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Effect of the AL_2O_3 and BaO Addition on the Thermal and Physical Properties of Ternary Glass System (B_2O_3-BaO-AL_2O_3)

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Abstract: In borate glasses, the main structural units are the $[BO_3]$ triangles and $[BO_4]$ tetradral which form different superstructural units like; boroxol rings, metaborate rings and chains, pentaborate, diborate, triborate and pyroborate. In this work, the Barium aluminoborate glasses were prepared. Some of properties were investigated by measure like density and chemical durability and the other by calculs. The dilatometric curves were determined and they revealed that the temperature of transition (T_g) and softening (T_s) and the dilatation coefficient increase by addition of Al_2O_3 and BaO content.

Key words: Barium aluminoborate glass, density, chemical durability, dilatometric curves.

Nomenclature

α:	Thermal dilation coefficient, 10^{-6}, k^{-1}
n_d:	Index of refraction
d:	Optical dispersion
E:	Longitudinal modulus of elasticity, kbar
σ:	Surface tension 10^{-3}, N/m
ρ:	Densities, $g{\cdot}cm^{-3}$
σ:	Compressive stress (σc) or with traction (σt), MN/m^2
Cp:	Heat capacity, J/gk
λc:	Thermal conductivity, W/mk
ε:	Electric permittivity

1. Introduction

In special glass systems, the chemical composition plays an important role in determining properties of the glass. The components of glass are distributed into three categories: network formers, network modifiers and intermediate species, which falls somewhere between network formers and modifiers and may substitute for a network former in the glassy state. The higher valence cations such as $Al^{3+}$are commonly used as intermediate species [1]. In borate glasses, the main structural units are the $[BO_3]$ triangles and $[BO_4]$ tetradral which form different superstructural units like; boroxol rings, metaborate rings and chains, pentaborate, diborate, triborate and pyroborate [2]. Also, in the pure B_2O_3 glass consists of $[BO_3]$ groups and with increasing alkali concentration, the first incorporation of alkali oxide leads to the coordination shift $[BO_3]$ to $[BO^{-4}]$ with alkali ions compensating the charge of the $[BO^{-4}]$ tetrahedra. A strengthening of the structure occurs, since the points of polyhedra linkage rise from three to four. At higher alkali concentrations, the structure weakened again due to the formation of $[BO_3]$ groups with nonbridging oxygens. This double change of coordination number explains minima or maxima of some properties which occur with increasing alkali concentration. Furthermore, this anomaly depends also on the temperature. According to Dietzel [3], the

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boron anomaly should not exist in glasses at temperatures above 1,000 °C, i.e., above this temperature only [BO_3] groups occur in the melt. The association of [BO_3] planar triangles with oxygen atoms into [BO^{-4}] groups should, however, occur at lower temperatures. Aluminum oxide acts as an intermediate in glass. Intermediates have a mid-position between network-formers and network-modifiers. Aluminum may either form tetrahedra and so reinforce the network (coordination number 4) or loosen the network in analogy to network-modifiers (coordination number 6). The ionic radius of barium ions is much larger than of aluminum oxide and boron oxide, which results in the coordination number 8. By contrast, the field strength of barium is much smaller resulting in the behaviour as network-modifier. In the BaO-Al_2O_3-B_2O_3 glass system, it was reported that Al_2O_3 behaves as AlO_4 and AlO_6 units in the glass structure [4]. It assumes that aluminium ions enter the structure in the form of three tetrahedral BO_4 and/or Al_2O_3 in the form of AlO_4 having an oxygen in common [5]. Owen [6] proposed for the glass systems of MO-Al_2O_3-B_2O_3; (M = Sr, Ca and Ba) that some of the M atom associate themselves with Al_2O_3 forming AlO_4 and the rest act with B_2O_3 producing BO_4 or non-bridging oxygen ions. The system BaO-Al_2O_3-B_2O_3, have also a negative thermal expansion coefficient, and therefore it is a potential candidate of a zero-expansion material [7, 8]. First research of this system with regard to the thermal expansion coefficient was carried out by MacDowell in 1989 [9, 10].

In the present study some properties of BaO-Al_2O_3-B_2O_3 glass system were investigated by measure like density and chemical durability and the other by calculs. The dilatometric curves were determined and they revealed that the temperature of transition (T_g) and softening (T_s) and dilatation coefficient increases by addition of Al_2O_3 and BaO content.

2. Experiments

2.1 Preparation of the Glass Samples

The glasses selected were prepared starting from the following chemical raw materials; barium carbonate, orthoboric acid and aluminum oxide. The finely crushed mixture was then placed in a platinum crucible and transferred to an electric furnace at temperature ranging from 1,300 °C to 1,400 °C with a stage for 1.5 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 350 °C for 1 h. The compositions of studied glasses are given in table 1.

2.2 DTA and TGA Analysis

The apparatus used was a simultaneous thermal analysis apparatus type STA 449C. 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 of Al_2O_3 and temperature range 25 to 1,550 °C. The type of the thermocouple used is Pt/Pt Rh.

The glass transition temperature (T_g) was determined from the second endothermic peak of DTA curve whereas the crystallization temperatures (T_c) was determined by the first exothermic peak of DTA curve [5].

2.3 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 (T_g) was determined from the expansion curve using the interception method, whereas the softening temperatures (T_s) was determined by the maximum temperature of expansion curve [5, 7, 8].

Table 1 Chemical composition of studied B_2O_3-BaO-Al_2O_3 glasses system.

	Composition (weight %)			Composition (molaire %)		
	B_2O_3	BaO	Al_2O_3	B_2O_3	BaO	Al_2O_3
G_1	95	5	-	97.70	2.29	-
G_2	85	10	5	91.73	4.88	3.76
G_3	75	15	10	84.92	7.69	7.77
G_4	65	20	15	77.5	10.83	12.25

Table 2 Values obtained of T_g and T_s of (BBA) glass system.

Samples	T_g (°C)	T_s (°C)
G_1	312.3	335.5
G_2	387.7	417.1
G_3	422.8	443.8
G_4	512.8	536.4

Table 3 Values obtained of density (ρ) and molecular volume (V_m) of BBA glass system.

Samples	ρ (g/cm^3)	V_m (cm^3/mol)
G_1	1.850	38.665
G_2	2.143	35.081
G_3	2.432	32.416
G_4	2.561	32.391

2.4 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 V_m was calculated from the molecular weight M and the density ρ according to the relation: V_m = M/ρ. The density results are illustrated in Table 3.

2.5 Determination of Chemical Durability

The chemical treatment of the samples under the various conditions (neutral, acidic and basic) was carried and the weight loss of samples was determined.

2.6 Theoretical Calculs of Properties

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].

3. Results and Discussion

3.1 DTA and TGA Analysis

The (DTA) curves of these glasses, show endothermic peaks between 100 and 200 °C (Fig. 1), knowing that towards the temperature 100 °C, the boric acid starts to lose its water, giving initially metaboric acid, and by dehydration supplements with 300 °C, it forms vitreous boric anhydride according to the following relation:

$$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O$$

This is accompanied by an important loss by mass presented in the relative curves TGA, however this loss of mass decreases with the reduction in the content of B_2O_3 (of G2 towards G4). The second endothermic peaks which this locate at various temperatures for various glasses represent the temperatures of vitreous transitions, their values increase with the increase in the oxide Al_2O_3 and BaO.

In parallel, various first exothermic peaks corresponding to the beginning of crystallization of the vitreous samples which show also an increase in the values with the increase in the oxide Al_2O_3 and BaO. Thus, the addition of the oxides Al_2O_3 and BaO in the systems of glasses (BBA) increases the temperatures of vitreous transition and the temperatures from crystallization of these glasses.

3.2 Dilatometric Analysis

The obtained curves of thermal dilation are represented in the Fig. 2. For glass G1 the thermal curve of dilation is representative of glass separated in two phases, because there are two glass transition temperatures represented by two points of inflection on the curve. The B_2O_3-BaO binary system is known by

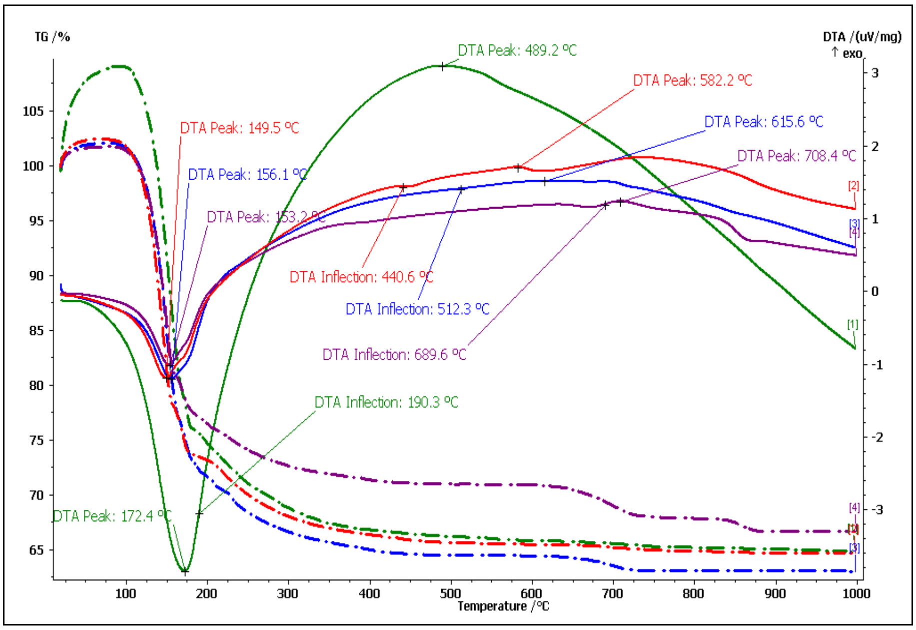


Fig. 1 DTA and GTA curves for obtained (BBA) glass system.

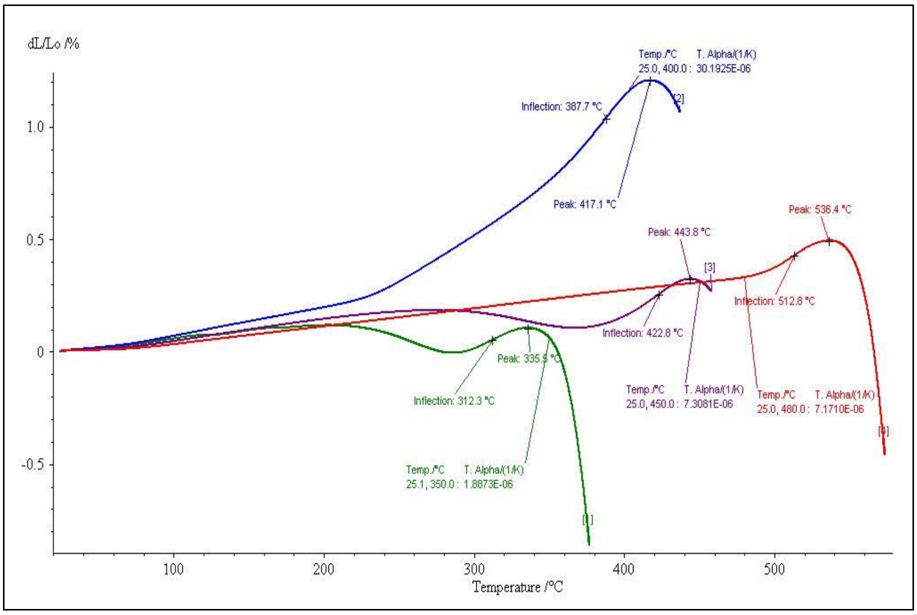


Fig. 2 Expansion curves of for obtained (BBA) glass system.

its mechanism of separation of phase [12, 13]. The G1 sample obtained has a translucent white aspect. With the addition of five percent of alumina (5% Al_2O_3), the phase separation decreases and the other glasses are homogeneous.

The temperatures of vitreous transition T_g and softening temperatures T_s increase by G1 towards G4 with the addition of Al_2O_3 and BaO, because these the last two oxides are known by their role to increase the viscosity of the molten bath but thermal dilation increases by G1 towards G4. Generally, glasses with the lower expansion coefficient have higher transition and softening temperatures and vice versa [11]. However, it can be seen in Fig. 2 that the expansion increases and the T_g and T_s temperatures increase with additions of Al_2O_3 and BaO oxides.

This is with the molar report/ratio Al_2O_3/B_2O_3 which increases by G1 towards G4, or the B^{3+} ions go to join with Al_2O_3 by forming the tetrahedrons AlO_4 and the remainder will act with the B_2O_3 by producing not bridging oxygen (NBO) what has to weaken the vitreous network and dilation has to increase. Substitution of BaO for B_2O_3 in the studied glass seems to lead to the conversion of NBO'S formation.

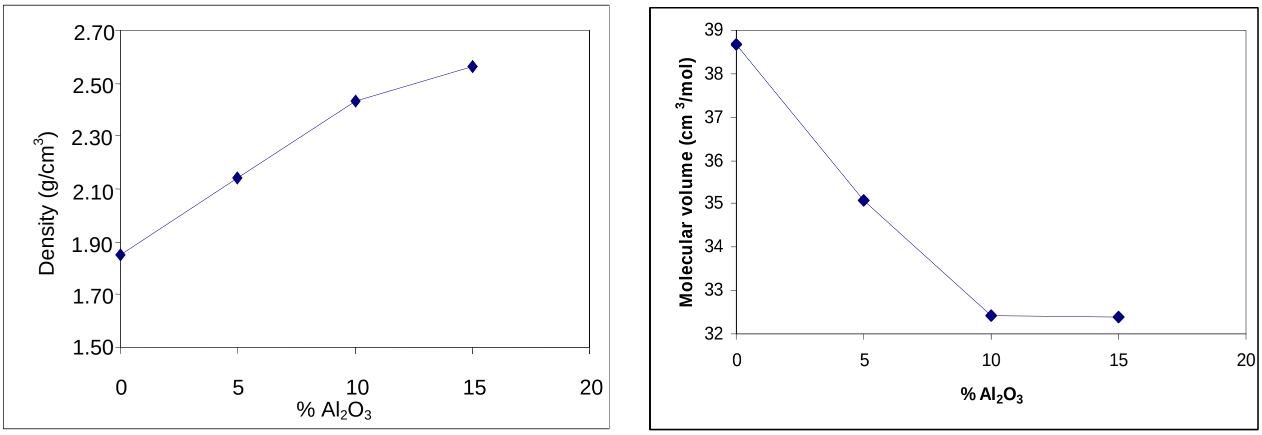
3.3 Density and Molar Volume

Density variation and molar volume for obtained (BBA) glass system as a function of Al_2O_3 mol% are given in Fig. 3a. Adding the BaO and Al_2O_3 oxides increase density: alkali earth ions (Ba) fill the free volume and Al_2O_3 behaves as AlO_4 and AlO_6 units in the glass structure so the molar volume decreases (Fig. 3b).

3.4 Chemical Durability

Results illustrated in Table 4 showed that the samples exhibited an increase in durability under the three media conditions studied (neutral, acidic and basic) with increase of aluminium content. Chemical attack decreases with increasing the aluminum content in all medium. The reactions between the ion H^+ and the "acid" network can be neglected since the components are packed too strongly to allow for any possibility of migration in the network to take place. On the other hand, the network modifiers have a certain freedom of displacement through vacuum and also the ability to pass through the solution that surrounds them if this vacuum borders the solution. The attack by the alkaline solutions on the other hand is governed by another mechanism.

The OH^- ion is in the case the determining factor, because its ability to react with the network. As a consequence, it appears that this result in a network division, which under certain conditions can result a complete dissolution of glass. It also appears that the solubility of glass increases under basic pH conditions [14]. When comparing the ratio of attack by acid versus water, this attack decreases with increasing Al_2O_3 content, which also reinforced the structure and reduces the chance of network division and destruction.



(a) (b)

Fig. 3 Variation of ρ and V for obtained (BBA) glass system as a function of Al_2O_3 mol%. (a) density (b) molecular volume.

Table 4 Chemical durability for obtained (BBA) glass system.

	Acid solution (HCl)			Basic solution (NaOH)			Neutral solution (distilled water)		
Sample	M_0 (g)	M_1 (g)	$\frac{M_0 - M_1}{M_0}$ (%)	M_0 (g)	M_1 (g)	$\frac{M_0 - M_1}{M_0}$ (%)	M_0 (g)	M_1 (g)	$\frac{M_0 - M_1}{M_0}$ (%)
G_1	2.759	1.640	40.55	4.271	3.940	92.74	2.139	0.259	87.89
G_2	1.443	0.775	46.29	2.228	0.380	89.94	2.382	0.622	73.88
G_3	2.211	1.715	22.43	4.256	0.947	77.74	4.752	3.264	31.31
G_4	1.262	1.235	2.13	2.508	1.652	34.13	2.691	1.865	30.69

Table 5 Theoretical properties calculated.

	Properties										
	α in % mass	n_d	*d*	*E*	*σ*	*ρ*	*δt*	*δc*	*Cp*	*λc*	*ε*	*α* in % molar
G1	0.813	1.48	0.006	252.5	94.5	1.95	64.25	857.5	0.219	0.04	5.84	0.43
G2	2.093	1.49	0.007	307.5	136.0	2.11	62.75	820	0.21	0.045	6.71	1.84
G3	3.364	1.51	0.007	362.5	177.5	2.26	61.25	782.5	0.201	0.050	6.96	3.15
G4	4.639	1.53	0.008	410	219.0	2.45	59.75	745	0.192	0.056	7.60	4.21

3.5 Theoretical Calcul of Properties

The results from the calculated properties are given in Table 5. According to Winckelmann and Appen, it is observed that the expansion values are respectively low in the range of 20-100 °C and 20-400 °C due to the presence of boron oxide B_2O_3 which generally reduces the coefficient of thermal expansion α of glasses [15]. The α values increases (which may be due to the decrease in boron oxide and the presence of BaO and Al_2O_3) and the formation of non-bridging oxygen. Results by Winkelmann and Appen are slightly different and are almost similar. The density increases with the addition of barium and alumina, as both ions have relatively large molar masses.

The presence of boron oxide also increases the refractive index of glasses which explains the high value of the refractive index calculated. Even alkaline earth oxides also contribute to the elevation of the refractive index and dispersion. With the reduction of other oxides such as boron oxide and the increase of barium and alumina the amount of non-bridging oxygen increases and this leads to an increase in the elastic modulus E and Poisson's ratio. Note that the compressive strength σ_c is higher than the tensile strength σ_t [14].

The mechanical strength of glass increases with the strength of the bonds of the glass structure. The samples prepared show low values of mechanical strength, the structure is not rigid enough, and with creation of NBO oxygen, there is a decrease in tensile strength and compression. Ordinary glasses generally are characterized by a specific heat value of about 0.8 CP (J/gk) by boric oxide increases against the property in the glasses. And with the decrease in B_2O_3 and higher alumina, there was decrease in specific heat value. With the addition of Al_2O_3, there was a slight increase in thermal conductivity *e*, non-bridging oxygen ions increase the heat transfer inside the glass.

A decrease in the surface tension value was observed in systems of binary or ternary glasses of borates, alkaline earth oxides are important to the surface. There is a relationship between the primitive and the index of refraction as a decisive influence on the polarizability of oxygen ions. When, the B_2O_3 content decrease, an increase of permittivity values with polarizability of ions (non-bridging oxygen ions) was observed with the same manner like the index of refraction.

4. Conclusions

In the studied glass system BaO-Al_2O_3-B_2O_3 samples have a transparent appearance (homogeneous), except that the sample G1 is heterogeneous and presents phase separation at binary BaO-B_2O_3 glass, then the phase separation disappears with addition of more amount of alumina.

The addition of the alumina at the same time as some barium in the component B_2O_3 contributed to the creation of non-bridging oxygen. Although the temperatures of transitions glassy T_g and softening *Ts* increased (because of the increase of the viscosity of the bath), Also densities and the coefficients of expansion increased. The creation of non-bridging oxygen led to an increase of the module of elasticity and this fact the reduction in the mechanical properties as the traction resistance and to the compression and the Poisson's ratio but there is an increase in chemical properties. The increase of the polarizability of the ions oxygen has to lead to the increase of the refractive index and the dispersal as well as the electric permittivity. The properties of transfer increased as the conduction of heat and the superficial tension on the other hand the specific heat decreased.

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