JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 2, February 2008, p. 246 - 250

FT-IR and Raman spectroscopic studies on $MnO-B_2O_3-PbO-Ag_2O$ glasses

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Glasses from $xMnO\cdot(100-x)[3B_2O_3\cdot0.7PbO\cdot0.3Ag_2O]$ 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. Both, FT-IR and Raman spectroscopic techniques have revealed changes in the local structure of the glasses when the composition modifies. The manganese ions modifier role is pointed out by the shape of the recorded spectra, changed at increasing of MnO content. 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 MnO content. The MnO content dependence of N_{BO4}/N_{BO3} ratio was studied. Raman data correlate well with the FT-IR results and complete them. By Raman scatering was detecting new structural groups as pyro-, ditri- and dipenta-borate, indicating structural changes in the short-range order of our glasses at the MnO addition.

(Received September 25; 2007; accepted February 7, 2008)

Keywords: FT-IR, Raman, Manganese ions, Local structure

1. Introduction

In the last few years, glasses have been frequently studied from fundamental and industrial point of view due to their large area of aplications, and wide variety of properties [1,2]. Today, the borate glasses - an important category of glasses, having interesting structural particularity - are known as important material for insulation (glass wool) and textile (continuous filament) fiberglass [3]. Lead borate oxide glasses are highly transparent in the visible and near-infrared regions and exhibit very good glass formation over a large compositional region [4]. Moreover, these glasses have the desired characteristic against irradiation since the naturally occurring stable boron isotope is a good absorber of thermal neutrons [5] and lead is known as a shielding material for γ-ray [6]. Lead oxide (PbO) can act both as a glass network former or modifier, depending on its concentration in the glasses [7,8]. Also, it is known that the lead oxide are influenced on the glass structure and is widely used in glasses because it enhances the resistance against devitrification, improves the chemical durability and lowers the melting temperature [9-13].

The borate glasses are very often investigated by a lot of methods because they are relatively easy to obtain, are relative stabile 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 modifier concentration [14,15]. 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 [16]. Raman studies on some ternary lead borate glasses indicate that PbO may be incorporated into the network in four-coordinated positions since the boron atoms in these glasses are both three (BO_3) and four coordinated (BO_4) [10,17-19]. 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 [20,21]. The nature and the amount of modifier oxide influenced the concentration of borate species which appear in the glass stucture.

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 [22-25] represent the mains points of interest on study of the glasses containing silver oxide.

This paper aims to present our result concerning the structural details of the $3B_2O_3\cdot0.7PbO\cdot0.3Ag_2O$ vitreous matrix gradually doped with manganese ions by means of FT-IR absorption and Raman scattering. Having different selection rules, these two spectroscopic techniques it proves to be very powerful complementary methods in elucidating the glasses structure. The research is part of a study focused on analyis of the local structural peculiarities and properties of the $3B_2O_3\cdot(1-y)PbO\cdot yAg_2O$ type vitreous matrix, doped with various amounts of MnO.

2. Experimental procedure

The starting materials used in present investigation were H_3BO_3, PbO, $AgNO_3$ and $MnCO_3$ of reagent grade purity. Samples from the xMnO·(100-x)[$3B_2O_3$·0.7PbO·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 950ºC. For melting, the samples were put into the electric furnace directly at this temperature. 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 (λ = 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, at room temperature, in the range 400-2000 cm^{-1}, using the KBr pellet technique. The Raman spectra of the bulk glass system were recorded with a Horiba-Jobin-Yvon Dilor Labram spectrometer 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).

3. Results and discussion

The experimental FT-IR spectra of xMnO·(100-x)[$3B_2O_3$·0.7PbO·0.3Ag_2O] glass system with various content of manganese oxide (0 ≤ x ≤ 20 mol%) are presented in Fig. 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 [26,27] and Condrate [28,29] by comparing the experimental data of glasses with those of related crystalline compounds. The characteristic absorption bands for vitreous B_2O_3 [2], PbO [2,10,30] and crystalline Ag_2O and MnO [31] were used as a reference point in the results discussion. In the case of borate glasses, the 400-780 cm^{-1}, 780-1150 cm^{-1} and 1150-1600 cm^{-1} represent the characteristic wavenumber ranges for B-O bonds, respectively structural units BO_4 and BO_3 [2,30,32,33].

Our experimental data indicate for the MnO-B_2O_3-PbO-Ag_2O glasses a structure built by: di- ($B_4O_7^{2-}$), tri- ($B_3O_5^{-}$), tetra- ($B_8O_{13}^{2-}$), penta- ($B_5O_8^{-}$) and ortho-borate (BO_3^{3-}) groups (O^- representing non-bridging oxygen atom) [2,30-33]. Characteristic vibrational modes of bonds from MnO, PbO and Ag_2O oxides were detected in the FT-IR spectra, being specified in Table 1.

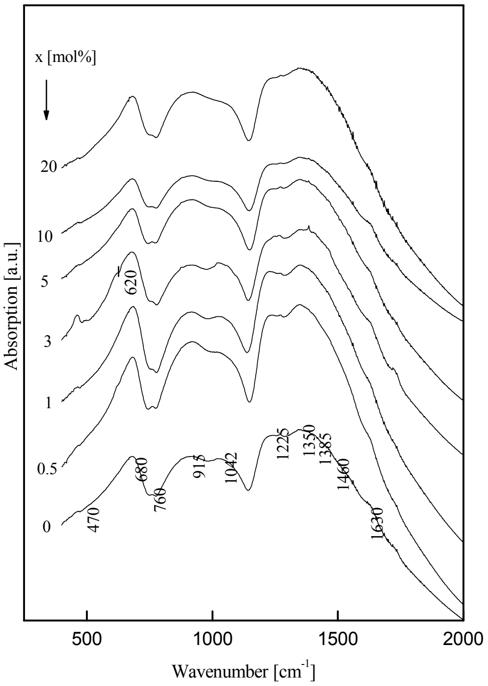

Fig. 1. FT-IR spectra of xMnO·(100-x)[$3B_2O_3$·0.7PbO·0.3Ag_2O] glasses.

The FT-IR absorption bands obtained for studied glass matrix are centered at ~470 cm^{-1}, ~680 cm^{-1}, ~760 cm^{-1}, ~915 cm^{-1}, ~1042 cm^{-1}, ~1225 cm^{-1}, ~1350 cm^{-1}, ~1385 cm^{-1}, ~1460 cm^{-1} and ~1630 cm^{-1}. 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 MnO addition. For x > 0, at this band may also contribute specific vibrations of Mn-O bond [31] and covalent Pb-O bonds [10,30]. For glasses with compositions x > 0 mol%, in the FT-IR spectra appear the shoulder located at ~620 cm^{-1} and attributed to the O-B-O bond bending vibrations [2]. On this shoulder also the contributions of the specific vibrations of Mn-O and Ag-O bonds [31] can be superposed. 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 [2,16]. The intensity of this band attains a maximum for samples with x = 1 mol% and decreases after that composition. The band situated at ~760 cm^{-1} is ascribed to O_3B-O-BO_3 bonds bending vibrations [2,16,30] and has approximately the same small amplitude for all the compositional range.

Table 1. The assignments for FT-IR and Raman bands of xMnO·(100-x)[3B$_2$O$_3$·0.7PbO·0.3Ag$_2$O] glasses.

Wavanumber [cm^{-1}]		**IR assignments**	**Raman assignments**
IR	**Raman**		
~ 470	~ 440	O-B-O bond bending vibrations, covalent Pb-O bond vibrations, Mn-O bond vibrations	isolated diborate groups, Pb-O bond vibrations
~ 620		O-B-O bond bending vibrations, Mn-O bond vibrations, Ag-O bond vibrations	
~ 680		B-O-B bonds bending vibrations from pentaborate groups	
~ 760	~ 765	O_3B-O-BO_3 bonds bending vibrations	Symmetric breathing vibrations of six member rings with one or two BØ$_3$ triangle replaced by BØ$_4^-$ tetrahedral
	~ 796		symmetric breathing vibrations of boroxol rings
~ 915		B-O bonds stretching vibrations in BO$_4$ units from diborate groups	
~ 1042		B-Ø bonds stretching vibrations of BØ$_4^-$ tetrahedra from tri-, tetra- and penta-borate groups	
	~ 1130		diborate groups
~ 1225	~ 1280	asymetric stretching vibrations of B-O bonds from pyro- and ortho-borate groups	pyroborate units
~ 1350	~ 1350	asymetric stretching modes of borate triangles BØ$_3$ and BØ$_2$Ø$^-$	BØ$_2$Ø$^-$ triangles linked to BØ$_4^-$ units
~ 1385 ~ 1460	~ 1470	B-O$^-$ bonds stretching vibrations in BO$_3$ units	BØ$_2$Ø$^-$ triangles linked to other borate triangular units
~ 1630	~ 1630	H-O-H bond bending vibrations	

Ø - represent oxygen atom bridging two boron atoms

At the ~ 915 cm^{-1} the FT-IR spectra present a relatively strong absorption band assigned to the B-O stretching vibrations in BO$_4$ units from diborate groups [2,30]. The intensity of this band increase up to x = 0.5 mol%, than decrease and remain the same at increasing of MnO content. The band at ~1042 cm^{-1}, which also increase up to x = 0.5 mol%, than decrease and remain the same as intensity in studied concentration range, is ascribed to the B-O stretching vibrations of BO$_4$ units in tri-, tetra- and penta-borate groups [2,16]. Absorption at ~1225 cm^{-1} can be attributed to the B-O asymetric stretching vibrations of BO$_3$ units in pyro- and ortho-borate groups [32]. The intensity of this band is maximum for the samples with x = 1 mol% and decrease a little for higher concentration of manganese ions. The absorption band at ~1350 cm^{-1} is ascribed to the asymetric stretching modes of borate triangles BØ$_3$ and BØ$_2$Ø$^-$ [2,30]. It was detected a small increasing up to x = 0.5 mol% of the intensity of this band at addition of MnO content. The shoulders at ~1385 cm^{-1} and ~1460 cm^{-1} has assigned to B-O$^-$ stretching vibrations of BO$_3$ units in varied borate rings [34]. Their intensity is small and relatively the same for all the compositional range.

The effect of increasing the manganese ions content on the structure glasses have been analyzed by the $A_r = A_4/A_3$ ratio (A_4 and A_3 were calculated as the integral of the absorption signal in the 770-1140 cm^{-1} (A_4) and 1140-1550 cm^{-1} (A_3) spectral ranges) [32]. 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. In Fig. 2 is shown the evolution of the A_r ratio with MnO content (the dotted line are just a guide for the eyes).

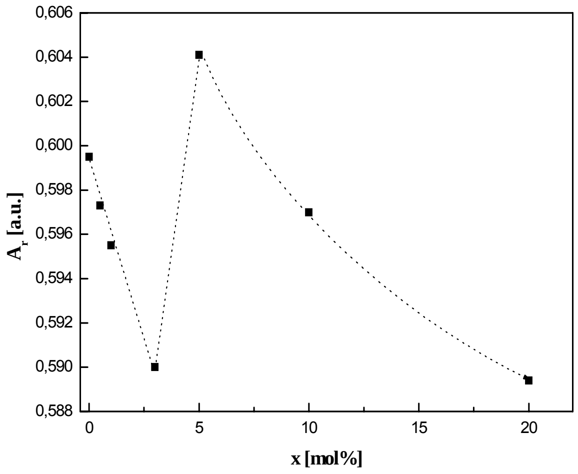

Fig. 2. A_r ratio evolution with the x values for xMnO·(100-x)[3B_2O_3·0.7PbO·0.3Ag_2O] glasses.

For all the investigated samples, the A_r values are lower than 1, showing the predominance of BO_3 units in the structure of studied glasses. The A_r ratio evolution with the MnO content denotes a relatively equilibrium between number of BO_4 and BO_3 units, values of the A_r being distributed in a restricted range (0.589-0.604). 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 in the 0-3 mol% and 5-20 mol% compositional ranges (fact that reveal an decrease of the fraction of $BØ_4^-$ units relative to the $BØ_3$ and $BØ_2Ø^-$ units). In the borate glasses, this aspect can be explayned by the isomerization process between the 3- and 4- coordinated boron species: $BØ_2Ø^- \leftrightarrow BØ_4^-$. When the glass composition is changed from 3 to 5 mol% MnO, an increase of the A_r value was detected. For the samples with x = 5 mol%, the A_r value attends its maximum.

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

The recorded Raman spectra for the xMnO·(100-x)[3B_2O_3·0.7PbO·0.3Ag_2O] glasses are presented in figure 3. In vitreoux glass matrix well defined Raman bands were detected at ~765 cm^{-1}, ~796 cm^{-1}, ~1130 cm^{-1}, ~1280 cm^{-1}, ~1350 cm^{-1}, ~1470 cm^{-1} and ~1630 cm^{-1}; also, a relatively wide envelope appears around ~440 cm^{-1}. The characteristic Raman bands at ~765 cm^{-1} and ~1350 cm^{-1}, respectively at ~796 cm^{-1}, ~1280 cm^{-1} and ~1350 cm^{-1} are correlated with the contribution of $BØ_4^-$, respectively $BØ_3$ and $BØ_2Ø^-$ structural units [2,16,20]. The presence of envelope centered at ~ 440 cm^{-1} is assigned to the Pb-O link vibration and also, isolated diborate groups [2,10,30].

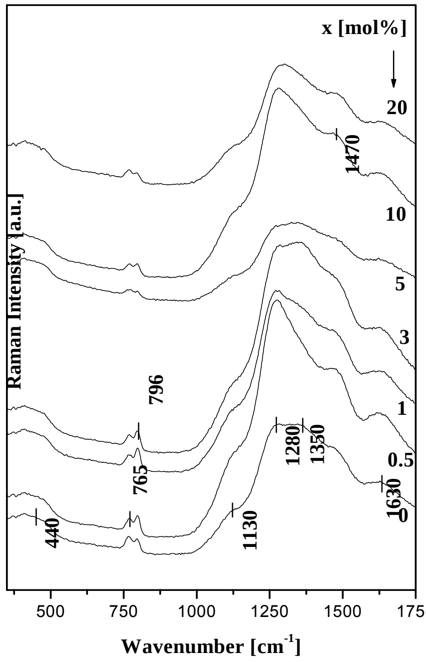

Fig. 3. Raman spectra of xMnO·(100-x)[3B_2O_3·0.7PbO·0.3Ag_2O] glasses.

The obtained data from Raman bands assignments confirm structures proposed by the FT-IR results, their evolution with the manganese oxide additions and moreover new structural groups were detected, i.e. boroxol rings [$B_3O_{4.5}$], pyro- [$B_2O_5^{4-}$], ditri- [B_3O_8] and dipenta-borate [B_5O_{11}] groups [3,4,6,10,30].

In most borate glasses, at ~ 806 cm^{-1} was detecting the Raman band characteristic of the breathing motions of the oxygen atoms inside the boroxol ring [1,2,16,20,21]. In our glasses, in the case of this band, the shift to lower wavenumber (~796 cm^{-1}) was observed. Since in B_2O_3-PbO glasses this tendency was not evidenced [6,10], this shift can be explained by the presence/influence of the silver ions in vitreous matrix.

No notable evolution in the intensities of the bands (~440 cm^{-1}, ~1130 cm^{-1}) coming from Pb-O bond vibration and diborate groups was evidenced when the MnO content increased. Also, the Raman band at ~765 cm^{-1} has the small intensity in all compositional range and is litlle influenced of the MnO content. The progressive addition of manganese ions implies an modification of the Raman bands intensities situated at ~796 cm^{-1}, ~1280 cm^{-1}, ~1350 cm^{-1} and ~1470 cm^{-1} characteristic of triangular borate units located in different environments, denoting the influence of the MnO on the structure of studied glasses.

4. Conclusions

Homogeneous glasses of the xMnO·(100-x)[3B_2O_3·0.7PbO·0.3Ag_2O] system were obtained within $0 \leq x \leq 20$ 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 manganese 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 highest value of the N_{BO4}/N_{BO3} ratio (A_4/A_3) was found in the case of x = 5 mol% composition.

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

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