

Infrared and Raman Spectroscopic Studies on mixed alkali tungsten based glasses

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Abstract—Quaternary tungstate glasses containing K_2O , Na_2O and B_2O_3 have been prepared by melt quench technique and studied by IR and Raman spectroscopy. Raman and infrared spectroscopy have been employed to investigate the $(30-x)Na_2O-xK_2O-10WO_3-60B_2O_3$ glasses in order to obtain information about the competitive role of WO_3 and B_2O_3 in the formation of glass network. IR spectral study reveals the existence of BO_3 and BO_4 groups with W-O-W vibrations in the present glasses. Raman scattering study of the present system to understand the role of the mass of the cation in determining the B-O network in glasses. Raman results show that lighter cations favour a stronger B-O network in which three-dimensional BO_4 groups are attached to a large borate ring while the heavy cations are not easily inserted in the network interstices. The introduction of heavy cations favours the formation of non-bridging oxygens which make the B-O network comparatively weak. The observation of disappearance and reappearance of IR and Raman bands as a function of various alkali concentrations is an important result pertaining to the mixed alkali effect in borate glasses. Acting as complementary spectroscopic techniques, both types of measurements, IR and Raman, revealed that the network structure of the studied glasses is mainly based on BO_3 and BO_4 units placed in different structural groups, the BO_3 units being dominant. The measured IR and Raman spectra of different glasses are used to clarify the optical properties of the present glasses correlating them with their structure and composition.

Keywords— Amorphous, Borate glasses, FTIR, Melt quenching, Mixed alkali effect, Raman scattering, X-ray diffraction.

1 INTRODUCTION

Raman and infrared spectroscopy have proven to be powerful and effective tools for characterizing the structure of local arrangements in glasses [1]. 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 non-linear variations in many physical properties associated with the alkali ion movement and structural properties, when one type of alkali ion in an alkali glass is gradually replaced by another, while total alkali content in the glass being constant [2].

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 elasto-opticity. The boron atom in borate crystals and glasses is usually coordinated with either three or four oxygen atoms forming $[BO_3]$ or $[BO_4]$ structural units. These two fundamental units can be arbitrarily combined to form either the so-called super-structure or different B_xO_y structural groups like boroxol ring, pentaborate, tetraborate, diborate groups etc. In the alkali borate glass systems, each alkali oxide is associated with a proportional quantity of B_2O_3 ; so that, the number of the structural units depends on both the nature and the total concentration of the added modifiers, and can often give rise to tightly organized structures resulting in intermediate order [3].

Tungsten ion containing glasses are the subject of a great deal due to their important non-linear optical absorption and electrical properties for technological applications [4]. Tung-

sten ions exist in hexavalent W^{6+} , pentavalent W^{5+} and also in tetravalent W^{4+} state, regardless of the oxidation state of the tungsten ion. W^{6+} ion participate in the glass network with different structural units like WO_4 (Td) and WO_6 (Oh) structural units and W^{5+} ions participate in the form of $W^{5+}O^{3-}$ and occupy octahedral positions [5].

Many investigations have been reported [6][7][8][9] on ternary alkali tungstate in phosphate, borate, tellurite, bismuthate and niobate glasses. More recently, Salem et al [10] presented physical, structural, optical and dielectric properties of $Li_2O-Bi_2O_3-GeO_2-WO_3$ glasses. A recent investigation Gaffar et al [11] studied the FTIR and ultrasonic properties on $Li_2O-WO_3-B_2O_3$ glasses. To the best of our knowledge, there are no reports on Raman and IR studies of mixed alkali borate tungsten glasses. To study the mixed-alkali phenomenon, borate glasses have proved to be promising hosts to investigate the influence of chemical environment, structural diversity of ligand groups, and spectroscopic properties of the materials [16]. Borate glasses with great variability in composition, structure and properties have a promising future in the fields of linear and nonlinear optics.

The objective of the present paper is to probe the structure of $xK_2O-(30-x)Na_2O-10WO_3-60B_2O_3$ ($0 \leq x \leq 30$ mol%) glasses using two complimentary spectroscopic techniques IR and Raman. This study is significant because the new findings will provide information about the basic units forming this multi-component glass structure.

2 EXPERIMENTAL

Glass samples of compositions $xK_2O-(30-x)Na_2O-10WO_3-60B_2O_3$ ($x=0, 5, 10, 15, 20, 25$ and 30) were prepared by melt quench technique. Details of the preparation and characterization of the glass specimens are given in ref. [12]. The amorphous nature of glass samples was confirmed by the

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absence of Bragg's peak in X-ray diffraction pattern.

The room temperature Raman measurements were performed in the range 200–1700 cm^{-1} on a micro Raman system from Jobin-Yvon Horiba (LABRAM HR-800) spectrometer. The system is equipped with high stability confocal Microscope for Micro Raman 10 \times , 50 \times , 100 \times objective lens to focus the laser beam. Ar⁺ laser beam of 488 nm ($E = 2.53$ eV) was used for excitation. The incident laser power is focused in a dia of $\sim 1\text{--}2\mu\text{m}$ and a notch filter is used to suppress Rayleigh light. In the present system Raman shifts are measured with a precision of ~ 0.3 cm^{-1} and the spectral resolution is of the order 1 cm^{-1} .

Infrared spectra of the powdered glass samples were recorded at room temperature in the range 300–1500 cm^{-1} using a spectrometer (Perkin-Elmer FT-1S, model 1605). These measurements were made on glass powder dispersed in KBr pellets.

3 RESULTS AND DISCUSSIONS

The IR absorption spectra of the present glasses were recorded in the range 300–2000 cm^{-1} . Fig. 1 shows the normalized FTIR absorption spectra of $\text{K}_2\text{O}\text{--}\text{Na}_2\text{O}\text{--}\text{WO}_3\text{--}\text{B}_2\text{O}_3$ glasses. The observed infrared spectra of these glasses arise largely from the modified borate networks and are mainly active in the spectral range 400–1600 cm^{-1} ; therefore the spectra are shown in 350–2000 cm^{-1} range for better clarity.

The infrared spectra of the present glasses show 11–12 absorption peaks. All the glass compositions show absorption peak at 467 cm^{-1} , 540 cm^{-1} , 697 cm^{-1} , 762 cm^{-1} , 874 cm^{-1} , 940 cm^{-1} , 1020 cm^{-1} , 1080 cm^{-1} , 1228–1266 cm^{-1} , 1346–1380 cm^{-1} , 1438 cm^{-1} and 1637 cm^{-1} . The peaks are sharp, medium and broad. Broad bands are exhibited in the oxide spectra, most probably due to the combination of high degeneracy of vibrational states, thermal broadening of the lattice dispersion band and mechanical scattering from powder samples.

The boron ion is a glass network-forming cation, and it may occupy the centers of oxygen triangles or tetrahedra. According to Krogh Moe's model [13] the structure of boron oxide glass consists of a random network of planar BO_3 triangles with a certain fraction of six-membered rings. In general, the infrared spectrum of vitreous B_2O_3 shows no active modes between 800 cm^{-1} and 1200 cm^{-1} , and the IR analysis of the modified borate glasses shows three distinct frequency regions in the mid-infrared range (400 cm^{-1} to 1600 cm^{-1}), where the vibrations of the B–O arrangements dominate, is only considered.

The broad IR bands as shown in Figure .1 are the overlapping of some individual bands with each other. Each individual band has its characteristic parameter such as its center which is related to some type of vibration of a specific structural group. A weak IR band around 415 cm^{-1} which was attributed to O–B–O bond bending vibrations and specific vibrations of K–O bond. In the present glass system, the IR band around 444 cm^{-1} is attributed to O–B–O bond bending vibrations and specific vibrations of Na–O, and K–O bonds. The

present IR spectra showed non-existence 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. In $\text{Li}_2\text{O}\text{--}\text{B}_2\text{O}_3\text{--}\text{Bi}_2\text{O}_3$ glasses the peak at around 700 cm^{-1} is assigned to pentaborate units. In alkali boro-tungstate glasses, the IR band around 700 cm^{-1} stands for B–O–B bond bending vibrations of bridging oxygen atoms. 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_2O content.

Since WO_3 is a conditional glass former, with the substitution of WO_3 with alkali oxides in borate glass network the intensity of vibrational band due to the BO_3 groups is observed to increase at the expense of BO_4 structural units. From XANES and FTIR studies in $\text{TeO}_2\text{--}\text{WO}_3$ glasses it was observed that W^{6+} prefers six-coordination and exhibits an absorption band at 930 cm^{-1} . 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.

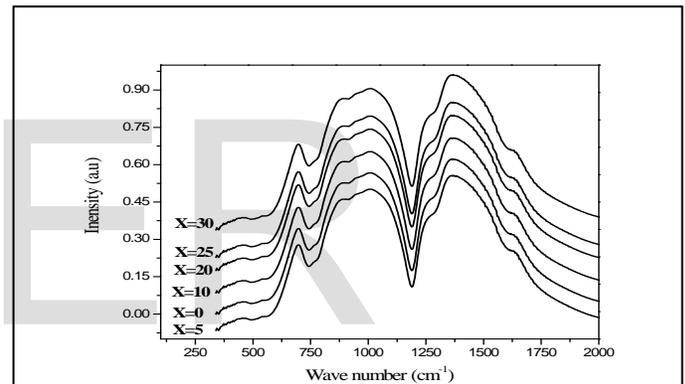


Fig. 1. Infrared spectra of $x\text{K}_2\text{O}\text{--}(30\text{--}x)\text{Na}_2\text{O}\text{--}10\text{WO}_3\text{--}60\text{B}_2\text{O}_3$ glass system. The peaks are sharp, medium and broad. Broad bands are exhibited in the oxide spectra, most probably due to the combination of high degeneracy of vibrational states, thermal broadening of the lattice dispersion band and mechanical scattering from powder samples.

Boudlich et al [14] reported a mixture of WO_4 and WO_6 units at 880 cm^{-1} and at 900–950 cm^{-1} respectively, in alkaline tungsten phosphate glasses. 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_4 units. This peak was observed around 866 cm^{-1} and at around 850 cm^{-1} in single alkali boro-tungstate glasses.

A broad band around 1020 cm^{-1} is assigned to stretching vibrations of B–O bonds in BO_4 units from tri, tetra and penta borate groups. 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. This indicates that tungsten enter the glass structure. The IR band around 1080 cm^{-1} is assigned to penta borate groups. The peak lying

in 1346 cm^{-1} -1380 cm^{-1} is attributed to asymmetric stretching vibrations of the B-O of trigonal $(\text{BO}_3)^{3-}$ units in meta-, pyro- and ortho-borate units. The band around 1438 cm^{-1} is assigned to antisymmetrical stretching vibrations with three non-bridging oxygens of B-O-B linkages. 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 OH bending mode of vibrations. The IR band in the range 1228 cm^{-1} -266 cm^{-1} is assigned to B-O stretching vibrations of $(\text{BO}_3)^{3-}$ unit in metaborate chains and orthoborates and these groups contain large number of non-bridging oxygens (NBO's). This suggests the conversion of the BO_4 tetrahedral to the non-bridging oxygen containing BO_3 triangles. 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 [15]. The assignments of IR bands are given in Table 1.

Raman spectra

Raman spectroscopy is one of the techniques used to investigate the structure of a glass. The room temperature Raman spectra of the present glass system is shown in Figure 2. There are three regions clearly visible in the Raman spectra: (i) 250 – 500 cm^{-1} , (ii) 500 – 1100 cm^{-1} and (iii) 1250 – 2000 cm^{-1} . In all the present glasses studied the total alkali content is 30 mol%. At this concentration of the alkali content in borate containing glasses, the boroxol rings get converted mostly into pentaborate groups. This is observed clearly by the strong presence of peaks around 787 and 684 cm^{-1} resembling the localized breathing motions of oxygen atoms in the boroxol ring.

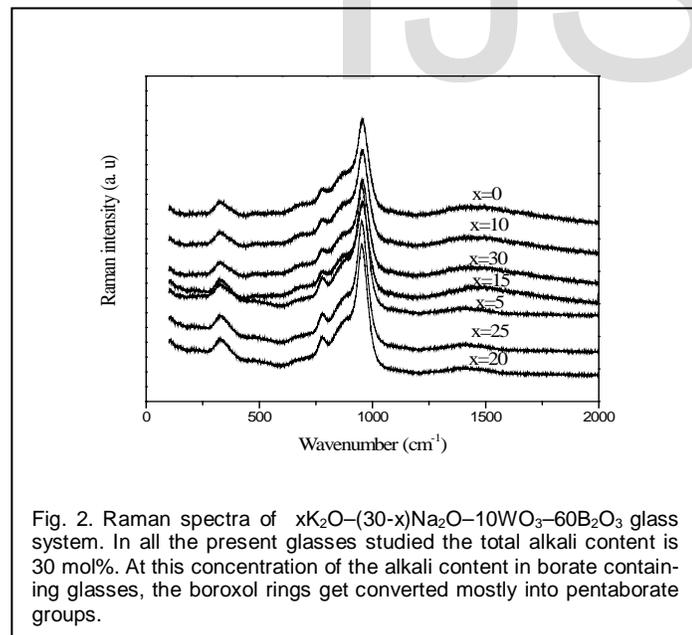


Fig. 2. Raman spectra of $x\text{K}_2\text{O}-(30-x)\text{Na}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ glass system. In all the present glasses studied the total alkali content is 30 mol%. At this concentration of the alkali content in borate containing glasses, the boroxol rings get converted mostly into pentaborate groups.

All the glass compositions show Raman peak at around 333 cm^{-1} , 554 cm^{-1} , 684 cm^{-1} , 787 cm^{-1} , 873 cm^{-1} , 957 cm^{-1} and 1464 cm^{-1} . The Raman band positions of all the glasses under study are given Table 1.

The vibrational Raman bands at 329 -340 cm^{-1} , 873-904 cm^{-1} and 951- 960 cm^{-1} belonging to tungstate groups undergo complex changes. In the Raman spectra of all the studied

glasses, there is a strong peak observed at $\sim 957 \text{ cm}^{-1}$ which is assigned to W-O- stretching vibrations in WO_4 tetrahedral. The peaks around 329-340 cm^{-1} are due to the bending vibrations of W-O-W in the WO_6 units. 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.

In the Raman spectra of all the glassy specimens, there is a peak observed around 774-793 cm^{-1} which is characteristic of a six membered ring with one or two BO_4 tetrahedra. Earlier, Brill [16] assigned this peak to the formation of six membered rings containing one BO_4 tetrahedron, and the shift of this peak towards lower frequency has been assigned to six membered rings with two BO_4 tetrahedra. The six membered rings with one BO_4 tetrahedron can be in triborate, tetraborate or pentaborate forms, and rings with two BO_4 tetrahedra can be in diborate, di-triborate or di-pentaborate forms. In the studied glasses, the presence of Raman band in the range at 675-692 cm^{-1} has been attributed to the pentaborate groups in the borate glasses. Similar results were observed in mixed alkali zinc borate glasses [17].

The Raman bands in the high frequency range 1429-1547 cm^{-1} has been assigned to stretching of B-O- bonds attached to large number of borate groups. The Raman band around 1490 cm^{-1} is attributed to BO_2O - triangles linked to other borate triangular units. In the present study 1464 cm^{-1} Raman band was assigned to stretching of B-O- bonds attached to large number of borate groups. The Raman band in the range 546-564 cm^{-1} is assigned to in plane-bending mode of BO_3 - units.

Raman spectroscopic studies of alkali borate glasses for different concentrations of R_2O reveal the possibility of two chemical processes by which the alkali ion can be dispersed in the glasses. The first process, operative at lower concentrations of R_2O , leads to the formation of boron in fourfold coordination, i.e. BO_4 - units, with the positive alkali ion (R^+) adjacent to the negative BO_4 - unit to provide local charge neutrality. The second process is the formation of a non-bridging oxygen (O^-) adjacent to the positive alkali ion.

4 CONCLUSIONS

Mixed alkali tungsten borate glasses in the form of $x\text{K}_2\text{O}-(30-x)\text{Na}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ ($0 \leq x \leq 30$) were prepared, and structural properties have been studied. The following conclusions were made: Homogeneous glasses of present glass system have been prepared by melt quench technique. The amorphous state of the prepared glasses was confirmed by X-ray diffraction spectra. Infrared and Raman spectra of these glasses have been analyzed to identify the spectral contribution of each component on the structure and to see the role of alkali as a modifier of the glass network. The infrared studies indicate the presence of BO_3 , BO_4 , WO_3 and WO_6 units in the structure of the studied glasses. The intensities and their peak position were affected by the alkali concentrations in each glass. The peak positions of few IR bands showed non-linear variation with alkali content manifesting mixed alkali effect. The Raman spectra of the investigated glasses exhibits several bands which are attributed to BO_3 , BO_4 tetrahedra and pentaborate groups linked to BO_4 tetrahedra. Raman spectra con-

forms the IR results regarding the presence of tungsten ions mainly as WO_6 groups

ACKNOWLEDGEMENTS

One of the authors A.Edukondalu is thankful to Dr. V. G. Sathe and T. Sripathi UGC, DAE, Indore for providing the Raman and FTIR facilities.

TABLE 1: Assignment of Infrared and Raman Bands in the Spectra of present glasses

Band positions (cm-1)		Band assignments	
IR	Raman	IR	Raman
~467	~329	Na / K cation vibrations	Bending vibrations of W-O-W in the WO_6 units
~540	~546	borate deformation modes such as the in-plane bending of boran-oxygen triangles	In plane bending mode of BO_3 -units
~697	~675	bending vibrations of pentaborate groups, which are composed of BO_4 and BO_3 units in the ratio 1:4	denotes the existence of BO_2O_2 -units
~762	~774	B-O-B bending vibrations of BO_3 and BO_4 groups with W-O-W vibrations in the borate network	ring breathing vibration of six membered ring contains both BO_3 triangles and BO_4 tetrahedral
~874	~873	stretching vibration of tri-, tetra- and penta- borate groups also due to the stretching vibration of non-bridging oxygen's of BO_4 groups overlapping with the stretching vibrations of WO_4 units.	Stretching vibrations of W-O-W in the WO_4 or WO_6 units
~940	~951	stretching vibrations of B-O linkages in BO_4 tetrahedra overlapping with the stretching vibrations of WO_6 units	W-O- stretching vibrations in WO_4 tetrahedra
~1020		stretching vibrations of B-O bonds in BO_4 units from tri, tetra and penta borate groups.	
~1080		penta borate groups	
~1266		B-O stretching vibrations of $(BO_3)_\beta$ - unit in metaborate chains and orthoborates	
~1346		asymmetric stretching vibrations of the B-O of trigonal $(BO_3)_\beta$ -units in meta-, pyro- and ortho-borate units	
~1438	~1464	antisymmetrical stretching vibrations with three non-bridging oxygens of B-O-B linkages	stretching of B-O- bonds attached to large number of borate groups
~1637		OH bending mode of vibration and change from BO_3 triangles to BO_4 tetrahedra	

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