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EFFECTS OF TEMPERATURE, AND SINGLE AND DOUBLE DOPINGS ON THE ELECTROMECHANICAL PROPERTIES OF QUATERNARY GLASSES

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ABSTRACT

Pure, single doped (Cr_2O_3) and double doped (Cr_2O_3/MnO_2) quaternary (alkali alumino-borosilicate) glasses have been prepared.

Several measurements of the temperature dependence of the DC electrical conductivity and the corresponding activation energies for conduction were evaluated in each case. Furthermore, the Vickers hardness numbers were examined as a function of glass composition and extent of doping.

The results obtained were discussed and correlated in detail. Finally, a correlation between the electrical and mechanical properties of the test glasses was deduced, and the optimum composition was recommended for the electronic glass industry.

INTRODUCTION

The mixed alkali effect is reflected in the final properties of a glass, related to the migration of ions, i.e., electrical characteristics, diffusion and internal friction [1–3]. Similar to the mixed alkali effect, the mixed cation effect is even found in glasses which contain non-alkali, monovalent cations [4–9]. Recently proposed theories [10–12] assume that interactions between alkali ions of different types occur, although the nature of the interaction is different; electrodynamic interactions occur in the former, and elastic dipole interactions in the latter. Recently, the effects of temperature and Cu-doping on the ionic conductivity of binary lithium borate glasses containing (BO_3) triangles were investigated [13]. The activation energies for conduction were also evaluated in each case and discussed in detail.

The phenomenon of microhardness indentation needs to be correlated not only with a single property such as strength, but also with viscous flow, compaction and local heating. The lubrication effect also seems to be

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involved [14]. Marsh [15] assumed that the Vickers diamond-hardness impression on glass was indicative of plastic deformation. Prod'homme [16] suggested that microhardness and viscosity are related. In order to support his idea, an optical glass was studied at various heat-treatment temperatures. The glasses with a weakly bonded molecular structure had a lower Vickers microhardness number and the value increased with the compactness of the glass network. Razumovskaya et al. [17] assumed that the mechanism of inorganic glass deformation during micro-indentation was carried out by two stress–relaxation processes. The first stage was associated with the elastic deformation of the glass network without rupture of the chemical bonds, and the second stage was associated with the diffusion of sodium ions at room temperature, or with the diffusion of oxygen ions at 100 to 200°C.

The present work aims to evaluate the electromechanical behaviour of a hard glass of long durability with the addition of Cr_2O_3 and/or Cr_2O_3–MnO_2 and with firing.

EXPERIMENTAL

Glass preparation

Glasses of compositions: $12\ Li_2O \cdot 12K_2O \cdot 3Al_2O_3 \cdot 20SiO_2 \cdot 53B_2O_3$; $12Li_2O \cdot 12K_2O \cdot 3Al_2O_3 \cdot 20SiO_2 \cdot 53 - xB_2O_3 \cdot xCr_2O_3$; and $12Li_2O_3 \cdot 12K_2O \cdot 3Al_2O_3 \cdot 20SiO_2 \cdot 53 - (x + \epsilon)B_2O_3 \cdot xCr_2O_3 \cdot \epsilon MnO_2$ (in moles), where $x = 0.0$–2.0 and $\epsilon = 0.0$–0.15 (Table 1) were prepared from acid-washed quartz sand, used for manufacturing optical glasses, and reagent grade chemicals in the form of carbonates. Either Cr_2O_3- or MnO_2-doping is undertaken at the expense of B_2O_3 content in the glass sample. Batches for the production of about 90-g glass samples were placed in platinum crucibles

TABLE 1

Compositions of the prepared and various doped alkali alumino–borosilicate glasses

Glass sample	Composition (mol%)					Cr_2O_3 (mol%)	MnO_2 (mol%)
	Li_2O	K_2O	Al_2O_3	SiO_2	B_2O_3		
I	12	12	3	20	53	0.00	0.00
II	12	12	3	20	52.95	0.05	0.00
III	12	12	3	20	52.90	0.10	0.00
IV	12	12	3	20	52.85	0.15	0.00
V	12	12	3	20	52.80	0.20	0.00
VI	12	12	3	20	51.00	2.00	0.00
VII	12	12	3	20	52.80	0.10	0.10
VIII	12	12	3	20	52.70	0.15	0.15
IX	12	12	3	20	49.00	2.00	2.00

and melted in an electric muffle furnace at 1400–1550°C for about 5 h. After refining, the melts were poured onto a steel plate to form cylindrical discs and annealed by placing them in the furnace preheated at 500–600°C.

Electrical conductivity measurements

The DC electrical conductivity was measured as described previously [13]. Discs of about 2.0 mm in diameter and 4 mm thick were used as specimens for the electrical measurements. Silver paste was applied to the two opposite faces of the specimen to form a guarded electrode system which consisted of a main electrode of 0.5 cm diameter, a ring-shaped guard electrode and another electrode opposite this. The measurements were carried out in a vertically wound tube furnace with the windings running in opposite directions to eliminate fields caused by the heating current. The measurements were made in the temperature range 40–300°C, at 15-min intervals 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 the measure of current for the second heating, to avoid the humidity effect.

Vickers hardness measurements

The prepared discs were ground and finely polished on one side until they exhibited a faultless surface. The samples were mounted on the objective stage of a Carl–Zeiss microhardness tester and brought into the focus of the viewfinder objective (magnification ×12). The part of the specimen suitable for indentation was placed at the centre of the field of view. The measuring objective (magnification ×40) was then engaged and the focus was adjusted. The indenter was set at its starting position and then released by a trigger. Under a load of up to 95 g the indenter penetrated slowly into the glass for 10 s, and was then raised. At least ten indentations were made and measured for each specimen. The diamond-shaped indentation produced was measured with an estimated accuracy of ± 0.5 μm. After the indenter had completed its descent, it was allowed to remain on the sample for 10 s before being raised. Testing with loads up to 100 g could be used without causing microcracks to emanate from the indentations [18]. The Vickers hardness, H_V (tetragonal pyramid) corresponding to an impression of diameter (diagonal) d (μm), was calculated from eqn. (1)

$$H_V = 1854.4(P/d^2)\ \text{kg mm}^{-2} \qquad (1)$$

where P is the load (g).

RESULTS AND DISCUSSION

Figures 1 and 2 show the variation of the temperature dependence of DC electrical resistivity for the prepared and various doped glasses as a function of doping. Since the graphs have a general trend in common, namely a positive temperature coefficient of electrical resistivity, all materials investigated possess a semiconducting conduction mechanism with ionic conductivity predominantly occurring in the relatively high temperature region.

Over the temperature range investigated (40–300°C) the conductivity measured in this way obeyed the Arrhenius equation

$$\sigma = \sigma_0 \exp(-E_0/RT) \tag{2}$$

where σ_0 is the pre-exponential factor, E_0 is the activation energy for ionic conduction, R is the gas constant and T is the absolute temperature (K). The activation energies (kJ mol^{-1}) in Table 2 were calculated using least-squares analyses of the experimental data.

Figures 3 and 4 show the variation of activation energy for conduction as a function of mol% Cr_2O_3 and (Cr_2O_3 + MnO_2) dopants, respectively. From Figs. 3 and 4 and Table 2, it can easily be seen that as the molar percentage

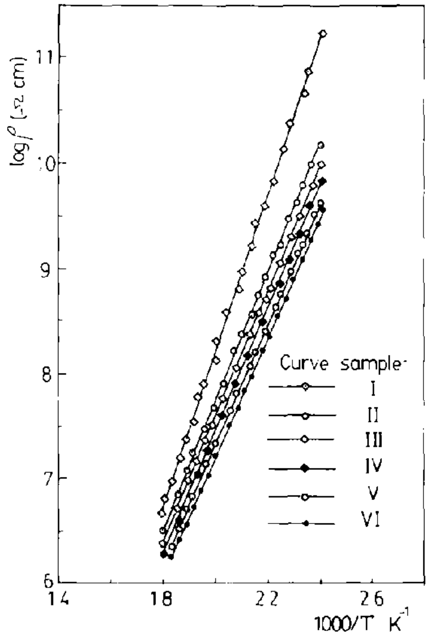


Fig. 1. Variation of electrical resistivity, log σ (Ω cm), as a function of temperature, 1000/T(K^{-1}), for pure and single (Cr_2O_3) doped alkali alumino-borosilicate glasses.

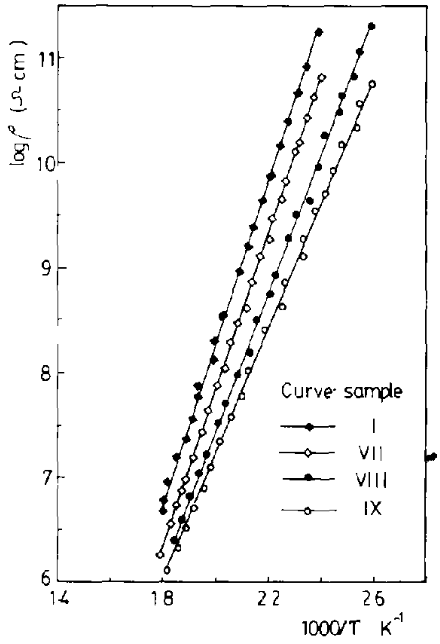


Fig. 2. Variation of electrical resistivity, log σ (Ω cm), as a function of temperature, 1000/T (K^{-1}), for pure and double doped (Cr_2O_3/MnO_2) alkali alumino-borosilicate glasses.

TABLE 2

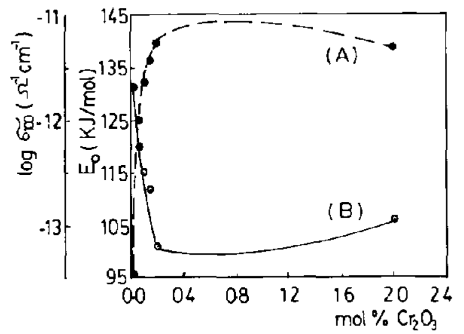
The values of electrical conductivity and activation energy (E_0) obtained for ionic conduction of pure single doped (Cr_2O_3) and double doped (Cr_2O_3/MnO_2) alkali alumino-borosilicate glasses

Glass sample	Cr_2O_3 (mol%)	MnO_2 (mol%)	log σ_{100} [a] (Ω^{-1} cm^{-1})	E_0 (kJ mol^{-1})
I	0.00	0.00	−13.50	133.80
II	0.05	0.00	−12.00	119.10
III	0.10	0.00	−11.60	115.80
IV	0.15	0.00	−11.40	112.00
V	0.20	0.00	−11.25	101.20
VI	2.00	0.00	−11.30	105.70
VII	0.10	0.10	−12.50	114.70
VIII	0.15	0.15	−11.40	115.40
IX	2.00	2.00	−11.00	105.70

[a] Logarithms of electrical conductivity at 100°C (where log $\sigma = -\log \rho$ and by extrapolation in some cases).

of Cr_2O_3 increases, the absolute values of the resistivity and its attendant activation energy for conduction decrease to 0.15 mol% Cr_2O_3, followed by a gradual slight rise. To explain this behaviour, we must consider the phenomenon of phase separation assumed in recent investigations [19,20].

The addition of Cr_2O_3 (up to 0.2 mol%) to replace B_2O_3 in the glass of composition: 12 mol% Li_2O + 12 mol% K_2O + 3 mol% Al_2O_3 + 20 mol% SiO_2 + 53 mol% B_2O_3, also decreases the electrical resistivity and activation energy for conduction (see Figs. 1–3 and Table 2). This may be because the amount of Cr_2O_3 dopant (0.2 mol%) is sufficient to effect complete nucleation for the formation of crystalline phases in glass. Furthermore, double



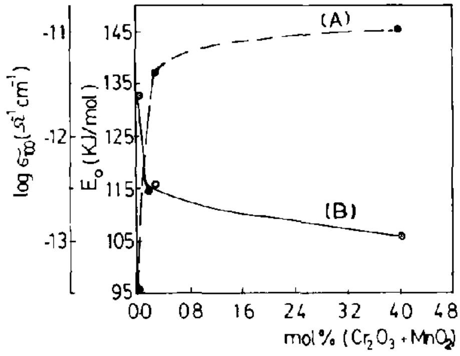


Fig. 3. Variation of log σ_{100} (A) and activation energy for conduction, E_0 (B), as a function of mol% Cr_2O_3 dopant.

Fig. 4. Variation of log σ_{100} (A) and activation energy for conduction, E_0 (B), as a function of mol% (Cr_2O_3 + MnO_2) dopant.

dopings with $Cr_2O_3 + MnO_2$ have a lower consistent effect (Figs. 3 and 4 and Table 2) on decreasing the absolute values of electrical resistivities and their attendant activation energy for ionic conduction, compared to single doping with Cr_2O_3 alone. These could most probably be correlated with the smaller ionic radius (r^+) and higher oxidation state for Cr^{3+} ions (0.69 Å) than for Mn^{4+} ions (0.80 Å). In addition, further interaction of douple dopants ($Cr_2O_3 + MnO_2$) with the glass composition and/or further phase separation leaves behind a decreased ionic mobility, and thus would increase electrical resistivities together with their attendant activation energies for ionic conduction.

This is further explained by the action of Cr_2O_3 or MnO_2 active mineralizer, which enhances the mobility of non-bridging ions. This is due to the high field strength and coordination requirements of these transition metal ions.

Beyond 0.20–2.0 mol% Cr_2O_3/MnO_2 dopants, the electrical resistivities and their attendant activation energies for ionic conduction tend to rise again. This could be correlated with the phase separation and changes in glass microstructures. This, in turn, may lead to the creation of a barrier energy, opposing current flow through the glass resulting in increased electrical resistivities and their attendant activation energies for conduction (see Figs. 1–4 and Table 2).

The increased Vickers microhardness in glasses containing higher contents (2 mol%) could be accounted for by a strongly bonded molecular structure and the compactness of the glassy network. Thus, the active role of Cr_2O_3 and/or MnO_2 as an active mineralizer enhancing glass nucleation (prior to the crystalization stage) is to increase the degree of compactness of the network [21]. Thus, supporting our view that microhardness is influenced by glass microheterogeneity.

Furthermore, single Cr_2O_3-doping for the glasses investigated has a more

TABLE 3

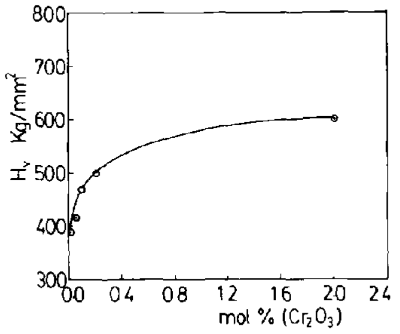
The Vickers hardnesses obtained of the glasses prepared containing Cr_2O_3 and Cr_2O_3/MnO_2 to replace B_2O_3

Glass	Glass composition (mol%)							Vickers number, DPH (kg mm^{-2})
	Li_2O	K_2O	Al_2O_3	SiO_2	B_2O_3	Cr_2O_3	MnO_2	
I	12	12	3	20	53	0.00	0.00	388.235
II	12	12	3	20	52.95	0.0	0.00	414.292
III	12	12	3	20	52.90	0.10	0.00	467.398
IV	12	12	3	20	52.85	0.15	0.00	480.168
V	12	12	3	20	52.80	0.20	0.00	495.116
VI	12	12	3	20	51.00	2.00	0.00	600.348
VII	12	12	3	20	52.80	0.10	0.10	486.776
VIII	12	12	3	20	52.70	0.15	0.15	509.129
IX	12	12	3	20	49.0	2.00	2.00	770.243

consistent effect on increasing the Vickers microhardness than double doping with Cr_2O_3 and MnO_2. This was ascribed to solute segregation in the former in accordance with earlier [22–24] deductions on other materials.

From Table 3 it is clear that the Vickers hardness increases with increasing Cr_2O_3/MnO_2 dopant content (network modifiers). This could be explained by the creation of potential barriers of various heights in presence of network modifiers [25,26]. Thus, the replacement of Cr_2O_3/MnO_2 and their combination for B_2O_3 in the glass composition permits a more efficient packing and thus produces a maximum diamond pyramid hardness (DPH). This is explained on the basis that the Cr^{3+} or Mn^{4+} ions coordinate with the highly polarisable non-bridging O^{2-} ions. This means that the highly polarisable O^{2-} ions are eliminated when either Cr^{3+} or Mn^{4+} ions are introduced.

Thus, from Table 3 and Figs. 5 and 6, the Vickers hardness increases with increasing molar ratio of Cr_2O_3, MnO_2 dopants, or a combination of the two. This could be correlated with the influence of dislocation-like defects,



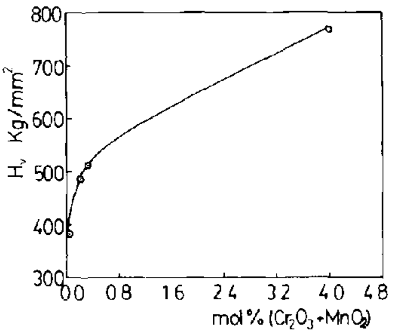


Fig. 5. Variation of Vickers hardness as a function of mol% Cr_2O_3 dopant.

Fig. 6. Variation of Vickers hardness as a function of mol% ($Cr_2O_3 + MnO_2$) dopant.

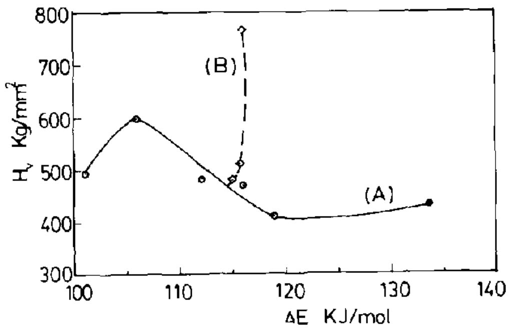


Fig. 7. Variation of Vickers hardness with values of the activation energy for conduction: (A) for single (Cr_2O_3) doped glasses; (B) for double ($Cr_2O_3 + MnO_2$) doped glasses.

the change in glass microstructure and the increased number of bridging ions in the same direction.

Figure 7 represents a correlation for Vickers hardness and activation energy for ionic conduction. It is clear that the relation has a general trend, namely an increase in Vickers hardness with increasing activation energy for ionic conduction. Thus, results of electrical properties agree with those of mechanical property for the investigated transition metal oxide-doped alkali alumino–borosilicate glasses. Accordingly, the role played by dopants, phase separation and the interaction of dopants with glass composition are clearly cut.

Alternatively, 2 mol% single doping (Cr_2O_3) or 2 mol% double doping ($Cr_2O_3 + MnO_2$) constitute an optimum composition for obtaining hard alkali alumino–borosilicate glasses of relatively low activation energy for conduction and moderate electrical conductivity for long durable electronic glasses.

CONCLUSION

It can be assumed that the electrical conduction and micro-indentation in the glasses investigated might have resulted largely from ionic mobility as the predominant mechanism (for electric conduction) and plastic deformation (for micro-indentations) through cooperative atomic movement depending on the bonding forces between the atoms, ease of mobility of the atomic aggregates and also on the field strength of the respective cations.

The close resemblance in behaviour of the microhardness data and the electrical properties of the glasses investigated indicated that the activation energy for the indentation in the microhardness phenomenon had some dependence on electrical parameters such as ionic and vacancy mobilization.

The relatively high value of diamond pyramid hardness (DPH) for these glasses can deteriorate through the combined presence of both Al_2O_3, in a minor proportion, and B_2O_3, in a high proportion. The glasses containing B_2O_3 are tough as a result of the disproportionation [27] of its binding forces into strong forces acting within the molecules and weaker ones acting between adjacent molecules. This distribution of binding forces produces a vibrational entropy and opposes the propagation of cracks.

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