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Structural investigation of $x\mathrm{Ag_2O} \cdot (100 - x)[2\mathrm{B_2O_3} \cdot \mathrm{As_2O_3}]$ glass system

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Abstract Structural analysis of $x\mathrm{Ag_2O} \cdot (100 - x)[2\mathrm{B_2O_3} \cdot \mathrm{As_2O_3}]$ 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 $2\mathrm{B_2O_3} \cdot \mathrm{As_2O_3}$ glass matrix with the addition and increase of silver ions content. Boroxol rings, pyro-, ortho-, di-, tri-, tetra-, and pentaborate groups, structural units characteristic to $\mathrm{As_2O_3}$ were found in the structure of the studied glasses. FT-IR spectroscopy measurements show that $\mathrm{BO_3}$ units are the main structural units of the glass system. The presence of structural units characteristic to $\mathrm{Ag_2O}$ were not directly evidenced by FT-IR spectroscopy. Raman analysis leads to similar conclusions as that obtained from FT-IR measurements.

Introduction

Over the last decade, many investigators have found that the analysis of vibrational spectra of glasses can be applied to the solution of both the industrial and basic research problems. In an applied study, the vibrational spectra can be used to identify the specific units that are present in the structure of the glasses [1].

$\mathrm{B_2O_3}$-based glasses have been widely studied over the years due to their interesting structural particularities, such as the occurrence of boron anomaly [2, 3], and because they are an important material for insulation (glass wool) and textile (continuous filament) fiberglass [4].

$\mathrm{As_2O_3}$ is also a network former in which we encounter $\mathrm{AsO_3}$ 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 [5, 6]. They have very high Raman scattering coefficients and are found to be suitable for active fiber Raman amplification [7]. Most of the studies available on $\mathrm{As_2O_3}$ glasses are on the understanding of their structure by X-ray and neutron diffraction studies, Raman spectra, IR spectra, etc. [8–10].

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 [11]. 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 [12].

Raman and infrared vibrational spectroscopies proved to be powerful tools to investigate the structure of borate glasses, which present extremely sharp peaks in the polarized Raman spectrum, similar to other glasses, such as $\mathrm{SiO_2}$ [13, 14].

The purpose of this study is to investigate the structural changes that occur in $x\mathrm{Ag_2O} \cdot (100 - x)[2\mathrm{B_2O_3} \cdot \mathrm{As_2O_3}]$ glasses, with $0 \leq x \leq 10$ mol%, by means of FT-IR and Raman spectroscopies.

Experimental

The $x\mathrm{Ag_2O} \cdot (100 - x)[2\mathrm{B_2O_3} \cdot \mathrm{As_2O_3}]$ glass system, with $0 \leq x \leq 10$ mol%, was prepared by mixing components of

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reagent grade purity: $AgNO_3$, 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 min. The melts were quickly cooled to room temperature by pouring onto stainless steel plates.

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 present 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 100 mW. The microscope used was Olympus BX with an objective of 100×. Signal acquisition was made with the help of a camera CCD (Photometric model 9000) and the software used was LabSpec 3.1. Spectra were obtained taking the average of 8 cycles of 20 s each and the spectral resolution was 1 cm^{-1}. For these measurements, bulk samples were used.

Results and discussion

The experimental FT-IR spectra of the $x\mathrm{Ag_2O} \cdot (100 - x)[\mathrm{B_2O_3} \cdot \mathrm{As_2O_3}]$ glasses, with $0 \leq x \leq 10$ mol% are presented, in Fig. 1. The vibrational assignments of the bands for the glasses spectra were made using the method given by Condrate [15] and Tarte [16], by comparing the experimental data of glasses with those of related crystalline compounds.

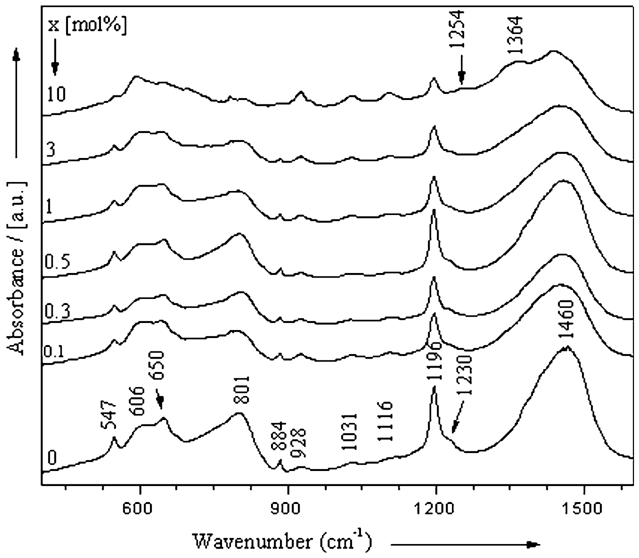

Fig. 1 FT-IR spectra of $x\mathrm{Ag_2O} \cdot (1 - x)[2\mathrm{B_2O_3}–\mathrm{As_2O_3}]$ glasses with $0 \leq x \leq 10$ mol%

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

- 600–800 cm^{-1}—due to B–O–B bending vibrations;
- 800–1,150 cm^{-1}—due to boron in tetrahedral oxygen coordination (BO_4);
- 1,200–1,500 cm^{-1}—due to borate units in which boron atom is coordinated with three oxygen atoms (both bridging and nonbridging types) [17–20].

The glass matrix $2B_2O_3$–As_2O_3 presents the FT-IR bands at: ~547 cm^{1}, ~606 cm^{-1}, ~650 cm^{-1}, ~801 cm^{-1}, ~884 cm^{-1}, ~928 cm^{-1}, ~1031 cm^{-1}, ~1116 cm^{-1}, ~1196 cm^{-1}, 1230 cm^{-1}, and ~1460 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 [21]. With the addition of silver ions, the band from ~547 cm^{-1} decreases in intensity and for $x = 10$ mol% is just a shoulder. The band from ~606 cm^{-1}, due to symmetric bending vibrations of As–O bonds [5], progressively increases in intensity with the addition of silver ions. The band from ~650 cm^{-1} is assigned to O–B–O bonds bending vibrations. With the addition of 0.1 mol% of silver oxide ions, the intensity of the band from ~650 cm^{-1} decreases. For small silver oxide ions concentrations, $0.1 \leq x \leq 0.5$ mol%, the intensity of the band from ~650 cm^{-1} increases, but with the increase of silver oxide concentration, the intensity decreases.

In the second region, there are five FT-IR bands. The band from ~801 cm^{-1} is due to the doubly degenerate stretching vibrations given by As–O bonds [15]; the bands from ~884 cm^{-1} and from ~928 cm^{-1} are due 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 di-borate groups, respectively; the band from ~1031 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 ~1106 cm^{-1} is due to asymmetric stretching vibrations of B–O bonds from BO_4 units. The intensity of the band from ~801 cm^{-1} increases with the increase of Ag_2O concentration till 0.5 mol%, and for higher concentrations the intensity of this band decreases. The intensity of the band from ~884 cm^{-1} progressively decreases with the addition and increase of silver oxide content. The intensities of the bands from ~928 cm^{-1}, ~1031 cm^{-1} and ~1106 cm^{-1} progressively increase with the addition and increase of silver oxide content.

In the third region, glass matrix $2B_2O_3$–As_2O_3 presents only three bands. The first one, from ~1196 cm^{-1}, is due to

Table 1 Wave numbers and band assignments of $x\mathrm{Ag_2O} \cdot (1 - x)[2\mathrm{B_2O_3} \cdot \mathrm{As_2O_3}]$ glasses

Wave number (cm^{-1})		FT-IR assignments	Raman assignments
FT-IR	RAMAN		
	~495		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	
~650	~691	O–B–O bonds bending vibrations	Vibrations of chain and/or ring type meta-and penta-borate groups
~801	~802	Doubly degenerate stretching vibrations of As–O	Symmetric breathing vibrations of boroxol rings
~884 ~1031	~879	B–O bonds stretching vibrations in $\mathrm{BO_4}^-$ units from tri-, tetra-, and penta-borate groups	Vibrations of ortho-borate groups
~928		B–O bonds stretching vibrations in $\mathrm{BO_4}$ units form di-borate groups	
~1116		Asymmetric stretching vibrations of B–O bonds from $\mathrm{BO_4}$ units	
~1196		Asymmetric stretching vibrations of B–Ø and/or B–O$^-$ bonds in borate triangular units ($\mathrm{BO_1}$ and $\mathrm{BO_2O^-}$) from pyro- and ortho-borate groups	
~1230	~1250	Asymmetric stretching vibrations of B–O bonds from ortho-borate groups	Vibrations of pyro-borate groups
~1364		B–O bonds stretching vibrations of $\mathrm{BO_1}$ units from various borate groups	
~1460		B–O bonds stretching vibrations in $\mathrm{BO_1}$ units from various borate groups	

the asymmetric stretching vibrations of B–Ø and/or B–O$^-$ bonds in borate triangular units ($\mathrm{BO_3}$ and $\mathrm{BO_2O^-}$) from pyro- and ortho-borate groups; the second one, from ~1230 cm^{-1}, is due to the asymmetric stretching vibrations of B–O bonds from ortho-borate groups; and the third one, from ~1460 cm^{-1}, is due to B–O bonds stretching vibrations of $\mathrm{BO_3}$ units from various borate groups. The intensity of the bands from ~1196 cm^{-1} and ~1460 cm^{-1} decreases with the addition of silver oxide. The intensity of these bands increases for small $\mathrm{Ag_2O}$ concentrations, $x \leq 0.5$ mol%, and decreases for higher silver oxide ions concentrations. The intensity of the band from ~1230 is slightly decreases with the addition of silver ions and for higher silver ions concentration, $x = 10$ mol%, it is shifted to higher wave numbers. The band from ~1364 cm^{-1}, which appears only for $x = 10$ mol%, is due to B–O bonds stretching vibration of $\mathrm{BO_3}$ units from various borate groups.

The structure proposed for $\mathrm{B_2O_3}$–$\mathrm{As_2O_3}$ glass matrix from FT-IR measurements is formed from tri- ($\mathrm{B_3O_5^-}$), tetra- ($\mathrm{B_8O_{13}^{2-}}$), penta- ($\mathrm{B_5O_8^-}$), di- ($\mathrm{B_4O_7^{2-}}$), pyro- ($\mathrm{B_2O_5^{4-}}$), and ortho ($\mathrm{BO_3^{3-}}$)-borate groups and also from structural units characteristic to $\mathrm{As_2O_3}$. The broadening of some bands with the increase of $\mathrm{Ag_2O}$ content is due to a depolymerization of the structure and an increase of the disorder degree of studied glasses. Considering the changes in intensity of the IR bands, with the increase of silver oxide content, and the fact that the bands broaden also with the increase of silver oxide content, we can conclude that silver oxide acts as a modifier of the network.

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 850–1150 cm^{-1} and 1150–1500 cm^{-1} denoted by A_4 and A_3, respectively [22]. A_4 and A_3 approximate the relative number of $\mathrm{BO_4}$ and $\mathrm{BO_3}$ units, respectively. The relative integrated intensity, $A_r = A_4/A_3$, is plotted in Fig. 2 versus $\mathrm{Ag_2O}$ content. It can be observed that $A_r < 1$, which means that the predominant structural units in the studied glasses are $\mathrm{BO_3}$ units. The proportion of $\mathrm{BO_4}$ rises with the increase of silver ions, reaching the maximum for $x = 10$ mol%. The addition and the increase

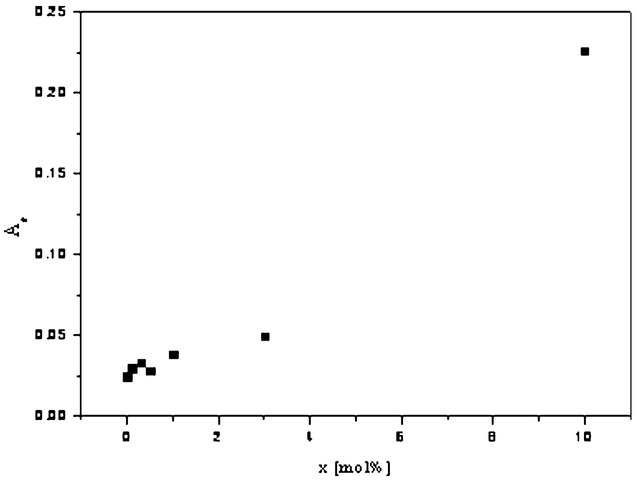

Fig. 2 A_r ratio as a function of $\mathrm{Ag_2O}$ content for $x\mathrm{Ag_2O} \cdot (100 - x)[2\mathrm{B_2O_3}$–$\mathrm{As_2O_3}]$ glasses

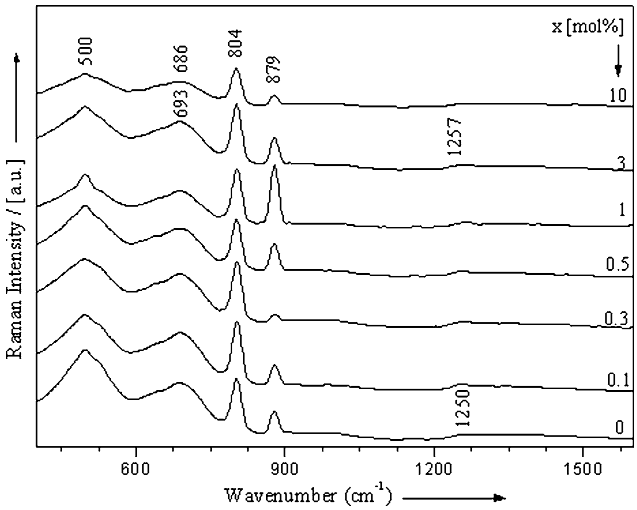

Fig. 3 Raman spectra of xAg$_2$O · (1 − x)[2B$_2$O$_3$–As$_2$O$_3$] glasses with $0 \leq x \leq 10$ mol%

of silver oxide ions cause a break of some linkages (possibly As–O–B or As–O) freeing the oxygen ions, which will attach to tricoordinated boron atoms transforming them into tetracoordinated boron atoms.

The Raman spectra of the studied glasses are presented in Fig. 3 and their structural assignments are summarized in Table 1. Due the fact that Raman bands for the investigated glasses are in the 400–2000 cm^{-1} spectral range, the spectra are presented only in this area. The 2B$_2$O$_3$–As$_2$O$_3$ glass matrix presents seven Raman bands at ~500 cm^{-1}, ~693 cm^{-1}, ~804 cm^{-1}, ~879 cm^{-1}, and ~1250 cm^{-1}. Their vibrational assignments are presented in Table 1.

The band from ~500 cm^{-1} is due to vibrations of isolated di-borate groups and/or to vibrations of As–O bonds. The intensity of this band decreases progressively with the increase of silver ions concentration.

The band from ~693 cm^{-1} is due to vibrations of chain and/or ring type meta- and penta-borate groups. With the addition of silver oxide, the intensity of this band decreases and is shifted to lower wave numbers for $x = 10$ mol%.

As we can observe in the Raman spectrum of these glasses there is an intense band at ~804 cm^{-1} attributed to symmetric breathing vibrations of boroxol rings, a fact that certificates the presence of boroxol rings in glass structure. Small Ag$_2$O concentrations do not affect the intensity of this band, but for higher Ag$_2$O concentrations, the intensity decreases.

The band from ~879 cm^{-1}, given by vibrations of ortho-borate groups, decreases for small Ag$_2$O concentrations, $x \leq 0.3$ mol%, and increases up to $x = 1$ mol%. For higher Ag$_2$O concentrations, the intensity of this band decreases.

The band from ~1250 cm^{-1} is due to vibrations of pyro-borate groups. Its intensity remains the same with the addition and the increase of silver ions content up to $x = 0.3$ mol% and then decreases. With the increase of silver ions, the band is shifted to higher wave numbers; for $x = 3$ mol% the band is centered at ~1257 cm^{-1}.

The structure proposed by Raman spectroscopy for B$_2$O$_3$–As$_2$O$_3$ glass matrix is formed from isolated di-borate groups [23], chain and/or ring type meta- and penta-borate groups [23], boroxol rings [24], ortho-[25] and pyro-borate groups [23], and also from the structural units characteristic to As$_2$O$_3$ [6].

Conclusions

Homogeneous glasses of the xAg$_2$O · (100 − x) [2B$_2$O$_3$ · AsO] system were obtained within $0 \leq x \leq 10$ mol%.

From FT-IR spectra it can be observed that the network structure of the studied glasses consists of randomly connected BO$_3$ and BO$_4$ structural units and also the characteristic structural units of As$_2$O$_3$. The infrared measurements reveal the presence of borate structural units (di-, tri-, tetra-, penta-, pyro-, and ortho-borate) and pyramidal units specific to As$_2$O$_3$. 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 increase of Ag$_2$O content the boron–oxygen network is modified 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 meta-borate 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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