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Properties of glasses in the ZrF_4–AlF_3–BaF_2–RF (R = Li, Na or K) system

XIUJIAN ZHAO, SUMIO SAKKA
Institute for Chemical Research, Uji-shi, Kyoto-fu 611 and Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606, Japan

Densities, molar volumes, refractive indices, molar refractivities, glass transition temperatures and elastic constants of glasses with compositions $(100 - x)(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xRF$, where R = Li, Na or K, were studied. All the properties vary continuously with increasing RF concentration for all three alkali atoms. The calculated molar refractivities of LiF, NaF and KF are constants which are very close to the values of the crystalline compounds LiF, NaF and KF, respectively, throughout the composition range studied, suggesting that no change occurs in the coordination state of the alkali ions by fluorine atoms. The comparison with crystalline compounds suggests that Li^+, Na^+ and K^+ ions are all coordinated by six fluorine atoms.

1. Introduction

In our previous papers [1, 2] we reported the glass formation, crystallization and electrical properties of alkali-containing fluoride glasses of the compositions $(100 - x)(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xRF$, where R = Li, Na, K or Cs. In this paper, the densities, molar volumes, refractive indices, molar refractivities, glass transition temperatures and Young's moduli of these glasses will be reported.

As to alkali-containing fluoride glasses, Lecoq and Poulain [3] reported the glass transition temperatures, densities, refractive indices and molar refractivities of compositions $(0.62 - 0.4x)ZrF_4 \cdot (0.3 - 0.5x)BaF_2 \cdot (0.08 - 0.1x)LaF_3 \cdot xRF$, where R = Li or Na, and x is changed in the range $0 < x < 0.3$. They attributed the variations of glass transition temperature, refractive index and contribution of RF to molar refractivity with x to the change of coordination state of Li^+ and Na^+ ions. It was proposed that Li^+ ions are coordinated by four F^- ions, behaving as a glass-former in the lower LiF concentration region, and by six F^- ions, behaving as a glass-modifier in the higher LiF concentration region, and that Na^+ ions are coordinated by six F^- ions, behaving as a glass-modifier over the whole region. In our previous studies on the alkali-containing fluoride glasses, no indication was found to show a change of the coordination state of alkali ions with the RF concentration. The present study has been undertaken in order to elucidate this matter.

2. Experimental procedure

2.1. Compositions of glasses

The compositions of glasses used in this study can be expressed by the formula

$$(100 - x)(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xRF$$

where R = Li, Na or K. The value of x was changed from 0 up to 55, 35 or 30 as shown in Tables I to III, respectively. The procedure for the preparation of glasses has been described in previous papers [1, 2].

2.2. Property measurements

The glass transition temperature was estimated from differential thermal analysis (DTA) curves measured

TABLE I Properties of $(100 - x)(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xLiF$ glasses*

x (mol %)	T_g (°C)	d (g cm^{-3})	V_m (cm^3 mol^{-1})	n_D	R_m	R_{LiF}
0	292	4.426	36.45	1.5174 ± 0.0013	14.38	–
5	276	4.406	35.08	1.5156 ± 0.0006	13.80	2.78
10	268	4.370	33.82	1.5101 ± 0.0011	13.20	2.58
15	256	4.340	32.49	1.5075 ± 0.0013	12.63	2.71
20	251	4.285	31.33	1.5056 ± 0.0008	12.15	3.23
25	240	4.247	30.02	1.5010 ± 0.0015	11.56	3.10
30	226	4.190	28.81	1.4985 ± 0.0011	11.06	3.31
35	220	4.138	27.54	1.4951 ± 0.0013	10.52	3.35
40	216	4.115	26.04	1.4925 ± 0.0013	9.904	3.19
45	209	4.068	24.68	1.4874 ± 0.0020	9.314	3.22
50	204	3.990	23.47	1.4825 ± 0.0013	8.791	3.20
55	194	3.908	22.23	1.4752 ± 0.0016	8.232	3.20

*T_g = glass transition temperature, d = density, V_m = molar volume, n_D = refractive index, R_m = molar refractivity, R_{LiF} = molar refractivity of LiF in glass.

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TABLE II Properties of $(100 - x)(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xNaF$ glasses*

x (mol %)	T_g (°C)	d ($g\,cm^{-3}$)	V_m ($cm^3\,mol^{-1}$)	n_D	R_m	R_{NaF}
0	292	4.426	36.45	1.5174 ± 0.0013	14.38	–
5	283	4.383	35.45	1.5131 ± 0.0019	13.90	4.78
10	271	4.333	34.48	1.5056 ± 0.0008	13.37	4.28
15	267	4.304	33.32	1.4985 ± 0.0011	12.79	3.78
20	257	4.260	32.27	1.4949 ± 0.0012	12.32	4.08
25	252	4.220	31.16	1.4874 ± 0.0020	11.76	3.90
30	245	4.185	29.99	1.4825 ± 0.0013	11.23	3.88
35	238	4.129	28.96	1.4776 ± 0.0009	10.77	4.07

*T_g = glass transition temperature, d = density, V_m = molar volume, n_D = refractive index, R_m = molar refractivity, R_{NaF} = molar refractivity of NaF in glass.

by using a heating rate of $10°C\,min^{-1}$ as shown in an earlier paper [1]. Density was measured by the Archimedes method using liquid paraffin as the immersion fluid at room temperature. Refractive index was measured by observing the motion of the Becke line in an optical microscope, using various reference liquids of given refractive indices. The average value of two refractive indices which cover the refractive index of the glass sample of the two reference liquids has been taken as the refractive index of the glass sample. The molar refractivity R_m was estimated using the formula

$$R_m = \left(\frac{n^2 - 1}{n^2 + 1}\right)\frac{M}{d} \quad (1)$$

where n is the refractive index, d the density and M the molecular weight.

3. Results

3.1. Glass transition temperature

The glass transition temperatures T_g of $(100 - x)(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xRF$ glasses are given in Tables I, II and III for R = Li, Na and K, respectively, and illustrated in Fig. 1 as a function of the RF concentration. T_g decreases with increasing RF concentration and increases with increasing radius of alkali ion. This tendency in the changes of T_g is consistent with those of Lecoq and Poulain [3] for $(0.62 - 0.4x)ZrF_4 \cdot (0.3 - 0.5x)BaF_2 \cdot (0.08 - 0.1x)LaF_3 \cdot xRF$ glasses, where R = Li or Na, except that no abrupt change is found in the evolution of T_g with respect to the RF concentration for the present alkali glasses. An abrupt change was observed in lithium glasses by Lecoq and Poulain [3].

3.2. Density and molar volume

The densities and calculated molar volumes are shown in Tables I to III and illustrated in Figs 2 and 3, respectively, as a function of the RF concentration. Both properties decrease almost linearly with increasing RF concentration. The density decreases and the molar volume increases with the increase in alkali ion radius.

3.3. Refractive index and molar refractivity

Refractive indices and molar refractivities are given in Tables I to III. Figs 4 and 5 show the refractive index and molar refractivity, respectively, as a function of the RF concentration. Both properties decrease continuously with increasing RF concentration. For glasses containing different alkali fluorides, the refractive index decreases and molar refractivity increases with increasing alkali ion radius.

The glass molar refractivity $R_{m,g}$, can be expressed by the formula assuming additivity:

$$R_{m,g} = \sum_i x_i R_i \quad (2)$$

where x_i and R_i are the molar fraction and molar refractivity, respectively. Since the $ZrF_4 : AlF_3 : BaF_2$ ratio is kept identical in the glass composition, the contribution to RF to the glass molar refractivity, R_{RF}, can be calculated from the equation

$$R_{RF} = \frac{R_{m,g} - (100 - x)R_{Zr\text{-}Al\text{-}Ba}}{x} \quad (3)$$

$R_{Zr\text{-}Al\text{-}Ba}$ may be put equal to the molar refractivity of the alkali-free glass, that is, 14.38. The calculated molar refractivities of RF are shown in Tables I to III

TABLE III Properties of $(100 - x)(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xKF$ glasses*

x (mol %)	T_g (°C)	d ($g\,cm^{-3}$)	V_m ($cm^3\,mol^{-1}$)	n_D	R_m	R_{KF}
0	292	4.426	36.45	1.5174 ± 0.0013	14.38	–
5	289	4.336	36.02	1.5082 ± 0.0018	14.02	7.18
10	280	4.286	35.23	1.4979 ± 0.0016	13.51	5.68
15	278	4.220	34.56	1.4950 ± 0.0013	13.19	6.45
20	271	4.148	33.92	1.4874 ± 0.0021	12.80	6.48
25	263	4.069	33.31	1.4825 ± 0.0013	12.48	6.78
30	257	3.996	32.62	1.4695 ± 0.0014	11.97	6.35

*T_g = glass transition temperature, d = density, V_m = molar volume, n_D = refractive index, R_m = molar refractivity, R_{KF} = molar refractivity of KF in glass.

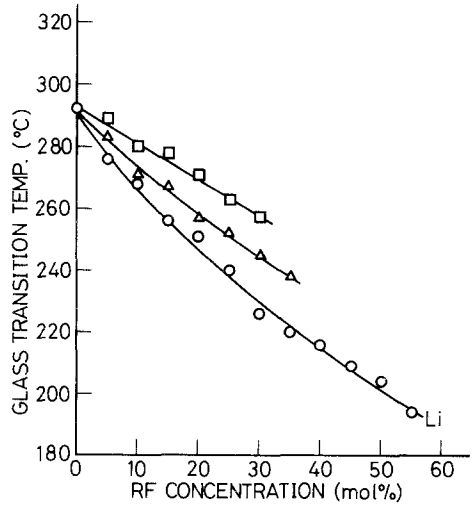

Figure 1 Glass transition temperature as a function of the RF concentration for $(100 - x)$ $(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xRF$ glasses. R = (○) Li, (△) Na, (□) K.

and illustrated in Fig. 6 as a function of the RF concentration. With some scattering in the low RF concentration region, the molar refractivities of RF converge on three horizontal straight lines for lithium glass, sodium glass and potassium glass. The molar refractivities of LiF, NaF and KF in glasses, about 3.2, 4.1 and 6.5, are very close to those of crystalline LiF, NaF and KF, i.e. 3.14, 4.13 and 6.74, respectively, calculated from the values of densities and refractive indices [4–6] of the crystals. These crystals have the NaCl-type structure in which all the lithium, sodium and potassium ions are coordinated by six fluorine atoms. No discontinuity is found in the evolution of R_{RF} with the RF concentration.

3.4. Elastic properties

The elastic properties of some of the $(100 - x)$ $(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xRF$ glasses were given in our previous paper [2]. Since the changes of shear modulus, Young's modulus and bulk modulus with the RF concentration were similar, only Young's modulus is illustrated in Fig. 7 as a function of the RF concentration. The data for Young's moduli are limited

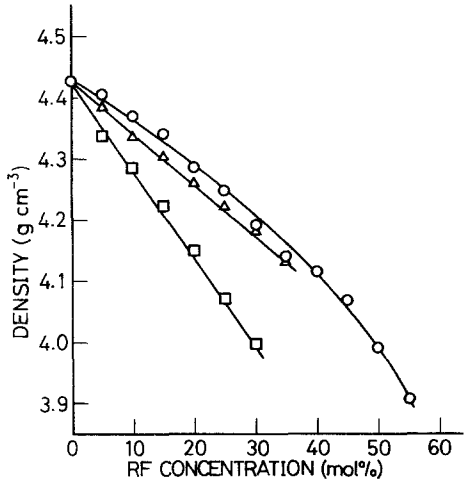

Figure 2 Density as a function of the RF concentration for $(100 - x)$ $(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xRF$ glasses. R = (○) Li, (△) Na, (□) K.

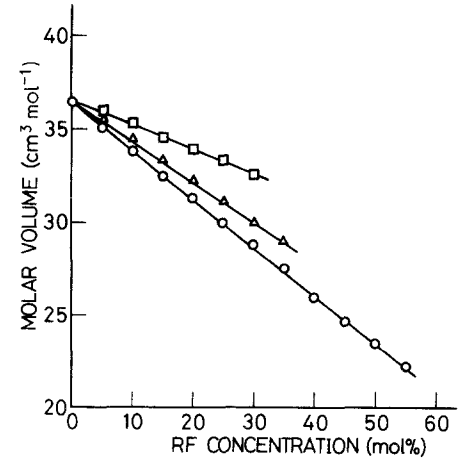

Figure 3 Molar volume as a function of the RF concentration for $(100 - x)$ $(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xRF$ glasses. R = (○) Li, (△) Na, (□) K.

to the RF concentration range of 10 to 30 mol% owing to the difficulty of sample preparation. It is found that Young's modulus decreases with increasing RF concentration and with increasing alkali ion radius.

4. Discussion

It has been found that all the studied properties including the glass transition temperature, density, molar volume, refractive index, molar refractivity, molar refractivity of RF and Young's modulus vary continuously with the RF concentration for all the LiF-, NaF- and KF-containing glasses. This indicates that no abrupt change occurs in the structure of the glasses. The fact that the molar refractivities of LiF, NaF and KF in glasses are very close to those in crystalline compounds and do not change with the glass composition suggests that Li^+, Na^+ and K^+ ions are coordinated by six fluorine atoms over the whole composition range studied. This is different from the case of $(0.62 - 0.4x)ZrF_4 \cdot (0.3 - 0.5x)BaF_2 \cdot (0.08 - 0.1x)LaF_3 \cdot xLiF$ glasses studied by Lecoq and Poulain [3], in which abrupt changes were present

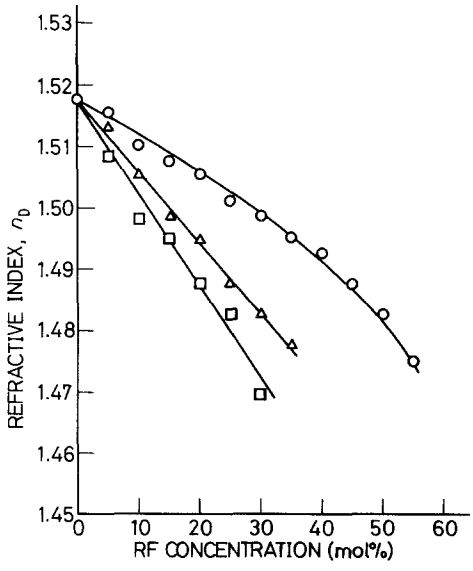

Figure 4 Refractive index as a function of the RF concentration for $(100 - x)$ $(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xRF$ glasses. R = (○) Li, (△) Na, (□) K.

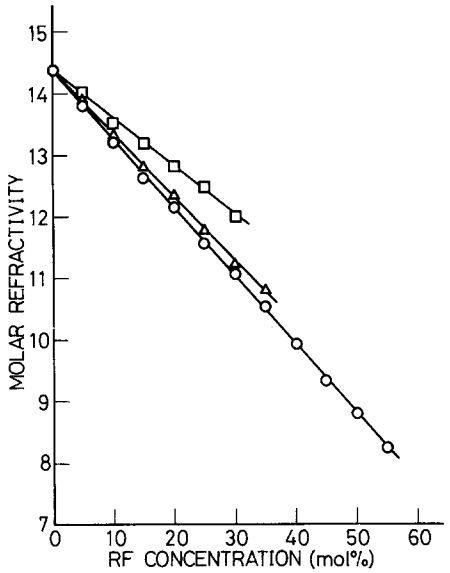

Figure 5 Molar refractivity as a function of the RF concentration for $(100 - x)$ $(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xRF$ glasses. R = (○) Li, (△) Na, (□) K.

in the evolution of glass transition temperature, refractive index, molar refractivity and molar refractivity of LiF with the LiF concentration and Li^+ ions were considered as being coordinated by four fluorine atoms in the lower LiF concentration region and by six fluorine atoms in the higher LiF concentration region. It is assumed that the Li^+ ion behaves as a glass-modifier in the present case. The difference between the present glasses and those of Lecoq and Poulain [3] may result from the fact that the only variable component in the present glasses is the alkali fluoride, whereas in their glasses the BaF_2 concentration was also varied.

Senegas *et al.* [7] explained their observation of the minimum found in the electrical conductivity against Li/F ratio curve as resulting from the change of Li^+ ion coordination state in ZrF_4–ThF_4–BaF_2–LiF glasses. However, the role of Li^+ ions as glass-former in the low LiF concentration region suggested by Lecoq and Poulain [3] is not common to all the cases of alkali-containing fluoride glasses. The present authors consider that this interpretation is not necessary in the cases of the present glasses [2]. The present

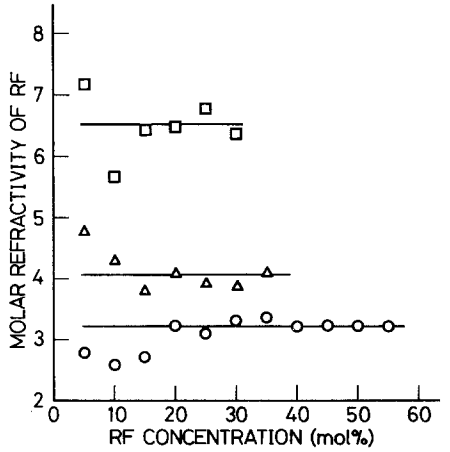

Figure 6 Molar refractivity of RF in glasses as a function of the RF concentration for $(100 - x)$ $(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xRF$ glasses. R = (○) Li, (△) Na, (□) K.

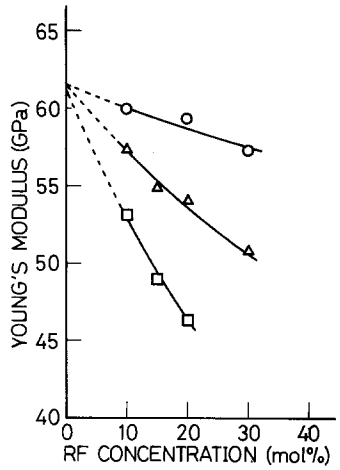

Figure 7 Young's modulus as a function of the RF concentration for $(100 - x)$ $(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xRF$ glasses. R = (○) Li, (△) Na, (□) K.

authors considered that the minimum or maximum found in the electrical conductivity or activation energy for conduction against the LiF concentration curve, which were similar to those of NaF- or KF-containing glasses, might be attributed to a change of the dominant electricity carrier from the discussion on the activation energies for diffusion of alkali ion and fluoride ion [2]. This change of the dominant electrical carrier with the RF concentration might be considered to have no direct correlation with the coordination state of the alkali ions. In the present glasses, no abrupt change of properties with the RF concentration has been seen. Thus, we consider that all the Li^+, Na^+ and K^+ ions behave as glass-modifiers in the present glasses.

5. Conclusions

The glass transition temperatures, densities, molar volumes, refractive indices, molar refractivities and elastic properties have been studied for glasses of the compositions $(100 - x)$ $(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xRF$, where R = Li, Na or K. All the properties vary continuously with the RF concentration, for all the glasses containing LiF, NaF and KF. This suggests that Li^+, Na^+ and K^+ ions play the same role of glass-modifier in these glasses. The calculated molar refractivities of LiF, NaF and KF are very close to the values for crystalline LiF, NaF and KF, suggesting that Li^+, Na^+ and K^+ ions are all coordinated by six fluorine atoms.

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