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The Ag_2O/PbO ratio influence on $3B_2O_3$-Ag_2O-PbO glasses

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Silver lead borate glasses were investigated through spectroscopic methods (FTIR absorption and Raman scattering) and X-ray diffraction in order to obtain information concerning the influence of the Ag_2O/ PbO ratio on the short range order of network structure. The obtained diffraction patterns prove the vitreous character of these samples in the $0 \leq y \leq 1$ compositional range. The FTIR data reveals a network structure mainly based on the di-, tri-, tetra-, penta- and orthoborate groups. The changes on the Ar (A_4/A_3) ratio, (where the values A_4 and A_3 reflect de relative amount of tetrahedral (BO_4, $BØ_4^-$) and triangular ($BØ_3$ and $BØ_2O^-$) borate species) were also followed in order to understand the Ag_2O/PbO relative amount influence on the boron atom coordination. For all analyzed samples, the amount of tricoordinated boron atoms is superior to tetracoordinated ones. A progressive increases of the tetracoordinated boron atoms versus tricoordinated ones up to y = 0.5 was observed. The Raman data is in agree with the structural information revealed by the FTIR spectroscopy and expose new structural groups such as pyroborate groups and boroxol rings.

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Keywords: Silver-lead-borate glasses, FTIR, Raman

1. Introduction

Boron oxide, which is a traditional glass former, along with lead oxide form stable glasses over a wide range of compositions [1, 2]. Lead borate glasses are highly transparent in the visible and near infrared region having the desired characteristics against irradiation [3]. Boron isotope is good absorber of thermal neutrons and lead is known as a shielding material for γ-rays [1]. Depending on the concentration, lead oxide plays both roles as network modifier or former of the glass. Network incorporated Pb has been found to be four-coordinated in various glass systems [4-7]. Previous FTIR and Raman studies [4-8] on ternary lead-borate glasses proposed a structure based on trigonal BO_3 and tetrahedral BO_4 groups. In the structure of those glasses were identified borate species such as di-, tri-, tetra-, penta-, pyro- and orthoborate groups besides the boroxol rigs. The structural conversion between BO_3 and BO_4 groups in the borate network depends on the chemical composition and on the type of the glass modifier [9,10]. On the other hand, oxide glasses containing silver oxide have many applications due to an important contribution of silver ions in the electrical conduction process [11-14]. In case of silver borate glasses at low concentrations of silver, the trigonal coordination of boron is partially changed into tetrahedral; all the oxigens bridge between two borons. At higher concentrations, the relative number of tetrahedral coordinated boron ions tends to decrease and the coherence breakdown commences with the formation of non-bridging oxygen ions (NBO). The silver ions are localized in the interstices of the network, near the BO_4 groups or the NBO, to ensure charge neutrality [15]. Earlier studies such us electron microscopy, electrical [16] and photoluminescence measurements [17], made on silver lead borate glasses shows that silver ions associated with oxygen bond reduce to metallic silver when the glasses are suitably heat treated.

The aims of the present study were to obtain information concerning the influence of the Ag_2O/ PbO ratio on the short-range order of the network structure through spectroscopic methods (FTIR absorption and Raman scattering) and X-ray diffraction.

2. Experimental procedure

The prepared glass compositions were $3B_2O_3\cdot(1-y)PbO\cdot yAg_2O$ with $0 \leq y \leq 1$. The batch of the mixture of the reagent grade H_3BO_3, PbO, $AgNO_3$ was melted in air, in sintered corundum crucibles, in an electric furnace at 950 °C for 15 minutes. The melts were quickly cooled at room temperature by pouring them onto stainless steel plates. The quenched glasses were submitted to thermal annealing (6 hours at 470°C) for internal stress relaxation.

To prove the vitreous character of the system X-ray diffraction measurements were performed using a diffractometer Philips X Pert MPD, with a monochromator of graphite for CuK_α (λ = 1.54 Å). The X-ray generator works at 40 KV and with an electric current of 50 mA. The diffractograms where performed in a 2θ degree range 10º- 90º with a variation speed of 3°/ minute. The analysis was made on powder samples, to satisfy the diffraction condition of Bragg law. The FT-IR absorption spectra were recorded with an Equinox 55 Bruker spectrometer, at room temperature, in the 400-2000 cm^{-1} range, using the KBr pellet technique. The FT-Raman spectra have been recorded for bulk glasses with a LabRam spectrometer using 514.5 nm and 100 mW output of a Spectra Physics argon ion laser, in a back–scattering (90°) geometry. The detection of Raman signal was carried out with a Photometric model 9000 CCD camera.

3. Results and discussion

The obtained diffraction patterns of the samples corresponding to the $3B_2O_3 \cdot yAg_2O \cdot (1-y)PbO$, where $0 \le y \le 1$ confirm their vitreous nature (Fig. 1).

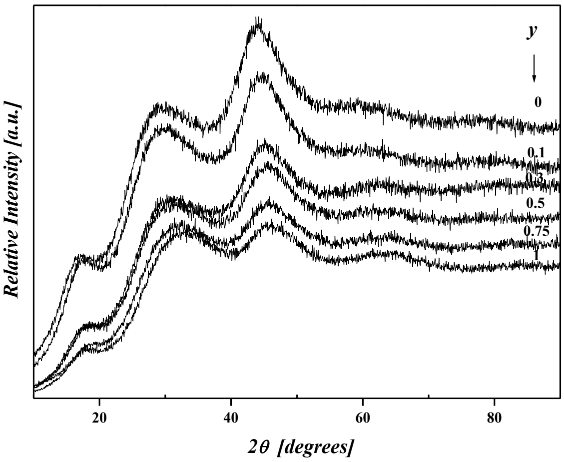

Fig.1. X-ray diffraction patterns of the $3B_2O_3 \cdot (1-y)PbO \cdot yAg_2O$ glass system.

X-ray patterns reveal the presence of three well-defined peaks, denoting a medium-range order (MRO) of the network. The progressively addition of silver oxide causes a decrease in the relative intensity of those peaks. This behavior can be explained by the fact that in the structure of the glasses there is no longer a MRO; some linkages break in the vitreous network, and the structural groups tend to be isolated and randomly disposed denoting a short-range order (SRO) of the network.

The experimental FT-IR spectra of the glass system are shown in figure 2 and the assignments of the detected absorption bands are presented in table I. The FT-IR data were analyzed based on the method given by Condrate and Tarte [19, 20] by comparing the experimental data of glasses with those of related crystalline compounds [4,12, 21-26].

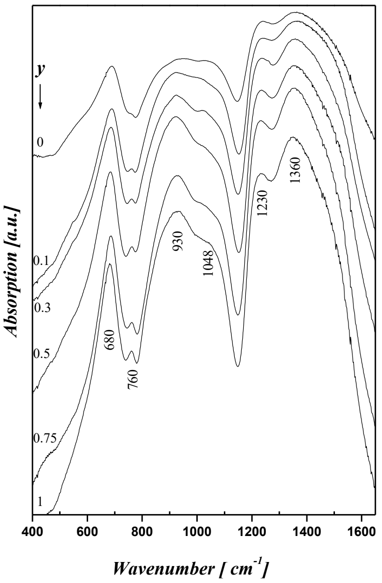

Fig. 2. FT-IR spectra of $3B_2O_3 \cdot (1-y)PbO \cdot yAg_2O$ glass system

Table 1. Assignments of the FT-IR and Raman bands in the spectra of $3B_2O_3 \cdot (1-y)PbO \cdot yAg_2O$ glass system.

Peak positions [cm^{-1}]		IR assignments	Raman assignments
IR	**Raman**		
~680	~760	B-O-B bonds bending vibrations from pentaborate groups	symmetric breathing vibrations of six member borate rings with one or two $\mathrm{BØ}_3$ triangle replaced by $\mathrm{BØ}_4^-$ tetrahedral
~760	~790	$O_3B\text{-}O\text{-}BO_4$ bonds bending vibrations	symmetric breathing vibrations of boroxol rings
~930	~1115	B-O bonds stretching vibrations in BO_4 units from diborate groups	diborate groups
~1048	~1260	B-Ø bonds stretching vibrations of $\mathrm{BØ}_4^-$ tetrahedra from tri-, tetra-, and penta-borate groups	pyroborate groups
~1230	~1370	asymmetric stretching vibrations of B-O bonds from orthoborate groups	$\mathrm{BØ_2O}^-$ triangles linked to $\mathrm{BØ}_4^-$
~1360	~1460	asymmetric vibrations of borate triangles $\mathrm{BØ}_3$ and $\mathrm{BØ_2O}^-$	$\mathrm{BØ_2O}^-$ triangles linked to other borate triangular units

For the sake of simplicity these spectra will be divided into three regions:

(a) the 400-800 cm^{-1} region is assigned to the bending vibrations of B-O-B linkages from various borate segments

(b) absorptions from 800-1150 cm^{-1} region correspond to borate arrangements containing BO_4 units

(c) the last region from 1150-1550 cm^{-1} is assigned generally to borate groups containing BO_3 units [4,5]. The absorption bands exposed by FT-IR spectroscopy indicate only the presence of borate units placed in di-, tri-, tetra-, penta- and orthoborate groups. Although the presence of vibrational modes from PbO or Ag_2O was not detected, the influence of Ag_2O/PbO ratio is noticeable. It is necessary to point the fact that even for the y = 0 in the glass network are present BO_4 units. Raising gradually the Ag_2O/PbO ratio the bands centered at 680 and 760 cm^{-1} corresponding to the bending vibrations of B-O-B linkages from various borate segments becomes sharp and increase in intensity for all the compositional range. The infrared spectra of the glass system indicate that the occurrence of Ag_2O induces structural rearrangements, which relates mostly to changes in the relative amount of triangular and tetrahedral borate units [12]. In order to quantify these changes a computer program (PeakFit v4.12) has been use to deconvolute the spectra (for example see Fig. 3 (a) and (b)) into their components band. Normalization procedure was applied before deconvolution analysis. The integrated absorption of the characteristic bands envelops between 800-1150 cm^{-1}, A_4, and 1150-1550 cm^{-1}, A_3, were calculated. The values A_4 and A_3 reflect de relative amount of tetrahedral (BO_4 and $BØ_4^-$) and triangular ($BØ_3$ and $BØ_2O^-$) borate species. The relative area and the center of each component band are presented in Table 2.

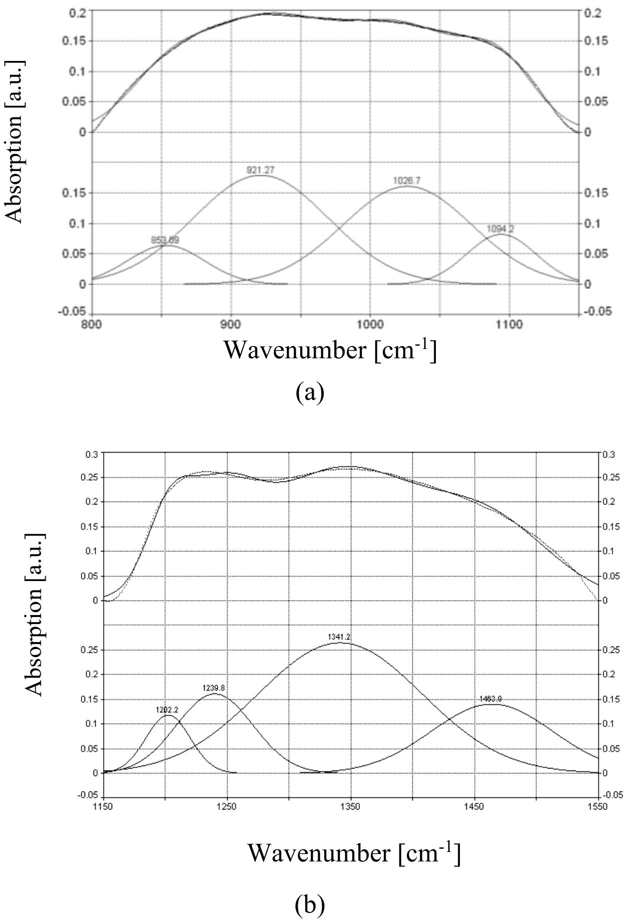

Fig .3. Deconvoluted infrared bands of $3B_2O_3{\cdot}0.9PbO{\cdot}0.1Ag_2O$ glass system between (a) 800-1150 cm^{-1} and (b) 1150 - 1550 cm^{-1} spectral range.

Table 2. Deconvolution parameters of the FT-IR spectra of $3B_2O_3{\cdot}(1\text{-}y)PbO{\cdot}yAg_2O$ glass system.

y	Deconvolution parameters Center (cm^{-1})/Relative area (%)							
0	856/3.1	940/15.2	1043/7.4	1092/2.0	1200/3.5	1238/8.8	1340/30.3	1459/10.7
0.1	853/4.4	921/21.8	1027/18.6	1094/5.1	1202/5.3	1240/12.4	1341/44.1	1464/17.2
0.3	855/4.7	930/28.0	1039/16.6	1096/4.2	1200/6.0	1236/14.6	1339/52.0	1458/18.8
0.5	854/6.5	928/36.2	1037/21.3	1096/5.7	1201/7.1	1236/16.4	1336/61.1	1458/23.7
0.75	855/7.1	927/41.6	1034/24.2	1093/6.9	1201/9.0	1236/19.5	1344/88.8	1469/23.4
1	856/8.5	935/44.1	1041/22.0	1092/6.9	1199/8.2	1233/19.1	1342/92.3	1468/24.3

The evolution of Ar (A_4/A_3) ratio as function of silver oxide is shown in figure 4. All the values of Ar ratio are sub unitary signifying the prevalence of boron connected with three oxigens present in $BØ_3$ and $BØ_2O^-$ borate species over the tetracoordinated boron ($BØ_4^-$).

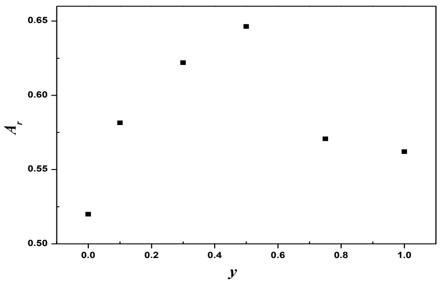

Fig. 4. Ar ratio as function of Ag_2O content for $3B_2O_3{\cdot}(1\text{-}y)PbO{\cdot}yAg_2O$ glass system.

In our case, the mechanism of conversion of the triangular units BO_3 into tetrahedral units BO_4 follows the next scenario: adding silver oxide into the network, causes a break of some linkages (possibly Pb-O-B or Pb-O linkages) freeing the oxygen ions, which will attach to tricoordinated boron becoming tetracoordinated. The proportion of BØ$_4^-$ units rises, reaching a maximum for y = 0.5 content. For y > 0.5, the decrease of the BØ$_4^-$ units relative to the BØ$_3$ and BØ$_2$O$^-$ units enhance the depolimerization degree of the network, inside the SRO limits.

Similar to FT-IR, Raman spectra of the glass system presented in Fig. 5 arise mainly from the modified borate network. The Raman spectra presents two bands in the range of 1250-1550 cm^{-1}, a small but sharp band at 790 cm^{-1} and two shoulders centered at 760 cm^{-1}and 1115 cm^{-1}. The assignments of the absorption bands are presented in Table 1.

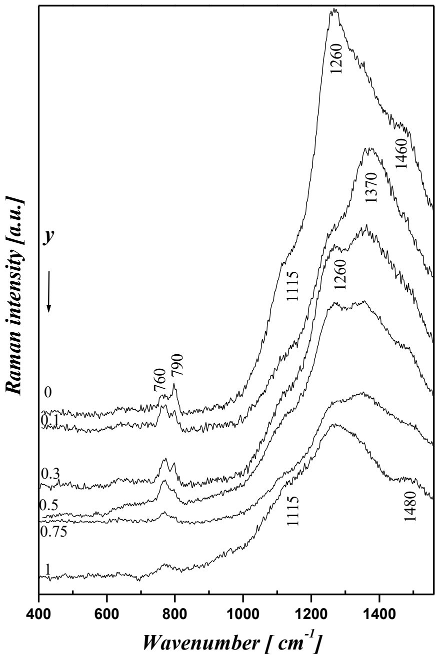

Fig. 5. Raman spectra of $3B_2O_3{\cdot}(1\text{-}y)PbO{\cdot}yAg_2O$ glass system.

Many Raman studies concerning the structure of lead borate glasses within a large compositional range have been made [1,4]. Depending on the concentration of the lead oxide, in the glass network are present boroxol rings (806 cm^{-1}), pentaborate (770 cm^{-1}) and diborate groups (1115 cm^{-1}).

In our system, the band corresponding to symmetric breathing vibrations of boroxol rings does not appear at 806 cm^{-1}; is shifted to a lower wavenumber (790 cm^{-1}). The change in the wavenumber and width of the bands depend on the kind and concentration of the network modifiers. This assumption is based on the results obtained by our research group on several glass systems that contain silver oxide and lead oxide (since in B_2O_3-PbO glasses this tendency was not evidenced) [8]. The weak intensity and the shift to lower wavenumber cause a distortion of the boroxol rings, probably due to a decrease of the bond force constant. Adding silver oxide up to y = 0.3 causes the disappearance of the band from 790 cm^{-1} on the expense of the band at 760 cm^{-1}, which may be do to the formation of the six-membered borate rings with one BO_4 unit called pentaborate or triborate groups. The Raman spectra reveal the presence of new structural groups such as pyroborate (1260 cm^{-1}) and BØ$_2$O$^-$ triangles linked to BØ$_4^-$ (1370 cm^{-1}). A kind of equilibrium between the amount of tricoordinated versus tetracoordinated boron for y = 0.5 silver oxide content is visible. Above y > 0.5 silver oxide, it take place a conversion between tetracoordinated and tricoordinated boron. In the network structure are present only diborate, pyroborate groups and BØ$_2$O$^-$ triangles linked to other borate triangular units, results there are in agreement with the structure revealed by FT-IR data.

4. Conclusions

X-ray diffraction patterns proved the vitreous nature of all samples. FT-IR data reveals a structure mainly based on the di-, tri-, tetra-, penta- and ortho-borate groups. The Ar (A_4/A_3) ratio as function of silver oxide has a maximum at y=0.5, denoting the fact that even there is an increase in BO_4 units, the number of BO_3 units is higher. Raman spectroscopic features support the FT-IR data revealing new structural groups such as boroxol rings and pyroborate groups. Still, no vibrational modes corresponding to Ag_2O or PbO were evidenced.

References

[1] H. Ushida, Y. Iwadate, T. Hattori, S. Nishiyama, K. Fukushima, Y. Ikeda, M. Yamaguchi, M. Misawa, T. Fukunaga, T. Nakazawa, S. Jitsukawa, J. Alloys Compounds **377**, 167 (2004).

[2] P. Nageswara Rao, C.Laxmi, D. Krishna Rao, N. Veeraiah, J. Quantitative Spectroscopy & Radiative Transfer **95**, 373 (2005).

[3] Z. Pan, S. H. Morgan, B. H. Long, J. Non-Cryst. Solids **185**, 127 (1995).

[4] M. Ganguli, K. J. Rao, J. Solid State Chemistry **145**, 65 (1999).

[5] I.Yasui, H. Hasegawa, Y. Saito and Y. Akasaka, J. Non-Cryst. Solids **123**, 71 (1990).

[6] A. Tawansi, I. A. Gohar, D. Holland, N. A. El-Shishtawi, J. Phys. D: Appl. Phys. **21**, 607 (1988).

[7] T. Takaishi, J. Jin, M Takaishi, T. Uchino, T. Yoko, Proc. Int. Congr. Glass. Volume 2. Extended Abstracts, Edinburgh. Scotland, 1-6 July 2001.

[8] R. Ciceo Lucacel, C. Marcus, V. Timar, I. Ardelean, J. Optoelectron. Adv. Mat., in press.

[9] H. Doweidar, J. Mater. Sci. **25,** 253 (1990).

[10] W. A. Pisarski, J. Pisarsk, W. Ryba-Romanowski, J. Mol. Struct. **744–747**, 515 (2005).

[11] O. Sipr, G. Dalba, F. Rocca, Phys. Rev. B **69**, 134201 (2004).

[12] C. P. Varsamis, E. I. Kamitsos, G. D. Chryssikos, Solid State Ionics **136–137,** 1031 (2000).

[13] M. Cutroni, M. Federico, A. Mandanici, P. Mustarelli, C. Tomasi, Solid State Ionics **113–115**, 681 (1998)

[14] J. A. Duffy, B. Harris, E. I. Kamitsos, G. D. Chryssikos, J. A. Kapoutsis, Phys. Chem. Glasses **39** (5), 275 (1998).

[15] M. C. Abramo, G. Carini, G. Pizzimenti, J. Phys. C: Solid State Phys. **21**, 527 (1988).

[16] A. O. Hulpus, J. Monteiro, S. K. Mendiratta, M. F. Carrasco, I. Ardelean, J. Non-Cryst. Solids **352**, 1495 (2006).

[17] A. O. Hulpus, J. Cascalheira, S. K. Mendiratta, M. F. Carrasco, I. Ardelean, poster M-510, ICANS-21, 2005, Lisbon, Portugal, Phys. Chem. Glasses, in press.

[18] H. Ushidaa, Y. Iwadate, T. Hattori, S. Nishiyama, K. Fukushima, M. Misawa, T. Fukunag, J. Alloys Compounds **327**, 121 (2001).

[19] P. Tarte, Physics of Non Crystalline Solids, Ed.By I. A. Prins, Elsevier, Amsterdam, (1964) p.549

[20] R. A. Condrate, J. Non-Cryst. Solids **84**, 26 (1986).

[21] Y. D. Yiannopoulos, G. D. Chryssikos, G. D. Kamitsos, Phys. Chem. Glasses **42**(3), 146 (2001).

[22] F. Bentley, L. D. Smithson, A.L. Rozek, Infrared-Spectra and Characteristic Frequencies 700-300 cm^{-1}, Interstice, New York, (1986) p. 103.

[23] E. I. Kamitsos, M. A. Karakassides, G. D. Chryssikos, J. Phys. Chem. **91**, 1073 (1987).

[24] G. Fuxi, Optical and Spectroscopic Properties of Glass, Springer, Shanghai Scientific Technical Pub., Shanghai, (1991) pp.32-35.

[25] E. Metwalli, J. Non-Cryst. Solids **317**, 221 (2003)

[26] S. G. Motke, S. P. Yawale. S. S. Yawale, Bull. Mater. Sci. **25**, 75 (2002).

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