Chemistry

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Behavior of monovalent ion in LiCl-KCl eutectic melt

Yoshihiro OKAMOTO*[1,2], Tsuyoshi YAITA[2], Hideaki SHIWAKU[2] Shinichi SUZUKI[1]
[1]Japan Atomic Energy Agency, Tokai-mura, Ibaraki 319-1195, Japan
[2]Japan Atomic Energy Agency, Sayo-cho, Hyogo 679-5148, Japan

Introduction

In the pyrochemial reprocessing of spent nuclear fuels, "a small amount of metal ion in LiCl-KCl eutectic melt" is a typical condition. Then, we have studied a mixing behavior of some polyvalent metal ions like U^{3+}[1] with the eutectic melt. Most XAFS works show that the 6-fold coordination structure like $(UCl_6)^{3-}$ is formed and stabilized by the mixing. The mixing behavior of monovalent ion in molten alkali chlorides is also important in the process. In the present work, the local structure around monovalent ion Rb^+ in LiCl-KCl eutectic melt was studied by using the high-temperature XAFS measurement.

Experimental

The XAFS measurements were performed at the BL-27B station in the KEK-PF. The Rb K-edge (E_0=15.20keV) XAFS for for molten pure RbCl and 15%RbCl-(eutectic LiCl-KCl) mixture were measured in the transmission method. The samples were sealed off in a quartz cell under reduced pressure. The measurement temperature is 1050K for the pure melt and 873K for the mixture melt, respectively. Details of the XAFS measurement and data processing of molten salts are described in ref.[2].

Results and discussions

Fig.1 shows XAFS functions $k^3\chi(k)$ of molten pure RbCl and 15%RbCl-(eutectic LiCl-KCl) mixture. Fig.2

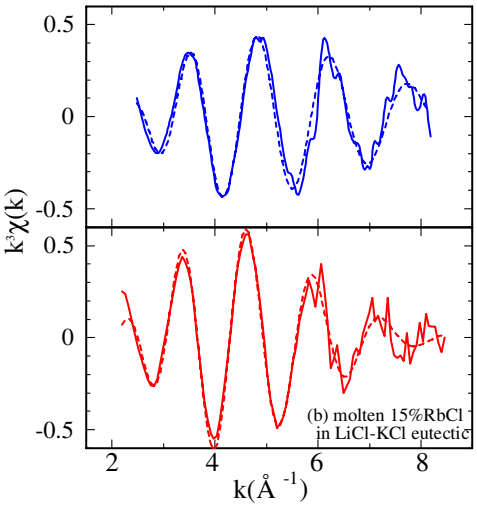

Fig.1 XAFS functions of molten (a)pure RbCl at 1050K and (b) 15%RbCl in LiCl-KCl eutectic melt.
(Solid : experimental, Dashed : fitting curve)

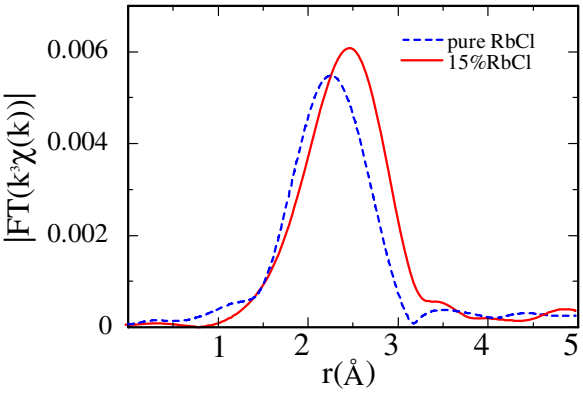

Fig.2 Fourier transform magnitudes |FT| of molten (a)pure RbCl at 1050K and (b) 15%RbCl in LiCl-KCl eutectic melt.

shows the Fourier transform magnitudes of these XAFS functions. The phase of the XAFS function and the first peak position of the |FT| result changed obviously in the mixture.

Structural parameters from the curve fitting analysis of the XAFS function are summarized in Table 1. The result for the pure melt shows the coordination number 5.3 with the averaged distance 3.20Å. These values are almost the same as the neutron diffraction result[3]. By the mixing, they increase and the Debye-Waller factor decreases. The coordination number is close to 6 in the mixture. It suggests that the 6-fold coordination structure $(RbCl_6)^{5-}$ is formed in the mixture melt. This result is compatible with the mixing behavior of polyvalent metal ion in the mixture. It can be concluded that all metal ions has a tendency to take the 6-fold coordination structure in LiCl-KCl eutectic melt.

Table 1 Structural parameters of the 1st Rb+-Cl- pair obtained from the curve fitting analysis

Rb^+-Cl^-	pure RbCl	15%RbCl
Coordination number	5.3	5.8
Averaged distance (Å)	3.20	3.25
Debye-Waller factor(Å^2)	0.0572	0.0475

References

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* okamoto.yoshihiro @jaea.go.jp