

STRUCTURE, THERMAL PROPERTIES AND MIXED ALKALI EFFECT IN Li₂O AND Na₂O DOPED BORATE GLASSES

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Abstract: The thermal and structural properties of melt-quenched Li₂O and Na₂O doped borate glasses were investigated. The non-crystalline nature of the as-quenched samples has been established by XRD studies. The structural and thermal properties of the present glasses have been studied using Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). The formation of both BO₃ and BO₄ units in the studied samples has been ascertained by the FTIR studies. The nonlinear variation of peak positions of B-O bonds of stretching vibrations validate the occurrence of mixed alkali effect. The glass transition temperature (T_g) and thermal stability (Δt) exhibited a non-linear variation with increase in (Li₂O+Na₂O) content. With increasing the concentration of dopants, the T_g and Δt respectively exhibited maxima and minima at x=0.30. This kind of behavior has been attributed to the structural modifications occurring in the network as a function of compositional variation. This is considered to be the signature for a possible mixed alkali effect taking place in the present glass systems.

Key words - Borate Glasses; Mixed Alkali Effect; FTIR; DSC.

I. INTRODUCTION

Alkali doped borate glasses are good candidates for ion conduction and are considered to be an important class of materials in optical fibers, optics, electrolytes in solid state batteries, cathode in electrochemical cells [1]- [3]. By combining the suitable network modifier to the glass former, their physical and electrical properties can be altered [4], [5]. It was reported that the borate glasses doped with alkali oxides exhibit a non-linear behavior in terms of the physical properties [6], [7]. Incorporation of alkali oxides into the borate system results in structural modifications such as transformation of BO₃ triangle to BO₄ tetrahedra. By combining these two fundamental structural units, various different structural groups viz., penta, tetra, tri, di, pyro, orthoborates and pyroxyl rings get formed [8]. When any glass system is doped with two different alkali ions, a phenomenon known as mixed alkali effect (MAE) may occur [9]. This MAE is long-time problem for understanding the conduction mechanism which still attracts the attention of the researchers [6], [10]. In the last few decades MAE was reported to have been observed in mixed crystals, cations and anions conducting glasses and also in the glass systems formed out of two glass formers [10]. Considering the structural aspects and the electrodynamic theories, few theories have been developed to explain this effect [11], [12]. However, no theory comprehensively explains the phenomenon of mixed alkali effect. Therefore, the MAE is still an open task in the field of oxide glasses.

Studies have revealed that the borate based glasses show rich structural chemistry in terms of their structure [13]. The formation of complex 3-dimensional network comprising of boron and oxygen in large structural units is usually the characteristic structure of alkali doped borate glasses. The incorporation of several alkali modifiers such as lithium, sodium and potassium to the borate glass makes radical variations in the structural units [14]. The arrangement of boron units in a borate glass system not only depends on the glass forming oxides, but also on the different glass modifier oxides and their doping concentrations as well [15].

The MAE has been reported in borate, phosphate, telluride and silicate glasses containing alkali or alkaline oxides [16], [17]. Isard [16] and Day [18] have observed that the with the increasing difference in size or mass of the involved alkali ions, the magnitude or strength of MAE increases. Bunde et al [20] formulated a theoretical model based on the ionic migration in glasses known as dynamic structural model (DSM). Lorosch et al. [20] assumed that when alkali oxide Li⁺ changed to Cs, different kinds of borate groups are formed due to ionic sizes.

In the present paper, we report the FT-IR spectra and thermal studies in the glass system; (1-x) (B₂O₃) – (Li₂O)_{1/2} - (Na₂O)_{1/2})_x, where x=0.20, 0.25, 0.30, 0.35 and 0.40 labelled as LNB1, LNB2, LNB3, LNB4 and LNB5. The objective of the present work is to study the structural and thermal properties in a glass system wherein two different alkali ions in equal concentrations are doped and the possibility of occurrence of MAE. To the best of our knowledge, there are no reports on structural and thermal studies in borate glasses doped with equal concentrations of lithium and sodium oxides.

II. EXPERIMENTAL

The glass samples in the above mentioned composition were prepared by melt-quenching method. Analytical grade chemicals of H₃BO₃, Li₂CO₃ and Na₂CO₃ were procured from Himedia Chemicals. The chemical quantities in required weight ratios were taken in porcelain crucibles and the composition was thoroughly mixed in order to get the uniformity. These porcelain crucibles were then placed in an electrical muffle furnace and melted at 1000°C. After confirming that a transparent melt was formed, it was poured on to a stainless steel plate maintained at room temperature and another stainless steel plate was covered onto it. The transparent samples of different size and shape were collected. The prepared samples were made fine powder in an agate mortar

before measuring their thermal and spectroscopic properties. As prepared samples were subjected to XRD to confirm their non-crystalline nature.

The FTIR spectra of the various powdered glass samples were recorded at room temperature in the range 650-4000 cm^{-1} using a spectrometer (Nicolet IS-10 Mid). These measurements were made on glass powder distributed in KBr pellets.

The TA instrument (Model DSC Q20 V24.11) has been employed for the thermal studies in all the glass samples. The thermal properties of a glass system such as glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) can be determined from DSC experiments. Here, under nitrogen flow, the heating rate was maintained at 10 K/min in the temperature range 30-480°C. The measurement of heat flow through the sample and temperature was measured simultaneously.

III. RESULTS AND DISCUSSION

3.1 XRD

The X-Ray diffraction pattern of LNB2 and LNB3 samples were depicted in Fig.1. No peak has been observed which confirms the non-crystalline nature of the glass samples. Similar profiles were found for the remaining samples.

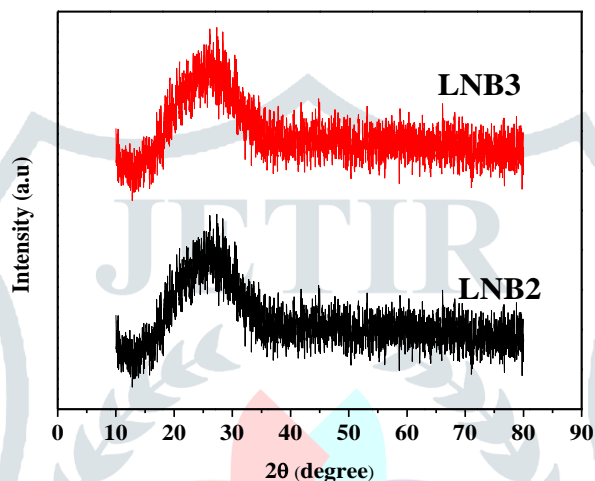


Fig.1- X-ray diffraction pattern of LNB2 and LNB3 samples.

3.2 FTIR STUDIES

The FTIR absorption spectra recorded in the present LNB glasses are shown in Fig. 2. The observed FT-IR spectra of these glasses is determined to arise largely due to the modified borate networks [23] and are mainly active in the spectral range 650-2500 cm^{-1} ; therefore, the spectra are shown in 650-2500 cm^{-1} range for better clarity. The present glasses exhibited 3-4 absorption peaks. All the glass compositions show absorption peaks at 701 cm^{-1} , 913 cm^{-1} and 1347 cm^{-1} . The analysis of these bands and their corresponding assignments is listed in Table 1. The broad band at $\sim 1347 \text{ cm}^{-1}$ is due to B-O stretching vibrations of BO_3 units in metaborates, pyroborates and orthoborates [21].

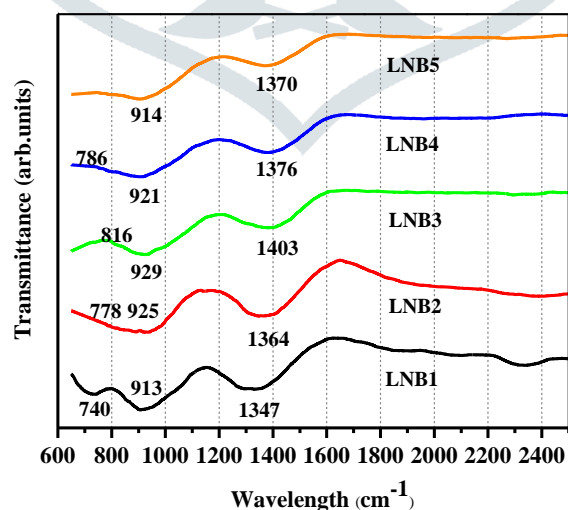


Fig. 2- FTIR absorption spectra of present glasses.

The broadening of this peak indicates the formation of pyroborate at the cost of metaborate which in turn cause a decrease in non-bridging oxygen's (NBO). This behavior was confirmed from the decrease in peak position of B-O bonds of stretching variation (Fig.3) with molar fraction of $(\text{Li}_2\text{O}+\text{Na}_2\text{O})$ at around $x=0.3$. A broad band at $\sim 913 \text{ cm}^{-1}$ is understood to be due to the stretching vibrations of B-O bonds in tetrahedral BO_4 units. The absorption band at $\sim 701 \text{ cm}^{-1}$ indicates the vibration of bridged oxygen and the B-O-B bending vibrations within the borate network [22]. This morphology combines two trigonal boron atoms [22].

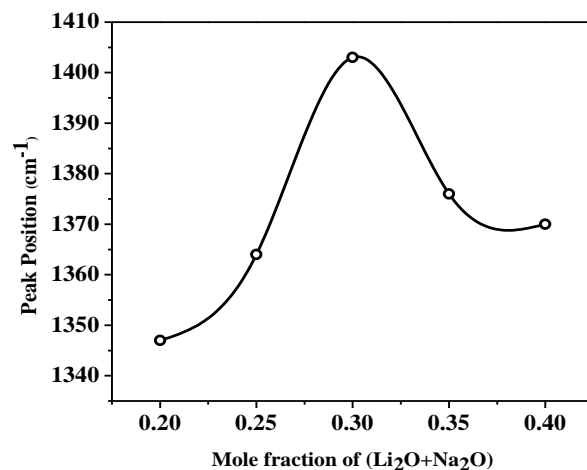


Fig. 3 - Peak position of B-O bonds of stretching variation with molar fraction of (Li₂O+Na₂O).

3.3 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Figure 4 shows the DSC thermograms for all the present glasses. From these plots the T_g and T_c were determined. The measured values of T_g and T_c are mentioned in Table 2. From the Table 2, it can be noted that the T_g in the present glass samples was determined to be in the range from 100°C to 480°C. The compositional dependence of T_g is depicted in Fig. 5. From Fig. 5, it can be observed that the T_g increased up to 0.3 mole fraction of (Li₂O+Na₂O) content and exhibits decreasing trend for further doping of (Li₂O+Na₂O). This may be due to the fact that lighter network modifiers (in the present system, Li₂O) having atomic radii 1.52Å are more effective in increasing the T_g as compared to another heavier network modifier (in the present case, Na₂O) having atomic radii 1.86Å [25]. The T_g increases in the present glasses up to 0.3 mole fraction of (Li₂O+Na₂O) because of the influence of lighter network modifier (Li₂O). As the concentration of (Li₂O+Na₂O) increases beyond 0.3 mole fractions, the effect of sodium ions is more prominent and hence a decrease in T_g has been observed.

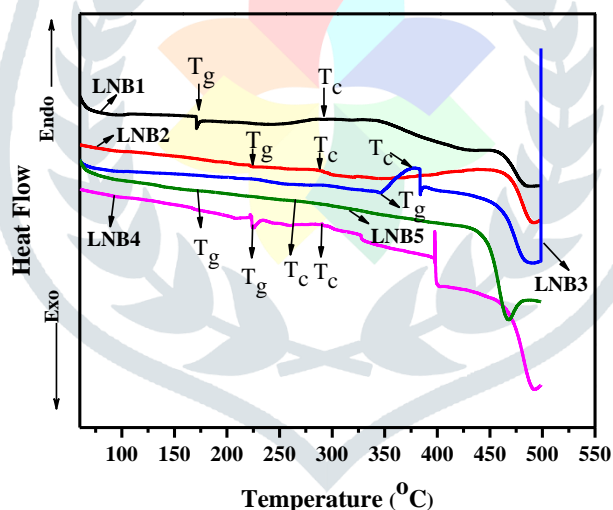


Fig. 4- DSC traces for LNB series glass samples.

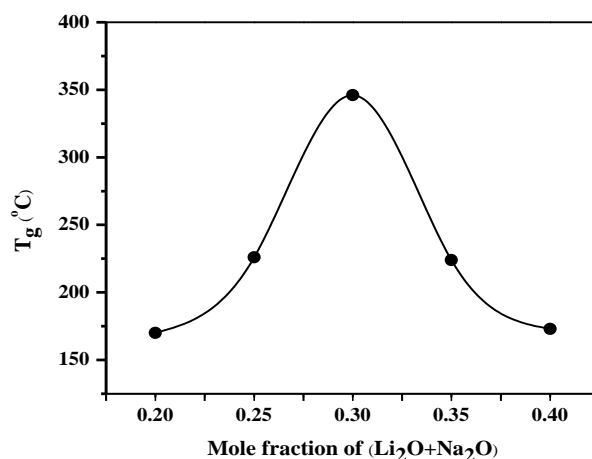


Fig. 5- Compositional variation of T_g with molar fraction of (Li₂O+Na₂O).

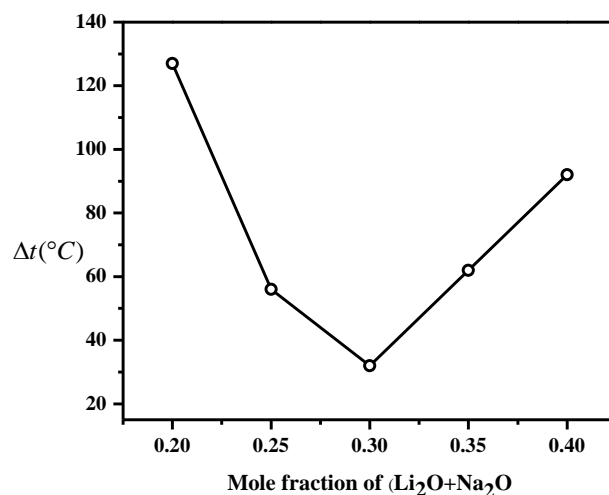


Fig. 6- Compositional variation of thermal stability, Δt with molar fraction of $(\text{Li}_2\text{O}+\text{Na}_2\text{O})$.

In the present glasses, the variation of both peak position and T_g with mole fraction of $(\text{Li}_2\text{O}+\text{Na}_2\text{O})$ is observed to be similar. These observations hint at the anomalous structural changes occurring at around $x=0.3$ mole fraction of $(\text{Li}_2\text{O}+\text{Na}_2\text{O})$.

Table 1: Band assignment for FTIR spectra of LNB glasses

Wavenumber (cm^{-1})	Band assignments	LNB1	LNB2	LNB3	LNB4	LNB5
~740	B-O-B bending vibrations of borate network	740	778	816	786	-
~913	Stretching vibrations of B-O bonds in tetrahedral BO_4 units	913	925	929	921	914
~1347	B-O stretching vibrations of BO_3 units in metaborates, pyroborates and orthoborates	1347	1364	1403	1376	1370

Table 2: Thermal properties of all LNB series glass system

Glass Code	T_g (°C)	T_c (°C)	$\Delta T=(T_c-T_g)$ (°C)
NLB1	170	297	127
NLB2	226	282	56
NLB3	346	378	32
NLB4	224	286	62
NLB5	173	265	92

The compositional variation of thermal stability in the present glass systems has been displayed in Fig.6. It can be noted from the figure that the thermal stability undergoes minima at $x=0.30$. This kind of behaviour can be attributed to the anomalous structural modifications taking place as the doping concentration is varied. The compositional dependence of thermal stability also hints at the MAE being taking place in the present glass systems at $x=0.3$.

CONCLUSION

The thermal and structural properties of a novel series of Li_2O and Na_2O doped borate glasses, prepared by melt quenching technique, have been studied. The XRD studies conformed the glassy nature of the samples. FTIR profiles showed clear structural modifications by confirming the presence of $[\text{BO}_3]$ and $[\text{BO}_4]$ units. The FTIR study also confirmed that these two fundamental structural units are interconvertible. The various absorption bands are assigned to antisymmetric vibrations of B-O-B linkages, symmetric stretches, and bending vibrations of B-O-B linkages. There are principally formed by sharing the vertices of BO_4 tetraborate polyhedral in the network. The non-linear variation of peak positions with alkali content hints at the possible occurrence of mixed alkali effect. The glass transition temperature (T_g) showed a non-linear behavior with the composition exhibiting maxima at $x=0.30$. The thermal stability in the present glasses varied non-linearly with molar fraction of $(\text{Li}_2\text{O}+\text{Na}_2\text{O})$ and showed minima at $x=0.3$. These results have been ascribed to the structural modifications that are occurring in the borate network. These results are the prominent signatures of a possible mixed alkali effect to be occurring at $x=0.30$ in the present glass systems.

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