X-Ray Structural Analysis of Molten KF-KX(X=Cl, Br, and I) Systems

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Abstract

The short range structures of molten KF-KX(X=Cl, Br, and I) systems with the common cation were investigated by an X-ray diffraction analysis. The results obtained were compared with those of the pure melts and molten alkali halide mixture melts with the common anions. The nearest neighbor configurations of the unlike ion pairs were similar to those in the pure melts. On the other hand, the nearest distance between like ions changed on mixing.

1. INTRODUCTION

Okada et al.(1) investigated the dynamical structure of molten LiCl-KCl(eutectic composition) system by the X-ray diffraction analysis and molecular dynamics simulation in detail. According to the report, the nearest neighbor distances of unlike ion pairs such as $\text{Li}^+\text{-Cl}^-$ and $\text{K}^+\text{-Cl}^-$ were almost the same as those in the pure melts. On the other hand, the nearest distances of like ion pairs such as $\text{K}^+\text{-K}^+$ and $\text{Cl}^-\text{-Cl}^-$ changed on mixing. Recently, Igarashi et al.(2-4) investigated the structures of molten alkali fluoride mixtures by the X-ray diffraction analysis and obtained a similar conclusion.

They were all the mixtures with the common anions. Also in the mixtures with the common cation, similar results may be expected. In this work, we chose molten KF-KCl(1:1), KF-KBr(1:1), and KF-KI(1:2) systems, which contain K^+ ion as the common cation. The mole ratios were close to the eutectic compositions of each system.

2. EXPERIMENTAL

Chemicals KF, KCl, KBr, and KI of analytical reagent grade were dried at 673 K under reduced pressure for 10 hours. They were mixed to the prescribed composition by weighing under dried N_2 gas, and melted in a platinum crucible. Experimental temperatures were 933 K for KF-KCl system, 973 K for KF-KBr system, and 873 K for KF-KI system. The temperature was controlled to a maximum error of 10 K.

X-ray scattering intensity was measured by a diffractometer having θ - θ type para-focusing reflection geometry using $\text{MoK}\alpha$ beam($\lambda=0.07107$ nm). Scattering beam was monochromatized with a curved graphite crystal. Intensity data were collected over the range of scattering angle 3° to 54° for KF-KCl and KF-KBr systems, and 4° to 45° for KF-KI system.

The corrections for background, polarization, absorption, and Compton radiation were applied to the observed data by the usual methods(5). The corrected data were scaled to the independent scattering factor(6,7) for stoichiometric unit by combined use of the high angle region method and Krogh-Moe-Norman method(8,9). The reduced intensity function $S_i(S)$, the radial distribution function $D(r)$, and the correlation function $G(r)$ were calculated by the following equations.

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$$D(r) = 4\pi r^2 g_0 + \sum (K_m)^2 \frac{2r}{\pi} \int_0^{S_{\max}} Si(S) \sin(rS) dS,$$

$$G(r) = 1 + \frac{\sum (K_m)^2}{2\pi^2 g_0 r} \int_0^{S_{\max}} Si(S) \sin(rS) dS,$$

$$Si(S) = S [I_{00}^{\text{coh}}(S) / \sum f_m^2(S) - 1],$$

$$g_0 = (\sum K_m)^2 \rho_0,$$

and

$$S = 4\pi \sin \theta / \lambda$$

where ρ_0 is the number of stoichiometric unit per nm^{-3} , K_m the effective electron number in the atom m , f_m the independent scattering intensity, $I_{00}^{\text{coh}}(S)$ the total coherent intensity, and $S_{\max}$ the maximum value of S reached in the experiment. Parameters used in the calculations are listed in Table 1.(10)

Table 1. Parameters used in the calculations of the $Si(S)$ and $G(r)$

	KF-KCl(1:1)	KF-KBr(1:1)	KF-KI(1:2)
Temperature/K	933	973	873
Density(10)/ gcm^{-3}	1.7531	2.0883	2.4094
Number density/ 10^3nm^{-3}	0.00796	0.00710	0.00620
Effective electron numbers			
$\bar{K}_K$	19.7889	18.6415	17.6950
$\bar{K}_F$	7.1749	6.7714	6.6380
$\bar{K}_X$	17.2454	37.9440	56.1370
$S_{\max}/10 \text{nm}^{-1}$	14.3	14.3	12.5

X=Cl, Br, and I

3.RESULTS AND DISCUSSION

(1)KF-KCl(1:1) system

$G(r)$ and $Si(S)$ curves for molten KF-KCl(1:1) system at 933 K are shown in Figures 1(a) and 2(a), respectively. $G(r)$ has the peaks at $r=0.310$, 0.370 , and 0.405 nm , and the shoulder at near 0.260 nm .

Zarzycki(11) investigated the structure of the pure KF melt and reported that the nearest neighbor distance and the coordination number of K^+ - F^- interaction were 0.265 nm and 4.9 (based on $D(r)$). Takagi et al.(12) reported that those of K^+ - Cl^- interaction in the pure KCl melt were 0.305 nm and $3.6(D(r)/r)$. From those results, it seems that the shoulder at near 0.260 nm and the peak at 0.310 nm are assigned to the nearest K^+ - F^- and K^+ - Cl^- interactions, respectively. The weak peaks at 0.370 and 0.405 nm seem to correspond to the second nearest neighbor interactions between like ions such as K^+ - K^+ and Cl^- - Cl^- . In order to separate and determine those contributions, the following equation reported by Narten et al.(13) was applied to the observed $Si(S)$ curve beyond $S=0.25 \text{ nm}^{-1}$.

Fig. 1 Correlation functions $G(r)$
(a)KF-KCl(1:1) at 933 K
(b)KF-KBr(1:1) at 973 K
(c)KF-KI(1:2) at 873 K

$$\sum f_i^2(S) S i(S) = \sum \sum N_{ik} \exp(-b_{ik} S^2) f_i(S) f_k(S) \sin(S r_{ik}) / r_{ik}$$

where N_{ik} represents the number of interactions between ions i and k , b_{ik} the temperature factor, and r_{ik} the average distance between ions i and k .

Structural parameters were obtained by the least squares method and are listed in Table 2. The nearest neighbor distance and the coordination number of K^+ - F^- interaction were 0.262 nm and 4.0. Although the distance of this interaction was in good agreement with that in the pure KF melt, the coordination number was slightly smaller than that in the pure melt. This seems to be caused by difference of the method of determining the coordination number, i.e., Zarzycki(11) assumed the symmetrical peak on $D(r)$ curve, but not in this work. Therefore, these values should not be carelessly compared. The nearest neighbor distance and the coordination number of K^+ - Cl^- interaction were 0.313 nm and 3.4, respectively. These values were in good agreement with those in the pure KCl melt. The nearest distance of K^+ - K^+ interaction was 4.02 nm. This value was shorter than that in the pure KCl melt, rather close to that in the pure KF melt. The nearest distance of Cl^- - Cl^- interaction was 0.369 nm, and shorter than that in the pure KCl melt. The calculated $Si(S)$ curve is shown in Figure 2(b). The degree of agreement between the observed and the calculated $Si(S)$ curves was $R=0.454$. The R value is defined by the following equation.

$$R = \frac{\sum [| Si(S)_{obs} - Si(S)_{cal} |]}{\sum [| Si(S)_{obs} |]}$$

(2) KF-KBr(1:1) system

$G(r)$ and $Si(S)$ curves for molten KF-KBr(1:1) system at 973 K are shown in Figures 1(b) and 3(a), respectively. $G(r)$ has the peak at 0.325 nm, and the shoulders at near 0.270 and 0.415 nm.

The shoulder at near 0.270 and the peak at 0.325 nm are expected to be the contributions of the nearest K^+ - F^- and K^+ - Br^- interactions, respectively. Ohno et al.(14) reported that the nearest neighbor distance and the coordination number of K^+ - Br^- interaction in the pure KBr

Fig. 2 Reduced intensity function $Si(S)$ for molten KF-KCl(1:1) system (a)observed (b)calculated

Fig. 3 Reduced intensity function $Si(S)$ for molten KF-KBr(1:1) system (a)observed (b)calculated

melt were 0.318 nm (based on $G(r)$ curve) and $3.5(D(r)/r)$. The shoulder around 0.415 nm seems to be due to the interactions of the like ion pairs.

As well as the foregoing system, structural parameters were obtained and are listed in Table 3. The nearest neighbor distances of the unlike ion pairs were almost the same as those in the pure melts. The nearest distance of K^+-K^+ interaction was 0.412 nm. This value was considerably shorter than that in the pure KBr melt, but longer than that in the pure KF melt. The nearest distance of $Br^- - Br^-$ interactions was 0.423 nm, and this value was also considerably shorter than that in the pure KBr melt. The calculated $Si(S)$ curve is shown in Figure 3(b). The R value in this system was 0.355.

(3) KF-KI(1:2) system

$G(r)$ and $Si(S)$ curves for molten KF-KI(1:2) system at 873 K are shown in Figures 1(c) and 4(a), respectively. $G(r)$ has the peak at 0.355 nm, and the shoulders at 0.265 and near 0.470 nm.

As well as the foregoing systems, the shoulder at 0.265 nm and the peak at 0.355 nm seem to be assigned to the nearest K^+-F^- and K^+-I^- interaction, respectively. Antonov(15) reported that the nearest neighbor distance of K^+-I^- interaction in the pure KI melt was 0.352 nm. This value was quite close to that in this system. As well as the foregoing systems, the shoulder around 0.470 nm seems to be attributed to the interactions of the like ion pairs.

The curve fitting to the observed $Si(S)$ in the same manner as the above systems was carried out. In the calculation, only $I^- - I^-$ interaction was employed as the interaction of the like ion pair, because the contributions of the other interactions were too small to separate and determine. The nearest distance of $I^- - I^-$ interaction was 0.464 nm, and slightly shorter than that in the pure melt. The calculated $Si(S)$ curve is shown in Figure 4(b). The R value was 0.486.

Fig. 4 Reduced intensity function $Si(S)$ for molten KF-KI(1:2) system
(a) observed (b) calculated

Table 2. Structural parameters of molten KF-KCl(1:1) system

	n_{ij}	r_{ij}/nm	$\langle \Delta r_{ij}^2 \rangle^{1/2}/10^{-2}nm$
$K^+ - F^-$	4.0	0.262	2.89
$K^+ - Cl^-$	3.4	0.313	3.26
$Cl^- - Cl^-$	6.1	0.369	4.94
$K^+ - K^+$	9.4	0.402	6.40

Table 3. Structural parameters of molten KF-KBr(1:1) system

	n_{ij}	r_{ij}/nm	$\langle \Delta r_{ij}^2 \rangle^{1/2}/10^{-2}nm$
$K^+ - F^-$	3.9	0.259	3.22
$K^+ - Br^-$	4.0	0.323	3.81
$Br^- - Br^-$	5.7	0.423	6.23
$K^+ - K^+$	7.9	0.412	6.43

Table 4. Structural parameters of molten KF-KI(1:2) system

	n_{ij}	r_{ij}/nm	$\langle \Delta r_{ij}^2 \rangle^{1/2}/10^{-2}\text{nm}$
$\text{K}^+ - \text{F}^-$	4.0	0.260	3.24
$\text{K}^+ - \text{I}^-$	4.3	0.348	4.39
$\text{I}^- - \text{I}^-$	4.6	0.464	6.70

Some experimental studies on the structures have been performed for pure alkali halide and their mixture melts, and are listed in Table 5. The nearest neighbor distances of $\text{K}^+ - \text{X}^-$ ($\text{X} = \text{Cl}$, Br , and I) interactions are found to be almost the same as not only those in the pure melts, but also those in the mixture melts with the common anions. On the other hand, the nearest distances of the like ion pairs are found to be slightly shorter than those in the pure melts. These results show that the conclusion reported for the mixture melts with the common anions by Okada et al.(1) and Igarashi et al.(2-4) applies well to the present systems.

Table 5. The interionic distances of the correlation functions and the radial distribution functions

Mixtures(Author)	$\text{K}^+ - \text{F}^-$	$\text{K}^+ - \text{Cl}^-$	$\text{K}^+ - \text{Br}^-$	$\text{K}^+ - \text{I}^-$	$\text{K}^+ - \text{K}^+ \text{ \& \& } \text{X}^- - \text{X}^- (\text{X})$	Temp.	Ref.
KF-KCl (this work)	0.262nm	0.313			0.402 0.369(Cl)	933K	
KF-KBr (this work)	0.259		0.323		0.412 0.423(Br)	973	
KF-KI (this work)	0.260			0.348	0.464(I)	873	
LiF-KF (Igarashi et al.)	0.270				0.357	818	(2)
FLINAK (Igarashi et al.)	0.259				0.343	793	(4)
LiCl-KCl(Okada et al.)		0.308			0.441 0.385(Cl)	668	(1)
KF (Zarzycki)	0.265*				0.420*	1143	(11)
KCl (Takagi et al.)		0.305				1173	(12)
KCl (Levy et al.)		0.310*			0.470 (Cl)		(16)
KBr (Ohno et al.)			0.318		0.465 (Br)	923	(14)
KBr (Antonov)			0.335*				(15)
KI (antonov)				0.352*	0.495* (I)		(15)

*the data based on r.d.f.

An influence by temperature should be considered in connection with the results in this work, because the experimental temperature in each system is considerably lower than the melting points of the constituent salts. Lantelme et al.(17) studied the effect of temperatures on the structures(646 K and 1096 K) for molten LiCl-KCl system at a eutectic composition by the molecular dynamics simulation. According to the report, the distance of the like ion pairs decreased at the low temperature(646 K). However, for the unlike ion pairs, despite the large difference in temperature amounting to 450 K, no change was detected. The similar conclusion was also reported for molten LiCl-KCl(eutectic

composition) system by Okada et al.(1). Although the observed temperature(668 K) in this system is considerably lower than the melting points of pure LiCl and KCl, no change was detected for the nearest neighbor distances of the unlike ion pairs. As shown in Table 5, it seems that the nearest neighbor distances of the unlike ion pairs are not appreciably influenced by the temperature, while the nearest distances of the like ion pairs decreased with a decrease in the temperature. Also in the mixture melts with the common cation, the results found in the mixture melts with the common anions are clearly obtained.

Molar volume of the melt is relatively sensitive to the structure, and generally decreases as temperature decreases. Lantelme et al. reported that the contraction of the melt at low temperature induced the decrease of the distance of the like ion pairs. The results obtained in this work seem to support the conclusion by Lantelme et al.

4.CONCLUSION

[1]In the mixture melts with the common cation, as well as the melts with the common anions, the nearest neighbor distances between unlike ions were similar to those in the pure melts.

[2]The nearest distances between like ions were changed on mixing. In molten KF-KX(X=Cl and Br) systems, the nearest distance of K^+-K^+ pair was close to that in the pure KF melt and considerably shorter than that in the pure KX melt. All of the nearest distances of $X^--X^-(X=Cl, Br, \text{ and } I)$ pair were considerably shorter than those in the pure melts.

[3]The decrease of the nearest distance between like ions is closely associated with the temperature, and attributed to the decrease of the molar volume at low temperature.

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