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Mixed alkali effect in elastic properties of glasses in the ZrF_4–BaF_2–AlF_3–RF system (RF = LiF–NaF, NaF–KF)

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The elastic properties, such as Poisson's ratios, shear modulus, Young's modulus and bulk modulus, have been determined with glasses of the compositions $48ZrF_4 \cdot 24BaF_2 \cdot 8AlF_3 \cdot 20RF$, where RF is the LiF–NaF or NaF–KF pair, and $42ZrF_4 \cdot 21BaF_2 \cdot 7AlF_3 \cdot 30RF$, where RF is the LiF–NaF pair, by measuring sound wave velocities. Non-linear variations, i.e. mixed alkali effects, were found in the sound velocities, shear modulus, Young's modulus and bulk modulus. The mixed alkali effect in the present systems is attributed to the strengthening of the glass structure and not to the mere compaction of the glass structure. The thermal expansion coefficient becomes higher when the two alkalis are mixed contrary to expectation from the change of the elastic moduli, indicating that the structural elements controlling the elastic moduli are different from those affecting the thermal expansion.

1. Introduction

In recent work [1, 2] on the properties of mixed alkali fluoride glasses of compositions $40ZrF_4 \cdot 20PbF_2 \cdot 10AlF_3 \cdot x\mathrm{RF} \cdot (30 - x)R'\mathrm{F}$, where R and R′ are different alkalis chosen from lithium, sodium and potassium, an appreciable mixed alkali effect, similar to that observed in mixed alkali oxide glasses, was found in the electrical conductivity. No marked effect was found, however, in the dielectric constant, molar volume, refractive index, thermal expansion coefficient and glass transition temperature, consistent with observations in oxide glasses [3–5].

It has been reported that a small mixed alkali effect is observed in the elastic moduli of the oxide glasses [6]. In this work, the elastic moduli of the mixed alkali fluoride glasses of the compositions $48ZrF_4 \cdot 24BaF_2 \cdot 8AlF_3 \cdot 20RF$, where RF is the LiF–NaF or NaF–KF pair, and $42ZrF_4 \cdot 21BaF_2 \cdot 7AlF_3 \cdot 30RF$, where RF is the LiF–NaF pair, have been measured, in order to study the effect of alkali mixing on the elastic properties.

2. Experimental procedure

Extra pure reagents $(NH_4)_2ZrF_6$, BaF_2, AlF_3, LiF, NaF and KF were used as starting chemicals for preparing glasses. The mixture of raw materials, containing about 10 wt % NH_4HF_2 as fluorinating agent, was preheated at about 450° C for 1 h and then melted at 850 to 900° C for 20 min in a platinum crucible under a nitrogen atmosphere in an electrically heated furnace. The melt was cast into a preheated brass mould to produce a glass plate of 20 g weight and about 6 mm thick.

Elastic constants were measured by the cube resonance method described by Goto and Soga [7]. A glass cube of about 5 mm × 5 mm × 5 mm polished with 400 grit polishing powder was placed between two transducers. Mechanical vibrations were given on one transducer by a synthesizer, controlled by a controller, and vibrations occurring on the other transducer were detected electrically and recorded through an a.c. voltmeter, a digital voltmeter, a controller and a plotter. A typical resonance spectrum is given in Fig. 1. The dimensionless frequencies, A_n, were calculated by dividing each observed frequency by the lowest resonance frequency (EV-1). By fitting these observed A_n values and the theoretical A_n against Poisson's ratio μ curves, the mode of each A_n was determined. Poisson's ratio was obtained by averaging the four Poisson's ratio values calculated from the observed resonance frequencies of EF-2, OS-2, OD-2 and OD-3 modes and the shear velocity was obtained by averaging the two shear velocities calculated from those of EV-1 and OD-1. Then the longitudinal wave velocity was calculated using the formula

$$v_l = [2(1 - \mu)/(1 - 2\mu)]^{1/2} v_s \qquad (1)$$

The shear modulus, G, Young's modulus, E, and the bulk modulus, K_s, were computed from Poisson's ratio, μ, the shear wave velocity, v_s, the longitudinal wave velocity, v_l, and the density, d, using the formulae

$$G = dv_s^2 \qquad (2)$$

$$E = 2G(1 + \mu) \qquad (3)$$

$$K_s = d(v_l^2 - 4/3v_s^2) \qquad (4)$$

The density was measured by the Archimedes method using a mineral oil as immersion liquid. The mean atomic volume, V, was calculated from the density.

Additionally, the thermal expansion was also

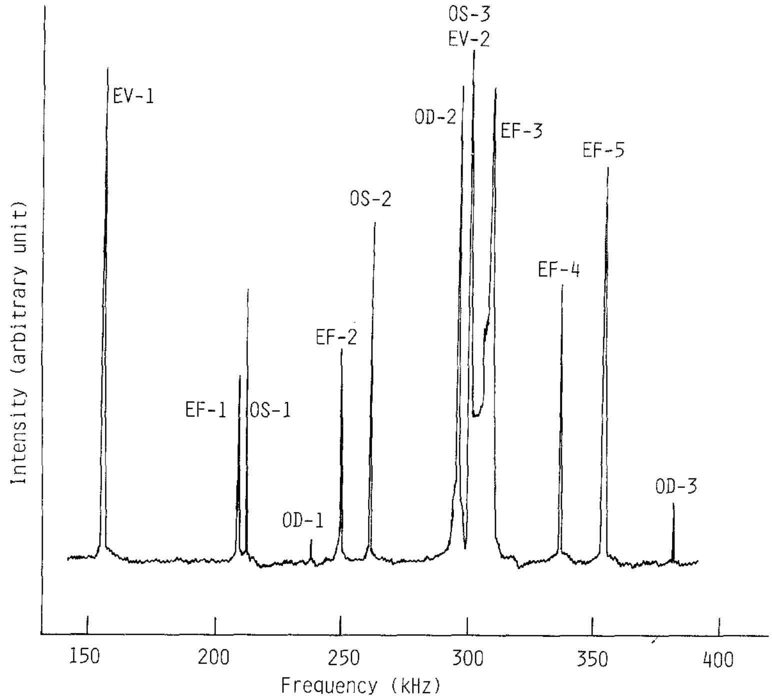

Figure 1 Resonance spectrum of $42ZrF_4 \cdot 21BaF_2 \cdot 7AlF_3 \cdot 25LiF \cdot 5NaF$ glass. EV, OD, EF and OS represent the vibrational modes for tortion, dilation, flexure and shear, respectively. The additional integer orders the modes in the subgroup by frequency.

measured with glasses containing 20 mol % RF using a Shimadzu TMA-30 dilatometer at a heating rate of 2° C. The thermal expansion coefficient and glass transition and dilatometric softening temperatures were estimated from the thermal expansion curve.

3. Results

Tables I and II give the densities, mean atomic volumes, shear and longitudinal wave velocities, Poisson's ratios, shear moduli, Young's moduli and bulk moduli of $48ZrF_4 \cdot 24BaF_2 \cdot 8AlF_3 \cdot 20RF$ and $42ZrF_4 \cdot 21BaF_2 \cdot 7AlF_3 \cdot 30RF$ glasses, respectively. The values of the elastic moduli of the present glasses are around 20, 50 and 45 GPa, respectively, for the shear moduli, Young's moduli and the bulk moduli, agreeing in order of magnitude with those of ZrF_4–BaF_2–LaF_3–NaF–AlF_3 glasses determined by Ota and Soga [8].

Figs 2 and 3 show the density and mean atomic volume as a function of the replacement of one alkali by another, for glasses with the total RF content of 20 and 30 mol %, respectively. It is seen from these figures that the density- and the mean atomic volume–alkali replacement curves exhibit a slight deviation from the additivity in Li–Na pair glasses and almost no deviation in the Na–K pair glasses.

TABLE I Densities, mean atomic volumes, sound velocities and elastic moduli of $48ZrF_4 \cdot 24BaF_2 \cdot 8AlF_3 \cdot 20RF$ glasses

RF	Density ($g\,cm^{-3}$)	Atomic volume (cm^{-3} g.atom^{-1})	Sound velocity ($km\,sec^{-1}$) long.	shear	Poisson's ratio	Shear modulus (GPa)	Young's modulus (GPa)	Bulk modulus (GPa)
20LiF · 0NaF	4.285	8.159	4.278	2.309	0.2945	22.9	59.4	48.2
15LiF · 5NaF	4.288	8.202	4.295	2.321	0.2937	23.1	59.8	48.3
10LiF · 10NaF	4.283	8.260	4.261	2.288	0.2974	22.4	58.2	47.9
5LiF · 15NaF	4.276	8.323	4.178	2.236	0.2993	21.4	55.5	46.1
0LiF · 20NaF	4.260	8.403	4.133	2.207	0.3005	20.8	54.0	45.1
20NaF · 0KF	4.260	8.403	4.133	2.207	0.3005	20.8	54.0	45.1
15NaF · 5KF	4.240	8.492	4.146	2.213	0.3008	20.8	54.0	45.2
10NaF · 10KF	4.210	8.603	4.063	2.140	0.3080	19.4	50.9	44.1
5NaF · 15KF	4.176	8.723	4.055	2.132	0.3090	19.0	49.7	43.4
0NaF · 20KF	4.148	8.832	3.957	2.077	0.3098	17.7	46.3	40.6

TABLE II Densities, mean atomic volumes, sound velocities and elastic moduli of $42ZrF_4 \cdot 21BaF_2 \cdot 7AlF_3 \cdot 30RF$ glasses

RF	Density ($g\,cm^{-3}$)	Atomic volume (cm^{-3} g.atom^{-1})	Sound velocity ($km\,sec^{-1}$) long.	shear	Poisson's ratio	Shear modulus (GPa)	Young's modulus (GPa)	Bulk modulus (GPa)
30LiF · 0NaF	4.190	7.981	4.276	2.294	0.2968	22.1	57.2	46.9
25LiF · 5NaF	4.202	8.011	4.268	2.284	0.2994	21.9	57.0	47.3
20LiF · 10NaF	4.211	8.046	4.281	2.294	0.2986	22.2	57.6	47.7
15LiF · 15NaF	4.213	8.095	4.254	2.269	0.3012	21.7	56.4	47.3
10LiF · 20NaF	4.204	8.165	4.205	2.250	0.2994	21.3	55.3	46.0
5LiF · 25NaF	4.185	8.261	4.225	2.238	0.3050	21.0	54.8	46.8
0LiF · 30NaF	4.180	8.320	4.067	2.160	0.3035	19.5	50.8	43.1

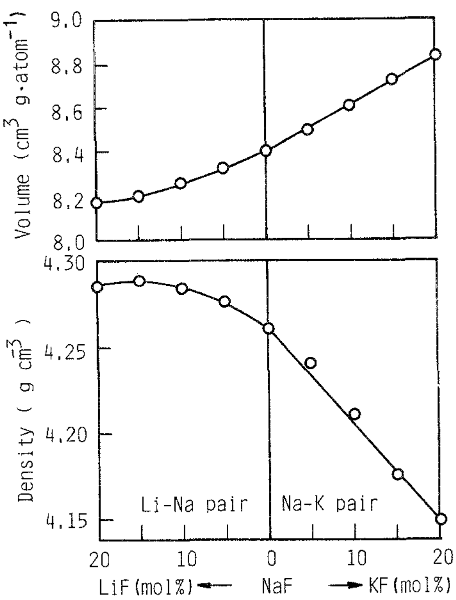

Figure 2 Density and mean atomic volume of $48ZrF_4 \cdot 24BaF_2 \cdot 8AlF_3 \cdot 20RF$ glass (RF = LiF–NaF, NaF–KF) as a function of alkali replacement.

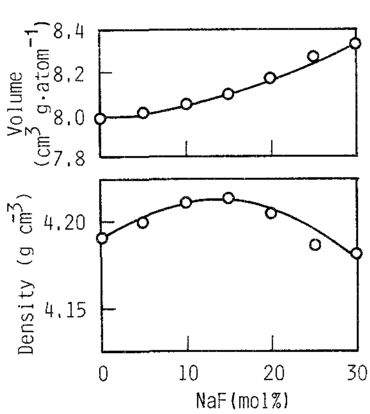

Figure 3 Density and mean atomic volume of $42ZrF_4 \cdot 21BaF_2 \cdot 7AlF_3 \cdot 30RF$ glass (RF = LiF–NaF) as a function of alkali replacement.

The variation of sound velocities with the alkali replacement are illustrated in Figs 4 and 5. It is found that the variation is non-linear, i.e. positive deviations can be found in these curves. The shear and bulk moduli are shown in Figs 6 and 7, respectively, for glasses with 20 mol % RF and in Figs 8 and 9, respectively, for glasses with 30 mol % RF. As shown in these figures the elastic moduli exhibit non-linear variations with alkali replacement for glasses of total alkali fluoride content of both 20 and 30 mol %. Comparison of Figs 6 and 7 with Figs 8 and 9 indicates that the degree of the non-linearity tends to increase with total alkali fluoride content. This tendency can also be found in the shear and longitudinal wave velocities. It should be noted that in all these mixed alkali glasses the elastic moduli and the sound velocities show positive deviations from the additivity of the two end members. These features agree with those observed in $Na_2O–Cs_2O–SiO_2$ glasses [6].

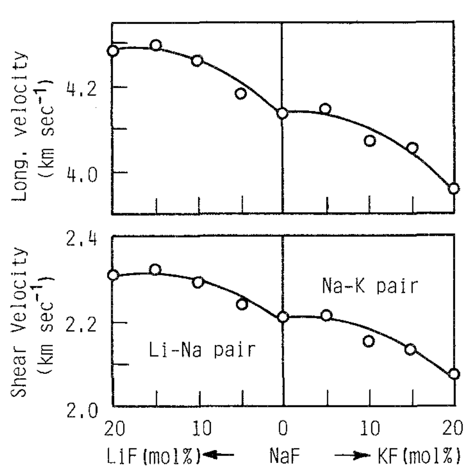

Figure 4 Sound wave velocities of $48ZrF_4 \cdot 24BaF_2 \cdot 8AlF_3 \cdot 20RF$ glass (RF = LiF–NaF, NaF–KF) as a function of alkali replacement.

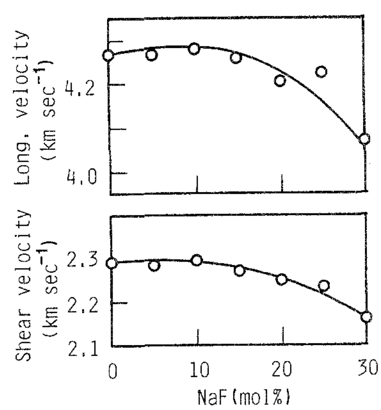

Figure 5 Sound wave velocities of $42ZrF_4 \cdot 21BaF_2 \cdot 7AlF_3 \cdot 30RF$ glass (RF = LiF–NaF) as a function of alkali replacement.

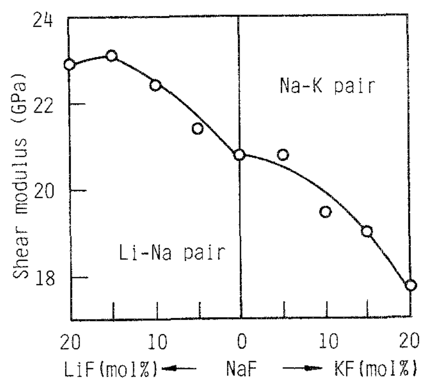

Figure 6 Shear modulus of $48ZrF_4 \cdot 24BaF_2 \cdot 8AlF_3 \cdot 20RF$ glass (RF = KiF–NaF, NaF–KF) as a function of alkali replacement.

The thermal expansion coefficient and glass transition and dilatometric softening temperatures are shown in Fig. 10 as a function of alkali replacement for $48ZrF_4 \cdot 24BaF_2 \cdot 8AlF_3 \cdot 20RF$ glasses. For the LiF–NaF pair, there are no simple positive or negative deviations in the curves. For the NaF–KF pair, there

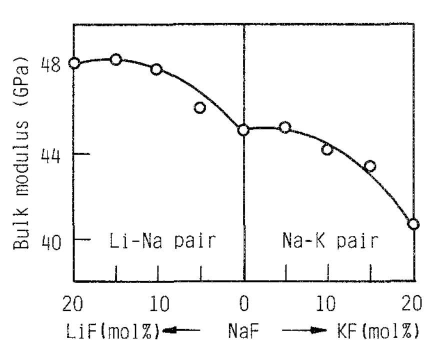

Figure 7 Bulk modulus of $48ZrF_4 \cdot 24BaF_2 \cdot 8AlF_3 \cdot 20RF$ glass (RF = LiF–NaF, NaF–KF) as a function of alkali replacement.

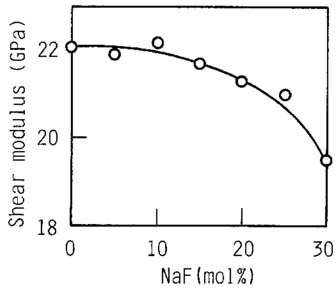

Figure 8 Shear modulus of $42ZrF_4 \cdot 21BaF_2 \cdot 7AlF_3 \cdot 30RF$ glass (RF = LiF–NaF) as a function of alkali replacement.

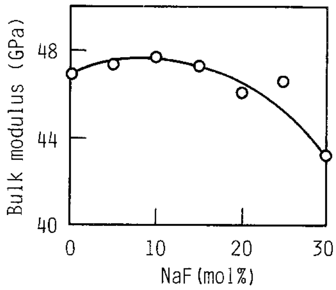

Figure 9 Bulk modulus of $42ZrF_4 \cdot 21BaF_2 \cdot 7AlF_3 \cdot 30RF$ glass (RF = LiF–NaF) as a function of alkali replacement.

are positive deviations in the thermal expansion coefficient and negative deviations in the glass transition and dilatometric softening temperatures in the curves.

4. Discussion

4.1. Relation between elastic moduli and mean atomic volume

The bulk moduli of glasses with 20 and 30 mol % RF are plotted against the mean atomic volume in the logarithmic scale, respectively, in Figs 11 and 12. It is interesting to see from Fig. 11 that the three single alkali glasses show a linear relation between log (bulk modulus) and log (mean atomic volume), whereas the mixed alkali glasses show an upward deviation from the straight line corresponding to the additivity of the two end members. For glasses containing 30 mol % RF, the mixed alkali glasses also show an upward

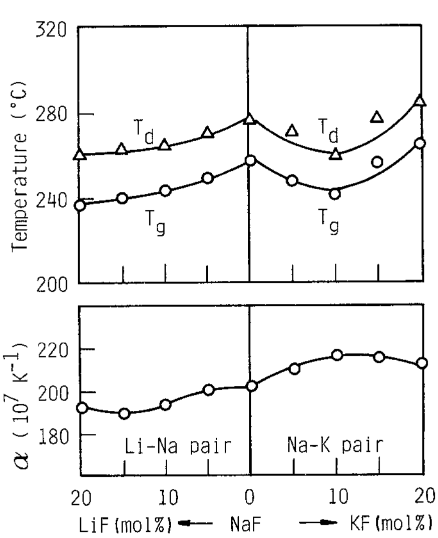

Figure 10 Thermal expansion coefficient, α, glass transition temperature, T_g, and softening temperature, T_d, of $48ZrF_4 \cdot 24BaF_2 \cdot 8AlF_3 \cdot 20RF$ glass (RF = LiF–NaF, NaF–KF) as a function of alkali replacement.

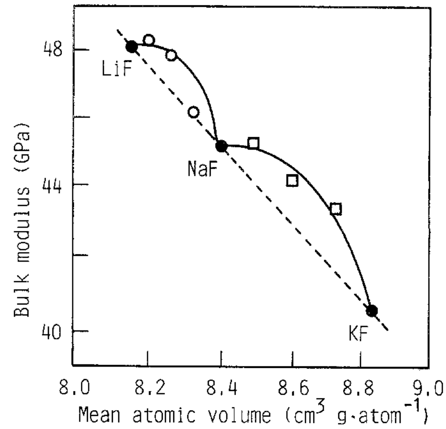

Figure 11 Relation between the bulk modulus and the mean atomic volume for $48ZrF_4 \cdot 24BaF_2 \cdot 8AlF_3 \cdot 20RF$ glasses. (○) Mixed alkali glasses for RF = LiF–NaF, (□) mixed alkali glasses for RF = NaF–KF, (●) single alkali glasses.

deviation from the additivity of the two end members. These suggest that the non-linear variations of the elastic moduli shown in Figs 6 to 9 are not originated from the mere compaction of the glass structure by mixing alkalis, but a certain strengthening of glass structure due to some other cause.

It is known [9] that in $MO \cdot mSiO_2$ glasses, where M is magnesium, calcium, strontium or barium or their mixture and $m = 1$ or 2, the bulk moduli lie on a straight line which expresses the dependence of the bulk modulus on the reciprocal four-thirds power of the mean atomic volume, indicating that there is no essential change in network structure when m is kept constant. Similarly, the bulk modulus of alkali halide and alkaline earth halide crystals has a reciprocal four-thirds power dependence on the mean atomic volume.

$$K_s = \text{const.}\ x z_1 z_2 V^{-4/3} \qquad (4)$$

where $z_1 z_2$ is the ionic charge product [8]. These indicate that the linear relationship between log (bulk modulus) and log (mean atomic volume) for single alkali fluoride glasses, shown in Figs 11 and 12 by the dashed line, is normal behaviour in the sense that no essential structural change takes place among those glasses. On the other hand, the behaviour of the mixed alkali glasses is abnormal in the sense that there is some structural effect caused by mixing alkalis.

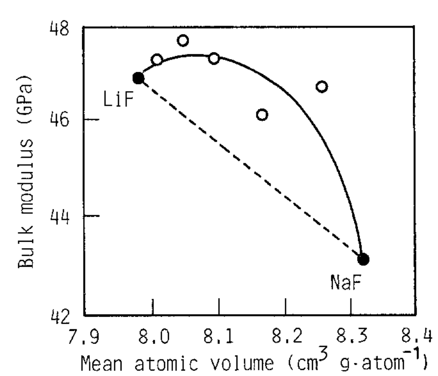

Figure 12 Relation between the bulk modulus and the mean atomic volume for $42ZrF_4 \cdot 21BaF_2 \cdot 7AlF_3 \cdot 30RF$ glasses. (○) Mixed alkali glasses for RF = LiF–NaF, (●) single alkali glasses.

4.2. Comparison of mixed alkali effect between elastic moduli and other thermal properties

The positive deviations in the elastic moduli suggest that the mixed alkali effect in the elastic modulus may be the strengthening of the glass structure in a broad sense. It has been stated above that this strengthening is not due to a simple compaction of glass structure. It is suspected that the present mixed alkali effect may be related to the thermal expansion coefficient and glass transition and softening temperatures, because these are other expressions of the strength of the glass structure. As shown in Fig. 10, the direction of the deviations of the thermal expansion coefficient and glass transition and softening temperatures by mixing alkalis is opposite to that expected from the strengthening of the glass structure.

Soga [10] noted that the mixed alkali effect in the elastic modulus, i.e. strengthening of the glass structure in mixed alkali silicate glasses, results in an increase of the characteristic temperatures θ_1 and θ_3, which are, respectively, related to the bond strength of the network former and the intermolecular bond strength from the additivity. θ_1 and θ_3 were assumed to be determined by the Si–O stretching and O–Si–O bending vibration modes in alkali or alkaline earth silicate glasses [11]. If this idea is applied to the present fluoride glasses, θ_1 and θ_3 may represent the Zr–F stretching and F–Zr–F bending vibration modes, respectively, and the mixed alkali effect in the elastic modulus occurs as a result of the strengthening of the Zr–F bond.

The increase in the Zr–F bond strength might correspond to a decrease in the length of the Zr–F bond and an increase in the bond angle of Zr–F–Zr. This would correspond to the weakening of the Zr–F–Zr bending mode. The linear variation of θ_E with the substitution of one alkali by another [11] indicates that the effect of mixed alkali on the thermal expansion is not related to the bonding between alkali ion and fluorine. Thus, if it is assumed that the thermal expansion in the present fluoride glasses is controlled by the Zr–F–Zr bonding, the difference in the direction of change with alkali mixing between bulk modulus and thermal expansion coefficient can be explained.

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