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Electrical Properties of Lead Borate Glasses Containing Different Alkali Metal Oxides

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The dc-electrical conductivity of lead borate glasses with different lead-boron ratios and lead borate glasses containing basic cations of Na^+, K^+ and Mg^{2+} were measured in the temperature range (308–789 K). The activation energy of electrical conduction was calculated. It was found that all samples have semiconducting properties and fit well with the Arrhenius equation. The ac-electrical conductivities for these samples were calculated from the dielectric loss data to give a comparison between the ac- and dc-conductivity of borate glasses taking into consideration the effect of polarization of the molecule at high frequency. Differential thermal analysis was carried out for two samples to identify phase transition, which occurs in the used temperature range. All results are discussed and correlated to the molecular structure of the prepared glasses.

Key Words: Electrical properties, Lead borate, Glasses, Alkali metal oxide

INTRODUCTION

Glasses of various chemical compositions offer a considerable interest from the point of view of their electrical conduction. A pure quartz glass (100% SiO_2) displays high resistivity. The content of other components decreases the electrical insulating properties of silicate glass. It was found that the presence of alkaline metal oxides reduces electrical resistivity due to the small size of alkaline metal ions and, therefore, to its high mobility. For this reason, from the point of view of reducing the resistivity of silicate glass, the presence of sodium in the composition is more harmful than the presence of potassium. On the other hand, the presence of heavy oxides such as BaO or PbO in the glass matrix increases electrical resistivity. Neutralizing or polyalkaline effect arising from the presence of two different alkaline oxides at the same time in glass, which tends to increase its electrical insulating properties much higher than the presence of only one alkaline oxide in a quantity equal to the total content of the two oxides. Moreover, it is sometimes possible to improve the electrical conducting properties of alkaline glass by adding another alkaline oxide contained previousiy in the glass (suppression effect)[1]. If optimum compositions are selected, glass with good electrical conducting properties with a high content of alkaline metal oxide can be obtained. The electrical conductivities as a function of temperature for lithium lead borate glasses samples containing different amounts of iron oxide up to 10 mol % have similar behaviours, from which the activation energy was deduced for each sample. DTA showed that the samples containing up to 5 mol % iron oxide are

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characterized by one crystallization temperature while samples containing 10 mol % iron oxide have two crystallization temperatures[2].

A sharp minimum in ac-resistivities of borate glasses containing pentavalent antimony or arsenic ions is observed for all samples at a temperature[3] around 315 K.

Dc-conductivity of zinc lead borate glasses was increased with increasing the oxygen-to-boron ratio in a common dependence regardless of glass composition. The results are discussed considering the dual role of ZnO and its effect on glass structure[4].

The ionic conductivities of the lithium lead borate glasses containing LiCl were found to be at least two orders of magnitude higher than those of the glasses containing Li_2Co. Although Cl does not substitute indirectly in the B—O network, it does serve to modify the network structure indirectly by affecting the O/B plus Pb ratio. NMR study shows the different activated processes in the Li_2Co prepared glasses:

(1) A short range motion with low activation energy at low temperature which is ascribed to the motion of Li^+ ions on the surfaces of PbO pyramids and BO tetrahedra.

(2) In the high temperature range with higher activation energy motion of Li^+ ions bonded to non-bridging of BO unites. In glasses with high LiCl content, the Li^+ ions associated with the Cl^- ions dominate the Li^+ ion motion in the temperature range measured[5].

EXPERIMENTAL

Lead borate glass samples with different ratios in addition to lead borate glass samples containing basic cations of Na^+, K^+ and Mg^{2+} with different concentrations were prepared as shown in Tables 1 and 2. All the raw materials used in the investigated glasses were AnalaR chemical reagents. The preparation of the samples was carried out according to the procedure reported previously[6].

Dielectrical conductivity measurements

The electrical conductivity was measured using Keithly 175 auto-ranging multimeter. Variable standard resistance box was connected in series with the sample where potential upon it was measured with the electrometer. Before measurements, the glass samples were in the form of pellets 13 mm in diameter and 1–3 mm in thickness[7]. By using the equation

$$R_X = R_S(V_S/V_X - 1)a/L \qquad (1)$$

where R_s is the standard resistance, V_s is the constant potential upon the sample, V_X is the measured potential, a is the diameter of the pellet and L is its thickness.

From this equation, the resistance of the sample (R_X) can be calculated. As $\sigma = 1/R$, the conductivity value for each sample can be calculated.

By using the well known Arrhenius equation,

$$\sigma = \sigma_0 \exp^{(-\Delta E/2KT)} \qquad (2)$$

The activation energy for each sample can be calculated.

Dielectrical properties measurements

The dielectric constant ε′ and dielectric loss ε″ were measured using a WTW-multidekameter type DK 06, of the Schering bridge with a frequency range of 0.1 to 12 MHz[8]. The measurements were based on the superheterodyne principle. The tuning condenser had 4500 uniform divisions enabling fine adjustment with a sensitivity of the order of 10^{-5}. The measured dielectric constant of each sample was obtained from the calibration curve of the scale readings of the tuning condenser and the corresponding dielectric constant.

The dielectric loss ε″ was obtained by using the difference substitution method with the relation:

$$\varepsilon'' = \varepsilon'/2\pi fR_x \Delta C \tag{3}$$

where f is the measuring frequency in MHz, R_x is the cathode resistance in MΩ and ΔC is the capacitance of the sample in pF. The accuracy for measuring ε′ was +0.0005 and for ε″ was +3 per cent.

Ac-electrical conductivity

The dielectric material corresponds in its electrical behaviour to a capacitor C, parallel to an ohmic resistor (RC circuit). The frequency response of this circuit can be expressed by the ratio of loss current to charging current, that is, the dissipation factor D or loss tangent tan δ as

$$D = \tan\delta = I_L/I_C = \sigma_{dc} V/W_{CV} = 1/W_{RC} \tag{4}$$

The values of tan δ calculated may not all agree with that actually observed because the conductance term need not stem from a migration of charge carriers, *i.e.*, dc- (or ohmic) conductance but can represent any other energy consuming process. It has therefore become customary to refer to the existence of loss current due to all dissipative effects, in addition to a charging current[9].

To obtain conductivity (σ_{ac}) due to the dielectric loss taking 0.9×10^{-2} as the ratio of the electrostatic unit of capacitance and of the mho to the electrostatic unit of conductance, and using the expression for the capacitance C_0 in farads of the empty condenser.

$$C_0 = A/4\pi d \times 0.9 \times 10^{12} \tag{5}$$

The following equation is used:

$$\sigma_{ac} = \varepsilon'' w/4\pi \times 0.9 \times 10^{12} = \varepsilon'' f/1.8 \times 10^{12}\ \text{ohm}^{-1}\ \text{cm}^{-1} \tag{6}$$

This dielectric conductivity sums over all dissipation effects and may represent as well as an actual conductivity caused by migrating charge carrier as referred to an energy loss associated with a frequency dependence[10] (dispersion of ε″) for example to the friction, accompanying the orientation of the dipoles.

Ac electrical conductivities for lead borate glass samples and lead borate glass containing alkaline metal oxide with different concentrations were calculated from the dielectric loss data obtained from a previous work[6] using equation (5).

Differential thermal analysis (DTA)

Differential thermal analysis was performed using a Shimadzu XD-30 thermal analyzer. A heating rate of 15°C min^{-1} was used. The glass samples were in the form of fine powder by using automatic mortar.

RESULTS AND DISCUSSIONS

The dc-electrical conductivities were measured within the temperature range 308–789 K for two series of lead borate glasses. The first series contains boron and lead oxides with different ratios. In the second series some of the PbO was replaced by alkali metal oxide namely Na^+, K^+ and Mg^{2+} with different concentrations.The data are graphically represented in Figs. 1 and 3. The lower and higher values of the conductivity in addition to the activation energies are listed in Tables 3 and 4.

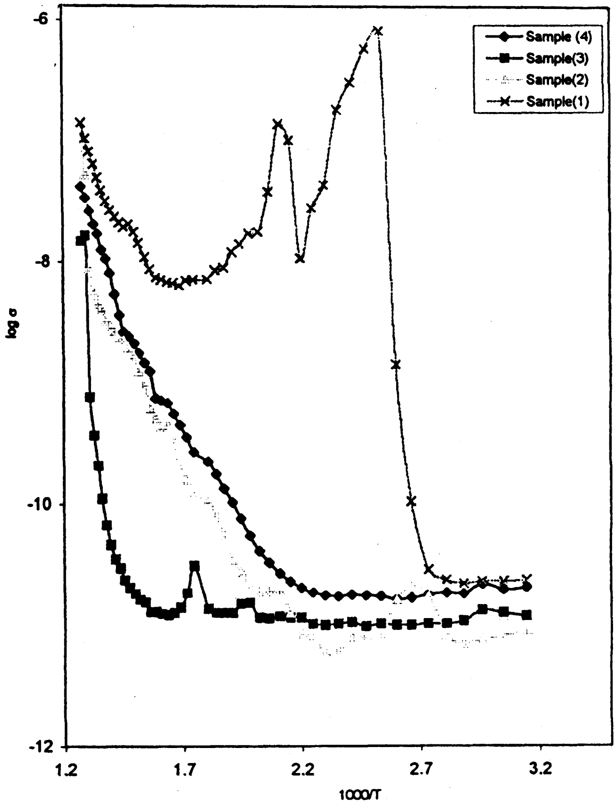

Fig. 1. The variation of the conductivity with reciprocal absolute temperature for samples 1, 2, 3 and 4

The measured conductivity values indicate semiconducting properties and fit the well-known Arrhenius eqation

$$\sigma = \sigma_0 \exp^{(-\Delta E/2KT)}$$

It is obvious from Figs. 1 and 3 that there is a major change within the two temperature ranges. The first one is at lower temperatures where the conductivity fits the Arrhenius type with a pre-exponential factor σ_0 and activation energy (ΔE) independent on temperature. This feature shows the relative stability of glass structure below the transition temperature[11].

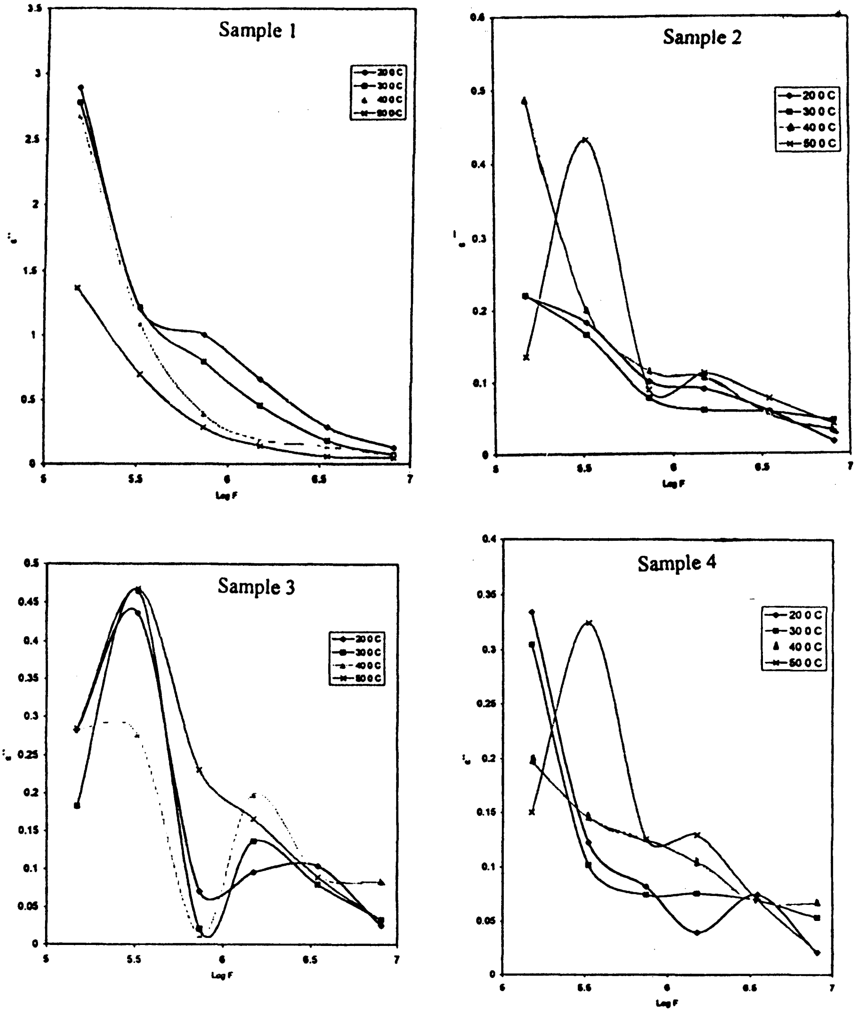

Fig. 2. The variation of dielectric loss values with frequency at different temperatures for samples 1, 2, 3 and 4 respectively

As the temperature approaches the spot where structural rearrangements become possible, the conductivity increases more rapidly with increasing temperature, leading to a second temperature region with a higher activation energy than at lower temperature[12].

Glasses containing boron and lead oxides

These glasses include the samples 1, 2, 3 and 4 with the constitution as shown in Table-1.

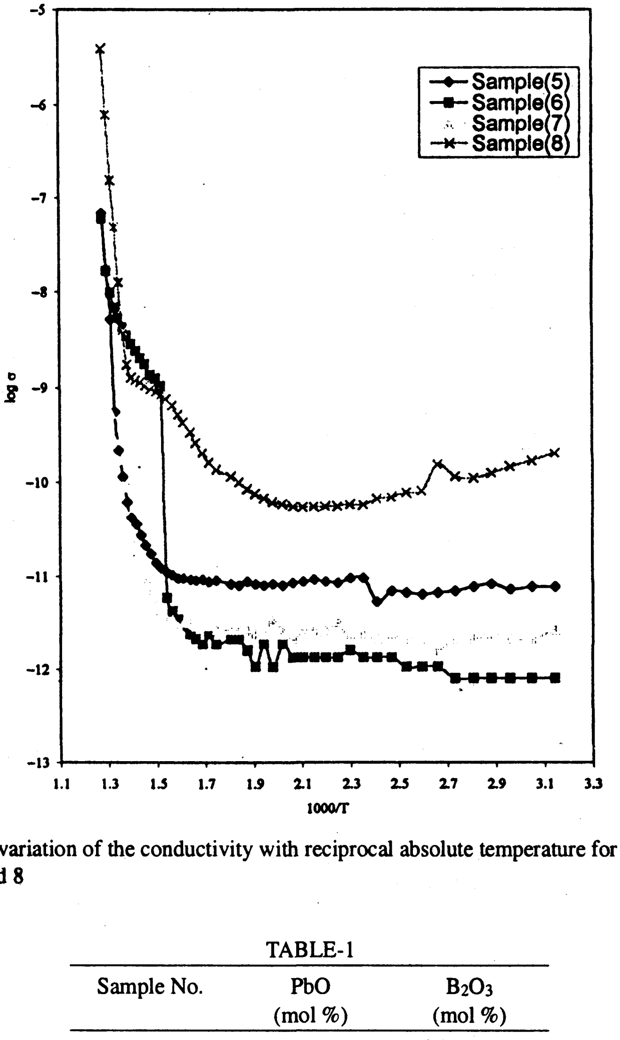

Fig. 3. The variation of the conductivity with reciprocal absolute temperature for samples 5, 6, 7 and 8

TABLE-1

Sample No.	PbO (mol %)	B_2O_3 (mol %)
1	90	10
2	75	25
3	65	35
4	60	40

The dc-electrical conductivities of the above mentioned glass samples within the temperature range 308–789 K are measured and graphically represented in Fig. 1. The data of the lower and higher values of the conductivity in addition to the values of the activation energy for this series is listed in Table-3.

From Fig. 1, it can be noticed that the four samples exhibit the general behaviour of semiconductors where the conductivity values ranged from 7.39×10^{-12} to 1.393×10^{-7}. The highest value was recorded for sample 1 (PbO 90% and B_2O_3 10%) and the lowest value was recorded for sample 3 PbO 65% and B_2O_3 35%) which may be due to the concentration of Pb^{2+} ions. Although the conduction mechanism in various "alkali-free" silicate and borate glasses containing lead, aiuminum and alkaline earth ions is uncertain it was found that in lead silicate and borate glasses the diffusion coefficient of oxygen gives too high conductivity and activation energy for oxygen diffusion[13]. It therefore seems likely that these experiments measure the diiffusion of molecular oxygen and its reaction with the lattice and that the diffusion of lattice oxygen is much slower. The electrical conductivity of lead silicate glass was affected by the presence of —OH group. Thus it seems possible that hydrogen ions are carrying the electrical current in this glass[14]. In most silicate glasses, the mobility of hydrogen ions is about three to four orders of magnitude lower than the mobility of sodium ions[15, 16] but it is possible that the mobility of protons is higher in alkaline earth, and alumina silicate glasses.

The diffusion coefficient of lead in lead silicate glasses gives the right value of conductivity; however, electrolysis experiments show that the lead ion is not conducting[14]. It is also possible that electrons carry part or all the current in these glasses.

The dielectric constant and dielectric loss of the glass samples in the temperature range from 293 K to 323 K and subjected to the alternations of the applied electric field which ranged from 10^5 to 10^7 Hz were measured and graphically represented in Figs. 2 and 4. These figures show dispersion and absorption bands. The dielectric dispersion was explained by the fact that the polarized parts in the lattice network in the glass molecules begin at some stage to lag behind the field oscillations at some high frequency. After this stage, only the dipoles or the flexible parts in lattices, which have sufficient rotational energy to allow frequency, passage over energy barriers can change their direction of equilibrium and then contribute to the deformation polarization. Also, it shows that at the lower frequencies and higher temperature of the dc-loss type is predominant over the Debye type loss, while the latter type become predominant at higher frequencies and lower temperatures.

In order to calculate the electrical conductivity from the measured dielectric loss, the measured absorption loss was corrected by determining the best-extrapolated value of $\varepsilon''_{\text{total}}$ from which the conductance term $\varepsilon''_{\text{ac}}$ could be calculate[17].

Using the equation

$$\sigma_{\text{ac}} = 5.56 \times 10^{-11} \varepsilon''_{\text{ac}} f \quad (7)$$

The dielectric loss used in the calculation of the conductivity was dc-type loss, which possessed equal values, *i.e.*, frequency independent. The values obtained for the complementary ac-electrical conductivity are listed in Table-5. It is clear that dielectric conductivity is higher than the dc-conductivity due to the high polarization of the B^{3+}, O^{2+} and Pb^{2+}, O^{2-} bonds and the other flexible bonds which gives rise to lattice defects and affect the vibrational configuration of the molecule.

The DTA curve of sample 1 is shown in Fig. 5. This curve reveals endothermic peak at 710 K corresponding to the α- and β-phase transformation. The peak observed is broad, and hence the reaction starts at lower temperatures and continues over a wide temperature range. These features are usually attributed to defects or disorders in the lattice that assist the start of the reaction. The presence of this phase transformation explains the decomposition of this sample at the conductivity curve. The activation energy of the transformation was calculated according to the simple method of Piloyan *et al.*[18] taking into consideration the precautions required for applying this methad[19]. Another feature of the DTA curve is tht presence of exothermic peak at relatively high temperature and takes place beyond the range of the conductivity measurements probably indicating the start of a dissociation process. The results are compiled in Table-7.

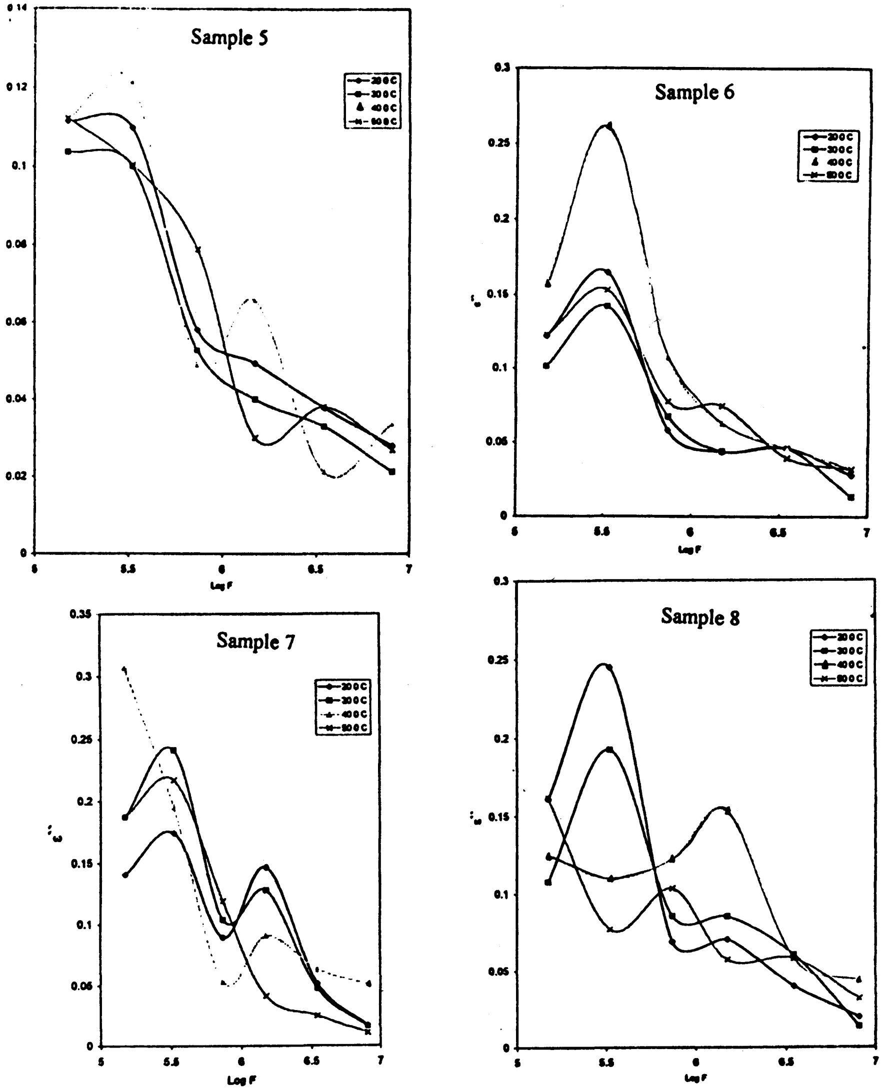

Fig. 4. The variation of dielectric loss values with frequency at different temperatures for samples 5, 6, 7 and 8 respectively

Borate glasses containing alkalines

These glasses include the samples 5, 6,7 and 8 with the constitution shown in Table-2.

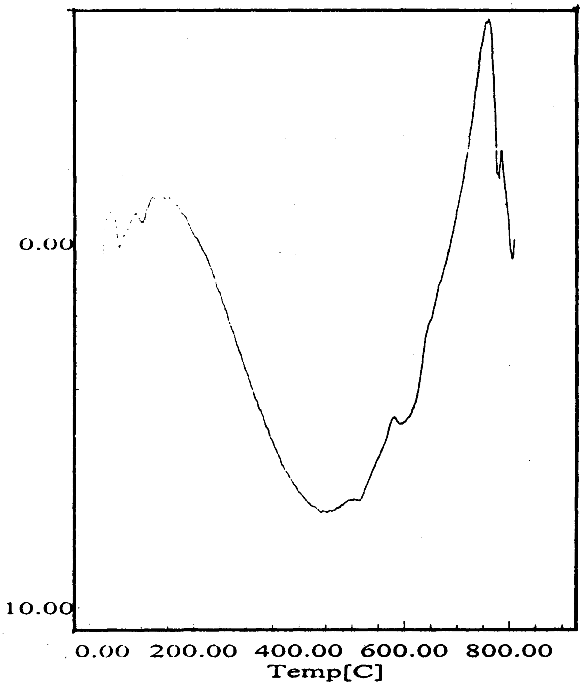

Fig. 5. DTA analysis of sample 1

TABLE-2

Sample No.	PbO (mol %)	B_2O_3 (mol %)	Na_2O (mol %)	K_2O (mol %)	MgO (mol %)
5	70	20	10	—	—
6	78	20	—	2	—
7	75	20	—	5	—
8	79	20	—	—	1

TABLE-3
CONDUCTIVITIES AND ACTIVATION ENERGIES OF THE GLASSES CONTAINING LEAD AND BORON OXIDE

Sample No.	Conductivity (Ω^{-1} cm^{-1})		Activation energy (ΔE eV)
	Room temp.	783 K	
1	2.061×10^{-11}	1.000×10^{-7}	1.560
2	7.396×10^{-12}	9.772×10^{-8}	1.435
3	1.531×10^{-11}	1.076×10^{-8}	3.431
4	7.852×10^{-11}	4.130×10^{-8}	1.500

The variation of dc-electrical conductivity with temperature are recorded and represented graphically in Fig. 3; from this figure it is clear that the general behaviour of Arrhenius equation is present where each sample has two temperature ranges. The first one is at lower temperature range with pre-exponential factor σ_0 and activation energy ΔE independent of temperature. The other one is at higher temperature range with a constant, although higher, activation energy than at lower temperature. The lower and higher values of conductivity in addition to the activation energy for each sample are calculated and listed in Table-4.

TABLE-4
CONDUCTIVITIES AND ACTIVATION ENERGIES OF THE GLASSES CONTAINING ALKALINE EARTH OXIDE

Sample No.	Conductivity (Ω^{-1} cm^{-1})		Activation energy (ΔE eV)
	Room temp.	783 K	
5	6.607×10^{-12}	6.887×10^{-7}	4.109
6	7.925×10^{-13}	6.012×10^{-8}	1.861
7	2.377×10^{-12}	3.327×10^{-8}	3.631
8	2.723×10^{-10}	3.900×10^{-8}	0.998

TABLE-5
THE VARIATION OF AC-CONDUCTIVITY FOR LEAD BORATE GLASSES WITH TEMPERATURE

Sample No.	log σ_{ac}			
	20°C	30°C	40°C	50°C
1	–6.676	–6.685	–6.800	–6.986
2	–7.745	–8.275	–7.585	–7.886
3	–7.993	–8.195	–7.575	–7.158
4	–7.735	–8.095	–7.826	–8.195

TABLE-6
THE VARIATION OF AC-CONDUCTIVITY FOR LEAD BORATE GLASSES CONTAINING ALKALINE EARTH METAL IONS WITH TEMPERATURE

Sample No.	log σ_{ac}			
	20°C	30°C	40°C	50°C
5	–8.305	–7.980	–8.185	–8.148
6	–7.835	–7.796	–7.375	–7.655
7	–7.675	–7.875	–7.835	–7.896
8	–7.795	–7.595	–7.825	–7.955

TABLE-7
DTA RESULTS OF SAMPLES 1 AND 6

Sample	Endothermic reaction		Exothermic reaction	
	Peak temp. (°C)	Activation energy (ΔE eV)	Peak temp. (°C)	Activation energy (ΔE eV)
1	440	11.46	761	1.06
6	565	2.56	624	2.90

The ionic conductivity of all oxide glasses results from the transport of monovalent cations. In most commercial glasses the conducting ion is sodium. Lithium ions also are quite mobile in oxide glasses. Potassium and hydrogen ions sometimes carry current, although their mobility is usually lower than that of sodium and lithium. Even in glasses with no nominal addition of monovalent ions, the conductivity results from transport of monovalent cations. In fused silica, the electrolysis experiments show that sodium and lithium ions are the conducting species even though they are present only in quantities of a few parts per million[20].

It is noteworthy that the lead borate glasses containing alkaline earth have nearly identical room temperature conductivity. The highest conductivity was for sample 8 which contained 1% of Mg^{2+} ion; the lowest conductivity was for samples 6 and 7 which contained 2% and 5% K^+ ion respectively. This observation leads to the assumption that the ionic conductivity of lead borate glasses is related to the ionic radius of the doped alkali metal. The maximum mobility is for Mg^{2+} (ionic radius 0.67 Å) and finally K^+ (ionic radius 1.33 Å).

Another feature that can be observed in Fig. 3 is the presence of a change in slope of the plot of log σ and 1000/T; this indicates a change in activation energy. In sample 8 this change in slope was observed around 475 K; in sample 5 this change was observed at around 649 K, while in samples 6 and 7 this change in slope was observed at around 611 K and 640 K respectively. The change in slope is generally attributed to some physical transformation. The effect of phase transition on the activation energy is the subject of some dispute in the literature. Hamann and Strobeck[21] believe that a phase transition should be associated with a change in activation energy, while Harrison and Ludwig[22] reported that such transitions would have no effect.

DTA curve of sample 6 (K^+, 5%) is shown in Fig. 6. The curve indicates endothermic peak at about 565 K corresponding to phase transformation. The observed peak is somewhat broad and hence this phase transformation continued over a wide temperature range. This feature is usually referred to defects or disorder in the lattice that assist the start of the reaction. Another feature of the DTA curve is the presence of exothermic peak at relatively higher temperature. The exothermic reaction is characterized by an activation energy of 2.56 eV and takes place beyond the range of the conductivity measurements probably indicating the start of a dissociation process. The results are compiled in Table-7.

The electrical conductivity resulting from the dielectric loss was calculated in the same way as described before. The values are recorded in Table-6. It is obvious

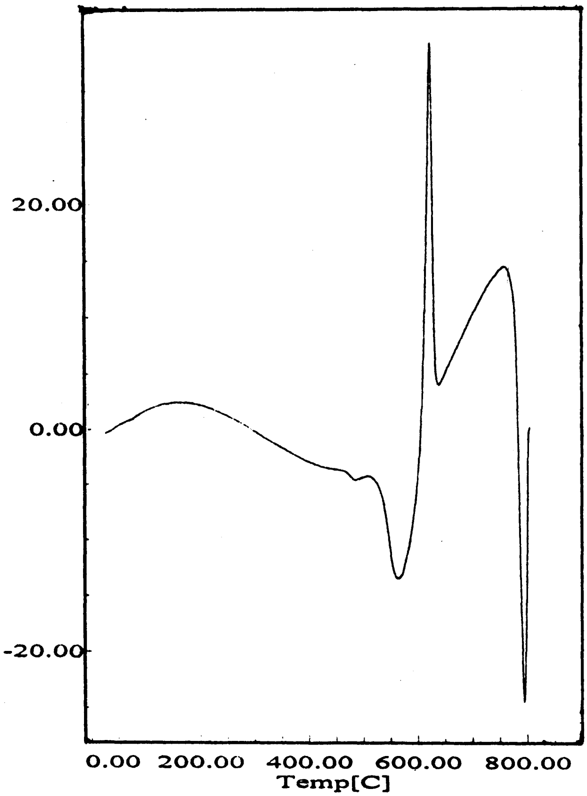

Fig. 6. DTA analysis of sample 6

that the ac-conductivity was higher than the dc-conductivity, which may be attributed to the presence of lattice defects and the polarization of flexible ions in the lattice. There is no big difference between the data of the four samples which means that the alkaline metal ions are not involved in this phenomenon and the only parameter controlled the dielectric conductivity in the vibration of polarizable bonds between B^{3+} and O^{2-} and Pb^{2+} and O^{2-}.

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