

Spectroscopic Studies on $\text{Li}_2\text{O}-\text{K}_2\text{O}-\text{MgO}-\text{BaO}-\text{B}_2\text{O}_3$ Glasses

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ABSTRACT: Mixed alkali alkaline earth oxide borate glasses of composition $(15-x)\text{Li}_2\text{O}-(15-x)\text{K}_2\text{O}-(15-x)\text{MgO}-(15-x)\text{BaO}-(40+4x)\text{B}_2\text{O}_3$ with $x = 0, 2.5, 5, 7.5,$ and 10 mol% were prepared by melt quenching method. X-ray diffractions studies on all the glass samples were made recorded at room temperature. Peak free X-ray spectra confirmed the amorphous nature of the glasses. Spectroscopic studies like Optical absorption and FTIR are carried out at room temperature. Optical absorption spectra are recorded in the wavelength range from $200\text{nm} - 1000\text{nm}$. From the optical absorption studies the values of the optical band (E_{opt}) for indirect, direct transition and Urbach energy (ΔE) have been evaluated. The values of $E_{\text{opt}}, \Delta E$ and density also show non linear behaviour with the compositional parameter, which also support the mixed alkali-alkaline effect in the present glass system. From FTIR spectra it is evident that present glasses consists of trigonal BO_3 and tetrahedral BO_4 structural units. The band $\sim 1360\text{ cm}^{-1}$ indicated the presence of tetrahedrally coordinated boron in the glass structure. The bands at 924 cm^{-1} and 1024 cm^{-1} suggest the presence of tri, tetra, penta and diborate units of BO_4 groups. The absence of band $\sim 806\text{ cm}^{-1}$ indicated the absence of boroxol rings in present glass system. The bands around 694 cm^{-1} might be due to formation of bridges by oxygen between two trigonal atoms.

KEYWORDS: borate glasses melt quenching, Optical absorption, band gap, Urbach energy, FTIR spectroscopy.

I. INTRODUCTION

Glasses are super cooled liquids, transparent, and amorphous in nature. They are inorganic product of fusion which has cooled to a rigid condition without any crystallization. The main distinction between glass and crystals is the presence of long-range order in the crystal structure [1]. The optimization of such properties as a function of composition and other processing parameters requires a good knowledge of the microscopic glassy structure. For many years, glasses containing transition metal ions have attracted attention because of their potential applications in electrochemical, electronic, and electro-optic devices. A host of borate rich glasses containing alkaline earth oxides along with ZnO , PbO , TeO_2 , Bi_2O_3 , MgO , CaO , SrO , and BaO as glass modifiers are optimistic materials for their probable applications in the fields of optical communications (optical fibers), laser hosts, optical filters, X- and γ -ray absorbers, photonic devices, and so forth. Infrared spectroscopy (IR) is an important tool for understanding the structure and dynamics of amorphous materials. It is also used to assign the observed absorption peaks to the proper vibration of the atoms in geometric grouping.

II. MATERIALS AND METHODS

The oxide borate glasses of composition $(15-x)\text{Li}_2\text{O}-(15-x)\text{K}_2\text{O}-(15-x)\text{MgO}-(15-x)\text{BaO}-(40+4x)\text{B}_2\text{O}_3$ with $x = 0, 2.5, 5, 7.5,$ and 10 mol% were prepared by melt quenching method. The starting materials were merck (gr grades) Boric acid (H_3BO_3), Lithium oxide (Li_2O), Potassium carbonate (K_2CO_3), Magnesium oxide (MgO), Barium oxide (BaO) (all are Sd fine). The calculated amounts by mol% of these compounds are thoroughly mixed in the agate mortar and pestle, grind to get the required composition. The ingredients are taken in a porcelain crucible and were melted for about 40-60 minutes in an electrical furnace maintained at 1150°C , to obtain homogeneity, the melt was shaken frequently. The melt was quickly poured onto a stainless steel plate and pressed with another stainless steel plate, both being maintained at 100°C , the samples are clear, transparent and bubble free. Samples of uniform thickness were employed in optical

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absorption measurement. the obtained bulk compounds were grounded into fine powders and were characterized by x-ray diffraction (xrd), optical absorption spectra (2092piuv/Vis-Analytical Technologies Limited) using UV-Vis Spectrophotometer (shimadzu) in the wavelength subsequently annealed at 383⁰ c temperatures for duration of about 12 h, and then sliced and polished. The glass samples thus obtained region 200 nm to 1000 nm, and FTIR (make-bruker optics, and model - tensor 27)arestudied at CFRD, OU (Central Facilities Research Development).

III.RESULT AND DISCUSSION

3.1 X-Ray Diffraction

Philips Xpert PRO XRD (PanAnalytic) model powder X-ray diffractometer with copper K α tube target with nickel filter operated at 40 kV, 30 mA was used to record the X-ray diffractograms. All the X-ray diffractograms are recorded at room temperature. All the recorded peak free X-ray diffractograms confirmed amorphous nature of the samples, used in the present studies.

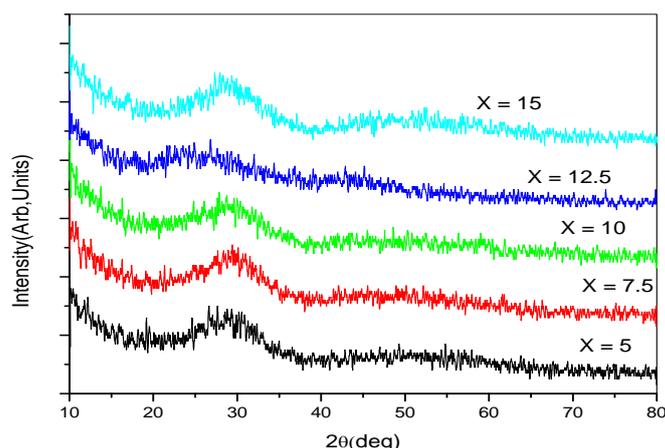


Fig.1 XRD patterns of KLMBB glasses.

Figure.1 shows the X-ray diffractograms of the present glass samples. It gives absence of sharp peaks and conform the amorphous nature of present all the glasses.

3.2 Optical Absorption

The optical absorption spectra of the present glasses are shown in Fig. 2. The optical absorption coefficient $\alpha(\nu)$ near the fundamental absorption edge of the curve is determined using the relation

$$\alpha(\nu) = \frac{1}{d} \log\left(\frac{I_0}{I_t}\right), \tag{1}$$

where I_0 and I_t are the intensities of the incident and transmitted beams, respectively, and d is the thickness of the glass sample. The factor $\log\left(\frac{I_0}{I_t}\right)$ corresponds to the absorbance. Davis and Mott [2] & Tauc and Menth[3] related this data to the optical band gap (E_{opt}) through the following general relation proposed for amorphous materials

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Table I.
Physical and optical parameters of KLMBB glasses.

Glass composition	x=5 LKMBB-5	x =7.5 LKMBB-7.5	x=10 LKMBB-10	x=12.5 LKMBB-12.5	x =15 LKMBB-15
Average molecular weight(M)(g/mol)	71.58	72.57	73.57	74.54	75.5
Density (ρ)(g/cc)	2.295	2.477	2.622	2.642	2.74
Molar volume (V _M)(cc/mol)	31.19	29.3	28.06	28.22	27.56
Oxygen Packing Density(g.atm/l)	83.36	81.91	78.4	70.88	65.32
Cut-off wavelength (nm)	380	353	350	373	367
Direct optical band gap(eV)	3.48	3.75	3.47	3.53	3.44
Indirect optical band gap(eV)	3.06	3.2	3.18	3.2	3.16
Urbach energy ΔE (eV)(±0.05)	0.54	0.43	0.33	0.32	0.37

Density(ρ)(g/cc) values calculated by Archimedes principle, Molar volume (V_M)(cc/mol) calculated from density and average molecular weight, Oxygen Packing Density(g.atm/l) calculated from molar volume and number of oxygens in the composition, Cut-off wavelength (nm) obtained from linear portion of curve, Direct and Indirect optical band gaps(eV) obtained from the Tauc model and Urbach energy ΔE (eV) width of localized states obtained from the Urbach plot.

$$\alpha(\vartheta) = B(h\vartheta - E_{opt})^n/h\vartheta, \tag{2}$$

where B is a constant and $h\vartheta$ is the incident photon energy. The index $n = 1/2$ for direct allowed transitions and $n = 2$ for indirect transitions. From eqns. (2) and (3) by plotting $(\alpha h\vartheta)^2$, $(\alpha h\vartheta)^{1/2}$ as a function of photon energy $h\vartheta$, optical energy band gap (E_{opt}) for direct and indirect transitions can be estimated respectively.

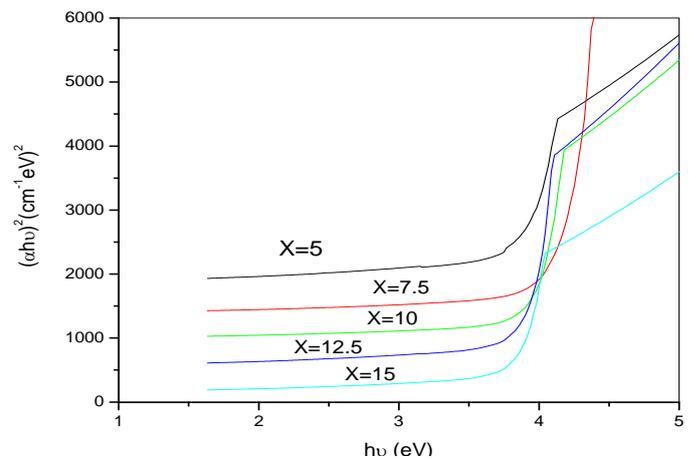
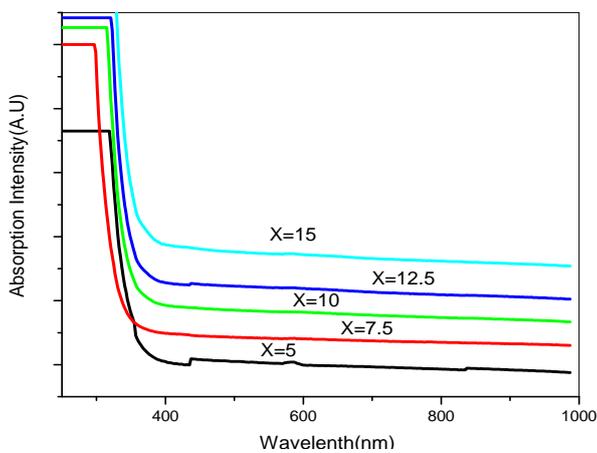


Fig. 2. Optical absorption spectra of KLMBB glasses. Fig. 3 Tauc plots $[(\alpha h\nu)^2 \text{ versus } h\nu]$ for the KLMBB glasses.

The cut-off wave length can be obtained from linear portion of curve from the Fig. 2 and Direct allowed band gap obtained from the (Fig.3) Tauc model, it gives the allowed energy transitions in between the valance and conduction band gaps.

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The respective values of E_{opt} were obtained by extrapolating to $(\alpha h\nu)^2 = 0$ for direct transitions and $(\alpha h\nu)^{\frac{1}{2}} = 0$ for indirect transition. Fig.3 and 4 represents the Tauc plots $[(\alpha h\nu)^2, (\alpha h\nu)^{\frac{1}{2}}$ versus $h\nu$] for the present glass samples. The values of the indirect band gap direct band gap are presented in Table I.

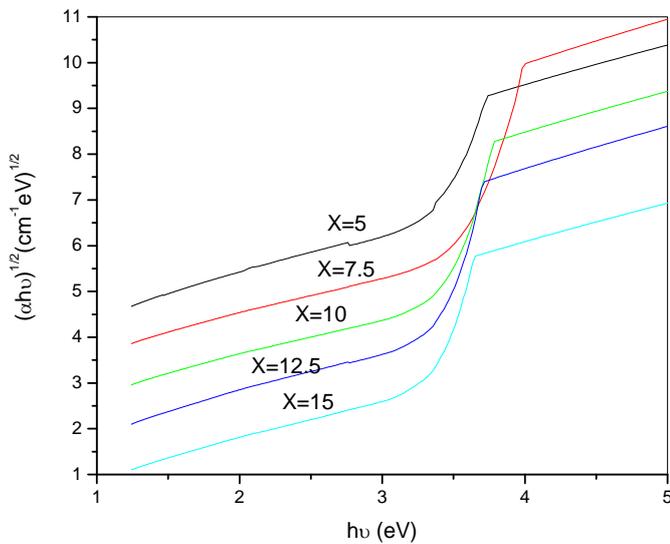


Fig. 4. Tauc plots $[(\alpha h\nu)^{\frac{1}{2}}$ versus $h\nu$] for the KLMBB glasses.

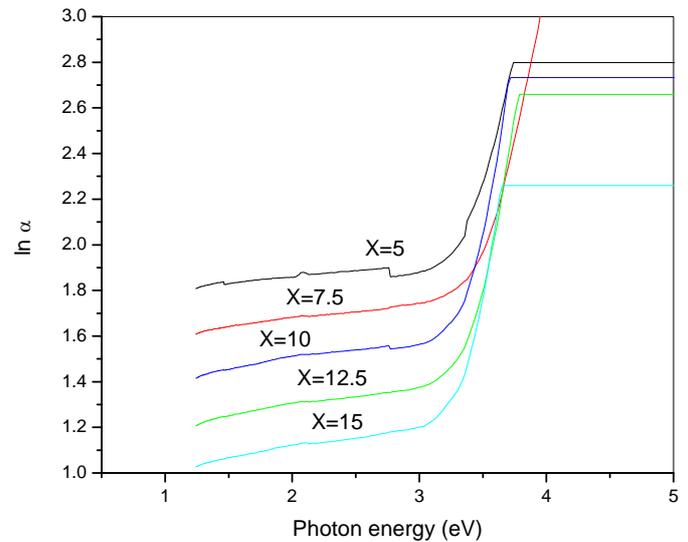


Fig. 7. Urbach energy $(\ln(\alpha)$ versus $h\nu$) of the KLMBB glasses.

The Indirect allowed band gap obtained from the (Fig.4) Tauc model, it gives the allowed energy transitions in between the valance and conduction band gaps and to conform the amorphous nature and Urbach energy ΔE (eV) width of localized states obtained from the Urbach plot from Fig.7.

Similar behavior was also observed by other workers [4, 5]. The variation of the direct and indirect band gap energy (E_{opt}) with the compositional parameter is shown in Fig. 5 and 6. It is observed that E_{opt} varies nonlinearly with composition. The main feature of the absorption edge of amorphous materials is an exponential increase of the absorption coefficient $\alpha(h\nu)$ with the photon energy $h\nu$, as given by the Urbach rule [6].

$$\alpha(h\nu) = C \exp(h\nu / \Delta E), \tag{3}$$

where C is a constant and ΔE is the Urbach energy, which is a measure of band shift. Fig.7. shows the variation of $\ln(\alpha)$ as a function of photon energy $h\nu$. The values of the Urbach energy (ΔE) were determined by taking the reciprocal of the slopes of the linear portion of the $\ln(\alpha)$ versus $h\nu$ curves. Fig.7 illustrates a fitted curve used to determine the Urbach energy for a typical glass samples. The Urbach energy values of the present glass samples are presented in Table I.

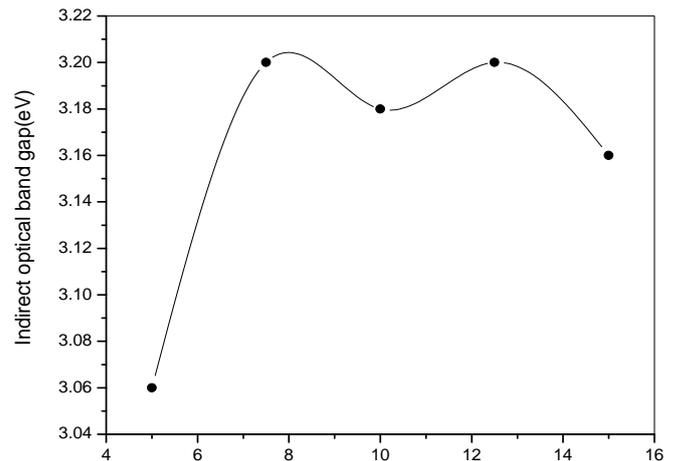
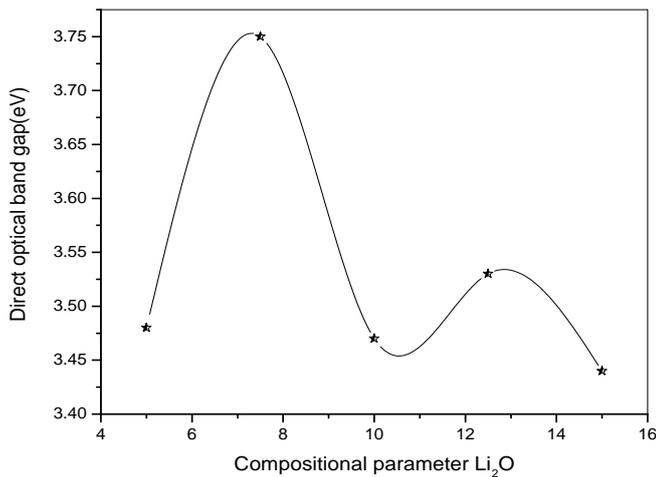


Fig.5.Compositional dependence of the direct band gap Fig.6.Compositional dependence of the indirect band gap.

The compositional dependence of the Urbach energy ΔE is shown in Fig. 8. Fig.9 shows the nonlinear variation of the indirect band gap and Urbach energy with Li₂O compositional parameter, and also fig.10 indicates molar volume and density shows opposite behavior with Li₂O content. It indicates the existence of the mixed alkali-alkaline effect.

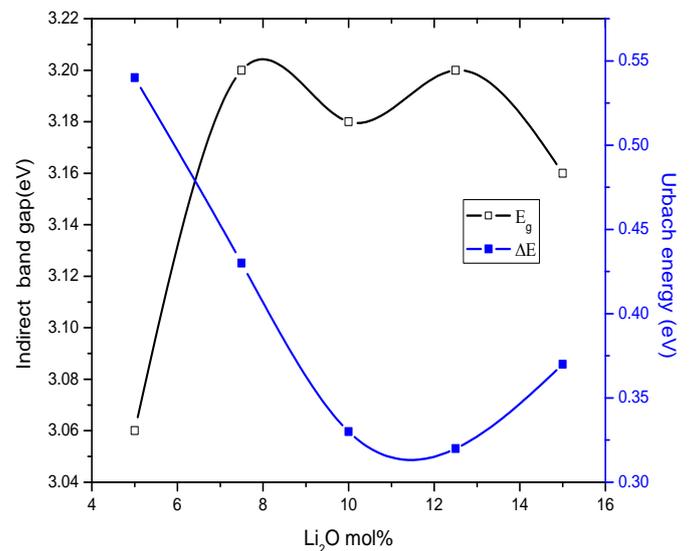
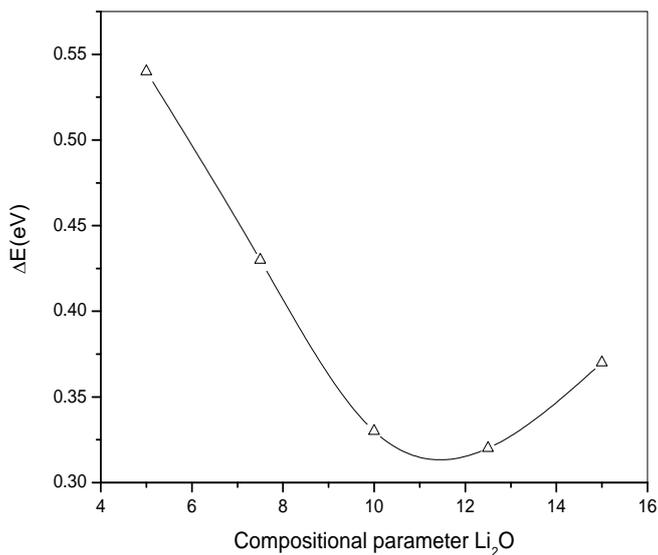


Fig.8.Compositional dependence of the Urbach energy (ΔE). Fig. 9. Variation of indirect band gap and Urbach energy as a function of Li₂O content.

3.3 Infrared Studies

The FTIR spectra of glass samples are shown in Figures 10. The infrared spectra have shown medium, weak and broad absorption bands and these are given in Table.2. The absorption peaks in FTIR Spectra can be divided into four main

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groups in the ranges $3600-2300\text{cm}^{-1}$, $1600-1200\text{cm}^{-1}$, $800-1200\text{cm}^{-1}$ and $700-400\text{cm}^{-1}$. The absence of absorption peak at $\sim 806\text{cm}^{-1}$ in all the glass systems shows that there is no boroxol ring formation in the glass network. The absorption bands around 3375cm^{-1} in the glasses (LKMBB-5 and LKMBB-7.5) are assigned to OH stretching vibration [7]. The peaks $2700-3000\text{cm}^{-1}$ are attributed to hydrogen bonding [8]. The presences of bands around 1740cm^{-1} in all the glass samples are attributed to the bending and stretching vibration of B–O–B in $[\text{BO}_3]$ triangles [9, 10].

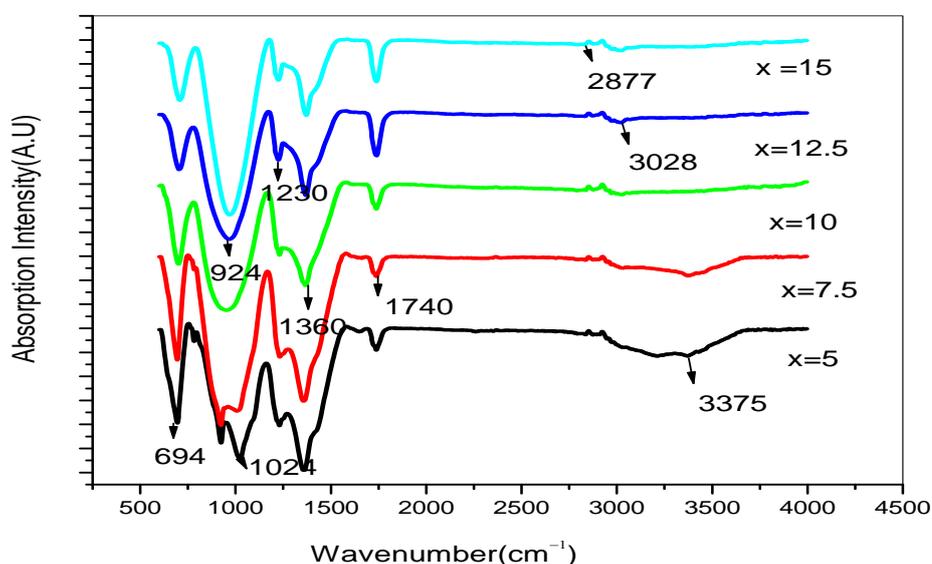


Fig. 10. FT-IR spectrum of KLMBB glasses.

The peaks around 1360cm^{-1} are due to asymmetric stretching vibrations of B-O and B-O⁻ bond in trigonal BO_3 units. The IR absorption peaks around 1230cm^{-1} are characteristic of =B-O-B= linkage with one of the boron in tetrahedral coordination [11]. The bands at 924cm^{-1} and 1024cm^{-1} suggest the presence of tri, tetra, penta and diborate units of BO_4 groups. The bands around 694cm^{-1} might be due to formation of bridges by oxygen between two trigonal atoms.

Table.2
Various IR bands observed in the glass systems.

S.No	Glass Systems	IR band positions wave number(cm^{-1})								
1	LKMBB-5	3373	--	--	1739	1360	1231	1024	924	694
2	LKMBB-7.5	3374	3032	--	1739	1357	1233	--	923	694
3	LKMBB-10	--	3030	2876	1739	1367	1231	--	953	700
4	LKMBB-12.5	--	3021	2873	1740	1370	1226	--	967	705
5	LKMBB-15	--	3023	2877	1740	1371	1225	--	969	708

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IV. CONCLUSIONS

- The oxide borate glasses of composition $(15-x) \text{Li}_2\text{O}-(15-x)\text{K}_2\text{O}-(15-x) \text{MgO}-(15-x) \text{BaO}-(40+4x)\text{B}_2\text{O}_3$ were prepared by melt quenching method. X-ray diffractograms studies revealed the amorphous nature of the prepared glasses.
- From the optical absorption studies the values of the optical band (E_{opt}) for direct, indirect transitions between conduction and valence bands and Urbach energy (ΔE) have been evaluated.
- The values of E_{opt} , ΔE and density have shown non linear behaviour with the compositional parameter, which also support the mixed alkali-alkaline effect in the present glass system.
- From FTIR spectra it is evident that present glasses consists of trigonal BO_3 and tetrahedral BO_4 structural units. The band $\sim 1360\text{cm}^{-1}$ indicated the presence of tetrahedrally coordinated boron in the glass structure. The bands at 924cm^{-1} and 1024cm^{-1} suggest the presence of tri, tetra, penta and diborate units of BO_4 groups. The absence of band $\sim 806\text{cm}^{-1}$ indicated the absence of boroxol rings in present glass system.

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REFERENCES

- [1] M. Yamane and Y. Asahara, *Glasses for Photonics*, Cambridge University Press, Cambridge, UK, 2000.
- [2] E.A. Davis and N.F. Mott, *Phil. Mag.* 22, 903 (1970).
- [3] J. Tauc and A. Menth, *J. Non-Cryst. Solids* 8, 569 (1972).
- [4] A. Agarwal, V.P. Seth, S. Sanghi, P. Gahlot, and S. Khasa, *Mater. Lett.* 58, 694 (2004).
- [5] R.P. Sreekanth Chakradhar, K.P. Ramesh, J.L. Rao, and J. Ramakrishna, *J. Phys. Chem. Solids* 64, 641 (2003).
- [6] F. Urbach, *Phys. Rev.* 92, 1324 (1953).
- [7] Baia.L and Simon.S, (2005), *Phys. Chem. Glasses*, 46(3) 279-283.
- [8] Veeranna Gowda.V.C and Anavekar.R.V. (2004), *Ionic's*, 10 (2004) 103-108.
- [9] Y. Cheng, H. Xiao, W. Guo, and W. Guo, *Ceramics International*, vol. 33, no. 7, pp. 1341–1347, 2007.
- [10] E. I. Kamitsos, A. P. Patsis, M. A. Karakassides, and G. D. Chryssikos, *Journal of Non-Crystalline Solids*, vol. 126, no. 1-2, pp. 52–67, 1990.
- [11] VirenderKundu, Dhilman. R.L., Maan. A.S, and Goyal D.R, (2008), *Advances in Condensed Matter Physics*, (2008) 1-7.