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Density Related Physical And Optical Properties Of Li_2O Added Cao-Zno-B_2O_3 Glasses

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Abstract:
Quaternary glass system of composition xLi_2O-5CaO-20ZnO-(75-x)B_2O_3 (x=0, 5, 10, 15 and 20 mole %) was prepared by the conventional melt-quenching technique. The amorphous nature of the prepared glasses was confirmed by the X-ray diffraction studies. The density (ρ) of the glass samples was measured by Archimedes' principle and it was found to vary linearly between 2.42-2.68 g/cm^3 with the addition of Li_2O mole concentration. Oxygen packing density (OPD) values also varied non-linearly between 53.13-54.5 g.atm/l. The Optical spectra confirms the shifting of cut-off wavelength towards higher wavelengths confirms the creation of non-bridging oxygens with the addition of Li_2O into the base glass matrix. The optical band gap energies were decreased with the additive content. The refractive index increased with Li_2O content.
Key Words*: Density, Molar volume, XRD, UV-Vis. spectra, Structural studies*

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I. INTRODUCTION

B_2O_3 is a well-known glass former oxide, which exhibits low melting point and good thermal stability. Borate glasses are widely used for the fabrication of superionic conductors and in many industrial applications [**1**]. B_2O_3 glass network consists of BO_3 and BO_4 structural units. The combination of these structural units' forms diborate, triborate, tetra borate and Penta borate groups in the glass network [**2**]. Borate glasses also possess both significant short-range order (SRO) and intermediate range order (IRO) units in the glass network when B_2O_3 host network is modified with alkali oxide or divalent oxides such as Li_2O and MgO etc. [**3**]. Zinc oxide containing glasses exhibit good optical and structural properties due to their unique properties like higher density, Infrared transparency and refractive index [**5, 6**]. When ZnO acts as a glass network modifier, it breaks the base glass former bonds (like B-O-B) and forms non-bridging oxygen (NBO).

The metal oxide CaO acts like network modifier and its show hygroscopic nature. The hardness of the network increases with content of CaO content. It contains an ionic concentration of Ca^{+2} ions and it disturb the glassy network, resulting in structural depolymerization and also the creation of non-bridging oxygen atoms (NBO). Lithium oxide (Li_2O) is a glass network modifier and acts as a good ionic conductor. Lithium oxide (Li_2O) consists of Li^+ cations which influence the physical, electrical transport and structural properties of the glass network. When high Li_2O content is added to borate glass network, the tetrahedral BO_4 units converted into BO_3 units with the creation of non-bridging oxygen (NBO). The creation of non-bridging oxygen forms more ionic bonds, which results in higher ionic conductivity and higher refractive index values [**7**]. Li_2O containing glasses have been widely used in battery, solar cell and superionic conductor applications. The aim of the present work is to prepare the effect of Li_2O on the optical and physical, structural properties for battery and non-linear optical device applications.

II. EXPERIMENTAL

Preparation of glasses

Glass compositions of x Li_2O-5CaO-20ZnO-(75-x) B_2O_3 with x=0, 5, 10,15 and 20 mol% were synthesized by conventional melt quench technique. AR grade chemicals like H_3BO_3, ZnO, CaO and Li_2CO_3 were taken in powder form in the stoichiometric ratios and mixed in a platinum crucible. The crucible that containing the starting materials was kept in the electrical carbide rod furnace which is maintained at 1060^0C for 30min. The molten mixtures were thoroughly stirred to get homogeneity and poured on the metal mould at 200^0C and quenched with a metal disc to get transparent glass samples of the desired shape. The obtained glass samples were annealed at 300^0C for 12 hours in the temperature-controlled furnace to subtract thermal strains. The prepared glasses were kept inside the paraffin oil to avoid hygroscopic nature. Various experimental studies were carried out on the prepared glass samples.

characterization techniques

X-ray diffraction studies:

X-ray diffraction patterns of the glass system were recorded on diffractometer (Philips PW 1140) at the room temperature with k_α radiation (1.54 A^o) to confirm the amorphous nature of the glass samples. The XRD spectrographs were recorded with Bragg's angle (2θ) from 10^0 to 80^0 with count 0.2/sec.

Physical parameters (Density related)

The density (ρ) of the glasses was measured on VIBRA HT analytical balance by using Archimedes' principle with xylene (ρ=0.86 g/cm^3) as the immersion liquid according to the following relation.

$$\text{Density}(\rho) = \frac{p}{p-q} \text{ x } 0.863 \qquad (1)$$

Where p- weight of glass in air, q - weight of glass in xylene

The molar volume (V_m) and the Oxygen packing density (OPD) can be calculated from the following relations

$$\text{Molar volume}(V_m) = \frac{M}{\rho} \qquad (2)$$

$$\text{Oxygen packing density}(\text{OPD}) = \frac{1000\rho C}{M} \qquad (3)$$

Where M-Molecular weight, ρ-density and C- No. of oxygen atoms per unit formula

III. RESULTS AND DISCUSSION

X-ray diffraction studies

The XRD patterns of the present glass system are presented in **Fig.1**. The intensity of the diffracted X-rays was measured as a function of the angle of diffraction (θ). There were no sharp peaks observed in the XRD patterns. A broad hump obtained at 280 Bragg's angle (2θ) for all the glass samples. In the present study, appearance of the broad hump and absence of sharp peaks in the spectra reveal the amorphous nature of the glasses. It also reveals the lack of periodicity or long-range order which is the characteristic nature of localized structured glasses [8]. From the XRD spectra the nature of the prepared glass system was confirmed as amorphous.

Density

In the present glass system, the mole concentrations of CaO, ZnO are fixed and Li_2O percent increases whereas B_2O_3 mole fraction decreases. The density was found to increase from 2.42 g/cm^3 to 2.68 g/cm^3 linearly as shown in **Fig.2**. The increase in the density value may be due to the different molecular weight of Li_2O than the glass former B_2O_3 and modifier CaO in the glass network. It may also be attributed to the Differ crystalline density of Li_2O (2.01 g/cm^3) than that of B_2O_3 (3.11 g/cm^3). The molar volume of the glass system decreased from 47.06cm^3/mol to 38.9 cm^3/mol with the increase of Li_2O mole percentage. Effect of the density is more pronounced on molar volume than that of molecular weight. It may also decrease due to the compactness of the glassy network and absence of voids in the structure [**9**]. The density and molar volume both are showing opposite behavior. The oxygen packing density increases with the addition of Li_2O except Third Sample. Oxygen packing density increases due to the accumulation of more number of oxygen atoms in the glass network as the mole percentage of Li_2O increases. All the physical parameters of the present glass system are presented in the Table.1.

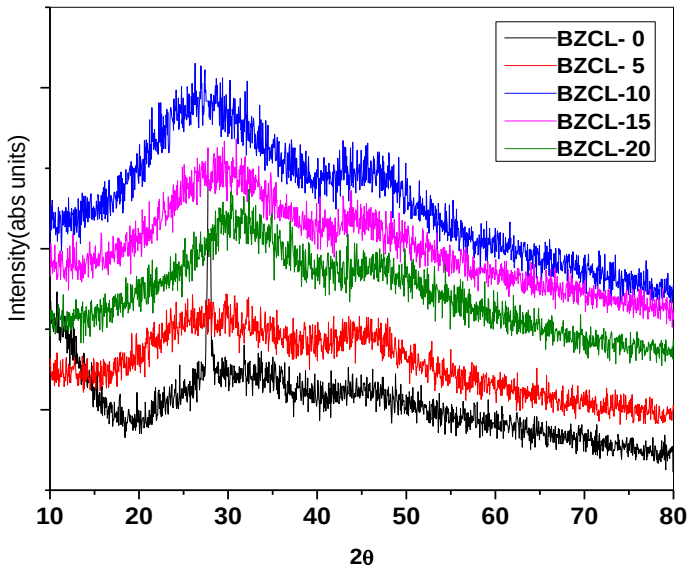

Fig.1.XRD spectra of BZCL glass system

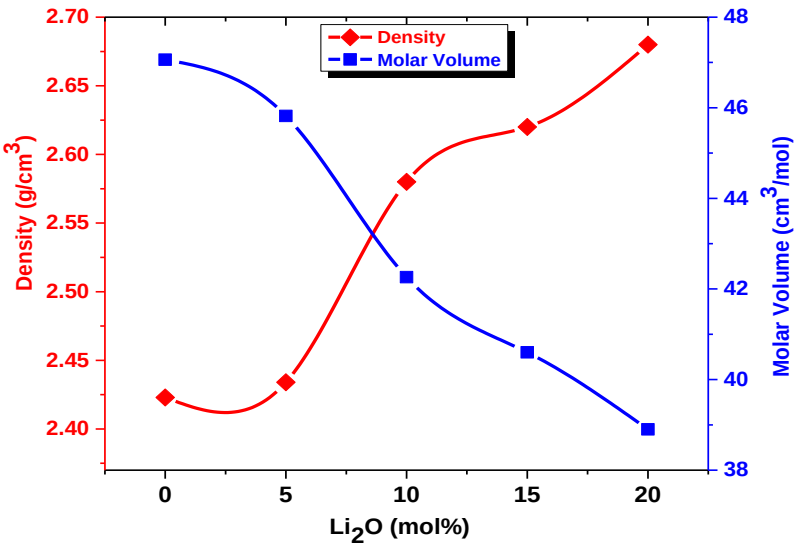

Fig.2.Variation of Density and Molar volume verses of BZCL glass system

TABLE. 1 Physical and optical properties of BZCL glass system

Properties	Li-0	Li-5	Li-10	Li-15	Li-20
Density (g/cm^3)	2.423	2.434	2.58	2.62	2.68
Molecular weight (g/mol)	114.03	111.54	109.05	106.5	104.07
Molar volume (cm^3/mol)	47.06	45.82	42.26	40.6	38.9
OPD (g atm/1)	53.13	52.71	54.5	54.1	54.12
Cut off wavelength (nm)	318	347	359	378	398
Indirect band gap energy (eV)	3.7	3.2	3	2.8	2.6
Direct band gap energy (eV)	4.7	4.2	4	3.7	3.4
Urbach energy(eV)	0.16	0.33	0.46	0.58	0.67
Molar refraction(cm/mol)	26.9	26.5	25.95	25.37	24.85
Refractive index	2.236	2.345	2.41	2.445	2.512
Electronic polarizability($*10^{-24}$ cm^{-3})	11.79	9.84	9.41	9.07	8.49

UV-Vis. absorption Spectra

UV-Vis. absorption spectra of the glass compositions xLi_2O -5CaO-20ZnO-(75-x) B_2O_3 with x=0, 5, 10,15 and 20 mol% with different mole fractions are shown in Fig.3. It is observed that the fundamental absorption edge is shifting towards higher wavelengths as the mole percentage of Li_2O increases. The shifting of λc towards higher values may be due to the creation of non-bridging oxygens (NBOs) which results in the lower rigidity of the glass system [10] as the concentration of Li_2O increases. The addition of Li_2O content into the glass network breaks the structure and causes the formation of bonds like Li-O-B or Li-O-Li bonds in the presence of network modifier CaO. In the present study, cut off wavelength of sample BZCL-20 is the highest (398nm). By adding Li_2O, the cut off wavelength suddenly falls down to 318nm for BZCL-0 sample, further, it goes on increasing. Cut-off wavelength varies between 318nm-398nm and shifts towards the higher wavelengths which is clear evidence of the creation of non-bridging oxygens (NBOs) in the glass system.

The indirect band gap values of the present system are obtained from the plots between hυ and $(\alpha h\upsilon)^{1/2}$ as shown in **Fig.4a**. The Indirect optical band gap energies increase from 2.6eV to 3.7 eV due to the creation of non-bridging oxygens. Generally, the direct band gap plots fit well at higher frequency range and the indirect band gap plots are good at the lower frequency range in amorphous materials such as polymers and glasses. The direct band gap energy values are greater than that of indirect band gap in the present system. The direct band gap can be calculated from the plots between hυ and $(\alpha h\upsilon)^2$ as shown in **Fig.4b**. The direct optical band gap energies decrease from 4.7eV to 3.4eV due to the creation of non-bridging oxygens. The shifting of direct and indirect band gap towards lower photon energies is a clear evidence for the creation of the non-bridging oxygens in the glass network[11-12].

The Urbach energy is a measurement of disorder in the glass network and hence the increase in Urbach energies confirms the increase of the disorderness in the glass [13]. Urbach plots of the present glass system shown in **Fig.5**. The Urbach energy is found to increase slightly and lie between 0.16-0.71 eV as the mole percentage of Li_2O is increased. The Urbach energy values of the present system are presented in the **Table.1.** The Urbach energy of sample BZCL-15 found to be the lowest through the system. It may be attributed to the structural rearrangement of the network modifiers [14-15].

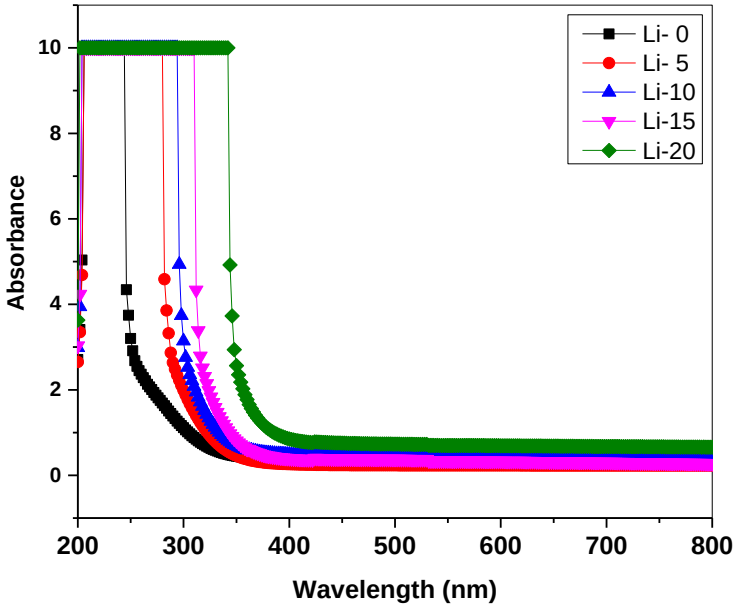

Fig.3.Optical spectra of BZCL glass system

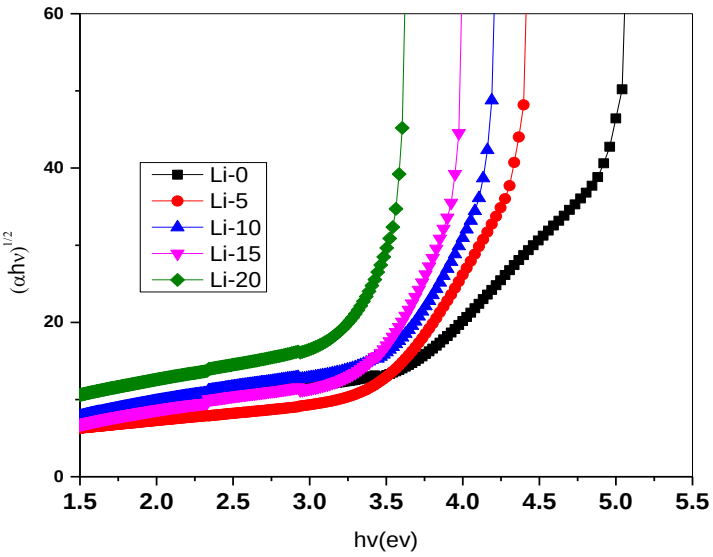

Fig.4a.Indirect band gap of BZCL glass system

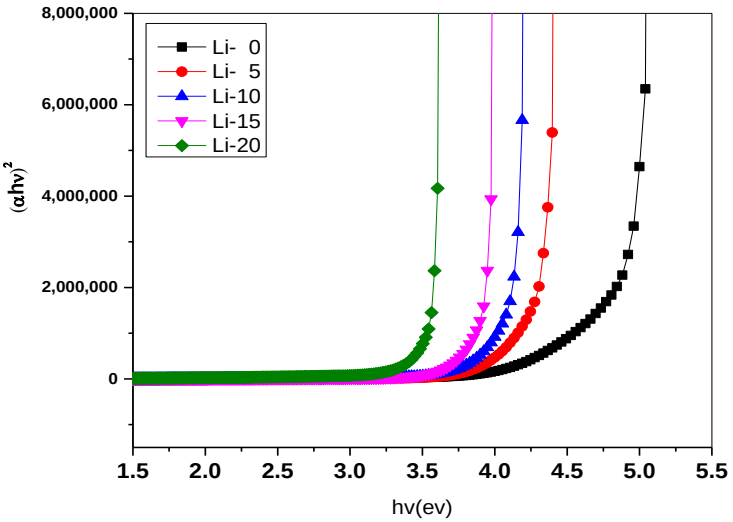

Fig.4b.Direct band gap of BZCL glass system

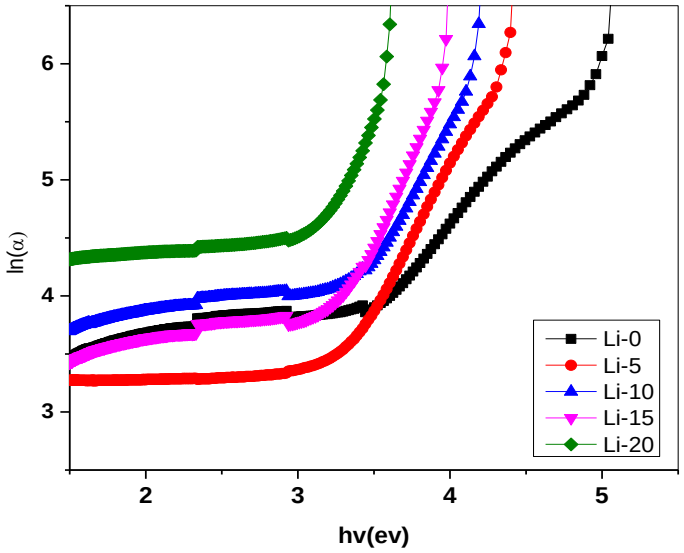

Fig.5.Urbach plots of BZCL glass system

When an alkali oxide like Li_2O is added to the pure borate glass, the basic structural BO_4 units convert into BO_3 units. The present system containing Li_2O and CaO causes the breaking of basic structural units and creates NBOs. It is evident that the increase of the disorderness or Urbach energy of the glass network depends on the creation of NBOs due to the conversion of BO_3 into BO_4 units [16].

Refractive index and molar refraction play a significant role in the glasses and closely related with the polarization process. The refractive index of the glass system varies between 2.236-2.512 and the molar refraction values change from 26.92 to 24.85cm^{-3}. The increase in the refractive index may be attributed to the NBOs in the glass network. The electronic polarizability decreases from 11.79 to 8.49 in the order of 10^{-24} cm^3 non-linearly [17]. Optical properties of the present glass system have improved compared to the earlier reports and finally, the present glass materials are suitable in the non-linear optical device applications with good optical properties.

IV.CONCLUSIONS

XRD measurements confirmed the amorphous nature of the studied glasses. The density of the glass system increased with increasing Li_2O content.The cut-off wavelength increased with Li_2O content. Optical band gap energies were decreased with Li_2O content. Urbach energy increased with Li_2O content. The refractive index increased with Li_2O content.

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