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RESEARCH ARTICLE

OPTICAL AND MECHANICAL STUDIES OF BORATE LITHIUM GLASSES DOPED WITH POTASSIUM OXIDE AND CALCIUM OXIDE

*,[1]Palani, R. and [2]Selvarasi, J.

[1]Associate Professor, Department of Physics, Annamalai University, Annamalai Nagar, Tamil Nadu, India
[2]Research scholar, Department of Physics, Annamalai University, Annamalai Nagar, Tamil Nadu, India

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ABSTRACT

Glasses with compositions $80B_2O_3$-$20Li_2O$, $80B_2O_3$-$(20\text{-}x)Li_2O$-xK_2O and $80B_2O_3$-$(20\text{-}x)Li_2O$-$xCaO$ (where x = 0 to 10 in steps of 2 mol %) have been prepared using normal melt quenching technique. Structure that was investigated using X-ray diffraction has indicated the amorphous state of the prepared glasses. The density and the molar volume have been determined. Decrease in density and the increase in molar volume of the glass samples indicated the largeness of glass network upon addition of K_2O and CaO. Furthermore, the optical and mechanical characterizations of these glasses were carried out. Variations in the different physical parameters such as the oxygen packing density, refractive index, dielectric constant, molar refractivity, molar electronic polarizability and metallization criterion of borate lithium glass with K_2O and CaO content have been analysed and discussed in terms of the changes in the glass structure. Results show anomalies with addition of K_2O and CaO confirming the changes in the rigidity and the content of non-bridging oxygens (NBOs). The Vicker's microhardness studies reveals the anisotropy nature of the material. It further confirms that the samples belong to soft glass category. Decreases in microhardness were attributed to decreases in elastic moduli and bond strength with increasing load. The effects of composition of the glasses on microhardness are discussed.

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INTRODUCTION

Nowadays, the increasing of glass researches is due to their interesting applications in photonics and nuclear fields (Aly Saeed *et al*., 2013). More recently, there has been a great deal of interest on the preparation and characterization of a wide variety of optical glasses comprising of oxides, silicates, borates, phosphates, fluorides etc., for their potential applications (Keerti Marita *et al.,* 2014). The borate glasses are the best glass formers, which can make glass alone with high chemical durability, good transparency, thermal stability and good rare-earth ion solubility (Abousely *et al.,* 2015). Borate glasses containing lithium ions are favourable for ionic conduction due to a fast ionic conductivity based on the mobility of light Li^+ ions. These glasses have been studied extensively due to their interesting advantages as electric materials (Aly Saeed *et al*., 2013). The addition of alkali, alkaline earth oxides in borate lithium glasses as it changes the properties such as density, refractive index, and microhardness, in a nonpredictive manner (Kjeldsen *et al.,* 2013).

Corresponding author: **Palani, R.**
Associate Professor, Department of Physics, Annamalai University, Annamalai Nagar, Tamil Nadu, India.

Refractive index is important parameter for the design of optical materials such as prisms, windows and optical fibres. Therefore, a large number of researchers have carried out investigations to ascertain the relation between refractive index and glass composition (Ma *et al.,* 1993). Mechanical strength of materials plays an important role in device fabrication. Microhardness is a property for assessing bond strength apart being a measure of bulk strength of a material. Hardness is one of the important mechanical properties of the materials. It can be used as a suitable measure of the plastic properties and strength of a material (Karthiga Devi, *et al.,* 2016). The hardness of a glass is usually expressed in terms of indentation hardness such as Vickers or Knoops hardness (Vijoy *et al.,* 1999). The general definition of indenters, is the ratio of the applied load to the projected area of indentation. Generally, the apparent hardness of the materials varies with applied load. This phenomenon, known as the indentation size effect (ISE), usually involves a decrease in the microhardness with increasing applied load (Sangwal, 2000). The decrease of microhardness with increasing applied load has been reported by various researchers (Anbukumar *et al.* 1986). In contrast to the ISE, a reverse type of indentation size effect (reverse ISE), where the microhardness increases with increasing applied load, is also known (Hanneman *et al.,* 1967). In view of the aforementioned aspects, $80B_2O_3$-$20Li_2O$ (BL), $80B_2O_3$-(20-x) Li_2O-xK_2O (BLK) and $80B_2O_3$-(20-x)Li_2O-xCaO (BLC) (where x =0 to 10 in steps of 2 mol%) glasses have been synthesized over a wide range of compositions to explore the relationship between the structure and the macroscopic behaviour of the glass for the design of optical materials suitable for specific applications. Optical and mechanical studies have been used for the present investigations.

MATERIALS AND METHODS

The glasses with chemical composition of $80B_2O_3$-$20Li_2O$ (BL), $80B_2O_3$-(20-x)Li_2O-xK_2O (BLK) and $80B_2O_3$-(20-x) Li_2O-xCaO (BLC) (where x =0 to 10 in steps of 2 mol%) were prepared by melt quenching technique, from high purity analytical grade chemicals of B_2O_3, Li_2CO_3, K_2CO_3, and $CaCO_3$. Appropriate amounts of these chemicals were mixed in an agate mortar and crushed thoroughly and the mixture was converted in to an alumina crucible and melted at a temperature 1373K about 1 hour using thermocyclic furnace. During melting, the mixture was shaken frequently to ensure homogeneity. The melt was then poured onto a preheated thick copper plate and annealed at 473K for about two hours to avoid the formation of air bubbles, to remove strains and to enhance the mechanical strength of the glass samples and then allowed to reach room temperature gradually. The prepared glasses were polished on both sides to obtain plainer surfaces before studying their optical and mechanical properties.

X-ray diffraction studies

The amorphous nature of glass samples was confirmed by X-ray diffraction technique using an X-ray diffractometer (Model: Diffractometers de rayons X- Inel- EQUNIOX 1000) at a range of $2\Theta = (10\text{-}100^{\circ})$ utilizing Cu radiation with an applied voltage of 40Kv and 30mA anode current.

Density studies

The density (ρ) of the glass samples at room temperature was measured using Archimedes' principle. The distilled water was used as an immersion liquid. The density was calculated using the formula.

$$\rho = [a / (a-b)]\, \rho_x \qquad \text{…………(1)}$$

where, 'a' and 'b' are the weight of the sample in air and in distilled water. ρ_x is a density of the distilled water at 303K.
The molar volume (V_m) was calculated by using the formula

$$V_m = M_{eff} / \rho \qquad \text{……………. (2)}$$

where, M_{eff} is the effective molecular weight.($M_{eff} = \Sigma\, x_iM_i$) where,$x_i$ and M_i are the mole percentage and molecular weight of the individual component in the mixtures.

The oxygen packing density (OPD) of the glass samples were calculated using the following relation (Padmaja *et al.,* 2009)

$$OPD = n\, (\rho / M_{eff}) \qquad \text{..…..………(3)}$$

where, n is the number of oxygen atoms in the composition.

Refractive index studies

Refractive Index (*n*) of the prepared glasses were measured at room temperature using a Metricon Prism Coupler Model 2010 at 632.8 nm.

The Lorentz – Lorentz equation (Lorentz, 1880.) relates molar refraction (R_m) to refractive index and molar volume of the substance by,

$$R_m = \left(\frac{n^2-1}{n^2+2}\right)V_m \qquad \text{……………(4)}$$

The dielectric constant (Ɛ) was calculated from the refractive index of the glass using the relation

$$\varepsilon = n^2 \qquad \text{………………….. (5)}$$

According to Clausius- Mosotti, the molar electronic polarizability α_m is given by the relation

$$\alpha_m = \left(\frac{3}{4\pi N}\right)R_m \qquad \text{………………….(6)}$$

where, *N* is Avogadro's number. (N= 6.023x10^{23} mol^{-1})

The metallization criterion (M) has been calculated using

$$M = 1 - R_m/V_m \qquad \text{………………..…(7)}$$

Microhardness studies

Microhardness measurements were carried out using SHIMADZU HMV Microhardness tester-2T-40X fitted with a Vickers diamond pyramidal indenter. All the indentation measurements were carried out on the freshly polished glass samples at room temperature. The indentation was made by varying the load from 0.05 to 0.1 Kg and time of indentation was kept at 10 sec. The indented impressions were approximately square. Diagonal lengths of the indented impression were measured using calibrated micrometre attached to the eyepiece of the microscope. Several indentations were made on each sample. The average value of the diagonal lengths of indentation mark was used to calculate the microhardness.

Vicker's microhardness value (H_v) (Chenthamari *et al.,* 2001) has been calculated using

$$Hv = 1.8544\, P/d^2 \qquad \text{…..………(8)}$$

where, P is the applied load, d is the mean diagonal length of the indentation impression and 1.8544 is a constant(a geometrical factor / Vicker's conversion factor for the diamond pyramid). According to Meyer's law (Bull, Page *et al.* 1989), the relation connecting the applied load is given by

$$P = a^{nd} \qquad \text{…………………...(9)}$$

where, 'n' is the Meyer's index number or work hardening exponent and 'a' is a constant for a given material. The value of work hardening exponent (n) was estimated from the plot of log P versus log d by the least square fit method. The 'n' value is useful to determine whether the material is hard or soft.

RESULTS AND DISCUSSION

X-ray diffraction studies

X-ray diffraction spectrum of the studied glass systems reveal the absence of any discrete or continuous sharp crystalline peaks, but show homogeneous glassy characters. The powder X-ray diffraction spectrum of some of the glass samples of BL, BLK3, and BLC3 are as shown in Fig 1.

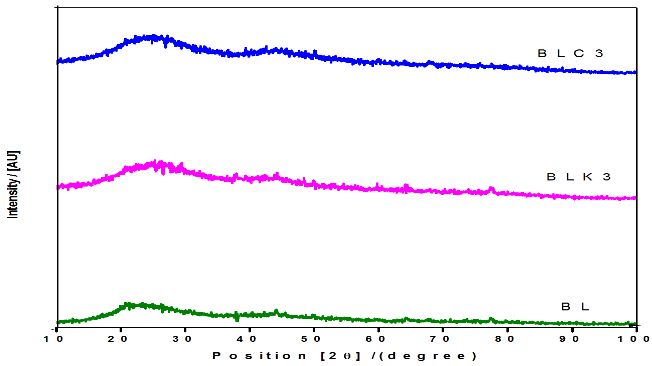

Fig. 1. The powder X-ray diffraction spectrum of glass samples of BL, BLK3, and BLC3 at room temperature

Refractive index studies

The structure of glasses can be determined from density and molar volume of glasses. The change in molar volume with molar composition of oxide is likely to explain the structural changes through a formation or modification process in the glass network (Thombre *et al.,* 2014). The oxygen packing density (OPD) also supports this idea. The decrease in oxygen packing density (Fig.2) suggests an increasing formation of NBOs and a loosely packed structure (Joao Coelho *et al.,* 2012). The density of a glass plays an important role in controlling the refractive index. Refractive index is another important property to be considered with respect to the optical features of glass. From the Fig.3 it is observed that the values of refractive index decreases in BLK glasses whereas the reverse trend occurs in the BLC series of glass. The refractive index of a substance is higher when its molecules are more tightly packed or in general when the glass is harder and with the increase of CaO content in borate lithium glasses, refractive index values also increases. It is important to note that the transparency of the glass depends upon the refractive index. Higher refractive index posses less transparency and vice versa.

value. Since the refractive index in the glasses are less than 1.7, they can be used as optical glasses (Edukondalu *et al.,* 2013). Furthermore, this behaviour is also supported by the variations of other parameters like dielectric constant (Ɛ), molar refractivity (R_m) and molar electronic polarizability (α_m). The prediction of glasses as metallic or insulator is based on metallization criterion. If the values are greater than unity and the material exhibits metallic nature and if less than unity, the material is treated as insulating nature. The metallization values (Table 1) of the present glasses are found to be less than one, which means that the width of both valence and conduction bands becomes large.

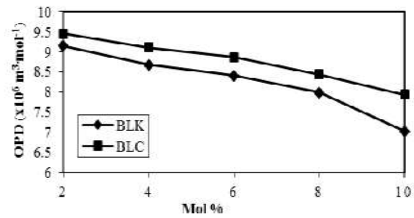

Fig.2. Variation of oxygen packing density (OPD) with K_2O/CaO mol % of borate lithium glass system.

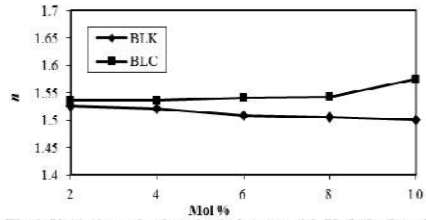

Fig.3. Variation of refractive index (*n*) with K_2O/CaO mol % of borate lithium glass system.

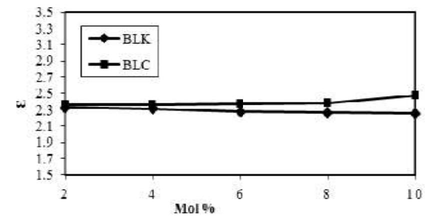

Fig.4. Variation of dielectric constant (Ɛ) with K_2O/CaO mol % of borate lithium glass system.

Table 1. Values of density (ρ), molar volume (V_m), oxygen packing density (OPD), refractive index (*n*), dielectric constant (Ɛ), molar refractivity (R_m), molar electronic polarizability (α_m),and metallization criterion (M) of the investigated glasses

Glass Samples Label	Composition (mol %)	ρ (kg.m^{-3})	V_m (x10^{-6} m^3. mol^{-1})	OPD (x10^6 m^3 mol^{-1})	*n*	Ɛ	R_m (x10^{-6} m^3 .mol^{-1})	α_m (x10^{-30} m^3)	M
B_2O_3+Li_2O (BL)									
BL	80 - 20	2334.6	30.19	8.6121	1.6668	2.778	11.235	4.456	0.628
B_2O_3+Li_2O+K_2O (BLK)									
BLK 1	80–18-02	2524.7	28.42	9.1484	1.5253	2.327	8.714	3.456	0.693
BLK 2	80-16-04	2437.6	29.97	8.6753	1.5209	2.313	9.124	3.618	0.696
BLK 3	80-14-06	2403.3	30.93	8.4061	1.5090	2.277	9.234	3.662	0.702
BLK 4	80-12-08	2323.2	32.55	7.9877	1.5055	2.267	9.662	3.832	0.703
BLK 5	80-10-10	2079.2	36.99	7.0289	1.5013	2.254	10.901	4.223	0.705
B_2O_3+Li_2O+CaO (BLC)									
BLC 1	80-18-02	2581.3	27.50	9.4545	1.5360	2.359	8.575	3.400	0.688
BLC 2	80-16-04	2506.3	28.54	9.1100	1.5370	2.362	8.913	3.535	0.688
BLC 3	80-14-06	2455.9	29.34	8.8616	1.5403	2.373	9.209	3.652	0.686
BLC 4	80-12-08	2356.4	30.79	8.4443	1.5425	2.379	9.698	3.846	0.685
BLC 5	80-10-10	2232.7	32.74	7.9414	1.5745	2.479	10.811	4.287	0.670

The increase in the refractive index could be attributed to the formation of non-bridging oxygen (NBOs) in the glass network. The NBOs create more ionic bonds, which manifest themselves in a larger polarizability over the covalent bonds of bridging oxygens (BOs), providing a higher refractive index

Hence, the present glass systems should exhibit an insulating nature. These glass samples are poor electronic conductors and have shown ionic conductivity.

Microhardness studies: Microhardness testing is one of the simplest and best methods to understand the strength of the materials (Dhanaraj *et al.,* 2011). From the Table 2, it is seen that the values of microhardness are decreases in BLK glasses whereas it increases in BLC series of glass. Further, it is noticed that the values of microhardness are decreases with increasing of load in all glasses.

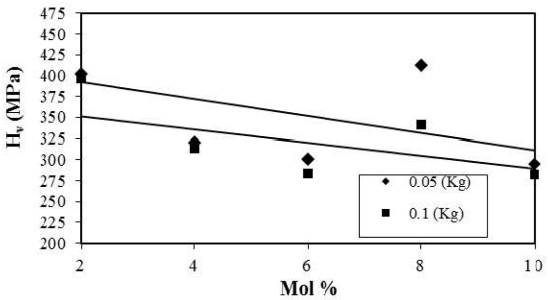

Fig.5. Variation of microhardness verus mol % of BLK glasses at room temperature.

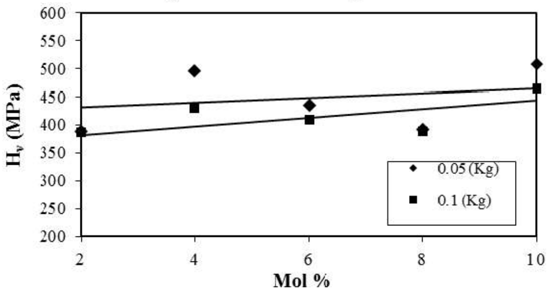

Fig.6. Variation of microhardness verus mol % of BLC glasses at room temperature.

Table 2. Values of microhardness (Hv) and Meyer's index number/ work hardening exponent (n) for various glass compositions with different applied load at room temperature

Glass Samples Label	Microhardness H_v/ (MPa) Load / kg 0.05	0.1	Meyer's index number / work hardening exponent (n)
B_2O_3+Li_2O (BL)			
BL	440	352	1.5137
B_2O_3+Li_2O+K_2O (BLK)			
BLK 1	402	396	1.9626
BLK2	321	313	1.9396
BLK 3	301	284	1.8550
BLK 4	413	341	1.5732
BLK 5	295	282	1.8940
B_2O_3+Li_2O+CaO (BLC)			
BLC 1	389	386	1.9878
BLC 2	496	430	1.6639
BLC 3	435	410	1.8520
BLC 4	392	389	1.9982
BLC 5	508	464	1.7795

The increasing value of microhardness in BLC glasses makes the glass harder and vice versa. The decrease of microhardness with the increasing of load is in agreement with the indentation size effect (ISE) (Balta-Celleja *et al.,*1995).The relation between load and the size of indentation can be interpreted using Meyer's law $P = ad^n$ and where 'a' is a constant and 'n' is the Meyer's number (or index).The slope of log P versus log d give the 'n' values. Meyer number is a measure of the indentation size effect (ISE). From the above table it is also noted that the values of 'n' are varies non-linearly with respect to BL glasses. According to Onitsch (Onitsch, 1947) and Hanneman (Hanneman, 1941) for the normal indentation size effect behaviour the exponent 'n' are less than 2, for softer ones. When 'n' greater than 2, there is the reverse indentation size effect (RISE) behaviour for hard materials which indicates the microhardness values increases with increasing load. It is evident from the above table the values of 'n' are less than 2 which indicates all the glasses belongs to the class of soft materials (Helen, *et al.,* 2015).

Conclusion

Increasing the K_2O and CaO content at the expense of Li_2O in the studied glass system reveals some remarkable features. Structure investigations using X-ray have indicated that the glass system is in the amorphous state. The density of the glass decrease, which is due to the lower atomic weight of Li_2O compared with that of K_2O and CaO. The increase in the molar volume, which is attributed to the open structure idea resulted from the conversion of the BO_4 unit with low density into the BO_3 unit with high density. The refractive index of glasses depended not only on the density but also on the polarizability of the glasses. Increasing of refractive index with increasing concentration of alkaline ions can be linked to increase in the non-bridging oxygen. The molar electronic polarizability shows a general trend of increase in refractive index. The metallization criterion shows the insulation behaviour of the present glasses. Additionally, this study provides a type of transparent glasses containing alkali/alkaline ions which can be used for optical materials. The microhardness studies revealed the anisotropic nature of the material and it further confirmed that the samples belong to soft glass category. The Vicker's hardness is strongly dependent upon composition but independent on applied load for all the glass samples. The increase in concentration of CaO in the glass composition was found to increase the rigidity of the glass structure and thereby to increase the microhardness. The decrease in hardness of the glasses is attributed to a decrease of elastic moduli and bond strength.

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