Composition Effect on Some Physical Properties and FTIR Spectra of Alumino – Borate Glasses Containing Lithium, Sodium, Potassium and Barium Oxides

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The composition effect on FTIR spectra, D. C. electrical conductivity, density and molar volume have been carried out for five glasses (G1 to G5) of (13 M_2O or M'O) – 78 B_2O_3 – x Al_2O_3 – y Nacl system, where M is Li, Na or K and M' is Ba; x = 9 and y = 0 for G1, while for G2, G3, G4 and G5: x = 3 and y = 6 mol %. FTIR spectra have been recorded in wavenumber range from 4000 cm^{-1} to 400 cm^{-1}. Eight absorption bands were observed in the rgion from 400 – 1750 cm^{-1}. The electrical conductivity yield activation energies for the investigated glasses. These activation energies as well as the density and the molar volume have been found to be in the fallowing order $Li^+ < Na^+ < K$. The molar volume, density and the activation energy for barium oxide seem to be constant whether Na Cl is present or not.

1. Introduction

1.1. Some remarks on the glass structure:

Chemical composition of the glasses plays an important role in determining properties of the glass. The glass is divide into main 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. Higher valence cations such as Al^{3+} are commonly used as intermediate species [1]. In the present study the influence of the network modifier (Li, Na, K and Ba) was determined from the experimental properties of the alumino - borate system.

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Infrared spectroscopy has been proven to be a useful tool for investigating the structure and dynamics of amorphous solids [2 and ref. therein]. The structure of glasses with composition $xB_2O_3 – (1-x)M_2O$, (M= Li, Na, K, Rb, Cs) is known to be consist of B – O network, built up from planner three- coordinated and tetrahedral four coordinated boron atoms [2], figure (1-a). Pure υ - B_2O_3 contains only three coordinated boron atoms $[BO_3]^{3-}$ and if an alkali oxide (M_2O) is added some of these units transform into four – coordinated tetrahedral [3] as shown in Fig. (1-b).
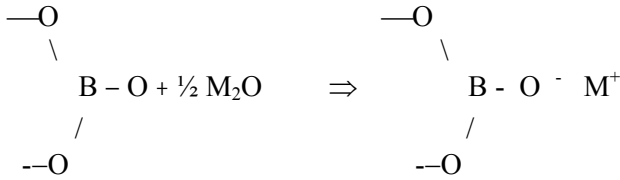
$$—O \qquad\qquad\qquad —O$$
$$\backslash \qquad\qquad\qquad\qquad \backslash$$
$$B – O + ½\, M_2O \quad \Rightarrow \quad B - O^{\,-} \ M^+$$
$$/ \qquad\qquad\qquad\qquad /$$
$$-\!—O \qquad\qquad\qquad -\!—O$$

Fig. (1-a): Formation of non-bridging oxygen [4] from addition of an alkali oxide (M_2O).

$$—O \qquad\qquad\qquad —O \qquad O—$$
$$\backslash \qquad\qquad\qquad\qquad \backslash \quad /$$
$$B – O + ½\, M_2O \quad \Rightarrow \quad B \qquad M^+$$
$$/ \qquad\qquad\qquad\qquad / \quad \backslash$$
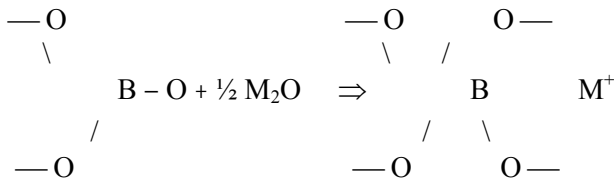$$—O \qquad\qquad\qquad —O \qquad O—$$

Fig. (1-b): The conversion of boron from a 3-coordinated state to a 4- coordinated state [4] as a result of the addition an alkali oxide M2O.

If an alkali impurity creates non-bridging, Fig.(1-a); the resulting network gets loose and the connectivity of B_2O_3 network decreases. This leads the glass properties such as thermal coefficient expansion, electrical conductivity and so on, all increase with increasing modifier content. If an alkali impurity causes boron atom to be tetrahedral, Fig (1- b), the connectivity increases followed by decreasing in the glass properties. The structure role of the network modifier is determined by its size and charge and by network forming agent of the glass.

In the present work four modifiers, Ba^{2+}, K^+, Na^+, and Li^+ have been used with the mol % in the glasses under investigation. In barium and lead alumino-borate glasses, it was reported that aluminum atoms have mainly a tetrahedral coordination with respect to oxygen [5]. In the glass system of BaO – Al_2O_3 – B_2O_3, it was assumed that aluminum ion enter the glass structure in the form of triclusters which consisted of three tetrahedral BO_4 and / or Al_2O_3 in

the form of AlO_4 having oxygen in common [6-8]. Owen [8] proposed, for the glass systems of $MO - AL_2O_3 - B_2O_3$ (M = SR, Ca and Ba), that some of M associate itself with Al_2O_3 forming AlO_4 and the rest act with B_2O_3 producing BO_4 or non- bridging oxygen ions. Sakae [9] concluded that the ratio Al_2O_3 / CaO has the same effect on the glass structure where ALO_4 dependent on B_2O_3. Prince [10] reported that the glass stability increases with respect to the devitrfication process when Al acting as a glass former in the $BaO - Al_2O_3 - B_2O_3$ system.

The aim of the present work is to study the influence of the glass composition on some physical properties and the IR spectra of the glasses under investigation.

2. Experimental:

2.1. Preparation of the glass samples

The investigated glasses have been prepared by mixing appropriate quantities from the reagent materials. These raw materials are barium carbonate, orthoboric acid, aluminum oxide, sodium chloride, lithium oxide, sodium oxide and potassium oxide. The required mixture from these reagents was melt in air in porcelain crucibles in an electric furnace.

The homogenized melts were cast into stainless steel moulds and subsequently cooled down to room temperature. Transparent glasses were obtained and its amorphous nature was confirmed by X-ray diffraction. The compositions of the studied glasses are given in Table (1).

Table (1): The compositions of the studied glasses in mole %.

	G1	G2	G3	G4	G5
BaO	13	-	-	-	-
BaO	-	13	-	-	-
Li_2O	-	-	13	-	-
Na_2O	-	-	-	13	-
K_2O	-	-	-	-	13
B_2O_3	78	78	78	78	78
Al_2O_3	9	3	3	3	3
Nacl	-	6	6	6	6

2.2. D.C. Electrical Conductivity Measurements

The resistances of three samples from each glass under investigation have been carried out using an Insulator Tester Type TM14 with $10^3 - 10^{13}$ ohm range. The thickness of each sample is (1 – 2 mm).

The glass surfaces were coated with silver paste to serve as electrodes. The resistivity of each sample has been calculated and the relation between ln ρ and $10^3 / T$ (K^{-1}) for the investigated glasses are shown in Fig. (2).
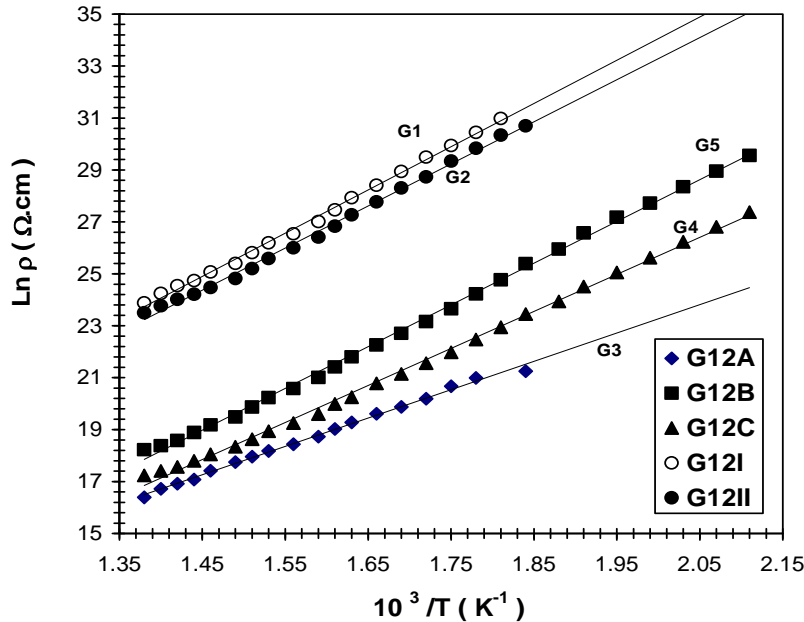

Fig. (2): Change of the natural logarithm of electric resistivity for the investigated glasses with temperature.

2.3. Infrared Spectroscopy

FTIR absorption spectra of the glasses under investigation have been recorded in the wavenumber range 4000 – 400 cm^{-1} using Mattson 5000 system.10 mg of each sample was mixed with 1000 mg of KBr in an agate mortar and then pressed into pellets of 13 mm diameter. The spectrum of each sample represents an average of 20 scans, which were normalized to the spectrum of the blank KBr pellet. A spectral resolution of 2 cm^{-1} was chosen and the spectrum has been carried for three samples from each glass to avoid any errors during the measurements.

2.4. Density and Molar Volume

The density measurements for the studied glass were carried out at room temperature using Archimedes method with xylene as immersion fluid. The measurements were carried out for three samples from each glass. 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: $V_m = M / \rho$

3. Results and Discussion

3.1. D.C. Electrical Conductivity

The electrical conductivity of the investigated glasses was measured as a function of temperature (from 470 – 730 K for the investigated glass) and found to fulfils the following Arhenius formula:

$$\sigma = \sigma_o \, e^{-E/KT} \tag{1}$$

and the resistivity

$$\rho = \rho_o \, e^{E/KT} \tag{2}$$

where E represents the activation energy for the electronic conduction, ρ_o is the pre-exponential factor contains several constants including the viberational frequency of the mobile ions [20,21] and is given by:

$$\rho_o = 2KT / N \, q^2 \, a^2 \, f \tag{3}$$

The relation between (ln ρ) and $10^3 / T$ (K^{-1}) is given in figure (2). It is obvious, from this figure, that (ln ρ) increases in the order Li$^+$ < Na$^+$ < K$^+$ < Ba^{++}. This means that the conductivity of the investigated glasses depends completely on the size and charge of the network modifiers in the glass. The calculated values of the activation energies are given in Table (2) and found to be inconsistent with the expected values.

Table (2): The calculated values for the activation energy, density and molar volume for the glasses under investigation

	Activation energy, E (ev)	Density, D (gm.cm^{-3})	Molar volume, V$_m$ (cm^3)
G1	1.4440	2.001	47.92
G2	1.3999	2.004	46.55
G3	0.9431	1.885	40.98
G4	1,2317	1.708	47.66
G5	1.3893	1.658	51.63

3.2. Analysis of FTIR spectra

Infrared spectroscopy is known to provide insights into the interaction between alkali metal ions and borate glass network. Absorption of these borate glasses is very high in the region of interest of wave numbers < 2000 cm^{-1}. The FTIR spectra were recorded in the wavenumber region 2000 – 400 cm^{-1}. The spectra can be divided into the following regions: (1) 600 – 800 cm^{-1} is related to the bending vibrations of various borate arrangements B – O – B, (2) 800 – 1200 cm^{-1}was attributed to the B – O stretching vibrations of tetrahedral [BO$_4$] and (3) 1200 – 1800 cm^{-1}, the peaks in this region were related to B – O stretching vibrations of [BO$_3$]. The bands in three active regions of the spectra are similar to those reported on alkali borate 11-13] and barium aluminoborate glasses [5,12]. In the forth absorption region (400 – 600 cm^{-1}), where the six-fold coordination of aluminum atoms can be detected [5,10] the bands appeared in this region is due to Al – O stretching vibration in the (AlO$_6$) groups.

Figures (3-5) represent the deconvolution spectra for the glass containing lithium oxide (G3) and barium oxide (G2 and G1). The FTIR absorption spectra of the investigated glasses have analyzed in more details using the Gaussian bands and the computer PeakFit program [19]. It is obvious from these figures that broad bands were observed and centered at 464 cm^{-1} for G3 and at about 435 cm^{-1} for G1. These bands have attributed to the vibration of cations of lithium and barium atoms at their network sits [14]. In some cases it was referred to the formation of units combined with the network [22 &23].
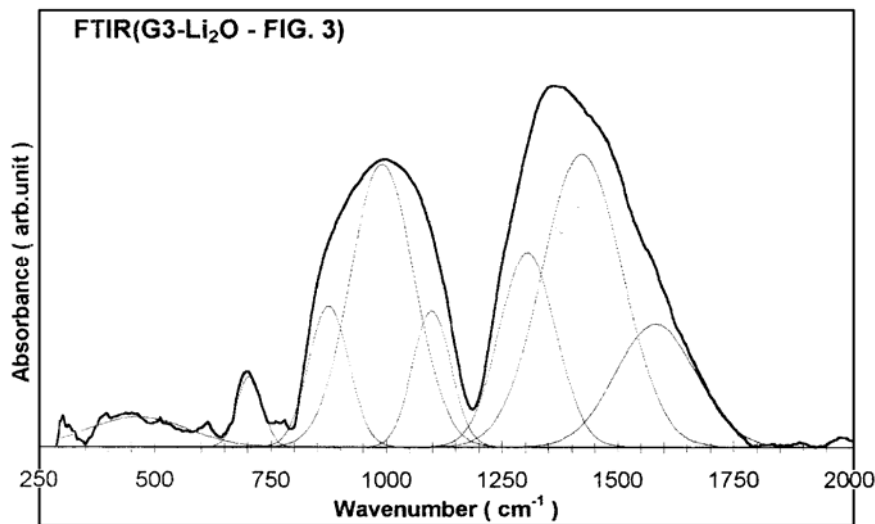

Fig. (3): Deconvolution result for 13 Li$_2$O-3 Al$_2$O$_3$-78 B$_2$O$_3$-6 Nacl, experimental absorption spectrum (solid line) and computer band (dashed lines), [G3].
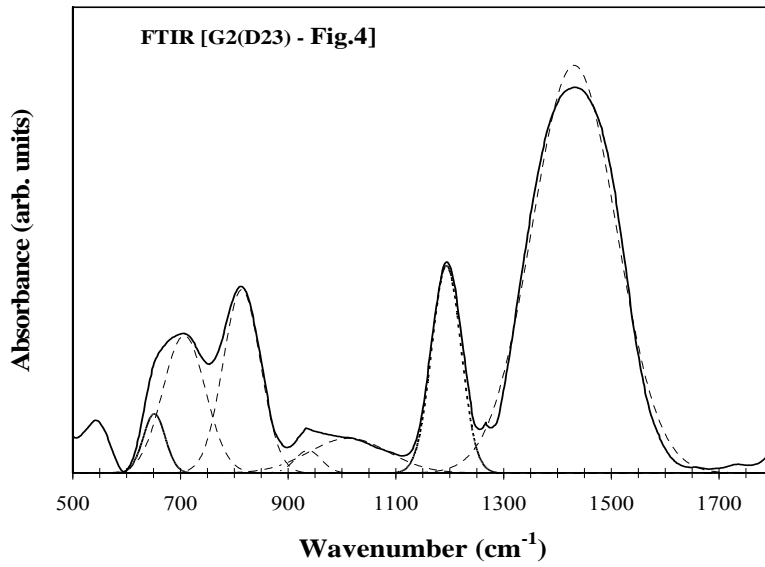
Fig. (4): Deconvolution result for 13 BaO -3Al$_2$O$_3$ −78 B$_2$O$_3$ 6Nacl, experimental absorption spectrum (solid line) and computer band (dashed lines), [G2].
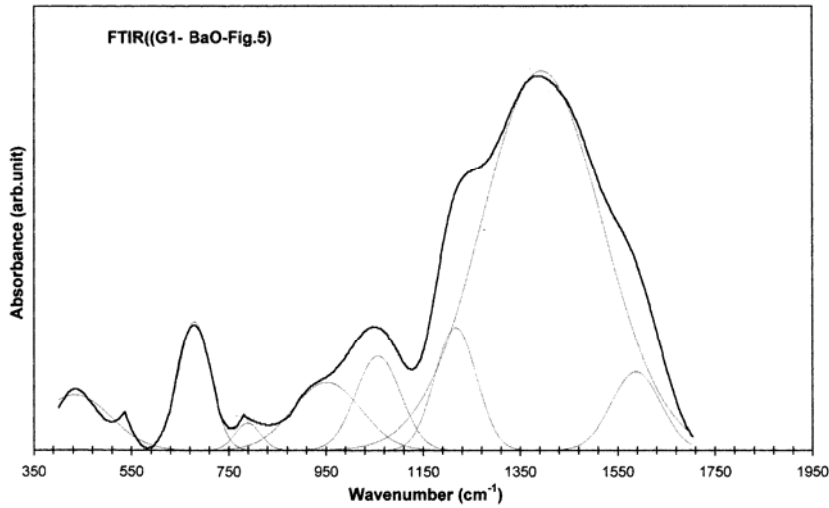

Fig. (5): Deconvolution result for 13 BaO -9 Al$_2$O$_3$ −78 B$_2$O$_3$, experimental absorption spectrum (solid line) and computer band (dashed lines), [G1].

We assign the intense bands centered at 1001 and 1427 cm^{-1} in the regions 800 – 1200 – 1700 cm^{-1} for G3 to the vibration of boron atoms with respect to the four oxygen atoms surrounding it.

The remaining peaks were attributed to B – O – B stretching vibrations associated with BO_4 tetrahedral which are connected to the other network unit. The four peaks in the spectral region $600 – 800$ cm^{-1} were appeared at 610, 686, 703 and 772 cm^{-1} and assigned to the bending vibration of borate segments [12 – 14].

In the barium aluminoborate glass (G1), Fig (5), the absorption peaks in the region $400 – 600$ cm^{-1} were at 600 cm^{-1} or less were assigned to the vibration of the modifier cations with respect to barium atoms. The more intense peaks in the region $600 – 800$ cm^{-1} are at 679 cm^{-1} where the tetrahedral BO_4 is obvious and the other peaks are related to the boroxol [BO_3] units. In the absorption band at 952 cm^{-1} is due to diborate network. The other peaks are due to the formation of pentaborate and that at 1395 cm^{-1}; the intensive peaks; are assigned to the metaborate chain [12] where BO_4 units are formed on the expense of BO_3 with non-bridging oxygen atoms. The peak at 1587 cm^{-1} is raised from B–O stretching vibration of triangle $[BO3]^{-3}$ units [11, 12, 16 and 17].

Each spectrum for all alkali atoms (Li, Na and K)- aluminoborate glasses contains the number of bands at approximately the same wavenumbers but may be with different intensities and widths. Therefore, one may conclude that, for example, the large potassium atoms open up the network and force BO_4 units to interconnect with the narrower distribution of B – O – B, resulting in the IR spectrum with narrower peaks.

3.3. Density (D) and Molar Volume (Vm)

The dependence of density, molar volume and activation energies on the glass compositions were given in Table (2). A slightly decrease in D, m_V and E were noticed from G1 up to G3, while a significant increase was observed in both V_m and E from G3 to G5.The Nacl contents has no effect on these physical properties of the studied glasses of barium alumino- borate.

4. Conclusions:

The conductivity of the studied glasses depends completely on the size and charge of the cations of the mole % content. The activation energies were found to be constant for BaO with or without Nacl while that of the alkaline oxides increases as $K^+ > Na^+ > Li^+$.The density, molar volume and the activation energies were found to be constant for G1 and G2. This means that Nacl contents has no effect on these physical properties of the present glasses containing BaO, while for that containing Li_2O, Na_2O and K_2O it was found that E and V_m increased from G3 to G5 and D decreases.

The FTIR spectra of the alkaline oxides (Li, Na, K) aluminoborate glasses have been found to have the equal number of peaks at approximately the

same wavenumbers. In barium aluminoborate glasses with or without Nacl the peaks in the regions 400 –600 cm^{-1} 600 – 800 cm^{-1} and at 793 cm^{-1} are assigned to the vibration of the cations in the network, to the boroxol [BO$_3$] and the formation of [BO$_4$], respectively. Peaks in the region 800 – 1200 cm^{-1} are due to diborate, pentaborate and the more intense one is assigned to metaborate. Two peaks observed at the region 1200 – 1750 cm^{-1} are due to pentaborate, one arise from B – O stretching vibration of [BO$_3$]$^{3-}$ and the intense one is due to the metaborate chain.

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