JOURNAL OF MATERIALS SCIENCE 15 (1980) 670–676

Diffusion of tin (IV) in silicate glazes and glasses

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The diffusion coefficients of Sn(IV) in an aluminosilicate glass and a commercial glaze have been measured from 809 to 1505° C. Two experimental techniques have been used. In one method, single crystals of SnO_2 were embedded in either the powdered glass or sealed into a bar of the glass. After the diffusion anneal, the Sn(IV) concentration profile was determined by EPMA. In the other method, radioactive ^{113}Sn was used as a tracer and the profile determined by measuring the X-ray emission. The results gave a good agreement between the two methods. The diffusion coefficients in the glaze ranged from 7×10^{-20} m² sec⁻¹ at 809° C to 1.9×10^{-14} m² sec⁻¹ at 1250° C and in the glass, from 5.6×10^{-15} m² sec⁻¹ at 1307° C to 1.6×10^{-11} m² sec⁻¹ at 1505° C.

1. Introduction

Few detailed investigations have been undertaken to study the diffusion of tin into molten and vitreous silicates. The diffusion of Sn(II) and Sn(IV) must play an important role in the production and properties of thin film resistors, semi-conducting glazes and the manufacture of float glass. This investigation was undertaken to obtain a better understanding of the factors which determine the electrical properties and microstructure of semiconducting glazes based on antimony-doped tin oxide.

Controlled-valence doped SnO_2 gives one of the more stable semi-conducting glaze systems [1] and until recently little was known of its detailed microstructure, conductivity mechanisms or failure modes. Scanning electron microscopy, EPMA and transmission electron microscopy [2, 3], have revealed that the glazes are a multiphase system. Their electrical properties, however, depend largely on only two phases, the undissolved grains of (semi-metallic) Sb-doped SnO_2, and the surrounding aluminosilicate glassy phase. The thermal activation energy for electronic conduction, the voltage non-linearity and the composition dependence of their conductivity, together with the direct observation of the microstructure via electron microscopy, lead to the conclusion that the electrical conductivity is determined by electron hopping within the glassy phase. This glass has been rendered conducting by dissolved SnO_2 and SbO_x [4] (the so-called solution rims), and not by a percolating network of grain-to-grain contacts or by, say, inter-grain electron tunnelling as occurs in thick-film resistor inks [5]. The measurements reported here have been undertaken on a commercial glaze* in order to aid the understanding of the processes which occur during the firing of the glaze and which determine their eventual microstructure and electronic properties.

The glazes show ionic conductivity above 300° C [4] so conductivity measurements have also been made [6] on a SnO_2/Sb-doped glass (glass A) chosen to have a relatively low viscosity and to have no group I mobile ions. The com-

*Doulton J8 glaze, Doulton Industrial Products Ltd, Stone, Staffordshire, UK.

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TABLE I Composition of the glaze and glass A (wt %)

	Glaze	Glass A
SiO_2	69.6	50.0
Al_2O_3	9.2	15.0
CaO	9.3	35.0
Na_2O	1.8	
K_2O	2.5	
ZnO	7.6	

positions of the glaze and glass A are given in Table I.

The diffusion of Sn(IV) in both silicate systems has been measured using a radioactive tracer method and electron microprobe analysis.

2. Experimental methods

The single-crystal anneal and the radioactive tracer methods have been used on the undoped glaze and glass A, in order to provide a check and an illustration of each method's applicability.

2.1. EPMA method

Single crystals of SnO_2 approximately 1 mm × 6 mm were pressed in the centre of a compacted pellet of glaze powder. The pellet was wrapped in platinum foil before firing. After firing and annealing, the position of the crystal in the pellet was found by taking X-ray radiographs of the pellet. Once the crystal had been located the glaze was ground away until the glass/crystal interface was reached, the surface was polished and vacuum coated with carbon and the profile then determined by EPMA. In order to show that this represented a true tin profile caused by tin diffusion and not X-ray fluorescence in the surrounding glass, the experiment was repeated without the high-temperature firing. A sharp drop in the tin concentration at the crystal interface was found in the second experiment.

This method appears to work well for the glaze which did not crystallize at the annealing temperatures and still had a high viscosity at the higher temperatures. The method is less suited for glass A which not only crystallizes at 1300° C or below, but also decreases rapidly in viscosity at higher temperatures. In samples fired below 1300° C, the SnO_2 crystal remains central within the pellet, and can be found by X-ray radiography and the profile determined. However, the diffusion is in the devitrified glass and not the glass itself. As the temperature is raised the viscosity of the glass decreases and the dense SnO_2 crystal tends to sink through the glass. The concentration profile may be distorted due to the viscous flow of the glass around the crystal. In addition there was a danger that the crystal might be ground away with the platinum foil.

A second technique was devised where the above problems did not occur. A bar of glass measuring approximately 80 mm × 5 mm × 5 mm was cast and two opposing long faces were ground flat. Parallel grooves to take the single crystals of tin oxide were cut across the bar at 10 mm intervals along the length. These grooves were approximately the same width as the crystals (~ 1 mm). The bar with crystals placed in the grooves on the upper ground surface was placed in a furnace at 1300° C for 4 min to seal the crystals into the glass. After cooling the bar was sliced into smaller pieces, each containing one crystal of SnO_2. These pieces were wrapped in Pt foil and annealed at known temperatures and times with the SnO_2 crystal at the bottom. All the temperatures were above 1300° C to avoid crystallization and the crystal could not sink through the glass. The crystal could be found easily after firing because the groove in the glass left an imprint on the platinum foil, and the glass/crystal interface was found by carefully grinding away the foil. When exposing the interface on quite a few samples the crystal fell out of the glass. This was due to the difference in expansion coefficient between SnO_2 and the glass, which caused the interface to crack on cooling. However, several samples which had been annealed between 1300 and 1500° C were prepared so that the diffusion profile of Sn in the glass could be determined by EPMA.

2.2. Radioactive tracer method

^{113}Sn was used for the tracer method. This is a radioactive isotope with a half-life of 115 days which decays by K capture to ^{113}In with the emission of In characteristic X-rays. Approximately 1.8% of decays result in emission of 0.255 MeV γ-radiation. The counter used was a gas-flow proportional counter (normally used for isotopes which emit low-energy electrons) which is sensitive to the X-rays, but has poor sensitivity for γ-rays. Hence the radiation monitored was principally the X-rays emitted by ^{113}In which have an energy of 24 keV and an absorption distance of the order of 1 mm in J8 glaze.

The diffusion experiments were carried out

TABLE II Diffusion of ^{113}Sn in glaze and glass A

Specimen no.	Sample	Anneal temp. (°C)	Anneal time (sec)	$D(m^2 sec^{-1})$
1	glaze	1250	7.2×10^3	1.9×10^{-14}
2	glaze	1000	2.52×10^4	8×10^{-17}
3	glaze	900	6.05×10^5	1.5×10^{-18}
4	glaze	809	1.5×10^5	$<7 \times 10^{-20}$
5	Glass A	1300*	7.2×10^3	2×10^{-11}

*This glass crystallized, refer to text.

using a "thin source" tracer technique. The ^{113}Sn tracer* was in the form of hexachlorostannate in solution in HCl. The glaze specimens (~ 200 μm thickness on an alumina tile) were preannealed for 2 days at 1350° C to establish a reasonably flat surface free from bubbles. With glass A, a preannealed block approximately 10 mm^3 was used. A drop of tracer solution was placed on the glaze surface and ammonia solution added until the drop was alkaline. This precipitated the tracer as stannic acid. The drop was then allowed to evaporate and the specimen heated to 500° C in air to evaporate the ammonium chloride and convert the tracer to SnO_2. The samples were then diffusion-annealed in air and an area ~ 20 mm x 20 mm which included the tracer, was cut from the tile. The specimens were then sectioned to determine the tracer penetration profile, the choice of method being determined by the expected penetration distance.

Techniques in which the activity of each section removed is measured are to be preferred for this isotope because of the relatively large escape depth of the 24 keV X-rays. Consequently, specimen 1 (Table II) was sectioned by precision grinding and counting the activity of the grindings [7]. Specimens 2, 3 and 4 could not be sectioned in this way because undulations in the glaze surface were larger than the penetration distances. Therefore these samples were sectioned by the r.f. sputtering technique [8] in which the activity of material removed by sputtering is measured. The penetration distance in specimen 5 was unexpectedly large and in this case the Gruzin technique of counting the residual activity was employed [7].

3. Results

The dissolution and diffusion of tin from the single crystal in the EPMA experimental arrangement produces a concentration profile for tin in the glaze similar to that expected around an SnO_2 particle in a commercial-doped glaze. A typical diffusion profile is shown in Fig. 1. However, the results of the radioactive tracer method showed less experimental scatter and these are described first.

Only a small quantity of SnO_2 is used in the tracer experiments so that the required solution of the diffusion equation is that for the thin source boundary condition

$$c(x, t) = \frac{A}{(\pi D t)^{\frac{1}{2}}} \exp\{-x^2/4Dt\} \tag{1}$$

where c is the activity per unit volume at penetration depth x, and A is the initial activity per unit area. Results were therefore plotted in the form log c versus x^2 in order to extract D, but only in the case of sample 1 was the interpretation straightforward (Fig. 2). The penetration profiles from samples 2 and 3 (Fig. 3) show a steep drop in activity near the surface before Equation 1 is obeyed and this is probably a result of tracer "hold-up" at the surface. The penetration profile in sample 4 could not be fitted to Equation 1. There are many possible reasons for this, the most likely of which is that transport of tracer may have been influenced by cracks in the surface region of the glaze. From this profile it was only possible to estimate an upper limit for D.

In the case of specimen 5, a modification of the Gruzin technique was used because the penetration depth was of the same order as the escape depth of the X-rays. The residual activity in a diffusion specimen after removal of the nth section, R_n, satisfies the equation [9]

$$\mu R_n - \frac{\partial R_n}{\partial x_n} = \frac{A}{(\pi D t)^{\frac{1}{2}}} \exp\{-x_n^2/4Dt\} \tag{2}$$

where μ is the absorption coefficient of the tracer radiation and is ~ 10 cm^{-1} in this case.

Fig. 4 shows R_n plotted against x_n^2 and hence

*^{113}Sn tracer was obtained from the Radiochemical Centre, Amersham, Buckinghamshire, UK.

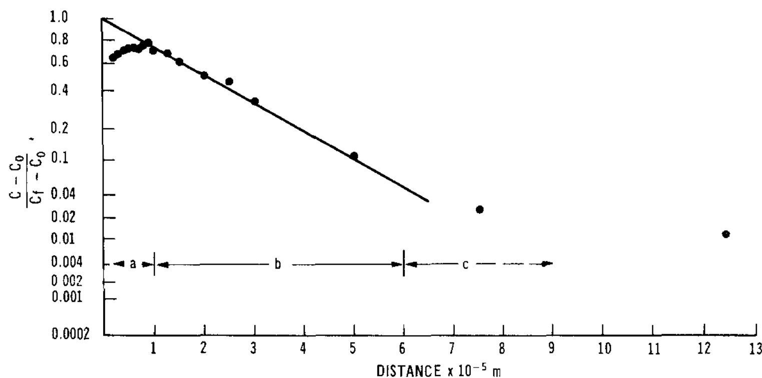


Figure 1 Diffusion profile from a single crystal of SnO_2 after a 5 min anneal at 1463° C. Region (a) shows reprecipitation part, (b) shows the central error function part and (c) shows the tail affected by viscous flow.

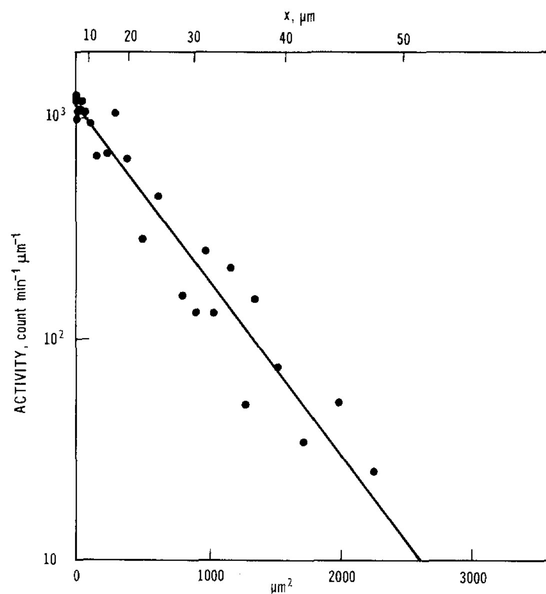


Figure 2 Diffusion of ^{113}Sn(IV) in a glaze at 1250° C.

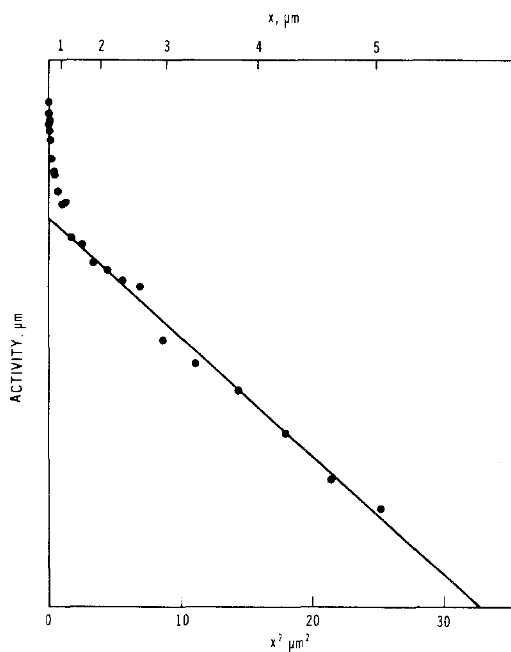


Figure 3 Diffusion of ^{113}Sn(IV) in a glaze at 1000° C showing tracer hold up at the surface.

R_n can be described by

$$R_n = R_0 \exp\{-x_n^2/4D_0t\} \quad (3)$$

where D_0 can be regarded as an initial estimate of D. Differentiating Equation 3 and substituting into Equation 2 gives

$$R_n\left(\mu + \frac{x_n}{2D_0t}\right) = \frac{A}{(\pi Dt)^{\frac{1}{2}}}\exp\{-x_n^2/4Dt\}; \quad (4)$$

the data are shown in Fig. 4, replotted according to Equation 4 and D was deduced from the modified plot.

The microprobe results were analysed by assuming diffusion from a constant source into a semi-infinite slab. This is a reasonable assumption because the maximum diffusion distance in most of the samples was 0.15 mm as opposed to the size of the crystal at 1 mm. The crystal size is much greater than the diffusion distance and the face of the crystal was considered as an infinite plane. In the case of the 1505° C sample, the diffusion distance was about 1 mm and so this assumption is not so good. It is not possible to be more accurate and to take the size of the crystal into account because, when the bottom surface is ground away, the position of the exposed glass/crystal interface is not known in relation to the original crystal.

A typical profile for the tin concentration is shown in Fig. 1. Three distinct regions are detectable in such a plot. Close to the crystal/glass interface, the drop in tin concentration is due to the reprecipitation of tin from solution back on to the SnO_2 crystal. This occurs because of the finite quenching time for the sample. The central

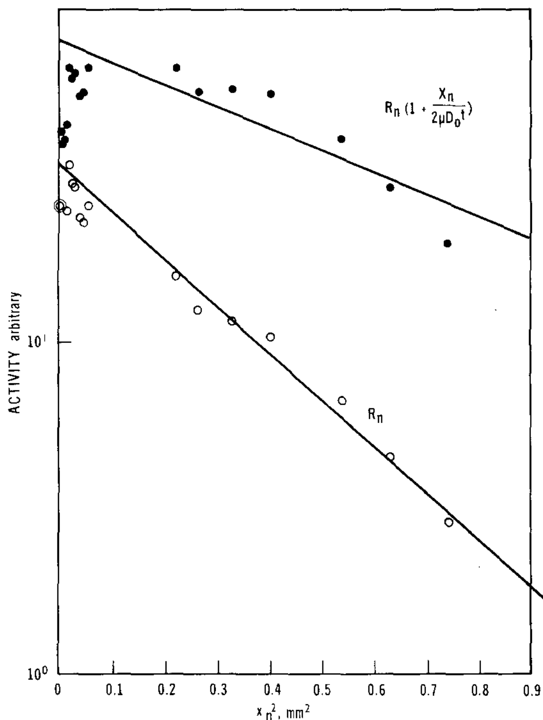


Figure 4 Extraction of diffusion coefficient from ratioactive tracer study using differentiation method, for specimen number 5.

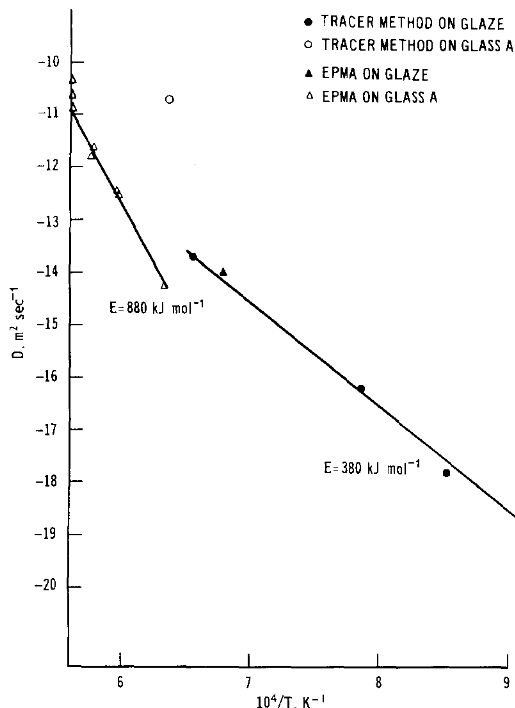


Figure 5 Temperature dependence of Sn(IV) diffusion as found by radioactive tracer method and by EPMA.

region corresponds to that of a complimentary error function while outside this region a higher than expected tin concentration occurs due to viscous flow of the glass around the crystal disturbing the diffusion profile. In view of the reprecipitation of tin at the crystal/glass interface, the concentration of tin at the interface was estimated by extrapolating the profile back from the central region to the interface. As the total amount of material that had been diffused from the crystal into the glass was relatively small, the position of the interface was assumed to have remained stationary.

The concentration, C, at a distance x from a semi-infinite slab obeys the equation

$$\frac{C - C_0}{C_f - C_0} = \mathrm{erfc}\left\{\frac{x}{2\sqrt{(Dt)}}\right\}, \quad (5)$$

with C_0 the background concentration and C_f that at the crystal/glass interface. The results were either plotted on error function graph paper to extract a value of D from a straight line plot, or Equation 5 was solved by a Newton–Raphson iteration process.

The results from the two methods are shown in Tables II and III. The diffusion coefficients for the glaze from Table II have been plotted against the reciprocal of temperature (Fig. 5) and give an activation energy of 380 kJ mol^{-1}.

The results from EPMA on both the glaze and glass A have also been plotted in Fig. 5 and the activation energy calculated from the points at 1307, 1410, 1415, 1455° C is 880 ± 180 kJ mol^{-1}. Three values for the diffusion coefficient at 1505° C are shown in Table III. These values were calculated from two different EPMA scans on the same specimen and highlight some of the difficulties. At this temperature the diffusion distance is large compared to that at lower temperatures; the glass is also more fluid. The most reliable result for the diffusion coefficient will therefore be calculated from an analysis close to the crystal/glass interface; the region least disturbed by viscous flow within the glass.

Interface concentrations (a) 5.2 and (b) 5.2 were calculated from runs conducted at different scanning speeds over adjacent areas of the same specimen. Estimating the surface concentration, C_f, is difficult due to the distortion of the concentration profile. Two values for C_f have therefore been used to interpret the data for this specimen. An interface concentration of 5.2 wt.%

TABLE III Diffusion coefficients determined by EPMA of commercial glaze and glass A

Specimen no.	Sample	Anneal temp. (°C)	Interface conc. C_f (wt %)	D(m² sec⁻¹)
6	Glass A	1505	(a) 5.2	2.5×10^{-11}
			(b) 5.2	6.0×10^{-11}
			(c) 7.8	1.6×10^{-11}
7	Glass A	1463	5.6	1.5×10^{-12}
8	Glass A	1455	5.7	2.5×10^{-12}
9	Glass A	1415	4.6	3.5×10^{-13}
10	Glass A	1410	3.0	5.3×10^{-13}
11	Glass A	1307	3.5	5.6×10^{-15}
12	Glass A	1300*	2.0	1.2×10^{-11}
13	Glaze	1220	nd	1.0×10^{-14}
14	Glaze	1180	0.76	7.7×10^{-15}

*This glass had crystallized, see text.

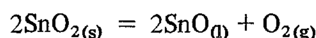
Sn was obtained from extrapolated profiles of two separate scans, while the value of 7.8 wt.% Sn used in (c) was that estimated from the observed trends in the solubility of SnO_2 in this glass with temperature and has been used to replace 5.2% in (b).

The diffusion coefficients calculated for specimens 5 and 12 in which crystallization occurred are compared using both experimental techniques. These two gave similar results, although much higher than the value for diffusion in a truly glassy specimen. This high value is thought to be due to diffusion of tin along the grain boundaries of the crystallizing specimens.

Two EPMA experiments were performed using the commercial glaze in place of glass A (see specimens 13 and 14, Table III). This enabled a direct comparison of the two methods to be made. Remarkably good agreement was obtained, as shown in Fig. 5.

4. Discussion

At high temperatures SnO_2 decomposes to SnO and oxygen. Above the melting point of SnO (977° C) the Gibb's free energy change for the reaction



$$2SnO_{2(s)} = 2SnO_{(l)} + O_{2(g)}$$

is given by

$$\Delta G^\circ = -RT \ln k = 635\,653 - 249T \text{ J/mole } O_2$$

where

$$k = \left(\frac{a_{SnO}}{a_{SnO_2}}\right)^2 P_{O_2}.$$

The ratio of the activites of SnO to SnO_2 can therefore be calculated for a given temperature and P_{O_2}. In the present study the samples were all annealed in an air atmosphere ($P_{O_2} = 0.2$ atm). The ratio a_{SnO}/a_{SnO_2} was therefore found to vary from 9.6×10^{-6} at 1400 K to 1.2×10^{-3} at 1700 K. The amount of Sn(II) which would be expected to form under the annealing conditions is therefore negligible. Mossbauer studies [10] on glass A containing added SnO_2 and prepared under similar conditions to those described here have been unable to detect the presence of Sn(II). It is therefore assumed that in both the glaze composition and glass A the diffusing species was Sn(IV).

An entirely different situation pertains when molten glass is in contact with a layer of tin, for example in the float glass process. In this case the P_{O_2} is 10^{-12} atm or less and under these conditions appreciable amounts of Sn(II) would be formed and the diffusion coefficients measured for tin would relate to the diffusion of Sn(II).

The values measured for the diffusion coefficient of any diffusing ion will be influenced by the composition of the medium and the local ionic environment. In a glass which contains a mixture of ionic and covalent bonds, small highly charged ions will be less mobile than ions with lower charges. However, as the charge on the Sn ion increases, the ionic radius decreases, thus partially compensating for the extra charge. The measured values for the diffusion coefficient would therefore depend on a number of factors including the temperature and the composition of the glass or glaze.

The activation energy for the diffusion of Sn(IV) in glass A is approximately twice that found for the glaze. The composition of the glaze was deliberately chosen to give a melt with a higher viscosity at the firing temperature and

furthermore one which changed relatively slowly with temperature. On the other hand, the viscosity of glass A, although not measured, was observed to change much more rapidly with temperature than that of the glaze. It is therefore not surprising that the observed activation energy for diffusion in the glass was higher than in the glaze.

Our own results are at variance with the only other reported study of the diffusion of tin into a silicate glass. Eremenko *et al.* [11] investigated the diffusion of tin into a soda-lime silica glass between 900 and 1150° C with a P_{O_2} of 10^{-16} to 10^{-18} atm. Mössbauer studies revealed the presence of both Sn(II) and Sn(IV). At 1050° C the diffusion coefficient of Sn(IV) is reported as 2.1×10^{-13} m^2 sec^{-1} and for Sn(II) as 9.3×10^{-15} m^2 sec^{-1}. The tin concentrations in the glass were determined by neutron activation analysis and the activation energy was found to be ~ 120 kJ mol^{-1} for the diffusion of Sn(IV).

The values obtained for the diffusion coefficients of Sn(IV) in the glaze are approximately six orders of magnitude less than those estimated for the diffusion of Sn(II) in the float glass process [12]. However, the activation energy for the two processes is very similar. These differences could well be accounted for by the difference in composition of the two glasses – the soda-lime silica glass being much more fluid than the glaze – and by the difference in ionic charge on the diffusing species.

The values for the diffusion coefficients and activation energies for a large number of ions in glasses and melts have been reported by Doremus [13] and Frischat [14]. The values obtained for the diffusion coefficients in the present investigation lie between those reported for Ca^{2+} and Ni^{2+}, although the activation energies were found to be much higher. In a glass of similar composition (CaO 39%, Al_2O_3 21% and SiO_2 41 wt.%) to that of glass A the activation energy for the self-diffusion of calcium varied between 200 and 300 kJ mol^{-1}. The activation energy for the diffusion of silicon [13, 15] is approximately 300 kJ mol^{-1}. In a review of the diffusivities of various elements in amorphous silica films [16] the activation energy for the diffusion of antimony is given as 844 kJ mol^{-1}, for arsenic between 386 and 473 kJ mol^{-1} and phosphorus between 122 and 389 kJ mol^{-1}.

The values for Sn(IV) diffusion in the commercial glaze may be used to explain the microstructure and overlapping solution rims reported in an earlier investigation [4].

5. Conclusions

The diffusion coefficients of Sn(IV) in the commercial glaze ranged from 7×10^{-20} m^2 sec^{-1} at 809° C to 1.9×10^{-14} m^2 sec^{-1} at 1250° C and in an aluminosilicate glass from 5.6×10^{-15} m^2 sec^{-1} at 1307° C to 1.6×10^{-1} m^2 sec^{-1} at 1505° C.

Acknowledgements

The assistance of P. W. Teare (CERL) with the EPMA analysis is gratefully acknowledged. The part of the work carried out at CERL is published with permission of the CEGB. Financial support from the SRC is gratefully acknowledged by one of us (SBM).

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Received 6 June and accepted 11 September 1979.