Optical band gap and FT-IR studies on Cu^{2+} doped $20ZnO + x\ Li_2O + (30\text{-}x)\ Na_2O + 50B_2O_3$ glasses

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The spectral studies on $20ZnO+xLi_2O+(30\text{-}x)Na_2O+50B_2O_3$ ($5 \leq x \geq 25$) doped with 0.1 mol% of paramagnetic CuO impurity are carried out. XRD patterns of powder glass samples confirm the amorphous nature. Urbach energies are shown the structural stability of the systems. The optical band gap energies varies non-linearly within the range of 3.818 – 4.073 eV for direct and 3.770 – 4.024 eV for indirect transitions with the increase of Li_2O content. The FT-IR spectral studies show that the glass systems contain BO_3 and BO_4 units in disordered manner. The structural changes have been observed with alkali contents of the systems. It is observed that the system is more stable at x = 20 mol%. Mixed Alkali Effect phenomenon has been explained in the glass host.

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1. Introduction

The transition metal ions doped alkali borate glasses have many technological applications due to their electrical and optical properties. Borate glasses are used as electro-optic switches, electro-optic modulators, solid state laser materials, non-linear optical parametric converters, insulting materials and cathode materials for batteries [1-5]. Zinc containing glasses have wide band gap, low melting point and have been widely used as a good sintering agents [6-9]. When one alkali is progressively substituted for another, many physical properties of oxide glasses show non-linear behavior as a function of alkali content. Mixed Alkali Effect (MAE) is one of the outstanding problems and is a poorly understood phenomenon in glass science [10-21]. The majority of existing literature on MAE is based on dynamic studies. The structure of pure vitreous B_2O_3 consists of a random network of boroxyl rings and BO_3 triangles connected by B–O–B linkage [22]. The addition of alkali oxides modifies the boroxyl rings; complex borate groups with one or two four co-ordinate borate atoms are formed [23]. MAE in phosphate glasses has been reported in which CuO is used as a paramagnetic probe [24-26]. Recently authors have been published MAE of different transition metal ions doped Alkali Zinc Borate Glasses and ascertained the site symmetry, bonding nature and physical parameters [27-33]. The aim of the present study is to examine the MAE in copper doped $20ZnO + x\ Li_2O + (30\text{-}x)\ Na_2O + 50\ B_2O_3$ ($5 \leq x \geq 25$) glasses using spectroscopic techniques like powder XRD, optical absorption and FT-IR studies to get a comprehensive view.

2. Experimental

2.1. Preparation of glasses

Analar grade ZnO (99.9%), B_2O_3 (99.9%), Li_2CO_3 (99.9%) and Na_2CO_3 (99.9%) are taken as starting materials for the present study. The host glass composition is taken in the ratio as mentioned in Table 1. For transition metal doping, 0.1 mol% of copper oxide is added to starting materials. These mixtures are sintered at 750 K and melted in an electric furnace in silica crucible around 1250 K for nearly 1h. The melt is then quenched at room temperature in air to form a glass. The glasses so formed are annealed at 700 K for 1h to relieve the structural stress.

Table 1. Composition of glasses studied in the present work.

Glass System	Glass Chemical Composition	Prepared temp.
ZLNB1	19.9 ZnO + 5 Li_2O + 25 Na_2O+ 50 B_2O_3 + 0.1 CuO	1175 K
ZLNB2	19.9 ZnO + 10 Li_2O + 20 Na_2O+ 50 B_2O_3 + 0.1 CuO	1188 K
ZLNB3	19.9 ZnO + 15 Li_2O + 15 Na_2O+ 50 B_2O_3 + 0.1 CuO	1213 K
ZLNB4	19.9 ZnO + 20 Li_2O + 10 Na_2O+ 50 B_2O_3 + 0.1 CuO	1223 K
ZLNB5	19.9 ZnO + 25 Li_2O + 5 Na_2O+ 50 B_2O_3 + 0.1 CuO	1223 K

2.2. Measurements

The X-ray diffraction patterns of powder glass samples are recorded on PANalytical XpertProdiffractometer with copper Kα radiation. The optical absorption spectra of polished glass samples are recorded on JASCO V670 spectrophotometer in the region of 200-1400 nm. The optical band gap energies for direct and indirect transitions and Urbach energies of all the samples are calculated. FT-IR spectra are recorded using KBr pellets on Thermo Nicolet 6700 FT-IR spectrophotometer in the region 400-4000 cm^{-1}.

3. Results and discussions

3.1. Powder X-ray diffraction studies

The x-ray diffraction pattern consists of a few broad diffuse haloes rather than sharp rings which is a sign of amorphous material. All the prepared glass samples confirm the amorphous nature. Fig. 1 shows the typical x-ray diffraction patterns for undoped and copper doped glasses.

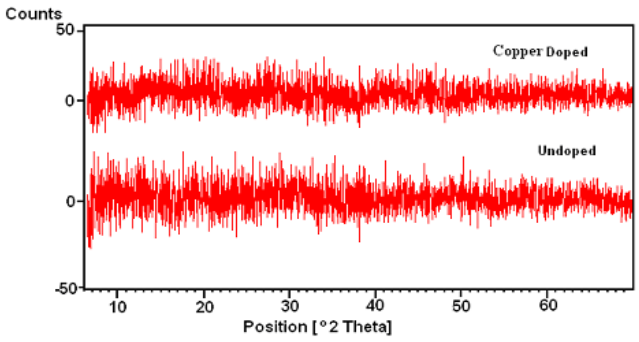

Fig. 1. Powder X-ray diffraction patterns of Cu^{2+} doped and undoped ZLNB glasses.

3.2. Optical band gap and Urbach energy studies

The study of the fundamental absorption edge in the UV region is a useful method for the investigation of optical transitions, electronic band structure in crystalline and non-crystalline materials. There are two types of optical transitions that can occur at the fundamental absorption edge of crystalline and non-crystalline materials. They are direct and indirect transitions. In both the cases, electromagnetic waves interact with the electrons in the valence band, which are raised across the fundamental gap to the conduction band. In glasses, the conduction band is influenced by the glass forming anions; the cations play an indirect but significant role. Classical optical transmission on the bulk samples with the thickness varying in the region 0.5 – 4 μm prepared by a glass blowing was measured [34]. Davis and Mott [35] gave the following forms of absorption co-efficient α(ν) as a function of photon energy for direct and indirect transitions. For direct transitions,

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

Where n = 1/2 for allowed transition, B is a constant and E_{opt} is direct optical band gap. For indirect transitions,

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

Where n = 2 for allowed transitions and E_{opt} is the indirect optical band gap. Using the above two equations and by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of photon energy hν, one can find the optical energy band gap (E_{opt}) for indirect and direct transitions respectively. The respective values of E_{opt} are obtained by extrapolating to $(\alpha h\nu)^{1/2} = 0$ for indirect transitions and $(\alpha h\nu)^2 = 0$ for direct transitions. In order to examine the optical band gap energy for these glasses, the optical absorption spectra are also recorded in the near ultra violet region (Fig. 2). Plots drawn between $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^2$ vs hν are shown in Fig. 3. The optical band gap energy is obtained by extrapolating the linear region of the curve to the hν axis. From these plots, the optical band gap energies calculated and are given in Table 2. The optical band gap energy equation for its calculation is as follows.

$$E_{opt} = hc/\lambda$$

The optical band gap energy increases and decreases alternately with the increase of x mol % and reaches to maximum at x = 20, which shows the significance of MAE in these glasses.

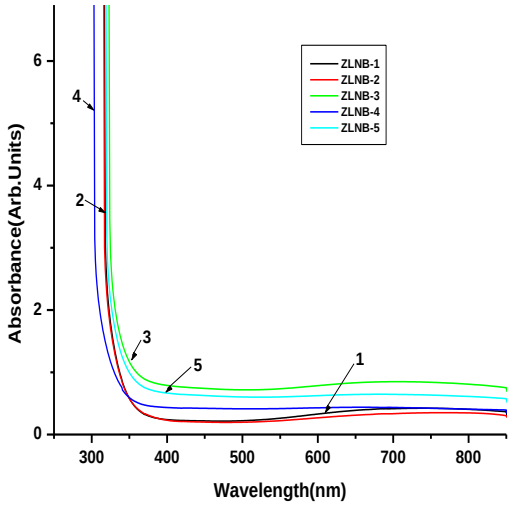

Fig. 2. Absorption edges of the optical spectra of Cu^{2+} doped ZNLB glasses.

Table 2. Absorption edge, thickness, direct, indirect optical band gaps and Urbach energies of Cu^{2+} doped ZLNB glass systems.

Glass System	Absorption edge (nm)	Thickness d (cm)	Optical band gap Energy E_{opt} (eV)			Urbach energy ΔE (eV)
			Theoretical	Experimental		
				Direct	Indirect	
ZLNB1	318	0.140	3.906	3.893	3.856	0.024
ZLNB2	317	0.140	3.919	3.910	3.870	0.023
ZLNB3	326	0.165	3.810	3.818	3.770	0.030
ZLNB4	305	0.094	4.073	4.073	4.024	0.018
ZLNB5	320	0.153	3.882	3.866	3.830	0.025

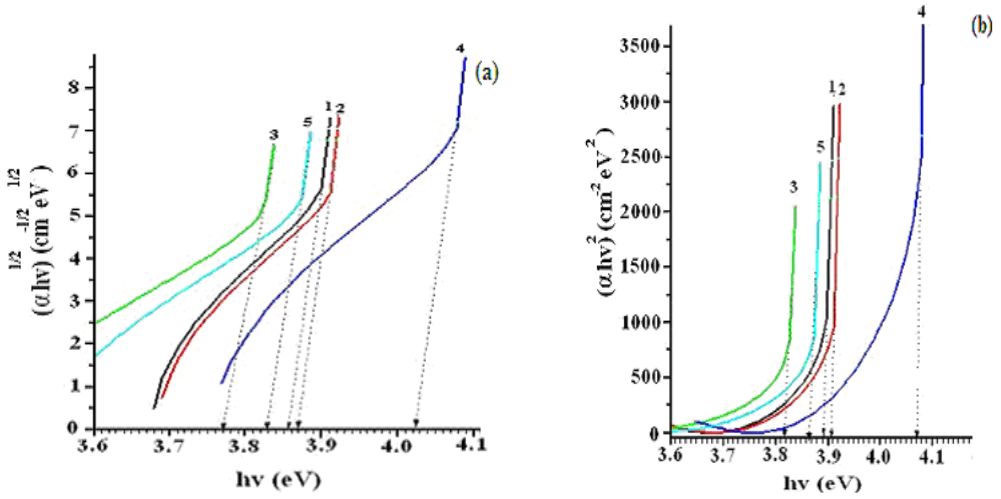

Fig. 3(a) Indirect (b) direct band gap energies of Cu^{2+} doped ZLNB glasses at room temperature.

The main feature of the absorption edge of amorphous materials is an exponential increase of the absorption coefficient α(ν) with photon energy hν in accordance with the empirical relation [36].

$$\alpha(\nu) = \alpha_o \exp(h\nu/\Delta E)$$

Where α_0 is a constant, ΔE is the Urbach energy which indicates the width of the band tails of the localized states and ν is the frequency of the radiation. Therefore, Urbach energy can be considered as a measure of disorder in amorphous and crystalline materials [37–39]. The nature of disorder can be different in crystalline and amorphous solids. The disorder can be both static and dynamic in crystalline materials. Dynamic disorder arises due to electron–phonon coupling in crystalline solids. In amorphous solids, the static atomic structural disorder dominates and can be due to presence of defects like dangling bonds or non-bridging oxygen's in glasses [40]. The higher the concentration of NBOs in the glass network, the smaller is the optical energy gap and the greater are the Urbach energy values in borate glasses [41]. The excitation levels at the absorption edges are determined by the random electric fields due to either the lack of long range order or the presence of defects [42]. Urbach energies (ΔE) are calculated by taking the reciprocals of the slopes of linear portion in the lower photon energy regions of these curves (Fig. 4) and are listed in Table 2. The Urbach energy decreases and increases alternately with the increase of Li_2O content (Fig. 5), which shows MAE. It also shows the structural disorder of the system, where the optical band gap energy is minimum, Urbach energy is maximum and vice-versa. Smaller is the value of Urbach energy, greater is the structural stability of the glass system. It is observed that the Urbach energy is minimum at x = 20 mol%.

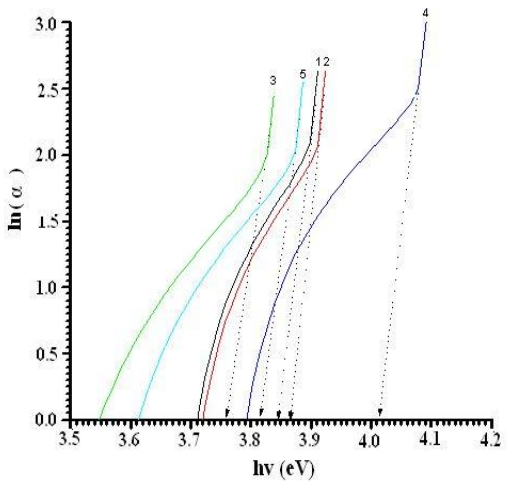

Fig. 4. Urbach energy plots of Cu^{2+} doped ZLNB glasses.

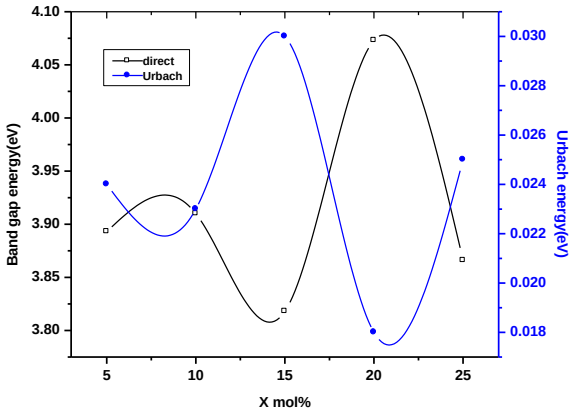

Fig. 5. Compositional dependence of band gap energy and urbach energy of Cu^{2+} doped ZLNB glasses.

3.3. FT-IR studies

The experimental FT-IR spectra of the Cu^{2+} doped (19.9 ZnO + x Li_2O + (30-x) Na_2O + 50 B_2O_3, (5≤ x ≥ 25)) glasses are presented in Fig. 6. The obtained absorption bands and their assignments are summarized in Table 3. In general, the FT-IR analysis of the studied borate glasses shows four distinct frequency regions. Two regions, from 1200 to 1600 cm^{-1} and from 800 to 1200 cm^{-1}, are assigned to the stretching vibrations of both triangular BO_3 and tetrahedral BO_4 borate units, respectively. Deformation modes of both types of units are active between 600 and 800 cm^{-1} [43]. Absorption bands in the region 400 - 550 cm^{-1} are due to ZnO tetrahedron in glasses [44]. The systematic changes in the infrared spectra of these glasses are mainly observed around 700, 1000 and 1400 cm^{-1}. The increase of alkali oxide up to 25 mol% leads to more number of BO_4 groups, which resulting a closely packed and strongly bonded structural glass network with less number of network BOs [45]. The B-O stretching vibration of BO_3 is assigned around 1600 cm^{-1}. The absorption bands around 715 cm^{-1} has been assigned to B-O-B bending vibrations, which exhibit shift towards lower wave number up to x = 15 and then to higher and lower wave numbers with the increase of Li_2O content, which shows MAE. The absorption bands around at 862 and 884, 935 - 960 and 1005 - 1026 cm^{-1} are assigned to symmetric stretching vibrations of B-O bonds in BO_4 units, which exhibits shift towards higher wave number and then to lower wave number up to x = 15 and then to higher and lower wave number with the increase of x mol%. The bands at 862 and 884 are attributed to non-bridging oxygen's which disappears with the increase of Li_2O content. It is observed that the alkali oxide modifies the structure by converting BO_3 groups into BO_4 groups. The absorption bands around 900 – 1300 cm^{-1} is assigned to characteristic zinc borate vibrations. Bands observed in the region 1335 -1495 cm^{-1} are assigned to symmetric stretching vibrations of B-O bonds in BO_3 Units. The band at 1606 cm^{-1} is assigned to asymmetric stretching vibrations of B-O bonds in BO_3 units, which shifts

alternately with x mol%. The absorption band at 457 cm^{-1} is assigned to characteristic vibration of Li cation which shifts towards lower to higher wave number and then to lower wave number with the increase of x %.

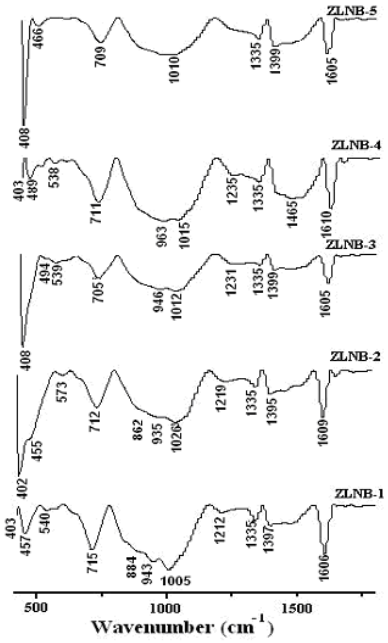

Fig. 6. FT-IR spectra of Cu^{2+} doped ZLNB glasses.

Table 3. Assignment of FT-IR bands in Cu^{2+} doped ZLNB glass systems.

Assignment	ZLNB1	ZLNB2	ZLNB3	ZLNB4	ZLNB5
	(bands in units of cm^{-1})				
Lithium Cation vibrations	457	455	494	489	466
B-O-B Bending vibrations	715	712	705	711	709
Vibrations of NBOs	884	862	----	----	----
B-O symmetric stretching	943	935	946	963	960
Vibrations of BO_4 units	1005	1026	1012	1015	1010
B-O stretching vibrations	1212	1219	1231	1235	----
of trigonal BO_3 units of	1335	1335	1335	1335	1335
boroxyl rings	1397	1395	1399	1402	1399
Vibrations of NBOs In BO_3 units	------	-----	------	1465	-----
B-O asymmetric stretching vibrations of BO_3 units	1606	1609	1605	1610	1609

4. Conclusions

From the spectral studies on Cu^{2+}doped 19.9 ZnO + x Li_2O + (30-x) Na_2O + 50 B_2O_3 ($5 \leq x \geq 25$) glasses the following conclusions are drawn:

(i) XRD patterns confirm the amorphous nature of all the systems.

(ii) From ultraviolet absorption edges the optical band gap energies and urbach energies are evaluated. Which also confirm the structural variations with the composition of x mol%, shows MAE.

(iii) FT-IR profiles have been used to understand the bonding nature of these glasses. Strongly bonded and stable structure is observed at x = 20mol%.

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