

FT-IR AND RAMAN SPECTROSCOPIC STUDIES OF IRON DOPED $3\text{B}_2\text{O}_3 \cdot 0.9\text{PbO} \cdot 0.1\text{Ag}_2\text{O}$ GLASSES

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Abstract

Glasses from $x\text{Fe}_2\text{O}_3 \cdot (100-x)[3\text{B}_2\text{O}_3 \cdot 0.9\text{PbO} \cdot 0.1\text{Ag}_2\text{O}]$ system, with $0 \leq x \leq 20$ mol%, were prepared and investigated by means of two complementary spectroscopic methods, FT-IR absorption and Raman scattering, in order to obtain information concerning network structure. The iron ions modifier role is pointed out by the shape of the recorded spectra, changed at increasing of 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 in the glasses of the BO_3 and BO_4 structural units, the network structure being mainly build 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 by the increasing of 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 possible bonds for iron and lead with the oxygen were detected in the FT-IR spectra. Raman data is in agreeing with the FT-IR results and complete them. By Raman scattering was detecting new structural groups as pyro-, ditri- and dipenta-borate groups, indicating structural changes in the structure of our glasses at the Fe_2O_3 addition.

Keywords: *Silver-lead-borate glasses, iron ions, FT-IR, Raman, structure.*

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 point of view in the last few

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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 metals ions that are accepted in glasses structure without forming crystalline microprecipitates depend on transitional ions 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 mains 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, thanks to their sensitivity at type and concentration of the structural groups from vitreous network [17]. Having different selection rules, these two spectroscopic techniques it proves 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 the amount of modifier oxide influenced the concentration of borate species which appear in the glass structure.

This paper aims to present our result concerning the structural details of the $3B_2O_3 \cdot 0.9PbO \cdot 0.1Ag_2O$ 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 $x\text{Fe}_2\text{O}_3 \cdot (100-x)[3\text{B}_2\text{O}_3 \cdot 0.9\text{PbO} \cdot 0.1\text{Ag}_2\text{O}]$ 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°C . 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 minutes 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 ($\lambda = 1.54 \text{ \AA}$). 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 $400\text{-}2000 \text{ cm}^{-1}$, 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 size. The spectral resolution used for the recording of 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 $x\text{Fe}_2\text{O}_3 \cdot (100-x)[3\text{B}_2\text{O}_3 \cdot 0.9\text{PbO} \cdot 0.1\text{Ag}_2\text{O}]$ glass system with various content of iron oxide ($0 \leq x \leq 20 \text{ mol\%}$) are presented in figure 1. The absorption bands detected in the FT-IR spectra and their assignments are summarized in table I. 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 $400\text{-}780 \text{ cm}^{-1}$, $780\text{-}1150 \text{ cm}^{-1}$ and $1150\text{-}1600 \text{ cm}^{-1}$ represent the characteristic wavenumber ranges absorption 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 bonds of iron and lead with the oxygen were indirect detected in the FT-IR spectra, while specific contribution from silver wasn't evidenced.

The FT-IR absorption bands obtained for studied glass matrix are centered at $\sim 470\text{ cm}^{-1}$, $\sim 670\text{ cm}^{-1}$, $\sim 680\text{ cm}^{-1}$, $\sim 760\text{ cm}^{-1}$, $\sim 915\text{ cm}^{-1}$, $\sim 1040\text{ cm}^{-1}$, $\sim 1222\text{ cm}^{-1}$, $\sim 1345\text{ cm}^{-1}$, $\sim 1460\text{ cm}^{-1}$ and $\sim 1630\text{ cm}^{-1}$. These experimental data indicate for the studied glasses a structure built by: di- ($\text{B}_4\text{O}_7^{2-}$), tri- (B_3O_5^-), tetra- ($\text{B}_8\text{O}_{13}^{2-}$),

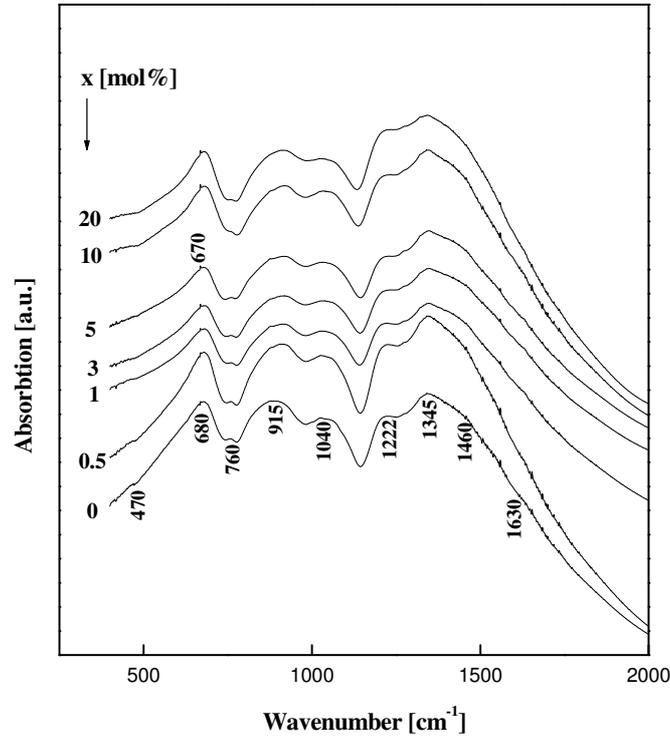


Fig. 1. FT-IR spectra of $x\text{Fe}_2\text{O}_3 \cdot (100-x)[3\text{B}_2\text{O}_3 \cdot 0.9\text{PbO} \cdot 0.1\text{Ag}_2\text{O}]$ glasses

penta- (B_5O_8^-) and ortho- (BO_3^{3-}) borate groups (O^- representing non-bridging oxygen atom) [2, 24, 25, 28, 29].

The band at $\sim 470\text{ cm}^{-1}$ 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 $\sim 670\text{ cm}^{-1}$, in the FT-IR spectra appear the small shoulder attributed to the O-B-O bond bending vibrations [2]. The absorption band centered at $\sim 680\text{ cm}^{-1}$ 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: attains a maximum for samples with $x = 0.5$ mol%, then little decreases after that composition and again easy increase for $x \geq 10$ mol%. This evolution confirm the presence of the FeO_4 units in the structure of studied glasses and indicate a relatively increasing of their number at increasing of the iron oxide content.

Table I. The assignments for FT-IR and Raman bands of $x\text{Fe}_2\text{O}_3 \cdot (100-x)[3\text{B}_2\text{O}_3 \cdot 0.9\text{PbO} \cdot 0.1\text{Ag}_2\text{O}]$ glasses

Wavenumber [cm^{-1}]		IR assignments	Raman assignments
IR	Raman		
~ 470	~ 455	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	~ 680	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
~ 760	~ 765	$\text{O}_3\text{B-O-BO}_4$ bonds bending vibrations	Symmetric breathing vibrations of six member rings with one or two BO_3 triangle replaced by BO_4^- tetrahedral units
	~ 800		symmetric breathing vibrations of boroxol rings
~ 915	~	B-O bonds stretching vibrations in BO_4 units from diborate groups	

~ 1040	~ 1080	B-Ø bonds stretching vibrations of $BØ_4^-$ tetrahedra from tri-, tetra- and penta-borate groups	diborate groups
~ 1222		asymmetric stretching vibrations of B-O bonds from pyro- and ortho-borate groups	
~ 1345	~ 1340	asymmetric stretching modes of borate triangles $BØ_3$ and $BØ_2Ø^-$	$BØ_2Ø^-$ 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 $\sim 760\text{ cm}^{-1}$ 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 $\sim 915\text{ cm}^{-1}$ and $\sim 1042\text{ cm}^{-1}$, 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 $x = 0.5\text{ mol}\%$, then decrease and remain the same at increasing of Fe_2O_3 concentration. Absorption at $\sim 1222\text{ cm}^{-1}$ 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 $x = 0.5\text{ mol}\%$ and decrease a little for higher concentration of iron ions. The absorption band at $\sim 1345\text{ cm}^{-1}$ is ascribed to the asymmetric stretching modes of borate triangles $BØ_3$ and $BØ_2Ø^-$ [2, 24]. Was detected a small increasing up to $x = 0.5\text{ mol}\%$ of the intensity of this band at addition of Fe_2O_3 content. The shoulder at $\sim 1460\text{ cm}^{-1}$, 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 $\sim 1630\text{ cm}^{-1}$, 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 $800-1135\text{ cm}^{-1}$ (A_4) and $1150-1550\text{ cm}^{-1}$ (A_3) spectral ranges) [28]. The quantities A_4 and A_3 reflect the relative content of

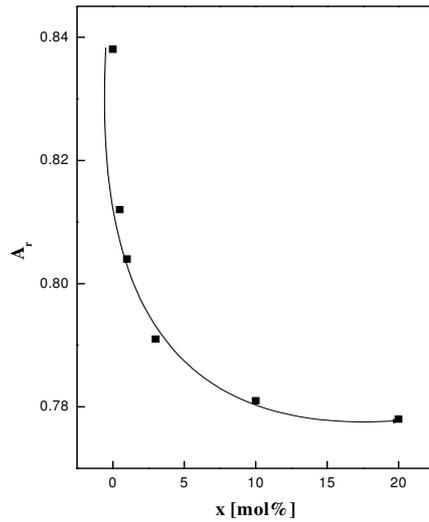


Fig.2. A_r ratio evolution with the x values for $x\text{Fe}_2\text{O}_3 \cdot (100-x)[3\text{B}_2\text{O}_3 \cdot 0.9\text{PbO} \cdot 0.1\text{Ag}_2\text{O}]$ glasses

tetrahedral (BO_4^-), respectively triangular (BO_3 and $\text{B}\text{O}_2\text{O}^-$) borate species. In figure 2 is shown the evolution of the A_r ratio with Fe_2O_3 content.

First of all, it is observed that the A_r values are lower than 1 for all the investigated samples, showing the predominance of BO_3 units in the structure of studied glasses. The tendency of the boron atoms from passing in structural positions which favored occurring the BO_3 structural units is reflected by decreasing of the A_r value (decrease of the number of BO_4^- units relative to the number of BO_3 and $\text{B}\text{O}_2\text{O}^-$ units) in 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: $\text{B}\text{O}_2\text{O}^- \leftrightarrow \text{B}\text{O}_4^-$.

The shape of the FT-IR spectra suggest that the controlled 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 $x\text{Fe}_2\text{O}_3 \cdot (100-x)[3\text{B}_2\text{O}_3 \cdot 0.9\text{PbO} \cdot 0.1\text{Ag}_2\text{O}]$ glasses are presented in figure 3. In vitreous glass matrix ($x = 0$) well defined Raman bands were detected at $\sim 765 \text{ cm}^{-1}$, $\sim 800 \text{ cm}^{-1}$, $\sim 1080 \text{ cm}^{-1}$ and $\sim 1340 \text{ cm}^{-1}$ and a wide envelopes appears around $\sim 455 \text{ cm}^{-1}$ and $\sim 680 \text{ cm}^{-1}$. As it can be seen for the Raman band assignments (Table I), the obtained data confirm structure proposed by the FT-IR results, their evolution with the iron oxide addition and moreover were detected boroxol rings [$\text{B}_3\text{O}_{4.5}$], pyro- [$\text{B}_2\text{O}_5^{4-}$], diti- [B_3O_8] and dipenta-borate [B_5O_{11}] groups [3, 8, 24].

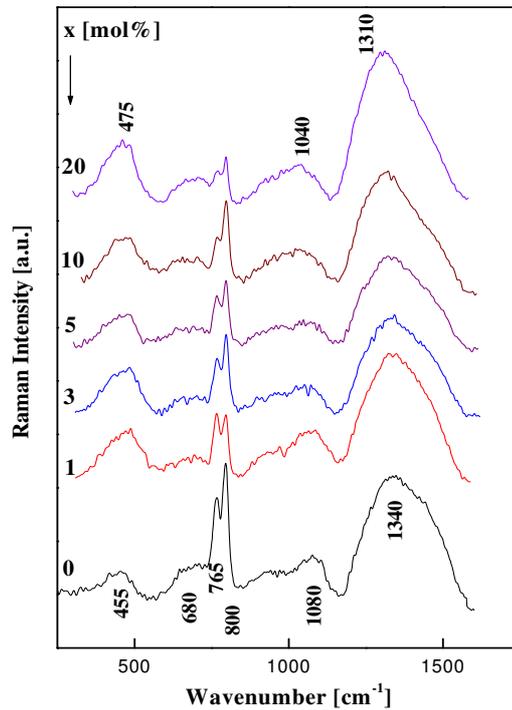


Fig.3. Raman spectra of $x\text{Fe}_2\text{O}_3 \cdot (100-x)[3\text{B}_2\text{O}_3 \cdot 0.9\text{PbO} \cdot 0.1\text{Ag}_2\text{O}]$ glasses

The presence of envelope centered at $\sim 455 \text{ cm}^{-1}$ is assigned to the isolated diborate groups and also Pb-O link vibration [2, 8, 24]. At increasing of the Fe_2O_3 content, was evidenced the shift to higher wavenumber ($\sim 475 \text{ cm}^{-1}$) and also an increasing to the intensity of this band. For band from $\sim 680 \text{ cm}^{-1}$, characteristic to symmetric breathing vibrations of metaborate rings [28], no notable evolution in the intensity was detected when the Fe_2O_3 content increased.

In most borate glasses, at $\sim 806 \text{ cm}^{-1}$ was detecting 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 was observed the shift to lower wavenumber ($\sim 800 \text{ cm}^{-1}$). 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 boroxol ring), since in $\text{B}_2\text{O}_3\text{-PbO}$ glasses this tendency was not evidenced [8, 30].

The presence in Raman spectra of bands from $\sim 765\text{ cm}^{-1}$ and $\sim 800\text{ cm}^{-1}$ in the entire studied compositional range and also their different intensities shown that the number of boroxol rings is higher than number of ditri- or dipenta-borate groups. Decreasing of intensity for these bands at increasing of the Fe_2O_3 content indicate an decreasing of these structural groups concentration in the glasses structure. Increasing of intensity band from $\sim 1080\text{ cm}^{-1}$ at increasing of the Fe_2O_3 content, in the same time with the shift to lower wavenumber ($\sim 1040\text{ cm}^{-1}$), shown an increasing of diborate groups concentration in the glasses structure. The progressive addition of iron ions implies an increasing of the Raman band intensity situated at $\sim 1340\text{ cm}^{-1}$, characteristic to BO_3 units located in different environments. Therefore, the Raman data evidenced the influence of the Fe_2O_3 on the structure of studied glasses.

4. Conclusions

Homogeneous glasses of the $x\text{Fe}_2\text{O}_3 \cdot (100-x)[3\text{B}_2\text{O}_3 \cdot 0.9\text{PbO} \cdot 0.1\text{Ag}_2\text{O}]$ system were obtained within $0 \leq x \leq 20\text{ mol}\%$. 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 coordination states, for all 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 $N_{\text{BO}_4}/N_{\text{BO}_3}$ ratio (A_4/A_3) decrease in the entire compositional range.

In agreement with the results gave by the 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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