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Structural studies of iron doped $3B_2O_3 \cdot 0.7PbO \cdot 0.3Ag_2O$ glasses by FT-IR and Raman spectroscopies

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Abstract. Glasses from $xFe_2O_3 \cdot (100-x)[3B_2O_3 \cdot 0.7PbO \cdot 0.3Ag_2O]$ system, with $0 \le x \le 20$ mol.%, were prepared and investigated by means of two complementary spectroscopic methods, FT-IR absorption and Raman scattering in order to obtain information concerning the network structure. Both FT-IR and Raman spectroscopic techniques have revealed changes in the local structure of the glasses when the composition is modified. The iron ions modifier role is pointed out by the shape of the recorded spectra, changed with increasing the Fe_2O_3 content. The influence of a gradual addition of the iron oxide on the local structure of silver lead borate based glasses has been studied. The FT-IR data indicate the presence of the BO_3 and BO_4 structural units in the glasses, the network structure being mainly built by: di-, tri-, tetra-, penta- and ortho-borate groups. The characteristic bands of the different structural groups evidenced in these glasses were identified and quantitatively analyzed after increasing the Fe_2O_3 content. The Fe_2O_3 content dependence of A_r (A_4/A_3) ratio (where the values A_4 and A_3 reflect the relative amount of tetra-, respectively tri-coordinated boron atoms) was studied. In addition, characteristic vibrational modes of bonds from iron, lead and silver oxides were detected in the FT-IR spectra. Raman data is in accordance with the FT-IR results and complete them. Using Raman scattering, we detected new structural groups as pyro-, ditri- and dipenta-borate groups, indicating changes in the structure of our glasses after Fe_2O_3 addition.

Keywords: silver-lead-borate glasses, iron ions, FT-IR, Raman spectra, structure.

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1. Introduction

Due to their unlimited theoretical variety of compositions, fact that leads to a very different properties and a large area of applications, glasses have been frequently studied from fundamental and industrial points of view in the last few years [1, 2]. The borate glasses – an important category of glasses, having interesting structural particularity – are known today as important material for insulation (glass wool) and textile (continuous filament) fiberglass [3]. Over the years, many studies about the structure and properties of borate glasses have been reported. The borate glasses are very often investigated because they are relatively easy to obtain, are relative stable glasses, representing good matrices for transitional metal ions and moreover because in their structure appears a large variety of structural units over a wide range of modifiers concentration [1, 4]. The proportions of transitional metal ions that are accepted in glasses structure without forming crystalline microprecipitates depend on the transitional ion nature and concentration [2], matrix composition [5] and melt temperature [6].

Glasses with complex matrices, containing several oxides formers and modifiers of the vitreous matrix, presents specific properties due to the particularity of these oxides. Thus, B_2O_3-PbO glasses have important structural and optical properties, such as thermal stability, IR transparency, high refractive index and also the desired characteristic against irradiation since the naturally occurring stable boron isotope is a good absorber of thermal neutrons and lead is known as a shielding material of γ-ray. The lead oxide (PbO) enhances the resistance against devitrification, improve the chemical durability, lower the melting temperature [7-10] and can act both as a glass network former or modifier, depending on its concentration in the glasses [11, 12]. The high ionic conductivity and numerous applications such as biomaterials with antibacterial and antimicrobial effects, biomaterials for cancer and HIV therapies, chemical sensors, electrochromic display devices and solid batteries [13-16] represent the main points of interest on study of the glasses containing silver oxide.

FT-IR and Raman spectroscopies represent two intensively employed techniques for study the structural details of the vitreous systems due to their sensitivity to the type and concentration of the structural groups from vitreous network [17]. Having different selection rules, these two spectroscopic techniques prove to be very powerful complementary methods in elucidating the glasses structure. A variety of anionic borate species, such as penta-, tri-, tetra-, di-, pyro- and ortho-borate, besides structural entities like boroxol rings have been identified in glasses containing B_2O_3 and PbO [18, 19]. The nature and amount of modifier oxide influenced the concentration of borate species that appear in the glass stucture.

This paper is aimed to present our result concerning the structural details of the $3B_2O_3{\cdot}0.7PbO{\cdot}0.3Ag_2O$ vitreous matrix gradually doped with iron ions by means of FT-IR absorption and Raman scattering.

2. Experimental procedure

The starting materials used in present investigation were H_3BO_3, PbO, Ag_2O and Fe_2O_3 of reagent grade purity. Samples from the $xFe_2O_3{\cdot}(100-x)[3B_2O_3{\cdot}0.7PbO\times$ $\times 0.3Ag_2O]$ system were prepared by weighing suitable proportions of the components, then the mixtures corresponding to the desired compositions were mechanically homogenized and melted in air, in sintered corundum crucibles, in an electric furnace at 1000 ºC. For melting, the samples were put into the preheated electric furnace directly at this temperature to avoid materials losses due to the evaporation. The molten material was kept at this temperature for 15 min and then quenched at room temperature by pouring on the stainless-steel plates.

The structure of samples was analyzed by means of X-ray diffraction using a Bruker D8 ADVANCE X-ray diffractometer with a graphite monochromator for CuK_α radiation ($\lambda = 1.54$ Å). The pattern obtained did not reveal any crystalline phase in the samples up to 20 mol.%.

The FT-IR absorption spectra were recorded with an Equinox 55 Bruker spectrometer, in the range 400-2000 cm^{-1}, 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 sizes. The spectral resolution used for recording the FT-IR spectra is 2 cm^{-1}.

The Raman spectra of the bulk glass system were recorded with a Dilor Raman spectrometer (Horiba-Jobin-Yvon, model LabRam) using the 514.5 nm excitation line from a Spectra Physics argon-ion laser. The spectra were collected in back-scattering geometry with a resolution of 2 cm^{-1}. Detection of the Raman signal was carried out with a CCD camera (Photometric 9000 Model).

All measurements were performed at room temperature.

3. Results and discussion

The experimental FT-IR spectra of $xFe_2O_3{\cdot}(100-x)$ $[3B_2O_3{\cdot}0.7PbO{\cdot}0.3Ag_2O]$ glass system with various content of iron oxide ($0 \le x \le 20$ mol.%) are presented in Fig. 1. The absorption bands detected in the FT-IR spectra and their assignments are summarized in Table. These data have been discussed on the basis of the method given by Tarte [20, 21] and Condrate [22, 23] by comparing the experimental data of glasses with those of related crystalline compounds. The characteristic absorption bands for vitreous B_2O_3 [2], PbO [2, 8, 24] and crystalline Ag_2O [25] and Fe_2O_3 [26, 27] were used as a reference point in the results discussion. In the case of borate glasses, the wavenumber ranges 400-780, 780-1150 and 1150-1600 cm^{-1} represent the characteristic absorbtion of B-O bonds in various borate segments, respectively in BO_4 and BO_3 structural units [2, 24, 28, 29]. Characteristic vibrational modes of the iron and lead bonds with the oxygen were indirectly detected in the FT-IR spectra, while any specific contribution from silver wasn't evidenced.

The FT-IR absorption bands obtained for the studied glass matrix are centered at approximately 470, 670, 680, 762, 910, 1045, 1225, 1350, 1460, and 1630 cm^{-1}. For the studied glasses, these experimental data indicate a structure built by: di- ($B_4O_7^{2-}$), tri- ($B_3O_5^-$), tetra- ($B_8O_{13}^{2-}$), penta- ($B_5O_8^-$) and ortho- (BO_3^{3-}) borate groups (O^- representing non-bridging oxygen atom) [2, 24, 25, 28, 29].

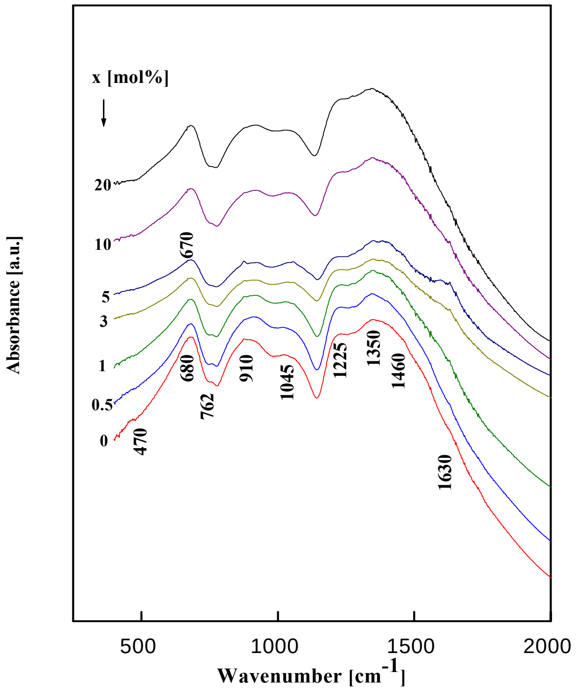

Fig. 1. FT-IR spectra of $xFe_2O_3{\cdot}(100-x)[3B_2O_3{\cdot}0.7PbO{\cdot}0.3Ag_2O]$ glasses.

The band at ~470 cm^{-1} is assigned to O-B-O bond bending vibrations [2], has a small intensity and is little influenced by the Fe_2O_3 addition. For compositions with $x > 0$, at this band may also contribute the Fe-O bonds stretching vibrations in FeO_6 units [26, 27] and covalent Pb-O bonds [8, 24]. At ~670 cm^{-1}, in the FT-IR spectra appear the small shoulder attributed to the O-B-O bond bending vibrations [2]. The absorption band centered at ~680 cm^{-1} dominate the 400-760 cm^{-1} spectral domain, being assigned to B-O-B bond bending vibrations from pentaborate groups [2,17] and also to specific vibrations of Fe-O bonds in FeO_4 units [26, 27]. The intensity of this band has a complex evolution with Fe_2O_3 addition: decrease for samples with $0 \le x \le 5$ mol.%, then increase after that composition. This evolution confirm the presence of the FeO_4 units in the structure of studied glasses and indicate a relativelly increasing of their number at increasing of the iron oxide content.

Table. The assignments for FT-IR and Raman bands of $xFe_2O_3 \cdot (100 - x)[3B_2O_3 \cdot 0.7PbO \cdot 0.3Ag_2O]$ glasses.

Wavenumber [cm^{-1}]		IR assignments	Raman assignments
IR	Raman		
~ 470	~ 465	O-B-O bond bending vibrations, covalent Pb-O bond vibrations, Fe-O bonds stretching vibrations in FeO_6 units	isolated diborate groups, Pb-O bond vibrations
~ 670		O-B-O bond bending vibrations	
~ 680	~ 700	B-O-B bonds bending vibrations from pentaborate groups. Specific vibrations of Fe-O bonds in FeO_4 units	Symmetric breathing vibrations of metaborate rings
~ 762	~ 770	O_3B-O-BO_4 bonds bending vibrations	Symmetric breathing vibrations of six member rings with one or two BØ$_3$ triangle replaced by BØ$_4^-$ tetrahedral units
	~ 800		symmetric breathing vibrations of boroxol rings
~ 910		B-O bonds stretching vibrations in BO_4 units from diborate groups	
~ 1045	~ 1040	B-Ø bonds stretching vibrations of BØ$_4^-$ tetrahedra from tri-, tetra- and penta-borate groups	diborate groups
~ 1225		asymmetric stretching vibrations of B-O bonds from pyro- and ortho-borate groups	
~ 1350	~ 1340	asymmetric stretching modes of borate triangles BØ$_3$ and BØ$_2$Ø$^-$	BØ$_2$Ø$^-$triangles linked to BØ$_4^-$ units
~ 1460		B-O$^-$ bonds stretching vibrations in BO_3 units	
~ 1630		H-O-H bond bending vibrations	

Ø – represent oxygen atom bridging two boron atoms,
O$^-$ – represent non-bridging oxygen atom.

The band situated at ~762 cm^{-1} is ascribed to the O_3B-O-BO_4 bonds bending vibrations [2, 17, 24] and has approximately the same small amplitude for all the compositional range. The absorption bands at ~910 and ~1045 cm^{-1}, assigned to the B-O stretching vibrations in BO_4 units from diborate groups [2, 24], respectively to B-O stretching vibrations of BO_4 units in tri-, tetra- and penta-borate groups [2, 17] presents the similar evolution of their intensity with the Fe_2O_3 content. The intensity of these bands increases up to $x = 0.5$ mol.%, than decrease and remain the same with increasing the Fe_2O_3 concentration. Absorption at ~1225 cm^{-1} can be attributed to the B-O asymmetric stretching vibrations of BO_3 units in pyro- and ortho-borate groups [28]. The intensity of this band is maximum for the samples with $x = 0.5$ mol.% and decrease a little for higher concentrations of iron ions. The absorption band at ~1350 cm^{-1} is ascribed to the asymmetric stretching modes of borate triangles BØ$_3$ and BØ$_2$Ø$^-$ [2, 24]. A small increase was detected up to $x = 0.5$ mol.% of this band intensity when growing the Fe_2O_3 content. The shoulder at ~1460 cm^{-1}, assigned to B-O$^-$ stretching vibrations of BO_3 units in varied borate rings [29], present the small and relatively the same intensity for all the compositional range. The appearance of the shoulder at ~1630 cm^{-1}, characteristic to the H-O-H bond bending vibrations, is due to the hygroscopicity of the studied glasses.

The structural changes involved by the Fe_2O_3 content addition have been analyzed on the basis of $A_r = A_4/A_3$ ratio (A_4 and A_3 were calculated as the integral of the absorption signal in the 800-1135 cm^{-1} (A_4) and 1150-1550 cm^{-1} (A_3) spectral ranges) [28]. The quantities A_4 and A_3 reflect the relative content of tetrahedral (BØ$_4^-$), respectively triangular (BØ$_3$ and BØ$_2$Ø$^-$) borate species. Shown in Fig. 2 is evolution of the A_r ratio with Fe_2O_3 content.

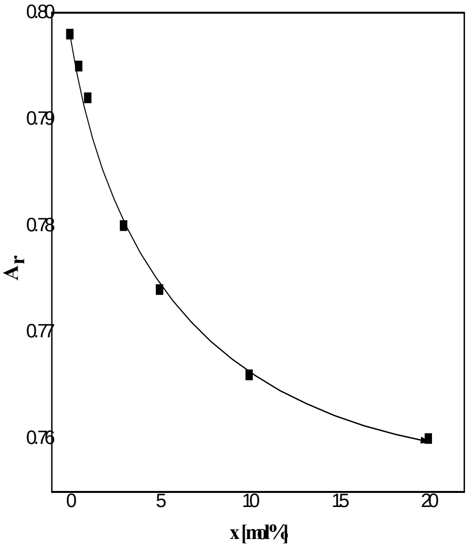

Fig. 2. A_r ratio evolution with x values for $xFe_2O_3 \cdot (100 - x) \times [3B_2O_3 \cdot 0.7PbO \cdot 0.3Ag_2O]$ glasses.

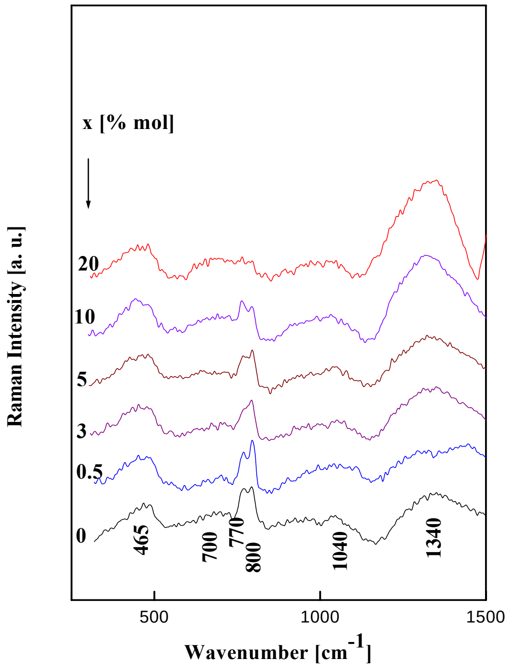

Fig. 3. Raman spectra of $xFe_2O_3·(100 – x)$ $[3B_2O_3·0.7PbO·0.3Ag_2O]$ glasses.

First of all, it is observed that the A_r values are lower than unity for all the investigated samples, which shows the predominance of BO_3 units in the structure of studied glasses. The tendency of the boron atoms from passing in structural positions which favourized occuring the BO_3 structural units is reflected by decreasing of the A_r value (decrease of the number of $BØ_4^-$ units relative to the number of $BØ_3$ and $BØ_2Ø^-$ units) within the entire compositional ranges. In the borate glasses, this aspect can be explained by the isomerization process between the 3- and 4- coordinated boron species: $BØ_2Ø^- \leftrightarrow BØ_4^-$.

The shape of the FT-IR spectra suggest that the controled addition of Fe_2O_3 (as vitreous network modifier) generates some rearrangements in the network structure at the short-range order.

The recorded Raman spectra for the $xFe_2O_3·(100 – x)[3B_2O_3·0.7PbO·0.3Ag_2O]$ glasses are presented in Fig. 3. In vitreous glass matrix ($x = 0$) well defined Raman bands were detected at ~770, ~800, ~1040, and ~1340 cm^{-1}, and a wide envelopes appear around ~465 and ~700 cm^{-1}. As it can be seen for the Raman band assignments (Table), the obtained data confirm the structure proposed by the FT-IR results, their evolution with the iron oxide addition and, moreover, presence of boroxol rings $[B_3O_{4.5}]$, pyro- $[B_2O_5^{4-}]$, ditri- $[B_3O_8]$ and dipenta-borate $[B_5O_{11}]$ groups [3, 8, 24].

The presence of envelope centered at ~ 465 cm^{-1} is assigned to the isolated diborate groups and also Pb-O link vibrations [2, 8, 24]. With increasing the Fe_2O_3 content, we observed the increase in the intensity of this band. As to the band ~700 cm^{-1}, characteristic to symmetric breathing vibrations of metaborate rings [28], no notable evolution in its intensity was detected when the Fe_2O_3 content was increased.

In most borate glasses, at ~806 cm^{-1} detected was the Raman band characteristic of the breathing motions of the oxygen atoms inside the boroxol ring [1, 2, 4, 17, 19]. In the case of this band, in our glasses the shift to the lower wavenumber (~800 cm^{-1}) was observed. This shift can be explained by the presence/influence of the silver ions in vitreous matrix (silver ions imposed some changes in the average bond characteristics of the boroxol ring), since in B_2O_3-PbO glasses this tendency was not evidenced [8, 30].

The presence in Raman spectra of bands from ~770 and ~800 cm^{-1} in the entire studied compositional range and also their different intensities showed that the number of boroxol rings is higher than that of ditri- or dipenta-borate groups. A decrease in the intensity for these bands with increasing the Fe_2O_3 content indicates the decrease of these structural groups concentration in the glass structure. The growth of the band ~1040 cm^{-1} intensity with increasing the Fe_2O_3 content showed the increase in the concentration of diborate groups in the glass structure. The progressive addition of iron ions implies the increase of the Raman intensity for the band located at ~1340 cm^{-1}, characteristic to BO_3 units being in different environments. Therefore, the Raman data evidenced the influence of Fe_2O_3 on the structure of studied glasses.

4. Conclusions

Homogeneous glasses of the $xFe_2O_3·(100 – x)\times$ $\times [3B_2O_3·0.7PbO·0.3Ag_2O]$ system were obtained within $0 \le x \le 20$ mol.%. FT-IR and Raman spectroscopies have been used in order to analyze the local structural peculiarities of our vitreous samples, to identify the contributions of each component on the structure and to point out the role of the iron ions as a modifier on the glass network.

The infrared data revealed the presence of boron atoms in both, three- and four-coordinate states, for all the investigated glasses. Over the entire compositional range, the number of four-coordinated boron atoms is lower than that of three-coordinated ones. The value of the N_{BO4} / N_{BO3} ratio (A_4/A_3) decrease in the entire compositional range.

In agreement with the results obtained using FT-IR data, the Raman data confirm the structure proposed on the basis of FT-IR spectroscopy and moreover, detect new structural groups (boroxol rings, pyro-, ditri- and dipenta-borate).

Both spectroscopic methods revealed the iron ions modifiers role, the recorded spectra changing continuously at these additions.

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