X-RAY DIFFRACTION ANALYSIS OF MOLTEN LaF_3–XF(X = Li, K) ①

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ABSTRRACT

The radial distribution functions of molten salt solution LaF_3–4LiF and LaF_3–4KF systems were derived from X-ray difraction data at 1,083 K. The interionic distances in the melts were obtained, e. g. La^{3+}–F^- interaction was 0. 238 and 0. 233nm respectively in molten LaF_3–4LiF and LaF_3–4KF systems. The temperature and coulombic force of La^{3+} were discussed concerning the results of interionic distances in melt.

Key words: X-ray melt LaF_3

1 INTRODUCTION

The molten salt has short range order and long range disorder. It is more difficult to describe than ordered crystal and disordered gas. The distribution function theory not based on any physical moldels but statistical theory and interaction is considered as an ideal theory, but its application is handicapped due to the fact that the mathematical and / or computational problems involved are at present insurmountable. Therefore, the radial distribu- tion function of molten salt is experimentally obtained by diffraction method[1-3]. In recent years, MD and MC have also been developed for the studies of molten salt[4].

In this note, the radial distribution functions of molten salt solutions LaF_3–4LiF and LaF_3–4KF were derived from X-ray diffraction data. The interionic distances were obtained and some problems concerning the structure were discussed.

2 EXPERIMENTAL

Dried LaF_3 and XF(X = Li, K analytical pure reagents) were mixed at a molar ratio of 1: 4, dewatered under reduced pressure at 400 ℃ for several hours, then melt, cooled, ground and conserved for use in the experiments.

Scattering intensity was measured on a θ–θ X-ray diffractometer (Mo target, λ = 0. 071,07 nm) with a curved graphite crystal mounted in the diffracted beam. The intensity data were collected over the angle range from 1 to 60(°). Several slit systems, angle intervals and counting time were used in different angle region as shown in Table 1. And the experimental temperatures were controlled at 1, 083 K(± 5K). The tube voltage was 50 kV with tube current 20 mA.

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Table 1 Experimental conditions

2θ / (°)	DS / (°)	SS / (°)	RS / mm	Step / (°)	t_c^* / s
2~9.2	1 / 2	1 / 2	0.15	0.2	60
8~16.1	1 / 2	1 / 2	0.15	0.1	40
15.6~26.1	1 / 2	1 / 2	0.15	0.1	20
25.2~41.2	1	1	0.15	0.2	15
38.6~120.6	2	2	0.30	0.6	10

* t_c—counting time

3 DATA ANALYSIS

Corrections for background, polarization, absorption and Compton scattering were applied to the measured scattering intensities by usual method[3]. Normalization was calculated by the radial distribution function method. The reducd intensity function $I(s)$, correlation $g(r)$ and radial distribution function RDF(r) are given by the following expressions

$$I(s) = 1 + [I_a^{'}(s) - \bar{f}^2 - I_{comp}(s)] / \bar{f}^2$$

$$g(r) = \{\int_0^{S_{max}} s[I(s) - 1]e^{-\alpha^2 s^2} \sin(sr)ds\} \times (2\pi^2 r \rho_a)^{-1} + 1$$

$$RDF(r) = 4\pi r^2 e_a + \frac{2r}{\pi}\int_0^{S_{max}} s[I(s) - 1] \times e^{-\alpha^2 s^2} \sin(sr)ds$$

where θ is the scattering angle; $s = 4\pi\sin\theta / \lambda$; f is the atomic scattering factor; $e^{-\alpha^2 s^2}$ the con-vergence factor; ρ_a the average atomic density; $I_a^{'}(s)$ the average total scattering intensity of one atom (electron unit); $I_{comp}(s)$ the average Compton scattering intensity.

4 RESULTS AND DISCUSSION

Correlation function $g(r)$ and radial distribution function RDF(r) obtained by X−ray diffraction are illustrated in Fig.1 and 2, respectively. Peaks in $g(r)$ curve of LaF_3−4LiF melt are observed at r = 0. 191 and 0. 238 nm and a shoulder is also observed at r = 0. 291 nm. Based on the parameters listed in Table 2, it can be concluded that peaks at r = 0. 191 and 0. 238 nm belong to the nearest neighbor distances of Li^+ −F^- and La_{3+} −F^- pairs, respectively, the shoulder at r = 0. 291 nm appears to correspond to the contribution of F^-− F^- interaction. Also, $g(r)$ curve of LaF_3− 4KF melt indicates that peaks at r = 0. 233, 0. 265,

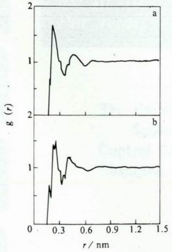

Fig.1 Corraltion functions of LaF_3−4XF

(a: X = Li; b: X = K) melts

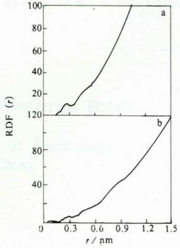

Fig.2 Radial distribution function of LaF_3−4XF

(a: X = Li; b: X = K) melts

Table 2 Data of relative crystal and melt and results of this work / nm

		$La^{3+}-F^-$	Li^+-F^-	K^+-F^-	K^+-K^+	F^--F^-	References
Crystal	LaF_3	0.242				0.287	[5]
	LiF		0.210			0.297	[1]
	KF			0.280	0.396		[1]
Melt	LiF		0.195			0.300	[1]
	KF			0.270	~0.386		[1]
	LiF–KF		0.184	0.270	0.357	0.299	[2]
	LaF_3–4LiF	0.238	0.191			0.291	This work
	LaF_3–4KF	0.233		0.265	0.351	0.290	This work

0. 290 and 0. 351 nm are contributed to the $La^{3+}-F^-$, K^+-F^-, F^--F^- and K^+-K^+ interactions, respectively.

From Table 2, we can see that distances of unlike ion pairs in melt are shorter than those in crystal. This agrees with the general property of molten salt–reduction of the coordination number in melt. Comparing simple melt with mixed melt, it is found that distances between unlike ions in mixed melt are close to those in simple melt, while distances between like ions are shorter. Distance of F^--F^- pair is even smaller in LaF_3–4XF (X = Li, K) melt than in LiF–KF melt.

Influence of temperature should be taken into consideration in connection with the results. Experimental temperature of mixed salt is considerably lower than the melting point of simple salt according to the eutectic action. The contraction of melt at low temperature induces the decrease of distance between like ions. On the other hand, F^- ions tend to be brought together by the strong Coulomb force of La^{3+}.

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