



Structural studies of lead lithium borate glasses doped with silver oxide

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ABSTRACT

Silver oxide doped lead lithium borate (LLB) glasses have been prepared and characterized. Structural and composition characterization were accessed by XRD, FTIR, Raman, SEM and EDS. Results from FTIR and Raman spectra indicate that Ag₂O acts as a network modifier even at small quantities by converting three coordinated to four coordinated boron atoms. Other physical properties, such as density, molar volume and optical basicity are also evaluated. Furthermore, they are also affected by the silver oxide composition.

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1. Introduction

For the last few years, heavy metal oxide (HMO) glasses are being intensively studied due to their optimal properties for photonics and electronic applications [1,2]. For instance, lead borate glasses present very interesting features such as optically transparency from the visible to the near-infrared range, wide compositional regions of PbO content in the host glass matrix, resistance against devitrification, high refractive index and density, good transmittance in the UV-region and enhanced radiation shielding for γ -ray [3–5]. In fact, lead borate glasses are already being used in enamels, photonics, and optoelectronic applications [3,4]. Boric acid is one of the best glass formers there is. When mixed with glass modifiers, such as Li₂CO₃ or other alkali oxides, its internal structure is rearranged due to the formation of non-bridging oxygens [6]. In turn, lead oxide is known as a non-conventional glass former, since it can act as a glass former or as a glass modifier. The role is determined by its concentration and by the type of bond between lead and oxygen [3,7]. Covalent bonding is associated with a network forming behavior, whilst an ionic bonding is related to glass modifier properties [4,8]. These two types of PbO–B₂O₃ bonds were proposed by means of NMR, IR and Raman spectroscopies, ESR and Neutron diffraction studies [8,9]. At high concentrations, PbO acts as a glass former [8,9], whilst at low concentrations it acts as a glass modifier [8]. Usually, heavy metal oxide glasses contain 50–78 wt.% of HM, such as lead oxide. It is known that lead oxide is very toxic for the environment. Thus, in the present work it is prepared a glass in the

system PbO–B₂O₃ with a lower concentration of lead oxide, which is expected to be more ecofriendly [10]. It is also known that silver ions present a high electrical conductivity in borate glasses [11]. Thus, the applicability of the lead–borate glasses can be enhanced by the addition of silver to the network. Thus, the proposed system will be also doped with different amounts of silver oxide. Silver ions are known due to their high-conductivity, resistance against humidity and possibility of being used in a large number of fields, such as biomaterials [4]. Thus, the purpose of this work is to prepare and deeply characterize glasses in the system PbO–B₂O₃, doped with different amounts of silver oxide. The characterization will be performed by FTIR, XRD and SEM. The changes produced by silver introduction in the glass will also be studied.

2. Materials and methods

2.1. Preparation of LLB glasses

Lead lithium borate (LLB) glasses doped with Ag₂O with the following chemical compositions (in mol%), 15PbO–5Li₂O–(80–*x*)B₂O₃–*x*Ag₂O, where *x*=0.5, 1, 2 and 4, were prepared by the quenching technique. A mixture of analytical grade PbO, B₂O₃, Li₂CO₃, Ag₂O raw chemicals (Sigma–Aldrich 99.99%) was melted in crucibles for about an hour, in an electrical furnace at temperature of 950 °C. In order to remove thermal strains in the glass, the samples were annealed at 200 °C for 1 h. The prepared glasses present circular shape, 2–3 cm in diameter with a thickness of about 0.33–0.38 cm and present good transparency.

2.2. Characterization of LLB glasses

Glass densities were measured by Archimedes' principle using water as an immersion liquid on a Mettler Toledo balance. Fourier

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transform infrared (FTIR) spectra were recorded in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} on a Jasco FT/IR – 460 PLUS spectrophotometer. The spectra were recorded by using 250 mg KBr pellets containing approximately 95% of KBr and 5% of silver oxide glass sample. In order to obtain a better results, the pellets were dried in a Buchi Glass Oven-B-585 at 120 °C for 1 h.

SEM was performed at CEMUP (Materials Centre of the University of Porto), using a FEI Quanta 400 FEG ESEM/EDAX Genesis X4M, a high resolution environmental Scanning Electron Microscope with X-ray microanalysis and backscattered electron diffraction pattern analysis. SEM images were obtained in a high vacuum mode and with an acceleration of 500 kV. In order to avoid superficial charge accumulation, the samples were covered with a carbon film.

The unpolarized micro-sampling Raman spectra of the LLB glass samples have been recorded in the back scattering geometry, at room temperature by using an Olympos BH2 UMA microscope and 50 \times lens. The 514.53 nm polarized line of a Ar+ laser was used for excitation with an incident power of about 150 mW impinging the sample. The scattered light was analyzed using a T64000 Jobin-Yvon spectrometer operating in the triple subtractive mode, and equipped with a LN2 cooled CCD. Identical conditions were kept constant for all measurements. The spectral slit width was about 1.5 cm^{-1} and the spatial resolution on the sample was about 1 μm .

3. Results and discussion

3.1. Physical parameters of silver oxide doped LLB glasses

The density of a glass is a powerful tool to examine the structural compactness of a glass network [12]. From Table 1, it is easily observed that changing the composition of silver oxide in the samples implies the variation of some physical properties, such as density and molar volume. In the present studies the molar volume increases along with the density. This behavior was reported by Rajendran et al. [13], and results of the creation of non-bridging oxygens (NBOs). These will break the bonds of the lithium borate host glass, increasing the free space in the network [6]. The oxygen packing density (O) also supports this idea. The decrease in O suggests an increasing formation of NBOs and a loosely packed structure [14,15]. The trend of r_i in the prepared glasses (Table 1) suggests a decrease of the available volume per atom. However, the total volume of the glass is increasing, as previously mentioned. In Table 1, the physico-chemical properties determined for the prepared glasses and presented.

3.2. XRD, SEM and EDS studies on silver oxide doped LLB glasses

The XRD pattern of the LLB glasses is shown in Fig. 1. Since silver content increase is not exhibiting any remarkable change in the XRD profiles, just two silver contents (0.5% and 4%) are presented. The overall features of these XRD curve confirm the amorphous nature of the glasses doped with silver oxide. The surface morphology (5000 \times) of the glasses doped with 0.5 mol% and 4 mol% of Ag_2O can be seen in Fig. 2. Besides the samples glassy nature, it is also observed the formation of very small metallic silver clusters ($\sim 0.75 \mu\text{m}$). Silver oxide XRD peaks are usually situated in the region $2\theta = 32.8^\circ$ (1 1 1) and 38.2° (2 0 0), and metallic silver at 38.2° (1 1 1) and 44.3° (2 0 0) [16–18]. In Fig. 1, two broad bands are present in these regions. Therefore silver diffraction peaks are not well identified, since they are present in the after mentioned bands. However, these profiles are in good agreement with literature [19,20].

There has been shown a great deal of interest in glasses with implanted metallic clusters. These materials present themselves as good candidates for many applications in optics and electronics.

Table 1
Composition and some physical properties of the LLB glasses doped with silver oxide.

Ag_2O (mol%)	Density (g/cm^3)	Average molecular weight (g/mol)	Molar volume (cm^3/mol)	Oxygen packing density (g/atom/l)	Refractive index (n)	Silver ion concentration ($\times 10^{22}$ ions/ cm^3)	Polaron radius (\AA)	Interionic distance (\AA)	Optical basicity	Electron polarizability ($\times 10^{-24} \text{cm}^3$)	Ionic factor (%)
0.5	3.90	87.48	22.43	118.99	1.596	1.34	3.66	0.909	0.4628	1.3834	3.0509
1	3.92	88.33	22.54	117.71	1.636	2.67	2.91	0.723	0.4621	1.3826	3.2373
2	3.94	90.03	22.85	116.40	1.656	5.27	2.32	0.575	0.4608	1.3810	3.3300
4	4.00	93.43	23.35	112.16	1.687	10.32	1.85	0.459	0.4581	1.3780	3.5293

Table 2
Assignments of FTIR and Raman spectra in LLB glasses doped with different amounts of silver oxide.

Wavenumber (cm ⁻¹)	FT-IR assignment	Ag ₂ O in mol%				Raman assignment	Ag ₂ O in mol%			
		0.5	1	2	4		0.5	1	2	4
480 [2]	Stretching vibration in PbO ₄	464	472	462	458					
510 [2]	Pb–O symmetrical bending vibration	529	530	526	530					
560 [2]	Ag–O vibrations	583	603	–	586					
669 [2]	Pb–O bonds vibrations of PbO _n									
722 [2]	units with n = 3 and/or 4	651	672	–	656					
690 [24]	B–O–B angle bending vibrations from pentaborate groups	684	693	686	686					
765 [4]						Symmetric breathing vibrations of six-member rings with one or two BØ ₃ triangles replaced by BØ ₄ tetrahedra	837	841	–	840
796 [4]						Symmetric breathing vibrations of boroxol rings				
870 [24]	Stretching vibrations of B–O bonds in BO ₄ units from tri-, tetra- and pentaborate groups	–	–	–	–					
960 [2]	Pb–O symmetrical stretching vibrations	910	936	936	908					
963 [24]	B–O stretching vibrations of BO ₄ units in diborate groups	–	–	–	–					
1090 [2]	Pb–O asymmetrical bending vibration	1037	1058	1055	1038					
1098 [24]	B–O stretching vibrations of BO ₄ units in pentaborate groups	1113	1121	1119	1115					
1110 [4]						Diborate groups				
1225 [24]	B–O stretching vibrations of BO ₃ units in orthoborate groups	1249	1239	1236	1250					
1275 [4]						Pyroborate units	1359	1049		1311
1328 [24]	B–O stretching vibrations of BO ₃ units in pyroborate rroups	1351	1342	1315	1352			1287		1412
1360 [4]						BØ ₂ O-triangles linked to BØ ₄ units				
1407 [24]	B–O stretching vibrations of BO ₃ units in chain and ring type metaborate groups	1438	1458	1448	1485					
1460 [4]						BØ ₂ O-triangles linked to other borate triangular units				
1600 [25]						Bending modes of O–H groups	1593	–	1594	1590
1647–1671 [23]	Bending modes of OH groups	1641	1637	1636	1638					

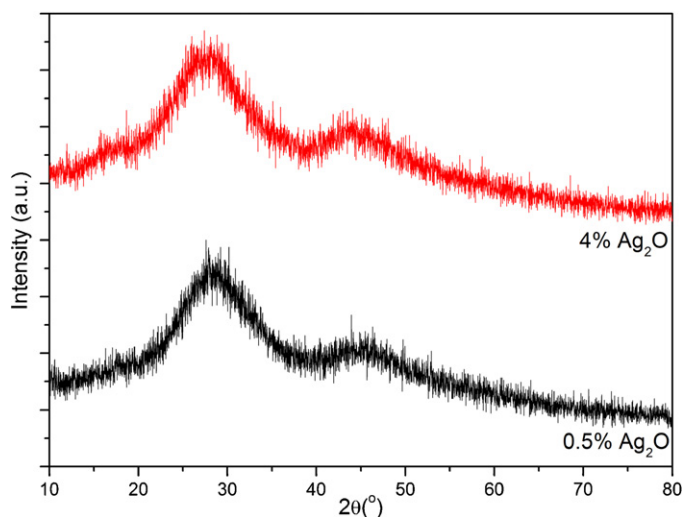


Fig. 1. X-ray diffraction patterns of the 0.5 and 4 mol% of Ag_2O LLB glasses.

The non-linearity of metal-doped glasses is of major importance for photonics and communications devices [21,22].

Fig. 2 also presents the EDS spectra for 0.5% and 4% silver oxide doped glasses. As expected the signal of silver increases in the 4% sample, due to a higher amount of Ag_2O . There were detected other unwanted elements in the samples. They probably result from dusts in the air, which present aluminosilicates in their composition. Moreover, the material used during the preparation could also be contaminated.

3.3. Fourier transform infrared (FTIR) and Raman studies on silver oxide doped LLB glasses

In order to obtain more information about the prepared glasses, FTIR measurements were performed. The positions of the bands for the LLB glass system are summarized in Table 2.

Fig. 3 shows the FTIR spectra for the silver doped LLB glasses. The bands in the region $2000\text{--}400\text{ cm}^{-1}$ are assigned to molecular vibrations of lead, boric acid and silver units. In this region is also visible the O–H bending mode [23]. The spectra are made of four different regions, composed of broad absorption bands with some shoulders. In Fig. 4(a) and (b) it is also shown the deconvolution

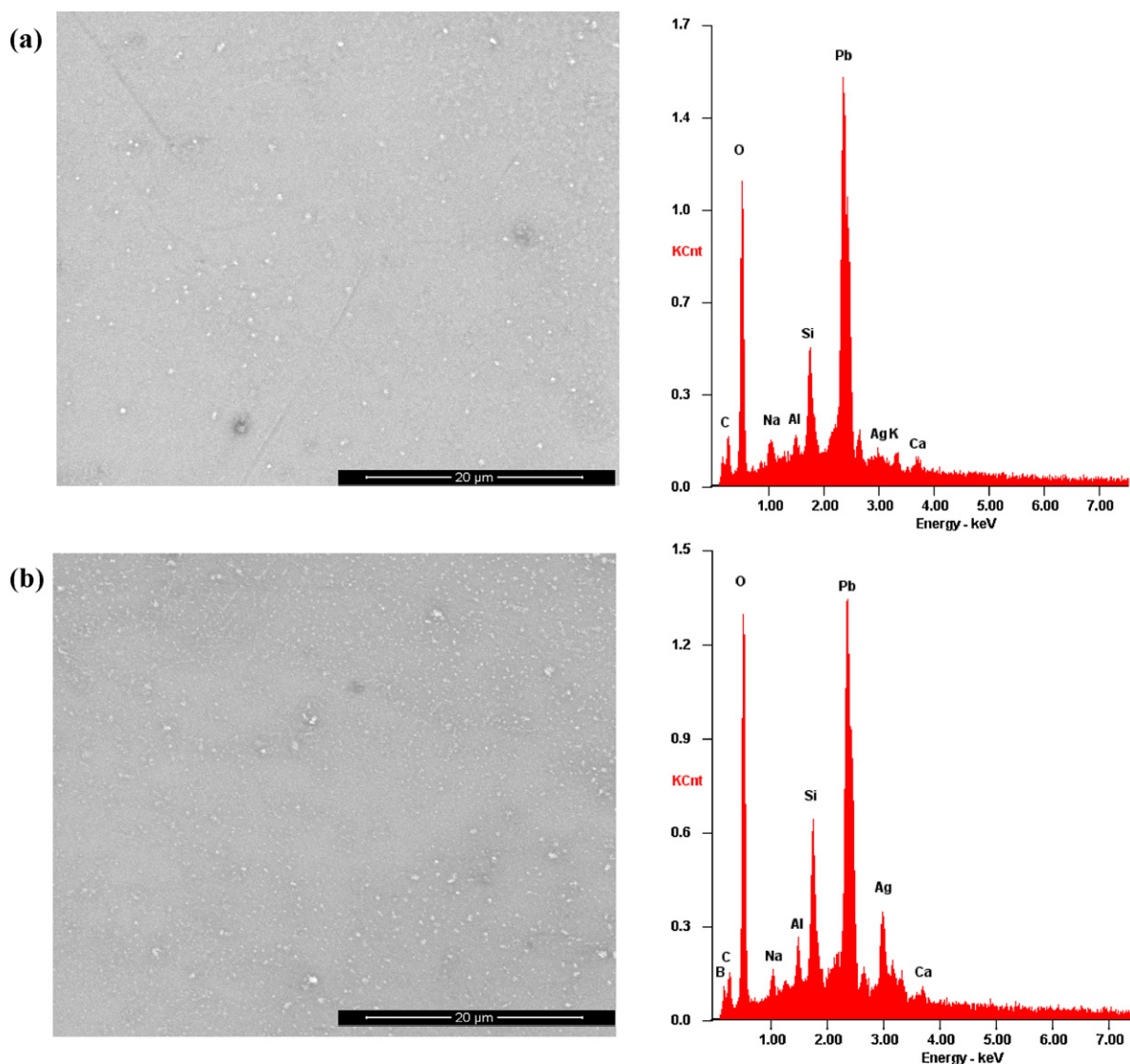


Fig. 2. SEM and EDS pictures of LLB glasses doped with (a) 0.5 mol% and (b) 4 mol% of silver oxide (SEM magnification of $5000\times$ (left) and EDS spectra recorded at 15 keV (right)).

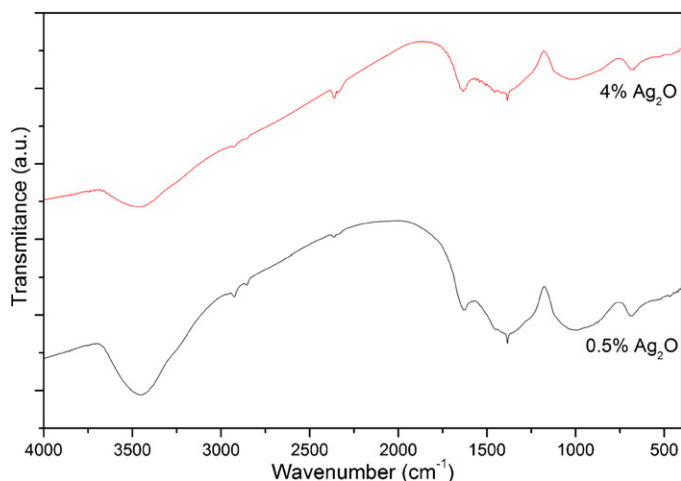


Fig. 3. FTIR spectra for the LLB glasses doped with 0.5 and 4 mol% of silver oxide.

of some bands present in the borate units vibration range. The first region below 600 cm^{-1} is usually assigned to the vibration of metals. The wavenumbers 480 and 510 cm^{-1} corresponds to the stretching and Pb–O symmetrical vibrations in PbO_4 . At 689 cm^{-1} is presented the B–O–B angle bending vibrations from pentaborate groups as the second region of the spectra. The next region, between 750 and 1170 cm^{-1} , is the typical vibration range of BO_4 units. There are present the stretching vibrations of B–O bonds in BO_4 units in the form of di-, tri-, tetra- and pentaborate groups, at

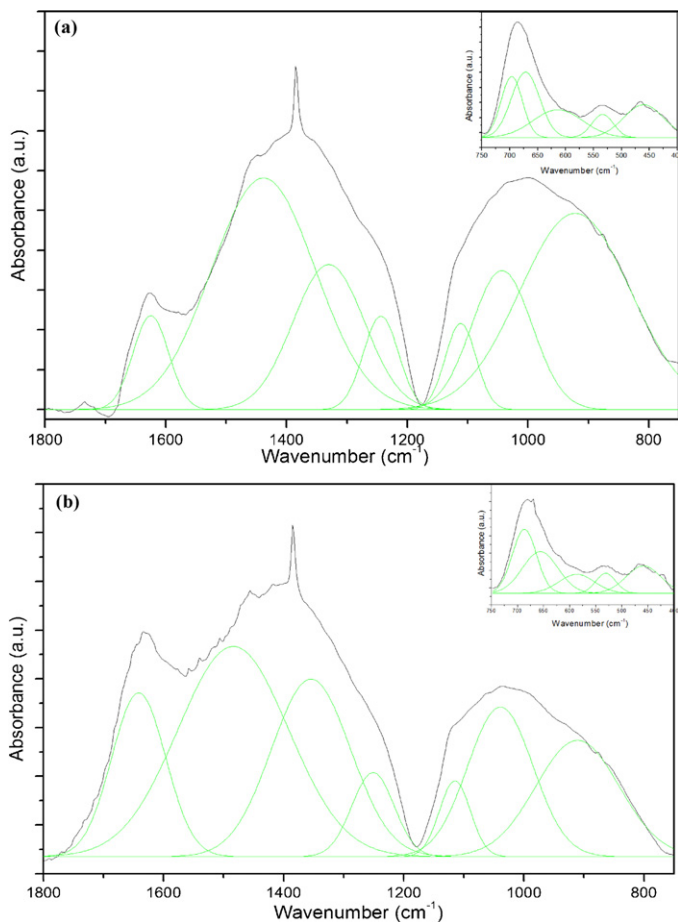


Fig. 4. Deconvolution of FT-IR spectra for (a) 0.5 mol% and (b) 4 mol% of silver oxide doped LLB glasses.

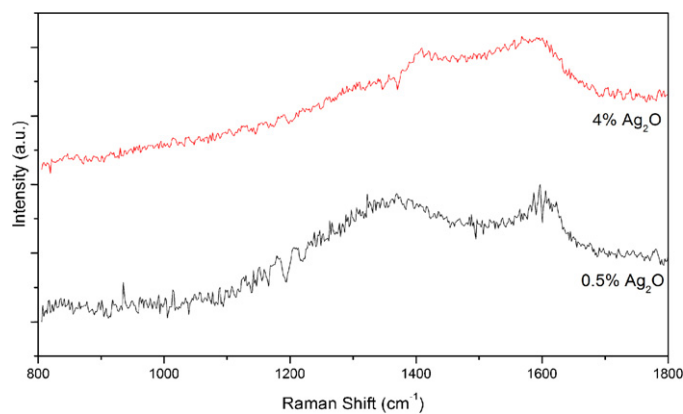


Fig. 5. Raman spectra for the LLB glasses doped with 0.5 and 4 mol% of silver oxide.

874 , 935 and 1100 cm^{-1} [24]. The positions of 935 and 1100 cm^{-1} can also be attributed to the Pb–O asymmetrical bending and symmetrical stretching vibrations, which present a very similar position in the spectra, as stated in Table 2. The last region of the absorption spectra is located between 1175 and 1702 cm^{-1} , corresponding to the BO_3 units vibrations. In a pure borate glass is always present at 806 cm^{-1} the vibration associated with boroxol rings. In the LLB samples that peak is not present. Therefore, all the boroxol units were converted into BO_3 and BO_4 units [14].

At 534 cm^{-1} there is a small band width could be assigned to the Ag–O vibration and no major difference in the region of silver with increasing concentration was observed. However it is verified a bands position shifting due to the addition of silver oxide. Small differences in the bands positions are usually present due to technical and software limitations. The larger differences result from the network re-arrangements induced by the silver oxide. Silver atoms break some of the X–O bonds (X = Pb, B), thus modifying the structure.

In fact, in borate glasses it is always present an isomerization process between 3 and 4 coordinated borons:



where \emptyset stands for an oxygen atom bridging two boron atoms. This idea is also supported in Fig. 4(a) and (b). As it is possible to observe from the deconvolution spectra that the areas of vibration bands and the bands themselves change with the addition of silver oxide in 0.5 mol% and 4 mol% in LLB glasses.

Raman analysis in the range of 800 – 1800 cm^{-1} was also performed in the samples. Fig. 5 shows the Raman results for the prepared different content of silver oxide doped LLB glasses. These spectra show a broad band around 1400 cm^{-1} , which is usually assigned to the $\text{B}\emptyset_2\text{O}^-$ triangles linked to $\text{B}\emptyset_4$ units, as stated in Table 2 [4].

For a better comprehension of these results a deconvolution of the 0.5% Ag_2O and 4% Ag_2O glass spectra was performed, and it is present in Fig. 6(a) and (b). Here it is clearly observed a band at 1361 cm^{-1} , due to borate units, which is slightly shifted to the right with an increasing amount of silver oxide. The band around 1600 cm^{-1} is assigned to the O–H bending vibrations, which is consistent in all samples [25]. The vibrations of the boroxol rings are usually located around 800 cm^{-1} . In the prepared samples it is observed a weak band at 837 cm^{-1} , which can be assigned to the boroxol rings vibration. Moreover, increasing the quantity of silver oxide results in the generation of new bands in the region 1200 – 1500 cm^{-1} . Thus, confirming the modifying behavior of silver oxide. All these results are in good agreement with the FTIR measurements.

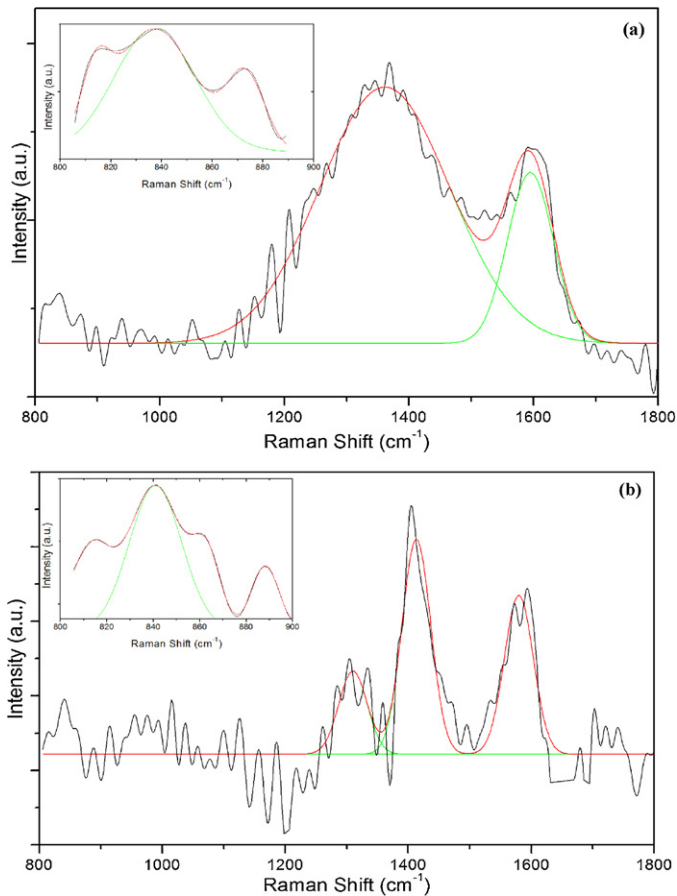


Fig. 6. Deconvolution Raman bands for (a) 0.5 mol% and (b) 4 mol% of silver oxide doped LLB glasses.

3.4. Polarizability and optical basicity of the LLB glasses

The optical basicity Λ , is related with the electron donor power of the oxygen in a sample. This power is higher for ionic solids due to the fact that the charges around oxygen are localized around each element. Therefore, the oxygen can share negative charge with other cations. In covalent bonding, the oxygen shares its electrons with other elements, reducing its donor power [26]. Facing this it is possible to estimate the type of bonds in the prepared glasses. A high Λ refers to a more ionic bonding, whilst a low value of Λ is typical of covalent bonding. Duffy determined that the Λ of a glass composed of mixed oxides can be calculated by the relation [27]:

$$\Lambda = \sum X_n \Lambda_n \quad (2)$$

where X_n is the equivalent fraction based on the amount of oxygen each oxide contributes to the overall glass stoichiometry and Λ_n is the single oxides optical basicity [27]. It is known that electron polarizability (α_o^{2-}) is strongly correlated with the optical basicity of a glass, and can be determined by [27]:

$$\Lambda = 1.67 \left(1 - \frac{1}{\alpha_o^{2-}} \right) \quad (3)$$

The electron polarizability (EP) is one of the most important properties of glasses used in optics. The non-linear effects are caused by the electron polarization of materials when exposed to intense light beams. Therefore, the development of optical devices is extremely connected with EP [27,28].

Based on Eqs. (3) and (4) it is possible to determine the optical basicity and EP of the prepared samples. In the literature is

found that $\Lambda(\text{Ag}_2\text{O}) = 0.91$ [29], $\Lambda(\text{Li}_2\text{O}) = 1.00$, $\Lambda(\text{B}_2\text{O}_3) = 0.41$ and $\Lambda(\text{PbO}) = 0.95$ [30]. In Table 1 is showed that optical basicity values are decreasing with an increasing amount of silver oxide. Thus the cation–oxygen bonds are progressively developing covalent behavior. The loss of ionic behavior can also be confirmed by calculating the ionic characteristic factor (I_c) [31]:

$$I_c = [1 - e^{-(\Delta\chi/4)}] \times 100 \quad (4)$$

where $\Delta\chi$ is the average electronegativity of the single oxides. The I_c value for the glasses were estimated from the molar contributions of each oxide. In Table 1, it is showed that I_c decreases with the addition of silver oxide. The values used for the electronegativity were 2.0 for B, 3.5 for O, 1.9 for Pb, 1.9 for Ag and 1.0 for Li [32]. If $I_c \geq 50\%$ it is assumed that the glass is essentially an ionic solid [31]. In the present results, I_c values are higher than 50%, however it is decrease with the addition of silver oxide. Therefore, this confirms the previous statement, that cation–oxygen bonds are becoming covalent.

4. Conclusion

By using different characterization techniques, some physical properties of glasses doped with silver oxide were analyzed. Through SEM and XRD analysis, we verified the vitreous nature of the samples. SEM analysis also indicates the formation of metallic silver in the glasses. Raman analysis supports these results, revealing that silver oxide induces a rearrangement of the borate network. The addition of silver oxide to the glass matrix, promotes the conversion of some BO_3 units to BO_4 .

The average electron polarizability and optical basicity of the LLB doped silver oxide glasses were calculated using the Duffy equations. It is observed a decrease of α_o^{2-} with increasing concentration of silver oxide, indicating an increasing number of covalent bonds in the sample. This behavior is also supported by the ionic characteristic factor. Further studies are under way to study optical properties of these glassy materials doped with different lanthanides.

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