Structural Studies of Mixed Alkali Borate Glasses with WO$_3$

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ABSTRACT
Raman and Infrared spectroscopy have been employed to investigate the xNaI-(30-x)Na$_2$O-10WO$_3$-60B$_2$O$_3$ (where x= 0, 5, 10, 15, 20, 25 and 30 mol%) glasses in order to obtain information about the competitive role of WO$_3$ and B$_2$O$_3$ in the formation of glass network. The IR spectral study reveals the existence of BO$_3$ and BO$_4$ groups with W-O-W vibrations in the present glasses. Raman spectra confirms the presence of tungsten ions mainly as WO$_6$ groups. In the present work, the mixed alkali effect (MAE) has been investigated in the above glass system through density, FTIR and Raman studies. The density of the present gasses varies non-linearly, the exhibiting the mixed alkali effect.

Key words
IR measurements; Raman spectroscopy; Density; Tungstanate glasses; Mixed alkali effect.

Introduction
When two types of alkali ions are introduced into a glassy network, a phenomenon known as mixed alkali effect (MAE) is observed. It represents the nonlinear variations in many physical properties associated with the alkali ion movement and structural properties, when one type of alkali ion with an alkali glass is gradually replaced by another, while total alkali content in the glass being constant [1]. The most evident manifestation of this effect has been observed in DC electrical conductivity as a function of composition where a deep minima is observed in the intermediate mixing ratio of alkali ions [2]. Another prominent MAE is observed in the activation energy, exhibiting a maximum as the relative composition is changed [3]. Interestingly, other “dynamical” properties such as internal friction, viscosity, glass transition, expansion coefficient also exhibit a more or less pronounced deviation. On the other hand, static properties like density appears to be linear [4].

Borate glasses are a very interesting class of materials, both from the fundamental and application point of view [5]. Alkali doping into borate glasses induces interesting structural variations by converting three-coordinated boron structure into four-coordinated structures, famously known as “boron anomaly” and also with the formation of non-bridging oxygen (NBO) ions in the glass network [6]. Cation clustering also must have an effect on several physical properties of the system. Clustering may possibly play an important role in controlling the bulk properties of the glass [7]. Our recent IR and Raman studies on the changes in structural units with the mixed alkali (Li/Na) doping have shown dramatic results with non-additive variation of the band intensities and positions [8]. In recent years MAE was found in mixed crystals [8], cation and anion conducting glasses [9] and also for glasses containing two glass formers [10]. In this present study, xNaI-(30-x)Na$_2$O-10WO$_3$-60B$_2$O$_3$ (0 ≤ x ≤ 30 mol%) glass system was investigated, by means of FT-IR and Raman spectroscopy, in order to obtain detailed structural information about the glass network and the alkali content role in its evolution.
Experimental

Glass samples of compositions xNaI-(30-x)Na2O -10WO3-60B2O3 (0 ≤ x ≤ 30) were prepared by melt quench technique using reagent grade chemicals NaI, WO3, H3BO3 and Na2CO3. The mixture of these chemicals taken in porcelain crucibles was calcinated at 450 °C for 1h and then melted at 1100-1200 °C depending on the glass composition. The liquids were agitated for 1h to ensure homogeneous mixture. The clear liquid was quickly cast in a stainless steel mold kept at 200 °C and pressed with another steel disc maintained at the same temperature. Thus obtained glasses were annealed at the 200 °C for a duration of about 12h to remove thermal stress and strain.

The amorphous nature of the glass samples was confirmed by X-ray diffraction study. The room temperature Raman measurements were performed in the range 100-1700 cm\(^{-1}\) on a micro Raman system from Jobin-Yvon Horiba (LABRAM HR-800) spectrometer. Infrared spectra of the powdered glass samples were recorded at room temperature in the range 400-2000 cm\(^{-1}\) using a spectrometer (Perkin-Elmer FT-IR, model 1605).

Results and discussions

The room temperature deconvoluted Raman spectra of the present glasses are shown in Figure 1.

![Figure 1. Room temperature deconvoluted Raman spectra of the glass system.](image)

The analysis of the Raman spectra reveals the following points: In the present study 1464 cm\(^{-1}\) Raman band was assigned to stretching of B-O \(^{-}\) bonds attached to the large number of borate groups [11]. The band around ~957 cm\(^{-1}\) which is assigned to W–O \(^{-}\) stretching vibrations in WO\(_4\) tetrahedral [12]. The Raman band around 873-904 cm\(^{-1}\) is assigned to stretching vibrations of W–O–W in the WO\(_4\) or WO\(_6\) units [13]. The Raman band ~ 825 cm\(^{-1}\) is assigned to W–O single bond stretching vibrations within W–O–W bonded units [14]. The peak observed around 774-793 cm\(^{-1}\) which is characteristic of a six membered ring with one or two BO\(_4\) tetrahedra [15]. The presence of the Raman band in the range at 675-692 cm\(^{-1}\) has been attributed to the pentaborate groups in the borate glasses [16]. In all the glasses a weak peak ~ 650 cm\(^{-1}\) resembling the localized breathing motions of oxygen atoms in the boroxol ring [17]. The Raman band in the range 546-564 cm\(^{-1}\) is assigned to in plane-bending mode of BO\(_3\)\(^{3-}\) units [18]. The band around 329-340 cm\(^{-1}\) are due to the bending vibrations of W–O–W in the WO\(_6\) units [19].
The FTIR spectra were recorded in the wave number region 2000 – 300 cm\(^{-1}\). Fig. 2 shows the normalized FTIR absorption spectra of xNaI-(30-x)Na\(_2\)O –10WO\(_3\)–60B\(_2\)O\(_3\) glasses. The analysis of the IR spectra reveals the following points:

![Infrared spectra of present glass system.](image)

**Figure 2. Infrared spectra of present glass system.**

The weak band observed around 1637 cm\(^{-1}\) indicates a change from BO\(_3\) triangles to BO\(_4\) tetrahedra, and this peak may also be assigned to the OH bending mode of vibrations [20]. The band around 1438 cm\(^{-1}\) is assigned to antisymmetrical stretching vibrations with three non-bridging oxygens of B-O-B linkages [21]. The peak lying in 1346-1380 cm\(^{-1}\) is attributed to asymmetric stretching vibrations of the B-O of trigonal (BO\(_3\))^3 units in meta-, pyro- and ortho-borate units [22]. The IR band in the range 1228-1266 cm\(^{-1}\) is assigned to B-O stretching vibrations of (BO\(_3\))^3 unit in metaborate chains and orthoborates and these groups contain a large number of non-bridging oxygens (NBO’s) [23]. The IR band around 1080 cm\(^{-1}\) is assigned to penta borate groups. A broadband around 1020 cm\(^{-1}\) is assigned to stretching vibrations of B-O bonds in BO\(_4\) units from tri, tetra and penta borate groups [24]. In the present IR spectra the peak at around 940 cm\(^{-1}\) is assigned to the stretching vibrations of B-O linkages in BO\(_4\) tetrahedra overlapping with the stretching vibrations of WO\(_6\) units [25]. In the present study the IR peak around 874 cm\(^{-1}\) is assigned to stretching vibration of tri-, tetra- and penta- borate groups and also due to the stretching vibration of non-bridging oxygens of BO\(_4\) groups overlapping with the stretching vibrations of WO\(_6\) units [26]. The weak peak at about 762 cm\(^{-1}\) can be attributed to B-O-B bending vibrations of BO\(_3\) and BO\(_4\) groups with W-O-W vibrations in the borate network [27]. In the present study, the IR peak around 697 cm\(^{-1}\) is assigned to bending vibrations of pentaborate groups, which are composed of BO\(_4\) and BO\(_3\) units in the ratio 1:4. The intensity of this band increases and then decreases with K\(_2\)O content [28]. The peak at around 540 cm\(^{-1}\) can be attributed to the borate deformation modes such as the in-plane bending of boron-oxygen triangles. A weak IR band around 467 cm\(^{-1}\) is assigned to the vibrations of Na\(^+\) cations through glass network. This IR band increases and then decreases in intensity as K\(_2\)O content is increasing [29].

**Conclusions**

Mixed alkali tungsten borate glasses in the form of xNaI-(30-x)Na\(_2\)O –10WO\(_3\)–60B\(_2\)O\(_3\) (0 ≤ x ≤ 30) were prepared and their structural properties have been studied. The following conclusions are made: XRD profiles have confirmed their amorphous nature more clearly. Raman spectra confirms the presence of tungsten ions mainly as WO\(_6\) groups. The infrared studies indicate the presence of BO\(_3\), BO\(_4\), WO\(_3\), WO\(_6\) and Li units in the
structure of the studied glasses. The peak positions of few IR bands showed non-linear variation with alkali content manifesting mixed alkali effect.

References