International Journal of Recent Research and Review, Vol. VIII, Issue3, September 2015

ISSN 2277 – 8322

Thermal and Structural Properties of Mixed Alkali and Transition Metal Ions in Sodium Borate Glass

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***Abstract-* Glasses with composition $20Na_2O$-(80-x) B_2O_3-xLi_2O (NBL) and $20Na_2O$-(80-x) B_2O_3-xWO_3 (NBW) (where x = 0 to 10 in steps 2 mol %) were synthesized by conventional melt-quenching method. The obtained glasses were characterized by X– ray diffraction (XRD), thermo gravimetric analysis (TGA), differential thermal analysis (DTA), and Fourier transform infrared spectroscopy (FTIR). The amorphous phase of the prepared glass samples was confirmed from their XRD, TGA, and DTA profiles. DTA profile yielded data of transition temperature (Tg), crystallization temperature (Tp) and the thermal stability (ΔT) range of glasses. FTIR spectra of the glasses were interpreted in terms of the structural transformations on the glass network by the changing composition. FTIR spectral study reveals the existence of BO_3 and BO_4 groups with Li-O-Li and W-O-W vibrations in the present glasses. The presence of varied types like di, tetra, penta, and ortho borate groups are confirmed in the glass matrix.**

***Keywords-* Glass, melt-quenching, X-ray diffraction, thermal analysis, and Fourier transform infrared spectroscopy.**

I. INTRODUCTION

The alkali-borate glasses are commonly used materials in the field of opto-acoustical electronics, in nonlinear devices for frequency conversion in the ultraviolet region and piezoelectric actuator. Meanwhile, these glasses and their crystalline counterparts are considered to be good candidates for the optically induced elastoopticity [1]. Alkali borate glasses have been studied for various technical and industrial applications. The insulating property of borate glasses turns into a semiconducting or electronic or ion conducting nature when metal oxides such as alkali and alkaline earth oxides are added to them. Alkali borate glass systems are good candidates for ion conduction and suitable for the fabrication of solid state batteries [2].

Borate glasses are very interesting class of materials both from the fundamental and application point of view [3]. Borate glasses, based on B_2O_3 network may provide an alternative bioactive glass for biomedical applications [4]. Pure borate glass is made up of random network of boroxyl units with boron in three-fold co-ordination (BO_3). The addition of modifier helps in forming BO_4 groups and non bridging oxygen, so increase of the non-bridging oxygen leads to open the network structure and the increase of durability [5]. The structure of borate glass not only depends on the glass forming oxides, but also on the glass modifier oxides and doping salts present in the glass composition. Among them, tungsten oxide is of intense interest and has been investigated extensively for its distinctive properties. With outstanding electrochromic, photo-chromic, gas chromic, gas sensor, photo-catalyst and photoluminescence properties, tungsten oxide has been used to construct ‘smart window’, anti-glare rear view mirrors for automobiles, non-emissive displays, optical recording devices, solid state gas sensors, humidity and temperature sensors, biosensors, photonic crystals and so forth. The tungsten ion exists in different valence states

W^{6+}, W^{5+}, W^{4+}, etc. Hence its doping can affect the structure and optical properties of host glasses [6]. Doping of materials with lithium ion is technologically very significant. It is important in preparation of optical waveguides and other optoelectronic elements [7]. Borate glasses containing Li^+ have been extensively studied due to their technological applications as solid electrolyte in electrochemical devices such as batteries [8]. Fourier transform infrared (FTIR) technique is one of the most sought spectroscopic investigations to probe the structural units present in the glass matrix. To the best of our knowledge, there are no detailed reports on thermal and structural studies on mixed alkali and transition metal ion sodium borate glasses. In the present paper $20Na_2O$-(80-x) B_2O_3-xLi_2O and $20Na_2O$-(80-x) B_2O_3-xWO_3 (where x = 0 to 10 in steps of 2 mol %), glasses are undertaken by using various thermal and spectroscopic techniques to get comprehensive view.

II. MATERIALS AND METHODS

A) Glass Preparation

The multicomposition sodium borate glass system of $20Na_2O$-(80-x)B_2O_3-xLi_2O and $20Na_2O$-(80-x)B_2O_3-xWO_3 (where x = 0 to 10 in steps of 2 mol %), were synthesised by conventional high temperature melt quenching techniques. The Nomenclature of prepared glass samples are listed in Table I. All starting oxide powder materials are in the range of 99.9% purity, were properly weighed (±0.0001g accuracy) and thoroughly mixed before melted in a closed-lid alumina crucible inside an electrical furnace for an hour at 1053 K. The melt was then rapidly cast into a preheated copper plate mould (at 623 K) and subsequently annealed in the second furnace at 573 K for 2 h in order to remove thermal strains in the glass. At the end of the annealing process the glasses were allowed to cool down naturally to room temperature and polished for thermal and FTIR measurements. The obtained glasses were confirmed bubble-free, homogenous and transparent, in a circular glass disc shape with dimension of 10 mm diameter and 6 mm thickness.

Table I

Nomenclature of prepared glass samples

Nomenclature	Composition in mol %	Remarks
$Na_2O - B_2O_3$ NB	$Na_2O - B_2O_3$ 20-80	
$Na_2O - B_2O_3 - Li_2O$	$Na_2O - B_2O_3 - Li_2O$	Mol % of Na_2O is constant
NBL 1 NBL 2 NBL 3 NBL 4 NBL 5	20-78-02 20-76-04 20-74-06 20-72-08 20-70-10	
$Na_2O - B_2O_3 - WO_3$	$Na_2O - B_2O_3 - WO_3$	Mol % of Na_2O is constant
NBW 1 NBW 2 NBW 3 NBW 4 NBW 5	20-78-02 20-76-04 20-74-06 20-72-08 20-70-10	

B) X-ray Diffraction

In general, the glassy nature of the obtained glass could be confirmed by crystallographic and thermal analysis. The crystallization of the glass was determined in powder form through X-ray diffraction (XRD) analysis on a Model: PW3040/60 X'pert PRO, X-ray diffractometer at a range of 2θ=(10-80°) utilizing Cu-Kα (1.5406 Å) radiation with an applied voltage of 40 KV and 30 mA anode current at a rate of $2^o / min^{-1}$, with a resolution of 0.001°.

C) Thermal analysis

In thermal study, a Model: NETZSCH STA 449F3 jupiter analyzer with heating rate of 20 K min^{-1} in the temperature range of 20-1000 °C, under N_2 gas ambient was used. The glass transition temperatures (Tg) were taken as the inflection point of the endothermic change of the calorimetric signal. Crystallization onset temperatures (T_P) were specified as the beginning of the reaction where the crystallization first starts and peak temperatures represent the maximum value of the exothermic.

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

$$\Delta T = Tp - Tg \qquad ......(1)$$

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

D) Fourier transform infrared spectroscopy

In order to reveal the structural of the glass network, room temperature Fourier transform infrared measurement has been performed with a Model: Bruker Optik GmbH, TENSOR 27, utilizing Middle-infrared light (MIR) excitation Source within the range of 400-4000 cm^{-1} using the KBr pellet technique. For each spectrum 64 scans were made and the spectral resolution of 4 cm^{-1}.

III. RESULTS AND DISCUSSION

X-ray diffraction profile of NB, NBL, and NBW glass sample (Fig. 1) shows no continuous or discrete sharp peak but exhibit broad halo, with reflects the characteristics of amorphous glass structure. This concludes the absence of long range atomic arrangement or three dimensional network periodicity in fabricated glass.

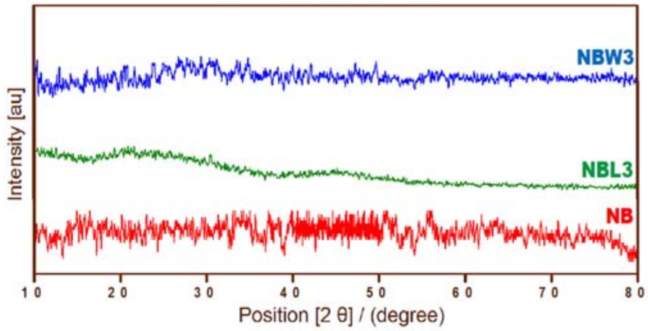

Fig. 1. XRD profile of glass samples of NB, NBL, and NBW at room temperature.

The TGA and DTA profile of the prepared glasses of NB, NBL, and NBW are shown in the Figs. 2-4. The TGA profile has shown only considerable weight loss which is less than of 20%. Meanwhile from the DTA, profile of the host glass (Figs 3-4), three important temperatures; glass transition temperature (Tg), crystallization temperature (Tp) and melting temperature (Tm) were identified. The glass transition temperature (Tg) is one of the basic characterizing properties of the glass and it confirms the amorphous nature of the glass as XRD [9]. Table II listed out some of the obtained physical quantities value of the host glass.

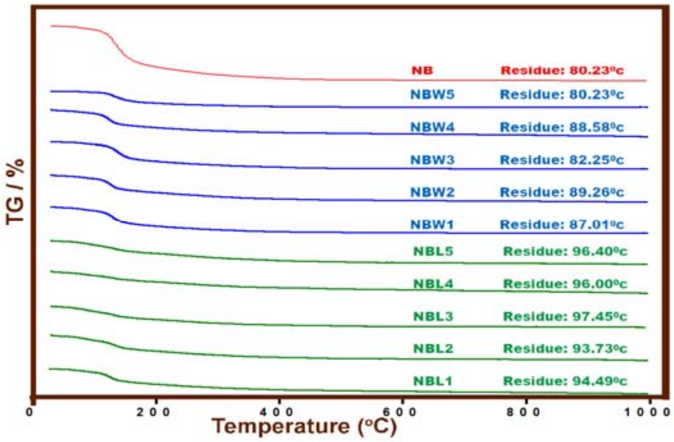

Fig. 2. TGA profile of for NB, NBL and NBW glasses at 20 $^{\circ}$c / min heating rate.

Table II

Values of glass transition temperature (Tg), crystallization peak temperature (Tp), melting temperature (Tm) and thermal stability (ΔT) of various glass samples.

Glass Samples label	**Glass transition temperature Tg / °c**	**Crystallization peak temperature Tp / °c**	**Melting temperature Tm / °c**	**Thermal stability ΔT / °c**
NB	308	568	768	260
NBL 1	310	601	732	291
NBL 2	319	640	715	321
NBL 3	323	645	732	322
NBL 4	329	650	746	321
NBL 5	334	656	755	322
NBW 1	312	594	742	282
NBW 2	337	598	747	261
NBW 3	342	609	751	267
NBW 4	351	612	757	261
NBW 5	356	621	762	265

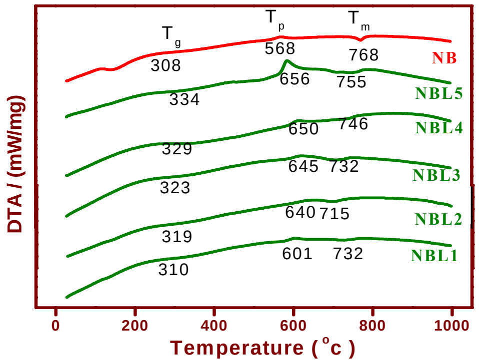

Fig. 3. DTA profile of NB and NBL glasses at 20 °c/ min heating rate.

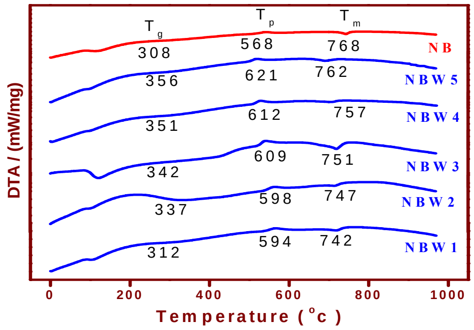

Figure 4. DTA profile of NB and NBW glasses at 20 °c/ min heating rate.

From the table II it is seen that all the value of T_g, T_p and T_m are increases with the doping of Li_2O and WO_3 content in sodium borate glass system. 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 change in the glass transition temperature T_g clearly shows that doping of Li_2O and WO_3 affects the glass structure. Specifically an increase in T_g with the addition of Li_2O and WO_3 contents indicates increase in the rigidity of the glass network (Table 2). The analysis of these results indicates the increase in T_g with the addition of Li_2O and WO_3 content might be associated with the augmented cross-link density of various micro-structural groups and closeness of their packing [10]. 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 glasses should decrease [11,12]. But in the present case this behavior was not observed. This could be due to the difference in cross-link densities of Li_2O and WO_3. Therefore, the increase in T_g may be ascribed to the higher bond strength of B-O ($\approx$ 808.8 KJ mol^{-1}) and W-O ($\approx$ 672 KJ mol^{-1}) in comparison with the bond strengths of Na-O ($\approx$ 270 KJ mol^{-1}) and Li-O ($\approx$ 322 KJ mol^{-1}) [13,14]. The T_g is also a measure of strength of the glasses [15]. The thermally stable glasses will have closed packed structure, whereas thermally unstable glasses will have packed structure [16]. The width of the glass transition region, ΔT, is a measure of stability of glasses [17]. Similarly, the observed increase in T_g, for glasses that are studied which is due to the destruction of non- bridging oxygen atoms (NBO) [18]. From this it is concluded that the strength of the glasses are increase with the doping of Li_2O and WO_3 contents in sodium borate glass systems. From the above table it is also found that the thermal stability of glasses tends to increase with doping of Li_2O or WO_3 content. This increasing trend of ΔT suggests that the chemical bond strength of Li-O and W-O bonds in the glasses is stronger than that of B-O bonds [19]. The higher values of ΔT correspond to delay in nucleation and thus, provide wider processing window for a glass composition to attain maximum densification. In the present study, increasing tungsten content in glasses decreases the value of ΔT, thus implying towards degradation in sintering behavior of glasses [20]. 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 [21]. The larger ΔT obtained for NBL glass has more thermal stability than NBW glass.

The FTIR transmittance spectra of NB, NBL, and NBW glasses were recorded over the range of 400-4000 cm^{-1} and are shown in Fig. 5. The obtained transmission band and their assignments are summarized in Tables III-IV.

The following informations are required for structural analysis of oxide glasses [22]:

1) Type of the bridging bonds of oxygen which link the coordination polyhedra of framework and the composition of chemical in homogeneities in the structure of glass;
2) The coordination number of the compound with respect to oxygen, especially of network formers;
3) The change in oxygen bonds of the framework, induced by the cation modifiers which combine with those bonds.

Moreover, the FTIR spectroscopy of borate containing compounds has vibrational modes mainly active in three infrared spectral regions [23,24]:

(i) The first group of bands occurring at 1200 - 1600 cm^{-1} is due to asymmetric stretching relaxation of the B-O bond of trigonal BO_3 units;
(ii) The second group occurs at 800 - 1200 cm^{-1} is due to B-O bond stretching of the tetrahedral BO_4 units;
(iii) The third group occurring at around 700 cm^{-1} is due to bending of B-O-B linkages in the borate networks.

In the studied glasses of NB, NBL and NBW, FTIR bands assignments have been revealed as follows:

The weak bands around 434-472 cm^{-1} are assigned to the vibrations of Li cations through glass network which are attributed to Li-O-Li bonds [25]. The band 472-478 cm^{-1} can be attributed to O-B-O bond bending vibrations [2]. The band 532 - 555 cm^{-1} may be due to vibrations of sodium cations through the glass network. The band 692 - 702 cm^{-1} can be attributed to B-O-B bond bending vibrations of bridging oxygen atoms [26]. The present FTIR spectra showed non-existance of band 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 [24]. The peaks at 926-929 cm^{-1} are assigned to the stretching vibrations of W-O$^-$ and W=O bonds associated with WO_4 and WO_6 units, respectively [27]. The bands 917-1022 cm^{-1} can be attributed to B-O stretching vibrations of BO_4 tetrahedra units [28]. The band that appears around 1034 cm^{-1} is assigned to stretching vibrations of B-O bonds in BO_4 units from tri, tetra and penta borate groups [25]. The bands at 1159-1163 cm^{-1} attributed to the vibrations of BO_4 tetrahedra units. The band in the region 1329-1423 cm^{-1} are attributed to the stretching vibrations of the B-O of trigonal $(BO_3)^{3-}$ units in metaborates, pyroborates and orthoborates groups [28]. The bands from 1624-3847 cm^{-1} are attributed to O-H bending that give rise to absorption in this region and the possibility of some adsorbed water [26].

In sodium borate glasses there are three types of structural groupings; namely boroxol rings, tetraborate units and diborate units. All of these groups share two distinct types of boron configurations; BO_3 triangles and BO_4 tetrahedra with bridging oxygen ions for each type. In high-sodium borate glasses (20 mol% of Na_2O), tetraborate groups are partially rearranged, and one Na_2O forms two diborate units at the expense of a tetraborate unit, As a result, one Na_2O forms two BO_4 units, which makes the network structure three-dimensional [29,30]. The positive deviation in glass transition temperature is explained due to the increase in cross link density, hence increase in Tg when compared with the end members. The Li^+ and Na^+ ion organized the structural arrangement of the planar BO_4 units slightly and favors the destruction of non-bridging oxygen in glass system. The destruction of non-bridging oxygen units cause the polymerization of the oxide network.

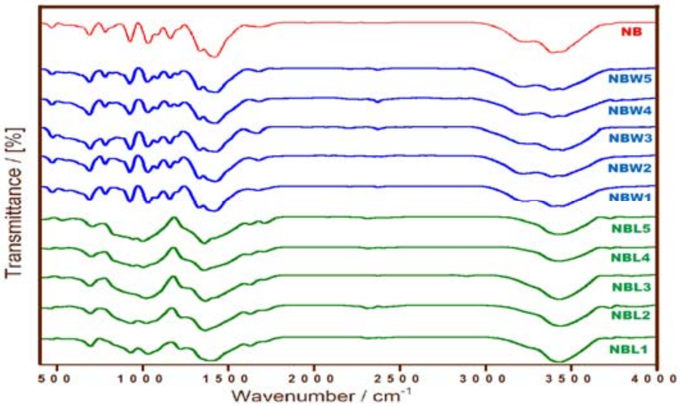

Fig. 5. FTIR spectra of NB, NBW and NBL glasses

Table III

FTIR bands assignment of Li^+ doped NB glass samples.

Glass samples label	Band position / cm^{-1}	Band assignment
NB	472, 555, 692, 785, 929, 1030, 1079, 1159, 1329, 1417,1680, 3234, 3394	457-472 cm^{-1} Vibrations of Li cation. 532-555 cm^{-1} Vibration of alkali Na cation. 692-702 cm^{-1} Bending vibrations of B-O linkages in the borate network. 917-1022 cm^{-1} B-O Stretching vibrations of BO_4 tetrahedra.
NBL 1	469, 532, 694, 929, 1034, 1223, 1385, 1627, 2316, 2403, 3432, 3729	
NBL 2	459, 520, 696, 931, 1022, 1228, 1367, 1631, 2314, 2407, 3440, 3729, 3845	
NBL 3	440, 532, 696, 1022, 1367, 1627 2378 2894 3434 3731 3847	
NBL 4	457, 528, 702, 943, 1005, 1361, 1624, 1708, 2316, 2407, 3434, 3731	

NBL 5	434, 532, 706, 944, 1005, 1361, 1629, 1714, 2316, 3432, 3731	~1034 cm^{-1} Stretching vibration of the BO structural units. ~1367 cm^{-1} Vibration due to triangular $(BO_3)^{3-}$ groups. 1624-3847cm^{-1} H-O-H Bending vibrations.

Table IV
FTIR bands assignment of W^{6+} doped NB glass samples

Glass samples label	**Band position / cm^{-1}**	**Band assignment**
NB	472,555, 692, 785, 929, 1030, 1079,1159, 1329, 1417, 1680, 3234, 3394	472-478 cm^{-1} Bending vibration of O-B-O bond. 551-557 cm^{-1} Vibrations of Na cation. 690-785 cm^{-1} Bending vibrations of B-O linkages in the borate network. 926–929 cm^{-1} Stretching vibrations of W–O^{-} and W=O bonds in tetrahedral $[WO_4]$ units or octahedral $[WO_6]$ units. 1030-1088 cm^{-1} Stretching vibrations of B–O bonds in BO_4 units from tri, tetra and penta borate groups. 1159-1163 cm^{-1} Vibration of BO_4 tetra hedra. 1329-1423 cm^{-1} Stretching vibrations of the B-O of trigonal $(BO_3)^{3-}$ units in metaborates, pyroborates and orthoborates. 1672-3945cm^{-1} Stretching vibration of OH, molecular water,
NBW 1	476, 555, 692, 782, 928, 1034, 1083, 1161, 1332, 1419, 1678, 2212, 2378, 3230, 3396	
NBW 2	474, 548, 690, 783, 926, 1032, 1083, 1161, 1206, 1332, 1423, 1680, 2212, 3222, 3388, 3454	
NBW 3	478, 555, 694, 785, 928, 1034, 1088, 1161, 1334, 1427, 1672, 2202, 2378, 3265, 3452, 3876, 3945	
NBW 4	472, 557, 690, 781, 926, 1034, 1082, 1163, 1207, 1332, 1429, 1687, 2333, 2376, 2883, 3222. 3392, 3456, 3764	
NBW 5	474, 551, 692, 783, 926, 1032, 1086, 1163, 1206, 1332, 1431, 1681, 2216, 2376, 2883, 3222, 3390, 3454, 3766	

The increase in Tg when compared with end members is attributed to the destruction of non-bridging oxygen BO_3 units in present glass system. FTIR studies in tungsten sodium borate glasses it was observed W^{6+} prefers six-coordination and exhibits a transmittance band at 929 cm^{-1}. In the presents study, the peak at 929 cm^{-1} is assigned to the stretching vibrations of B-O linkages BO_4 tetrahedra overlapping with the stretching vibrations of WO_6 units [25]. Infrared investigations on present glass systems reveal no significant changes in the overall structure of the glasses with composition. These glasses contained BO_3 and BO_4 units of various types as di, tetra, penta and ortho borates groups [2].

IV. CONCLUSION

The effect of Li^+ and W^{6+} ions are doped with sodium borate glass have been investigated using XRD, TGA, DTA and FTIR measurements. The glassy state of the samples are characterized using XRD, TGA and DTA measurements. Further, the increasing behavior of Tg and ΔT indicates increasing the strength and thermal stability of the investigated glass systems with the doping of Li_2O and WO_3 content in sodium borate glass. From the ΔT values it has been found that NBL glass has more thermal stability than NBW glass. The FTIR result suggests that the glass consists of BO_3, BO_4, Li-O-Li and W-O bridging bonds forming a large glass network. The characteristic boroxol ring (806 cm^{-1}) was not observed in the present glass samples. Further, it has also been observed that Li_2O and WO_3 contents help in converting BO_3 group to BO_4 units. This reveals that these ions also enter the glass structure as a network modifier. In the investigated glass system the four-fold boron atoms are dominated compared with the three-fold ones. As most of the band positions remained the same in the infrared spectra, it can be concluded that the structure of the glasses is stable and the impact of variation of composition on the structure is not much significant.

V. ACKNOWLEDGEMENTS

The authors wish to express their grateful thanks to Dr.S.Barathan. Professor and Head, Department of physics, Annamalai University for his kind help and encouragements which he extended to them throughout the period of this study.

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