Original Paper

Diffusion of zinc, cadmium, strontium, lead, barium divalent cations in silicate glasses

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Diffusion of zinc, cadmium, strontium, lead, barium divalent cations from molten halide or nitrate salts into soda-lime-aluminosilicate glasses was investigated at 580 to 640 °C. The diffusion concentration of these divalent cations in the glass surface was measured by ion microprobe analysis. The results show that the diffusion coefficients (D^*), frequency factors (D_0) and activation energies (E) of divalent cations depend on their ionic radii. The diffusion coefficients decrease with the ionic radii increasing; one can state that $D^*_{Zn} > D^*_{Cd} > D^*_{Sr} > D^*_{Pb} > D^*_{Ba}$. But the diffusion activation energies and frequency factors of divalent cations increase with their ionic radii increasing. The influence of ionic field strength and polarization on diffusion behavior is also discussed.

Diffusion von zweiwertigen Zink-, Cadmium-, Strontium-, Blei- und Bariumkationen in Silicatgläsern

Die Diffusion von zweiwertigen Zink-, Cadmium-, Strontium-, Blei- und Bariumkationen aus Halogenid- oder Nitratsalzschmelzen in ein Kalk-Natron-Alumosilicatglas wurde bei Temperaturen von 580 bis 640 °C untersucht. Die Messungen der Diffusionskonzentration dieser zweiwertigen Kationen an der Glasoberfläche erfolgten mit der Ionenstrahlmikrobereichsanalyse. Die Ergebnisse zeigen, daß die Diffusionskoeffizienten (D^*), die Frequenzfaktoren (D_0) und die Aktivierungsenergien (E) der zweiwertigen Kationen vom Ionenradius abhängen. Die Diffusionskoeffizienten nehmen mit zunehmendem Ionenradius der Kationen ab, dies wird beschrieben durch die Reihe $D^*_{Zn} > D^*_{Cd} > D^*_{Sr} > D^*_{Pb} > D^*_{Ba}$. Dagegen nehmen die Aktivierungsenergien und die Frequenzfaktoren der zweiwertigen Kationen mit größer werdendem Ionenradius zu. Der Einfluß der Ionenfeldstärke und der Polarisation auf das Diffusionsverhalten wird ebenfalls diskutiert.

1. Introduction

Many investigators have reported on diffusion studies of monovalent cations in silicate glasses. Divalent cations diffuse much more slowly than monovalent cations in silicate glass thus giving rise to increased difficulties in determining diffusion coefficients and therefore have been much less studied [1]. Frischat measured the diffusion coefficient of calcium in soda-lime-silicate [2] and Infrasil (= fused silica) glasses [3]. He also described Ca^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+} diffusion in his review [4]. Varshneya [5] gave the diffusion coefficient of calcium in solid glass. Measurements of D^*_{Ca} in soda-lime-silicate glass and slag glass were carried out by Terai [6]. Takahashi reported on the diffusion behavior of Cd^{2+}, Ni^{2+}, Co^{2+} in molten sodium borates [7] and Ni^{2+} in three series of molten alkaline earth borate glasses [8]. Diffusion behavior of Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{2+} ions in glasses with electric field was reported by Frischat [9]. Rauschenbach [10] applied SIMS for the measurement of Ca^{2+}, Mg^{2+} diffusion coefficients in the $Na_2O-Al_2O_3-SiO_2$ system. In this paper the diffusion of zinc, cadmium, strontium, lead, barium divalent ions from molten halide or nitrate salts into soda-lime-silicate glasses is discussed.

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2. Experimental

The glass used in this work consists of 70 SiO_2, 11.5 Al_2O_3, 10 CaO, 8.5 Na_2O (in mol%). The glass batches were melted by using a platinum crucible in an electric furnace, then the glass melts were cast in the form of plates. The glass plates were annealed at 600 to 700 °C for 1 to 2 h. Sample plates of $(10 \times 10 \times 1)$ mm^3 size were smoothed by mechanical grinding and polishing. Before the diffusion experiment the specimens were rinsed with distilled water, then washed in propanone, alcohol and deionized water and finally air-dried. Diffusion experiments were made by immersing the silicate glasses in molten halide or nitrate salts. The conditions of the diffusion processes are shown in table 1.

A Hatchi IMA-2A ion microprobe was used to examine the depth profiles of diffusion ions in silicate glasses. The experimental conditions were: primary ion O^+, accelerative voltage 10 to 15 kV, sample current 1.2 to 2.0 μA, beam diameter 200 to 924 μm, chamber pressure 2.66 to $8 \cdot 10^{-6}$ mbar.

3. Results and discussion

When glass samples were immersed in molten halide or nitrate, interdiffusion between molten salt and

glass occured. The self-diffusion coefficient of divalent ion is much lower than that of alkali so that the interdiffusion coefficient is approximately equal to the self-diffusion coefficient of divalent cation. The diffusion equation is the well-known expression:

$$C(x,t) = C_0 \operatorname{erfc}\left(x/2\sqrt{Dt}\right) \tag{1}$$

where C_x is the concentration at depth x (after diffusion time t) and C_0 is the initial concentration of divalent ion.

The calculated equation is given by:

$$I_x/I_0 = C_x/C_0 \tag{2}$$

where I_0 is the secondary ion intensity on the surface and I_x is the secondary ion intensity at depth x. C_0 and C_x are the concentrations at the surface and depth x, respectively. Therefore it holds

$$I_x/I_0 = C/C_0 = \operatorname{erfc}\left(x/2\sqrt{Dt}\right). \tag{3}$$

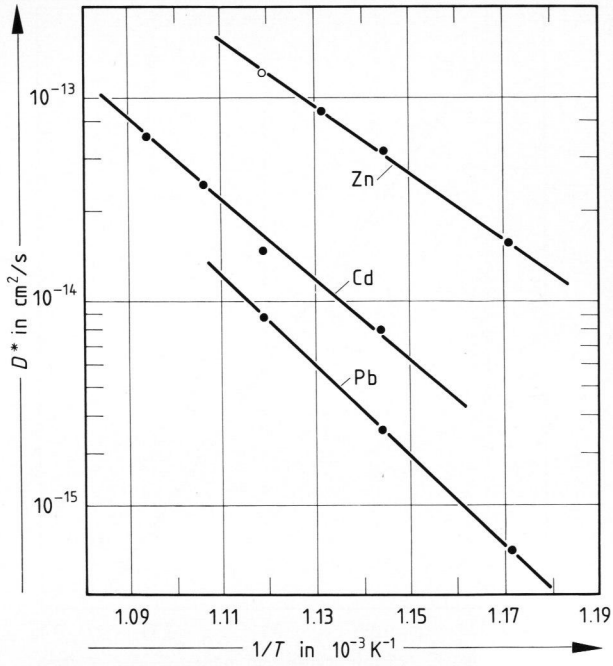

Figure 1. Dependence of zinc, cadmium, lead ion diffusion coefficients on temperature.

Table 1. Conditions of the diffusion processes

sample no.	molten salt	diffusion temperature in °C	diffusion time in h
Zn−1	$ZnCl_2$	580	4
Zn−2	$ZnCl_2$	600	4
Zn−3	$ZnCl_2$	610	4
Zn−4	$ZnCl_2$	620	4
Cd−1	CdI_2	600	4
Cd−2	CdI_2	620	4
Cd−3	CdI_2	630	4
Cd−4	CdI_2	640	4
Sr−1	$Sr(NO_3)_2$	600	4
Sr−2	$Sr(NO_3)_2$	610	4
Sr−3	$Sr(NO_3)_2$	625	4
Sr−4	$Sr(NO_3)_2$	640	4
Pb−1	$PbBr_2$	580	4
Pb−2	$PbBr_2$	600	4
Pb−3	$PbBr_2$	620	4
Ba−1	$Ba(NO_3)_2$	600	4
Ba−2	$Ba(NO_3)_2$	610	4
Ba−3	$Ba(NO_3)_2$	620	4
Ba−4	$Ba(NO_3)_2$	640	4

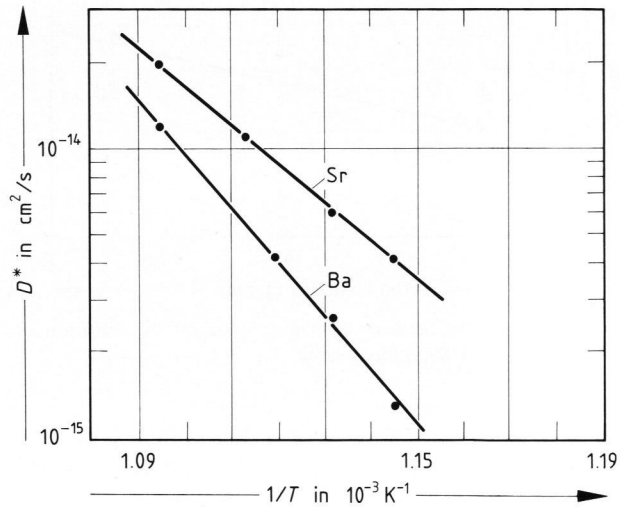

Figure 2. Dependence of strontium, barium ion diffusion coefficients on temperature.

Table 2. The diffusion coefficients (at 600 °C), frequency factors, and activation energies of various divalent cations

divalent cation	ionic radius r in nm	diffusion coefficient D^* in cm^2/s	frequency factor D_0 in cm^2/s	activation energy E in kJ/mol	ionic field strength $z/(r + r_0)^2$ in 10^{20} m^{-2}
Zn	0.074	$3.26 \cdot 10^{-14}$	$8.28 \cdot 10^{-2}$	207.6	0.4367
Cd	0.097	$8.10 \cdot 10^{-15}$	1.27	253.1	0.3561
Sr	0.116	$4.12 \cdot 10^{-15}$	1.20	258.6	0.3052
Pb	0.124	$3.60 \cdot 10^{-15}$	$1.20 \cdot 10^{3}$	293.0	0.2870
Ba	0.136	$1.30 \cdot 10^{-15}$	$4.50 \cdot 10^{6}$	359.6	0.2625

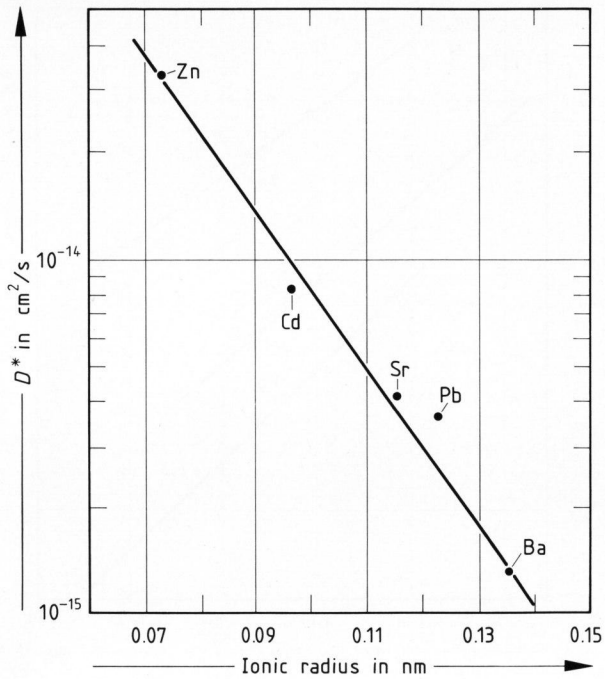

Figure 3. Relation between diffusion coefficients of divalent cations at 600 °C and their ionic radii.

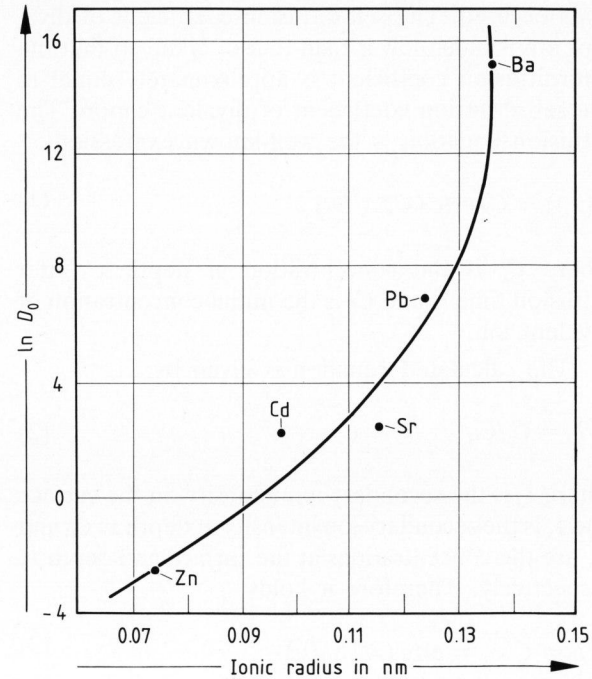

Figure 4. Relation between frequency factors of divalent cations at 600 °C and their ionic radii.

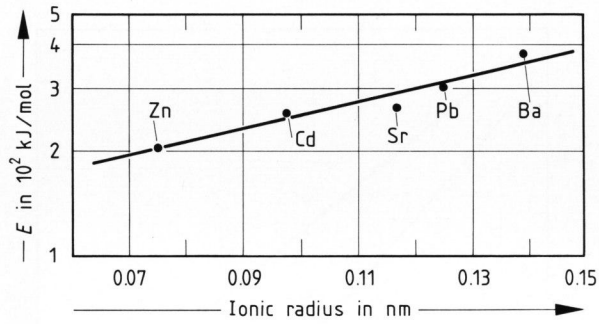

Figure 5. Relation between activation energies for diffusion of divalent ions and their ionic radii.

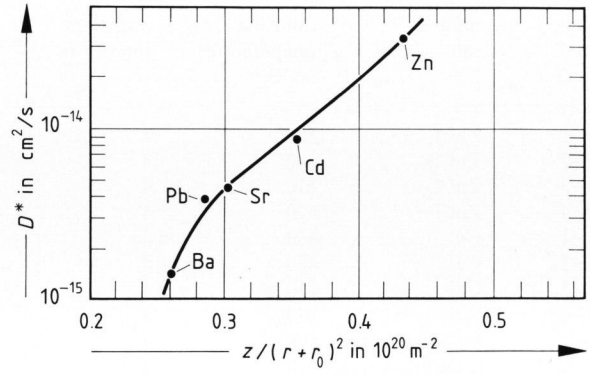

Figure 6. Diffusion coefficients of divalent cations correlated with their ionic field strength (r = radius of divalent cations, r_0 = radius of oxygen ion).

The values of I_x, I_0 and x were obtained by using ion microprobe analysis. According to equation (3) the diffusion coefficient of divalent ion is calculated. The dependence of divalent cation diffusion coefficient on temperature is shown in figures 1 and 2. The diffusion coefficients (at 600 °C), frequency factors and activation energies of various divalent cations are listed in table 2.

Figures 3 to 5 show diffusion coefficients, frequency factors and activation energies of divalent ions correlated with their ionic radii, respectively. It is seen that the diffusion coefficients decrease with the increase of ionic radii (figure 3), but the diffusion activation energies and frequency factors increase with the increase of ionic radii (figures 4 and 5). These experimental observations can be explained by ionic size effects: The larger the ions are, the slower the speed they have. Moreover, the blocking effect is attributed to the larger ions in the glass network and subsequently activation energies are enhanced. The plots of diffusion coefficients (figure 6) and the activation energies with frequency factors (figure 7) versus the ionic field strength correspond with the plots versus ionic radii. This result could be interpreted with the ionic field strength which affects the polarizing power of a cation. The distortion of neighboring oxygen increases with increasing polarizing power of the cations, hence the reduction of the "blocking effect" in the ionic diffusion passage occurs.

4. Conclusion

The correlation between diffusion coefficients of divalent cations and ionic radii agress with ion size

effects. The order of the diffusion coefficients is as follows: $D^*_{Zn} > D^*_{Cd} > D^*_{Sr} > D^*_{Pb} > D^*_{Ba}$. The influence of ionic field strength on the diffusion coefficients of divalent cations is similar to that of their ionic radii. The diffusion mechanisms of divalent cations are the subject fraught with difficulties and needs further study.

5. References

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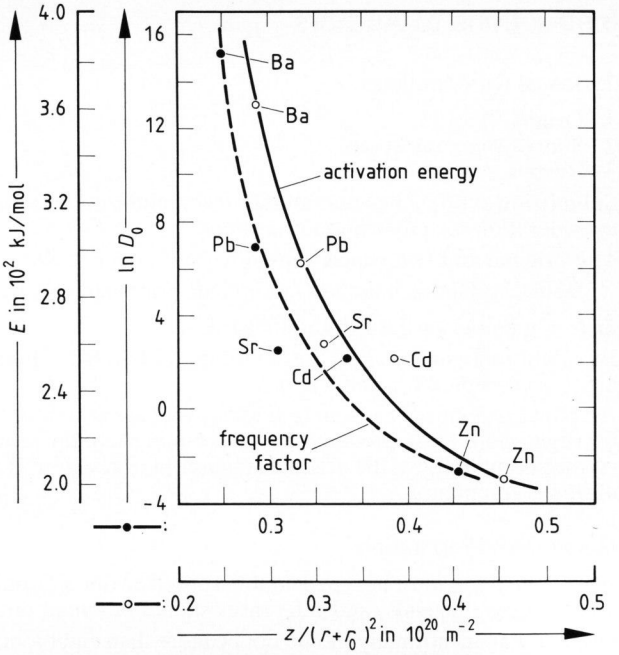

Figure 7. Frequency factors and activation energies for diffusion of divalent cations correlated with their ionic field strength.

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