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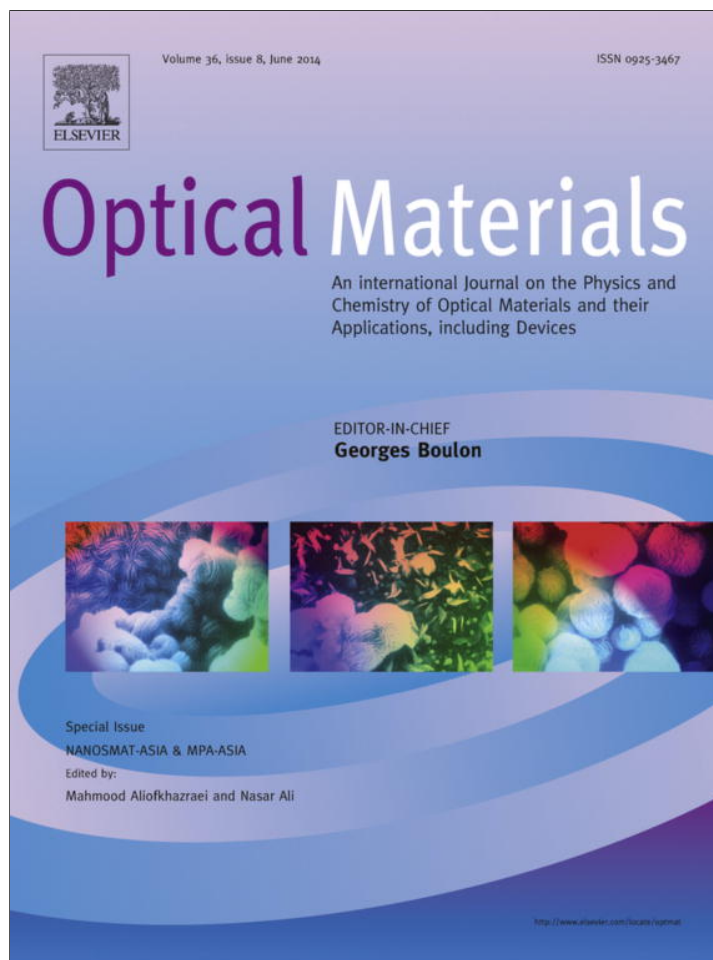


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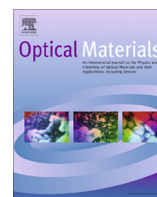
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Characterization of Cr³⁺ doped mixed alkali ions effect in zinc borate glasses – Physical and spectroscopic investigations



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ABSTRACT

The physical and structural properties of Cr³⁺ doped 19.9 ZnO + xLi₂O + (30 – x) Na₂O + 50B₂O₃ (5 ≤ x ≤ 25) (ZLNB) glasses have been studied. Powder X-ray diffraction patterns indicated the amorphous nature of the glass samples. The physical parameters of all the glasses were also evaluated with respect to the composition. They exhibit the non-linearity providing the evidence for mixed alkali ions effect. The infrared spectra of the glasses in the range 400–4000 cm^{−1} showed the presence of BO₃ and BO₄ local structures in all the glass systems. No boroxol ring formation was observed in the structure of these glasses. Optical absorption and electron paramagnetic resonance studies were carried out at room temperature. From the optical absorption data various optical parameters such as optical band gap, Urbach energy were evaluated. Crystal field and Racah parameters are evaluated from optical absorption spectra. The EPR spectra of Cr³⁺ doped ZLNB glasses exhibited resonance signals at g = 4.066 and g = 1.9779 characteristic of Cr³⁺ ions. The evaluated bonding parameters suggest the covalent nature.

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1. Introduction

Glasses obtained from a variety of non-linear materials are widely used for multi-facets applications in modern technology due to their unusual physical and optical properties [1]. The investigation of the changes in the physical properties of glasses with controlled variation of chemical composition and dopants of transition metal ions is of considerable interest in the application point of view. Its physical properties can be improved with the addition of Li, which results in increased humidity resistance and capacity to concentrate transition metal ions. Among all the classical network formers, boric oxide (B₂O₃) is one of the significant glass former and flux material due to their high phonon energies [2]. However, glasses based on borates have special features such as high thermal stability and good solubility, making them promising candidates for a vast amount of technological applications [3,4]. Alkali doping into borate glasses induces interesting structural variations by converting three-coordinated boron structure into four-coordinated structures, famously known as “boron anomaly”

and also with the formation of non-bridging oxygen (NBO) ions in the glass network which pertains mixed alkali effect [5,6].

The most important part of the investigation on the mixed alkali ions effect on borate glasses containing transition metal ions shows non-linear behavior, which has applications in solid state devices, electro-optic modulators, electro-optic switches, electric and electro-optical devices and non-linear optical parametric converters [7]. These applications of glass materials have created many more arenas where it triggered to explore for new variety of glasses. Therefore, demand for glasses with high optical non-linearity and higher damage resistance at reduced cost have been increased. More recently in our previous papers, we have reported the mixed alkali ions effect in transition metal ions doped alkali zinc borate glasses [8–14].

Oxide glasses containing transition metal oxides (TMOs) possess both scientific and technological interest because of their wide range optical properties depending on the presence of such transition metal (TM) ions in varying valences or coordination's and with respective different colors [15–17]. Also, semiconducting properties are expected from these glasses which arise from the electron hopping process between TM ions having at least two valence states [18,19]. Glasses containing Cr₂O₃ have interesting optical properties due to the presence of chromium ions in two possible oxidation states, namely trivalent and hexavalent forms [20]. The

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optical properties of Cr^{3+} ions can be tuned by the random disordered structural units of glasses, since the environment of each Cr^{3+} ion in the glass network varies due to differences in bonding to nearest-neighbor ions [21]. Glasses doped with chromium are still attractive in active laser media, especially for tunable solid-state lasers based on the Cr^{3+} ions, localized in the low-field sites of crystal lattice or glass network. Subhadra et al. [22,23] carried out physical and optical studies transition doped bismuth borate glass system to understand the effect of progressive doping of Li^+ ion with K^+ ion. Recently the Hassan et al. [24] reported the effect of halides on Cr^{3+} doped alkali borate glasses and Moustafa et al. [25] reported the effect of gamma radiation on the chromium doped alkali borate glasses.

Recently we have reported the physical and spectroscopic investigations of Fe^{3+} doped ZLNB glass system also exhibited MAE and Fe^{3+} ion occupies distorted octahedral sites [26]. The aim of the present study is to observe the physical and structural behavior of the new quaternary system of trivalent ion, Cr^{3+} doped $19.9 \text{ ZnO} + x\text{Li}_2\text{O} + (30 - x) \text{ Na}_2\text{O} + 50\text{B}_2\text{O}_3$ ($5 \leq x \leq 25$) (hereafter referred as ZLNB) glasses by using spectroscopic techniques and correlated their properties.

2. Experimental

2.1. Preparation

About 0.1 mol% of Cr^{3+} doped mixed alkali zinc borate glasses are prepared by using analar grade chemicals of ZnO , Li_2CO_3 , Na_2CO_3 , B_2O_3 and Cr_2O_3 as starting materials with 99.9% of purity using melt quenching technique. Appropriate amounts of these starting materials are weighed and thoroughly mixed and ground in an agate mortar about an hour. The batch mixture was transferred to a silica crucible and it is sintered at 750 K and melted in an electric furnace in a silica crucible around 1250 K for nearly 1 h. The melt is then fast quenched to room temperature in air to form a glass. The glass samples are quickly transferred to another furnace previously kept at 700 K, and annealed at this temperature for 1 h to reduce thermal stresses generated by rapid cooling. All glass samples are disk-shaped (about 1 cm diameter and thickness of 1–2 mm). The opposite faces of the samples are ground and polished with different grades of emery powder for spectroscopic measurements. The glass compositions are taken as $19.9 \text{ ZnO} + x\text{Li}_2\text{O} + (30 - x)\text{Na}_2\text{O} + 50\text{B}_2\text{O}_3 + 0.1\text{Cr}_2\text{O}_3$ ($5 \leq x \leq 25$ or $x = 5, 10, 15, 20, 25 \text{ mol\%}$), hereafter named as ZLNB glass systems prepared at the temperatures 1175, 1188, 1213, 1223 and 1223 K respectively.

2.2. Characterization

A programmable VIBRA HT density measurement kit was used to determine the densities (ρ) and molar volumes of bulk samples automatically (with readability 0.0001 g/cm^3) by means of Archimedes' principle with O-Xylene (99.99% pure) as buoyant liquid. Refractive indices (n_d) of prepared glasses are measured by using NAR-4T Atago Abbe's Refractometer. X-ray diffraction patterns of powdered glass samples are recorded on PANalytical Xpert Pro diffractometer with $\text{Cu K}\alpha$ wavelength of 1.5406 \AA . The EPR spectra of powdered samples are recorded at room temperature on JEOL JES TE 100 ESR spectrometer at X-band frequency with 100 kHz field modulation. FT-IR spectra are recorded by using Bruker FT-IR spectrometer in the region $500\text{--}4000 \text{ cm}^{-1}$. The optical absorption spectra of polished glass samples (thickness 1 mm) are recorded on JASCO V670 spectrometer in the region of $200\text{--}1400 \text{ nm}$. By using measured values of density (ρ), refractive index (n_d) some more physical parameters like molar refractivity (R_M), optical

dielectric constant (ϵ), ionic concentration (N), electronic polarizability (α_e), polaron radius (r_p) and inter ionic distance (r_i) are evaluated.

3. Results and discussion

3.1. Powder X-ray diffraction studies

The typical powder X-ray diffraction patterns for undoped and Cr_2O_3 doped glasses reveals the amorphous nature and the absence of crystalline characteristics. All the prepared glass samples confirm the glassy nature. Fig. 1 shows the X-ray diffraction patterns of undoped and chromium doped glasses.

3.2. Physical properties

From the refractive index (n_d) and density values of the glass samples, the other physical parameters like molar refractivity, ionic concentration, electronic polarizability, inter-ionic distances and polaron radii are evaluated and tabulated in Table 1.

The dielectric constant (ϵ) was calculated from the refractive index of the glass using the relation by Bendow et al. [27]:

$$\epsilon = n_d^2 \quad (1)$$

The reflection loss from the glass surface was computed from the refractive index using the Fresnel's formula [28]:

$$R = [(n_d - 1)/(n_d + 1)]^2 \quad (2)$$

For each glass sample the molar refractivity (R_M) can be evaluated by using the given formula [29]

$$R_M = [(n_d^2 - 1)/(n_d^2 + 2)]M/D \quad (3)$$

where M is the average molecular weight and D is density in g/cm^3 .

Electronic polarizability (α_e) can be calculated by using the following expression [30]

$$\alpha_e = 3(n_d^2 - 1)/4\pi N(n_d^2 + 2) \quad (4)$$

where N is the number of chromium ions per unit volume.

The polaron radius and inter-ionic separation can be determined by using formulae [31]

$$r_p = (1/2)[\pi/6N]^{1/3} \text{ and } r_i = (1/N)^{1/3} \quad (5)$$

The error in density measurements and refractive indices are estimated to be $\pm 0.004 \text{ g/cm}^3$ and ± 0.0001 respectively. The density (D) of the glass samples at room temperature was measured by the Archimedes principle using a sensitive micro balance with xylene as the immersion liquid. The mean atomic volume (V) of each glass was obtained from the values of densities (D) and mean

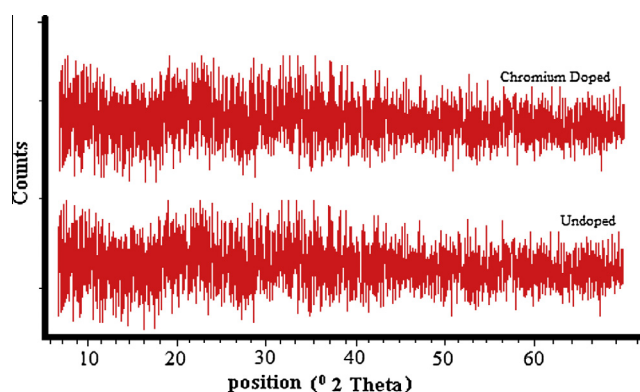


Fig. 1. Powder X-ray diffraction patterns of Cr^{3+} doped and undoped ZLNB glasses.

Table 1
Physical properties of ZLNB glass systems at room temperature.

Sl. No	Physical parameter (units)	Glass code				
		ZLNB1 $x = 5$	ZLNB2 $x = 10$	ZLNB3 $x = 15$	ZLNB4 $x = 20$	ZLNB5 $x = 25$
1.	Average molecular weight (g/mol)	81.3485	79.7437	78.1389	76.5343	74.9289
2.	Density (ρ) (g/cm ³) (± 0.004)	2.7989	2.8186	2.8032	2.8138	2.8108
3.	Refractive index (μ) (± 0.0001)	1.6552	1.6551	1.6556	1.6551	1.6552
4.	Optical dielectric constant (ϵ)	2.7397	2.7393	2.7410	2.7393	2.7396
5.	Reflection loss	0.0608	0.0608	0.0609	0.0608	0.0608
6.	Molar refractivity (R_M) (cm ³) (± 0.005)	10.6680	10.3832	10.2363	9.9823	9.7845
7.	Ionic concentration (N) (10 ²² ions/cm ³) (± 0.005)	0.3149	0.3235	0.3284	0.3365	0.3434
8.	Electronic polarizability (α_e) (10 ⁻²⁴ × cm ³) (± 0.005)	27.8349	27.0919	26.7085	26.0458	25.5297
9.	Inter-ionic distance (r_i) (Å) (± 0.005)	6.8220	6.7610	6.7276	6.6728	6.6282
10.	Polaron radius (r_p) (Å) (± 0.005)	2.7488	2.7242	2.7107	2.6886	2.6707

atomic weights. The number of chromium ions (N) was determined from the glass composition and its density value. The refractive index (n_d) of the glass was measured with an Abbe's Refractometer at sodium wavelength ($\lambda = 5893$ Å). With an increase in Li₂O content, it is pragmatic that the above physical parameters vary non-linearly. The dielectric polarization is strong for borate glasses with compositions close to the diffusivity crossover composition where the ionic conductivity is weak [32].

Fig. 2 shows the compositional dependence of density and refractive index of Cr³⁺ doped ZLNB glass systems. The density values reaches a maximum value at $x = 10$ mol% from a minimum value at $x = 5$ mol% and then decrease and increase with increase of x mol%. Similarly, the refractive index values also decrease and increase with increase of x mol% and the maximum value of refractive index is observed at $x = 15$ mol%. However, in the present investigation of Cr³⁺ doped ZLNB glasses, experimentally determined density and refractive index values are varied with in the composition. For Cr³⁺ doped ZLNB glasses, ionic concentration and electronic polarizability are correlated with respect to Li₂O content and depicted in Fig. 3. It is observed that both these parameters are changed with increase of x mol%.

3.3. FT-IR studies

FT-IR (Fourier Transform Infrared) spectra of Cr³⁺ doped ZLNB glasses are shown in Fig. 4. The obtained absorption bands and their assignments are summarized in Table 2. The infrared transmission spectra of ZLNB glasses have exhibited two main groups of bands: (i) in the region 600–800 cm⁻¹ the bands are due to the bending vibrations of B–O–B linkages (ii) in the region 800–1140 cm⁻¹, the bands are identified due to the B–O symmetric stretching vibrations of BO₄ units [33]. In the present IR analysis

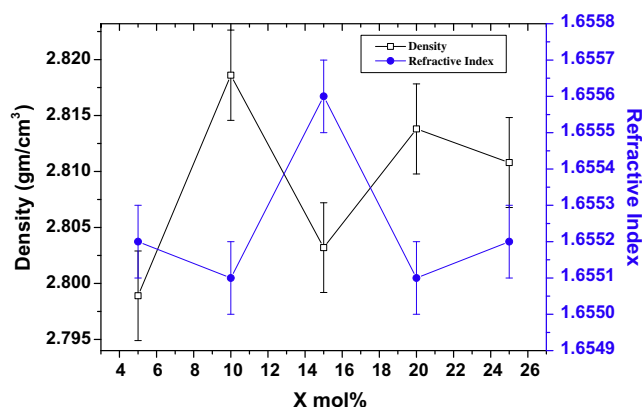


Fig. 2. Correlation between density and refractive index of Cr³⁺ doped ZLNB glasses.

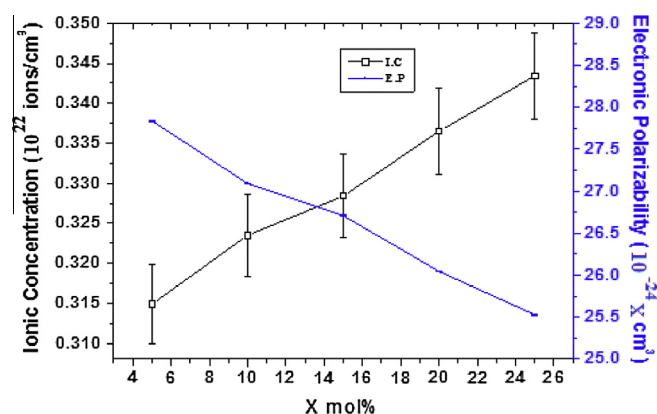


Fig. 3. Correlation between ionic concentration and electronic polarizability of Cr³⁺ doped ZLNB glasses.

of the glasses, bands observed in the region 1200–1520 cm⁻¹ are assigned to asymmetric stretching vibrations of B–O units in different borate groups [34]. The vibrational band observed at around 1679 cm⁻¹ is ascribed to the vibrational modes of hydroxyl or water groups present in the glass systems.

3.4. Optical absorption studies

The electronic configuration of Cr³⁺ gives rise to the free ion terms ⁴F, ⁴P, ²G and several other doublet states out of which ⁴F is the ground state. The absorption spectrum of ZLNB3 consists of peaks at 271 (36,890 cm⁻¹), 422 (23,690 cm⁻¹), 607

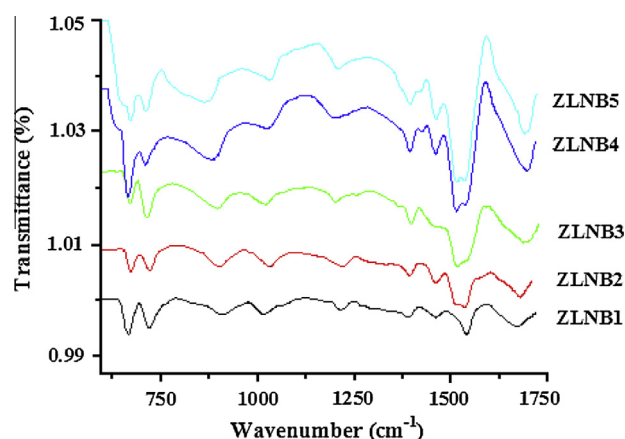


Fig. 4. FT-IR spectra of Cr³⁺ doped ZLNB glass systems.

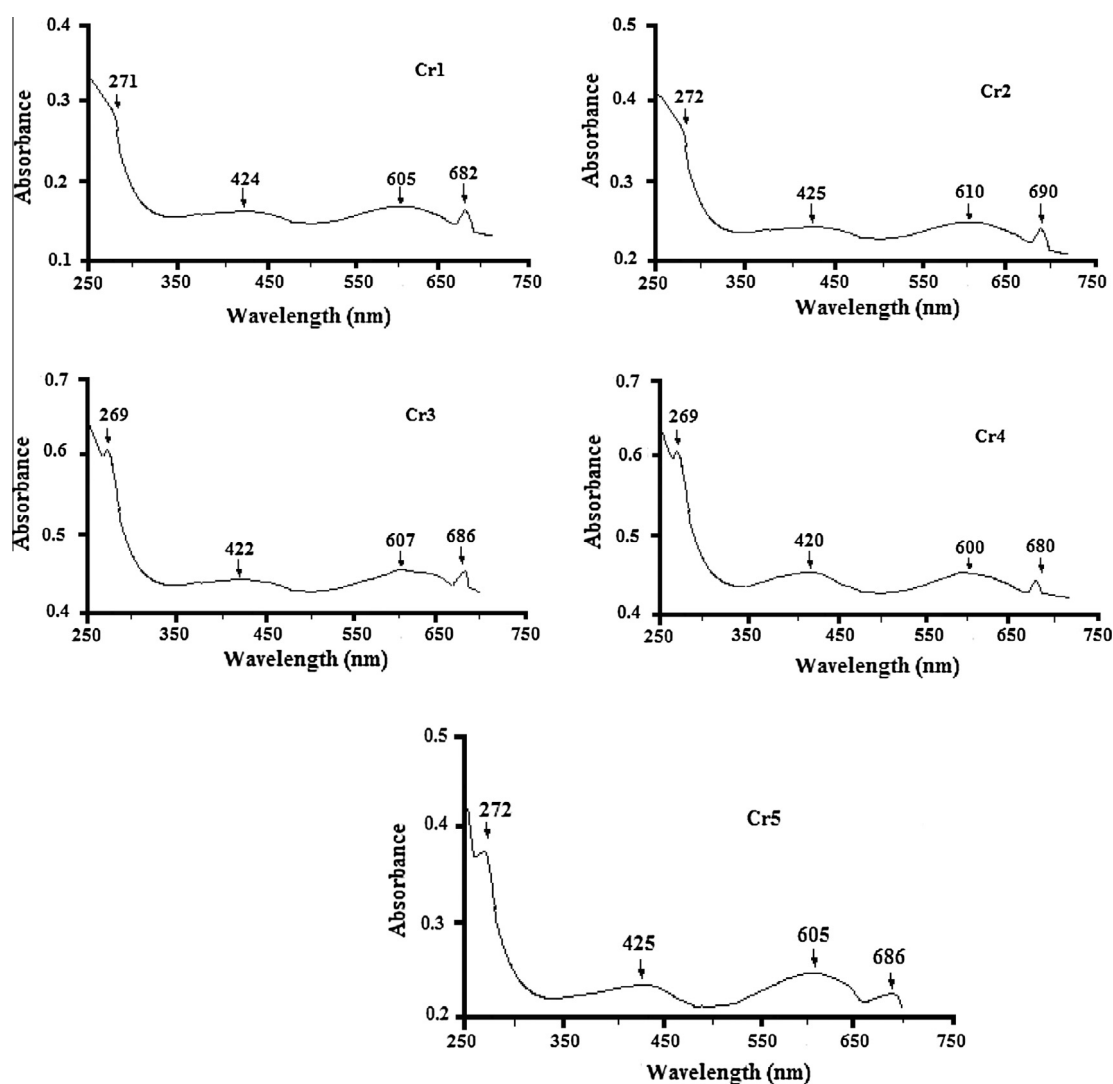
Table 2

Assignments of FT-IR bands in ZLNB glass systems.

Assignment (bands in units of cm^{-1})	ZLNB1	ZLNB2	ZLNB3	ZLNB4	ZLNB5
B–O–B bending vibrations Involving oxygen atoms Outside borate ring	560	559	560	559	559
Stretching vibrations of NBOs in BO_4 units	820	820	820	820	820
B–O symmetric stretching Vibrations of BO_4 units	978 1140	978 1140	977 1142	978 1140	978 1143
B–O stretching vibrations of trigonal BO_3 units	1284 1310 1462	1284 1305 1455	1284 1310 1460	1284 1310 1457	1284 1310 1457
H–O–H bending vibrations	1673	1673	1675	1676	1675

($16,469 \text{ cm}^{-1}$) and 686 nm ($14,573 \text{ cm}^{-1}$) as shown in Fig. 5. The broad absorption band observed at 607 nm has been attributed to Cr^{3+} ions in octahedral symmetry. Cr^{3+} ions belong to $3d^3$ configuration, the ground state is always $^4A_{2g}(\text{F})$ irrespective of strength of crystal field. In general Cr^{3+} ions are characterized by three spin allowed transitions $^4A_{2g}(\text{F}) \rightarrow ^4T_{2g}(\text{F})$, $^4A_{2g}(\text{F}) \rightarrow ^4T_{1g}(\text{F})$ and $^4A_{2g}(\text{F}) \rightarrow ^4T_{1g}(\text{P})$. In general, in octahedral symmetry, the optical

absorption spectra of Cr^{3+} exhibit two intense broad bands in the visible region corresponding to the transitions $^4A_{2g}(\text{F}) \rightarrow ^4T_{2g}(\text{F})$ and $^4A_{2g}(\text{F}) \rightarrow ^4T_{1g}(\text{F})$ and the third broad band in the ultraviolet region corresponding to $^4A_{2g}(\text{F}) \rightarrow ^4T_{1g}(\text{P})$ transition is less intense due to double electron jump ($t_{2g}^3 \rightarrow t_{2g}^1 e_g^2$). In addition to this a number of doublet states also possible, which are spin-forbidden transitions. In the present study, two broad bands are observed

**Fig. 5.** Optical absorption spectra of Cr^{3+} doped ZLNB glasses.

at around 420 and 605 nm. The intensity and position of this main band around 600 nm is suggest that this band to be related to d-d electronic transition and is assigned to the transition ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ of Cr^{3+} ions in octahedral symmetry. The intense band position ν_1 at $16,469\text{ cm}^{-1}$ corresponding to the transition ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ gives the value of $10 Dq$. The wavenumber corresponding to ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ at $23,690\text{ cm}^{-1}$ gives ν_2 and the Racah parameter B is given by the equation:

$$B = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)/(15\nu_2 - 27\nu_1) \quad (6)$$

The value of B is evaluated to be 760 cm^{-1} and it is significantly lower than the free ion value of Cr^{3+} , $B_{free} = 918\text{ cm}^{-1}$. The value of B is a measure of inter-electronic repulsion in the d-shell and is useful in discussing the ionic/covalent properties of Cr–O ligand bonding. The bonding can be predicted using the expression [35]

$$h = ((B_{free} - B)/B_{free})/K_{Cr^{3+}} \quad (7)$$

where h and k are nephelauxetic parameters of the ligands and the central metal ion, respectively. For Cr^{3+} ion, the value of $k = 0.21$ [36]. The calculated values of h are 0.9233, 0.8714, 0.8195, 0.9492 and 1.0270 for ZLNB1 to ZLNB5 glasses. The value of h indicates increased delocalization of the d-electrons suggesting covalent nature of bonding between Cr^{3+} and the ligands. The Racah parameter C can be calculated from the position of the ${}^4A_{2g}(F) \rightarrow {}^2E_g(G)$ absorption peak using the following equation [37],

$$C/B = 1/3.05[E^2E]/B - 7.9 + 1.8(B/Dq) \quad (8)$$

The calculated value of C is 3020 cm^{-1} . These values of crystal field and Racah parameters and Dq/B are in tune with other Cr_2O_3 containing glasses [38,39]. By using d^3 energy matrices the values of Dq , B and C are evaluated and give a good fit between the observed and calculated positions of the bands as shown in Table 3.

3.5. Optical band gap and Urbach energies

The analysis of optical absorption spectrum is one of the most productive tools for understanding and developing the band structure and energy band gap (E_g) of crystalline and non-crystalline material structures. 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 the case of glasses, the conduction band is influenced by the anions; the cations play an indirect but major role. The absorption coefficient $\alpha(\nu)$ is a function of photon energy for direct and indirect transitions [40]. For direct transitions,

$$\alpha(\nu) = A(h\nu - E_{opt})^n/h\nu \quad (9)$$

Here A is a constant, E_{opt} is direct optical band gap and $n = 1/2$ for allowed transitions. For indirect transitions, $n = 2$ for allowed transitions. Using the above equation, plots for $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ as a function of photon energy $h\nu$ are drawn and shown in Fig. 6. The respective values of E_{opt} for direct and indirect transitions are obtained by extrapolating to $(\alpha h\nu)^2 = 0$ for direct transitions and $(\alpha h\nu)^{1/2} = 0$ for indirect transitions. The optical band gap energy is obtained by extrapolating the linear region of the curve to the $h\nu$ axis. From these plots, the obtained optical band gap energies are given in Table 4. Using the following equation, optical band gap energy can be calculated theoretically,

$$E_{opt} = hc/\lambda \quad (10)$$

The optical band gap energy shows the non-linear behavior of these ZLNB glasses and it is maximum at 20 mol%. The main feature of the absorption edge of amorphous materials is an exponential increase of the absorption coefficient $\alpha(\nu)$ with photon energy $h\nu$ in accordance with the empirical relation [41].

$$\alpha(\nu) = \alpha_0 \exp(h\nu/\Delta E) \quad (11)$$

Here α_0 is a constant, ν is the frequency of the radiation and ΔE is the Urbach energy which indicates the width of the band tails of the localized states and depends on temperature, induced disorder, static disorder, and on average photon energies. Hence, Urbach energy provides a measure for the disorder in amorphous and crystalline materials [42]. The nature of disorder is different for crystalline and amorphous solids. In amorphous solids, the static atomic structural disorder dominates and can be due to presence of defects like dangling bonds or non-bridging oxygens in glasses [43]. Urbach energies (ΔE) are calculated by taking the reciprocals of the slopes of linear portion in the lower photon energy regions of the curves and are listed in Table 4. It shows the structural disorder of the system. Smaller is the value of Urbach energy, greater is the structural stability of the glass system. It is also observed

Table 3
Band head data of ZLNB glass systems.

Glass system	Transitions from ${}^4A_{2g}(F)$	Wavelength (nm)	Wavenumber (cm^{-1})		Dq (cm^{-1})	B (cm^{-1})	C (cm^{-1})	Dq/B
			Observed	Calculated				
ZLNB1	${}^2E_g(G)$	682	14,658	14,623	1645	740	3080	2.22
	${}^4T_{2g}(F)$	605	16,524	16,450				
	${}^4T_{1g}(F)$	424	23,578	23,616				
	${}^4T_{1g}(P)$	271	36,890	36,833				
ZLNB2	${}^2E_g(G)$	690	14,488	14,331	1635	750	2965	2.18
	${}^4T_{2g}(F)$	610	16,388	16,350				
	${}^4T_{1g}(F)$	425	23,523	23,570				
	${}^4T_{1g}(P)$	272	36,754	36,729				
ZLNB3	${}^2E_g(G)$	686	14,573	14,567	1650	760	3020	2.17
	${}^4T_{2g}(F)$	607	16,469	16,500				
	${}^4T_{1g}(F)$	422	23,690	23,807				
	${}^4T_{1g}(P)$	269	37,164	37,092				
ZLNB4	${}^2E_g(G)$	680	14,701	14,660	1665	735	3100	2.26
	${}^4T_{2g}(F)$	600	16,662	16,650				
	${}^4T_{1g}(F)$	420	23,803	23,807				
	${}^4T_{1g}(P)$	269	37,164	37,167				
ZLNB5	${}^2E_g(G)$	686	14,574	14,407	1650	720	3050	2.29
	${}^4T_{2g}(F)$	605	16,525	16,500				
	${}^4T_{1g}(F)$	425	23,523	23,534				
	${}^4T_{1g}(P)$	272	36,754	36,765				

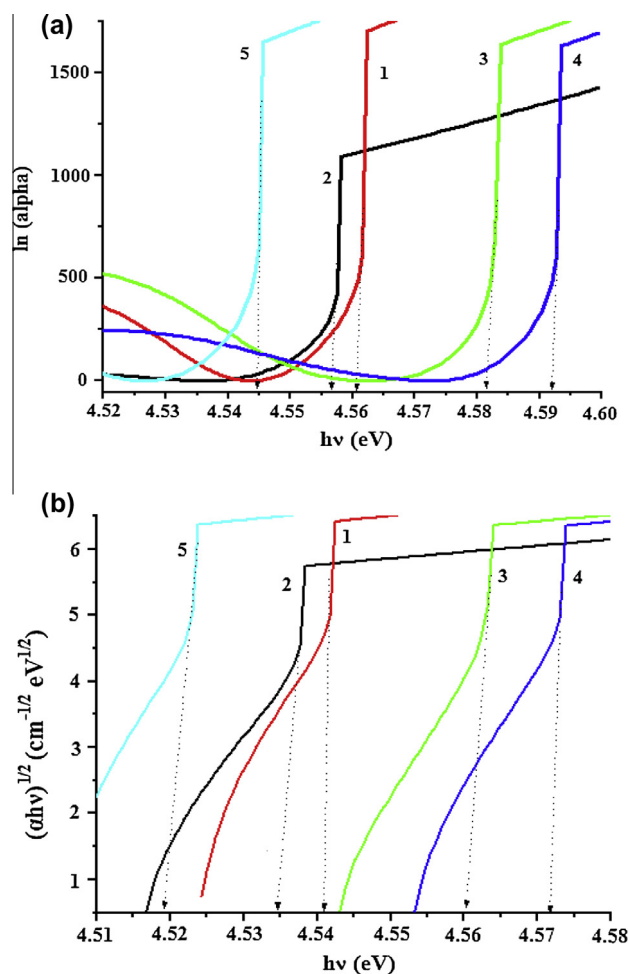


Fig. 6. (a) Direct, (b) indirect band gap energies of Cr³⁺ doped ZLNB glasses.

that all the systems have low value of structural disorder, which indicates the strong structural stability. The band gap energy calculations indicate that the glass systems are direct semiconductors with the calculated band gaps close to the observed ones. In the present investigations absorption edge is more when compared to divalent ions doped in ZLNB glasses [10–12], this may be due to Cr³⁺ ions incorporated in to the host glass network. The chromium doped ZLNB glasses shows more absorption edge and optical band gap energies values which were also observed in similar other glass systems [44–46].

3.6. Electron paramagnetic resonance studies

The optical absorption and electron spin resonance spectroscopy of Cr³⁺ ion in a variety of inorganic glasses have been studied because of their technological importance in the development of tunable solid-state lasers and new luminescence materials [47].

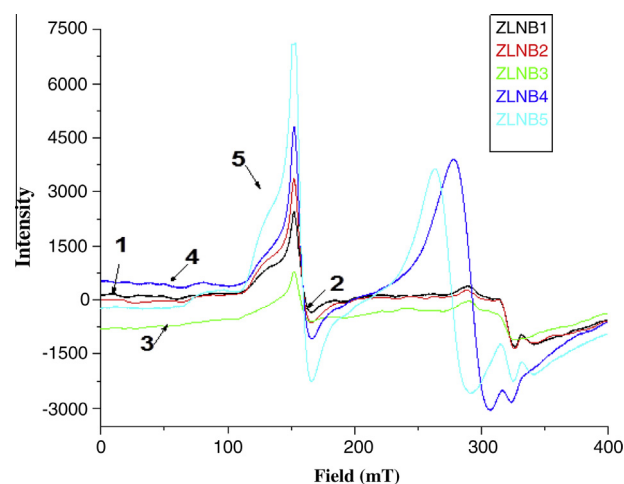


Fig. 7. EPR spectra of Cr³⁺ doped ZLNB glasses.

The Cr³⁺ free ions have 3d³ electronic configuration and ⁴F_{3/2} ground state. In octahedral crystal field the ground state of Cr³⁺ ions is fourfold degenerated to spin ⁴A_{2g} level. The spin–orbit interaction taken as a perturbation on the crystal-field states yields the splitting of the ⁴A_{2g} ground orbital singlet level of the Cr³⁺ ions into two Kramer's doublets with the effective electron spin quantum numbers Ms = ± 1/2 and Ms = ± 3/2. The Cr³⁺ ions in glassy network may exist as both isolated Cr³⁺ ions and exchange coupled Cr³⁺–Cr³⁺ ion pairs [38]. EPR spectra of Cr³⁺ ions in borates [48], Borosulphates [49,50] were reported by many authors. In all these glasses, two resonance signals have been observed at observed at g ~ 4.80 and g ~ 1.98; these resonance signals have been attributed to isolated Cr³⁺ ions in strong distorted sites and Cr³⁺ ion pairs respectively [51].

In the present studies EPR spectra shown in Fig. 7 exhibits the two resonances at g = 4.066 and 1.9779 for glass sample ZLNB1. Accordingly the resonance at g = 1.9779 to exchange coupled Cr³⁺–Cr³⁺ pairs primarily and the resonance at g = 4.066 is assigned to the isolated chromium ions. The line shape of the EPR spectra of chromium ions in glasses is more complicated than in single crystal or polycrystalline substances. They are influenced by the absence of long-range order in glasses connected with various small distortions of the local environment of the ions from site-to-site. In addition to that, the symmetry axes of the ligand fields relative to the direction of the applied magnetic field are randomly oriented. Therefore the line shape is highly broadened [52]. The g-values (4.066, 1.9779, 4.065, 1.9775, 4.065, 1.9781, 4.065, 1.9837 and 4.178, 1.9800 for ZLNB1 to ZLNB5) obtained from EPR results of Cr³⁺ doped ZLNB glasses indicate the distorted octahedral site. Similar g values are also observed in the glass network [53]. By correlating optical and EPR data the chemical bonding parameter α is evaluated using the formula [54]

$$g_o = g_e - 8\alpha/\Delta \quad (12)$$

Table 4

Absorption edge, thickness, direct, indirect optical band gaps and Urbach energies of 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	271	0.1120	4.575	4.545	4.519	0.026
ZLNB2	272	0.1050	4.562	4.557	4.534	0.023
ZLNB3	269	0.1215	4.607	4.561	4.541	0.020
ZLNB4	269	0.1104	4.616	4.581	4.560	0.021
ZLNB5	272	0.1220	4.566	4.592	4.572	0.02

where g_e is free electron g factor (2.0023), λ is the spin-orbit coupling constant (91 cm^{-1}), Δ is the gap between the excited and ground levels. From experimental values $g_0 = 1.9779$ and $\Delta = 16524\text{ cm}^{-1}$, the value of α is evaluated to be 0.5515 for ZLNB1 glass. The evaluated values of α (0.5569, 0.5485, 0.4253 and 0.5054 for ZLNB2 to ZLNB5) indicate the covalent nature of the Cr^{3+} ions in the glass matrix.

4. Conclusion

From the physical and spectral properties of 0.1 mol% of Cr^{3+} doped $19.9\text{ ZnO} + x\text{ Li}_2\text{O} + (30 - x)\text{ Na}_2\text{O} + 50\text{B}_2\text{O}_3$ ($5 \leq x \leq 25$) glasses, the following conclusions are drawn:

- (i) Powder X-ray diffraction patterns confirm the glassy nature of all the ZLNB glass samples.
- (ii) Non-linear behavior is observed in the physical parameters like density, refractive index, molar refractivity, ionic concentration, electronic polarizability, inter-ionic distances and polaron radii with respect to the changes in the concentrations of alkali content ($5 \leq x \leq 25\text{ mol}\%$). This is due to the phenomenon of MAE.
- (iii) The FT-IR spectral analysis confirms the presence of BO_3 and BO_4 local structures in all the glass systems.
- (iv) Optical absorption spectra confirm the distorted octahedral site symmetry for Cr^{3+} ions with partial covalency of ZLNB glasses. The crystal field (Dq) and Racah parameters (B and C) were evaluated.
- (v) From optical absorption edges, optical band gap energies and Urbach energies were evaluated. A non-linear behavior is observed and found to be in good agreement with theoretical values. It also confirms the structural variations with $x\text{ mol}\%$ of alkali ions.
- (vi) EPR spectra of the prepared ZLNB glass systems exhibited well intense resonance signals which are characteristic of Cr^{3+} ions in distorted octahedral symmetry. The non-linear behavior in g values was observed by changing the concentrations of alkali contents ($5 \leq x \leq 25\text{ mol}\%$) which is the manifestation of mixed alkali effect in the present glass systems. The evaluated bonding parameter predominantly indicates the covalent nature of Cr^{3+} in glass systems.

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