency. The temperature dependence of ϵ' of the glasses containing different concentrations of CuO at 1 kHz is shown in Fig. 3 and at different frequencies for the glass C_8 is shown as the inset. The value of ϵ' is found to exhibit a significant increase at higher temperatures particularly at lower frequencies; it is observed that the rate of increase of ϵ' with the temperature is higher for the glass that contains 0.6 mol. % of CuO.

A comparison plot of variation of $\tan \delta$ with temperature, measured at a frequency of 10 kHz is shown in Fig. 4 and the temperature dependence of $\tan \delta$ for the glass C_6 in different frequencies is presented in the inset of Fig. 4. The curves of CuO doped glasses have revealed distinct maxima; with increasing frequency, the temperature maximum shifted upwards and with the increase of the temperature, the frequency maximum also shifted upwards, indicating the relaxation character of dielectric losses of these glasses. Further, the studies on dielectric loss variation with the temperature indicated an increase of the width and $(\tan \delta)_{\text{max}}$ of relaxation curves with the increase of the concentration of CuO up to 0.6 mol. %. Using the relation [35]:

$$f = f_0 \exp(-W_d/KT) \quad (1)$$

the effective activation energy, W_d , for the dipoles is calculated for different concentrations of CuO. The activation energy is found to decrease with the increase of the content of CuO up to 0.6 mol. % in the glass matrix (Table 2). The ac conductivity σ_{ac} is evaluated in different temperatures using the equation [35]:

$$\sigma_{ac} = \omega \epsilon' \epsilon_0 \tan \delta \quad (2)$$

(where ϵ_0 is the dielectric constant and ω is the frequency) for different frequencies and the plot of $\log \sigma_{ac}$ against $1/T$ for all the glasses at 10 kHz (Fig. 5) and for one of the glasses viz., C_4 at different frequencies is shown as the inset of the Fig.5, the conductivity is found to increase considerably with the increase of the concentration of CuO in any given frequency and temperature up to 0.6 mol. % of CuO (Fig. 6). From these

plots, the activation energy for the conduction in the high region of temperatures on which a near linear dependence of $\log \sigma_{ac}$ with $1/T$ noticed, is calculated and presented in Table 2.

Fig. 7 represents the optical absorption spectra of PbO-Bi₂O₃-B₂O₃: CuO glasses recorded at room temperature in the wavelength region of 200-1200 nm. The absorption spectra of all the glasses exhibited two kinks in the region of 380-450 nm followed by another two, one broad band with a metacenter between 730 and 790 nm. Half-width and intensity of the principal band are found to increase for the concentration of CuO up to 0.6 mol. % and a gradual decrease in the intensity of this band could be noticed beyond this concentration. Of the rims of absorption observed, we have calculated the optical band gaps (E_o) of these glasses by drawing the Urbach plot between $(\alpha\hbar\omega)^{1/2}$ and $\hbar\omega$ according to the equation:

$$\alpha(\omega)\hbar\omega = c(\hbar\omega - E_o)^2 \quad (3)$$

$\alpha(\omega)$ is the absorption coefficient, $\hbar\omega$ is the energy of photon and c is a constant that represents the slope of the curve drawn between $(\alpha\hbar\omega)^{1/2}$ and $\hbar\omega$. Higher the value of c represents the high optical band gap. The values of optical band gap (E_o) (the intercepts on the x-axis) are determined from the extrapolation of the linear portions of the curves of Fig. 8 and are tabulated in the Table 3; the value of E_o is identified to be the highest for the glass C₁₀. The excitation spectrum for copper ions ($\lambda_{\text{emission}} = 552$ nm) of the glass C₄ is shown in the Fig. 9; the spectrum exhibited three discrete bands at 274, 292 and 332 nm. The spectra of all other glasses continue the same structure. Of these spectra, the λ_{exc} is determined ~ 274 nm and the same one was used to recording spectra of emission of these glasses. The fig. 10 shows luminescence spectra of PbO-Bi₂O₃-B₂O₃ glasses that contain different concentrations of CuO recorded at the room temperature. The spectra of all these samples exhibited emission bands at about 452 and 550 nm. When the concentration of CuO is increased beyond 0.6 mol. %, it is observed that the intensity and the half width of these two bands are increase gradually. The ESR spectra (Fig. 11) of CuO free PbO-Bi₂O₃-B₂O₃ glasses recorded at room temperature have not exhibited any signal. With the addition of CuO into the pure glass matrix, an asymmetric strong additional signal with a hyperfine structure partially resolved with a value of $g_{\perp} \sim 2.04$ and a shallow quadruplet in approximately $g_{\parallel} \sim 2.35$ is noticed. The components of g are identified to change significantly with the concentration of CuO (Table 4). It is observed that the width of line of hyperfine parallel and perpendicular peaks (of spectra of all the glasses) increases with the order of the quantum magnetic number m_l . When the concentration of CuO is increased beyond 0.6 mol. %, decrease in the intensity of the signal is observed.

The infrared transmission spectra (Fig. 12) of PbO-Bi₂O₃-B₂O₃: CuO glasses have exhibited a few different groups of bands corresponding to: (i) BO₃ units (ii) BO₄ units (iii) B-O-B linkages and (iv) PbO₄/BiO₆ structural units. The details of the band positions [9, 29, 36-39] are listed in Table 5.

Table 1: Various physical parameters of PbO-Bi₂O₃-B₂O₃ glasses doped with different concentrations of CuO

Sample	Density (g/cm ³)	Avg. Mol. Wt. \overline{M}	Dopant ion Conc. N_i ($\times 10^{21}$ ions/cm ³)	Inter ionic distance r_i	Polaron radius (Å)	Field strength F (10^{15} cm ²)
C ₂	6.443	258.58	3.00	6.93	2.79	2.56
C ₄	6.437	258.30	5.98	5.50	2.21	4.06
C ₆	6.430	258.01	8.96	4.80	1.93	5.32
C ₈	6.424	257.72	11.9	4.36	1.76	6.45
C ₁₀	6.417	257.44	15.0	4.05	1.63	7.49

Table 2: Summary of data on dielectric studies of PbO–Bi₂O₃–B₂O₃ glasses doped with different concentrations of CuO

Sample	Temp. Region of relaxation (°C)	A.E. for conduction (eV)	A.E. for dipoles (eV)	(Tan δ _{max}) _{avg}	N(E _F) (x 10 ²⁰ , eV ⁻¹ /cm ³) (± 0.01)
C ₂	99–134	0.44	2.15	0.83	4.73
C ₄	90–131	0.37	1.96	0.86	5.24
C ₆	88–133	0.31	1.77	0.89	5.65
C ₈	111–152	0.57	2.44	0.91	3.46
C ₁₀	125–158	0.66	2.79	0.92	3.04

Table 3: Absorption band positions and optical band gaps of PbO–Bi₂O₃–B₂O₃ glasses doped with different concentrations of CuO

Sample	Cut-off Wave length (nm)	Band positions ² B _{2g} → ² B _{1g} (nm)	Optical Band Gap (eV)
C ₂	240	773	3.61
C ₄	248	779	3.52
C ₆	259	792	3.36
C ₈	233	764	3.87
C ₁₀	219	760	4.18

Table 4 : Data on ESR spectra of PbO–Bi₂O₃–B₂O₃ glasses doped with different concentrations of CuO

Sample	g	g _⊥	α ²	β ₁ ²
C ₂	2.353	2.045	0.739	0.927
C ₄	2.358	2.048	0.766	0.895
C ₆	2.361	2.049	0.787	0.866
C ₈	2.354	2.047	0.749	0.927
C ₁₀	2.337	2.043	0.709	0.936

Table 5 FTIR spectral band positions (in cm^{-1}) of $\text{PbO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses doped with different concentration of CuO

Band positions (cm^{-1})	Assignment	Ref
470	A band due to PbO_4 structural units and in the same region a band due to symmetrical bending vibrations of BiO_6 units.	[9, 39]
710	A band due to bending vibrations of B-O-B linkages	[40, 41]
1100-1200	A band due to the vibrations of BO_4 structural units	[40, 42]
1300-1400	Conventional stretching relaxation of B-O bond of the trigonal BO_3 units and Bi-O^- (NBO) of BiO_3	[32, 39]

4. DISCUSSION

B_2O_3 is a well-known network former with BO_3 and BO_4 structural units. PbO converts sp^2 planar BO_3 units into more stable sp^3 tetrahedral BO_4 units in addition to non-bridging oxygens (the NBO's), When incorporated in the glass network B_2O_3 . The IR spectra of $\text{PbO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glass network is the clear evidence of presence of BO_3 and BO_4 structural units. Bray et al. [40] mentioned that the fraction of fourfold coordinated boron in $\text{PbO-B}_2\text{O}_3$ is ~ 0.53 . Consequently, the composition of this glass can be obtained in the form of the following chemical structural units: $0.5 \text{Pb}_{1/2}^{+2} [\text{BO}_{4/2}]^- + 0.5 \text{Pb}_{1/2}^{+2} [\text{O}^- \text{BO}_{2/2}]$

PbO in general takes part in the glass network both with covalent and ionic bonds and participate in the glass network with $[\text{PbO}_{4/2}]$ pyramidal units connected in puckered layers. Further PbO enters in to the glass network by breaking the B-O-B bonds and introduces coordinate defects known as dangling together with NBO ions.

Bi_2O_3 , network former does not readily form glass but does so in the presence of modifiers like PbO with triangular BiO_3 pyramids. Bi_2O_3 takes part octahedral positions in the glass network with BiO_6 structural units and nevertheless, Bi_2O_3 also acts as the modifier and enters the glass network breaking bonds of Pb-O-B . The ions of copper exist in state of Cu^{2+} and act as a modifier; however, the reduction of Cu^{2+} ions into Cu^+ ions is possible during melting and processes of subsequent annealing since $\text{Cu}^{2+} + \text{e}^- = \text{Cu}^+$ happen only with reduction potential $E^\circ = 0.153 \text{ V}$ [41]. Such a type of the reduction of copper ions has been mentioned in several other glass systems earlier [42].

4.1. Optical spectrums of absorption

The free ion term for $\text{Cu}^{2+} (3d^9)$ is rarely found in octahedral regularly. In an octahedral crystal field, it splits into e_g and t_{2g} ; e_g is the low level and it splits due to the effect of Jahn- Teller. In the present glass network, it is assumed that Cu^{2+} is octahedrally coordinated, tetragonal and in the square planar coordination. In tetragonally deformed octahedral environment, the e_g level splits into ${}^2A_{1g}$ and ${}^2B_{1g}$, and the t_{2g} level splits into 2E_g and ${}^2B_{2g}$, the ground state being ${}^2B_{1g}$. The broad absorption band noticed in the absorption spectra of these glasses is corresponds to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition [37]. The broadening of this band can be recognized due to the super position of three electron transitions in d orbitals corresponding to ${}^2B_{1g} \rightarrow {}^2E_g$, ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions. When the concentration of CuO is increased beyond 0.6 mol. %, a significant reduction of the intensity of the broad band is observed. Such a reduction reveals the conversion of a part of Cu^{2+} ions into Cu^+ ions [43]. The weak kink in the violet region in the absorption spectra is anticipated due to $3d^{10} \rightarrow 3d^9$

$4s^1$ charge transfer transition of copper ions [44]. The highest intensity of this kink is identified in the spectrum of glass C_{10} , indicating the largest existence of concentration of Cu^+ ions. Further two considerable kinks observed in the region of 380-450 nm and another in between 730-790 nm in the optical absorption spectra are characterized to $^3P_0 \rightarrow ^1S_0$, 1D_2 transitions of Bi^{3+} ions [45]. The synchronized octahedrally Cu^{2+} ions acts as the modifier similar to Pb^{2+} ions and induces NBOs in the glass network. The concentration of Cu^{2+} modifier ions, results the concentration of NBOs in the glass matrix this causes, the degree of localization of electrons and hence the donor centers in the glass network is expected. The existence of smaller concentration of donor centers (lower concentration of Cu^{2+} modifier ions) increases the optical band gap and shifts the absorption edge towards the lower wavelength side as shown in Fig. 8 when the concentration of CuO is increased beyond 0.6 mol. %. The increase of the optical band gap with the increase of the concentration of the CuO from 0.6 to 1.0 mol. % can be explained accordingly: the gradual reduction of the concentration of Cu^{2+} ions causes the extinction of a number of donor's centers; then the excited states of localized electrons originally trapped on Cu^+ sites continue to overlap with the empty $3d$ states on the adjacent Cu^{2+} sites. As consequent, the impurity band extended into the main band gap this might shifted the absorption edge in the higher energy as given in Table 3, which results a substantial growth in the band gap.

4.2 ESR Spectra

The observed g_{\parallel} and g_{\perp} values (Table 4) in ESR spectra of $PbO-Bi_2O_3-B_2O_3: CuO$ glasses are the attributes of Cu^{2+} ions coordinated by six ligands with the octahedron extended along the z-axis [46]. Because $g_{\parallel} > g_{\perp} > 2.0023 g_e$, the ground state of the paramagnetic electron is $d_{x^2-y^2}$ orbital ($^2B_{1g}$ state). The ESR and optical absorption spectral data can be interrelated to know the environment of Cu^{2+} ions in $PbO-Bi_2O_3-B_2O_3$ glass network as follows [47]:

$$g_{\parallel} = 2.0023 \left[1 - \frac{4\lambda\alpha^2\beta_1^2}{E(^2B_{2g})} \right] \quad (4)$$

$$g_{\perp} = 2.0023 \left[1 - \frac{\lambda\alpha^2\beta^2}{E(^2E_g)} \right] \quad (5)$$

where λ is the spin-orbit coupling coefficient and the bonding coefficients α^2 , β_1^2 and β^2 (~ 1.00) characterize, respectively, the in-plane σ bonding, in-plane π bonding and out of-plane π bonding of the $Cu(II)$ complexes. Their values exist between 0.5 and 1, the limits of pure covalent and pure ionic bonds. Since only one absorption band corresponding to the transition $^2B_{1g} \rightarrow ^2B_{2g}$ has been identified, the position of the second band has been assessed using the equation [48]:

$$E(^2B_{1g} \rightarrow ^2E_g) = \frac{2k_{\perp}^2\lambda}{2.0023 - g_{\perp}} \quad (6)$$

Where k_{\perp} is the orbital reduction factor ($k_{\perp}^2 = 0.77$) and λ is the spin-orbit coupling constant ($= -828 \text{ cm}^{-1}$) [49]. The values of α^2 and β_1^2 obtained using Eqs. (4) and (5) are listed in Table 4. α^2 is the bonding coefficient due to covalency of the σ bonds with the equatorial ligands that determines the electron density delocalized on ligand ions and β_1^2 accounts for the covalency of π bonding between ligands and $^2B_{2g}$ excited state. The values of α^2 and β_1^2 are far from unity (when the concentration of CuO is greater than 0.6 mol. %), representing a gradual modification of Cu^{2+} ions from ionic to covalent nature in the concentration of 0.6-1.0 mol. % of CuO in the glass network.

4.3. IR spectra

In the IR spectra of $\text{PbO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$: CuO glasses, the intensity of the bands due to more ordered BO_4 tetrahedral units, is observed to be the highest for glass C_6 ; with the increase of CuO content beyond 0.6 mol. %, the intensity of band due to BO_3 structural units is observed to be build up at the expense of tetrahedral bands. These observations confirm that in the glasses containing CuO beyond 0.6 mol. %, there is an increasing degree of disorder in the glass network by creating more and more dangling bonds.

4.4. Luminescence emission spectra

Emission spectra exhibited an intense yellow emission band centered at about 550 nm and a relatively broad blue emission band at about 452 nm. Since these bands were not identified in the spectra of CuO free glasses, the bands are evidently due to copper ions. The emission bands observed under the excitation of 270 nm can be attributed to the $^3\text{D}_1 \rightarrow ^1\text{S}_0$ (452 nm) transition of isolated Cu^+ ions and $^3\text{D}_1 \rightarrow ^1\text{S}_0$ (550 nm) transition of $(\text{Cu}^+)_2$ pairs, respectively [50–53]. The intensity of these bands is observed to be feeble for the glass C_6 and increases gradually with increasing concentration of CuO beyond 0.6 mol. %; this indicates that there is an increasing reduction of Cu^{2+} ions into Cu^+ in samples C_8 to C_{10} .

4.5. Dielectric properties

The dielectric constant of a material is due to electronic, ionic, dipolar and space-charge polarizations. Amongst these, the space-charge contribution depends on the purity of the glasses. The substantial increase of ϵ' with temperature in the present glass system $\text{PbO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ can be attributed to space-charge polarization because of the bonding defects produced by the modifiers [54]. With a gradual increase of the dopant (CuO) concentration from 0.2 to 0.6 mol. % in the present glasses, the rate of increase of ϵ' with the temperature is gradually increased, causing a degree of increases of disorder that leads to the space-charge polarization. From the results of optical absorption and studies of ESR, the copper ions especially exist at the state of divalent as modifiers and create bonding defects by breaking the bonds Bi-O-Pb, Bi-O-Bi in this range of concentration. As a consequence, the easy pathways for the migration of charges that would develop space-charge polarization and allow an increase in the dielectric parameters as observed [55, 56]. When the concentration of the CuO is changed between 0.8 and 1.0 mol. % in the glass system $\text{PbO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$, as mentioned earlier, a significant proportion of ions of copper exists in the state of Cu^+ in addition to the state of Cu^{2+} ; these ions are in network forming positions and increase the insulating strength of the glass network which results in the decrease of dielectric parameters identified.

The change in dielectric constant and the loss changes with the frequency and the temperature of these glasses they exhibit effects of dielectric relaxation. The effects of dielectric relaxation are observed when the metallic ions are present in the state of divalent [57]. The effects of dielectric relaxation are observed for the different concentrations of $\text{PbO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses are due to the formation of dipoles from the divalent copper ions together with a pair of cationic vacancies. The switching of relaxation region towards lower temperatures and decrease in the activation energy for the dipoles with increase in the concentration of CuO from 0 to 0.6 mol. % (Table 3) indicates growing degree of freedom for dipoles to orient in the field direction in the glass network. As stated earlier there is a significantly higher concentration of Cu^+ ions that take network forming positions in the glass matrix, provides the decrease in the intensity of the relaxation effects beyond 0.6% of CuO.

A near linear relationship is identified in Fig. 6; when a plot is made between $\log \sigma(\omega)$ versus activation energy for conduction (in the high temperature region), this observation implies that an increase in conductivity is directly related to the thermally stimulated mobility of the charge carriers in the high temperature region. The conductivity isotherm shown in Fig.13 as a function of the concentration of CuO, it is observed that the conductivity is maximum at 0.6 mol. %. The observed tendency of increase of conductivity and decrease of activation energy up to 0.6 mol. % (zone-I), and decrease of conductivity and increase of activation energy beyond 0.6 mol. % of CuO (zone-II), propose the plug in influence of the conduction mechanism from ionic to electronic [58]. The mobile electrons, or polarons, participated in the process of

conversion of $\text{Cu}^+ \leftrightarrow \text{Cu}^{2+}$ are attracted by the cations and this results a neutral entity. The migration of this pair is not associated with any net displacement of the charge and does not provide electrical conductivity thus we predict a decrease in the conductivity, as observed in zone-II. In other words, the electronic paths are gradually blocked, causes hindering of the electronic current, with the entry of Cu^+ ions into the glass network.

Our systematic investigation on dielectric parameters of $\text{PbO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3\text{:CuO}$ glasses, as stated earlier, indicate the rate of increase of $\tan \delta$ (which is inversely proportional to breakdown strength) with temperature is the highest for glass C_6 and the lowest for glass C_{10} . The experiments on dielectric properties of these glasses also exhibit that there is an increase in the dielectric breakdown strength of the glasses with the concentration range of 0.8 to 1.0 mol. % of CuO . In accordance with these revelations the copper ions significantly occupy network forming positions with the gradual reduction of $\text{Cu}^{2+} \rightarrow \text{Cu}^+$, with the concentration of CuO beyond 0.6 mol. % and increase the rigidity of the glass network.

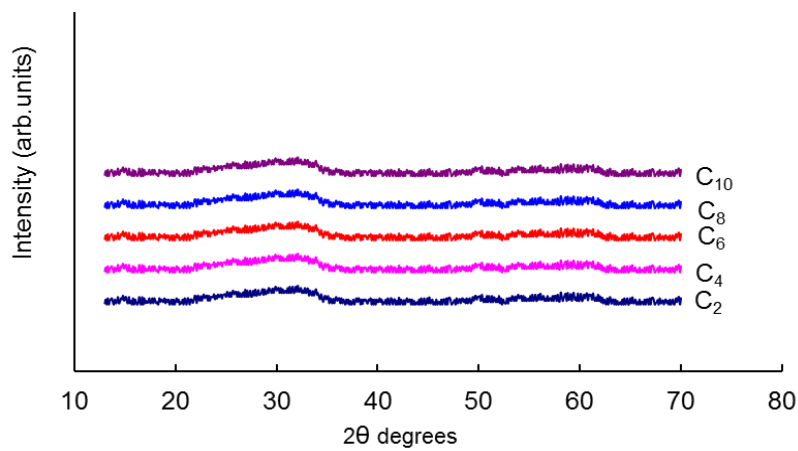


Fig. 1 X-Ray diffraction patterns of $\text{PbO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3\text{:CuO}$ glasses.

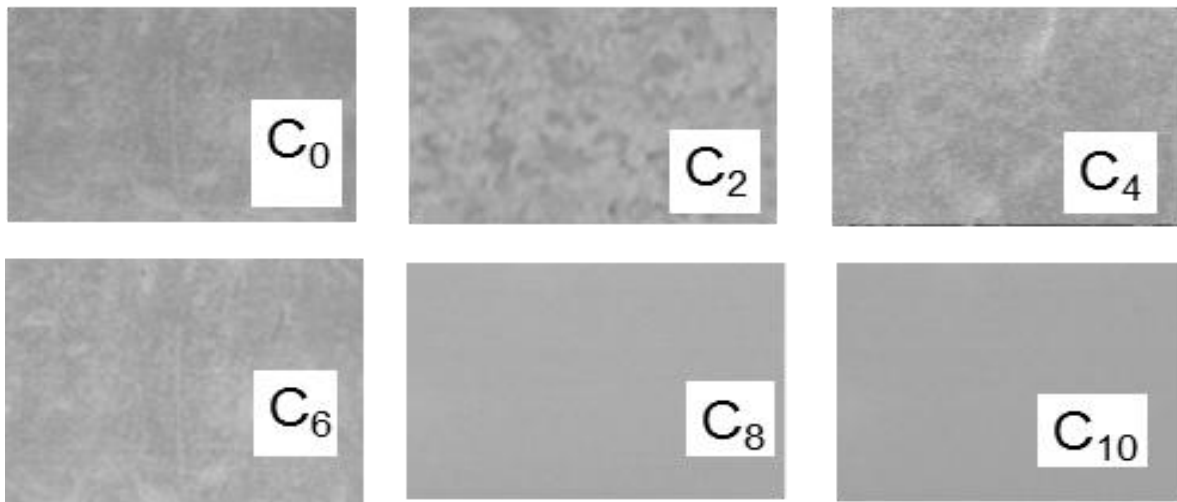


Fig. 2 SEM photographs of $\text{PbO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3\text{:CuO}$ glasses

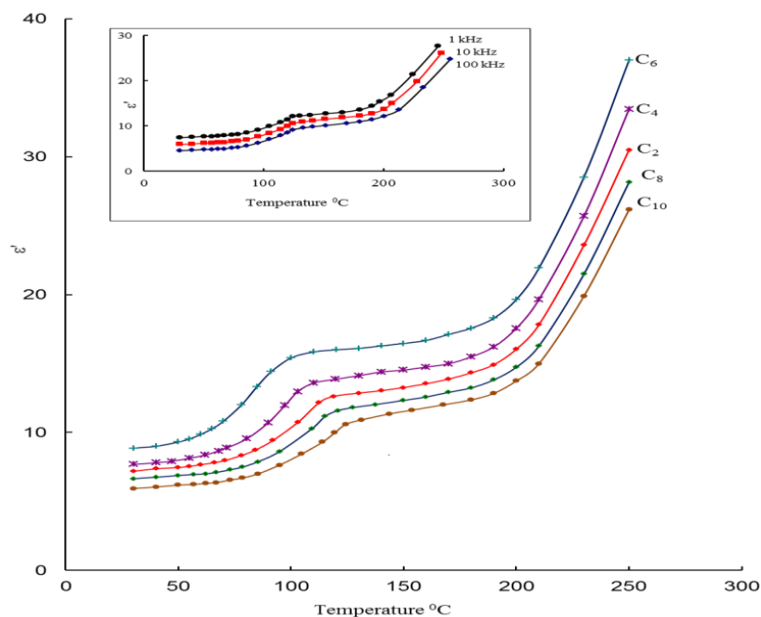


Fig. 3 A comparison plot of variation of dielectric constant with the temperature for PbO–Bi₂O₃–B₂O₃: CuO glasses at 1 kHz. Inset gives the variation of dielectric constant with temperature at different frequencies for the glass C₄.

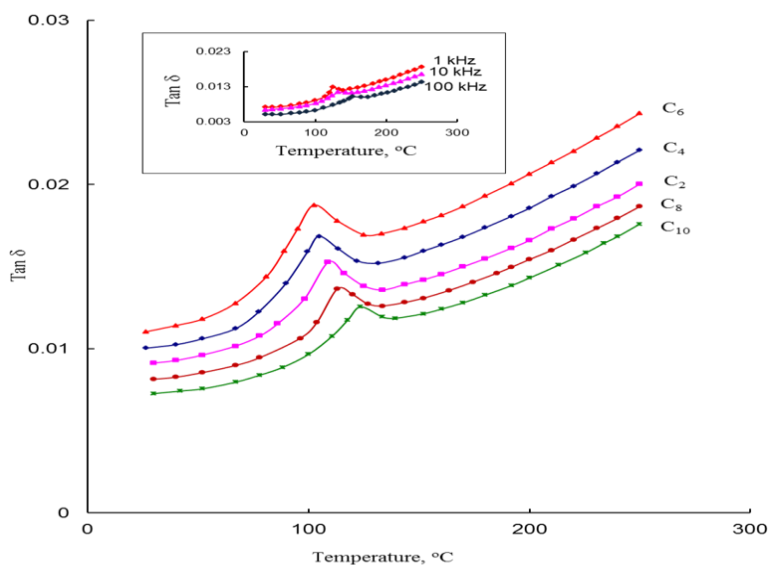


Fig. 4 A comparison plot of variation of dielectric loss with the temperature for PbO–Bi₂O₃–B₂O₃: CuO glasses at 10 kHz. Inset shows the variation of dielectric constant with temperature at different frequencies for the glass C₆.

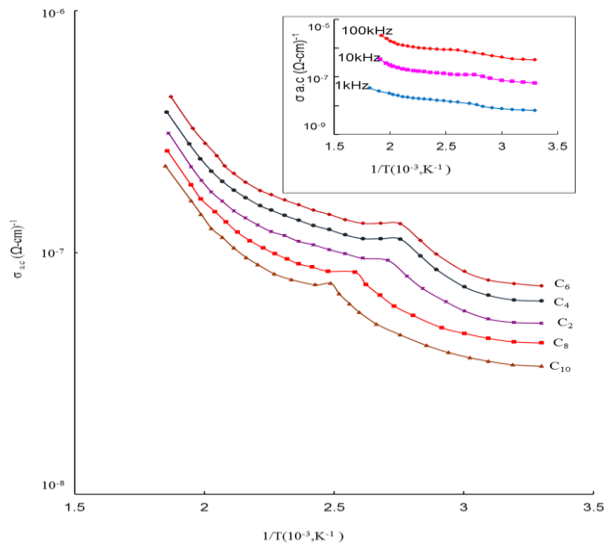


Fig.5 Variation of σ_{ac} with $1/T$ for PbO-Bi₂O₃-B₂O₃: CuO glasses at 10 kHz. Inset shows the variation of σ_{ac} with $1/T$ at different frequencies for the glass C₈

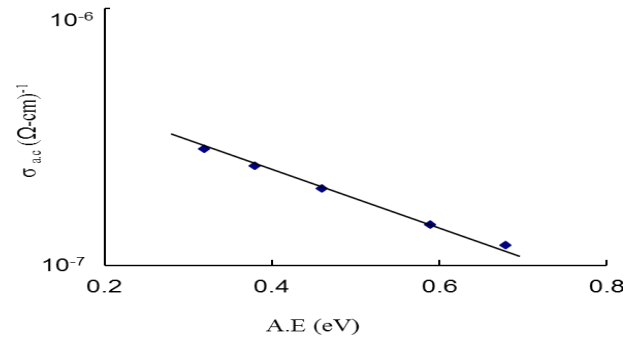


Fig. 6 Variation of conductivity with the activation energy for conduction

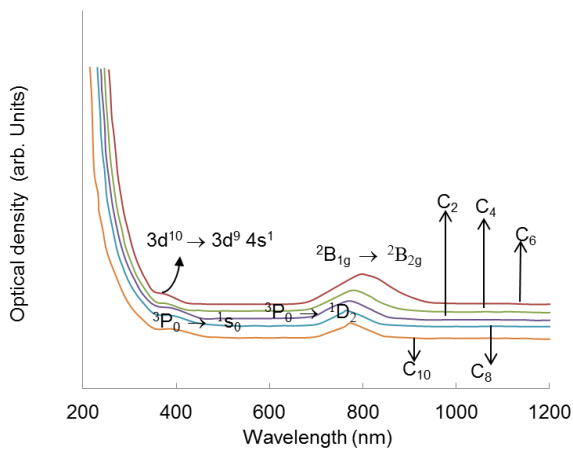


Fig. 7 Optical absorption spectra of PbO-Bi₂O₃-B₂O₃: CuO glasses.

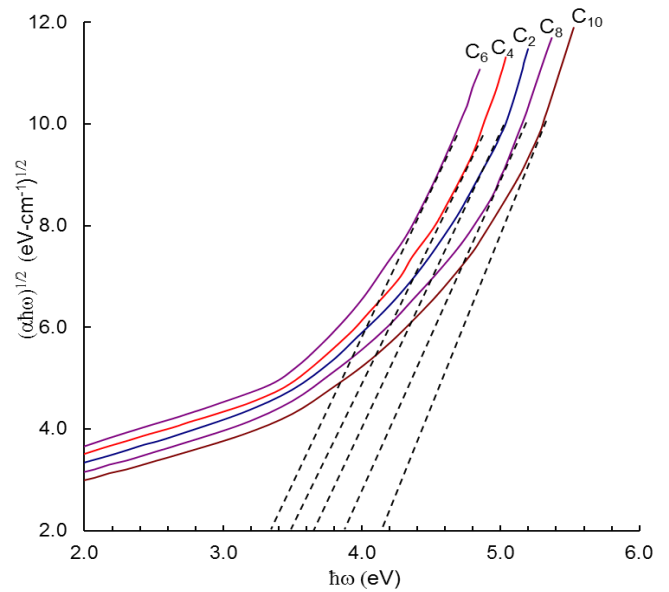


Fig. 8 Urbach plots to evaluate optical band gaps for PbO-Bi₂O₃-B₂O₃: CuO glasses

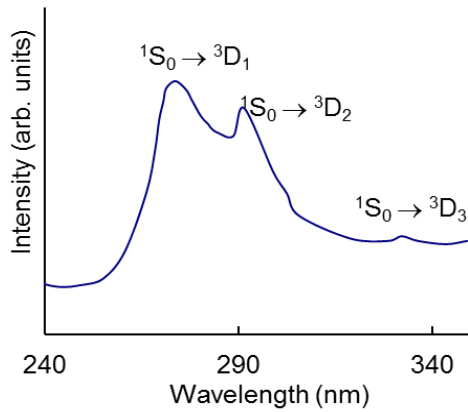


Fig. 9 Excitation spectrum of the glass C₄ ($\lambda_{\text{emission}} = 552 \text{ nm}$).

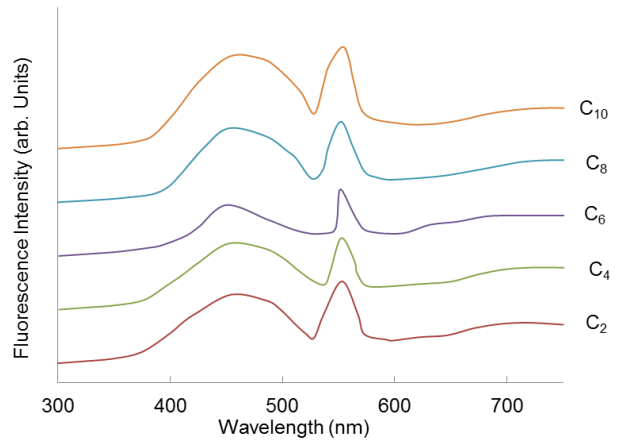


Fig. 10 Emission spectra of PbO-Bi₂O₃-B₂O₃: CuO excited at $\sim 270 \text{ nm}$

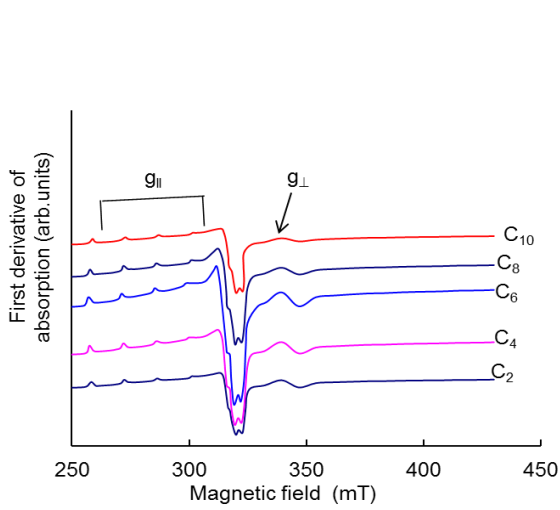


Fig.11 ESR spectra of PbO-Bi₂O₃-B₂O₃: CuO glasses.

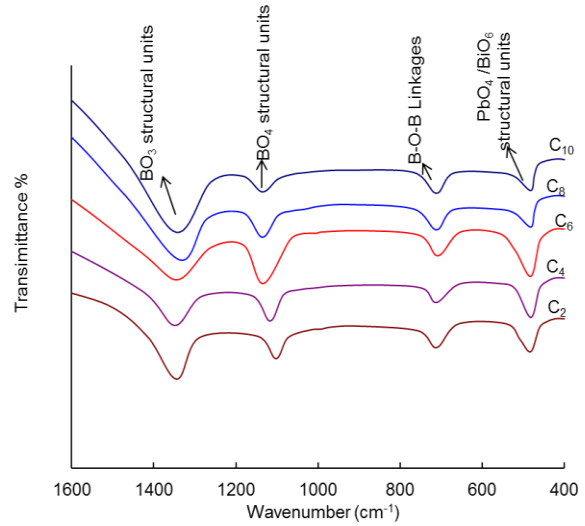


Fig.12 Infrared spectra of PbO-Bi₂O₃-B₂O₃: CuO glasses.

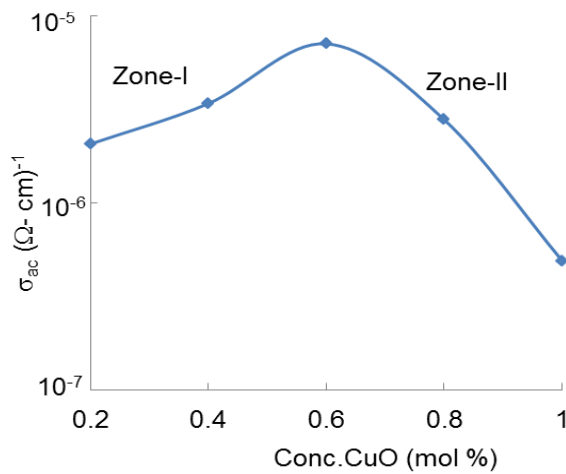


Fig.13 Variation of σ_{ac} as a function of CuO concentrations at 100 kHz.

5. CONCLUSIONS

The summary of the data from the study of various physical properties of PbO–Bi₂O₃–B₂O₃ glasses doped with different concentrations of CuO is as follows:

- i. The results of dielectric properties connected with the data on optical absorption, luminescence, ESR, IR spectral studies of PbO-Bi₂O₃-B₂O₃: CuO glasses pointed out that there is a possibility of conversion of a part of Cu²⁺ ions into Cu⁺ ions, particularly in the glasses containing CuO beyond 0.6 mol. %.
- ii. The dielectric parameters viz., ϵ' , $\tan \delta$, and σ_{ac} are found to increase where as the activation energy for ac conduction is decrease with the increase in the concentration of CuO up to 0.6 mol. %, suggesting an increase in the concentration of Cu²⁺ ions act as modifiers in this concentration range.
- iii. The optical absorption and the ESR spectral studies have revealed that the presence of copper ions predominantly in the state of Cu²⁺ with tetragonally distorted octahedral positions when the concentration of CuO is in the range, 0-0.6 mol. %.
- iv. The IR spectral studies indicated a gradual increase of the degree of disorder of the glass network with the increase of the concentration of CuO up to 0.6 mol. %.
- v. The phenomenon of ac conductivity is explained in terms of varied conduction mechanism viz., electronic and ionic. (Ionic nature up to 0.6 mol. % of CuO and electronic conduction beyond 0.6 mol. % of CuO)

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