Sodium Self-Diffusion in Mixed-Alkali Glasses

The physical properties of oxide glasses cannot generally be related to the composition accurately by means of linear functions of the amounts of each component. However, for many properties, and for a wide range of compositional changes, the departures from linearity are not excessive, so that linear factors often may be used to a first approximation. One important exception is the effect of changing the relative proportions of the alkali oxides in glasses containing more than one alkali. The variation with composition is often so non-linear that the initial trend is later reversed. This extreme departure from linearity is called "mixed-alkali" effect [1]. The property which normally shows the largest mixed-alkali effect is the electrical conductivity. As has been demonstrated by several authors [2-6] alkali ion diffusion in different glasses is also dependent on the ratio of the different alkalis, but comprehensive data are still scarce.

TABLE I Compositions (mole-%) and sodium self-diffusion results of the investigated mixed-alkali glasses.

No.	Na_2O	K_2O	Al_2O_3	SiO_2	x	D_0[cm^2/s]	Q[kcal/mole]
1	31.8	—	5.8	62.4	0	$(1.78 \pm 0.20) . 10^{-3}$	15.8 ± 0.1
2	31.1	0.7	5.8	62.4	0.022	$(3.77 \pm 1.02) . 10^{-3}$	16.8 ± 0.3
3	25.0	6.8	5.8	62.4	0.21	$(4.60 \pm 0.64) . 10^{-3}$	19.0 ± 0.2
4	15.9	15.9	5.8	62.4	0.50	$(5.39 \pm 0.84) . 10^{-3}$	20.7 ± 0.2
5	6.8	25.0	5.8	62.4	0.79	$(3.06 \pm 0.98) . 10^{-3}$	20.8 ± 0.3
6	—	31.8	5.8	62.4	1	$(3.59 \pm 1.08) . 10^{-1}$	26.7 ± 0.3

This paper is concerned with the investigation of sodium self-diffusion in a series of glasses of the system Na_2O/K_2O–Al_2O_3–SiO_2, ranging from pure soda to pure potash glasses. Table I contains the compositions of these glasses together with their $x = [K]/([K] + [Na])$ values. Glasses were prepared by holding the melts in a Pt crucible for 1.5 h at 1450°C. The melts were stirred for homogenisation. Prior to the diffusion measurement the glasses were annealed for 0.5 h at 490°C, followed by slow cooling to room temperature.

One drop of an aqueous solution of ^{22}NaCl was put on the surface of a polished specimen (20 mm, thickness 2 mm). A sandwich of two such specimens was subjected to an appropriate diffusion anneal. Then the samples were sectioned by grinding off thin layers (between 5 and 50 μm, depending on the penetration depths of the diffusion) parallel to the surface. The residual activity of the sample after each layer had been ground away was measured with a scintillation counter, using a discriminator for the 1.28 MeV γ-rays of the ^{22}Na emission spectrum. With the initial condition of an instantaneous source one obtains an erfc-type expression for the residual activity [7]. Applying this function to a measured diffusion profile the diffusion coefficient, D, can be calculated using a computer least-squares method.

Sodium self-diffusion in the potash-free glass 1 is known from previous work [8]. In fig. 1 the diffusion results for temperatures between about 200 and 400°C are plotted for all glasses according to the Arrhenius equation $D = D_0 \exp(-Q/RT)$. D_0 and Q values are listed in table I. As expected D decreases in a markedly non-linear manner with increasing x but a reversal in this dependence, such as is found in the electrical conductivity [1], was not observed although the diffusion parameters for the soda-free glass 6 are somewhat different from those of the other glasses.

Addition of a small amount of K_2O to the original glass did not change D significantly (see glasss 2) but resulted in more complex diffusion profiles. In [9] similar profiles were evaluated assuming a superposition of two diffusion processes with different diffusion coefficients. As was discussed there, addition of a small amount of a second alkali to a single-alkali glass may lead to loss of structural homogeneity with respect to diffusion of the primary alkali ion. This effect is in accordance with the internal friction behaviour

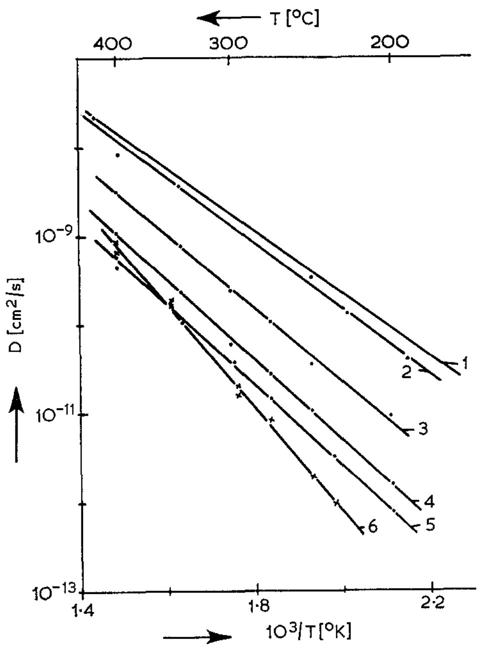

Figure 1 Temperature dependence of sodium self-diffusion in several soda-potash-aluminosilicate glasses.

of mixed-alkali glasses where a second alkali damping peak was observed after addition of only small portions of the second alkali [10]. For the glasses of table I with x values > 0.2 diffusion profiles were describable by a single diffusion process, again in accord with internal friction where only one alkali peak could be found for these compositions [10]. Therefore such mixed-alkali glasses with $x > 0.2$ may be regarded as structurally homogeneous with respect to ionic transport. In current theories for the explanation of the mixed-alkali effect [1] such further concentration-dependent effects in diffusion and internal friction have not been considered so far.

Comparing electrical conductivity and self-diffusion of ionic crystals (e.g. AgBr) by means of the Nernst-Einstein equation a correlation factor $f < 1$ normally results, demonstrating a defect mechanism for diffusion [11]. As has been shown especially by Haven and Verkerk [12] the theory of this correlation effect should also be valid for glasses, the resulting experimental f values being between 0.4 and 0.5. A similar f value has been found for glass 1 [8]. Using Zener's standard theory [13] for the discussion of the frequency factor D_o (which contains information on the atomic structure of the diffusion medium) a diffusion entropy factor $(\Delta S/R) = -0.99$ was calculated for this glass [8]. These results demonstrated that ionic transport in such glasses may also be seen in terms of a defect mechanism. Similar to the formation of a Frenkel pair in the Ag^+ sublattice of AgBr, Na^+ ions near $[SiO_{4/2}]$ tetrahedra must occupy energetically suitable sites in the glass. Complexes like $[Na^+SiO_{4/2}]$ and $[SiO_{3/2}O^-]$ can formally account for "interstitial" and "vacancy" sites. The mechanism of forming them may be seen as a dissociation process in the glass structure [14].

In comparison with crystalline materials both the size of the correlation factor and the sign of the entropy factor tend to the conclusion that an interstitialcy (indirect interstitial) is more probable than a vacancy mechanism. This is the same as the conclusion drawn by Barr *et al.* [15] from the measured isotope effect of sodium self-diffusion in glass. Except for the soda-free glass 6, D_o values of the other glasses in table I are of the same order as that of glass 1, therefore similar conclusions concerning the diffusion mechanism may be possible.

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Shaped Mesas on Gallium Arsenide

Gallium arsenide is now widely used to make microwave semiconductor devices and is of interest in acoustic surface wave research. A preferential etching effect which we have observed is of interest in both areas.

The etch used was potassium cyanide, hydrogen peroxide and water (15:400:400 parts by weight). At room temperature (24°C) the etch rate on the (100) face of GaAs was 2.6 μm/min. Conventional positive photoresist techniques were used to define the mesa pattern. The effect observed with a circular mesa is shown in fig. 1. The [110] direction was determined from the cleavage behaviour of the GaAs slice. Fig. 2 shows scanning electron microscope photographs of (*a*) an outward sloping section (*b*) a vertical section and (*c*) an inward sloping section. This behaviour can be explained in terms of preferential etching of the (111) planes when etching the (100) surface. Fig. 3 shows the four (111) planes in the GaAs (Zinc Blende) structure, with the two [110] directions which fall in the (100) plane. When etching a circular mesa an etchant which attacked (111) planes only would give two inward sloping sections on opposite sides of the mesa at 54° 45′ to the surface of the sample, parallel to the [110] direction. Two similar outward sloping sections would be formed perpendicular to this [110] direction. This is just the observed behaviour shown in figs. 1 and 2a, b and c.

Fig. 2d shows a shaped mesa on epitaxial gallium arsenide used to make Schottky barrier gate field effect transistors. The sloping edges (at both ends of the mesa) allow evaporated metal leads to be taken from the transistor over the edge of the mesa to contact bonding pads on the semi-insulating substrate. This gives an important reduction in interelectrode capacitances.

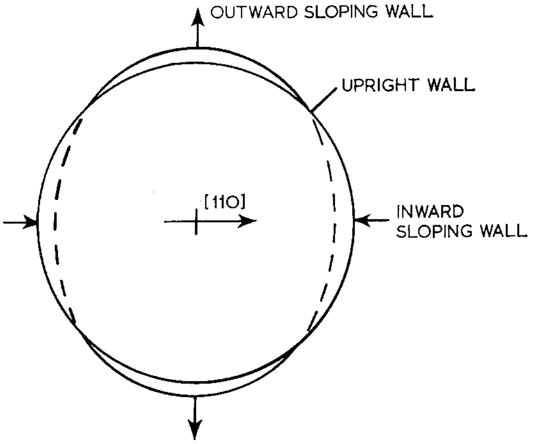

Figure 1 Etching effect observed on a circular mesa.

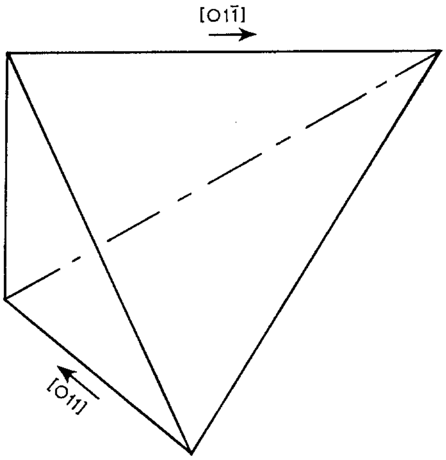

Figure 3 The four (111) planes in GaAs and the two [110] directions which fall in the (100) plane.