Lithium Oxide Effect on the Thermal and Physical Properties of the Ternary System Glasses (Li_2O_3-B_2O_3-Al_2O_3)

D. Aboutaleb, B. Safi

***Abstract*—**The borate glasses are known by their structural characterized by existence of unit's structural composed by triangles and tetrahedrons boron in different configurations depending on the percentage of B_2O_3 in the glass chemical composition**.** In this paper, effect of lithium oxide addition on the thermal and physical properties of an alumina borate glass, was investigated. It was found that the boron abnormality has a significant effect in the change of glass properties according to the addition rate of lithium oxide.

***Keywords*—**Borate glasses, triangles and tetrahedrons boron, Lithium oxide, Boron anomaly, thermal properties, physical properties.

I. Introduction

IT is known that the glass is part of our daily life. In glass industry, Countless applications are constantly changing. The oxide glasses are among the most studied and used over other glass types; they are composed of several related oxides in a well defined mixture [1], [2]. The boric anhydride B_2O_3, sometimes used as the only trainer of network in enamels and very fuse glasses. It confers to the glass many valuable properties such as improving the fusibility; increasing the mechanical resistance, high thermal resistance; a decrease in the surface tension and increases the chemical resistances [3], [4]. The boron is a very small cation; initially it is tri-coordinated vis-à-vis oxygen and forms a network or are all oxygens fixed (if B_2O_3). Normally the oxygen apport decreases the number of bridges (bridging oxygen's: Y). Here there there's first modification of the coordination number which increases from 3 to 4. During Y increases, this phase only when all boric trihedral turned into tetrahedrons, Y begins to decrease. This occurs for the percentages about of 17% of Na_2O in B_2O_3 [5], [6]. In the alkaline glasses - borate, alkaline-borate glass structure consists of alkaline borate units. Motif units $[(BO_4)^{5-}\ Me^{+}]^{+4}$ cause increased melting temperature and lowering of the dilatation coefficient of the glass based on boron oxide but a large amount of alkali oxides leads to the destruction of the bonded structure of glass and causes also the variation of properties of the boro-silicate glass (Me: is an alkali on) [7], [8]. For this, the work aim is to study the ternary glass system B_2O_3-Al_2O_3-Li_2O_3, after its preparation and determination of some properties depending on the chemical composition (influence of composition chemical on the properties of glass) and his structure.

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II. Experimental Study

A. Preparation of Studied Glasses

The glasses selected were prepared starting from the following chemical raw materials; orthoboric acid, lithium carbonate, and aluminum oxide. The finely crushed mixture was then placed in a platinum crucible and transferred to an electric furnace at temperature ranging 1450°C with a stage for 1 h. The liquid was then cast in a graphite mold preheated to approximately 250°C to limit the thermal shocks during hardening. The samples were annealing then at 250°C for 1 h. The compositions of studied glasses are given in Table I. To study the system-glass B_2O_3-Al_2O_3-Li_2O_3, five variants were chosen. From the first variant G1, whenever 5% of lithium oxide is added and in parallel, 5% of boron oxide is reduced. The content of aluminum oxide is kept constant at 5%. Samples G1 and G4 are opaque by against other samples which are transparent.

TABLE I
Chemical Compositions of Studied Glasses (B_2O_3-AL_2O_3-LI_2O_3)

Glass	B_2O_3 (%wt)	Li_2O_3 (%wt)	Al_2O_3 (%wt)
G1	90.00	05.00	05.00
G2	85.00	10.00	05.00
G3	80.00	15.00	05.00
G4	75.00	20.00	05.00
G5	70.00	25.00	05.00

B. Test Methods

1. Dilatometric Analysis

The expansion curves of samples were determined using a dilatometer DIL 402C (Materials Mineral Composite Laboratory (MMCL-Boumerdes-Algeria) 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 expansion curve using the interception method, whereas the softening temperatures (Ts) was determined by the maximum temperature of expansion curve [9]-[12].

2. Density 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. Molar volume samples is determined by the following formula: Vm = Pm /MV (molecular weight of glass/ Density) in mol / cm 3.

III. Results and Discussions

A. Thermal Properties

Determination of glass transition temperatures Tg and Td dilatometric deformation temperature: From the thermal expansion curves it was determined transition temperatures and thermal expansions of the glasses prepared.

TABLE II
GLASS TRANSITION TEMPERATURES (TG) AND DILATOMETRIC DEFORMATION (TS) OF GLASSES STUDIED

Glass	Tg (°C)	Ts (°C)
G1	318.6	359.1
G2	429.0	454.5
G3	426.8	449.6
G4	258.7	308.3
G5	414.4	434.5

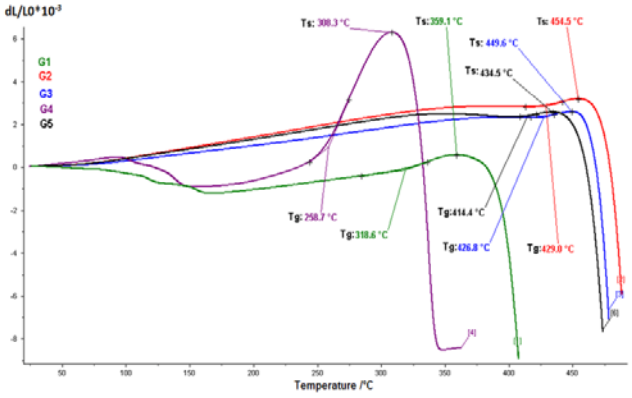

Fig. 1 Curves of dilatation thermal of glasses studied

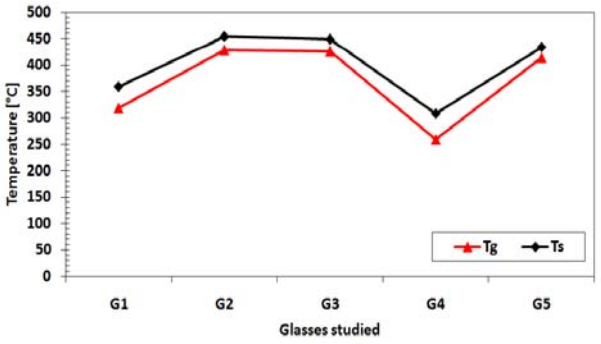

Fig. 2 Variation of the Glass transition temperatures (Tg) and dilatometric deformation (Ts) of glasses studied

Fig. 2 gives the variation of the Glass transition temperatures (Tg) and dilatometric deformation (Ts) of glasses studied. It was noted that between the G1 and G2 glasses, there is increase in the glass transition temperatures Tg and TS dilatometric deformation given the decrease in oxide and increase in boron lithium oxide (10%). While it was found that a decrease in glass transition temperature, this is explained by the transformation the units borates triangular tetrahedral units which consolidated the glass structure of the variant G2.

The glass G2 is less than the opaque glass G1 which has a phase separation is characterized by two inflection points in the thermal expansion curve (Fig. 1).

Variations between G2 and G3; there is a decrease in glass transition temperatures and dilatometric with increasing percentage of lithium (15%) (Modifier network based) and the decrease in the percentage of boron oxide (forming the network), as here there was creation of non-bridging oxygens and the structure became less rigid. G3 glass is transparent, so there was disappearance of the phase separation.

Between variants G3 and G4; there is a large decrease of the glass transition temperatures and dilatometric with increasing percentage of lithium (20%), but here again became opaque glass (phase separation), a curve of expansion of the glass is observed with two inflection points.

Between variants G4 and G5; the glass transition temperatures and dilatometric increased with increasing the percentage of lithium (25%), but here is once again transparent glass and there was suppression of the phase separation.

So we can say that whenever there is a phase separation (immiscibility) glass, the glass transition decreases, and increases with its disappearance. Because when a glass is generally separated into two phases, it minimizes its glass transition temperature by searching a more stable energy state [3].

B. Physical Properties

Table III gives the density of all studied glasses. In Table IV, the molar volume is also presented.

It is noted that the density of the samples increased with the addition of lithium oxide, which is explained by filling the voids between the structural units (silica tetrahedra, boron, boron triangles) by the Network modifiers (Ion of Li +), thus decrease the molar volume and density increase (see Fig. 3).

TABLE III
DENSITY OF GLASSES STUDIED

Glass	Mv (g/cm^3)
G1	2,05
G2	2,09
G3	2,18
G4	2,23
G5	2,25

TABLE IV
MOLAR VOLUME OF THE SAMPLES PREPARED

Glass	Vm (mol/cm^3)
G1	38,89
G2	35,38
G3	34,40
G4	33,80
G5	32,30

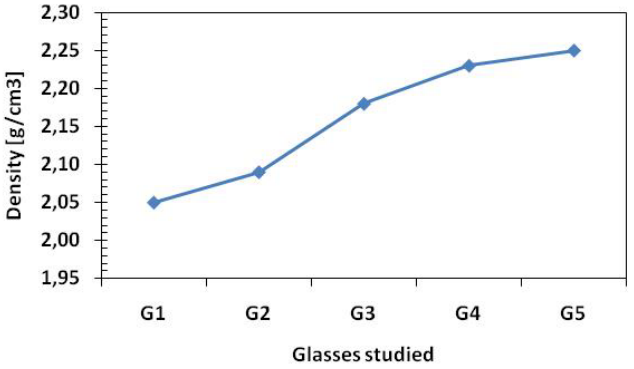

Fig. 3 Density of glasses studied

TABLE V
PROPERTIES OF GLASSES STUDIED

Glass	α	nd	E	σ	δt	δc	λc	ε
G1	2 .150	1.47	260	97.4	67.30	863	0.048	6.42
G2	3.340	1.49	312	147	65.80	843	0.053	7.84
G3	3.969	1.53	350	173.8	64.50	793	0.058	7.96
G4	5.350	1.54	381	206	64.35	757	0.061	8.12
G5	6.779	1.57	420	249.7	63.00	747	0.066	8.57

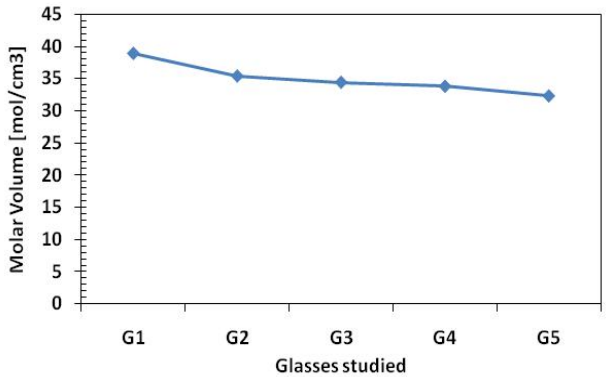

Fig. 4 Molar volume variation of glasses studied

C. Theoretical Calculus of Properties of Glasses

In the structure of glass, the various components contribute a share defined in the effect of certain properties. There would be thus a possibility of calculating by means of additive formulas these properties to leave the composition [11].

According to the calculation methods, there is an increase in the coefficients of thermal expansion as and is added lithium oxide, and by reducing the boron oxide as the structure becomes less rigid and network modifiers contribute to the creation of non-bridging oxygens which increases the expansion of the network (see Table V). But it must be taken into account in the phase separation phenomenon which occurs substantially by increasing the coefficient of expansion.

Note the increase in density with the addition of lithium oxide, as Li + ions fill the voids structural units and this causes the decrease of the molar volume (Fig. 4).

The refractive index is an optical property related to the polarizability of oxygen atoms, we also notice an increase in the refractive index as we add lithium oxide which promotes the creation of non-oxygen bridging and therefore their polarizability increases. The same behavior is observed for the dispersion.

Increases were observed in the values of modulus of elasticity, and this behavior is similar to the same coefficient of thermal expansion (non-bridging oxygen's of creation by adding modifiers network) and the opposite fish louse coefficient (decrease). Decreases observed in the values of mechanical strength and this is due to the creation of non-bridging oxygen that caused voids in the glass structure so open and less rigid structures.

Generally the specific heat borates glasses increases with increasing content of boron oxide. Decreased values were observed with decreasing boron oxide.

As the thermal conductivity is a property related to transport phenomena in matter, we note in the case of our glasses, an increase in value with the increase in modifier ions (Li^+) thus facilitating the transfer of thermal conductivity through the vitreous mass.

The surface tension increases with the non-bridging oxygen's created by the addition of lithium.

The electrical permittivity is also related to the polarizability of oxygen ions, which notes the increase in its value with the increase in non-bridging oxygen's created with the Li_2O_3 addition.

IV. CONCLUSION

The study of the glass system B_2O_3-Al_2O_3-Li_2O_3 allowed us to draw the following conclusions and remarks:

This system of lenses is one of known lenses by their low glass transition temperature and glass silicates having phenomena relative immiscibility borates;

By studying this system, it was noted that with the addition of lithium oxide (10% and 15% Li_2O_3) there was suppression of phase separation, but at 20% of Li_2O_3 has recurred. Then 25% of Li_2O_3 glass is completely transparent, so the lithium oxide has a great influence on the structural configuration of the glasses studied, and according Li_2O_3/B_2O_3 report the structure changes (abnormal boron which is manifested by the existence of boron is the tetrahedral shape is triangular).

The properties of glasses prepared change according to the structural condition. Generally good properties are shown in glasses having a high glass transition temperature.

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