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FT – IR and Raman spectroscopic studies of $xAg_2O\cdot(100\text{-}x)[3B_2O_3\cdot As_2O_3]$ glass system

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Structural analysis of $xAg_2O(100\text{-}x)[3B_2O_3\cdot As_2O_3]$ glass system, with $0 \le x \le 10$ 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 $3B_2O_3\cdot As_2O_3$ glass matrix with the addition and increasing of silver ions content. Boroxol rings, pyro-, ortho-, di- , tri-, tetra- and penta-borate groups and structural units characteristic to As_2O_3 were found in the structure of the studied glasses. At small silver oxide content the predominant structural units are those in which boron is three-fold coordinated. For higher silver oxide concentrations ($x \ge 5$ mol%) the number of four-fold coordinated boron units is increasing. The changes in the $A_r = A_4/A_3$ (A_4 and A_3 reflect the relative amount of tetrahedral (BO_4 and $B\varnothing_4^-$) and triangular ($B\varnothing_3$ and $B\varnothing_2O^-$) borate species) ratio also shows the fact that silver oxide influence the boron coordination number. The Raman analysis leads to similar conclusions as FT – IR measurements.

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1. Introduction

B_2O_3 based glasses have been widely studied over the past decades due to their technological applications and for understanding the structural particularities as the occurrence of boron anomaly. Today, borates are important materials for insulation (glass wool) and textile (continuous filament) fiberglass [1]. Borate glasses are host of widespread optical, electrical, magnetic and other technologically interesting properties [2].

Pure boron oxide B_2O_3 in the glass state consists of three coordinated boron atoms, which can be associated to form six-member boroxol rings [3].

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 transmission because of the exceptionally high transmission potential in the far infrared region [4, 5].

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 [6]. 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 [7].

The purpose of this study is to investigate the structural changes which occur in $xAg_2O(100\text{-}x)[3B_2O_3\text{-}As_2O_3]$ glasses, with $0 \le x \le 10$ mol %, by means of FT – IR and Raman spectroscopies.

2. Experimental

The $xAg_2O\cdot(100\text{-}x)[3B_2O_3\text{-}As_2O_3]$ glass system, with $0 \le x \le 10$ 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.

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 $xAg_2O\cdot(100-x)[3B_2O_3-As_2O_3]$, with $0 \le x \le 10$ 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 [8] and Tarte [9], by comparing the experimental data of glasses with those of related crystalline compounds.

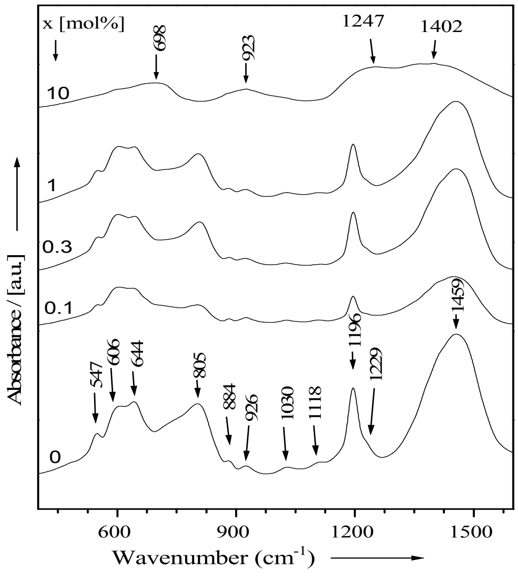

Fig.1. FT – IR spectra of $xAg_2O\cdot(1-x)[3B_2O_3-As_2O_3]$ *glasses with* $0 \le x \le 10$ *mol %*

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

- 600 - 800 cm^{-1} – due to B-O-B bending vibrations;
- 800 - 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) [10 - 13];

The glass matrix $3B_2O_3-As_2O_3$ presents the following FT - IR bands at: ~ 547 cm^{1}, ~ 606 cm^{-1}, ~ 644 cm^{-1}, ~ 805 cm^{-1}, ~ 884 cm^{-1}, ~ 926 cm^{-1}, ~ 1030 cm^{-1}, ~ 1118 cm^{-1}, ~ 1196 cm^{-}1, ~ 1229 cm^{-1} and ~ 1459 cm^{-1}. Their structural assignments are presented in Table 1.

In the first region there are three FT-IR bands. The band from ~ 547 cm^{-1} is assigned to B-O-B bonds bending vibrations involving oxygen atoms outside borate rings [14]. The band from ~ 606 cm^{-1} is due to symmetric bending vibrations of As – O bonds [4]. The band from ~ 644 cm^{-1} is assigned to O–B–O bonds bending vibrations. With the addition of 0.1 mol% of silver ions, the intensities of these bands decrease, then increase with the increase of silver ions content up to 1 mol%. For the sample with x = 10 mol% it can be observed that these bands are covered by a broad band with a maximum at ~ 698 cm^{-1}.

In the second region there are five FT-IR bands. The band from ~ 805 cm^{-1} belongs to doubly degenerate stretching vibrations given by As-O bonds [4]. With the addition of 0.1 mol% of silver ions content, the intensity of the band is decreasing and, with the increase of silver oxide content its intensity is progressively increasing up to 1 mol%. For the sample with x = 10 mol%, it disappears. The bands from ~ 884 cm^{-1} and from ~ 926 cm^{-1} belongs to B-O bonds stretching vibrations of BO_4 tetrahedra from tri-, tetra- and penta-borate groups, and B-O bonds stretching vibrations in BO_4 units from diborate groups, respectively. The band from ~ 1030 cm^{-1} is due to B-O bonds stretching vibrations of BO_4 tetrahedra from tri-, tetra- and penta-borate groups and the band from ~ 1118 cm^{-1} is due to asymmetric stretching vibrations of B-O bonds from BO_4 units. With the increase of silver ions content, the bands from ~ 884 cm^{-1}, ~ 926 cm^{-1}, ~ 1030 cm^{-1} and ~ 1118 cm^{-1} remains the same up to 1 mol %. For the sample with x = 10 mol%, these bands are covered by a broad band centered at ~ 923 cm^{-1}.

In the last region there are only three FT-IR bands. The first one, from ~ 1196 cm^{-1} is given by the 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. The second band, from ~ 1229 cm^{-1} is given by the asymmetric stretching vibrations of B-O bonds from orthoborate groups and the third band is due to B-O bonds stretching vibrations of BO_3 units from various borate groups. With the addition of 0.1 mol% of silver ions, the intensities of these bands are decreasing and, with the increase of silver oxide content, the intensities of the bands from ~ 1196 cm^{-1} and ~ 1459 cm^{-1} are progressively increasing up to 1 mol%. The shoulder from ~ 1229 cm^{-1} remanis the same up to 1 mol%. For the sample with x = 10 mol% there are only two broad bands with maxima at ~ 1247 cm^{-1} and at ~ 1402 cm^{-1}, respectively.

The structure proposed for $3B_2O_3-As_2O_3$ glass matrix from FT-IR measurements is formed from tri- ($B_3O_5^-$), tetra- ($B_8O_{13}^{2-}$), penta- ($B_5O_8^-$), di- ($B_4O_7^{2-}$), pyro- ($B_2O_5^{4-}$) and ortho-borate (BO_3^{3-}) groups and also from structural units characteristic to As_2O_3. With the addition of silver ions the proportion of the structural units is changing.

The broadening of the bands with the increase of silver ions content is due to a depolymerization of the structure and an increasing of the disorder degree.

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 800-1150 cm^{-1} and 1200 - 1500 cm^{-1} denoted by A_4 and A_3 respectively [15]. 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 Fig. 2 versus Ag_2O content.

Table 1. Wavenumbers and band assignments of $xAg_2O\cdot(1\text{-}x)[3B_2O_3\text{-}As_2O_3]$ glasses.

Wavenumber [cm^{-1}]		FT-IR assignments	Raman assignments
FT-IR	RAMAN		
	~ 490		Vibrations of isolated di–borate groups, Vibrations of As-O bonds
~ 547		B–O–B bonds bending vibrations involving oxygen atoms outside borate rings	
~ 606		Symmetric bending vibrations of As – O bonds	
~ 644	~ 690	O–B–O bonds bending vibrations	Vibrations of chain and/or ring type meta- and penta- borate groups
~ 805	~ 800	Doubly degenerate stretching vibrations of As-O bonds	Symmetric breathing vibrations of boroxol rings
~ 884	~ 875	B-O bonds stretching vibration of BO_4 tetrahedra from tri-, tetra- and penta-borate groups	Vibrations of ortho-borate groups
~ 926		B-O bonds stretching vibrations in BO_4 units from diborate groups	
~ 1030		B-O bonds stretching vibrations of BO_4 tetrahedra from tri-, tetra- and penta-borate groups	
~ 1118		Asymmetric stretching vibrations of B-O bonds from BO_4 units	
~ 1196		Asymmetric stretching vibrations of B-Ø and / or B-O^- bonds in borate triungular units (BO_3 and BO_2O^-) from pyro- and ortho-borate groups	
~ 1229	~ 1250	Asymmetric stretching vibrations of B-O bonds from orthoborate groups	Vibrations of pyro-borate groups
~ 1459		B-O bonds stretching vibrations of BO_3 units from various borate groups	

∅ - Oxygen atom bridging two boron atoms

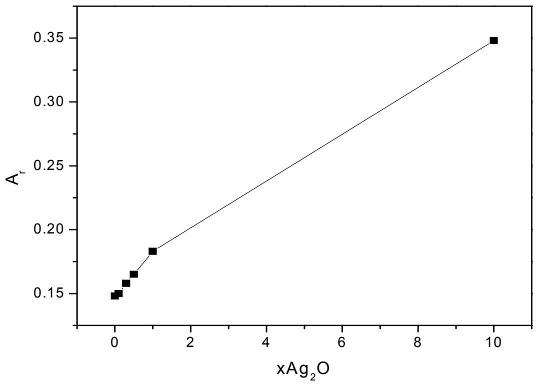

Fig. 2. A_r ratio as a function of Ag_2O content in $xAg_2O\cdot(100\text{-}x)[3B_2O_3\text{-}As_2O_3]$ glasses

It can be observed that $A_r < 1$, which means that the predominant structural units in the studied glasses are BO_3 units. The increase of A_r ratio with the increase of silver ions content indicates a progressively change of boron coordination from three to four.

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 – 2000 cm^{-1} spectral range, the spectra will be presented only in this area. The $3B_2O_3\text{-}As_2O_3$ glass matrix presents five Raman bands at ~ 490 cm^{-1}, ~ 690 cm^{-1}, ~ 800 cm^{-1}, ~ 875 cm^{-1} and ~ 1250 cm^{-1}. Their vibrational assignments are presented in Table 1.

The band from ~ 490 cm^{-1} is due to vibrations of isolated di–borate groups and/or to vibrations of As-O bonds. The intensity of the band decreases with the addition and increasing of silver ions content. The band from ~ 690 cm^{-1} belongs to vibrations of chain and/or ring type meta- and penta-borate groups; its intensity is increasing with the adding and increasing of silver ions content. The band from ~ 800 cm^{-1}, which is due to symmetric breathing vibration of boroxol rings, increases progressively with the increasing of silver ions up to 1 mol% and than decreases for 10 mol%. The band from ~ 875 cm^{-1}, given by vibrations of ortho-borate groups, decreases progressively with the addition of silver ions content. The band from ~ 1250 cm^{-1} is due to vibrations of pyroborate groups. Its intensity remains the same with the addition and the increasing of silver ions content.

The structure proposed by Raman spectroscopy for $3B_2O_3$-As_2O_3 glass matrix is formed from isolated di-borate groups [16], chain and/or ring type meta- and penta-borate groups [16], boroxol rings [17], ortho-[18] and pyro-borate groups[16] and also from the structural units characteristic to As_2O_3 [5].

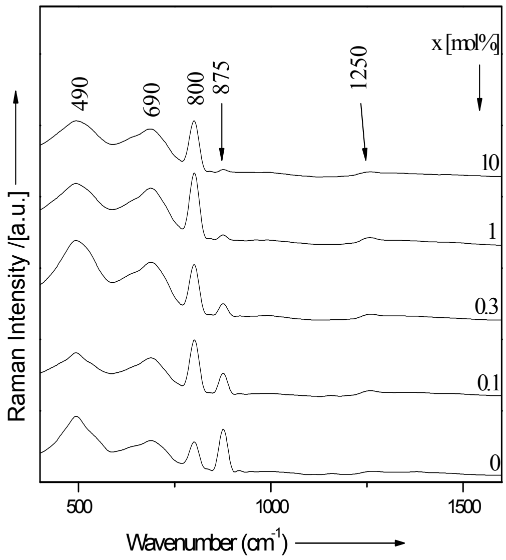

Fig. 3. Raman spectra of $xAg_2O\cdot(1-x)[3B_2O_3$-$As_2O_3]$ *glasses*

4. Conclusions

From FT-IR spectra it can be observed that the network structure of $xAg_2O\cdot(1-x)[3B_2O_3$-$As_2O_3]$ glasses consist of randomly connected BO_3, BO_4 structural units and also from As_2O_3 structural units. The infrared measurements reveal the presence of borate structural units (di-, tri-, tetra-, penta-, pyro- and ortho- borate) and As_2O_3 pyramidal units. Boron atoms are present in the structure in both, three and four coordination states. The A_r 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 silver ions content, the boron-oxygen network is modifying by changing the coordination number of some of the boron atoms from three to four. The broadening of the FT-IR bands with the increase of silver ions content is due to a depolymerization of the structure and an increasing of the disorder degree.

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 don't evidence directly the presence of silver structural units in the studied glasses.

References

[1] Ryiuichi Akagai , Norikazu Ohtori , Norimasa Umesaki , J. Non-Cryst. Solids **293**, 471, (2001)
[2] S.A. Feller, Phys. Chem. Glasses **41**, 211, (2000)
[3] M. Massot, S. Souto, M. Balkanski, J. Non-Cryst. Solids **182**, 49, (1995)
[4] G. Srinivisarao , N. Veeraiah , J. Alloys Compounds **327**, 52, (2001)
[5] R. Ciceo Lucacel, I. Ardelean, J. Optoelectron. Adv. Mater **8**(3), 1124, (2006)
[6] T. Minami, J. Non-Cryst. Solids **73**, 273, (1975)
[7] G. Calas, L. Cormier, L. Galoisy, P. Jollivet, C. R. Acad. Sci., Ser. IIc: Chim. **5**, 831, (2002)
[8] R. A. Condrate, J. Non-Cryst. Solids **84**, 26 (1986)
[9] P. Tarte, Physics of Non Crystalline Solids 549, (1964)
[10] U. Selvara , K. J. Rao, Spectrochim. Acta A, **40**, 1081 (1984)
[11] E. I. Kamitsos, M. A. Karakassides, G. D. Chryssikos, Phys. Chem. Glasses **28**, 203 (1987)
[12] E. I. Kamitsos, M. A. Karakassides, G. D. Chryssikos, J. Phys. Chem. **91**, 1073, (1987)
[13] E. I. Kamitsos, A. P. Patsis, M. A. Karakassides, G. D. Chryssikos, J. Non-Cryst. Solids **126**, 52 (1990)
[14] J. F. Ducel, J. J. Videau, M. Couzi, Phys. Chem. Glasses **34**, 5, (1993)
[15] Y. D. Yiannopoulos, G. D. Chryssikos, E. I. Kamitsos, Phys. Chem. Glasses **42**, 164 (2001)
[16] D. Maniu, T. Iliescu, I. Ardelean, S. Cinta-Pinzaru, N. Tarcea, W. Kiefer, J. Molec. Structure 651, (2003)
[17] D. Maniu, T. Iliescu, I. Ardelean, R. Ciceo-Lucacel, M. Bolboaca, W. Kiefer, Vibr. Spectroscopy **29**, 241, (2002)
[18] Munia Ganguli., K. J. Rao, Solid State Chem. **145**, 65, (1999)

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