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Thermal and Structural Properties of Borate Lithium Glass Doped With Potassium Oxide and Calcium Oxide

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

[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.*

E-mail: [1]palani_physics06@yahoo.co.in

***Abstract* - Glasses in the system $80B_2O_3$-$20Li_2O$, $80B_2O_3$-$(20-x)Li_2O$-xK_2O and $80B_2O_3$-$(20-x)Li_2O$-$xCaO$ (where x= 0 to 10 mol% in steps of 2 mol%) have been prepared using melt quenching technique. The samples were characterized by using X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR) respectively. The amorphous and glassy states of the glasses are evidenced by the X-ray diffraction and thermal analysis respectively. The weight loss has been noticed from the TGA profile. Based on the DSC profile the precursor chemical mix glass transition temperature (T_g), crystallization peak temperature (T_p), melting temperature (T_m) and the thermal stability (ΔT) have been identified. FTIR is used to characterise their structural approach. The infrared spectra of the glasses reveal the presence of three- and four- coordinated boron atoms. The specific vibrations of Li-O, K-O, and Ca-O bonds were observed in the present IR study. Tetrahedral BO_4 units transformed into BO_3 units has evidenced from the FTIR spectrum of prepared glasses.**

Keywords - X-ray diffraction, TGA, DTA, DSC, and FTIR.

I. INTRODUCTION

B_2O_3 glasses are found to be very interesting amorphous materials whenever the specific structure and physical properties of which taken into consideration. In these glasses, two groups of bands are obtained: (i) due to trigonal BO_3 and (ii) due to the tetrahedral BO_4 units. By the addition of alkali/alkaline earth oxides to the borate glasses, they would exhibit specific physical properties. When these glasses are grafted with alkali/ alkaline earth oxides, the resultant glasses are found to have several potential applications such as radiation dosimetry, solar energy converters, phosphors, vacuum ultraviolet (VUV) optics and semiconductors lithography and in a number of electronic device [1]. Borate glasses have a random network consisting of tetrahedral (BO_4) and trigonal (BO_3) units and their combination form diborate, triborate, tetraborate and pentaborate groups [2]. However, the borate glass still requires the incorporation with modifiers such as alkali/ alkaline earth oxides to improve the mechanical stability and reduce the hygroscopic property of their glass network [3]. As ionic radius of Li is smaller than the ions in the network, it easily enters into the glass network interstitially forming a new environment. This leads to a change in the structure of the studied glass samples and hence all its related properties have been changed accordingly with the concentration of Li_2O content [4]. Lithium borate glasses are classical glass systems formed over a wide range of compositions. These glasses have been studied extensively because of their important advantages as solid electrolytes in storage batteries. Apart from these technological applications, the understanding of the conduction mechanism of the Li^+ ions requires some structural studies on the host glass, e.g., spectroscopic studies [5].

Differential scanning calorimetry (DSC) is used to characterize the glasses and determine glass transition temperature (T_g) [6]. Fourier transform infrared (FTIR) technique is one of the most sought spectroscopic investigations to probe the structural units present in the glass matrix. The structure of borate glass not only depends on the glass forming oxides, but also on the glass modifier oxides and dopant salts present in the glass composition [7]. So, it should be mentioned that the study of optical, mechanical, thermal, and structural properties are necessary, worthy and comprehensive to obtain more comprehension about the nature of materials [8]. In the present investigation, potassium oxide and calcium oxide containing borate lithium glass samples were prepared and then they were subsequently characterized by thermal and FTIR techniques.

II. MATERIALS AND METHODS

High purity analytical grade chemicals such as B_2O_3, Li_2CO_3, K_2CO_3, and $CaCO_3$ have been used as the main constituents to prepare the K_2O and CaO doped borate lithium glass following the melt quenching technique. The chemical composition follows as $80B_2O_3$-$20Li_2O$ (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% , Table 1). Each batch of composition of about 10 g were taken 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 in a muffled furnace. Simultaneously, the melt mixture was stirred for getting homogeneous mixture. 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 measuring their thermal and spectroscopic properties. 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 2ϴ = (10-100°) utilizing Cu radiation with an applied voltage of 40 kV and 30 mA anode current.

Thermal properties like the glass transition (T_g), crystallization peak (T_p), and melting temperatures (T_m) were measured using differential scanning calorimetry (DSC). Thermal studies were performed on all samples on SDT Q600 V8.3 Build 101 (universal V4.7A TA Instruments) system in the temperature range of 0 to 1000°C at heating rate of 20°C / min in air. Samples amounts of 4.35mg were used during DSC measurements. The same instrument has been used for thermogravimetric analysis (TGA), differential thermal analysis (DTA), measurements.

The thermal stability of glasses can be described by ΔT, which is defined as

$$\Delta T = T_p - T_g$$

where, ΔT gives the information about the devitrification tendency of the glasses. The difference between glass transition temperature and the onset crystallization temperature, ΔT, has been commonly used as a rough criterion of the glass thermal stability against devitrification.

The FTIR transmission spectra of the glass samples were recorded at room temperature using KBr pellet technique with a spectrum RX-1 FTIR spectrometer (Perklin Elmer, USA) in the spectral range 400-4000 cm^{-1}. For, this powdered glass samples were thoroughly mixed with dry KBr in the ratio 1:30 by weight and the pellets were formed using a pellet machine. A SIC Globar source and a DTGS detector cooled with liquid nitrogen were used. For each spectrum 10 scans were made and the spectral resolution was 4 cm^{-1}.

III. RESULTS AND DISCUSSION

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.

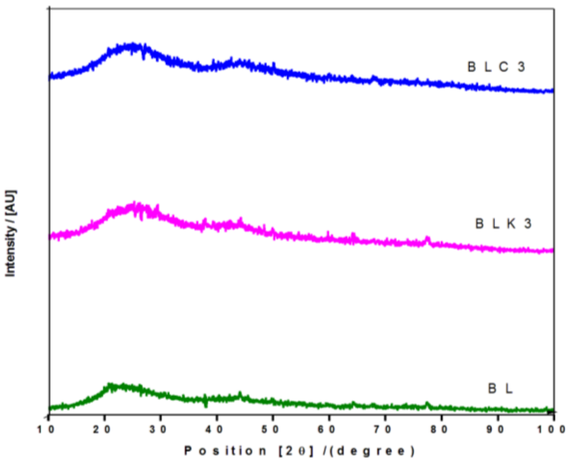

Fig.1 The powder X-ray diffraction spectrum of glass samples of BL, BLK3, and BLC3 at room temperature.

Thermo gravimetric analysis, differential thermal analysis and differential scanning calorimetry scan for the prepared glasses (BL, BLK and BLC) are shown in Fig. 2 to 6. The TGA curves show only considerable weight loss less than ±10% in the complete range of investigation i.e. from 20 to 1000°C in all the glasses are studied.

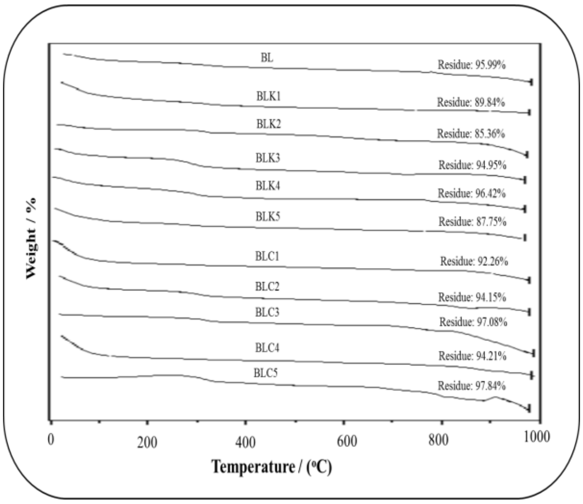

Fig. 2 TGA curves of BL, BLK and BLC glasses at 20°C / min heating rate.

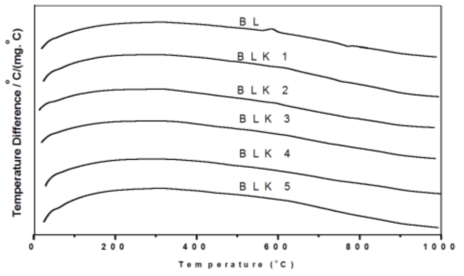

Fig. 3 DTA curves of BL and BLK glasses at 20°C/ min heating rate.

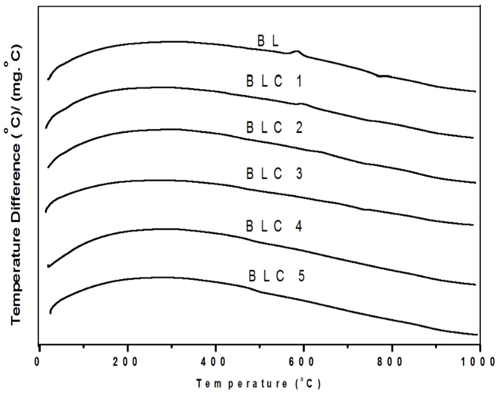

Fig. 4 DTA curves of BL and BLC glasses at 20°C/ min heating rate.

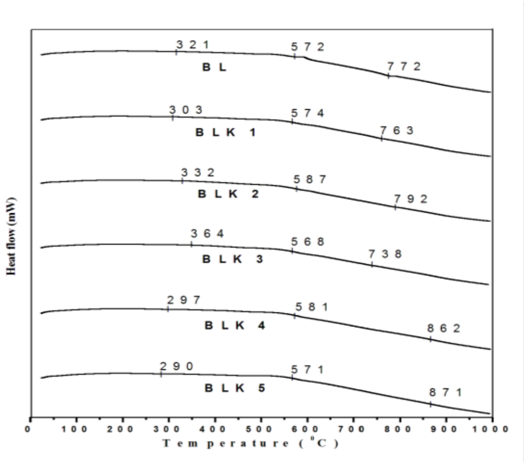

Fig. 5. DSC patterns of BL and BLK glasses at 20°C/ min heating rate.

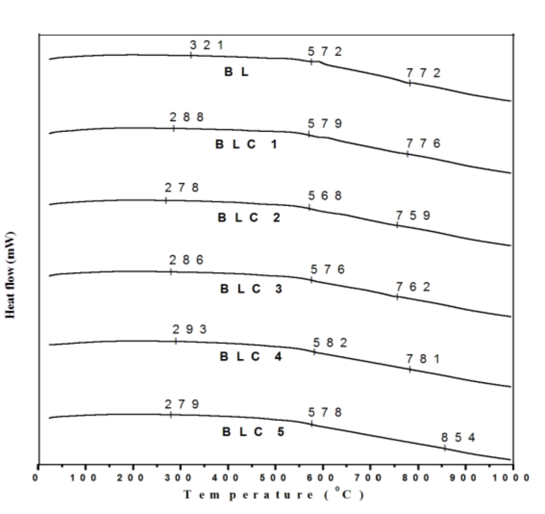

Fig. 6 DSC patterns of BL and BLC glasses at 20°C/ min heating rate.

The TGA and DTA thermograms of the present glasses also showed the amorphous nature of the glasses like XRD. From the DTA scans, it is also observed that the lack of sharp endothermic and exothermic peaks evidently specify the formation of homogeneous glass. The endothermic peaks corresponding to the glass transition (T_g) and exothermic peaks due to the crystallization (T_p) are clearly observed in the DSC curves. It is therefore, concluded that all melt-quenched samples prepared are glass. The values of glass transition temperature, crystallization temperature, melting temperature and thermal stability (ΔT) estimated from DSC scans are summarized in Table I. It is seen that all the values of T_g and T_p decrease with the doping of K_2O and CaO content in borate lithium glass system. The T_g is also a measure of strength of the glasses [9]. Similarly, the observed decrease in T_g, for glasses that are studied may be due to the increasing number of non-bridging oxygen atoms (NBO) [10]. The change in the glass transition temperature T_g clearly shows that doping of K_2O and CaO affecting the glass structure. Specifically a decrease in T_g with the addition of K_2O and CaO contents indicates the decrease in the rigidity of the glass network. The analysis of these results indicates the decrease in T_g with the addition of K_2O and CaO content might be associated with the augmented cross-link density of various micro-structural groups and loosened of their packing [11]. Further, it has been known from the literature of the glasses that when a higher cross-link density of cation is replaced by a cation of lower cross-link density, T_g of respective glass should decrease [12]. But in the present study this behaviour was clearly observed. This could be due to the variation in cross-link density of the network and the bond energy between constituent atoms. However, in the present case, in BLK and BLC, the glass transition temperature decreases due to decreased cross-linking density and bond strength between the atoms involved [13]. The decreasing T_g values may be related to the forming role of K_2O and CaO which competes with B_2O_3 for oxygen atoms supplied by the Li_2O describing the decrease in the formation of BO_4 units and consequently the decrease in the connectivity of the network structure. Also, the bond strength plays a competitive role in decreasing the T_g values. The bond strengths of K-O, Ca-O, Li-O, and B-O are (≈ 277.8 KJ mol^{-1}), (≈ 402.1 KJ mol^{-1}), (≈ 333.5 KJmol^{-1}) and (≈ 808.8 KJmol^{-1}) respectively [14], so the decrease in T_g values is attributed to the replacement of B-O linkage by the weaker K_2O and CaO linkage which indicating the overall decrease in the total strength of links in the glass structure [15]. Further, from the Table I, it is also found that the thermal stability of glasses tends to increase with doping of K_2O or CaO content. The increasing nature of ΔT suggests that the chemical bond strength of K_2O and CaO bonds in the glasses is stronger than that of B-O bonds [16]. The thermal stability criterion ΔT of glasses is larger than 100°C, indicating that these glasses have good thermal stability and can easily be obtained in bulk forms [17]. The higher values of ΔT (or lower tendency of crystallization) suggest that the BLC glasses are more stable than BLK and BL glasses [18].

The transmission spectra of IR radiation gives information about molecular vibrations or rotation associated with a covalent bond [19]. The IR spectra results because of a change in the dipole moment of the molecule. IR spectroscopy involves the twisting, bending, rotating and vibrational motions in a molecule. Upon interaction with IR radiation are absorbed at particular wavelength. This characterizes the functional groups comprising the molecule and the overall configuration of the atoms as well. The FTIR transmission spectra of BL, BLK & BLC glasses are given in Figs 7 & 8. The assignments of the transmission bands as detected in the IR spectra are summarised in Table II. In the infrared spectral region, the vibrational modes of the borate network have three prominent bands:

(i) The band around 700 cm^{-1} is due to the bending vibration of B-O-B linkages in the borate networks.

(ii) The band between 800-1200 cm^{-1} is due to the B-O bonds stretching of tetrahedral BO_4 units, and

(iii) The band between 1200-1600 cm^{-1} is due to asymmetric stretching relaxation of the B-O bonds in the trigonal BO_3 units.

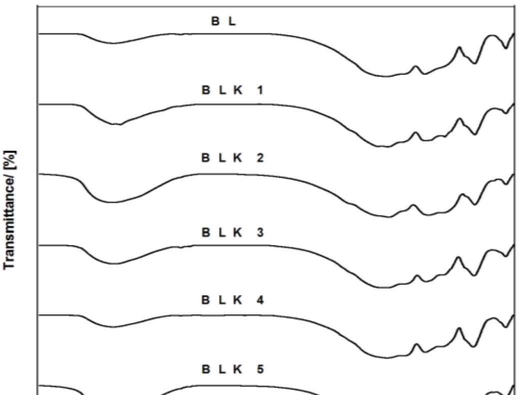

Fig. 7 FTIR spectra of BL and BLK glasses

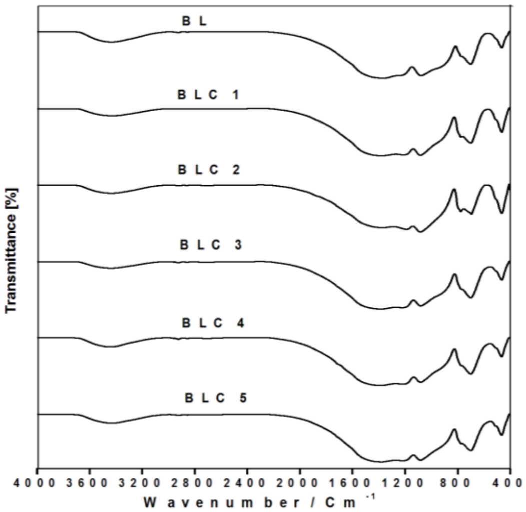

Fig. 8 FTIR spectra of BL and BLC glasses

In the studied glasses of BL, BLK and BLC FTIR bands assignments have been revealed as follows:

The weak IR bond around 466 cm^{-1} is assigned to the vibrations of Li cations through glass network which was attributed to Li-O-Li bands [20]. The weak bond around 463 cm^{-1} is assigned to the O-B-O bonds bending and stretching vibrations of Li-O, K-O and Ca-O bond vibrations [21]. In present study, the bending and stretching vibrations of B-O-B bonds in BO_3 triangles appear in the region 698-711cm^{-1} and 1200-1350 cm^{-1} respectively. The present FTIR spectra showed non-existence of bond at 806 cm^{-1}, which reveals the absence of boroxol rings in glasses and hence it consists of only BO_3 and BO_4 groups. Stretching vibrations of BO_4 units in various structural groups gives rise to IR bands in the regions 777-936 cm^{-1} and around 1083cm^{-1}. The absorption peak around 1720-1730 cm^{-1} is due to the H-O-H bending. The bands around 2280cm^{-1} and 2340cm^{-1} are attributed to –OH group. The absorption peak observed at 3400cm^{-1} is attributed to hydroxyl group present in the glass [22]. The addition of alkali/alkaline earth oxides to borate lithium glass slightly changes its bond strength. The following changes are observed in the FTIR spectra of BL, BLK, and BLC glasses with increased K_2O and CaO content.

(i) The bending vibration of B-O-B in BO_3 triangles (peak around 698cm^{-1}) is shifted to higher wave number with increased intensity in K_2O and CaO content.

(ii) The shifting of the band at 1079cm^{-1} to higher wave number indicates the conversion of BO_4 units (of tri, tetra and penta borate) to BO_3 units (pyro and ortho borate groups) with increased K_2O and CaO content.

(iii) The intensities of the peaks corresponding to the stretching vibrations of the B-O bonds of triangle BO_3 units (in the region 1200-1600cm^{-1}) is higher than B-O bond stretching of tetrahedral BO_4 units (in the region 800-1200cm^{-1}) in BLK and BLC glasses. This is due to the conversion of some BO_4 units to BO_3 units with NBOs.

IV. CONCLUSION

In the present paper, the transparent glasses of composition $80B_2O_3$-$20Li_2O$, $80B_2O_3$-$(20-x)Li_2O$-xK_2O and $80B_2O_3$-$(20-x)Li_2O$-xCaO (where x= 0 to 10 mol% in steps of 2 mol%) were prepared by melt quenching technique and were studied by X-ray diffraction, TGA, DTA, DSC and FTIR techniques . The amorphous nature of glasses were confirmed from its XRD, TGA and DTA profile. The weight loss, glass transition temperature (T_g), crystallization peak temperature (T_p), and melting temperature (T_m) and thermal stability (ΔT) have been noticed and identified from the thermal profile of precursor chemical mix. The decrease in T_g indicates a decrease in the cross-linking network density, which causes the decrease in strength and compactness of the glass network. From DSC study it is found that the thermal stability of BLK and BLC glasses increase in K_2O and CaO contents. The BLC glass posses the highest thermal stability. The FTIR spectra also support the structural changes by composition effect. The FTIR studies indicate the presence of BO_3, BO_4, Li-O, K-O, and Ca-O units in the structure of the studied glasses. The intensities and their peak position may be affected by the alkali/alkaline metal oxides concentrations in each glass. It has also been observed that alkali/alkaline metal oxides content help in converting BO_4 units to BO_3 units. This reveals that these oxides also enter the glass structure as a network modifier. In the investigated glass system the three-fold boron atoms are dominated compared with four-fold ones.

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Table I

Values of glass transition temperature (T_g), crystallization peak temperature (T_P), melting temperature (T_m), and thermal stability (ΔT) of various glass samples.

Glass sample Label	**Composition (mol %)**	**Glass transition temperature T_g/°C**	**Crystallization Peak temperature T_p/°C**	**Melting temperature T_m/°C**	**Thermal stability $\Delta T = T_p - T_g$**
B_2O_3+Li_2O (BL)					
BL	80 - 20	321	572	772	251
B_2O_3+Li_2O+K_2O (BLK)					
BLK 1	80-18-02	303	574	763	271
BLK 2	80-16-04	332	587	792	255
BLK 3	80-14-06	364	568	738	204
BLK 4	80-12-08	297	581	862	284
BLK 5	80-10-10	290	571	871	281
B_2O_3+Li_2O+CaO (BLC)					
BLC 1	80-18-02	288	579	776	291
BLC 2	80-16-04	278	568	759	290
BLC 3	80-14-06	286	576	762	290
BLC 4	80-12-08	293	582	781	289
BLC 5	80-10-10	279	578	854	299

Table II

FTIR band assignments of potassium oxide and calcium oxide doped borate lithium glass systems

Glass sample Label	**Band Position (cm^{-1})**	**Band assignments**
BL	464, 700, 1079, 1368, 2852, 2922, 3426	≤ 625 cm^{-1} - Due to specific vibrations of Li-O, and K-O and Ca-O bonds. 600 - 750 cm^{-1} - Bending vibrations of B-O linkages. 860 - 1200 cm^{-1} - B-O bond stretching of the BO_4 tetrahedral BO_4 units. 1200-1600 cm^{-1} - Asymmetric stretching vibrations of BO_3 groups in ortho- and meta- borate units. ~ 3400 cm^{-1} - O-H group
BLK 1	462, 507, 698, 926, 1077, 1254, 1361, 1431, 3382, 3442	
BLK 2	465, 699, 936, 1055, 1351, 3444	
BLK 3	466, 705, 1072, 1238, 1363, 1419, 2921, 3426	
BLK 4	464, 711, 1077, 1237, 1364, 2852,2921, 3441	
BLK 5	462, 562, 709, 930, 1062, 1348, 3444	
BLC 1	463, 698, 776, 1083, 1209, 1382, 2708, 2925, 3424	
BLC 2	463, 695, 777, 1083, 1189, 1371,2707, 2923, 3442	
BLC 3	464, 698, 1081, 1221, 1385,2705, 2853, 2923, 3442	
BLC 4	465, 699, 1082,1221, 1383,2712, 2854, 2924, 3443	
BLC 5	464, 698, 774, 1083,1220, 1382, 2713, 2923, 3431	