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EFFECTS OF TEMPERATURE AND Cu-DOPING ON IONIC CONDUCTIVITY OF BINARY LITHIUM BORATE GLASSES CONTAINING (BO_3) TRIANGLES

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Pure and several Cu_2O-doped binary lithium borate glasses have been prepared and annealed.

Extensive measurements of the temperature-dependence of DC electrical conductivity were made on these samples and the corresponding activation energies of conduction were evaluated in each case. The results obtained are discussed in detail. They indicate that the phenomena of the formation of BO_3 triangles and a mixed alkali metal effect appear.

As discussed by Mott [1] and Cohen [2], the application of Anderson's theory [3] concerning the effect of disorder on the nature of eigenstates in a covalently bonded material should give rise to a band region of localized states and a region in which the states are extended. In the band tail the carriers are localized and move by phonon-assisted hopping, while in the energy range above the mobility edge the carriers are in extended states and can diffuse throughout the material without phonon assistance, but with short mean free paths. Borate glasses have the advantageous property of good thermal shock resistance, which can be utilized for sealing to metals. Alkali metal ion motion in glass is important because of its fundamental relation to properties such as electrical conductivity, chemical durability and ion-exchange kinetics. Previous work has concentrated on binary silicate glasses, and there are relatively few data on borate glasses. Below the glass transformation temperature (T_g), the electrical conductivity and alkali metal diffusion coefficients (D_{Na}) are much lower in $Na_2O-B_2O_3$ glasses [4] than in Na_2O-SiO_2 glasses [5–10], but the reasons for this are not known. Borate glasses [11] also exhibit smaller internal friction peaks than those found in alkali silicate glasses. $Ag_2O-Na_2O-B_2O_3$ glasses exhibit a mixed alkali metal internal friction peak [12], as well as a small minimum in electrical conductivity [13] as Ag_2O replaces Na_2O. Tsuchiya et al. [14] worked on the electrical propoerties of silver-containing oxide glasses in the temperature range 20–130°. In the case of conductivity, an anomaly was found for boric oxide at the composition 16 mol % Na_2O in the $Na_2O-B_2O_3$ glasses, but no anomaly was found in the $Ag_2O-B_2O_3$ glasses. Sekkina [15] studied the effects of heat treatment and active mineralizers on

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the electronic conductivity and related properties of silicate glasses, and a useful tool for controlling the desired quality of silicate semiconductors was put forward to suit their application for industry.

The behaviour of Ag^+ impurity diffusion has been emphasized since silver, which is present mostly as Ag^+, has been reported to behave similarly to lithium and other alkali metal ions in borate glasses [16]. The present work was undertaken to study the action of Cu^{2+} on the temperature-dependence of the electrical conductivity of lithium borate glasses.

Experimental

1. *Glass preparation*

Binary lithium borate glasses to which copper was added were prepared from high-purity boric acid*, lithium carbonate** and cuprous oxide powders*** (batch weight to give 5 g glass). One definite composition (24 mol % Li_2O + 76 mol % B_2O_3) was selected as base, as it contains (BO_3) triangles [17, 18]. Increasing amounts of cuprous oxide from 0.1 up to 8 mol % were introduced into this composition at the expense of the B_2O_3 content to give compositions (Table 1) still containing (BO_3) triangles.

Table 1 Compositions of the prepared Cu_2O-doped lithium borate glasses

Glass sample	Cu_2O, mol %
24 Li_2O · 76 B_2O_3	0.0
24 Li_2O · 75.9 B_2O_3 · 0.1 Cu_2O	0.1
24 Li_2O · 75.7 B_2O_3 · 0.3 Cu_2O	0.3
24 Li_2O · 75.5 B_2O_3 · 0.5 Cu_2O	0.5
24 Li_2O · 75 B_2O_3 · 1.0 Cu_2O	1.0
24 Li_2O · 74 B_2O_3 · 2.0 Cu_2O	2.0
24 Li_2O · 72 B_2O_3 · 4.0 Cu_2O	4.0
24 Li_2O · 68 B_2O_3 · 8.0 Cu_2O	8.0

Although the glasses were not analyzed, the final compositions are not expected to show much deviation from the nominal compositions. After the batch constituents had been throughly mixed, they were melted under normal atmospheric conditions in Pt–2 Rh crucibles in an electric furnace at 1050±5° for 3 h after the last traces of the batch had disappeared.

The molten glass was poured into rectangular rods (0.5 X 1.0 X 1.0 cm) and then annealed at the appropriate temperatures.

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* Extra-pure (> 99.5%), E. Merck, Darmstadt, Federal Republic of Germany.

** Anhydrous extra-pure (> 99.5%), E. Merck.

*** Analar (> 99.9%), BDH, England.

2. *Electrical conductivity measurements*

The DC electrical conductivity was measured for pure and copper-doped various binary lithium borate glasses. The two parallel faces of each pallet were coated with conducting paste for a good electrode contact area. The sample was placed between copper electrodes in a tubular electric furnace and the electrical resistivity was measured with a level Insulation Tester TM14 Electrometer in the temperature range 49–283°. The temperature was measured with a Cu-constant thermocouple fitted into the furnace. Measurements were made within 15 minutes for each temperature equilibration and were checked several times in order to attain reproducible and reliable data. The conductivity (1/resistivity) was calculated from the applied field and measured current for the second heating, to avoid the humidity effect. Over the temperature range from 49 to 283°, the conductivity (σ) measured in this way obeyed the Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_0}{RT}\right) \tag{1}$$

where σ_0 is the pre-exponential factor, E_0 the activation energy for ionic conduction, R the gas constant and T the absolute temperature in K.

Results and discussion

The temperature-dependence of the electrical conductivity is shown in Fig. 1. The activation energies (kJ mol^{-1}) in Table 2 were calculated from Eq. (1) using least squares analyses of the experimental data.

Table 2 Obtained values of the activation energy (E_0) for the electrical conductivity of pure and Cu_2O-doped lithium borate glasses

Sample	Cu_2O, mol %	E_0, kJ mol^{-1}
$24\ Li_2O \cdot 76\ B_2O_3$	0.0	96.2
$24\ Li_2O \cdot 75.9\ B_2O_3 \cdot 0.1\ Cu_2O$	0.1	93.6
$24\ Li_2O \cdot 75.7\ B_2O_3 \cdot 0.3\ Cu_2O$	0.3	85.8
$24\ Li_2O \cdot 75.5\ B_2O_3 \cdot 0.5\ Cu_2O$	0.5	85.9
$24\ Li_2O \cdot 75\ B_2O_3 \cdot 1.0\ Cu_2O$	1.0	83.1
$24\ Li_2O \cdot 74\ B_2O_3 \cdot 2.0\ Cu_2O$	2.0	83.2
$24\ Li_2O \cdot 72\ B_2O_3 \cdot 4.0\ Cu_2O$	4.0	85.9
$24\ Li_2O \cdot 68\ B_2O_3 \cdot 8.0\ Cu_2O$	8.0	85.3

The Cu_2O molar percentage dependence of the electrical resistivity, as well as the activation energy for conduction, shown in Figs 2 and 3, respectively, are very similar, reaching a minimum at 2 mol % Cu_2O addition. The present activation energy data

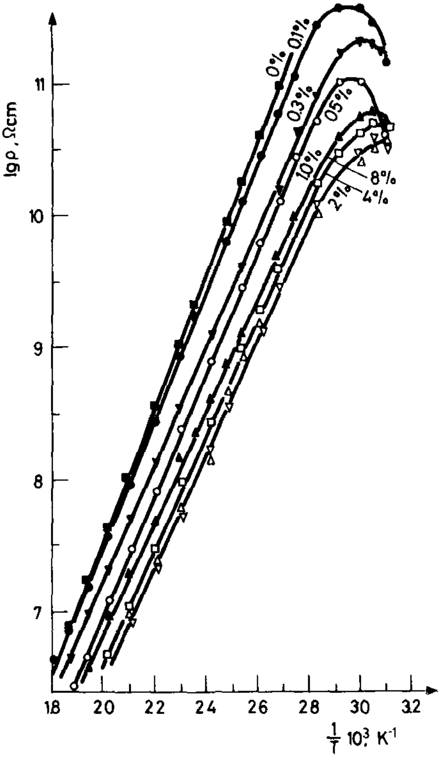

Fig. 1 Temperature dependence of electrical resistivity for lithium borate glasses containing (0.0–8.0 mol %) Cu_2O

for electrical conductivity are in accordance with previous results on borate glasses [13]. From Figs 2 and 3, it can be seen that as the molar percentage of Cu_2O increases, the absolute values of the resistivity and its attendant activation energy for conduction decrease to 2 mol % Cu_2O, followed by their gradual slight rise.

To explain this behaviour, we must consider the phenomenon of phase separation assumed in our previous investigation on borate glasses [19]. It is known that all borate glasses have criteria of structural changes as functions of composition and heat treatment. Thus, at certain compositions, the physical properties of borate glasses may pass through a minimum or a maximum as the alkali metal oxide content increases. Our previous work [19] on lithium borate glasses showed that as the Li_2O content in binary lithium borate glasses rises up to 12 mol %, there is a continuous transition from tricoordinated (B_2O_3) to tetracoordinated boron ions (BO_4) with the network being densified. Throughout these processes, the activation energy for conduction remains nearly constant. Beyond 12 mol % Li_2O in borate glasses, the formed (BO_4) groups begin to convert into (BO_3) triangles, so that the activation energy for conduction falls for glasses containing up to 24 mol % Li_2O. The addition of Cu_2O

(<2 mol %) to the glass composition (24 mol % Li_2O + 76 mol % B_2O_3) also decreases the electrical resistivity and activation energy for conduction (see Figs 2 and 3). This may be due to the amount of added Cu_2O still being below that needed and/or not consumed for the enhancement and commencement of nucleation and crystallization. At this stage, copper is assumed to act (most probably) as a bridge for current transfer through the interamorphous barriers and/or intercrystalline barrier if present.

For Cu_2O additions of from 2 mol % up to 8 mol %, the slight increase in electrical resistivity and its attendant activation energy for conduction (Figs 2 and 3) could readily be explained on the basis of the phenomenon of the mixed alkali metal effect [20], which may lead to the concept called the independent path model, in which alkali metal ions of one type can only move through vacancies left by ions of the same type. The probability that cations of one type could jump into the sites of cations of another type must be very small.

Accordingly, to a first approximation, the replacement of alkali metal ions of one type by dissimilar alkali metal ions causes a dilution, that is an increase in interionic separation for alkali metal ions of one type, and this may lead to an increase

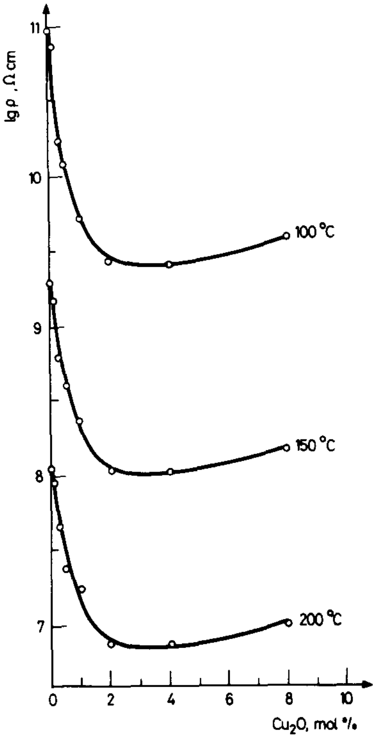

Fig. 2 Behaviour of electrical resistivity of binary lithium borate glasses as a function of Cu_2O content at constant temperatures of 100, 150 and 200 °C

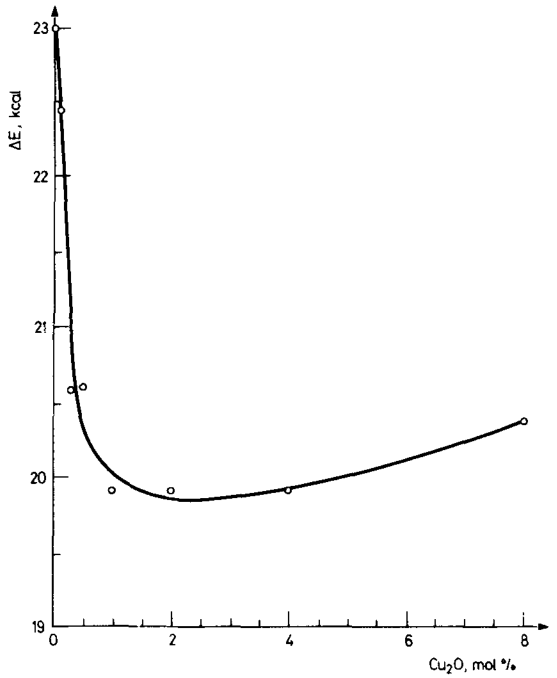

Fig. 3 Behaviour of activation energy for conduction as a function of Cu_2O (mol %)

in activation energy for conduction and a decrease in conductivity by the particular alkali metal ions. Since a particular interaction between dissimilar alkali metal ions is not assumed, a similar decrease in conductivity upon substitution of alkali metal ions by alkaline earth metal ions should be found according to the independent path model. This is the case, as can easily be seen in Figs 2 and 3.

The effect of dilution of the charge-carrying alkali metal ions on the activation energy for conduction will be discussed on the basis of the Anderson and Stuart method [21], in which the activation energy E is expressed as the sum of the elastic strain energy ΔE_s and the electrostatic energy E_b:

$$E = \Delta E_s + \Delta E_b \tag{2}$$

In this case, ΔE_s is the energy required to change the radius of a spherical cavity from r_d to r, the radius of the diffusing ion, which is Cu^{2+} in the present study. *

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* Since Cu^+ is oxidized to Cu^{2+} during glass melting and sample preparation.

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Zusammenfassung — Reine und einige mit Cu_2O versetzte binäre Lithiumboratgläser wurden hergestellt und getempert. Eingehende Messungen der Temperaturabhängigkeit der Gleichstrom-Leitfähigkeit wurden ausgeführt und in jedem einzelnen Fall die Aktivierungsenergie der Stromleitung bestimmt. Die in Einzelheiten diskutierten Ergebnisse weisen darauf hin, daß die Phänomene der Bildung von dreigliedrigen BO_3-Ringen und des Alkalimetallmischeffektes in Erscheinung treten.

Резюме — Были получены и отожжены чистые и легированные окисью одновалентной меди двойные литийборатные стекла. Проведены обширные измерения температурной зависимости их удельной электропроводности и в каждом случае были оценены энергии активации проводимости. Полученные результаты свидетельствуют об образовании треугольных BO_3 и появлении смешанного эффекта щелочного металла. Приведено детальное обсуждение результатов.