

# FTIR and Raman Studies of $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{Bi}_2\text{O}_3-\text{ZnO}-\text{B}_2\text{O}_3$ Glasses

Kalsani Venkateshwarlu<sup>a</sup>, Bachchewal Sreenivas<sup>b</sup>

<sup>a</sup>Department of Physical Sciences, Kakatiya Institute of Technology & Science, Warangal, India

<sup>b</sup>Department of Physics, Osmania University, Hyderabad, India

## ABSTRACT

Glasses with composition  $x\text{Li}_2\text{O} - (25-x)\text{Na}_2\text{O} - 45\text{Bi}_2\text{O}_3-10\text{ZnO}-20\text{B}_2\text{O}_3$  with  $5 \leq x \leq 25$  have been prepared by conventional melt quench technique. The amorphous phase of the prepared glass samples was confirmed from their X-ray diffraction and SEM studies. FT-IR and Raman spectroscopic studies were employed to investigate the structure of all the prepared glasses. Acting as complementary techniques, both IR and Raman measurements revealed that the network structure of the present glasses mainly based on of  $[\text{BiO}_3]$  pyramidal and  $[\text{BiO}_6]$  octahedral units and also on  $\text{BO}_3$  and  $\text{BO}_4$  units placed in different structural groups. The formation of Zn in tetrahedral coordination was observed. Raman and infrared studies have been employed on these glasses in order to obtain information regarding the competitive role of  $\text{Bi}_2\text{O}_3$  in the formation of glass network.

**Keywords** : Amorphous, Glasses, IR, Melt Quench Technique, Raman Spectroscopy, Samples, X-Ray Diffraction.

## I. INTRODUCTION

$\text{Bi}_2\text{O}_3$  based glasses attracted the scientific community due to their important applications in the field of glass ceramics, thermal and mechanical sensors, reflecting windows etc [1]. The interest in Heavy Metal Oxide (HMO) glasses is due to their long infrared (IR) cutoff and optical non-linearity [2]. Especially ZnO based glasses / ceramics have special applications in the area of varistors, dielectric layers and transparent dielectric and barrier ribs in plasma display panels [3-6].

Despite the fact that  $\text{Bi}_2\text{O}_3$  is not a classical glass former, due to high polarizability and small field strength of  $\text{Bi}^{3+}$  ions, in the presence of conventional glass formers (such as  $\text{B}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{SiO}_2$  etc.) it may build a glass network of  $[\text{BiO}_n]$  ( $n = 3, 6$ ) pyramids [7]. However, the structural role played by  $\text{Bi}_2\text{O}_3$  in glasses is complicated and poorly understood. This is because the  $[\text{BiO}_n]$  polyhedra are highly distorted due to the lone pair electrons. Several techniques have been employed in an attempt to identify the local environment of the different elements in bismuthate glasses. X-ray and infrared studies have shown that  $\text{Bi}^{3+}$  ions participate in the glass network structure above 45 mol %  $\text{Bi}_2\text{O}_3$  [8]. The addition of Cd, Th, Li, Ba, Zn, and Fe oxides results in the large glass formation domain.

Raman and infrared spectroscopy provide important information regarding the local structure in vitreous and ceramic materials [9-15]. The aim of the present study is to obtain by means of Raman and infrared spectroscopy, specific data regarding the local structure of  $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{Bi}_2\text{O}_3-\text{ZnO}-\text{B}_2\text{O}_3$  glass system. Further, some physical properties such as density and glass transition temperature have also been studied. Also optical absorption studies were performed on these glass samples. The presence of two glass forming oxides, the classical  $\text{B}_2\text{O}_3$  and the unconventional  $\text{Bi}_2\text{O}_3$ , increase the interest of the present study.

## II. EXPERIMENTAL PROCEDURE

Glass samples of compositions  $x\text{Li}_2\text{O} - (25-x)\text{Na}_2\text{O} - 45\text{Bi}_2\text{O}_3-10\text{ZnO}-20\text{B}_2\text{O}_3$  ( $5 \leq x \leq 25$ ) were prepared by melt quench technique using reagent grade chemicals  $\text{Bi}_2\text{O}_3$ ,  $\text{ZnO}$ , and  $\text{H}_3\text{BO}_3$ . The mixture of these chemicals taken in porcelain crucibles was calcinated at  $450^\circ\text{C}$  for 1h and then melted at  $1100-1200^\circ\text{C}$  depending on the glass composition. The liquids were agitated for 1h to ensure homogeneous mixture. The clear liquid (free of bubbles) was quickly cast in a stainless steel mould kept at  $200^\circ\text{C}$  and pressed with another steel disc maintained at the same temperature. The samples were transparent and their colour varied from yellow to light brown as the content of bismuth is increased. Thus obtained glasses

were annealed at 200 °C for a duration of about 12h to remove thermal stress and strain. The amorphous nature of all the samples was confirmed by the absence of Bragg's peak in X-ray diffraction pattern.

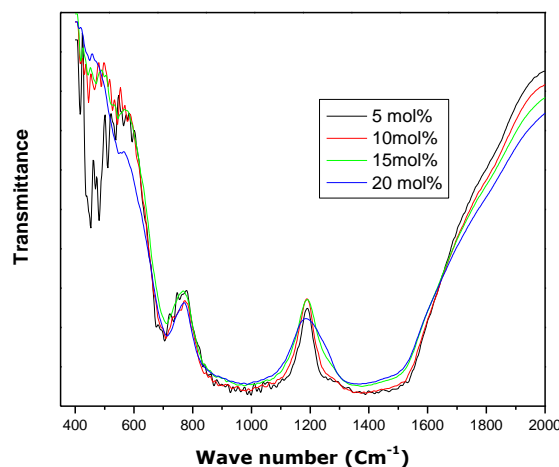
The room temperature Raman measurements were performed in the range 100-1700  $\text{cm}^{-1}$  using a micro Raman system from Jobin-Yvon Horiba (LABRAM HR-800) spectrometer. The system is equipped with a high stability confocal Microscope for Micro Raman 10x, 50x, 100x objective lens to focus the laser beam.  $\text{Ar}^+$  laser beam of 488 nm ( $E = 2.53 \text{ eV}$ ) was used for excitation. The incident laser power is focused in a diameter 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  $\sim 0.3 \text{ cm}^{-1}$  and the spectral resolution is of the order  $1 \text{ cm}^{-1}$ . Infrared spectra of the powdered glass samples were recorded at room temperature in the range 400-2000  $\text{cm}^{-1}$  using a spectrometer (Perkin-Elmer FT-IS, model 1605). These measurements were made on glass powder dispersed in KBr pellets.

### III. RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra of the present ternary class system in the spectral range 100-1700  $\text{cm}^{-1}$  consisting of broad peaks and shoulders. The broadening of peaks is due to the disorderness. To find out the exact mode of vibrations and also the Raman shifts, the spectrum with superimposed broad peaks was deconvoluted into six peaks using a Gaussian distribution. In the Raman spectra the strong band that appears at all concentrations around 133  $\text{cm}^{-1}$  becomes stronger as  $\text{Bi}_2\text{O}_3$  content increases. Weak shoulder is observed for all compositions around 254  $\text{cm}^{-1}$  and 586  $\text{cm}^{-1}$ . The band around 394  $\text{cm}^{-1}$  that grows in intensity shifts towards lower wavenumbers with increasing  $\text{Bi}_2\text{O}_3$  content. For all compositions a strong band around 925  $\text{cm}^{-1}$  and a weak band around 1278  $\text{cm}^{-1}$  are observed that grows in intensity and shifts towards lower wave numbers with increase in  $\text{Bi}_2\text{O}_3$  concentration.

Figure 2 illustrates the infrared spectra of the present glass system. For all glass compositions, bands around 420-450  $\text{cm}^{-1}$ , 480  $\text{cm}^{-1}$  and 700  $\text{cm}^{-1}$  were observed. The observed IR band at 900  $\text{cm}^{-1}$  increases in intensity

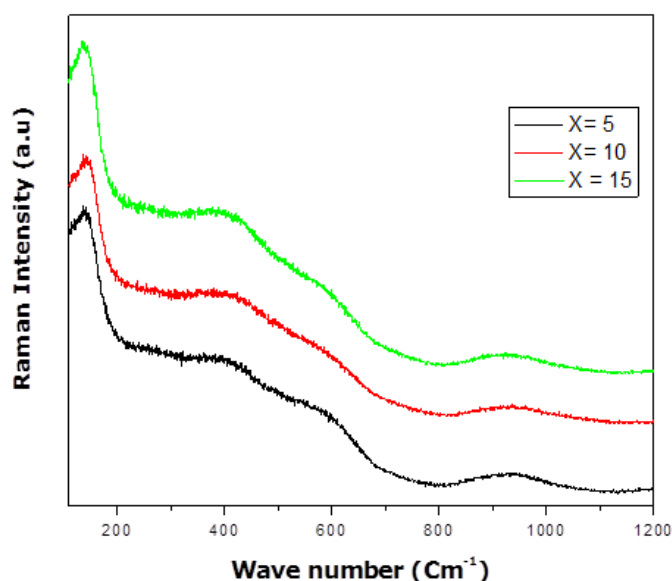
and shifts to higher wave numbers as  $\text{Bi}_2\text{O}_3$  content is increased. Also a convoluted band around 855  $\text{cm}^{-1}$  and bands around 1258  $\text{cm}^{-1}$  and 1319  $\text{cm}^{-1}$  were observed.



**Figure 1.** FTIR spectra of the present glass system

Raman and infrared spectra of the investigated glasses with 45-70 mole% bismuth oxide content are dominated by bands associated to the structural units of the heaviest cation,  $\text{Bi}^{3+}$ . The Raman bands due to heavy metal oxides such as  $\text{Bi}_2\text{O}_3$ , can be classified into four regions: 1) low wave number Raman modes ( $<100 \text{ cm}^{-1}$ ), 2) heavy metal ion vibrations in the range 70-160  $\text{cm}^{-1}$ , 3) bridged anion modes in the intermediate 300-600  $\text{cm}^{-1}$  region and 4) non-bridging anion modes at higher wave numbers [16]. An evidence for the existence of  $[\text{BiO}_3]$  and  $[\text{BiO}_6]$  polyhedra in the glass structure is the presence of band around 135  $\text{cm}^{-1}$  in the Raman spectra [17]. In the present Raman spectra this band was observed at 133  $\text{cm}^{-1}$  and its intensity increases with  $\text{Bi}_2\text{O}_3$  content. Therefore, we assume that  $\text{Bi}^{3+}$  cations are incorporated in  $[\text{BiO}_3]$  and  $[\text{BiO}_6]$  groups. This is confirmed by the IR spectra as the shift of the band from 480  $\text{cm}^{-1}$  to 523  $\text{cm}^{-1}$  which is due to the change of local symmetry in  $[\text{BiO}_6]$  polyhedra as the bismuth oxide content decreases. Having in view that the bismuth group vibrations appear at significantly smaller wave numbers in comparison with the boron units vibrations, we can assume that in the 120-650  $\text{cm}^{-1}$  spectral region of the Raman spectra, only the bismuth unit vibrations as bridged anion and angularly cation-anion-cation constrained modes appear [34,37]. Thus, the broad but strong band occurring in the present Raman spectra centered around 394  $\text{cm}^{-1}$  can be attributed to Bi-O-Bi vibrations of both  $[\text{BiO}_3]$  and  $[\text{BiO}_6]$  octahedral units,

while the shoulder at  $586\text{ cm}^{-1}$  can be attributed to Bi-O<sup>-</sup> stretching vibrations in distorted linked [BiO<sub>6</sub>].



**Figure 2.** The Raman spectra of the present glass system

In the Raman spectra the band around  $927\text{ cm}^{-1}$  can be ascribed to isolated orthoborate group [18] while the weak band from  $1258\text{--}1278\text{ cm}^{-1}$  is due to BiO<sup>-</sup> (NBOs) of BiO<sub>3</sub> units in the entire composition range. This is confirmed from the fact that in the present glasses, the band observed at  $696\text{--}720\text{ cm}^{-1}$  in infrared spectra is assigned to B-O-B bending vibrations in [BO<sub>3</sub>] triangles [39] while the strong bands in the range  $1258\text{ cm}^{-1}$  and  $1319\text{ cm}^{-1}$  arises from Bi-O<sup>-</sup> stretching vibrations of BiO<sub>3</sub> units. The band in the present IR spectra around  $855\text{ cm}^{-1}$  represents the convolution of the absorbance bands reported for different bismuthate glasses at  $840$  and  $860\text{ cm}^{-1}$ , assigned to the total symmetric stretching vibrations of the [BiO<sub>3</sub>] and [BiO<sub>6</sub>] polyhedra respectively [19-23]. In the present study this band is observed at  $900\text{ cm}^{-1}$  which increases in intensity and shifts to  $966\text{ cm}^{-1}$  as Bi<sub>2</sub>O<sub>3</sub> content is increased from 45 to 70 mol%.

The presence of Raman peak at  $254\text{ cm}^{-1}$  and IR band in the range  $400\text{--}600\text{ cm}^{-1}$  indicates the presence of Zn-O tetrahedral bending vibrations in the present glass system [24-27]. It is clearly observed that with increase in the zinc oxide content the peak around  $254\text{ cm}^{-1}$  increases in intensity which indicates the formation of the ZnO<sub>4</sub> units.

## IV. CONCLUSIONS

The structural studies of the present quaternary glass system revealed the following conclusions. XRD profiles have confirmed their amorphous nature more clearly. 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 BiO<sub>3</sub>, BiO<sub>6</sub>, BO<sub>3</sub>, BO<sub>4</sub> and LiO<sub>2</sub> units in the structure of the studied glasses, but their position and intensity depend on the concentration of bismuth ion added. There is a formation of ZnO<sub>4</sub> units with the increase in the alkali oxide content.

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