Original Paper

Ion-exchanged versus as-melted mixed alkali glasses

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Assuming that the glass network structure containing channels for ionic migration is established at the glass transition temperature during cooling and is perfectly rigid below this temperature, the properties of ion-exchanged and as-melted mixed alkali glasses are compared. Alkali ions introduced by ion exchange below the glass transition temperature bring the glass matrix into a state of internal strain by elastic expansion or contraction of ionic sites. In an as-melted mixed alkali glass, an ion-channel mismatch produces a similar strained state, resulting in large internal friction and the so-called thermometer effect. The change in molar volumes due to ion exchange is calculated on the basis of Eshelby's misfitting sphere theory. The molar volumes of ion-exchanged glasses calculated are close to those observed for as-melted mixed alkali glasses. The mixed alkali effect is also expected in ion-exchanged mixed alkali glasses from the standpoint of the ion-channel match model.

Vergleich zwischen ionenausgetauschten und konventionell geschmolzenen Mischalkaligläsern

Die Eigenschaften von ionenausgetauschten und konventionell geschmolzenen Mischalkaligläsern werden verglichen. Dabei wird angenommen, daß sich die Netzwerkstruktur, die Kanäle für die Ionenwanderung enthält, bei der Transformationstemperatur während des Kühlens bildet und daß sie unterhalb dieser Temperatur völlig starr ist. Alkali-Ionen, die durch Ionenaustausch unterhalb der Transformationstemperatur in das Glas eingeführt werden, versetzen die Glasmatrix durch elastische Dehnung oder Kontraktion von Ionenplätzen in einen internen Spannungszustand. In einem konventionell geschmolzenen Mischalkaliglas erzeugt eine Fehlanpassung zwischen Ionen und Kanälen einen ähnlichen Spannungszustand, was zu großer interner Reibung und dem sogenannten Thermometer-Effekt führt. Die Veränderung im molaren Volumen infolge des Ionenaustausches wird auf Grundlage der Misfitting-Sphere-Theorie von Eshelby berechnet. Das berechnete molare Volumen von ionenausgetauschten Gläsern stimmt ziemlich genau mit dem für homogene Mischalkaligläser beobachteten überein. Der Mischalkalieffekt wird auch für ionenausgetauschte Mischalkaligläser unter Zugrundelegung des Ion-Channel-Match-Modells erwartet.

1. Introduction

When glass solidifies at the glass transition temperature and attains the network structure which it retains at all lower temperatures, the thermal migration of alkali ions is still violent [1]. Paths for the ionic transport are constructed and fixed to match with the size of moving ions. The concept of an ion-channel match has been used to explain ion transport processes in mixed alkali glasses [2 and 3]. The activation energy for migration of a majority ion was shown to be always smaller than that for migration of an impurity ion, be it larger or smaller than the majority ion [3], where not only narrow gates but also wide spots are expected to be saddle points for migration as shown schematically in figure 1.

In a mixed alkali glass, the substitution of a second alkali modifies the ionic channels; the ion-channel match for the host ion is gradually lost. The mean channel radius increases or decreases according to the size of the ion substituted. The ion-channel mismatch for both ions is an essential feature of mixed alkali glasses [2 and 3]. In low-temperature ion exchange, the network structure is thought to be perfectly rigid. However, larger ions introduced into misfitting sites are supposed to widen the channel elastically. Then, the ion-channel mismatch is expected to appear also for original ions. In this article, the special characteristics of ion-exchanged and as-melted mixed alkali glasses originating in this ion-channel mismatch are discussed.

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2. Anelasticity and thermometer effect

Low frequency peaks observed in internal friction measurements were first demonstrated in alpha-iron containing carbon and nitrogen [4]. The positions occupied by interstitial solute atoms in b.c.c. lattices are of the type (0,1/2,1/2), or (1/2,0,1/2) or (1/2,1/2,0). In the absence of an externally applied stress, the interstitial atoms will be distributed at random among the three types of positions designated as x, y and z. When a tensile stress is applied along, say, the z-axis, the equilibrium distribution of solute atoms will be one in which more atoms are in the z-type position than in the other two. The continual striving of solute atoms to maintain the equilibrium distribution during cycle vibration gives rise to the anelastic effects. Wert and Zener [5] reported experimental results showing internal friction peaks of Debye

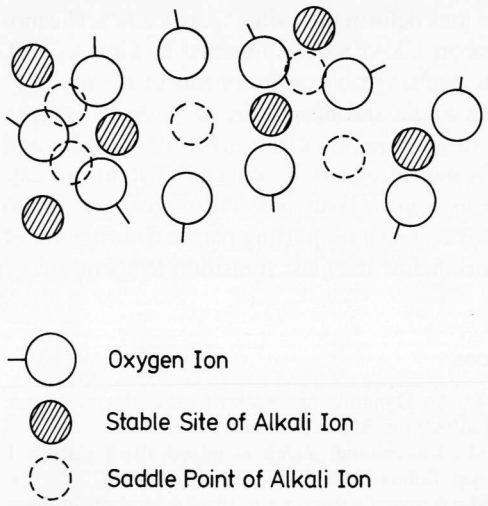

Figure 1. Schematic representation of alkali ions in a glass network, showing minimum energy positions and activated states.

type with slight excess in the breadth. The interaction of solute atoms with one another is much less than in the case of ionic movement.

It is difficult to establish such a clear mechanism in the case of glasses, but alkali peaks observed in alkali-containing glasses [6] suggest that there are many excess sites of various sizes into which cations can easily move. Boltzmann distribution of alkali ions among those sites is expected to hold even below the glass transition temperature. Under externally applied stress, smaller sites become more acceptable for ions in a tensile field and, vice versa, in a compressed field. Ions change their distribution, seeking a more favorable site to lower the total elastic energy, resulting in anelastic extension or contraction.

As discussed above, ion-channel mismatch is an essential feature of mixed alkali glasses. A favorable change of sites for mismatched larger or smaller ions under an external stress field will reduce a large amount of elastic energy, resulting in a large mixed alkali peak [6]. It has been reported that the maximum height of the mixed-alkali internal friction peak occurs at the composition where the diffusion coefficients of both alkali ions are equal [7 and 8]. The height of the peak is likely to be controlled by the interdiffusion coefficient D given by

$$D = D_A D_B/(D_A N_A + D_B N_B) \quad (1)$$

where D_i is the self-diffusion coefficient of i and N_i is mole fraction of i, because D becomes maximum closely at the composition, where the diffusion coefficients of both alkali ions are equal. In spite of the large difference of ionic radii, the relatively small mixed peak for Li–Cs glasses [9] is explained by their small interdiffusion coefficients estimated from the self-diffusion coefficients of both ions.

The same is true for ion-exchanged glasses. There were some reports on internal friction of ion-exchanged glasses [10 to 12]. They found a similar peak to that occurring in conventionally melted mixed alkali glasses of the same composition. It was experimentally confirmed that the peak was associated with the mixed-alkali surface layer. The results demonstrated a resemblance between the ionic structure of ion-exchanged and as-melted mixed alkali glasses.

Table 1. Molar volumes in cm^3 of as-melted and ion-exchanged glasses

glass	radius of alkali ion in nm [16]	as-melted (observed)	ion-exchanged (calculated)	
			$+V_0$	$+\Delta V$
$Na_2O \cdot 3SiO_2$	Na^+ 0.097	24.90	–	–
$K_2O \cdot 3SiO_2$	K^+ 0.133	28.32	26.72	28.17
$Rb_2O \cdot 3SiO_2$	Rb^+ 0.148	30.95	27.83	30.19
$Cs_2O \cdot 3SiO_2$	Cs^+ 0.167	33.58	29.62	33.40

The large thermal after-effect in mixed alkali glasses, usually referred to as the thermometer effect, can equally be explained by the above concept of the ion-site mismatch. The phenomenon is actually a nonequilibrium-to-equilibrium transition, that is, a stabilization process in ionic distribution [13]. There is a spread of relaxation times in ionic movement; some of them are as large as hours or days near room temperature. Thermally activated mismatched ions in narrow sites relax slowly to an equilibrium position, where significant volume shrinkage occurs in mixed alkali glasses.

3. Volumetric consideration

The molar volumes of R_2O_3–SiO_2 glasses, calculated from the densities given in [7 and 9], are listed in table 1. They show larger differences between different alkali species than is expected from the difference in ionic radii of alkalis. Larger ions seem to enlarge not only their sites but also paths through which they move. The linear change of molar volumes of mixed alkali glasses with the content of a second alkali [14] suggests that the width of ionic channels changes exactly in proportion to the amount of the second alkali.

In ion-exchanged glasses, the network structure is constructed to accomodate original ions. A second alkali ion introduced by low temperature ion exchange deforms the network structure only elastically. Larger ions extend channels, so that successive introduction of larger ions becomes progressively easier. Surface compressive stress may hinder the extension at an early stage of exchange processes. However, if all the original ions are replaced by the larger ions, the glass becomes stress-free and extends without restraint.

To estimate the dilatation of glasses caused by an ion exchange, the classical "misfitting sphere theory" proposed by Eshelby [15] may be applied. According to this theory, the increase in volume of the glass, ΔV, is not correctly given by the difference in volume, V_0, between

two exchanged ions. The increase in volume, V_i, due to the additional image displacements caused by surface tractions must be considered. When the constancy in ionic radii of cations in glass network is assumed.

$$\Delta V = V_0 + V_i = \gamma V_0 \tag{2}$$

where

$$\gamma = 3(1 - \sigma)/(1 + \sigma) \tag{3}$$

and σ is the Poisson ratio of the glass matrix. If σ is taken to be 0.25, γ becomes 1.8.

As shown in table 1, the calculated molar volumes of ion-exchanged glasses, produced by replacing sodium ions with larger alkali ions, are close to those of melt-formed glasses of the same compositions. The width of ionic channels in ion-exchanged mixed alkali glasses is then almost identical to that in as-melted mixed alkali glasses of corresponding compositions. From the standpoint of the ion-channel match model, the conduction anomaly observed in as-melted mixed alkali glasses is also expected in ion-exchanged mixed alkali glasses.

4. Concluding remarks

There are some conductivity and diffusion measurements on ion-exchanged mixed alkali glasses, but inhomogeneous composition and remaining stress complicate the analysis of experimental results. The problem as to whether ion-exchanged mixed alkali glasses exhibit the mixed alkali effect is still in controversy. Tomandl and Schaeffer [17] denied the mixed alkali effect in ion-exchanged glasses in analyzing their results of conductivity measurements. Frischat [18], however, reported no deviation from the mixed alkali effect in comparing the electrical conductivity of ion-exchanged and as-melted mixed alkali glasses. The interdiffusion coefficients obtained from ion-exchanged layers showed a clear mixed alkali effect [19 to 21].

Berg and Ludwig [22] have found that ion-exchanged silver-sodium silicate glasses with uniform compositions show typical features of the mixed alkali effect. However, the silver-sodium substitution takes place without any volume expansion of glass samples [23]. The ion-channel match model can not directly be applied to explain the mixed alkali effect in this case. The local deformation of ionic channels due to high covalency of Ag–O bonds, as designated by low coordination numbers of silver ions and shorter Ag–O distances [23 and 24], must be considered. Anyway, more experimental work, especially measurements of pressure dependence of diffusion coefficients of alkali ions in mixed alkali glasses are desirable to prove the adequacy of the ion-channel match model.

Recently, Maass, Ingram and Bunde [25 and 26] have developed the dynamic structure model for ionic transport in glass, assuming that the glass network is not completely rigid below the glass transition temperature and mobile ions deform their sites "plastically". The model is based on EXAFS data obtained by Greaves [27], which show unchangeable environments of K^+ and Cs^+ ions in both single and mixed silicate glasses. However, ionic sites in glass network can deform elastically and the EXAFS data demonstrate only the stability of cationic radii in a glass structure. There seems to be no experimental evidence supporting plastic deformation of glass network below the glass transition temperature.

5. References

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