SPECTROSCOPIC EXPLORATION OF 2% COPPER OXIDE DOPED BINARY ALKALI BOROSILICATE GLASS

Nagamani^{1,2,✉} and C. Srinivasu^{1,3}

¹Department of Physics, Krishna University, Machili patnam-521 001, (Andhra Pradesh) India.

²Department of Physics, Dr. LHR Government Degree College, Mylavaram-521231, (Andhra Pradesh) India.

³Department of Physics, Andhra Loyola College, Vijayawada - 520 004, (Andhra Pradesh) India.

✉Corresponding Author: nagamani1411@gmail.com

ABSTRACT

Glasses are prepared with the oldest accepted technique of melting the silica, boron oxide and alkali oxides with 2% copper oxide and quenching in air. XRD, SEM with EDX, optical methods are employed to study the microstructure of the material. The ductile nature of glass is observed from DTA studies. Glass formation is confirmed by X-ray diffraction spectra. The measured band gaps from both reflectance spectra and absorption spectra are compared and show they are in good agreement. To know the degree of the covalency of bonds, bonding parameters are calculated from EPR data. The Covalency of bonds in host glasses influences the Luminescence emission of Cu²⁺ ions in the visible region. The molecular structure of glasses is studied using FTIR. The covalent nature of molecular orbitals and molecular structure in the prepared samples is analysed systematically. Also, the various physical properties evaluated concerning the concentration of Alkali ions are reported. The covalent nature of glasses is observed from metallisation criterion.

Keywords: Borosilicate Glass, Melt-Quench Method, Spectroscopic Techniques, Covalent Nature, Electron Paramagnetic Resonance.

RASAYANJ. Chem., Vol. 14, No.3, 2021

INTRODUCTION

Borosilicate glasses are well thought of materials for their huge melting points, non-corrosiveness and bioactive nature.¹⁻³ The properties of any material depending on its composition, chemical bond and molecular structure. In the present paper authors prepared borate glasses with alkali mixed of composition 38SiO₂-30 B₂O₃-xNa₂O-(30-x)K₂O-2CuO (where mol% x = 5 to 25, of five samples). On these glasses, the structural, spectroscopic studies are carried out systematically with a special focus on the environmental chemical bonds formed in the composition. For a better understanding of the structure of the glasses, XRD, SEM, EDX, DTA, Optical absorption technique, Photo Luminescence, EPR, FTIR techniques are employed. Many researchers reported Calibration techniques like Kubelka-Munk function makes quantitative Diffuse Reflectance Spectroscopy (DRS) technique is competitive with absorption spectroscopy in some cases.⁴ Literature reveals the energy gap magnitudes are extracted from reflectance spectra similar as in absorption spectra with Tauc plots.^{5,6}

Further, it is known that Copper has multi oxidation states +1, +2, +3 like other transition metals. Out of which +2 oxidation states are most stable and have paramagnetic nature. Cu²⁺ ion electronic configuration is 3d⁹. The surrounding ligand structure of Cu²⁺ ions can be studied with EPR. Spectroscopic properties of transition metals are affected largely by their local environment. In another word, one can say the transition metal copper helps explore the structure of the glass.

In the present work, the authors attempted to measure bandgaps from both reflectance spectra and absorption spectra are compared. The degree of the covalency of bonds and bonding parameters are evaluated from EPR data. The Covalency of bonds in host glasses also influences the Luminescence emission of Cu²⁺ ions in the visible region.⁷ The various bonds that are present in the structure of the studied glasses are reported using FTIR.

EXPERIMENTAL

The various constituents and assigned codes involved in the preparation of glass are specified in Table-1. The studied glasses are prepared by melt- quenching method. Analytical-grade reagents of SiO_2 , B_2O_3 (99.5 - Loba) and Na_2O , K_2O anhydrous carbonates, 2mol% CuO are weighed commensurable to their mol% as shown in Table - 1 for each glass. The powdered batch chemicals of glass are melted at 1100°C for a one-hour duration of time in a vertical furnace. The molten form of the material is quickly cooled in air pouring on a brass plate. To eliminate internal stress the obtained glasses are annealed in an oven at 350°C for 3 hours.

The non-periodic arrangement of atoms in glasses is examined by XRD obtained from an X-ray diffractometer. Exterior surface smoothness and structural inhomogeneities are observed using Field emission SEM and X-ray energy dispersive analysis. The glass density is measured by density meter. To find out the electron transitions of energies nearer to bandgap are obtained using Perkin Elmer lambda 950 UV-VIS-NIR spectrophotometer. Magnetic resonance is measured and noted using EPR spectrometer. JY Fluorolog-3-11 fluorimeter is used to record photoluminescence spectra of glasses.

Table -1: Details of Chemical Composition of $38\text{SiO}_2\text{-}30\text{B}_2\text{O}_3\text{-}x\text{Na}_2\text{O-(}30\text{-}x\text{)K}_2\text{O-}2\text{CuO}$ ($x = 5, 10, 15, 20, 25$)

Glass Code	Constituents of Glass (All in mol%)
Cu_5	$38\text{SiO}_2\text{-}30\text{B}_2\text{O}_3\text{-}5\text{Na}_2\text{O-}25\text{K}_2\text{O-}2\text{CuO}$
Cu_{10}	$38\text{SiO}_2\text{-}30\text{B}_2\text{O}_3\text{-}10\text{Na}_2\text{O-}20\text{K}_2\text{O-}2\text{CuO}$
Cu_{15}	$38\text{SiO}_2\text{-}30\text{B}_2\text{O}_3\text{-}15\text{Na}_2\text{O-}15\text{K}_2\text{O-}2\text{CuO}$
Cu_{20}	$38\text{SiO}_2\text{-}30\text{B}_2\text{O}_3\text{-}20\text{Na}_2\text{O-}10\text{K}_2\text{O-}2\text{CuO}$
Cu_{25}	$38\text{SiO}_2\text{-}30\text{B}_2\text{O}_3\text{-}25\text{Na}_2\text{O-}5\text{K}_2\text{O-}2\text{CuO}$

Physical Parameters

Prepared glasses Physical properties are assessed utilizing density, molecular weights (M) of glass by traditional formulae⁸, which are specified in Table-2. From glass samples Cu_5 to Cu_{25} , the mol% of potassium (K^+) ions decrease by 5% and monovalent sodium ions replace potassium ions. Molar volume decreases due to the more electropositive potential of monovalent potassium ions compared with sodium ions. With this effect ionic concentration, the intensity of ionic Field increases and separation between ions and polaron radius decreases. The evaluated values of physical parameters are presented in Table-2. Making use of indirect band energies from Table-3, refractive index and Molar Polarizability and Metallization Criterion are also evaluated.⁹ $\frac{Rm}{Vm} < 1$ for all studied glasses indicates their nonmetallic nature. Metallization criterion M value is proportional to the material bandgap. Cu_{10} shows more ionic nature among the other studied glasses from $\frac{Rm}{Vm}$ values.

Table-2: Physical Parameters of $38\text{SiO}_2\text{-}30\text{B}_2\text{O}_3\text{-}x\text{Na}_2\text{O-(}30\text{-}x\text{)K}_2\text{O-}2\text{CuO}$ Glasses

Physical Parameter(units)	Glasscode				
	Cu_5	Cu_{10}	Cu_{15}	Cu_{20}	Cu_{25}
Average molecular weight (g/mol)	71.95	70.34	68.73	67.12	65.51
Density ρ (g/cm ³)	2.601	2.595	2.591	2.587	2.586
molar volume(cm ³)	27.9	27.1	26.5	25.9	25.3
Transition metal ion concentration	7.91	8.08	8.26	8.44	8.64
Inter ionic distance r_i (Å)	2.33	2.31	2.30	2.28	2.26
Polaron radius r_p (Å)	0.94	0.93	0.92	0.92	0.91
Field strength F (10 ¹⁵ cm ²)	2.27	2.30	2.33	2.37	2.41
Refractive index (at band edge)	1.75	1.78	1.75	1.76	1.75
Molar Refraction (Rm)	16.7	17.4	15.9	15.6	15.2
Molar Polarizability	6.60	6.91	6.32	6.21	6.04
$\frac{Rm}{Vm}$	0.601	0.643	0.601	0.603	0.601
Metallization Criterion (M)	0.397	0.357	0.399	0.397	0.399

Micro Structure Analysis Techniques

The XRD spectrum Fig.-1 of cupric ions doped glass Cu_{15} shows clearly it consists of the broad scattered band and no characteristic peaks. This ensures the non-crystallinity of the materials.

Fig.-1: XRD Spectra of Undoped 40SiO_2 - $30\text{B}_2\text{O}_3$ - $15\text{Na}_2\text{O}$ - $15\text{K}_2\text{O}$ Glass and CuO Doped Glass

In a comparison of SEM pictures (two sets of magnifications) in Fig.-2, the surface structure of undoped glass and Cu_{15} glass, it is noticed that the glass texture becomes rough by embedding CuO . This informs structural changes that may occur in the doped glass.

Fig.-2: (a), (b) 25 K times magnified SEM pictures of 40SiO_2 - $30\text{B}_2\text{O}_3$ - $15\text{Na}_2\text{O}$ - $15\text{K}_2\text{O}$ undoped and Cupric oxide doped glass (c), (d) 10,000 times enlarged SEM pictures of without cupric oxide and with cupric oxide glass.

EDX spectra (Energy Dispersive X-Ray spectroscopy) for Cu_{15} glass is shown in Fig.-3 all the elements present in glass and the elements weight% and atomic % are almost the same as the true composition and details are shown in Fig.-3.

Optical Bandgap Measurement

Both Optical Absorption and DRS (Diffuse Reflectance Spectroscopy) techniques are utilized to study the energy gaps that occur in the present glass samples.

Optical Absorption Technique

The Optical absorption spectra of Cu^{2+} ions in present glasses in the wavelength region $200\text{nm} - 1300\text{nm}$ are recorded in Fig.-4a. This spectrum reveals a lone intense wide-ranging band expected of ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$

transition in all glasses.^{10,11} This wide and asymmetric absorption band from 450nm – 900nm partially covers the other absorption bands. A slight nonlinear change in the peak position of the band is observed from Fig.-4a). This is due to the ligand field effect on central metal cation Cu^{2+} with a change in Na/K alkali ratio.

Fig.-3: EDX Spectrum of 38SiO₂-30B₂O₃- 15Na₂O-15K₂O-2CuO Glass

Applying, Tauc Optical absorption technique^{12,13} of noncrystalline materials, Tauc plots of absorption are drawn. The related Tauc plots of absorption data are depicted in Fig.-4b, 4c and 4d. In these plots, optical absorption coefficient $\alpha(\nu)$, optical band energies (for both direct, indirect transitions) are estimated with standard expressions which involve the glass thickness and absorbed photon intensity. $E_{\text{direct}} > E_{\text{indirect}}$ implies that the phonon-assisted oblique transitions need less energy compared with the vertical allowed photon transitions. Along with these energies, Urbach energy, the mean energy of defected states is also reported.

Cupric ion has 3d⁹ configuration. Cu^{2+} ion is 6-coordinated octahedral complex. The trans ligands on z-axis experience less force by nuclear charge and the ligands in x-y plane more. These two long bonds produce tetragonal elongation to Cu^{2+} ion octahedron structure. The Energy level picture of 3d⁹ electron is illustrated in Fig.-5 with the recorded transition in reported glasses.

DRS Technique

The Tauc plots of reflectance spectra are studied Using Kubelka – Munk function relations with scattering coefficient S and absorption spectroscopy band gap E_{opt} . The corresponding plots are shown in Fig.-6a, 6b, 6c, 6d. The band gaps deduced corresponding to both Reflectance and absorption spectra plots are found to be nearly equal. These values are tabulated in Table -3.

Table-3: Comparison of Optical Bandgaps from Absorbance and Reflectance Data

Glass Code	Absorbance Plots					Reflectance Plots		
	Band Position (nm)	Cut-off Wave Length (nanometer)	Direct Energy (electron volt)	Indirect Energy Gap (eV)	Urbach Energy (eV)	Direct Band Gap (eV)	Indirect Energy (eV)	Urbach Energy (electron Volt)
Cu ₅	816	416	3.34	3.15	0.28	3.4	3.01	0.33
Cu ₁₀	826	470	2.87	2.55	0.42	3.05	2.45	0.43
Cu ₁₅	796	390	3.44	3.19	0.29	3.5	3.20	0.34
Cu ₂₀	816	440	3.37	3.15	0.35	3.3	2.93	0.32
Cu ₂₅	814	393	3.43	3.18	0.31	3.5	3.27	0.32

Fig.-4: (a) Absorption spectra of 38SiO₂-30B₂O₃- xNa₂O-(30-x)K₂O-2CuO glasses; Tauc absorption graphs to evaluate (b) direct energy gaps ;(c) indirect energy gaps ; (d) Urbach energy of 38SiO₂-30B₂O₃- xNa₂O-(30-x)K₂O-2CuO reported glasses

Fig.-5: Energy Level picture of 3d⁹ electron in octahedral and tetragonal crystal field

From the Table-3 it is understood that among the glasses studied, the direct and indirect bandgaps are minimum and Urbach energy is maximum for Cu₁₀ glass. Also, the data shows nonlinear variation in bandgap energies in the studied glasses. It is because of the change in NBO with variation in alkali ratio (Na/K). These observations strengthen that the structural changes of glass due to the mixed alkali phenomenon. Similar reports have been observed in other host glasses also.^{14,15}

Photoluminescence Studies

When oxide glasses are excited by UV radiation, charge transfer bands are formed due to oxygen ligands around the cation. The Charge transfer from ligand to metal results in emission bands. All the present

glasses detect invisible radiation, provided if they are exposed to radiation of wavelengths at 250 nm and 820 nm and are shown in Fig.-7.

By exciting with UV radiation blue emission centers at 452 nm and 470 nm are found for all studied glasses. When excited in the infrared region at 820 nm wavelength corresponding to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition, red luminescence is observed. Blue and red emissions are reported in copper doped glasses earlier also.^{16,17} Hence these glasses are useful as invisible radiation sensor materials. Also, the present glasses could be employed in display technology.

Fig.-6:(a) Reflectance spectra of 38SiO₂-30B₂O₃- xNa₂O-(30-x)K₂O-2CuO glasses ;Tauc Plots to calculate (b) direct energy bandgaps ; (c) indirect energy bandgaps ; (d) Urbach energy of 38SiO₂-30B₂O₃- xNa₂O-(30-x)K₂O-2CuO glasses using Kubelka- Munk function

EPR Spectra

EPR technique is employed to understand the arrangement of the ligands on Cu²⁺ ions and the covalent nature of the metal-ligand bonds in glasses. The association of electron spin with the spin of the copper nucleus ($I = \frac{3}{2}$), a four-line hyperfine splitting is observed and is conveyed through Fig.-8(a). In the studied glasses in between 200 – 300 mT applied magnetic field three parallel components are observed and the last parallel peak is partly covered with perpendicular peak. The Perpendicular signal components formed between 320-340 mT are not resolved well. EPR spectral lines are broadened because of the more dipolar interaction of Cu²⁺ with ligands, which may be because of a higher concentration of Cu²⁺ ions.

The computed g-factors show that $g_{\parallel} > g_{\perp} > g_e (2.0023)$. This recommends that the octahedral site of Cu^{2+} ion has tetragonal elongation due to Z-out john – Teller distortion and the ground state is ${}^2B_{1g}$ ($d_{x^2-y^2}$). Spin- Hamiltonian for paramagnetic ions of EPR spectra is interpreted by Abragam and Pryce¹⁸. Bleany and Abragam gave an expression for spin Hamiltonian $\hat{H}$ for a paramagnetic ion in tetragonal axial distortion along the z-axis in EPR spectra as in expression (1).¹⁹

$$\hat{H} = \beta_e g_{\parallel} B_z S_z + \beta_e g_{\perp} (B_x S_x + B_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (I_x S_x + I_y S_y) \quad (1)$$

Fig.-7: Photo luminescence spectrum of $38\text{SiO}_2\text{-}30\text{B}_2\text{O}_3\text{-}x\text{Na}_2\text{O}\text{-(}30\text{-}x\text{)K}_2\text{O-}2\text{CuO}$ glasses (a) at excitation wavelength 800nm ; (b) at excitation wavelength 250nm

Perturbation due to ligand field leads to nonlinear deviation in Spin Hamiltonian parameters in studied glasses. g value depends on the local magnetic field and it differs from unpaired electron $g_e = 2.0023$ for transition metals because of their large spin-orbit coupling constant λ and of their low transitional energies from which we get information about ligand – central metal atom bond. In copper complexes, g shift was positive due to their filled orbitals. The degree of tetragonal distortion was calculated by a parameter G.

$$G = \frac{g_{\parallel} - g_e}{g_{\perp} - g_e} \quad (2)$$

G magnitude is nearer to 5 in studied glasses suggests strong magnetic coupling among non-equivalent Cu^{2+} ions. Less degree of tetragonal distortion means the axial ligands do not move much away from d_{xy} & d_{xz}, d_{yz} ; orbitals of central metal ion and so E_{xy} and E_{xz}, yz energies increase. ΔE_{xy} and ΔE_{xz} are $E_{xy} \rightarrow E_{x^2-y^2}$ and $E_{xz}, yz \rightarrow E_{x^2-y^2}$ transition energies respectively.^{20,21}

P is Dipolar distortion constant and κ is Fermi contact term. These two parameters are measures of anisotropic and isotropic interactions of electrons magnetic moment with the nucleus magnetic moment.²²

$$P = 2\gamma_{\text{Cu}}\beta_o\beta_N(r^{-3}) = 0.036 \text{ cm}^{-1} \quad (3)$$

Here, copper ion magnetic moment is denoted as γ_{Cu} , Bohr magneton with β_o , nuclear magneton with β_N and the separation from the nucleus center to the outer electron with r.

κ quantifies a part of the hyperfine splitting induced by 's' electrons because of the symmetric orbital shape and closest position of s- orbital to the nucleus.

$$\kappa = \left(\frac{A_{\text{iso}}}{P}\right) + \Delta g_{\text{iso}} \quad (4)$$

$$g_{\text{iso}} = \frac{(2g_{\perp} + g_{\parallel})}{3} \quad (4.1)$$

$$A_{\text{iso}} = \frac{(2A_{\perp} + A_{\parallel})}{3} \quad (4.2)$$

And $\Delta g_{\text{iso}} = g_{\text{iso}} - g_e$, and $g_e = 2.0023$ (free electron).

The calculated value of $\kappa \sim 0.31$, coincides with the standard value of κ in copper complexes and it is an independent property of Cu^{2+} ion. The calculated values of spin-Hamiltonian parameters and bonding coefficients are indicated in Table-4.

Table-4: Spin Hamiltonian Parameters and Molecular Orbital Coefficients

GlassCode	$g_{\parallel}$	$A_{\parallel}$	$g_{\perp}$	$A_{\perp}$	G	α^2	β_1^2	β^2	κ	Γ_{σ}	Γ_{Π}
		10^{-4} cm^{-1}		10^{-4} cm^{-1}							
Cu ₅	2.23	141	2.05	33	4.7	0.68	0.31	1.2	0.31	127	62.8
Cu ₁₀	2.3	125	2.05	37	6.2	0.70	0.38	1.1	0.30	123	64.8
Cu ₁₅	2.28	139	2.05	30	5.7	0.72	0.36	1.1	0.31	128	61.0
Cu ₂₀	2.29	133	2.05	25	6.1	0.72	0.37	1.1	0.30	125	60.4
Cu ₂₅	2.27	135	2.05	26	5.6	0.70	0.35	1.1	0.29	129	64.7

Covalent Nature of Metal-Ligand Bond

Spin Hamiltonian parameters of paramagnetic ions depend on separation between electrons and nuclei. This decides the nature of the bonds between transition metal ions and the ligands. Using hyperfine splitting parameters molecular bonding coefficient α^2 is calculated by Kuska's formula.²³

$$\alpha^2 = \frac{7}{6} \left\{ \left(\frac{A_{\parallel}}{P} \right) + (g_{\parallel} - g_e) + \frac{3}{7} (g_{\perp} - g_e) + 0.04 \right\} \quad (5)$$

The Spin Hamiltonian splitting parameters are correlated with electron energy levels measured from optical absorption data. This gives information about the interaction of central molecular ion Cu^{2+} with its chemical environment.²⁴ Using Klonkowski formulae the bonding parameters β_1^2 and β^2 are calculated.²⁵

$$g_{\parallel} = g_e \left[1 - \frac{4\alpha^2 \beta_1^2 \lambda}{\Delta E_{xy}} \right] \quad (6)$$

$$g_{\perp} = g_e \left[1 - \frac{\alpha^2 \beta^2 \lambda}{\Delta E_{xz,yz}} \right] \quad (7)$$

Figure-8(b) depicts the variation of covalent nature of ligand-metal bond with alkali ratio. The normalized covalencies Γ_{σ} , Γ_{Π} of Cu^{2+} -O inplane σ - and inplane Π - bonds are calculated using formulas (12), (13) given below. Γ_{Π} and Γ_{σ} are proportional to the covalent nature of Cu^{2+} - O bond.

$$\Gamma_{\sigma} = \frac{200(1-S)(1-\alpha^2)}{1-2S} \% \quad (8)$$

$$\Gamma_{\Pi} = 200(1 - \beta_1^2) \% \quad (9)$$

Where $S = 0.076$ is overlap integral and is due to the overlap of copper $d_{x^2-y^2}$ orbital with ligand orbitals. The SHP and distortion parameters P , κ from EPR spectra and bonding parameters are calculated correlating with absorption spectrum and values are tabulated in Table-4 and all resemble the values obtained in previous studies on Cu^{2+} doped glasses.²⁶⁻²⁹ From the calculated metal-ligand wave functions α^2 , β_1^2 , β^2 it is found that the in-plane σ - bond and inplane Π bond formed among transition metal ion-ion and the ligands is moderately covalent and out of a plane Π - bonding is ionic respectively. The lower value of $\alpha^2 > 0.5$ suggests that the electrons in $d_{x^2-y^2}$ orbital are more localized on copper atom than ligand and in plane σ bond among Copper ion and the ligands is moderately covalent. Similarly $\beta^2 < 0.5$ indicates d_{xy} electrons are more shared by ligand orbitals than a metal atom. The low value of $\alpha^2 = 0.68$, $\beta^2 = 0.31$ for Cu₅ than other glasses of this series indicate better covalency of bonds in this glass and less z-out tetragonal distortion. This is also supported by the low value of tetragonal distortion measure G

= 4.7 for Cu₅. Similarly higher tetragonal elongation of Cu₁₀ is also explained by more localization of d_{x²-y²} orbital on metal atom ($\alpha^2 = 0.70$) and d_{xy} electrons ($\beta^2 = 0.38$) than other glasses of this series. So Cu₁₀ is more ionic, this is also strengthened from the metallization criterion values evaluated in Table 3. Higher normalized covalency Γ_σ and low Γ_Π for Cu₁₀ also confirms the same.

These results suggest MAE phenomenon in present glasses. From the calculated metal-ligand wave functions α^2 , β_1^2 , β^2 it is found that the in-plane σ - bond and in-plane Π - bonding between Copper ion and its ligands is moderately covalent and out of a plane Π - bonding is ionic respectively.

Fig.-8: (a) EPR spectra of Cu²⁺ ion of 38SiO₂-30B₂O₃- xNa₂O-(30-x)K₂O-2CuO glasses
(b) Dependence of ionic nature on tetragonal distortion ($G = \frac{\Delta g_{||}}{\Delta g_{\perp}}$)

Vibrational Spectra of Glasses

Using vibrational spectra, structural groups present in glasses can be known. Infrared spectra of materials are sketched in the region 400-4000cm⁻¹. The bands present in our investigating glasses are represented in Fig.-9 and the assigned bands in Table-5.

The band centers at 450 and 470 cm⁻¹ in FTIR spectra indicate the existence of SiO₄ tetrahedra.^{30,31} The presence of Silica phase (SiO₄ tetrahedra) in glass indicates less corrosiveness of studied glasses. Due to high alkali content (30%) boroxol rings are replaced by other borate structural units. This was evident by the replacement of the band at 808 cm⁻¹ with 720 cm⁻¹ band. The presence of asymmetric stretching vibration bonds of (BO₃)³⁻ entities of pyro borates³⁰ is also revealed by the band centers at 875 cm⁻¹, 1265cm⁻¹, 1415-1453 cm⁻¹. Asymmetric vibrational modes of SiO₄ with one NBO are also confirmed by the bands at 1020 and 1050cm⁻¹. Weak Si-O-B band at 670 cm⁻¹ also informs boron ions are not incorporated much in silica network.^{31,32}

Table-5: Wavenumber assignment to infrared transmittance band of 38SiO₂-30B₂O₃ - xNa₂O-(30-x) K₂O-2CuO glasses (x = 5,10,15,20,25)

S. No.	Centre of Band Position	Assigned Band
1	455, 470	Si-O-Si symmetric vibrations of SiO ₄ tetrahedra
2	670	bending vibration of B - O-Si
3	720	bending mode of B -O-B center
4	875	stretching vibrations of tetrahedral BO ₄ ⁻ units
5	1020	SiO ₄ with one NBO
6	1415-1453	antisymmetric stretching vibration of BO ₃

Fig.-9: FTIR spectra of 38SiO₂ - 30B₂O₃ - xNa₂O - (30-x) K₂O - 2CuO glasses

CONCLUSION

The studied non-crystalline glassy materials surface smoothness decreases with doping Cu²⁺ ions. This indicates there is a change in the structure of glass by doping transition metal ions. The glasses may have good ductile nature because of their large supercooled liquid range $\Delta T_c = 189^\circ\text{C}$. Nonlinear variation in bandgaps is observed due to the Mixed Alkali Effect phenomenon. Metallization criterion values indicate these inorganic glasses are non-metals and Cu₁₀ glass is less covalent than other glasses. The studied glasses exhibit blue and red fluorescence when excited in UV region and IR region respectively. The Hamiltonian parameters confirm the tetragonal elongated octahedron site of Cu²⁺ ion. The bonding parameters α^2 , β_1^2 estimate that the in-plane σ - bond and in plane Π bonding among Copper ion and the ligands is moderately covalent. The trend of $\frac{R_m}{V_m}$ which measures the metallic nature of glasses obtained from bandgaps is similar to the tetragonal distortion. FTIR spectra identify the vibrational bands corresponding to various structural groups of borate BO₄ tetrahedra, BO₃ triangles, B-O-Si linkages and also of vitreous Silica phase in studied glasses.

REFERENCES

1. Weidong Xiang, Haihong Gao, Li Ma, Xin Ma, Yunyun Huang, Lang Pei and Xiaojuan Liang, *ACS Applied Materials and Interfaces*, **7(19)**, 10162 (2015), <https://doi.org/10.1021/acsami.5b00218>
2. Francesco Baino, Sepideh Hamzehlou and Saeid Kargozar, *Functional Biomaterials*, **9(1)**, 25 (2018), <https://doi.org/10.3390/jfb9010025>
3. F. Foroutan, J. McGuire, P. Gupta, A. Nikolaou, B.A. Kyffin, N.L. Kelly, J.V. Hanna, J. Gutierrez-Merino, J.C. Knowles, S.Y. Baek and E. Vellio, *ACS Biomaterials Science & Engineering*, **5(11)**, 6054 (2019), <https://doi.org/10.1021/acsbiomaterials.9b01291>
4. R. W. Frei, Research of the National Bureau Standards. Section A. *Physics and Chemistry*, **80A(4)**, (1976), <https://doi.org/10.6028/jres.080A.055>
5. A. Escobedo-Morales, M. de L. Ruiz-Peralta, L. Tepech-Carrillo, M. Sánchez-Cantú, and J.E. Moreno-Orea, *Heliyon*, **5**, e01505 (2019), <https://doi.org/10.1016/j.heliyon.2019.e01505>
6. Li Yang and B. Kruse, *Journal of the Optical Society of America*, **21(10)**, 1933 (2004).
7. M. Rajesh Yadav, B. Jaya Raja, M. Avinash, Ch. Rama Krishna and R. V. S. S. N. Ravikumar, *Materials Science: Materials in Electronics*, **27**, 1318 (2016), <https://doi.org/10.1007/s10854-015-3892-4>

8. F. Auzel, spectroscopy of solid state lasers, Plenum Press, Newyork (1987), https://doi.org/10.1007/978-1-4613-0899-7_10
9. J. A. Duffy, *Journal of Solid State Chemistry*, **62(2)**, 145(1986), [https://doi.org/10.1016/0022-4596\(86\)90225-2](https://doi.org/10.1016/0022-4596(86)90225-2)
10. O.I .Sallam, A. Abdeldaym, and F.M. Ezz-Eldin, *Materials Chemistry and Physics*, **252**, 123241(2020), <https://doi.org/10.1016/j.matchemphys.2020.123241>
11. B. Ashok, A . Hameed, B. Srinivas , , G. Ramdevudu and , M .N Chary, *i-Manager's Journal on Material Science*, **8(2)**, 9 (2020).
12. J. Tauc, R. Grigoroviceand A. Vancu, *Physica Status Solidi (b)*, **15**, 627(1996), <https://doi.org/10.1002/pssb.19660150224>
13. E.A. Davis and N.F. Mott, *ThePhilosophical Magazine: A Journal of Theoretical Experimental and Applied Physics*, **23**, 2500(1970) , <https://doi.org/10.1080/14786437008221061>
14. S. Kojima, *Solids* , **1(1)**, 16 (2020), <https://doi.org/10.3390/solids1010003>
15. C. Calahoo, Y.Xia, R. Zhou, *International Journal of Applied Glass Science*, **11(3)**, 396 (2020).
16. R. Hashikawa, Y. Fujii, A. Kinomura, T. Saito, A. Okada , T. Wakasugi, K. Kadono, *Journal of the American Ceramic Society*, **102(4)**,1642(2019).
17. M.A. Ouis, M.A.Marzouk, *Journal of Luminescence*, **1(223)**, 117242(2020).
18. A. Abragam and M.H.L. Pryce, *Proceedings of The Royal SocietyA*, **205**, 135(1951), <https://doi.org/10.1098/rspa.1951.0022>
19. B. Bleaney and A. Abragam, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford p. 650 (2013).
20. Chee Chow, Kun Chang and R.D. Willet, *Chemical Physics*, **59**, 2629(1973), <https://doi.org/10.1063/1.1680380>
21. D. Kivelson and R. Neiman, *Chemical Physics*, **35**, 145(1961), <https://doi.org/10.1063/1.1731880>
22. G. Fuxi, *Optical Spectroscopic Properties of Glass* (Berlin; Springer) 1992.
23. H.A. Kuska, M.T. Rogers and R.E. Durringer, *Physics and Chemistry*, **71(1)**, 109(1967), <https://doi.org/10.1021/j100860a015>
24. R.M. Krishna and S.K. Gupta, *Bulletin of Magnetic Resonance*, **16(3-4)**, 239(1994).
25. A. Klonkowski, *Physics and Chemistry of Glasses*, **24**, 166(1983), [https://doi.org/10.1016/S0022-3093\(87\)80134-5](https://doi.org/10.1016/S0022-3093(87)80134-5)
26. A.K. Maki and B.R. McGarvey, *Chemical Physics*, **29**, 31(1958), <https://doi.org/10.1063/1.1744456>
27. V. Kumar Chavan, M. Sreenivasulu, and B.R.V. Rao, *Optik*, **221**, 16529(2020), <https://doi.org/10.1016/j.ijleo.2020.165291>
28. O.I. Sallam, A. Alhodaib, S. Abd El Aal, and F.M. Ezz-Eldin , *Inorganic Chemistry Communications*, **124**, 108388(2021), <https://doi.org/10.1016/j.inoche.2020.108388>
29. J.S. Krishna, D.S. Raju, V.V. Krishna, and C. L. Raju, In Proceedings of international Conference on Research Frontiers in Sciences (ICRFS 2021) 5th-6th February 2021, Nagpur, India, *Journal of Physics: Conference Series*, IOP Publishing, 1913(1), 012013(2021).
30. W. B. White, S. A. Brawer, T. Furukawa and G.J. McCarthy, Structure of Borate Glasses by Raman Spectroscopy, in: L.D. Pye ,V. D. Frechette and N.J. Kreidl, (Eds), *Borate Glasses. Materials Science Research*, Vol 12. Springer, Boston, MA, pp. 281-296 (1978), https://doi.org/10.1007/978-1-4684-3357-9_12
31. B. Nagamani and Ch. Srinivasu, *Material Research Express* , **7(1)**, 015207(2020), <http://dx.doi.org/10.1088/2053-1591/ab67f6>
32. W. L. Konijnendijk and J. M. Stevels, *Non-Crystalline Solids*, **18**, 307(1975), [https://doi.org/10.1016/0022-3093\(75\)90137-4](https://doi.org/10.1016/0022-3093(75)90137-4)

[RJC-5757/2020]