Influence of PbO molar fraction and Se doping on borate glasses

M. Rodríguez[1], I. Aguiar[1], L. Fornaro[1], A. C. Hernandes[2]

[1] *Compound Semiconductor Group, Faculty of Chemistry, Universidad de la República, Montevideo, Uruguay*

[2] *Laboratorio de Crescimento de Cristais e Materiais Ceramicos, Instituto de Fisica de Sao Carlos, Universidade de Sao Paulo, SP, Brasil*

mrodrig@fq.edu.uy

Glasses of $xPbO(1-x)B_2O_3$ composition, with x = 0.2, 0.4, 0.5 and 0.6, and doped with Se (0.01, 0.02, and 0.03 mol) were synthesized from H_3BO_3, PbO, Pb_3O_4 and Se powders, homogenized and then fused at about 700 - 800 ºC. The fused mixing was annealed at temperatures lower than the glass transition one, about 400 ºC and during 3 hours. Samples were then slowly cooled down to room temperature. PbO concentration correlates with an increase on the color intensity of the samples. Final glasses were cut, mechanical etched and then characterized by spectrometry in the 400 - 830 nm range and by differential scanning calorimetry (DSC) and thermal gravimetry (TG). The influence of PbO and Se concentrations on the spectra was confirmed studying the correlation between molar fraction and intensity of the 435 nm and 610 nm peaks. TG results indicate that, when heated up to 800 ºC, samples with Se decompose. However, sample color as far as increases for the 435 nm absorption peak, indicating the possible incorporation of Se to the glass structure. DSC diagrams show a glass transition in the 443-436 ºC temperature range. DSC also indicate the glasses have up to three crystalline phases. Future work will confirm these phases and Se incorporation by X-ray diffraction.

Keywords: Lead borate glasses, Glass structure

1. INTRODUCTION

Borate glasses have attracted many researchers for years in order to obtain information about their structure [1]. But in the past ten years, these glasses have been studied because of their electrochemical and optical applications, namely solid state batteries, optical waveguides and luminescent materials. The glassy materials, which consist of oxides of the heaviest metals, such as lead, are more promising for photonics and electronics [2]. Since naturally occurring stable boron isotope is a good absorber of thermal neutrons [3], borate glasses may be used to shield such radiation. Furthermore,

borate glass is an advantageous material for radiation dosimetry applications [4]. On the other hand, the use of glasses with high content of lead as shielding materials dates from many years ago.

Lead borate glasses have unique properties such as their low melting temperatures and wide glass formation regions, showing technological as far as industrial interest. Different techniques were used to determine the borate glass structure and the role of PbO in such structure. The current model for the structure of vitreous boric oxide involves triangles, which are connected by BO at all three corners to form a completely linked network. Although this network is planar rather three-dimensional, the three dimensional linkage is produced by weak unions, such as Van der Waals bonds, between two network planes. Since the union between two network planes is very weak, this structure is easily disrupted. The low glass transition temperature, in the case of borate glasses, is an example of this weak interaction [5]. In accordance with this, Raman studies have demonstrated that borate glass network consist of many boroxol rings [6]. NMR investigations of lead borate glasses have shown that at low PbO addition, lead enters the glass as modifier Pb^{2+} ions. Above a PbO molar fraction of x=0.2, it becomes a glass former with more covalent bonding [7]. Beyond a PbO molar fraction of x=0.5, the glass shows a disruption of diborate groups which disappear at a fraction of x=0.65. This reduction in the number of boroxol rings is hence due to PbO acting both as network modifier and network former. The changing nature of PbO bond, from ionic to covalent, with the increase of PbO content, had been determined previously. For high lead content (> 0.75) back conversion of B_4 units to B_3 units takes place [6].

Thermal expansion and viscosity measurements were performed for the system $xPbO.(1-x)B_2O_3$ containing up to x=0.6 PbO. The existence of a phase separation region up to x=0.195 was reported [8]. Differential scanning calorimetric (DSC) studies, and heat capacities of $xPbO.(1-x)B_2O_3$ glasses with x = 0.2, 0.27, 0.33 ,0.42, 0.50, 0.65 were also made. These measurements, together with Raman studies, have confirmed the structural model proposed [9]. Recently, IR spectroscopy of lead borate glasses has been performed [10] apart from previous one [11]. Other system, with BO_3 unit, like Bi_2O_3-B_2O_3 was studied by IR and DSC measurements [12].

In the present work we study the system $xPbO.(1-x)B_2O_3$ with x= 0.2, 0.4, 0.5, 0.6, in order to see the influence of PbO molar fraction on borate glasses. We also doped the system with Se (0.01, 0.02 and 0.03 mol) for investigating the possible action of Se in such glass. The influence of PbO molar fraction and Se doping was evaluated by DSC and TG measurements and IR and visible spectra.

2.   EXPERIMENTAL

H_3BO_3, PbO, Pb_3O_4 and Se commercially available were used as starting materials. The glasses' compositions are summarized in Table 1. The dry powders were mixed, homogenized and then melted in a temperature range of 700-800 ºC, in ceramic crucibles in air using an electric furnace. Once a homogeneous free bubble liquid was obtained, it was poured into an iron mold and then annealed at a temperature below the glass transition temperature for 3 hours, to eliminate internal stress. Then the glasses were cooled down to room temperature. Transparent and homogenous glasses were

obtained. All glasses were mechanically cut and polished until homogeneous and smooth surfaces were observed.

The infrared spectra of the glasses were recorded at room temperature, using the KBr disc technique. A FTIR Shimadzu 8101A spectrometer was used to obtain the spectra in a wavenumber range between 400 and 2000 cm^{-1} with a resolution of $\pm$ 4 cm^{-1}. DSC measurements were performed using NETZSCH STA 409C on 50 mg of glass pieces at a heating rate of 10 ºC/min. Visible spectra were made using a Shimadzu 210 spectrometer in the wavelength range of 400-830 nm. The density determination was performed using distilled water as inmersion liquid (25 $\pm$ 2 ºC) by the Arquimedes method.

3. RESULTS AND DISCUSSION

Reproducible and stable glasses were obtained, whereas no interaction between the crucible and the studied glasses was observed. Various starting materials were used (PbO, Pb_3O_4) and no differences were observed between the glasses obtained.
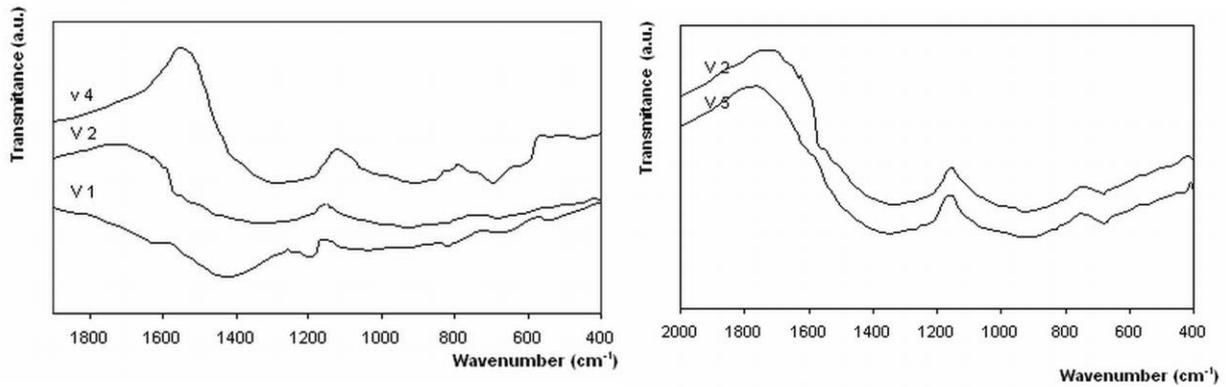
Table 1.

Summary of same physical properties of the synthesized borate glasses

Nome	Composition	Calculated Molecular Weigth (g/mol)	Thickness (mm)	Density (g/cm^3)
V1	$0.2PbO.0.8\ B_2O_3$	97.01	35	1.72
V2	$0.4PbO.\ 0.6\ B_2O_3$	124.62	30	3.48
V3	$0.5PbO.0.5\ B_2O_3$	138.39	20	2.41
V4	$0.6PbO.\ 0.4\ B_2O_3$	152.15	15	3.72
V5	$0.4PbO.0.6\ B_2O_3 + 0.01$ mol Se	-	30	4.36
V6	$0.2PbO.0.6\ B_2O_3 + 0.02$ mol Se	-	20	5.54
V7	$0.2PbO.0.6\ B_2O_3 + 0.03$ mol Se	-	30	3.52

Table 1 shows the density of the obtained samples. It can be seen that the highest the PbO content, the highest the glass density. It is well known that the density of a glass plays a role in controlling the refractive index, the highest the density of the glass, the highest the refractive index. Pb^{2+} ions are used to produce very high refractive index glasses and fine annealing is essential to minimize local index variation. It is also well known that, decreasing the cooling rate of the fused glass, the refractive index increses [5]. To confirm this, refractive index measurement need be done and the correlation of the PbO content with the variation on the refractive index may be determined.

The infrared absorption spectra are shown in Fig 1a and 1b for $xPbO(1-x)B_2O_3$.

Figure 1a. Infrared absorption spectra of xPbO(1-x)B$_2$O$_3$ with x = 0.2, 0.4, 0.6.
1b. Infrared absorption spectra of 0.4PbO0.6B$_2$O$_3$ undoped and doped with 0.01 mol Se

Table 2 and Table 3 summarize the major absorption bands observed in the V1, V2, V4 and V5 glasses an the vibration types, respectively.

Name	IR absortion bands (cm^{-1})				
V1	1625	1420	1180	830	670
V2		1350		900	660
V4		1280		910	700
V5		1350		935	670

Table 2
Observed IR absorption bands in xPbO(1-x)B$_2$O$_3$

With the increase in the PbO content a shift to a lower wavenumber for the 1400 cm^{-1} peak was observed, whereas the 1180 cm^{-1} peak tends to disappear. The spectra for the V1 sample is similar to the one of pure B$_2$O$_3$ glass, with two broad absorption bands at 1300-1700 and 720 cm^{-1} [10].

Figure 1 b shows the spectra for V2 and V5 glasses; for both glasses the same pattern is observed. The incorporation of Se produces a little shift to upper wavenumber for the 900 cm^{-1} peak and a little shift to lower wavenumber for the 1350 cm^{-1} peak observed in the V2 glass. According to this result, the incorporation of Se does not produce any structural change on the lead borate network. The infrared absorption spectra obtained in this work is similar to the previous one reported for the system xPbO(1-x)B$_2$O$_3$ with x = 0.1 – 0.8 [10].

Frequencies (cm^{-1})	Assigment
≤ 630	Characteristic vibration of PbO [13]. B-O-B and Pb-O-B bending vibration as well as borate ring deformation [2].
680- 720	Bending vibration of B-O-B in BO$_3$ triangles [14,15].
850-1050	B-O streching in BO$_4$ units. 1050 correspond to the antysimetric streching modes; whereas symetric streaching is located 850-900 [16].
1300-1600	Antysimetric B-O streching of BO$_3$.

Table 3
Vibration type of different IR wavenumbers.

DSC and TG curves for the $0.4PbO.0.6B_2O_3$ (V2) and $0.4PbO.0.6B_2O_3 + 0.01$ mol Se (V5) samples are shown in Figs 2a and 2b. Characteristic temperatures of the glass sample were obtained from the curves, such as glass transition temperature, Tg, temperature of the onset of crystallization, Tx, and temperature of the maximum crystallization peak, Tp. ΔT (ºC) = T_x- T_g and S (ºC) = (T_x- T_g) (T_p- T_x)/T_g factors were calculated to provide an indication of the tendency toward crystallization. For the V2 glass the characteristic temperatures determined were Tg=443 ºC, Tx=516 ºC, Tp= 594 ºC, ΔT=73 ºC, S(ºC)=13.7, while for the V2 glass Tg=435.7 ºC, Tx=496.7 ºC, Tp=560 ºC, ΔT=61 ºC, S(ºC)=8.86. A decrease of Tg and ΔT was observed with the addition of Se to the V2 glass used as a reference. The largest ΔT´s and S´s represent the best stability against devitrification [17]. It is well known that a glass which is stable against devitrification has a $\Delta T \sim 80$ ºC. Therefore, the obtained results indicate that our glasses are reasonable stable. The result of the thermal parameters determined for the V2 glass were different compared to previous reported ones, for glasses with the same composition. These differences may be due to a different heating rate used during the calorimetry studies or may be due to differences in the size of the grains used for the analysis.

Three exothermic peaks were found in the DSC curve, while only one peak was found in a previous report [10]. This founding suggest a crystallization in three steps or the crystallization of three different phases. In order to confirm our results, new DSC analysis and XRD analysis must be done. TG curve for the V5 glass shows a loss of mass near to 1 %. This loss may be due to the release of the incorporated Se. For the V5 glass no endothermic peak is observed.
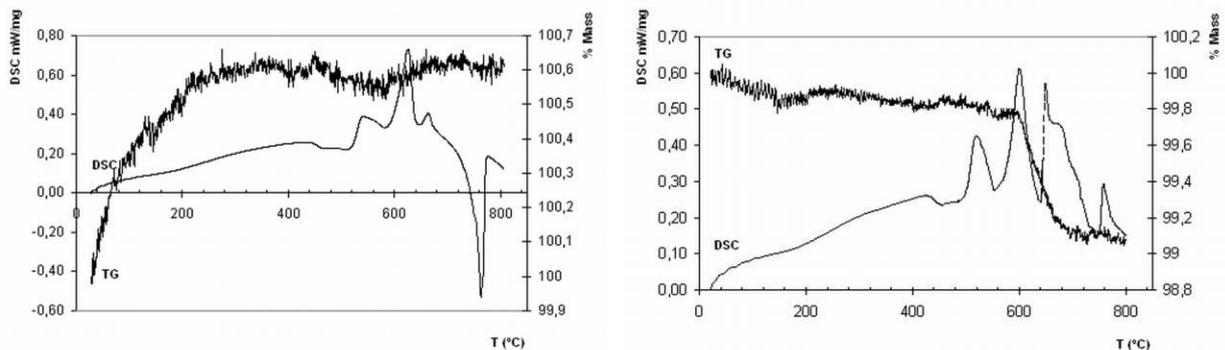

Figure 2a. DSC and TG for the $0.4PbO.0.6B_2O_3$ (V2) glass. **2b** DSC and TG for the $0.4PbO.0.6B_2O_3 + 0.01$ mol Se (V5) glass

The optical absorption spectra, in the 400-830 nm range, for the glasses of composition $xPbO(1-x)B_2O_3$ with x = 0.2, 0.4, 0.5, 0.6 are shown in Fig. 3a and 3b**.** From Fig.3 it can be deduced that the highest the PbO content, the highest the intensity of the peaks. A transmission peak in the yellow region of the visible spectrum (610 nm) was found. This result confirms the change in the appearance of the sample, which turns from transparent to yellowish, in accordance with a previous report [9].

The spectra for the glasses doped with Se are shown in Fig. 3b**.** The optical absorption for the doped sample follows the same pattern observed in the undoped glasses, showing one peak at 610 nm. The increase in the transparency peak may be due to the

increase in the content of Se as dopant, since no significant changes were observed, during the fusion, comparing with the $0.4PbO.0.6B_2O_3$ sample used as reference.
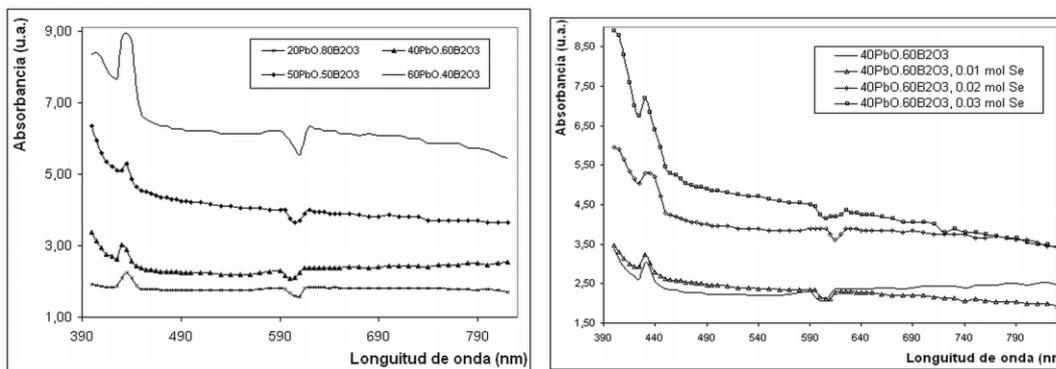
Figure 3a. *Absorbance spectrum of xPbO-(1-x)B_2O_3 glasses with x= 0.2, 0.4, 0.5, 0.6*
3b *Absorbance spectrum of 40PbO.60B_2O_3 doped with 0.01, 0.02, 0.03 mol of Se.*

4. CONCLUSIONS

The increase in the PbO content changes the structure of the borate glasses but also produces an increase in the density and in the refractive index of the samples. The existence of a wide glass forming region for the system xPbO.(1-x), x=0.2 – 0.6, without a phase separation, the transparency from the visible to the near-infrared range, create an excellent host to incorporate ions in order to obtain luminescents materials. The possible existence of crystalline phases must be confirmed by XRD, whereas the study of the crystallization mechanisms is promising in order to obtain a non-linear optical crystal. The incorporation of Se to lead borate glasses does not produce any appreciable change in their structure; the incorporation in the structure must be confirmed by XRD.

1. P.J. Bray, *J. Non-Crystalline Solids*, 75; 29-36 (1985).

2. W.A.Pisarski, T.Goryczka, B.Wodecka-Duś, M.Plońska, J. Pisarska, Structure and properties of rare earth-doped lead borate glasses, Materials Science & Engineering B, 122; 94-99 (2005).

3. V.F. Sears, Neutron News, 3; 29 (1992).

4. M.Santiago et. al.Phys. Status Solid A, 185 (2); 285 (2001).

5. Shelby J.E., Introduction to Glass Science and Technology, Chapter 10, Ed. The Royal Society of Chemistry, Cambridge, 1997.

6. B.N.Meera, J.Ramakrishna, J.Non-Crystalline Solids, 159; 1-21 (1993).

7. P.J.Bray, M.Levethal, H.O.Hope, Phys. Chem. Glasses, 4;47 (1963).

8. J.E.Shelby, J.Non-Crystalline Solids, 49; 287 (1982).

9. A.M.Zahra, C.Y.Zahra, B.Piriou, J. Non-Crystalline Solids, 155; 44-55, (1993).

10. Yin Chen et. al., Structure and crystallization kinetics of PbO-B2O3 glasses, Ceramics International, 33; 1341-1347 (2006).

11. P. Tarte, M.J. Pottier, in: P.H. Gaskell (Ed.), The Structure of Non-Crystalline Solids, 227 (1976)

12. Y.Chemg, H.Xiao, W.Guo, W.Guo, Thermochimica acta, 444; 173-178 (2006).

13. W.L.Konijnendijk, H. Verweij, Structural aspects of vitrous PbO-2B2O3 studies by Raman scaterring, J. Am.Ceram. Soc., 59;459-461 (1976).

14. A.K. Kamitsos, A.P. Patsis, M.A.Karakassides, G.D.Chryssikos, Infrared reflectance spectra of lithium borate glasses, J. Non-Cryst. Solids, 126; 52-67 (1990).

15. A.K.Hassan, L.Börjesson, L.M.Torell, The boson peak in glass formers of increasing fragility, J.Non-Cryst.Solids, 172/174; 154-160 (1994).

16. S.D.Ross, Spectrochim. Acta 28 A;1555 (1972).

17. N.C.de Souza, R. Lebullenger, M.C.C.Custódio,A.C.Hernandes, J.Non-Cryst. Solids, 273;94-99 (2000).