

FT – IR AND RAMAN SPECTROSCOPIC STUDIES OF $x\text{Ag}_2\text{O} \cdot (100-x)[\text{B}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ GLASS SYSTEM

S. C. Baidoc¹, S. Filip² and I. Ardelean^{1*}

¹Faculty of Physics, Babes-Bolyai University, 400084 Cluj
Napoca, Romania

²Department of Physics, University of Oradea, 410087
Oradea, Romania

Abstract:

Structural analysis of $x\text{Ag}_2\text{O} \cdot (100-x) \cdot [\text{B}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ glass system, with $0 \leq x \leq 10$ mol%, was performed by means of FT – IR and Raman spectroscopies. The purpose of this work is to investigate the structural changes that appear in the $\text{B}_2\text{O}_3 \cdot \text{As}_2\text{O}_3$ glass matrix with the addition and increasing of silver ions content. Boroxol rings, pyro-, ortho-, di-, tri-, tetra- and penta-borate groups, structural units characteristic to As_2O_3 were found in the structure of the studied glasses. FT-IR spectroscopy measurements show that BO_3 units are the main structural units of the glass system. The presence of structural units characteristic to Ag_2O were not directly evidenced by FT-IR spectroscopy. The Raman analysis leads to similar conclusions as FT – IR measurements.

1. Introduction

B_2O_3 is one of the most important glass forming oxides and has been incorporated into various kinds of glass systems in order to attain the desired physical and chemical properties [1]. Binary borate glass systems are known to show interesting properties. Today, borates are an important material for insulation (glass wool) and textile (continuous filament) fiberglass. Therefore, precise knowledge of the structure and properties of B_2O_3 – based glasses and melts is increasingly required from both fundamental and industrial points of view [2].

In structural analyses of borate glasses, the boron–oxygen configurations have been determined by means of X-ray diffraction [3–5], neutron diffraction [6], molecular dynamics [7], Raman spectroscopy [8 - 11] and ^{11}B -nuclear magnetic resonance (NMR) [12–14].

As_2O_3 is also a network former in which we encounter AsO_3 pyramidal units and its glasses were identified as low loss materials for long distance optical

*Corresponding author: arde@phys.ubbcluj.ro

transmission because of the exceptionally high transmission potential in the far infrared region [15, 16]. They have very high Raman scattering coefficients and are found to be suitable for active fiber Raman amplification [17]. Most of the studies available on As_2O_3 glasses are on the understanding of their structure by X-ray and neutron diffraction studies, Raman spectra, IR spectra, etc. [18 - 20].

Silver borate glasses in particular have attracted a lot of attention because of their high ionic conductivity, especially when mixed with AgI. This property makes a basis for their applications in electrochemistry as solid electrolytes [21]. The optimization of such properties requires a good knowledge of the microscopic glass structure. In particular, a deeper knowledge of the local environment of the moving ions is highly desirable [22].

The purpose of this study is to investigate the structural changes which occur in $x\text{Ag}_2\text{O} \cdot (100-x)[\text{B}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ glasses, with $0 \leq x \leq 10$ mol %, by means of FT – IR and Raman spectroscopies.

2. Experimental

The $x\text{Ag}_2\text{O} \cdot (100-x)[\text{B}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ glass system, with $0 \leq x \leq 10$ mol %, was prepared by mixing components of reagent grade purity as: AgNO_3 , H_3BO_3 and As_2O_3 . The mixtures were melted in sintered corundum crucibles, in an electric furnace directly at 1250 °C for 30 minutes. The melts were quickly cooled at room temperature by pouring onto stainless steel plates.

By X – ray diffraction it was observed that the XRD patterns obtained are characteristic to vitreous solid in all compositional range.

The FT-IR absorption spectra of the glasses in the 400 - 4000 cm^{-1} spectral range were obtained with an Equinox 55 Bruker spectrometer. Because the studied glasses presents IR absorption in the 400 – 2000 cm^{-1} spectral range, the spectra will be analyzed within this spectral range. The spectral resolution was about 0.5 cm^{-1} . The IR absorption measurements were done using the KBr pellet technique. In order to obtain good quality spectra the samples were crushed in an agate mortar to obtain particles of micrometer size. This procedure was applied every time to fragments of bulk glass to avoid structural modifications due to ambient moisture.

The Raman spectra of the samples were recorded in the 50 - 4000 cm^{-1} spectral range with a Dilor Labram spectrometric machine using the line from 514.5 nm of the laser with argon ions. The power of the laser was 100mW. The microscope used was Olympus BX with an objective of 100x. Signal acquisition was made with the help of a camera CCD (Photometric model 9000) and the soft used was LabSpec 3.1. Spectra were obtained making the average of 8 cycles of 20 seconds each and the spectral resolution was 4 cm^{-1} . For these measurements, bulk samples were used.

3. Results and discussion

The experimental FT – IR spectra of the $x\text{Ag}_2\text{O} \cdot (100-x)[\text{B}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$, with $0 \leq x \leq 10$ mol % glasses are presented in figure 1. The vibrational assignments of the bands for the glasses spectra were made using the method given by Condrate [23] and Tarte [24], by comparing the experimental data of glasses with those of related crystalline compounds.

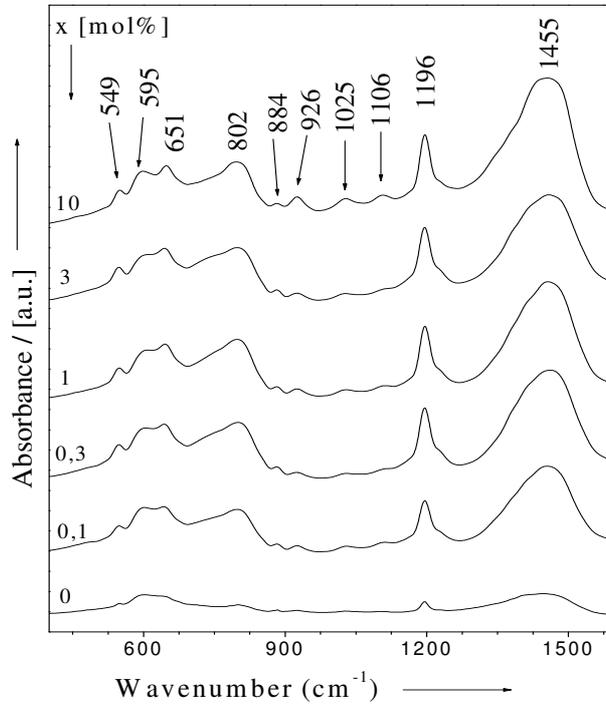


Fig.1. FT – IR spectra of $x\text{Ag}_2\text{O} \cdot (1-x)[\text{B}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ glasses with $0 \leq x \leq 10$ mol %

In general, the IR absorptions of borate glasses occur in three regions:

- 600 - 850 cm^{-1} – due to B-O-B bending vibrations;

- 850 - 1150 cm^{-1} - due to boron in tetrahedral oxygen coordination (BO_4);

- 1200 -1500 cm^{-1} – due to borate units in which boron atom is coordinated with three oxygen (both bridging and nonbridging types) [25 - 28].

The glass matrix $\text{B}_2\text{O}_3 \cdot \text{As}_2\text{O}_3$ presents the following FT - IR bands at: $\sim 549 \text{ cm}^{-1}$, $\sim 595 \text{ cm}^{-1}$, $\sim 651 \text{ cm}^{-1}$, $\sim 802 \text{ cm}^{-1}$, $\sim 884 \text{ cm}^{-1}$, $\sim 926 \text{ cm}^{-1}$, $\sim 1025 \text{ cm}^{-1}$, $\sim 1106 \text{ cm}^{-1}$, $\sim 1196 \text{ cm}^{-1}$ and $\sim 1455 \text{ cm}^{-1}$. Their structural assignments are presented in Table 1.

In the first region there are three FT-IR bands. The band from $\sim 549 \text{ cm}^{-1}$ is assigned to B-O-B bonds bending vibrations involving oxygen atoms outside

borate rings [29]. The band from $\sim 595 \text{ cm}^{-1}$ is due to symmetric bending vibrations of As – O bonds [15]. The band from $\sim 651 \text{ cm}^{-1}$ is assigned to O–B–O bonds bending vibrations. With the addition of 0, 1 mol% of silver oxide ions the intensities of the peaks are increasing and with the increase of silver oxide content the intensities are progressively increasing up to 10 mol%.

In the second region there are five FT-IR bands. The band from $\sim 802 \text{ cm}^{-1}$ belongs to doubly degenerate stretching vibrations given by As-O bonds [15]; the bands from $\sim 884 \text{ cm}^{-1}$ and from $\sim 926 \text{ cm}^{-1}$ belongs to B-O bonds stretching vibrations in BO_4 units from tri-, tetra- and penta-borate groups and B-O bonds stretching vibrations in BO_4 units from diborate groups, respectively; the band from $\sim 1025 \text{ cm}^{-1}$ is due to B-O bonds stretching vibrations in BO_4 units from tri-, tetra- and penta-borate units and the band from $\sim 1106 \text{ cm}^{-1}$ is due to asymmetric stretching vibrations of B-O bonds from BO_4 units. With the addition and increasing of silver oxide content the intensities of the peaks are progressively increasing up to 10 mol%.

In the third region there are only two FT-IR bands. The first one, from $\sim 1196 \text{ cm}^{-1}$ is given by the asymmetric stretching vibrations of B-O and/or B-O bonds in borate triangular units (BO_3 and BO_2O^-) from pyro- and ortho-borate groups and the second one from $\sim 1455 \text{ cm}^{-1}$ is due to B-O bonds stretching vibrations of BO_3 units from various borate groups. The intensity of the band from $\sim 1196 \text{ cm}^{-1}$ increases with the addition of silver oxide up to 0, 3 mol% and then remains constant up to 10 mol%. The intensity of the band from $\sim 1455 \text{ cm}^{-1}$ increases progressively with the addition and increase of silver oxide concentration.

The structure proposed for $\text{B}_2\text{O}_3\cdot\text{As}_2\text{O}_3$ glass matrix from FT-IR measurements is formed from tri- (B_3O_5^-), tetra- ($\text{B}_8\text{O}_{13}^{2-}$), penta- (B_5O_8^-), di- ($\text{B}_4\text{O}_7^{2-}$), pyro- ($\text{B}_2\text{O}_5^{4-}$) and ortho-borate (BO_3^{3-}) groups and also from structural units characteristic to As_2O_3 . With the addition of silver ions it can be observed an increase in intensity for all the bands.

Table 1. Wavenumbers and band assignments of $x\text{Ag}_2\text{O}\cdot(1-x)[\text{B}_2\text{O}_3\cdot\text{As}_2\text{O}_3]$ glasses

Wavenumber [cm^{-1}]		FT-IR assignments	Raman assignments
FT-IR	RAMAN		
	~ 495		Vibrations of isolated di-borate groups, Vibrations of As-O bonds
~ 549		B–O–B bonds bending vibrations involving oxygen atoms outside borate	

		rings	
~ 595		Symmetric bending vibrations of As – O bonds	
~ 651	~ 691	O–B–O bonds bending vibrations	Vibrations of chain and/or ring type meta- and penta- borate groups
~ 802	~ 802	Doubly degenerate stretching vibrations of As-O bonds	Symmetric breathing vibrations of boroxol rings
~ 884 ~ 1025	~ 880	B-O bonds stretching vibrations in BO_4^- units from tri-, tetra- and penta-borate groups	Vibrations of pyroborate groups
~ 926		B-O bonds stretching vibrations in BO_4 units from diborate groups	
~ 1118	~ 1000	Asymmetric stretching vibrations of B-O bonds from BO_4 units	Vibrations of orthoborate groups
~ 1196		Asymmetric stretching vibrations of B-Ø and / or B-O ⁻ bonds in borate triangular units (BO_3 and BO_2O^-) from pyro- and ortho-borate groups	
	~ 1250	Asymmetric stretching vibrations of B-O bonds from ortho-borate groups	Vibrations of pyroborate groups
~ 1455		B-O bonds stretching vibrations in BO_3 units from various borate groups	

To quantify the silver ions effect to the changes in the relative population of triangular and tetrahedral borate units we have calculated the integrated intensity of the absorption envelopes $850\text{-}1150\text{ cm}^{-1}$ and $1200\text{ - }1500\text{ cm}^{-1}$ denoted by A_4 and A_3 respectively [30]. A_4 and A_3 approximate the relative number of BO_4 and BO_3 units, respectively. The relative integrated intensity, $A_r = A_4/A_3$, is plotted in figure 2 versus Ag_2O content. It can be observed that $A_r < 1$, which means that the predominant structural units in the studied glasses are BO_3 units. The decrease of A_r up to $x = 3\text{ mol}\%$ indicates the fact that the formation of structural units in which boron atoms are tri-coordinated is favoured. The increase of A_r ratio from $x \geq 3\text{ mol}\%$ silver ions concentration indicates a progressively change of boron coordination from three to four.

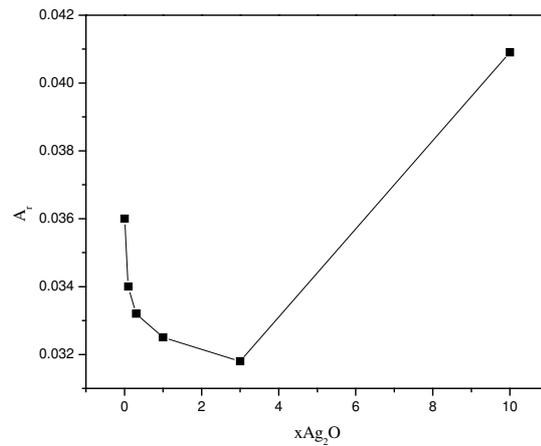


Fig. 2. A_r ratio as a function of Ag_2O content in $x\text{Ag}_2\text{O}\cdot(100-x)[\text{B}_2\text{O}_3\cdot\text{As}_2\text{O}_3]$ glasses

The Raman spectra of the studied glasses are presented in figure 3. Due to the fact that the Raman bands for the investigated glasses are in $400\text{ - }2000\text{ cm}^{-1}$ spectral range, the spectra will be presented only in this area. The $\text{B}_2\text{O}_3\cdot\text{As}_2\text{O}_3$ glass matrix presents seven Raman bands at $\sim 495\text{ cm}^{-1}$, $\sim 691\text{ cm}^{-1}$, $\sim 802\text{ cm}^{-1}$, $\sim 880\text{ cm}^{-1}$, $\sim 912\text{ cm}^{-1}$, $\sim 1000\text{ cm}^{-1}$ and $\sim 1250\text{ cm}^{-1}$. Their vibrational assignments are presented in Table 1.

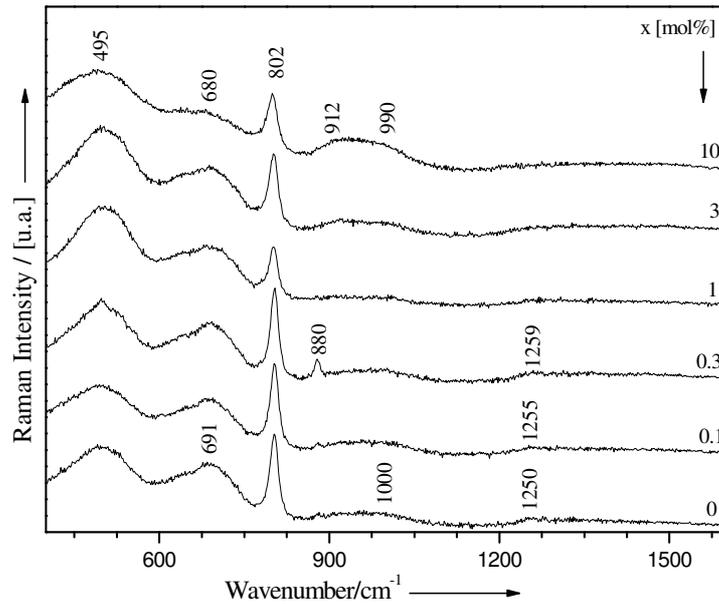


Fig. 3 – Raman spectra of $x\text{Ag}_2\text{O} \cdot (1-x)[\text{B}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ glasses with $0 \leq x \leq 10 \text{ mol } \%$

The band from $\sim 495 \text{ cm}^{-1}$ is due to vibrations of isolated di-borate groups and/or to vibrations of As-O bonds. The intensity of this band increases with the increase of silver ions concentration up to 3 mol% and then decreases for $x = 10 \text{ mol}\%$. The band from $\sim 691 \text{ cm}^{-1}$ belongs to vibrations of chain and/or ring type meta- and penta-borate groups. With the addition of silver oxide the intensity of this band is decreasing.

The intensity of the band from $\sim 802 \text{ cm}^{-1}$, which is due to symmetric breathing vibration of boroxol rings, remains the same with the addition of silver ions up to 0.3 mol%, then decreases for $x = 1 \text{ mol}\%$, increases for $x = 3 \text{ mol}\%$ and for $x = 10 \text{ mol}\%$ it decreases.

The band from $\sim 880 \text{ cm}^{-1}$, given by vibrations of pyro-borate groups, increases with the addition of silver oxide ions up to 0.3 mol% and for $x \geq 3 \text{ mol}\%$ it's shifted to higher wavenumbers ($\sim 912 \text{ cm}^{-1}$). The band from $\sim 1000 \text{ cm}^{-1}$ originates from orthoborate groups; the intensity of this band is decreasing with the addition of silver ions up to $x = 1 \text{ mol}\%$ and then increases up to $x = 10 \text{ mol}\%$.

The band from $\sim 1250 \text{ cm}^{-1}$ is due to vibrations of pyro-borate groups. Its intensity remains the same with the addition and the increasing of silver ions

content up to $x = 0.3$ mol% and then decreases. With the adding and the increase of silver ions the band is shifted to higher wavenumbers.

The structure proposed by Raman spectroscopy for $B_2O_3 \cdot As_2O_3$ glass matrix is formed from isolated di-borate groups [31], chain and/or ring type meta- and penta-borate groups [31], boroxol rings [32], ortho-[33] and pyro-borate groups [31] and also from the structural units characteristic to As_2O_3 [16].

4. Conclusions

From FT-IR spectra it can be observed that the network structure of $xAg_2O \cdot (1-x)[B_2O_3 \cdot As_2O_3]$ glasses consist of randomly connected BO_3 , BO_4 structural units and also from characteristic structural units of As_2O_3 . The infrared measurements reveal the presence of borate structural units (di-, tri-, tetra-, penta-, pyro- and ortho- borate) and pyramidal units specific to As_2O_3 . Boron atoms are present in the structure in both, three- and four-coordination states. The A_T ratio is lower than the unity, so the number of tetracoordinated boron atoms is smaller than the number of tricoordinated boron atoms. With the increasing of Ag_2O content, $x \geq 3$ mol%, the boron-oxygen network is modifying by changing the coordination number of some of the boron atoms from three to four.

Raman spectra confirm the structure proposed by FT – IR measurements and also reveal the presence of boroxol rings and chain and/or ring type metaborate groups.

Both, FT – IR and Raman measurements do not evidence directly the presence of silver structural units in the studied glasses.

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