



OPTICAL AND EPR STUDIES ON BARIUM ZINC SODIUM TETRABORATE GLASSES MODIFIED WITH Cu^{2+} IONS

¹M. Sreepad, K. Chandra Sekhar², Md. Shareefuddin³, G. Pushpa Chakrapani¹

¹Department of Physics, Dr. B. R. Ambedkar Open University, Hyderabad, Telangana, 500033, India

²Department of Physics, University College of Science, Saifabad, Osmania University, Hyderabad, Telangana, 500004, India.

³Department of Physics, University College of Science, Osmania University, Hyderabad, Telangana, 500007, India

Corresponding author mail: pushpanig@gmail.com, msreepad1980@gmail.com

In the present work, the authors prepared the glasses with the chemicals, BaO, ZnO, CuO and $\text{Na}_2\text{B}_4\text{O}_7$ in which CuO is used as probe for getting EPR signal and to evaluate the ligand field environment around the Cu^{2+} ion. The sample were prepared with the compositional formula $x \text{ BaO} - 10 \text{ ZnO} - 1 \text{ CuO} - (89-x) \text{ Na}_2\text{B}_4\text{O}_7$ in which $x = 0, 10, 20, 30$ & 40mol% using melt quenching method. The samples initially exposed to XRD spectra in the range 10 to 80degrees. The XRD spectra revealed no sharp peaks in the spectra that confirms the non-crystalline nature of the glass samples. The polished samples were next subjected to UV- Visible spectra in the wavelength range 200nm to 1200nm. All the absorption spectra shown similar kind and one broad absorption band is noticed for all the spectra of the samples. The absorption band is assigned to $^2\text{B}_{1g}$ to $^2\text{B}_{2g}$ transition. The calculated band gap values were clearly reduced from 3.457 eV to 2.679 eV. The decrease in the band gap values were ascribed to the enhancing the non bridging oxygen in the structure of the glasses. Urbach energy values were evaluated from Urbach plot and the evaluated values are smaller and hence the samples have less defects in the structure. Studies using electron paramagnetic resonance (EPR) are essential for comprehending the local composition and characteristics of glasses, especially when examining the context of coordination and oxidation state of paramagnetic ions (such as transition metals) doped within the glass matrix. By doing so, researchers examine the glass network at the atomic level and detect changes in the local environment based on the features of the EPR signals.

IndexTerms – Tetra borate glasses, optical band gap, Spin-Hamiltonian.

1. INTRODUCTION

Borate glasses offer several benefits especially when it concerns glass formers. Borate glasses have been shown to reduce thermal expansion, enhance toughness, endure thermal shocks, and offer excellent mechanical durability [1, 2]. Furthermore, the borate glasses' limited applicability in specific applications was caused by their weak chemical stability. To overcome this unwanted fault, oxides can be added to borate glasses to increase their chemical endurance. The addition of modifiers like ZnO, BaO greatly enhances the physicochemical characteristics of the borate network through two important scenarios [3, 4]. Given its affordability and environmental friendliness, zinc oxide is a worthy metal oxide to mix with sodium borate glasses. Additionally, ZnO serves as a former and/or modifier in the glass network.. Zinc borate glasses' unique qualities, made them suitable for a range of industrial uses [5, 6]. The capacity of borate glasses to produce BO_3 units is improved by the incorporation of alkaline earth metal oxides. Additionally, alkaline earth borate glasses are establishing themselves as attractive glassy solids for shielding against radiation and bioactive applications [7, 8]. Sodium tetra borate is another name for borax, which is a combination of Na_2O and B_2O_3 in a 1:2 ratio. In the so-called binary glass system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$, it is widely recognized that when Na_2O is added, BO_3 is changed into BO_4 units up until its mole percentage rises to one-third of the borate. When more Na_2O is added above this eutectic composition, BO_4 units become BO_3 . Sodium tetra borate is the glass that forms at the composition, which is 33.3 mol% Na_2O and 66.7 mol% B_2O_3 [9, 10]. One of the TM ions that generate a basic EPR spectrum from which useful structural information about the copper ions' ligand surroundings can be obtained is the copper ion. A tiny amount of Cu^{2+} ions added to the glasses expands the potential uses in flipping and storage devices [11, 12]. Explaining how BaO affects spectroscopic analyses of glasses made with zinc and sodium with a Cu^{2+} spin probe is the innovative aspect of the current study. Thus, the sodium tetra borate glass system including BaO and ZnO doped with Cu^{2+} ions was the subject of extensive spectroscopic analyses in the current study. The following article presents the specifics of the composition-dependent analysis.

2. EXPERIMENTAL

2.1. Sample preparation

Glass samples with the following composition: $x\text{BaO}-10\text{ZnO}-1\text{CuO}-(89-x)\text{Na}_2\text{B}_4\text{O}_7$ and $0 \leq x \leq 40$ mole% were made by melt quenching. After combining the required amounts of analar-grade BaO, ZnO, CuO, and $\text{Na}_2\text{B}_4\text{O}_7$, the mixtures had been melted in a crucible made of porcelain in an electrically operated furnace for 45 minutes at a temperature of around 1100°C under normal atmospheric conditions. The glasses are formed by quenching the melt on a prepared stainless steel plate and then annealing them at a temperature 200 degrees Celsius below the glass transition point. The glass compositions are listed in Table 1. Glasses were then created by pressing the molten fluid onto a steel plate using a second plate. In order to relieve the tensions in the glasses, these specimens are additionally placed in a second furnace that is kept at 200°C .

2.2. Characterization

After the BZCN samples were prepared, they were subjected to XRD spectra. The produced materials' crystalline or non-crystalline nature can be determined from the XRD spectrum. The spectra are required to demonstrate the materials' amorphous nature. At room temperature, X-ray diffraction spectra in the range of 10° to 80° were recorded using the Philips Xpert Pro X Ray Diffractometer. Additionally, UV-Vis spectra were applied to the polished samples. Absorption spectra are used to determine the band gap, Urbach energy, and refractive index in addition to providing the absorption bands present in the spectra associated with the TMI. Using a JASCO V-670 UV-VIS spectrophotometer, the optical absorption spectra of the glasses were recorded between 200 and 1000 nm. EPR spectra were used to know about the environment around the TMI in the glass structure. Using a BRUKER EPR spectrometer set to operate at 9.7 GHz with a modulating frequency of 100 KHz, the EPR spectra of the glass samples were captured at ambient temperature. The atmosphere surrounding the TMI in the glass structure was ascertained using EPR spectra.

3. RESULTS AND DISCUSSION.

3.1. X-Ray Diffraction.

XRD is a helpful instrument for the growth of research in the glass industry since it can be used to understand the fundamental properties of glasses and develop new materials. XRD can be used to identify and characterize any crystalline states or particles that might be embedded in bulk glass and cause defects or alters the properties of the glass. XRD studies, especially high-energy XRD, can show the short- and medium-range atomic arrangements in glass-forming liquids and glasses that influence their properties like viscosity and crystal nucleation. Each glass system's X-ray diffraction spectra was analyzed; the lack of distinct, sharp peaks indicated that the glasses were amorphous. The current glasses' X-ray diffraction patterns are shown in Fig. 1.

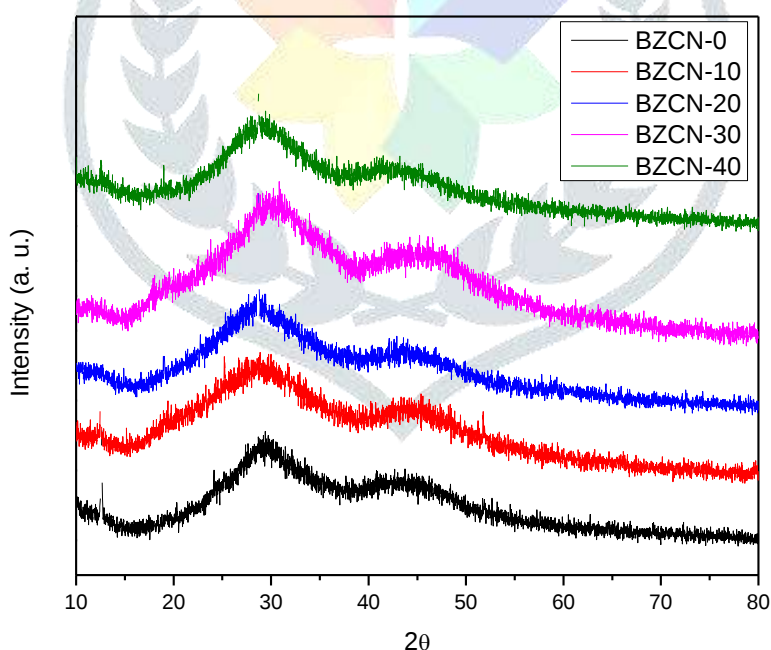


Figure 1 XRD spectra of BZCN glasses

3.2. UV Measurements.

Knowledge regarding the chemical circumstances of glass ingredients, such as the existence and quantity of dopants or impurities, can be obtained via UV-Vis spectroscopy. Additionally, it can assist in detecting modifications to the glassy network architecture brought on by irradiation, doping, or other processes. Additionally, it can be used to describe the hue of glasses, which is frequently associated with the presence of specific impurities called dopants. Numerous glass types and formulations can be studied using it.

Table 1 Glass composition, optical band gap (eV), Urbach energy (eV), and refractive index

Glass	Composition (Mole %)				E_{opt}		$\Delta E(eV)$	n
	BaO	ZnO	CuO	$Na_2B_4O_7$				
BZCN-0	0	10	1	89	3.457		0.2542	2.2838
BZCN-10	10	10	1	79	0.2776		2.3014	75.33
BZCN-20	20	10	1	69	3.191		0.2666	2.3475
BZCN-30	30	10	1	59	3.125		0.2489	2.3642
BZCN-40	40	10	1	49	2.679		0.5792	2.4894

Figure 2 displays the optical absorption spectra of each manufactured glass sample. The produced glasses' amorphous nature is confirmed by the lack of a distinct optical absorption edge.

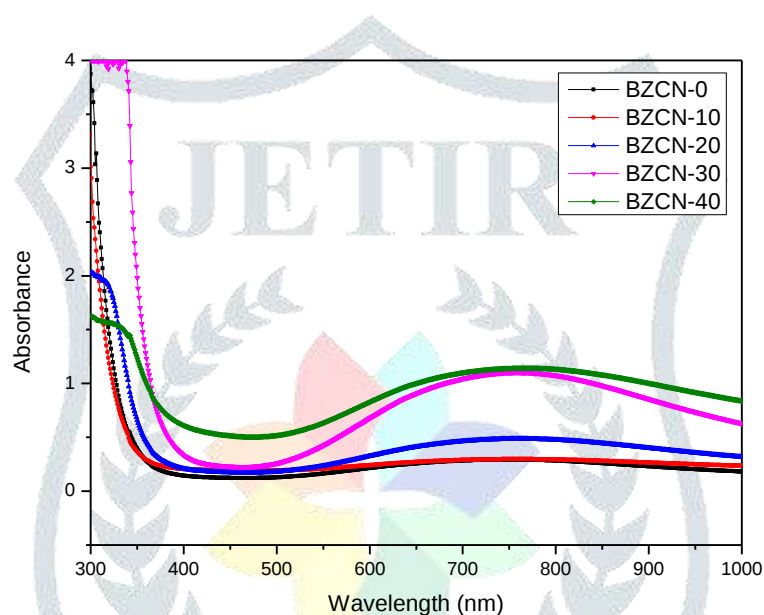


Fig 2 Optical absorption spectra of BZCN glasses

For amorphous materials, Davis and Mott presented the following relation: for both direct and indirect transitions, the absorption coefficient $\alpha(\nu)$ is a function of photon energy ($h\nu$) [13].

$$\alpha(\nu) = B(h\nu - E_{opt})^2 / h\nu \quad (1)$$

Where E_{opt} is the optical band gap, [14]. Table 1 displays the values of E_g , which are derived by projecting the linear portion of the curve to the ($h\nu$) axis, or $(\alpha h\nu)^{1/2} = 0$ for indirect transitions.

It became apparent that when the BaO mole% increased, the obtained band gap values for BZCN glasses decreased from 3.457 to 2.679 eV. This decline indicates the structural alterations taking place in the glass. Generally speaking, the production of bridging oxygens (BOs) and non-bridging oxygens (NBOs) is responsible for the change in the band gap. When BAO is added to sodium tetra borate glasses, it may increase the production of NBOs, which could further reduce the band gap values for BZCN glasses. The same explanation explains why the E_{opt} values for the samples in Fig. 3 tend to decrease as the BaO content rises. It is evident that the composition has a significant impact on the E_{opt} value. By calculating the reciprocal of the slopes of the linear component of the curves, the ΔE values are calculated from the Urbach's plots of $\ln(\alpha)$ vs ($h\nu$) and are shown in Table 1[15]. Figure 4 displays the change in Urbach energy (ΔE) with BaO concentration. The Urbach energy changes nonlinearly as the BaO content rises. The BZCN glasses have lower levels of glass structural flaws, as indicated by their Urbach's energy values, which vary from 0.2542 to 0.5792 eV

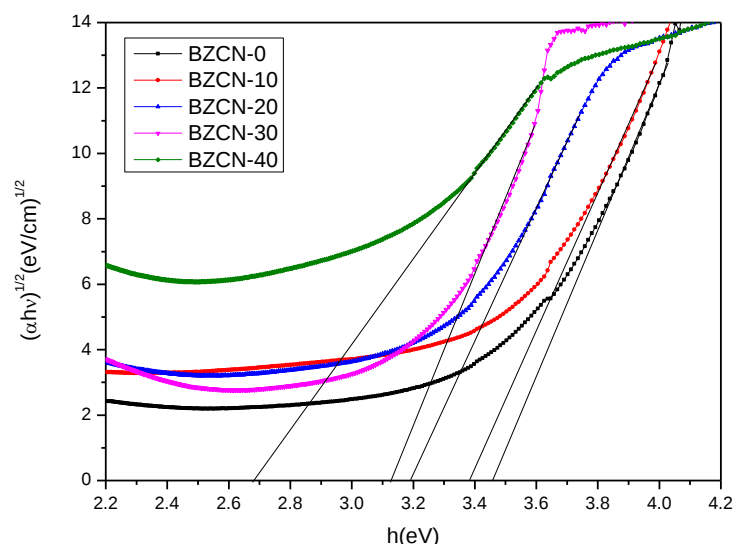


Fig 3. Tauc plots of BZCN glasses

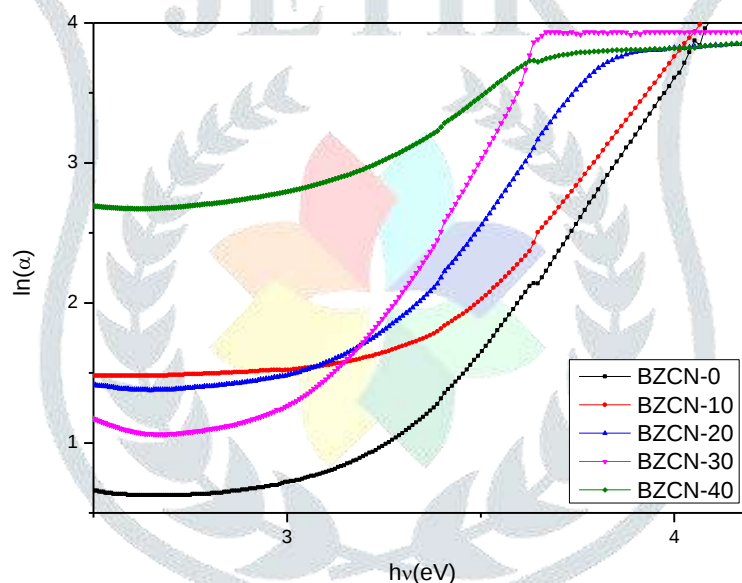


Fig 4. Urbach plot of the BZCN glasses

3.3. EPR spectra

Because of its exceptional sensitivity, EPR spectroscopy may identify minimal quantities of paramagnetic species—molecules or ions having a single electron that is unpaired. EPR aids in the research concerning semiconductor and coated properties as well as the characterization of material flaws such as oxygen vacant spaces in nanomaterials. Due to its high sensitivity, EPR can detect even minute levels of paramagnetic species. The primary goal of this effort is to understand the structure around the copper ions in the BZCN glasses. The EPR spectra of every BZCN glass are displayed in Figure 5. All these different spectra showed three distinct and noticeable parallel signals, as well as the predicted resonance signal. However, because it is combined together with the predicted four perpendicular signals that are visible in the large resonance trace in the spectra, the predicted fourth parallel signal is unclear and cannot be detected. A few key physical parameters must be computed in order to obtain additional information on the TMI environment. The parameters influencing EPR spectra are examined using the spin-Hamiltonian (SHP) approach [3, 11].

$$\mathcal{H} = \beta[g_{\parallel}H_ZS_Z + g_{\perp}(H_XS_X + H_YS_Y)] + A_{\parallel}I_ZS_Z + A_{\perp}(I_XS_X + I_YS_Y) \quad (2)$$

The SHP of BZCN glasses have been investigated and are shown in **Table 2**. The surroundings free condition is typically shown by the free electron's $g = 2.0023$. The g value will shift from the pure g value to an alternative one if the ligand field influences it. In this instance, $g_{\parallel}$ values range from 2.408 (BZCN-0) to 2.437 (BZCN-20), but $g_{\perp}$ values fall between 2.146 and 2.153. Whereas $A_{\perp}$ values varied from 22 cm⁻¹ to 32 cm⁻¹, $A_{\parallel}$ numbers fluctuated between 134 cm⁻¹ (BZCN-20) to 154 cm⁻¹ (BZCN-0). As far as we recognize, the $d_{x^2-y^2}$ orbital (2B_{1g} state) is the ground state of Cu²⁺ because the significance of $g_{\parallel}$ is bigger than that of $g_{\perp}$ ($g_{\parallel} > g_{\perp} > g_e$ ($g_e = 2.0023$)) and the quantity of $A_{\parallel}$ is higher for $A_{\perp}$ ($A_{\parallel} > A_{\perp}$) [16].

Table 2 Spin-Hamiltonian parameters, number of spins, susceptibility and bonding parameters of BLTC glasses

Glass	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (10^{-4} cm^{-1})	$A_{\perp}$ (10^{-4} cm^{-1})	ΔE_{xy}	α^2	β^2	β_1^2	$N (10^{22})$ per kg
BZCN-0	2.408	2.146	154	32	13280	0.938	0.574	0.866	1.614
BZCN-10	2.433	2.146	144	22	13157	0.936	0.581	0.912	1.438
BZCN-20	2.437	2.153	134	32	13154	0.916	0.593	0.941	1.429
BZCN-30	2.424	2.146	144	25	13422	0.928	0.574	0.921	1.441
BZCN-40	2.408	2.146	153	28	13089	0.938	0.583	0.854	1.526

The most significant bonding factors that are very helpful in describing the type of bond that occurs between the copper ions and their ligands are determined with the aid of UV and EPR data. Firstly the α^2 (in-plane σ -bonding) values observed from the table 2 that ranged between 0.916 (BZCN-20) and 0.938 (bzcN-40). These are all above 0.9 hence the nature banding can made as ionic. Secondly, β^2 (in-plane π -bonding) values ranged between 0.574 (BZCN-0) and 0.593 (BZCN-20). These are all under 0.6, with these numbers one can made conclusion that the bonding is covalent. Finally β_1^2 (out of plane π -bonding) numbers fall under 0.854 (BZCN-40) and 0.941 (BZCN-20), which gives the conclusion that the bonding is moderately ionic[3, 11]. Spin plays most important role in the magnetic resonance process hence it is required to find the number that participate in the spin (N). The same can obtained by the relation given by Weil et al[17]. Table 2 gives that the N values altering with BaO randomly in the order of 10^{22} per Kg.

4. CONCLUSIONS

CuO is employed as a probe to obtain an EPR signal and assess the ligand field environment around the Cu^{2+} ion in the glasses that the authors made in this work using the chemicals BaO, ZnO, CuO, and $\text{Na}_2\text{B}_4\text{O}_7$. Using the melt quenching process, the sample was generated using the compositional formula $x \text{ BaO} - 10 \text{ ZnO} - 1 \text{ CuO} - (89-x) \text{ Na}_2\text{B}_4\text{O}_7$, where $x = 0, 10, 20, 30 \text{ \& } 40 \text{ mol\%}$. The materials were first subjected to XRD spectra between 10 and 80 degrees. The absence of strong peaks in the XRD spectra supports the glass samples' non-crystalline character. Next, UV-visible spectra in the wavelength range of 200 nm to 1200 nm were applied to the polished samples. One broad absorption band is visible in all of the samples' spectra, and all of the absorption spectra displayed a similar kind. The 2B1g to 2B2g transition is identified as the absorption band. It was evident that the computed band gap values had decreased from 3.457 eV to 2.679 eV. The enhancement of the non-bridging oxygen in the glasses' structure was credited with lowering the band gap values. The samples have fewer structural flaws because the estimated Urbach energy values, which were derived from the Urbach plot, are smaller. The Cu^{2+} ions are tetragonally deformed in the octahedral configuration, according to the values of the spin-Hamiltonian parameters. First, the values of α^2 (in-plane σ -bonding) that were found in Table 2 varied from 0.916 to 0.938. Since all of these are higher than 0.9, the nature banding can be classified as ionic. The values of β^2 (in-plane π -bonding) varied from 0.574 to 0.593. Since all of these are less than 0.6, it may be concluded that the bonding is covalent. Out of plane π -bonding (β_1^2) numbers fall between 0.854 and 0.941, indicating a moderately ionic bonding.

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