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EFFECT OF La_2O_3 ON THE STRUCTURE AND THE PROPERTIES OF STRONTIUM BORATE GLASSES

Article Highlights

- Selected lanthanum-strontium-borate glasses were prepared by conventional melt--quenching technique
- The density and the molar volume were increasing with increasing La_2O_3 content
- Oxygen molar volume values were increasing opposite to oxygen packing density values
- The HSM results were employed for obtaining the viscosity curves using VFT equation and GS

Abstract

The selected lanthanum-strontium borate glasses were prepared by a conventional melt-quenching technique. The compositions of the investigated glasses were chosen to be: 5.7, 9.5, 14.3, 19.1 mol% for La_2O_3, 22.9, 19.1, 14.3, 9.5 mol% for SrO and 71.4 mol% for B_2O_3. The density, molar volume, oxygen molar volume, oxygen packing density, oxygen/boron ratios and structural transformations in the glass network were investigated according to the substitution of SrO by La_2O_3. The density and the molar volume increased in parallel with La_2O_3 content increase. Simultaneously, oxygen molar volume values increased while the oxygen packing density values decreased. A hot stage microscope (HSM) and a differential thermal analysis (DTA) were used to determine the characteristic temperatures. By increasing the content of lanthanum, the glass transition temperatures, changed with the same trend as the molar volume. Glass stability parameters were calculated from the temperatures obtained by DTA and HSM. The HSM results were used to obtain the viscosity curves by applying the Vogel--Fulcher-Tamman (VFT) equation.

Keywords: glass, DTA, HSM, glass viscosity.

A growing interest recently has been focused on alkaline earth-borate glasses due to their applications as laser hosts, nonlinear optical and other photonic devices [1]. The structure of vitreous B_2O_3 consists of a random network of [BO_3] triangles connected by bridging oxygen at all three corners to form completely linked network. The addition of a network modifier in B_2O_3 glass could induce the conversion of [BO_3] triangles to [BO_4] tetrahedra. This conversion of boron from 3- to 4-fold coordination occurs only until the network reaches some critical concentration of tetrahedral coordinated boron, and is then followed by a formation of non-bridging oxygen (NBO) caused by additional network modifier [2]. Therefore in borate glasses, the main structural units are both [BO_3] triangles and [BO_4] tetrahedra forming boroxol rings and chains with different number of NBO [2].

The present study aims to characterize the physical and structural properties of the selected lanthanum-strontium borate glasses. Glass compositions for the synthesis were selected within the glass forming range of increasing content of La_2O_3, decreasing content of SrO and constant content of B_2O_3. Also, the goal of this work was to determine glass stability and viscosity behavior of the selected glasses. The physical and structural properties of the glasses were investigated by measuring the densities of the glass samples, and calculating the molar volume, oxygen molar volume, oxygen packing density values and

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ratios of oxygen to boron atoms [2,3]. Differential thermal analysis (DTA) was applied to determine the glass transition temperature, T_g, the crystallization onset, T_x, and the crystallization peak temperature, T_p. Hot stage microscope (HSM) was acquired for estimation the temperatures of: the first shrinkage (T_{FS}), the maximum shrinkage (T_{MS}), the deformation (T_D), the sphere T_S, the half-ball temperature (T_{HB}) and the flow temperature (T_F). The glass stability (GS) parameters were calculated on the basis of these characteristic temperatures. Viscosity curves of the glasses were set based on the results from the HSM using the Vogel-Fulcher-Tamman (VFT) relation [4].

EXPERIMENTAL

The glasses with nominal composition $y$$La_2O_3$-$x$SrO-(100-$x$-$y$)$B_2O_3$, where y = 5.7, 9.5, 14.3 and 19.1 and x = 22.9, 19.1, 14.3 and 9.5 (Table 1), were melted in a covered platinum crucible in an electric furnace and melted at 1200 °C for 30 min. The reagent grade of H_3BO_3, $SrCO_3$ and $La_2(CO_3)_3$ were used as raw materials, mixed and homogenized in an agate mortar. Covered crucible and relatively short melting time at relatively low temperature were applied in order to minimize boron evaporation. The melt was cast and cooled on a stainless steel plate in air at room temperature. The measurements of the weight loss due to the melting indicated that the glasses were within 1-2 wt.% of the desired compositions. The obtained glasses were transparent without visible bubbles.

Table 1. The glass compositions, density, molar volume, oxygen molar volume and oxygen packing density

Parameter	Glass sample			
	1	2	3	4
La_2O_3, mol%	5.7	9.5	14.3	19.1
SrO, mol%	22.9	19.1	14.3	9.5
B_2O_3, mol%	71.4	71.4	71.4	71.4
ρ, g cm^{-3}	3.21	3.25	3.56	3.66
V_m, cm^3 mol^{-1}	28.65	30.90	31.21	33.26
V_o, cm^3 mol^{-1}	11.28	11.81	11.50	11.84
OPD, mol dm^{-3}	88.68	84.70	86.95	84.45
O/B	1.78	1.83	1.90	1.97

The densities of the glasses were determined by using the pycnometer method, with uncertainty ±0.01.

A hot-stage microscope (E. Leitz Wetzlar) equipped with a Cannon camera, and differential thermal analysis (DTA) were used to determine the characteristic temperatures during the heating of the glass powder. The samples were prepared by crushing and grinding the bulk glass in an agate mortar and sieving to grain size < 0.048 mm. The DTA curves were recorded by a Netzch STA 409 EP instrument at the heating rate 10 °C min^{-1}, using Al_2O_3 as a reference material.

HSM analysis was performed on the previously prepared glass powder pressed into cylinders, which were placed on a platinum plate, on an alumina support, contacted with a (Pt/Rh/Pt) thermocouple. The heating rate was 10 °C min^{-1}. With temperature increase, the geometric shape of the samples changed. Micrographs obtained were used to determine the temperatures corresponding to the typical glass viscosity points [5-7]. Combination of the DTA and HSM methods enabled determination of the GS parameters. The HSM results were applied to obtain viscosity curves using the VFT relation [4,5].

RESULTS AND DISCUSSION

The densities (ρ) of the glass samples determined in the present study are shown in Table 1. The molar volume (V_m) of the glass samples was calculated using the relative molecular mass (M) and density (ρ) by the following relation [8]:

$$V_m = \frac{M}{\rho} \tag{1}$$

These values are included in Table 1 together with the values of oxygen molar volume (V_o) and oxygen packing density (*OPD*), calculated using the following relations:

$$V_0 = V_m \frac{1}{n} \tag{2}$$

$$OPD = 1000 \frac{\rho}{M} n \tag{3}$$

where n is the number of oxygen atoms per formula unit.

The following equation, based on the glass stoichiometry, was used for the calculated number of oxygen:

$$\text{Number of oxygen} = x + 3y + 71.4 \tag{4}$$

where x is mol% of the SrO, y is mol% of the La_2O_3 and 71.4 is constant content of the B_2O_3 in the glasses.

The density and the molar volume of the glasses increased in parallel with La_2O_3 content increase in the glasses. The increase of the density could be explained considering the higher relative molecular mass of lanthanum oxide as compared to the relative molecular mass of strontium oxide. With the increase

of La_2O_3 content in the glasses, the oxygen content rises as well, increasing the molar volume of the glass. The oxygen molar volume increases opposite to the oxygen packing density with the increasing La_2O_3 content in glasses, indicating a less tight packing of the glass network and more open glass network [9]. The O/B ratios increased together with La_2O_3 content increase. The ratios of the O/B indicated the presence of the metaborate structures, so the both $[BO_3]$ triangles and $[BO_4]$ tetrahedra units are present in the glass systems.

The characteristic temperatures obtained by HSM and DTA measurements are summarized in Table 2. The T_g exhibits the same trend of the changes as of V_o. The increase in the T_g could be attributed to the greater bond strength of the La-O (244 kJ mol^{-1}) bond in comparison with the Sr-O bond (134 kJ mol^{-1}). The addition of the La_2O_3 increased the T_g, which can be explained by higher field strength of La^{3+} (0.52 $Å^{-2}$) with respect to Sr^{2+} (0.32 $Å^{-2}$) [10]. The decline in the Tg for the sample 3 could be explained by stoichiometry composition of this glass [11].

Table 2. Characteristic temperatures (°C) obtained by HSM and DTA

Temperature	Glass sample			
	1	2	3	4
T_{FS}	600	600	600	680
T_{MS}	680	719	739	740
T_D	700	720	760	760
T_S	740	760	800	800
T_{HB}	840	900	1000	1050
T_F	890	950	1020	1060
T_g	622	640	638	644
T_x	735	763	723	765
T_p	809	792	749	792

The photomicrographs for the glass sample 3, obtained by HSM, with the graphs of the shrinkage are shown in Figure 1 [11]. The shrinkage of the samples is determined by the ratios of A/A_0 and H/H_0, where A_0 is the initial area of the sample whereas A is the area at the temperature T, H_0 is the initial height and H is the height at the temperature T.

The temperatures corresponding to the typical viscosity points were determined from the photomicrographs, by observing the geometric shape of the specimens, obtained by HSM (Figure 1). The temperature of the first shrinkage (T_{FS}) is the temperature at the typical viscosity, log η = 9.1±0.1, where η is in dPa·s. At this temperature the sample shrinks to about 3-5% of its initial height. The temperature of the maximum shrinkage (T_{MS}) is the temperature where the sample shrinks to the maximum possible level, but still has sharp edges, before softening, at viscosity log η = 7.8±0.1. The T_D is the point of log η = = 6.3±0.1 when the first signs of softening could be observed and the edges of the samples are rounded. The T_S is the temperature at which the sample becomes spherical, at log η = 5.4±0.1, whereas the half-ball temperature (T_{HB}), at log η = 4.1±0.1, is the temperature at which the observed section of the sample forms a semicircle. The flow temperature (T_F) is the temperature at which the height of the drop of molten glass corresponds to a unit on the microscopic scale, at log η = 3.4±0.1 [5].

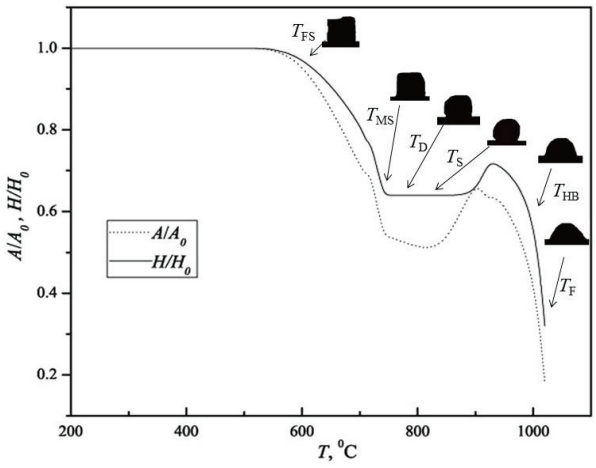

Figure 1. The photomicrographs obtained by HSM with the graphs of the shrinkage.

These temperatures obtained by DTA and HSM were used to determine the GS parameters, the Hruby parameter, K_H, the Weinberg, K_W, and the parameter K_{LL} proposed by Lu and Liu [12]. Within this work, the used T_F was determined by HSM.

The glass stability parameters are defined by the equations:

$$K_H = \frac{T_x - T_g}{T_F - T_x} \quad (5)$$

$$K_W = \frac{T_p - T_g}{T_F} \quad (6)$$

$$K_{LL} = \frac{T_p}{T_g + T_F} \quad (7)$$

The calculated parameters for the glasses are shown in Table 3. The resistance of a given glass against crystallization upon reheating defines GS. High values of the parameters indicate high glass stability, higher stability of the glass with respect to

devitrification. The lowest values of the parameters are related to the sample 3. This glass shows the smallest GS and the highest tendency toward crystallization [11]. Increase of lanthanum content in the glasses was followed with decrease of the GS.

Table 3. Glass stability parameters

Glass sample	K_H	K_W	K_{LL}
1	0.73	0.21	0.53
2	0.66	0.16	0.50
3	0.29	0.11	0.45
4	0.41	0.14	0.46

The viscosity values of the glasses and VFT parameters were determined based on the photomicrographs and the typical temperatures, obtained by HSM:

$$\log\eta = A + \frac{B}{T - T_0} \tag{8}$$

where η is viscosity in dPa·s, A, B and T_0 (K) are constants. These constants were obtained from Eq. (8) by resolving a couple equations, using temperatures and viscosity values obtained by HSM (Table 4). These equations are used to calculate the viscosity for the glasses, $\log\eta = f(T)$ as shown in Figure 2 in the upper left corner. The activation energy of the viscous flow is obtained from the Arrhenius equitation, from the slope of the $\log\eta = f(1/T)$ curves (Figure 2, Table 4).

Table 4. VFT parameters and the activation energies of the viscous flow

Parameter	Glass sample			
	1	2	3	4
A	-0.315	-3.30	-6.12	1.22
B	1780	5103	11603	808
T_0 / K	684	462	135	1142
E_a / kJ mol^{-1}	365	340	297	543

CONCLUSION

The investigation of the physical properties of the glasses showed that the substitution of SrO by La_2O_3 increased the density, molar volume, oxygen molar volume and decreased oxygen packing density. The density increase was attributed to the higher relative molecular mass of the glass containing more La_2O_3. The decrease of the oxygen packing density indicated a less tightly packed the glass network. The increase in the T_g could be attributed to the greater

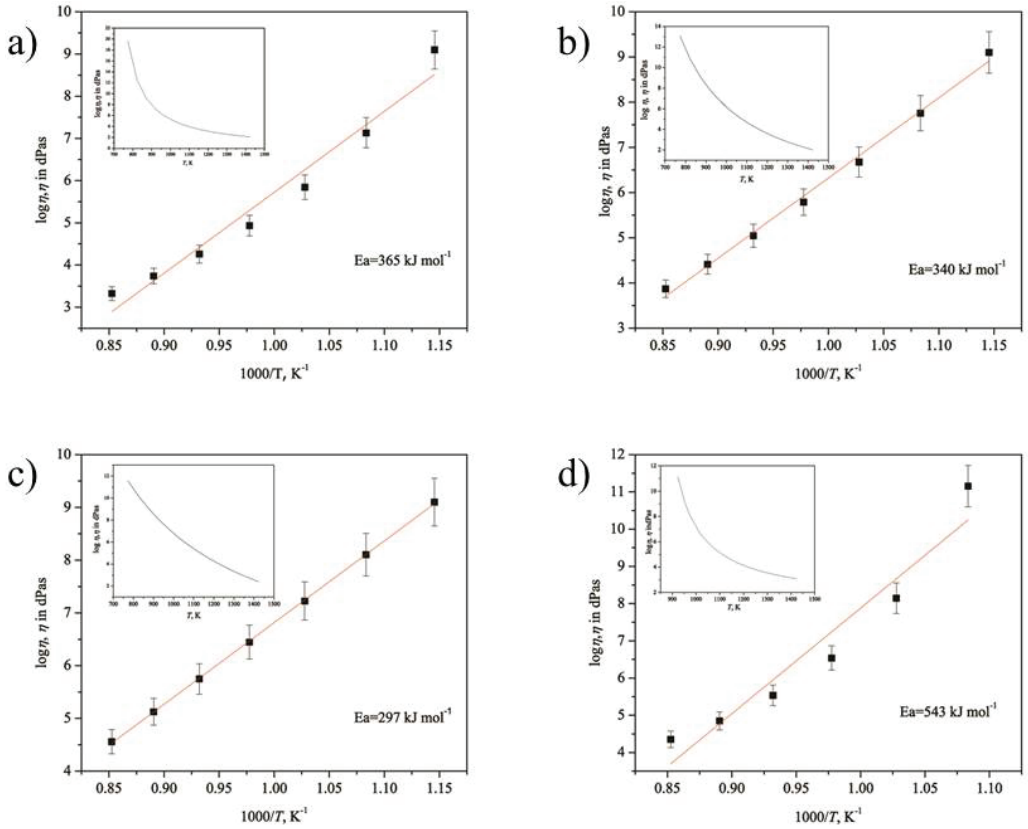

Figure 2. Log η versus reciprocal temperature curves for the glass samples: a) 1, b) 2, c) 3 and d) 4.

bond strength of the La-O (244 kJ mol^{-1}) bond in comparison to the Sr-O bond (134 kJ mol^{-1}). Parallel with lanthanum content increase, the GS decreased.

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NAUČNI RAD

UTICAJ La_2O_3 NA STRUKTURU I SVOJSTVA STRONCIJUM-BORATNIH STAKALA

Izabrana lantan-stroncijum-boratna stakla su dobijena uobičajenom tehnikom topljenja i naglog hlađenja rastopa stakla. Sastavi ispitivanih stakala su: 5,7; 9,5; 14,3; 19,1 mol% La_2O_3; 22,9; 19,1; 14,3; 9,5 mol% SrO i 71,4 mol% B_2O_3. Ispitivan je uticaj izmene SrO sa La_2O_3 na: gustinu, molarnu zapreminu, molarnu zapreminu kiseonika, gustinu pakovanja kiseonika, odnose kiseonik/bor kao i strukturalne transformacije u mreži stakla. Gustina i molarna zapremina se povećavaju sa porastom sadržaja lantan-oksida. Primećen je trend rasta molarne zapremine kiseonika dok gustina pakovanja kiseonika opada. Za određivanje karakterističnih temperatura korišćene su diferencijalna termijska analiza (DTA) i termomikroskop (TM). Sa porastom sadržaja lantan-oksida temperature transformacije stakla su se menjale na isti način kao i molarna zapremina. Parametri stabilnosti stakla izračunati su na osnovu temperatura određenih TM i DTA. Na osnovu rezultata dobijenih termomikroskopom postavljene se krive viskoznosti upotrebom Vogel-Fulcher-Tamman (VFT) jednačine.

Ključne reči: staklo, DTA, TM, viskoznost stakla.