Effect of Li_2O and Na_2O Addition on Structure and Properties of Glass System (B_2O_3-ZnO)

D. Aboutaleb, B. Safi, S. Laichaoui, and Z. Lemou

***Abstract*—This work present the study of the effect of adding alkali oxides Li_2O and Na_2O on the variation of the structure and properties of the glass system (B_2O_3-ZnO) prepared by melt quenched method. Several tests and characterization methods were used in this study. Some of properties were investigated by measure like density and others by calculations. The dilatometric curves were obtained and they revealed that the transition temperature (Tg) and softening (Ts) have increased by addition of Li_2O and Na_2O content. It was also noted that this finding has been proven by Differential Thermal Analysis (DTA) and an improvement of mechanical properties of studied glasses.**

***Index Terms*—Glass (B_2O_3-ZnO), melt quenched, density, glass structure, DTA analysis, dilatometrie.**

I. Introduction

Borate glasses are glasses known for their low glass transition temperature and their boron anomaly which is manifested by the double coordination of the boron which can have either coordination three or coordination four according to the composition of the glass bath and the configuration of the atoms of the neighborhood [1]-[4]. Borate glasses, in particular, have been the subject of numerous infra-red studies due to their structural peculiarities [5]-[8]. In pure B_2O_3 glass structure most of the boron is involved in B_3O_6 (boroxol) ring. Addition of modifier breaks boroxol ring and thereby produced BO_3 and BO_4 units [6]-[8]. In addition, modifier also changes the physical properties along with structural modifications.

Recently, a study of oxide glasses doped with transition metal ions (TMI) has received considerable attention due to their attractive combination of physical and chemical properties. TMI doped borate glasses have application in microelectronics, optical glasses and solid state laser [9]-[11]. Structural characterization and optical properties of manganese and zinc oxide containing B_2O_3 glass with an intention to precipitate Mn-doped ZnO crystal in the borate glass matrix, which may lead to a new composite spintronics material, were investigated [12].

In this work, network modifiers Li_2O and Na_2O have been introduced, which are alkaline oxides, in order to study their influence on the structure and properties of the glasses in B_2O_3-ZnO system.

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II. Experimental Study

A. Preparation of Studied Glass System

Two glass systems were studied; Li_2O - B_2O_3 - ZnO (LBZ) and Na_2O-B_2O_3-ZnO (NBZ). The glasses selected were prepared starting from the following chemical raw materials, lithium carbonate, sodium carbonate, orthoboric acid and zirconium oxide. The finely crushed mixture was then placed in a platinum crucible and introduced to an electric furnace at temperature ranging 1000 ℃ with a bearing for one (01) h. The liquid was then cast in a graphite mold preheated to approximately 250 ℃ to limit the thermal shocks during hardening. The compositions of studied glasses are given in Table I and Table II.

TABLE I: Chemical Compositions of Studied Glasses Li_2O_3- B_2O_3-ZnO (%wt.)

Glass	Li_2O_3	B_2O_3	ZnO
LBZ 1	70	25	05
LBZ 2	65	30	05
LBZ 3	60	35	05
LBZ 4	55	40	05
LBZ 5	50	45	05

TABLE II: Chemical Compositions of Studied Glasses Na_2O-B_2O_3-ZnO (%wt.)

Glass	Na_2O	B_2O_3	ZnO
NBZ 1	70	25	05
NBZ 2	65	30	05
NBZ 3	60	35	05
NBZ 4	55	40	05
NBZ 5	50	45	05

B. Test Methods

DTA and TGA Analysis: The apparatus used was a simultaneous thermal analysis apparatus type STA 449 C. Jupiter. It can give the differential variations in temperatures, changes in weight during treatment and thermal enthalpies exchanged. It works at high temperature furnace with protective tube and of Al_2O_3 and temperature range 25 to 1550 ℃. The type of the thermocouple used is Pt/Pt Rh. The glass transition temperature (Tg) was determined from the second endothermic peak of DTA curve whereas the crystallization temperatures (Tc) was determined by the first exothermic peak of DTA curve.

Dilatometric Analysis: The expansion curves of samples were determined using a dilatometer DIL 402C (at an average speed of heating of 5 K•min-1. The sample had a rectangular shape with an 8 mm width and a 20-25 mm length. The glass transition temperature (Tg) was determined from the

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expansion curve using the interception method, whereas the softening temperatures (Ts) was determined by the maximum temperature of expansion curve.

Density and molar volume Measurements: The densities were determined out using Archimedes' method with xylene as an immersion fluid. The relative error in these measurements was about ± 0.03 g•cm^{-3} and the molar volume *Vm* was calculated from the molecular weight *M* and the density ρ according to the relation: *Vm* = *M*/*ρ*.

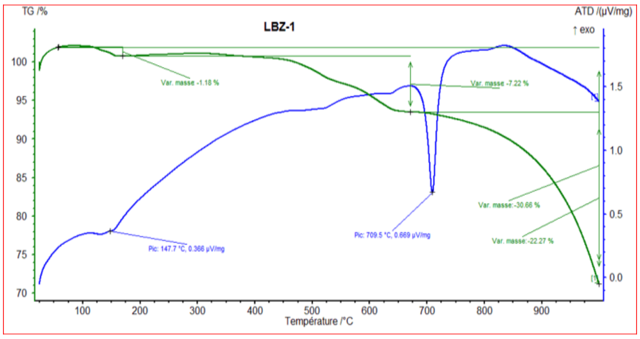
III. Results and Discussions

A. DTA and TGA Analysis

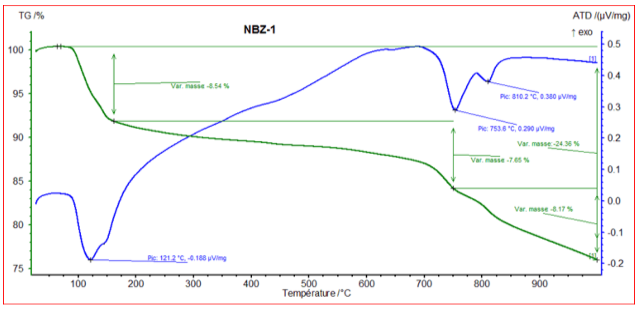
DTA analyzes were carried out on two samples (LBZ1) and (NBZ1). The determined curves are shown in Fig. 1. The glass transition temperature (Tg) was determined from the second endothermic peak of DTA curve whereas the crystallization temperature (Tc) was determined by the first exothermic peak of DTA curve. This is shown in Table III.

TABLE III: Tg and Tc Temperatures of Glasses LBZ1 and NBZ1

Glass	Tg	Tc
LBZ1	147.7	675
NBZ1	149	679



(a)



(b)

Fig. 1. DTA curve of studied glasses (a) LBZ (b) NBZ.

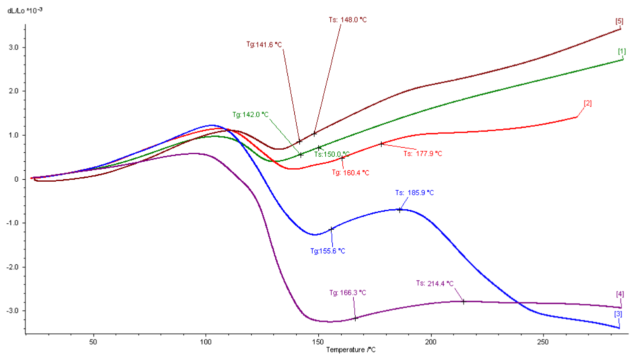
It is realized that the glass transition temperature of the glass LBZ1 is lower than that of the glass NBZ1; this is at the low melting point of the lithium carbonates relative to the sodium carbonates, (same for the crystallization temperatures).

B. Dilatometric Analysis

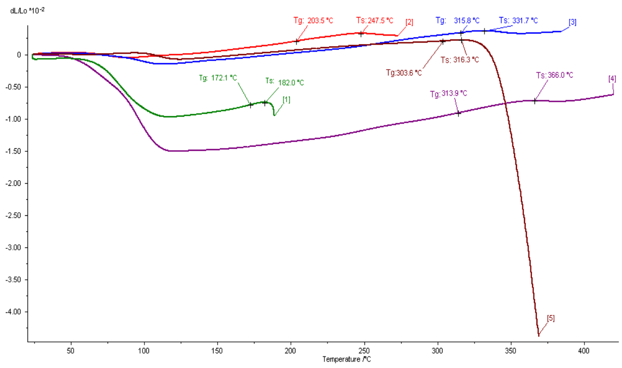
LBZ glass system: Fig. 2(a) shows the shape of thermal expansion curves of the LBZ glasses, this vitreous system exhibits show a clear phase separation, and for this reason the thermal expansion curves represent somewhat special shapes (note the existence of two peaks For the two phases present in the glass); the maximum peak was taken for the determination of Ts and the maximum inflection point for the determination of Tg.

NBZ glass system: For these thermal expansion curves, NBZ1 and NBZ4 samples have, in particular, the curves of the lenses separated in phases (Fig. 2(b)). In contrast, the other glasses are transparent and homogeneous and their curves of thermal expansion have the appearance of those of homogeneous glasses.

From the thermal expansion curves recorded in Fig. 2, the glass transition temperatures Tg and the dilatometric deformation temperature Ts were determined. Table IV gives the obtained results Tg and Ts of all glass samples.



(a) LBZ



(b) NBZ

Fig. 2. Thermal expansion curves.

TABLE IV: Glass Transition Temperatures (Tg) and Dilatometric Deformation (Ts) of Glasses Studied

Glass	Tg (℃)	Ts (℃)
LBZ 1	142.0	150.0
LBZ 2	160.4	177.9
LBZ 3	155.6	185.9
LBZ 4	166.3	214.4
LBZ 5	141.6	148.0
NBZ 1	172.1	182.0
NBZ 2	218.0	246.2
NBZ 3	322.1	330.4
NBZ 4	323.3	363.2
NBZ 5	306.8	316.8

LBZ glass system: Elaborated glasses have low glass transition temperatures (their chemical compositions contain large amounts of fluxes Li_2O and B_2O_3). The system lenses (LBZ) are completely opaque (milky white color) and have phase separations. With the addition of B_2O_3 content and decrease of % Li_2O, the glass transition and dilatometric transitions increase except for the LBZ5 glass which decreases (see Fig. 3).

The structure becoming rigid probably due to the creation of bridging oxygens with the tetrahedral configuration of boron in favor of the boron trigonal configuration with respect to the first glass (NBZ1); But the structure becomes less rigid for glass LBZ5 (transformation of the tetrahedral form of boron to the triangular form).

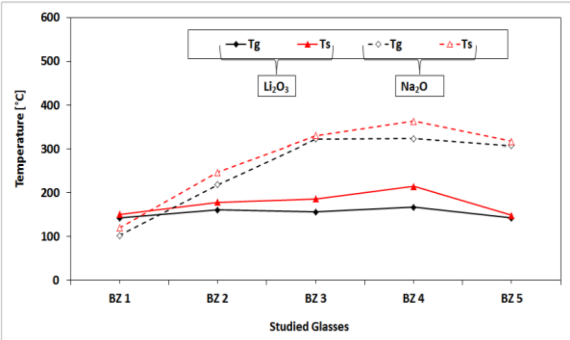


Fig. 3. Temperatures variation Tg and Ts of the glasses elaborated as a function of Li_2O and Na_2O content.

Fig. 4. Effect of Li_2O addition on the structure and opacity of studied glass system (B_2O_3-ZnO).

TABLE V: DENSITY AND MOLAR VOLUME OF STUDIED GLASSES

Glass	ρ (g /cm^3)	*Vm* (mol /cm^3)
LBZ 1	4.08	36.08
LBZ 2	3.76	37.17
LBZ 3	3.11	38.78
LBZ 4	1.92	39.99
LBZ 5	1.33	41.69
NBZ 1	2.35	27.27
NBZ 2	2.34	27.62
NBZ 3	2.33	27.84
NBZ 4	2.32	28.15
NBZ 5	2.20	29.79

NBZ glass system: It can be noted that NBZ glasses are almost all opaque except for the variants NBZ2 and NBZ5 (see Fig. 4)). As the percentage of B_2O_3 and decrease of Na_2O in the composition is added, an increase in glass transition and dilatometric temperature is observed such as the system (LBZ).

C. Determination of Glass Properties

It is noted that the density of elaborated glasses decreases with the decrease of lithium or sodium oxide and increase of boron oxide (Fig. 5). This can be explained that due to the increase in the molar volume by Boron oxide addition.

The structure of these glasses is composed of tetrahedral or triangles boron which make up the main unit, while lithium or sodium and zinc ions are modifiers which occupy the voids between the structural units and The quantity of modifying ions that fill the voids so the density has decreased (Fig. 6).

D. Theoretical Calculs of Properties

In the glass structure, the various components contribute a share defined in the effect of some properties. There would be thus a possibility of calculating by means of additive formulas these properties to leave the composition [1]. After calcul all these properties are given in Table VI.

According to the calculation methods, a decrease in the coefficients of thermal expansion is observed as the oxides of lithium or sodium are decreased, and by increasing the boron oxide, the non-bridging oxygens decrease and the structure becomes rigid.

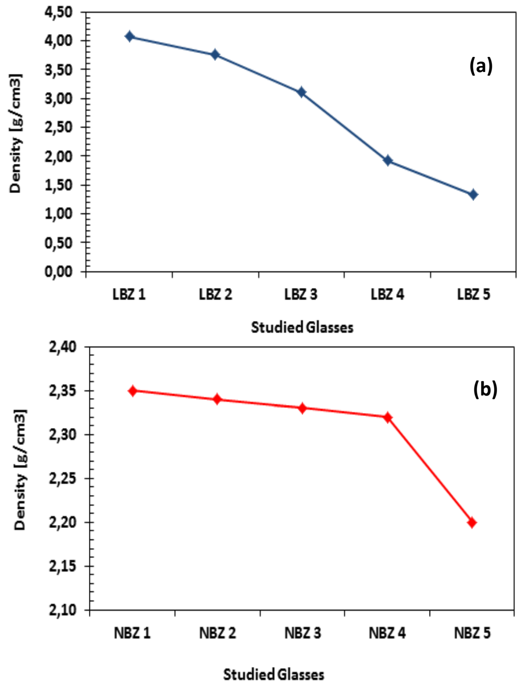


Fig. 5. Density variation of elaborated glasses as a function of Li_2O and Na_2O content for tow studied glass system (LBZ and NBZ).

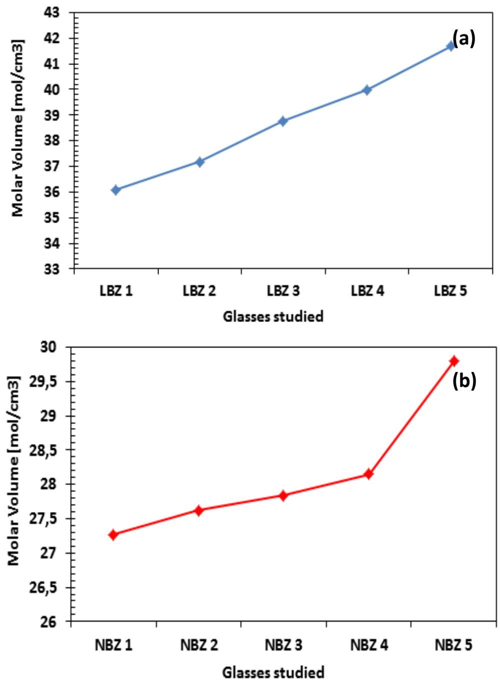


Fig. 6. Molar volume variation of elaborated glasses as a function of Li_2O and Na_2O content for tow studied glass system (LBZ and NBZ).

The refractive index is an optical property related to the polarizability of the oxygen atoms, so a decrease in the refractive index is observed as the lithium or sodium oxide is decreased, decreasing the Oxygens and therefore their polarizability decreases. The same behavior is observed for dispersion.

TABLE VI: CALCULATED PROPERTIES OF STUDIED GLASSES

Glass	α	nd	d	μ	E	G	σt	δc	σ
LBZ 1	15.56	1.72	0.0132	0.0883	923.66	357.40	23.75	255	365.5
LBZ 2	14.51	1.71	0.0130	0.1025	957.06	372.48	27.00	300	346.5
LBZ 3	12.17	1.70	0.0129	0.1167	991.74	388.16	30.25	345	327.5
LBZ 4	6.81	1.68	0.0127	0.1309	1019.58	400.80	33.50	390	308.5
LBZ 5	8.52	1.69	0.0123	0.1451	1066.16	421.82	36.75	435	289.5
NBZ 1	23,17	1,61	0,0129	0.3900	873,60	317.33	37,75	269	147.2
NBZ 2	22,06	1,60	0,0125	0.3826	930,74	339.97	40.00	313	143.8
NBZ 3	20,41	1,60	0,0121	0.3753	989,00	367.78	42.25	357	140.4
NBZ 4	18,76	1,59	0,0117	0.3679	1048,05	376 .21	44.50	417	137 .0
NBZ 5	17,11	1,59	0,0089	0.3606	1107,45	382.35	46.57	460	133.49

α : Thermal dilation coefficient, (10 -6 k-1); nd: Index of refraction; d: Optical dispersion; E: Longitudinal modulus of elasticity, (kbar); G : shear Modulus, (kbar) ; μ: Poisson Coefficient; σ : Compressive stress (σc) or with ttensile stress (σt), (MN/m^2); δ : Surface tension (10-3 N/m)

An increase in the shear modulus and modulus of elasticity is observed with the decrease in the fish coefficient. This is due to the improvement in the rigidity of the structure of these glasses with the decrease of Li_2O and Na_2O and increase of B_2O_3, which also leads to the improvement in the values of the mechanical resistances due to the creation of the bridging oxygens.

A decrease in the surface tension of the samples is observed as a result of the addition of the boron oxide B_2O_3 which is known by its influence on the reduction of the surface tension of the glass baths.

However, for the LBZ5 and NBZ5 glasses, an anomaly of the calculated values (ie increase or decrease contrary to the preceding variations) is observed and this is due to the creation of the non-bridging oxygens at the rate of 50% of the network modifiers.

IV. CONCLUSION

The addition of the network modifying oxides Li_2O or Na_2O has a content greater than 50% (by weight in %) in a system glass (B_2O_3-ZnO), contributes to the creation of the non-bridging oxygens and the reduction in the structural rigidity of Vitreous network, thus weakened the mechanical and thermal properties. The influence of two alkaline oxides Li_2O or Na_2O is similar in glasses (B_2O_3-ZnO), although the glasses of the system (Li_2O-B_2O_3-ZnO) exhibit sharper phase separations than system glasses Na_2O-B_2O_3-ZnO).

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