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Diffusion and electrical conductivity studies in some heterophase glasses containing bismuth

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Self-diffusion coefficients of sodium in the temperature range 300 to 375° C have been measured for glasses in the system $Na_2O-B_2O_3-Bi_2O_3-SiO_2$, by using a radioactive tracer technique. All these glasses have a two-phase structure. The d.c. resistivities of these glasses were also measured over the temperature range 30 to 375° C. The correlation factors, f, of all the samples have been calculated by using the diffusion coefficients and d.c. resistivity values for temperatures above 300° C. The anomalously large f values in the case of Bi_2O_3-containing glasses are thought to be due to a distribution of sodium ions in the dispersed as well as the continuous phases in these systems.

1. Introduction

Diffusion of alkali ions in oxide glasses has been studied extensively to understand the glass structure [1–5]. Most of these studies have been made on homogeneous glasses with either SiO_2 or B_2O_3 as the network former.

It has been shown recently that certain borosilicate glasses containing Bi_2O_3 when subjected to a sodium ⇌ silver ion-exchange followed by a reduction treatment, show memory switching [6]. The results of $Na^+ \rightleftharpoons Ag^+$ interdiffusion measurements carried out on these glasses predict a two-phase structure, one of which is rich in alkali ions forming a dispersed phase in a continuous matrix [7]. The microstructure of these Bi_2O_3-containing glasses has been previously described as consisting of a two-phase structure, one of which contains bismuth particles [6]. It is, therefore, necessary to clarify whether both the alkali ions and the bismuth particles are present in the same droplet phase distributed in a homogeneous matrix. To throw more light on this aspect of the structure of the $Na_2O-B_2O_3-Bi_2O_3-SiO_2$ glass system, self-diffusion coefficients of sodium ions as well as the electrical conductivities were measured in several compositions. The results are reported in this paper.

2. Experimental

The compositions of the glasses studied are given in Table I. The glasses were prepared from reagent grade chemicals which were melted in pure alumina crucibles in an electric furnace at temperatures ranging from 1250 to 1450° C. Rectangular glass slabs were cast by pouring the melt into an aluminium mould and these were subsequently annealed. For diffusion experiments glass plates of dimension 10 mm x 10 mm x 3 mm were cut from the cast slabs. All the faces of the samples were polished by using 1 μm size alumina powder. The microstructure of the glasses was studied by a Phillips EM 300 electron microscope. The method

TABLE I Compositions of glasses investigated

Glass no.	Composition (mol %)				Density (g cm^{-3})
	Na_2O	B_2O_3	Bi_2O_3	SiO_2	
1	10.7	19.7	0.0	69.6	2.4
2	10.0	18.0	8.0	64.0	3.3
3	23.0	15.1	8.0	53.9	3.3

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of sample preparation has been described elsewhere [8].

The self-diffusion of sodium was studied by a radio tracer technique. The radionuclide ^{22}Na was obtained from M/s International Chemical and Nuclear Corporation, California, USA. The diffusion anneal of the glass specimens was carried out by immersing them in a molten bath of sodium nitrate containing the ^{22}Na radioisotope kept in a pyrex crucible. The latter was mounted inside a stainless steel cup. The entire assembly was placed in an electrically heated furnace. The temperature of the furnace was maintained constant to within ± 1° C by an electronic controller over a temperature range 250 to 400° C. After a diffusion run lasting for a period ranging from 12 to 50 h the sample was taken out, cooled to room temperature and washed under tap water to remove any solidified sodium nitrate on its surface. Diffusion taking place through the faces of dimensions 10 mm x 10 mm was utilized for analysis. Hence all the other faces were ground off and polished to avoid surface diffusion effects.

The diffusion coefficients were measured by the residual activity method [4]. Layers of approximately 1 to 2 μm were removed by grinding from the diffused surface using a specially constructed sample holder and alumina powder of 0.5 μm size. The residual activity of the exposed surface was detected with a scintillation counter using a Tl-doped NaI crystal. The counting system was calibrated by plotting the pulse height spectra of Cs^{137} and Na^{22} respectively. The analyser was set in integral mode, and the preset timer was set to a period of 300 sec. The thickness changes of the sample were measured by a micrometer to an accuracy of 1 μm.

The solution of Fick's second law under the present experimental conditions is given by [4],

$$A/A_0 = \sqrt{\pi} \int_{\xi}^{\infty} \mathrm{erfc}\, \xi \,\mathrm{d}\xi = \sqrt{\pi}\, \mathrm{i\,erfc}\, \xi, \quad (1)$$

$$\text{with } \xi = x/2\sqrt{(Dt)} \quad (2)$$

A is the activity left in the sample after removal of a thickness x, A_0 is the total activity of the sample after diffusion anneal, D is the diffusion coefficient, t is the time, and erfc is the conjugate error function. The values of D were found by comparison of the experimental curve with one plotted from tabulated values of the error function integral [4].

For electrical measurements circular gold electrodes of diameters varying between 1 and 2 cm were vacuum-evaporated onto the faces of the specimens polished to a thickness of approximately 1 mm. The d.c. resistivities of the specimens were measured in the temperature range 30 to 375° C by plotting their voltage–current characteristics over a decade of voltage using a General Radio 1230A Electrometer. The I–V curves were linear for all the specimens.

3. Results and discussion

Figs. 1, 2 and 3 give the transmission micrographs of compositions 1, 2 and 3 respectively. It is evident that glass 1 has an interconnected two-phase

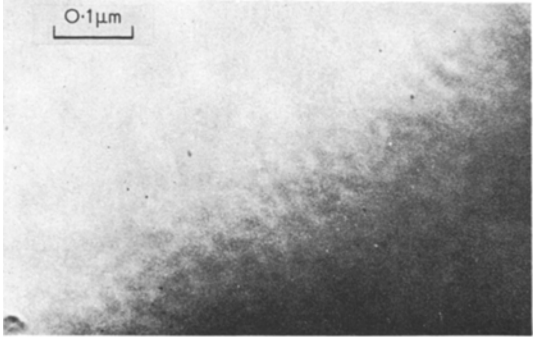

Figure 1 Electron micrograph of glass 1.

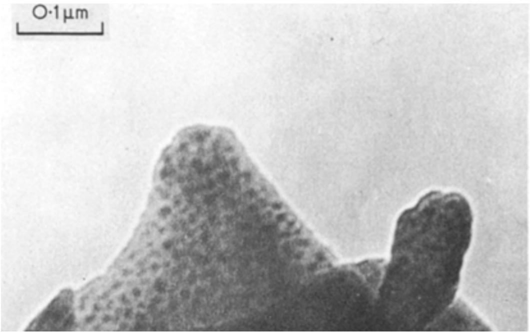

Figure 2 Electron micrograph of glass 2.

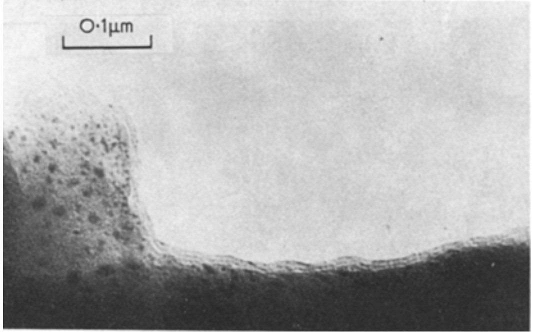

Figure 3 Electron micrograph of glass 3.

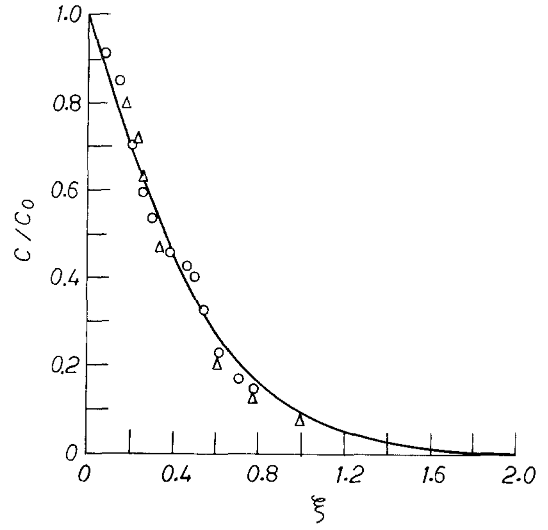

Figure 4 Diffusion profile of ^{22}Na in glass 1. ○ 333° C for 48 h; △ 360° C for 12 h.

TABLE II Diffusion coefficients of sodium in different glasses of the system $Na_2O-B_2O_3-Bi_2O_3-SiO_2$

Glass no.	Temperature (° C)	D (cm^2 sec^{-1})
1	333	8.0×10^{-12}
	360	1.1×10^{-11}
2	333	3.6×10^{-12}
	353	5.0×10^{-12}
3	330	1.1×10^{-11}
	352	2.5×10^{-11}

structure, one of which seems to be rich in SiO_2 judging from the contrast obtained in the micrograph. This is in agreement with the observation of Charles [9], for a similar glass composition. Glasses 2 and 3, on the other hand, have a microstructure consisting of a dispersed electron-dense phase in a continuous matrix. The dimension of the spherical phase varies from 50 to 200 Å. It has been shown previously from X-ray analysis of bulk samples in the present glass system that this droplet phase contains bismuth particles [6].

Fig. 4 shows a typical diffusion profile of sodium ions obtained in the different glasses. The line in this figure has been drawn from Equation 1 and the points represent the calculated values of A/A_0 from experimental data assuming a constant D value. The D values obtained from diffusion measurements on the three glasses compositions are shown in Table II.

In Fig. 5, the d.c. resistivity data of different glasses have been plotted as $\log(\rho/T)$ versus $1/T$. For glass 1, a straight line is obtained whereas in the other two compositions the slope decreases for temperatures lower than ~180° C. This has been attributed to a conduction mechanism involving electron tunnelling between bismuth particles present in such glass systems [10]. However, the slope obtained from these curves in the higher

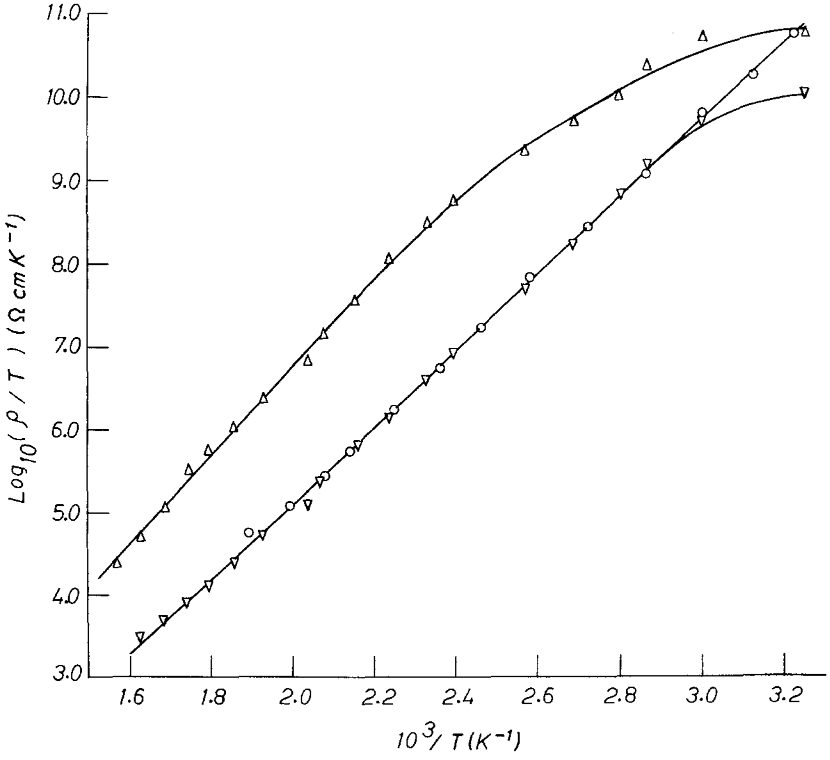

Figure 5 Resistivity–temperature plots for different glasses. ○ glass 1; △ glass 2; ▽ glass 3.

TABLE III Pre-exponential factor and activation energy for sodium ion migration in different glasses

Glass no.	ρ (Ω cm)	E (eV)
1	1.1×10^{-4}	0.9 ± 0.0
2	6.3×10^{-4}	1.1 ± 0.0
3	1.2×10^{-4}	0.9 ± 0.0

temperature region (temperatures above ~ 180° C) is controlled by the ionic contribution to the electrical conductivity [9]. The activation energies of sodium ion migration and the pre-exponential factors as obtained from the resistivity data of the different glasses are summarized in Table III.

The values of the correlation factor f for the different glasses were calculated [3] by the modified Nernst–Einstein relation,

$$\rho D = \frac{kT}{Ne^2} f \tag{3}$$

where, ρ is the resistivity of sample,
D is the diffusion coefficient at temperature T K,
k is the Boltzmann constant,
N is the number of sodium ions per cm^3,
and e is the electronic charge.

These values are given in Table IV. The value of f for glass 1 (0.14 to 0.18) is found to be unusually small. The conducting phase in glass 1 has an interconnected structure as is evident from Fig. 1 and has a large concentration of sodium ions [9]. The volume fraction of this phase is estimated from the micrograph to be ~ 0.5. The sodium ion concentration in this phase, which controls the electrical conduction of glass 1, is therefore twice the value calculated on the basis of the density and glass composition. The modified f values obtained by using this effective sodium ion concentration are shown in the last column of Table IV. These values, ranging between 0.28 and 0.36, indicate that a vacancy mechanism of sodium ion migration with mixed co-ordination of the sodium sites is operative in the conducting phase of glass 1 [3].

TABLE IV Correlation factor for different glasses

Glass no.	Temperature (° C)	f	f_{modified} (two-phase model)
1	333	0.18	0.36
	360	0.14	0.28
2	333	3.16	0.79
	353	2.51	0.63
3	330	0.79	0.74
	352	0.73	0.69

This phase consists largely of sodium borate [9], and it is interesting to note that similar f values were obtained earlier in the case of some sodium alumino borate glasses [5]. The large values of f found in glasses 2 and 3 at first appear to be anomalous because they imply that conduction mechanisms other than sodium ion movement are present in these glass compositions. However, the resistivity data show that the activation energy of conduction in all these compositions is almost identical to that of glass 1 over the temperature range under consideration. A two-phase structure of the Bi_2O_3-containing glasses with sodium ions distributed over both the phases [7] can explain this apparent anomaly as explained below.

From Fig. 5, it is evident that the pre-exponential factor in the case of glass 2 is larger than that of glass 1. According to Stevel's model [11] the resistivity of a glass arising due to the ionic migration is given by;

$$\rho = \frac{6kT}{N\nu s d^2 e^2} \exp(E/kT) \tag{4}$$

where N is the concentration of sodium ions per cm^3,
ν is the frequency of vibration of the sodium ion about its mean position,
s is the total number of interstitial sites available for any ion to jump to,
d is the distance between two neighbouring sites for an alkali ion
and e is the electronic charge.

The change in value of the pre-exponential factor as observed in the case of glass 2 cannot be explained on the assumption of changes in the values of either ν, s or d. Assuming the latter situation to be valid, the complete identity of resistivity values of glass 1 and 3 is difficult to explain. It is thus concluded that the above changes are brought about because of a variation in the effective value of N influencing the resistivities in the Bi_2O_3-containing glasses. As mentioned earlier, in glass 1 most of the alkali ions are concentrated in one of the interconnected phases and both D and ρ values in this specimen are determined by the transport of ions in that phase. In the other glasses containing Bi_2O_3 the two-phase structure consists of a dispersed phase in a continuous matrix. Assuming that the alkali ions present in these glasses are distributed in both the phases, the transport properties will evidently be determined by the number of such ions present in the matrix phase only. This implies that the effective value of N contributing to either the diffusion coefficient or the resistivity of these glasses should be a fraction of that calculated on the basis of composition and density. For glass 2 this fraction is estimated by taking the ratio of its pre-exponential factor with that for glass 1, since both of them have the same mol% of Na_2O in their overall compositions. For glass 3, the effective N value should be identical to that for glass 1 which follows from their resistivity data. In these calculations the effective value of N in glass 1, as estimated above on the basis of an interconnected conducting phase, has been used. The correlation factors of the Bi_2O_3-containing glasses calculated using these modified N values are shown in the last column of Table IV. The f values obtained by using the two-phase structure model of these glasses show that in both phases the diffusion occurs by a combination of vacancy and indirect interstitial mechanisms for sodium ion migration [3].

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