ORIGINAL ARTICLE

Ultrasonic measurement and elastic properties of the PbO-SrO-B₂O₃ glass system

Medidas ultrassônicas e propriedades elásticas do sistema vítreo PbO-SrO-B₂O₃

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Abstract: The PbO-SrO-B₂O₃ glass system with the of molar ratio of R (= PbO/B₂O₃) were prepared by fusion method. The elastic properties have been investigated using longitudinal and transversal ultrasonic wave velocity. Measurements were performed at room temperature and using pulse-echo technique at frequency of 5 MHz. The results indicate that, when increasing R value, the glass network stability decreases. This decrease indicates, of the increase the number of borate structures with non bridging oxygen (NBOs) at the expense of the decrease of borate units with tetrahedral structures. This feature may lead to the more open glass network structures and lower stiffness of the samples studied.

Palavras-chave: vidro, método de fusão, densidade, medidas ultrassônicas.

Resumo: Vidros do sistema PbO-SrO-B₂O₃, em função da razão molar R (=PbO/ B₂O₃), foram preparados usando a técnica de fusão. As propriedades elásticas tem sido investigadas a partir das medições das velocidades longitudinais e transversais das ondas ultrassônicas. As medidas foram realizadas a temperatura ambiente usando a técnica de pulso-eco a 5 MHz. Os resultados indicam que, com o aumento do valor de R, a estabilidade da rede do vidro diminui. A diminuição da estabilidade da rede vítrea indica o aumento do número de estruturas boratos com oxigênios não ligados às expensas da diminuição das unidades boratos com estruturas tetraédricas. Esta característica pode levar à ter no vidro estruturas mais abertas e a ter menor rigidez das amostras estudadas.

Keywords: glass, fusion method, density, ultrasonic measurements.

1 INTRODUCTION

Oxide glasses containing boron, lead and strontium have a history of glass formation, showing good properties such as high refractive index, density and infrared transmission. Lead-oxide (PbO) containing glasses provide low melting glasses [1].

There are wide applications of different types of glass, with lead oxide and silica content, among many others, being the quality control of the final properties of the product of paramount importance, since high quality controlled glass is applied in the fields of nanotechnology and optics such as lasers, sensors, semiconductors, etc [2], [3].

Borate glasses have been widely studied for their interesting properties, have high optical transparency and thermal stability. Luminescent borate glasses gain importance in application as a laser amplifier due to their high transparency

over a wide range of the electromagnetic spectrum in the visible region, which is extremely important for glass application in many optical devices as most of them act by light transmission.

The interest in the B_2O_3-PbO-SrO glass system was due to the fact that boron oxide and strontium oxide are network forming in the glass structure; in small additions of lead oxide, it acts as a network modifier and in larger additions PbO plays a network forming role, being a double behavior component in glass.

The propagation of the ultrasonic wave in solids, such as glass, provides valuable information on the mechanical properties and overall solid state molecular motion in the material [4]. Sonic waves are classified as ultrasound waves at frequencies exceeding 20 kHz. The measurement technique is based on the analysis of ultrasound wave propagation at 5 MHz and its relationship with the elastic properties of the material [5]-[6].

The objective of this work is to correlate the microstructure with the elastic properties of the investigated glass samples. For this, the samples were characterized by measurements of longitudinal and transverse ultrasonic wave propagation velocities, density and infrared absorption spectroscopy (FTIR).

2 CHARACTERIZATION TECHNIQUES

2.1 Sample preparation

For the preparation of glass based on boron, lead and strontium oxides, the melt fusion technique was used. The amounts of each powdered reagent have been carefully mixed to give the glass homogeneity; The material was then placed in a porcelain crucible to make the melting process in an electric oven up to 1000 ° C for one hour. After melting, the viscous mass was poured into a preheated steel mold at a temperature of 60 ° C for the molding process. After being placed in another oven for annealing at a temperature of 300 ° C for three hours, this procedure serves to remove the internal stresses of the glass. All samples followed the same procedure at the same temperature to have a similar history and to make a useful comparison between the different structures. After cooling, the samples were cut in the form of slabs, sanded, polished and also crushed to be subsequently subjected to proper characterization.

2.2 Density and molar volume

The density of the samples was estimated by the Archimedes principle method, using a scale whit precision of 0,0001g and a pycnometer, where the pieces (splinters of glass) of the samples were immersed in acetone solution, applying the expression 1.0:

$$\rho = \rho_H \left(\frac{m_a}{m_d} \right)$$

(Eq. 1.0)

Where, ρ is the density, ρ_H is the density of the water, m_a and m_d are the mass of the sample in the air and the mass of the submerged sample, respectively. The molar volume of the glass can preferably be used to describe the structure of the network and the disposition of the constructive units, since it deals directly with the spatial structure of the Oxygen network [7].

The measurement was made three times to obtain an average, this being a value with greater precision for calculating the density. The molar volume was calculated from the expression. 1.1:

$$V_m = \frac{\sum x_i M_i}{\rho}$$

(Eq. 1.1)

In which x_i is the molar fraction and M_i, the molar mass of the glass component. Table 1 illustrates the glasses compositions and values obtained for the different properties.

2.3 Ultrasonic measurements

The elastic modules of glass are influenced by many physical parameters, which in turn can be studied by measuring ultrasonic velocities. The variation of the ultrasonic velocity in the glass samples indicates the various changes in the structural configuration between the network former and the modifiers, directly and indirectly affecting other properties [8].

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Table 1 Chemical composition (% molar), proportion of the content of PbO/ B_2O_3 (R), thickness, density (ρ), molar volume (Vm) and glass sample packaging density (V_T).

Glasses	B_2O_3 (%)	SrO (%)	PbO (%)	R (=PbO/ B_2O_3)	Thickness (mm)	ρ (g/ cm³)	Vm (cm³)	V_T (cm³)
BPS-1	60	25	15	0,25	0,6	4,26	23,75	61,03
BPS-2	60	20	20	0,33	0,9	4,35	24,63	60,34
BPS-3	60	15	25	0,42	0,96	4,43	25,53	59,64
BPS-4	60	10	30	0,50	1,18	4,52	26,35	59,20
BPS-5	60	5	35	0,58	0,94	4,68	26,72	59,75
BPS-6	60	0	40	0,67	0,64	4,82	27,19	60,08

Source: the autors (2018).

For ultrasonic measurements, samples were used in a rectangular slabs and thickness varying from 0.6 to 1.18 cm (Table 1). The measurement was performed using an equipment that uses the pulse-echo technique for ultrasonic speed measurements, this measures the sound velocity in the samples with a given thickness with the pulse-echo system working at a frequency of 5 MHz, with the Transverse (Vs) and longitudinal (VL) velocities were calculated using the Equation 1.2:

$$V_s = \frac{2x}{\Delta t} \quad V_L = \frac{2x}{\Delta t}$$

(Eq. 1.2)

Having x as the sample thickness in (mm) and the time interval given as Δt. The other elastic properties of the studied glass were measured using the following relationships:

Longitudinal Module: $L = \rho V_L^2$,

Shear Module: $G = \rho V_s^2$,

Bulk Module: $K = L - \frac{4}{3}G$,

Young's Module: $E = (1+\sigma)2G$,

Poisson Coefficient: $\sigma = \frac{(L-2G)}{2(L-G)}$, e

Debye Temperature: $\theta_d = \left(\frac{h}{k}\right) \cdot \left(\frac{9N_A}{4\pi V_m}\right)^{\frac{1}{3}} V_{ms}$

Where L, G, K and E are the longitudinal, shear, bulk and Young modulus modules, respectively. The ρ is the density of the samples, σ is the Poisson coefficient, θ_d is the temperature of Debye, V_{ms} is the average speed of sound, V_m is the molar volume, h is the Plank constant, k is the Boltzmann constant and N_A is the Avogadro number.

The average sound velocity (V_{ms}) is defined by the relationship 1.3:

$$V_{ms} = \left[\frac{1}{3}\left(\frac{2}{Vs^3}\left(\frac{1}{V_L^3}\right)\right)\right]^3$$

(Eq. 1.3)

Other properties can be calculated as the acoustic impedance (Z) and the coefficient of thermal expansion (A) [6]. Acoustic impedance is: $Z = \rho V_L$.

2.4 FTIR infrared spectroscopy

For infrared measurements, a Fourier transform Nicolet Nexus 670 FTIR spectrometer was used, which measures from the near-infrared region of 4000 cm⁻¹ to 400 cm⁻¹ in the mid-infrared. The powdered samples were mixed with potassium bromide (KBr) and prepared as a pellet; these were prepared using the ratio of 1 mg of powder sample and 150 mg of KBr, this mixture was subjected to a loading of 3 t / cm² resulting in a thin and compact tablet shape.

This is a structural characterization technique that qualitatively and quantitatively determines different molecular groups.

3 RESULTS AND DISCUSSION

3.1 Density and volume molar

As the substitution of strontium oxide by lead oxide in the samples, there is an increase in the density provided by the high molecular weight of lead oxide, when compared to the other components of the glass system studied. The increase in density is also explained considering the formation of BO_4 units in the network of glass by the introduction of lead oxide in the sample.

The molar volume of the samples, Figure 1, showed unexpected behavior, since as the density increases, the molar volume also increases. The expansion in the structure of the vitreous matrix can be explained by the formation of non-bridging oxygen in the material during the substitution of the glass components [9].
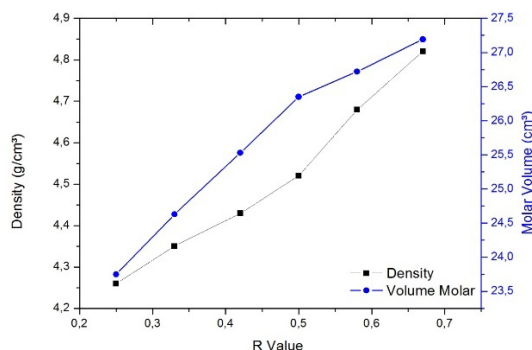

Figure 1. Density variation in R function of vitreous system and molar volume. Source: the autors (2018).

3.2 Ultrasonic study

Pulse-echo thickness measurement has a high sensitivity in detecting small internal discontinuities, so measurements were made at room temperature using a 5 MHz frequency ultrasonic meter.

Table 2 shows the variation of longitudinal ultrasonic velocities in the prepared samples. It is observed that velocities decrease as the value of the ratio R is increased. The longitudinal modulus (L) of the samples are calculated by the expression 1.4:

$$V_L{}^2 = \sqrt{\frac{k}{\rho}}$$

(Eq. 1.4)

Having k as volumetric modulus of elasticity, V_L as longitudinal velocity of sound and ρ as glass sample density.

When the substitution of components in the glass matrix occurs, new bonds between the ions are formed, causing the network expansion, which increases the molar volume, leading to a decrease in the packaging volume. Non-bridging oxygen formation decreases the peak pulse resistance, consequently contributing to the decrease in ultrasonic velocity [9]. Table 2 shows the results of ultrasonic velocity measurements and the various elastic modules.

Table 2 Longitudinal Velocity (V_L), Transverse velocity (V_s), Average sound velocity (V_{ms}), Longitudinal Module (L), Transversal Modulus (G), Bulk Module (K) e Young's Module (E).

Glasses	V_L (m/s)	V_S (m/s)	Vms (m/s)	L (10^{10} N/m²)	G (10^{10} N/m²)	K (GPa)	E
BPS-1	4918,67	2951,20	3264,75	103,06	37,10	53,59	75,42
BPS-2	4626,00	2775,60	3070,49	93,09	33,51	48,41	68,24
BPS-3	4541,33	2724,80	3014,29	91,36	32,89	47,51	66,99
BPS-4	4361,00	2616,60	2894,60	85,96	30,95	44,69	63,12
BPS-5	4209,00	2525,40	2793,71	82,91	29,85	43,11	60,92
BPS-6	4104,00	2462,40	2724,01	81,18	29,23	42,21	59,68

Source: the autors (2018).

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Elastic modules allow a macroscopic view of material rigidity from inter atomic bonding energies and material connectivity. Figure 2 shows a decreasing trend in elastic modulus which may be associated with the number of unit bonds per glass unit formula and the average strength of these bonds, which are related to the values of the forces between cations and anions. Thus, both decreasing average bond strength and number of bonds explain the decrease values in elastic modulus [10].
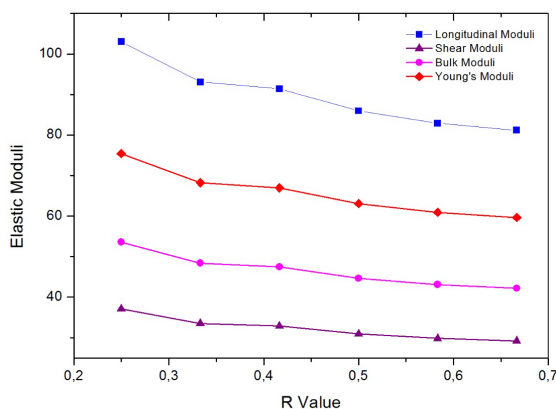

Figure 2. Variation of elastic modules for the BPS glass system. Source: the autors (2018).

Debye temperature is the value at which all vibration modes in a solid are excited, which is directly proportional to the average speed of sound [11]. The decrease is observed in the average speed of sound and the temperature Debye values, Table 3; that can be attributed to the formation of non-bridging oxygen due to the substitution of the components in the glass matrix, leading to a decrease in the stiffness of the glass [4], [12].

Table 3 Debye Temperature (θ_d), Poisson Coefficient (σ), Acoustic Impedance (Z) and Coefficient of Thermal Expansion (A).

Glasses	θ_d	σ	Z $(10^{-7}$ kg / m^2.s)	A
BPS-1	411,7409	0,21879	2,09	114099,81
BPS-2	382,5736	0,21878	2,01	107309,87
BPS-3	371,1051	0,21874	2,01	105345,53
BPS-4	352,6334	0,21869	1,97	101161,87
BPS-5	338,7643	0,21872	1,96	97635,47
BPS-6	328,3990	0,21867	1,98	95199,47

Source: the autors (2018).

The increasing behavior of acoustic impedance indicates that we have increased resistance to ultrasonic wave propagation in the sample, which can be verified by decreasing velocity as glass increases its density [13].

3.3 FTIR infrared spectroscopy

The properties that certain glass provide us can be analyzed by the structural study conducted by spectroscopy techniques. Infrared absorption spectroscopy allows us to verify if the material has presented significant structural changes, so it is important to know what are the peaks of the characteristic absorption bands of each structure. Table 4 shows the positions of the spectra absorption peaks obtained for each sample. It is possible to verify the displacement of some bands by the insertion of the network modifier in the matrix, such as lead oxide, and by the formation of tetrahedral units of BO$_4$; It is possible to verify the displacement of some bands by the insertion of the network modifier in the matrix, such as lead oxide and by formation of tetrahedral units of BO$_4$; therefore the increase of non-bridging oxygen to bridging oxygen's in the 800 to 1200 cm^{-1} range [13].

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Table 4 position of the peaks for the FTIR spectra of the vitreous systems.

Glasses	Vitreous system B_2O_3 - SrO – PbO				
	Peaks in the middle infrared (cm^{-1})				
BPS-1	2350	1640	1360	1030	682
BPS-2	2370	1640	1370	993	682
BPS-3	2360	1640	1420	1050	682
BPS-4	2360	1640	1430	1100	661
BPS-5	2350	1640	1390	1050	661
BPS-6	2350	1640	1390	1000	682

Source: the autors (2018).

Figure 3 shows the infrared absorption spectra for all samples of the glass system B_2O_3 – PbO – SrO, most peaks are in the same position.
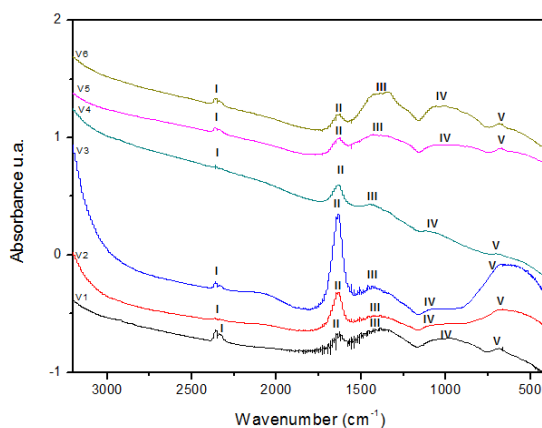

Figure 3. Samples absorption spectra in infrared. Source: the autors (2018).

For qualitative analysis, the spectrum was divided into five regions: (I) 2300-2350 cm^{-1}; (II) 1500-1700 cm^{-1}; (III) 1200-1550 cm^{-1}; (IV) 800-1200 cm^{-1} and (V) 700-1000 cm^{-1} respectively.

The spectrum in region (I) has bands close to 2300-2350 cm^{-1}, the vibrations of different C-O bonds or ambient CO2 concentrations in the Infrared [14] are attributed, these are not part of the glass structures. In region (II), bands between 1500-1700 cm^{-1} are attributed to molecular vibrations of hydroxyl (water) [15]. In region (III), the bands found between 1200-1500 cm^{-1} are attributed to molecular vibrations of borate group units with non-bridging oxygen [15]. In region (IV), bands between 800-1200 cm^{-1} are assigned to borate groups with BO4 tetra borate structures, extending in the range 1200-1600 cm^{-1} are related to BO3 triborate groups [16]–[17]. In the last region, region (V), bands close to 700 cm $^{-1}$ are assigned to borate group bonds [15]-[18]. From 700 to 400 cm^{-1} the bands do not appear explicitly, but there may be bonds due to the Sr-O and Pb-O of the heavy atoms in the glass.

3 CONCLUSIONS

PbO-SrO-B_2O_3 glass samples are potential candidates for transparent ultraviolet and gamma ray protection materials [1]. The results of the ultrasonic velocity measurements of the PbO-SrO-B_2O_3 glass system indicate non-bridging oxygen formation with increasing PbO to B_2O_3 ratio. In addition, the glass structure becomes less rigid at higher R ratio values. On the contrary, the gamma ray protection properties improve with increasing PbO / B_2O_3 ratio of the glass samples.

FTIR spectral studies indicated the conversion of BO3 to BO4 structural units, caused by the addition of PbO in the matrix. These changes contributed significantly to obtaining denser glasses, a fact confirmed by the ultrasonic study. For these reasons, the characterization of the samples through ultrasonic and spectroscopic studies was presented as a powerful tool to explore the structural characterization of the glass type.

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