

ANALYSIS OF INFRARED AND RAMAN SPECTROSCOPY OF BISMUTHCHLORIDE ADDED WITH LITHIUM DIBORATE GLASSES.

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ABSTRACT

The oxyhalide glass system $60\text{B}_2\text{O}_3 + 30\text{Li}_2\text{O} + (10 - x)\text{BiCl}_3$. With x changing from 05 – 30 mol % have been prepared by technique of melt quenching method. FTIR and Raman spectroscopy were used to how the distribution of functional groups and chemical structure of glass samples were analyzed in the absorption peaks changes with wavenumber. Its detailed analysis of glass network is added with Bi^{3+} ions, which changes in the number of BO_3 and BO_4 structural units in the glass network are observed, the four-coordinated boron units and groups, such as the boroxol ring, diborate, tetraborate, and pentaborate etc. may be simultaneously present in a single glass matrix, by the addition of modifiers. The band vibration is attributed to the trigonal BO_3 units in B-O-B are stretching vibrations in the meta, pyro, and ortho-borates. The glasses sample spectrum band overlap, which can be resolved by using of technique of the Gaussian deconvoluted graphs. Detailed analysis of the Bi-O-B, B-O-B and B-O stretching vibration at absorption peaks in the Raman spectroscopy.

KEYWORDS: Borate glass, stretching vibrations, Bending vibration, absorption peaks and Bonding.

1. INTRODUCTION.

Glasses are transparent, isotropic and amorphous supercooled liquids. They are an inorganic fusion product that has cooled to a hard state without crystallization. The existence of long-range organization in crystal structure distinguishes glass from crystals. Infrared spectroscopy (IR) is a useful technique for studying the structure and behavior of amorphous materials (Arti Yadav, et al 2018). It is also utilized in geometric grouping to assign measured absorption peaks to the correct vibration of the molecules.

Over the past few decades, detailed investigations on borate glasses have been pursued for both an academic and technological interests. B_2O_3 is a well-known glass former and is present in several crucial glasses, used for many commercial applications (D. Ramachari et al 2017 and G. Chandrashekaraiah et al 2018). It is the most fundamental glass forming materials because of its better bond strength, reduced cationic size, and low heat of fusion. The "boron anomaly" in borate glasses is a major aspect that promotes scientific interest in investigating borate glass features (B. N. Meera et al 1990). Oxygen atoms trigonally coordinate B^{3+} ions, and these triangular units are randomly corner-bounded. Some of the trigonally coordinated units are transformed into four-coordinated boron units and groups, such as the boroxol ring, diborate, tetraborate, and pentaborate etc. may be simultaneously present in a single glass matrix, when addition of modifiers are added. The number of structural units which depends on the concentration of the modifiers added to the glass network (Arti Yadav, et al 2018 and D. Ramachari et al 2017). Glasses containing Bi_2O_3 are a good choice for use in infrared transmission components, photonic devices and ultrafast optical switches, due to their lengthy infrared cut-off and strong third-order nonlinear optical susceptibility. These glasses have also been used in the development of electrical, mechanical, and thermal sensors (B. N. Meera et al 1990 and G. Chandrashekaraiah et al 2018).

Additionally, glasses with few glass formers, such as bismuth borate oxide glasses, are better for a variety of applications due to their excellent qualities, including strong polarizability and high refractive index valued. For usage in opto-electronic devices, lithium bismuth borate glasses can be used as optical fibers, WLEDs, and photosensitive waveguides. Additionally, these glasses are good hosts for the construction of luminous devices in photonics applications when doped with rare earths (G. Chandrashekaraiah et al 2020 and B. N. Meera et al 1990). Because bismuth may function as a network former and moderator, bismuth oxide has a special effect on the structure of borate glasses. On the other hand, the borate anomaly, which is characterized by an increase in the number of BO_3 and BO_4 structural units in the glass network, was seen in lithium-borate glasses (C. Narayana Reddy et al 2007). The creation of the higher coordinated species and the structural processes causing the anomaly continue to be of interest to the glass science. In the present investigation FTIR and Raman spectroscopic study used to understand how the distribution of functional groups and chemical structure with the variation of $BiCl_3$ content in the lithium diborate glass systems.

2. METHODOLOGY

2.1. Experimental

The melt quenching process was used to synthesis the glass system with the chemical compositions $(100 - x)[60B_2O_3 + 30 Li_2O] + x BiCl_3$ (LB) where $0 \leq x \leq 30$. Analar-grade Li_2CO_3 , H_3BO_3 and $BiCl_3$ chemical are taken in accordance with the above glass equation formula. The detailed synthesis of above glass network have shown in my elsewhere publication.

2.2. Characterization

Using a Vertex 70 model IR spectrometer from Bruker Germany and a KBr pellet at ambient temperature, the infrared spectra of LB glasses were prepared. With the use of a high resolution Jobin-Yvon-Hariba (Model LABRAM-HR visible) spectrometer, the Raman spectra of the glass samples were recorded.

3. RESULT AND DISCUSSION

3.1. Infrared spectroscopy

Because of its distinctive features, such as low melting temperatures, large glass forming regions, and strong radiation shielding qualities, lithium diborate glasses ($\text{Li}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) are of technological interest. The IR spectra of absorption band of wavenumber range of $400 - 4000 \text{ cm}^{-1}$ have shown in the Fig 1 and 2 of the LB glass samples. In this systems identified here, several observed absorption peaks at 490 cm^{-1} , 592 cm^{-1} , 668 cm^{-1} , 780 cm^{-1} , 785 cm^{-1} , and 1193 cm^{-1} , among others. In the first glass system (LB 05) observed many absorption peaks at lower wavenumber region, which are due to are attributed to vibration of Bi^{3+} ions acts as bridging in the BO_3 units (C. Narayana Reddy et al 2007). Hence, the observed absorption peaks 490 cm^{-1} , 592 cm^{-1} , and 668 cm^{-1} are assigned to the formation of bridging bonds B-O-Bi at the asymmetric stretching vibration (B.K. Chethana, et al 2012). Further, absorption bands at 780 cm^{-1} , and 785 cm^{-1} are observed due to the stretching vibrations BO_4 units, which indicate that BO_4 units is formed from the BO_3 units. The absorption band at 1193 cm^{-1} is assigned to stretching vibration and bending vibration of BO_3 triangle units in B-O-B bonding. The final band seen at 1193 cm^{-1} is attributed to the trigonal BO_3 units' B-O-B are stretching vibrations in the meta, pyro, and ortho-borates (Y. Cheng et al, 2006.) (P. M. Yamane and Y. Asahara, 2000) and (E. Culea et al, 2005)

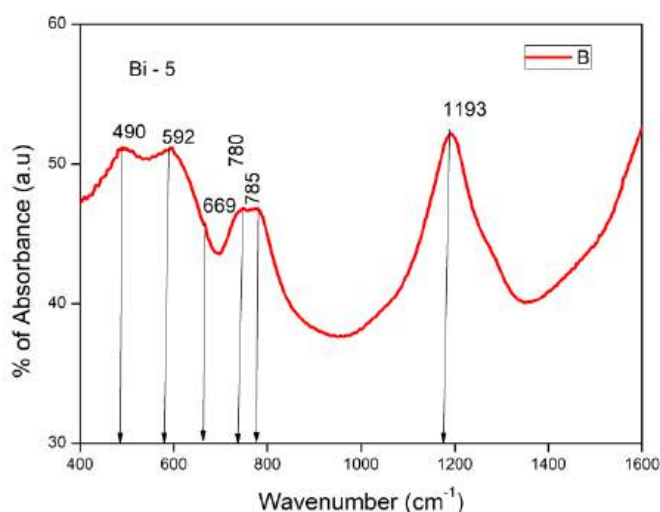


Fig 1. FTIR spectra of 05, 15 and 25 mol% LB glasses.

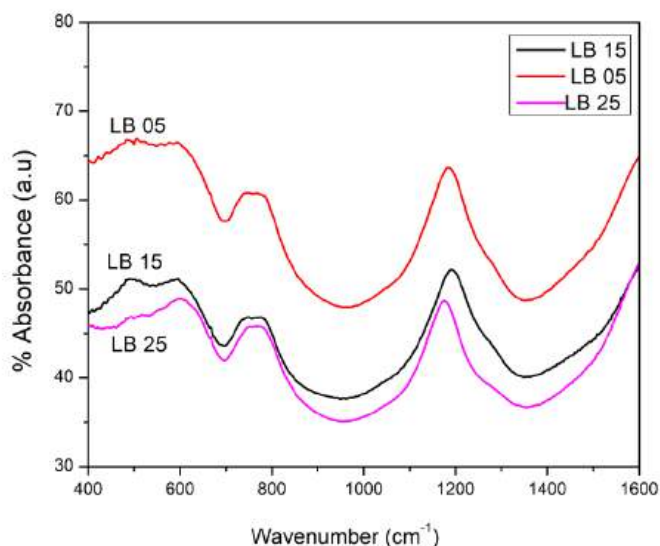


Fig 2. FTIR spectra of 25 mol% LB glasses

Furthermore, when bismuth content increased from 5 to 15 to 25 mol%, smaller peaks in the lower area of wavenumber decreased. Because the stretching force constant of Bi-O-B bonding is significantly lower than that of B-O, the stretching vibration of Bi-O-B may tend to be lower (M. Yamane and Y. Asahara), (2000). While addition of Bi^{3+} ions in the borate glass network does not affect more but can observe changes in the glass system. Furthermore, the Bi^{3+} concentration increases, the vibration of the $[\text{BO}_4]$ unit moves from 1193 cm^{-1} to a lower wavenumber in glass samples LB 15 and LB 25, owing to the development of Bi-O-B bridging bridges. Because the stretching force constant of Bi-O bonding is significantly lower than that of B-O bonding, the stretching vibrations of Bi-O-B may be lower. The structure of the glass network is influenced by the electrostatic fields of the strongly polarizing Bi^{3+} ions, which might serve to increase the wavenumber of B-O-B bending vibrations (E. Culea et al 2005). Therefore, the addition Bi^{3+} does not affect much in the borate glass network.

3.2. Raman spectroscopy

The vibrational modes, which are the "breathing modes" of the fundamental structural units that are found in the structure of borate glasses, are studied using Raman spectroscopy. The raw spectrum of the tested glasses was in the asymmetric in nature and our spectra of 05, 15 and 25 mol% BiCl_3 have shown in Fig 3. It is challenging to determine the active band location with accuracy, however curve fitting techniques like the Gaussian deconvoluted spectra of a glass sample LB 25 have shown in the Fig 4. With further addition of concentration of BiCl_3 , peak intensity is a decrease which is due to the growth of Raman lines with small changes in the absorption band spectrum (B. N. Meera et al, 1990).

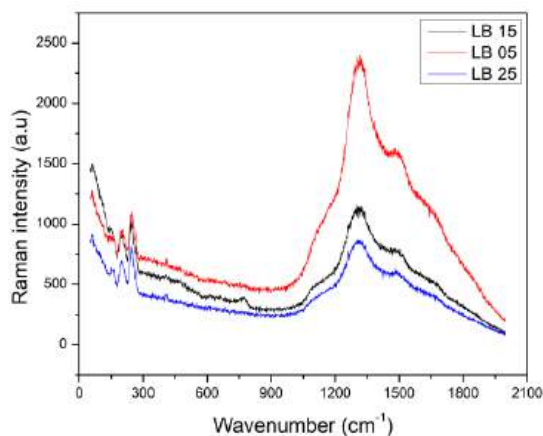


Fig 3. Raman spectra of 05, 15 and 25 mol% LB glasses

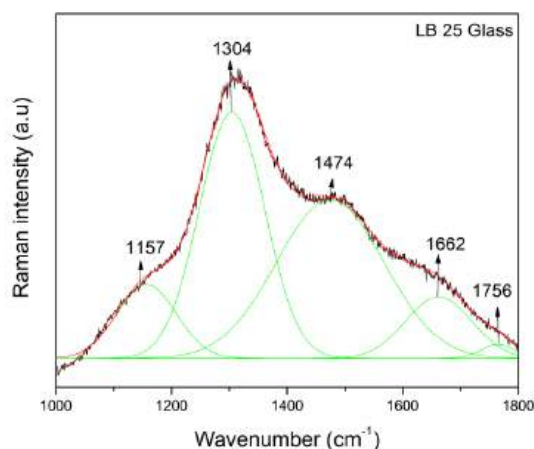


Fig 4. Deconvoluted Raman spectra of LB 25 mol% LB glasses

In diborate, trigonal, tetrahedral, pentaborate, metaborate, and boron rings, the potential cation-oxygen connections B-O, B-O-, and B-O-B are found using Raman spectroscopic analysis. To support the network links, Raman investigations are used to further examine the groupings. The stretching vibration of 1662 cm^{-1} and 1474 cm^{-1} is due to B-O-vibrations are present in pyro- and ortho-borate groups. The presence of diborate groups is shown by the band at 1157 cm^{-1} (H. Fan et al, 2010). The centre of the B-O vibration in the pyro and ortho borate groups is 1063 cm^{-1} . B-O vibrations are present in diborate groups and are centered at 739 cm^{-1} . Due to the bending vibrations of B-O-B in boroxyl rings not due to the Bi^{3+} a weak band at 540 cm^{-1} is observed (M. S. Dahiya et al, 2018). The bismuth structural units are responsible for the spectra's moderately strong band in the area of 181 cm^{-1} . The vibrational modes observed at 345 cm^{-1} are bismuth-oxygen polyhedral. (Y. Cheng et al, 2006) (N. Elkhoshkhanya, et al, 2019).

4. CONCLUSION.

Using FTIR and Raman spectroscopy techniques the distribution of functional groups and chemical structure of glass samples were analyzed. Its analysis of glass network is added with Bi^{3+} ions, which changes in the number of BO_3 and BO_4 structural units in the glass network are observed. The trigonal BO_3 units in B-O-B are stretching vibrations in the meta, pyro, and ortho-borates are confirmed. In Raman spectroscopy absorption peaks due to B-O, B-O-B and Bi-O stretching vibration are analyzed.

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