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Optical and IR studies of Cr³⁺ doped Li₂O-K₂O-B₂O₃ glasses

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ABSTRACT:

The glasses of Cr³⁺ doped Lithium potassium borate (LKB) glasses with variable concentrations of alkali content were prepared by melt quenching technique. The prepared samples were characterized by UV-vis absorption, EPR and FT-IR spectroscopy. Various physical parameters are evaluated and non-linear variation in physical parameters for different glasses was observed, which gives the evidence of MAE. optical absorption studies reveals the covalent nature of the Cr³⁺ doped LKB glasses. The evaluated bonding parameters suggest the covalent nature. The FT-IR spectra of the glasses showed the presence of trigonal BO₃ and tetrahedral BO₄ structural units.

KEYWORDS: Borate glass; Mixed alkali effect; Optical absorption; Melt quenching.

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1. INTRODUCTION

Glasses are more preferred as host matrix because of their high transparency, ease of mass production and shaping. Moreover, glasses show high dispersibility of many additives, large inhomogeneous broadening, and chemical durability as well as unique thermal and mechanical properties^{1,2} that have applications especially in lasers, phosphors, solar energy converter, plasma display panels and in a number of electronic devices. In order to identify new optical devices for specific utility, or devices enhanced performance, an appropriate host has to be prepared. Borate glass is considered to be a suitable host for optical materials because of their special properties. This interest is partly because of the anomalous behaviour of the glass in that it forms super structural units: well defined arrangements of the basic BO_3 and BO_4 structures. Furthermore, doping of these glasses by traces of other elements such as transition metals modifies its structural network and consequently changes its basic properties rendering them useful in a variety of applications. The local network structure and the formation of glass, though being studied for decades, are still puzzling problems.

Transition metal ions can be used to probe the glass structure since their outer d-electron orbital functions have a broad radial distribution. Among various transition metal ions, chromium ions, a paramagnetic probe, when doped in glass structural matrices in very small amounts affects strongly the optical transmission and the insulating strength of the glasses. This is due to the existence of chromium in different oxidation states, where Cr^{3+} may act as a network modifier while Cr^{6+} acts as network former with CrO_4^{2-} structural units^{3,4} Such multiple chromium oxidation states that can simultaneously be present in the glass depend on the modifier-former properties, size of the ions, their field strengths and mobility of the modifier cation. The optical absorption transition, ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ of Cr^{3+} ions is found to be very sensitive to the chemical environment. In recent years, investigations on the optical absorption, luminescence and electron spin resonance spectroscopy of Cr^{3+} ions in a variety of inorganic glasses have been made because of their technological importance in the development of tunable solid-state lasers and new luminescence materials.⁵⁻¹²

The authors selected the glass composition as described in Table 1, to know the effect of alkali ions on the site symmetry around the transition metal ions and also on the nature of bonding present in these glasses. Mixed-alkali effect (MAE) is one of the most widely studied component interactions in glasses. Many physical properties measured in mixed-alkali systems show initial non-linear growth and subsequent reversal in trends leading to a maxima or minima as a function of modifier fraction¹³ Lithium is used in high-capacity energy storage devices for next-generation electric vehicles, in light weight high-power-density lithium ion batteries for heart pacemakers, mobile phones and laptop computers¹⁴⁻¹⁵. Zinc-containing glasses have a low melting point and have

been widely used as good sintering agents. The aim of this study is to use detailed spectroscopic data to form a complete picture of the physical and spectroscopic properties of Cr³⁺ ions in LKB glasses. The interesting Electron Paramagnetic Resonance (EPR) and optical absorption spectra are known to be valuable sources of information with respect to the local environment of transition elements which are introduced in the vitreous matrix, thus giving certain knowledge of structure. The results that are obtained from these studies are discussed with respect to the composition of the mixed alkali elements.

2. EXPERIMENTAL PROCEDURE:

2.1 Preparation Technique:

A series of glass samples of formula $x\text{Li}_2\text{O} + (50-x)\text{K}_2\text{O} + 50\text{B}_2\text{O}_3$ with $10 \leq x \leq 30$ mol% were prepared by using melt quenching technique. Using B₂O₃ in the composition of these glasses make them more fusible, so they can be readily melted in conventional laboratory glass furnaces. The required amount of chemicals Li₂CO₃, K₂CO₃, B₂O₃ and Cr₂O₃ were thoroughly mixed in a porcelain mortar to obtain fine powder and then were melted in silica crucibles at a temperature of 1173 K for 60 minutes. The melt is then quenched at room temperature in air to form a glass. The glasses are annealed at 700 K for 60 minutes to remove structural stress. Subsequently, the samples were cooled down naturally to room temperature. All glass samples are disk-shaped (about 1cm diameter and thickness of 1–2 mm). The opposite faces of the samples are ground and polished with different grades of emery powder for UV–Visible spectroscopic measurements. The glass composition is taken in the ratio as mentioned in Table 1 and is here after named as LKB glasses.

Table 1: Composition of Cr³⁺ doped LKB glasses

Glass System	Chemical composition	Prepared temperature (K)
LKB1	9.9Li ₂ O+40K ₂ O+50B ₂ O ₃ +0.1Cr ₂ O ₃	1173
LKB2	19.9Li ₂ O+30K ₂ O+50B ₂ O ₃ +0.1 Cr ₂ O ₃	1173
LKB3	29.9Li ₂ O+20K ₂ O+50B ₂ O ₃ +0.1 Cr ₂ O ₃	1173

2.2 Characterizations:

The density of the glasses was determined by standard principle of Archimedes' using O-xylene (99.99% pure) as the buoyant liquid using VIBRA HT/HTR instrument. The refractive indices of the samples are measured by ATAGO's Abbe refract meter. One of the most definite methods to determine whether a glass sample has an amorphous structure or not, involves the XRD measurements. X-ray diffraction patterns of powdered glass samples are recorded on PANalytical Xpert Pro diffract meter with Cu K_α wavelength of 1.5406 Å. EPR spectra of the samples are

measured by using JEOL-JES TE100 ESR spectrometer at X-band frequency with 100 KHz field modulation. Optical absorption spectra of the samples are recorded using JASCO V-670 spectrophotometer in 200-1400 nm region. FT-IR spectra of the samples are recorded using KBr pallets on Shimadzu IRAffinity-1S in the range of 2000–400 cm^{-1} .

3. RESULTS AND DISCUSSION:

3.1 Powder X-Ray Diffraction Studies:

The observed powder X-ray diffraction patterns for Cr_2O_3 doped LKB glasses reveal the amorphous nature and the absence of crystalline characteristics. All the prepared glass samples confirm the glassy nature.

3.2 Physical Properties:

The physical parameters of the samples like dielectric constant, molar refractivity, molar volume, reflection loss and oxygen packing density are calculated from the measured values of the densities and refractive indices of Cr^{3+} doped LKB glasses.

Dielectric constant of the glass sample can be calculated by using refractive index.¹⁶

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

By using refractive index, the reflection loss of the sample is given by Fresnel's formula¹⁷

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

Molar refractivity of the glass sample can be calculated by using the formula¹⁸

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

The molar volume of the samples can be obtained by using the formula

$$V_m = M/\rho \quad (4)$$

Here, M is the molecular weight and ρ is the density of the sample. The oxygen packing density of the glass sample can be calculated by using the following expression¹⁹

$$O = n/V_m \quad (5)$$

Where n is the number of oxygen atoms in the composition. The electronic polarizability of the glass samples can be evaluated by using the formula²⁰

$$\alpha_e = 3(n_d^2 - 1)/4\pi N(n_d^2 + 2) \quad (6)$$

Here N is the number of Chromium ions per unit volume.

The inter ionic distance and polaron radius can be calculated by using the following formulae

$$r_i = (1/N)^{1/3} \quad (7)$$

$$r_p = (1/2)(\pi/6N)^{1/3} \quad (8)$$

Physical properties of the glasses are important and provide useful information about the structure and conduction mechanism due to transport of ions. In the glass production density is the most important property and is used to measure other physical parameters such as refractive index, elastic properties and thermal conductivity. The calculated values of density, refractive index, optical dielectric constant, reflection loss and other physical parameters of Cr³⁺ doped glasses are listed in the Table 2. The error in density and refractive index measurements are expected to ± 0.004 gm/cm³ and ± 0.0001 respectively. Density increases with increase of Li₂O content where as refractive index decreases. Similarly when ionic concentration increases then electronic polarizability decreases with increase of Li₂O content.

Table 2: Physical properties of Cr³⁺ doped LKB glasses at room temperature

Physical parameter	LKB1	LKB2	LKB3
Average molecular Weight (g/mol)	75.59	69.16	62.73
Density (ρ)(g/cm ³) (± 0.004)	2.388	2.417	2.403
Refractive index (n_d) (± 0.0001)	1.7342	1.7042	1.7371
Optical dielectric constant (ϵ) (± 0.005)	3.028	3.007	3.017
Reflection loss (R)	0.0729	0.0720	0.0724
Molar refractivity (R_m) (cm ³) (± 0.005)	12.766	11.569	10.402
Molar Volume (V_m) (cm ³ /mol)	31.64	28.77	25.94
Oxygen Packing density (O) (cm ³ /mol)	63.25	69.56	77.13
Cr ³⁺ ion concentration (N) (10 ²² ions/cm ³) (± 0.005)	0.190	0.209	0.232
Electronic polarizability (α_e) (10 ⁻²⁴ ions/cm ³) (± 0.005)	50.709	45.952	41.277
Inter ionic distance (r_i) (A) (± 0.005)	1.739	1.627	1.685
Polaron radius (r_p) (± 0.005)	0.639	0.601	0.627

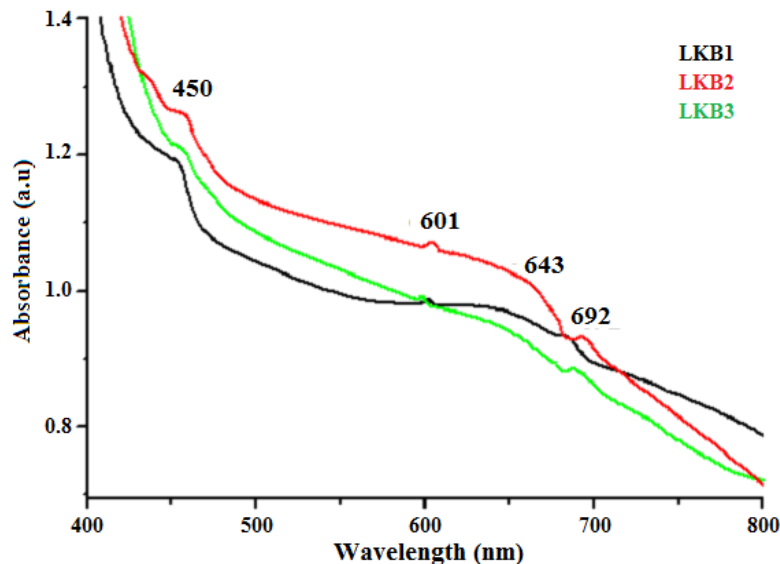
3.3 Optical Absorption Studies:

From the crystal field theory, Cr³⁺ ions are usually assumed to occupy approximately octahedral symmetry sites in inorganic solids. This is due to the ionic radius and the strong ligand field stabilization energy of Cr³⁺ ions in six fold coordination. The parity-forbidden d-d transitions can be due to partially allowed by the weak distortion of the crystal field or by instantaneous distortion due to molecular vibrations²²⁻²⁴ The assignments of the bands are given in Table 3.

Table 3: Absorption edge, thickness, indirect band gap & Urbach energies of Cr³⁺ doped LKB glasses

S. No	Glass system	Absorption edge (nm)	Thickness d(cm)	Optical band gap energy			Urbach energy ΔE (eV)
				E_{opt} (eV)			
				Theoretical	Experimental		
Direct	Indirect						
1	LKB1	410	0.182	3.029	3.028	3.027	0.039
2	LKB2	408	0.171	3.044	3.044	3.045	0.025
3	LKB3	414	0.185	3.000	2.995	2.996	0.041

The energy levels of transition elements, with electronic configuration '3d', can be described by crystal-field strength Dq and interelectronic interactions expressed as Racah parameters B and C. The chromium ion, Cr³⁺ (d³) gives rise to the free ion terms ⁴F, ⁴P, ²G and several other doublet states of which ⁴F is the ground state.

**Figure.1: Optical absorption spectrum of Cr³⁺ doped LKB3 glass**

Optical absorption spectrum of Cr³⁺ doped LKB3 glass is depicted in Fig. 1. It exhibits three characteristic spin allowed bands at 450 nm (22216 cm⁻¹), 643 nm (15548 cm⁻¹) and 692 nm (14447 cm⁻¹). These bands, according to their positions, are ascribed to the transitions ⁴A_{2g}(F) → ⁴T_{1g}(F), ⁴A_{2g}(F) → ⁴T_{2g}(F) and ⁴A_{2g}(F) → ²E_g(G) respectively. The broad absorption band observed at 643 nm has been attributed to Cr³⁺ ions belonging to 3d³ configuration, the ground state is always ⁴A_{2g}(F) irrespective of strength of crystal field. The band observed at 15548 cm⁻¹ (ν_1) attributed to ⁴A_{2g}(F) → ⁴T_{2g}(F) gives $10Dq$ and this band is to be related to d-d electronic transition of Cr³⁺ ions in octahedral symmetry. The wave number corresponding to the transition ⁴A_{2g}(F) → ⁴T_{1g}(F) is 22216 cm⁻¹ (ν_2). The band observed at 692 nm is attributed to the transition ⁴A_{2g}(F) → ²E_g(G). In addition to this a peak observed at 601 nm is the spin forbidden transition and it assigned to ⁴A_{2g}(F) → ²T_{1g}(G) with

the help of Tanabe-Sugano diagram. The Racah parameters (B and C) are determined by the following expressions^{25, 26}

$$B = (2v_1^2 + v_2^2 - 3v_1v_2)/(15v_2 - 27v_1) \quad (9)$$

$$C/B = 1/3.05[E(^2E)/B - 7.9 + 1.8 (B/D_q)] \quad (10)$$

The approximate value of B is evaluated to be 684 cm^{-1} . Based on the above assignments the energy matrices of d^3 configuration are solved for different values of crystal field (Dq) and inter electronic repulsion parameters (B and C). A good fit with the experimental results is obtained with $Dq = 1555$, $B = 684$ and $C = 3143 \text{ cm}^{-1}$. The errors in these values are $\pm 1 \text{ cm}^{-1}$. The free-ion value (B_{free}) is 918 cm^{-1} . The bonding in Cr^{3+} doped can be predicted by Nephelauxetic parameters of ligands and the central metal ions, which is evaluated using the expression²⁷

$$h = [(B_{\text{free}} - B)/B_{\text{free}}]/K_{\text{Cr}^{3+}} \quad (11)$$

In the above expression, the value of $K_{\text{Cr}^{3+}} = 0.21$ is used to evaluate²⁸ h value. The calculated values of h for LKB1, LKB2 and LKB3 glasses are 1.19, 1.09 and 1.21 respectively. The value of h indicates increased delocalization of the d -electrons suggesting covalent nature of bonding between Cr^{3+} and the ligands.

The value of Dq/B in the present case is 2.2733. This indicates moderately weak crystal field suggesting a covalent character for the chemical bonding in the glass²⁹

some of the Cr^{3+} ions is affected by changing x , which suggests that the structural changes take place with composition and the intensity of the resonance signal.

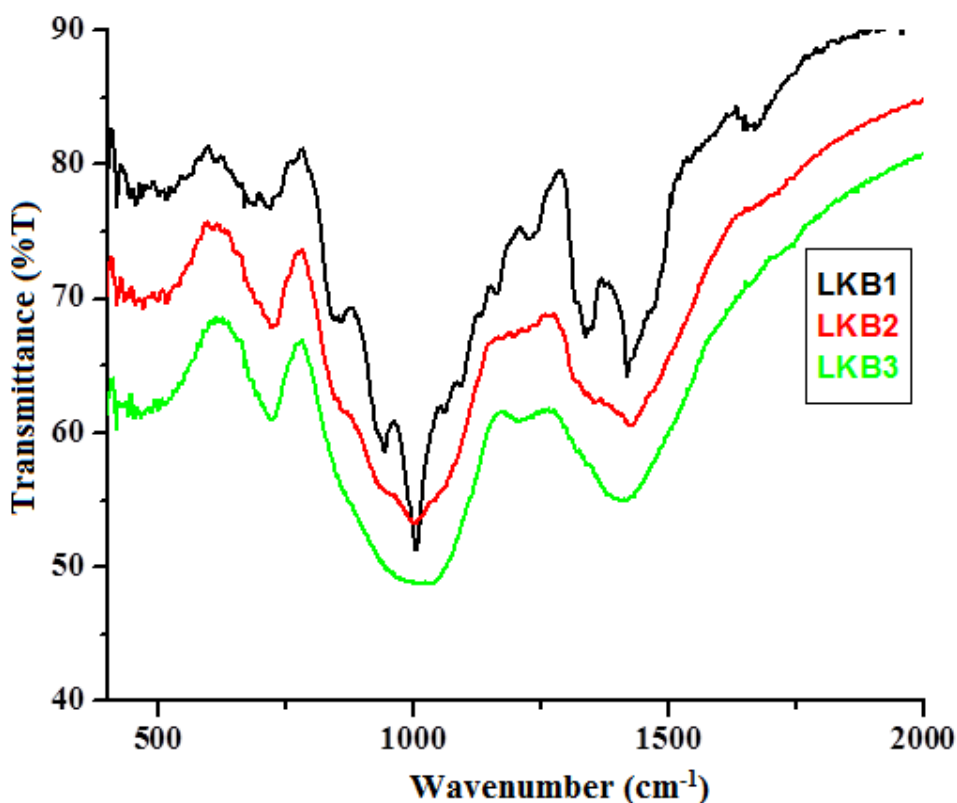
3.4 FT-IR STUDIES:

Borate glasses in particular, have been the subject of numerous infrared studies in order to study their structure peculiarities. The IR spectroscopy is the most advantageous tool for the study of structural features of amorphous materials. FTIR absorption spectra of the glasses under investigation have been recorded in the wave number range $4000\text{--}400 \text{ cm}^{-1}$ using Bruker FT-IR spectrometer.

Table4: Assignments of FT-IR bands in Cr³⁺ ions doped LKB glasses

LKB1	LKB2	LKB3	Assignments
458	471	464	Specific vibrations of Li cations
609, 686, 715	603, 724	721	B-O-B bending vibrations
846, 942, 1007, 1068, 1097, 1132, 1167	862, 1001, 1065	---	B-O symmetric vibrations of BO ₄
1334	1235, 1427	1209, 1408	B-O stretching vibrations of BO ₃
1674	1745	1748	H-O-H bending vibrations

Infrared spectroscopy is known to provide insights into the interaction between alkali metal ions and borate glass network.

**Figure.2: FT-IR spectra of Cr³⁺ doped LKB glasses**

In general the IR analysis of borate shows four distinct frequency regions. The region 1200-1600 cm⁻¹ and 800-1200 cm⁻¹ are assigned to stretching vibrations of both triangular BO₃ and tetrahedral BO₄ borate units respectively. Deformation modes of both types of units are active between 600 and 800 cm⁻¹²⁸. The bands observed in the region 900-1500 cm⁻¹ are the characteristic vibrations of LKB glasses²⁹. Fig. 2 shows the FT-IR spectra of Cr³⁺ doped LKB glasses. Specific vibrations of Li cations are observed at 458-471 cm⁻¹ region⁴². The absorption peaks in the region 603-724 cm⁻¹ are due to B-O-B bending vibrations. The absorption bands in the region 846-1167cm⁻¹

¹ are assigned to B-O symmetrical stretching vibrations of BO₄ units. The absorption bands observed in the region 1209-1427 cm⁻¹ is assigned to B-O stretching vibrations of BO₃ units with non-bridging oxygen atoms. The absorption bands around 1674-1748 cm⁻¹ region are assigned to H-O-H bending vibrations²⁵⁻²⁷. The origin of this weak band may be due to the trapping of water molecules in the glass matrix during the decomposition of boric acid. The obtained absorption bands and their assignments are summarized in Table 4.

4. CONCLUSIONS:

From the physical and spectral properties of 0.1 mol% of Cr³⁺ doped xLi₂O + (50-x) K₂O + 50B₂O₃ (x=10 ≤ x ≤ 30) glasses, the following conclusions are drawn:

- (i) The observed X-ray patterns of the samples studied in the present investigation indicate that the samples are amorphous.
- (ii) The physical parameters like density, refractive index, molar refractivity, ionic concentration, electronic polarizability, inter-ionic distances and polaron radii exhibited non-linearity with respect to the changes in the concentrations of alkali content (5 ≤ x ≤ 25 mol%). This is due to the phenomenon of MAE.
- (iii) The FT-IR spectral analysis confirms the presence of BO₃ and BO₄ local structures in their structural units for all the glass systems.
- (iv) Optical absorption spectra confirm the distorted octahedral site symmetry for Cr³⁺ ions with partial covalency of LKB glasses. The crystal field (Dq) and Racah parameters (B and C) were evaluated.

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