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DC electrical conductivity of Na_2O-ZnO-B_2O_3 glass system

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Abstract. The d.c. electrical conductivity of Na_2O-ZnO-B_2O_3 glass system has been measured as a function of temperature in the range of 350–600°K. The conductivity data show that the activation energy of Na^+ ions is dependent on ZnO concentration. The results have been discussed in the light of the cluster model of glasses.

Keywords. Na_2O-ZnO-B_2O_3 glass; electrical conductivity; density; activation energy.

1. Introduction

It is well known that glasses containing alkali ions are essentially solid cationic electrolytes, the current being carried by relatively mobile alkali ions. The motion of alkali ions in glasses is important, not only because of its relation to electrical conductivity, but also to chemical durability and to ion exchange kinetics. Similar work has been earlier reported on binary silicate and binary borate glasses. Some studies on borate glasses containing two different alkali oxides and alkali-alkaline earth oxides have also been reported (Israd 1969; Erzukyan 1969; Day 1976; Sakka *et al* 1979; Mutusita *et al* 1980). In the present work we report the d.c. electrical conductivity of sodium borate glasses with different concentrations of ZnO. The behaviour of activation energy of Na^+ ions has been discussed on the basis of the cluster model of glasses (Rao and Rao 1982).

2. Experimental

Analytical grade chemicals were used to prepare glasses corresponding to their glass-forming region (Rawson 1967). Appropriate quantities of boric acid (H_3BO_3), sodium carbonate (Na_2CO_3) and zinc oxide (ZnO) were taken and melted in a crucible at 1100°C for about 2 hr. The melt was then poured on a brass-block and it was quickly pressed with a polished copper-block. The glasses formed were annealed at about 400°C for 2 hr. X-ray studies showed that the glasses were amorphous. Samples of dimensions ($\sim 20 \times 20 \times 2$ mm) suitable for the measurement of electrical conductivity were prepared by grinding and polishing (using rough powder) the two flat surfaces. Silver paint was applied to these flat surfaces to serve as electrodes.

Measurements were made with glasses of the compositions listed in table 1. To measure the resistance of the samples, a special sample holder was designed following Mahadevan *et al* (1977). The resistance of the samples was determined by measuring the

Table 1. Glass composition, density and activation energy (E_a).

Mol% composition			Density	Activation energy (eV)	
Na_2O	ZnO	B_2O_5	(gm/cm^3)	(600–500) °K	(500–400) °K
10	5	85	2·04	0·77	—
10	10	80	2·49	0·97	0·15
10	15	75	2·60	0·95	0·17

current through the sample for an applied voltage (25 V); the voltage was briefly applied to avoid polarization. The temperature was measured with a chromel-alumel thermocouple placed very close to the sample. The d.c. electrical conductivity was measured as a function of temperature over the range 350–600°K. Density was also measured by the Archimedes method using benzene and the values are given in table 1.

3. Results and discussion

The variation of the d.c. electrical conductivity as a function of $1/T$ for three different compositions is shown in figure 1. The activation energies are calculated from the Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy for conduction and k is the Boltzmann constant. The variation of E_a as a function of ZnO concentration is shown in figure 2. The values of activation energy obtained are shown in table 1. The conductivity behaviour in figure 1 shows that the glass with 5 mol% ZnO has a single activation barrier and also has a higher conductivity, while the glass with 10 and 15 mol% ZnO has two conductivity regions and lower overall conductivity. In order to understand the behaviour of $\ln\sigma$ in figure 1, we note the following features about borate glasses.

In borate glasses the principal structural elements present are boroxol, tetraborate and diborate groups. The diborate groups get converted into triborate and pentaborate units. In the glasses investigated here the extent of any such borate grouping which consist of tetrahedral borons depends upon the total quantity of added oxides ($Na_2O + ZnO$). In order to investigate the role of Zn^{2+} ion in these glasses, we note that the e/r^+ ratio (2·7) is quite high. It is likely that it acts as a network former, particularly in low Zn^{2+} concentration. Such Zn^{2+} positions in the network also help in cross-linking the borate chains. Zn^{2+} ions in such situations can modify the diborate groups into more open rings without affecting the extent of tetrahedral borons (Selvaraj and Rao 1983). However at higher concentrations Zn^{2+} ions act as network modifiers and may ultimately lead to phase separation. In glasses containing 5 mol% ZnO, therefore, $\ln\sigma$ variation as a function of $1/T$ is linear. Addition of 5 mol% ZnO is unlikely to cause any phase separation. The activation energy of Na^+ ions (0·77 eV) may be compared with that of (0·60 eV) 10 mol% Na_2O-90 mol% B_2O_3 glass (Chakravorty and Chakraborti 1980). This may perhaps reflect the fact that incorporation of Zn^{2+}

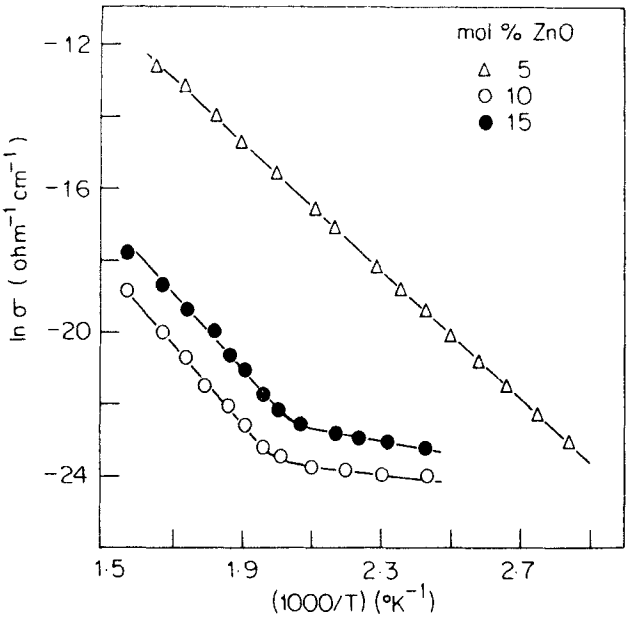

Figure 1. Variation of d.c. conductivity with temperature.

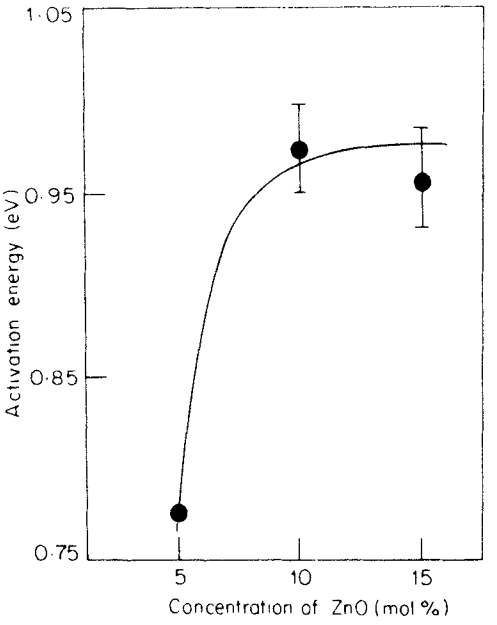

Figure 2. Variation of activation energy with concentration of ZnO.

into cross-linking positions increases the cohesion and density, thereby increasing the activation barrier for migration of Na^+ ions. In samples with 10 mol% ZnO and 15 mol% ZnO there appears to be two regions of conductivity (figure 1) characterized by two values of activation energy (E_a). This possibly indicates the presence of two distinct regions which act as precursors to phase separations. We feel that the two

phases correspond to oxide-poor and oxide-rich regions (oxide representing the total quantity of Na_2O and ZnO). The oxide-poor region can be expected to be less dense with lower E_a and lower conductivity (low concentration of charge carriers and perhaps even low mobility). The oxide-rich region corresponds to high E_a and high conductivity. The charge carriers being primarily Na^+ ions, one can see that the conductivity is slightly lower for lower effective concentration of Na^+ ions. The activation barriers for both glasses (10 mol% and 15 mol% ZnO) are virtually constant (figure 2) which should be the case if conduction is mainly by the oxide-rich region and hence we find that the results support a two-region model for these glasses.

The two-region model is essentially a cluster model recently described by Rao and Rao (1982). The more ordered cluster region is likely to be an oxide-rich region while the oxide-poor region corresponds to the tissue (less order) region. Indeed AgI-Ag_2O-MoO_3 glasses (Senapati *et al*, private communication) also exhibit such two-region conductivity behaviour in accordance with the cluster model of glasses. In 5 mol% ZnO glass, the regions are not sufficiently differentiated to exhibit two-region conductivity at high temperatures; it is likely to be seen in low temperature measurements.

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