

Behavior of trivalent metal ion in LiCl-KCl eutectic melt

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Introduction

In the pyrochemical reprocessing of spent nuclear fuels, a small amount of polyvalent metal ion like U^{3+} in LiCl-KCl eutectic melt is an important condition. In the present work, the local structure around trivalent ions; U^{3+} and Y^{3+} in LiCl-KCl eutectic melt was studied by using the high-temperature XAFS measurement and the molecular dynamics simulation.

Experimental

The XAFS measurements were performed at the BL-27B station in the KEK-PF. The U L_{3} -edge ($E_0=17.167\text{keV}$) XAFS for 5% UCl_3 -(LiCl-KCl eutectic) and the Y K-edge ($E_0=17.080\text{keV}$) XAFS for molten pure YCl_3 and 5% YCl_3 -(eutectic LiCl-KCl) mixture were measured in the transmission method. The samples were sealed off in a quartz cell under reduced pressure. Details of the XAFS measurement and data processing of molten salts are described in ref.[1].

Simulation

The molecular dynamics simulation using polarizable ionic model(PIM) was performed to simulate XAFS functions of molten UCl_3 and YCl_3 systems[2]. The functions were obtained by averaging FEFF computations from position data of the MD simulation[3].

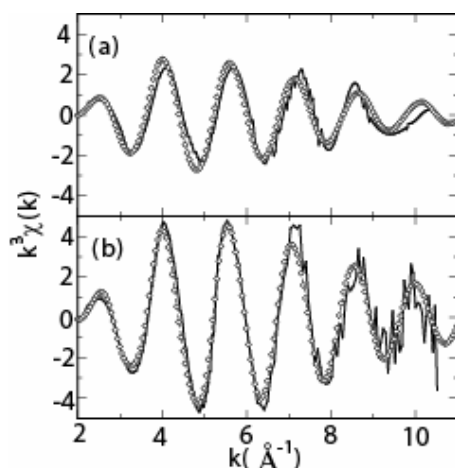


Fig.1 XAFS functions of molten (a) pure YCl_3 and (b) 5% YCl_3 in LiCl-KCl eutectic melt.
(Solid : experimental, open circle : simulation)

Results and discussions

Fig.1 shows XAFS functions of molten pure YCl_3 at 1023K and 5% YCl_3 in LiCl-KCl eutectic melt at 773K. In this system, very small changes in the nearest Y^{3+} -Cl⁻ coordination number and separation distance were observed by mixing with LiCl-KCl. Therefore no oscillation phase shift was observed in the XAFS function as shown in the Fig.1. Only a fluctuation factor such as Debye-Waller factor in the XAFS analysis was changed by the mixing. It is concluded that YCl_3 has $(YCl_6)^{3-}$ octahedral coordination unit both in the pure melt and in the mixture melt.

Fig.2 shows XAFS function of molten 5% UCl_3 in LiCl-KCl eutectic at 823K. From the MD simulation optimized by the XAFS data, the nearest U^{3+} -Cl⁻ distance is 2.76Å and its coordination number is 6.5. They are smaller than 2.85Å and 8.0 in the pure melt[2]. The local structure of molten pure UCl_3 is different from that of YCl_3 melt. On the other hand, they have similarly $(MCl_6)^{3-}$ coordination unit in the mixture with LiCl-KCl.

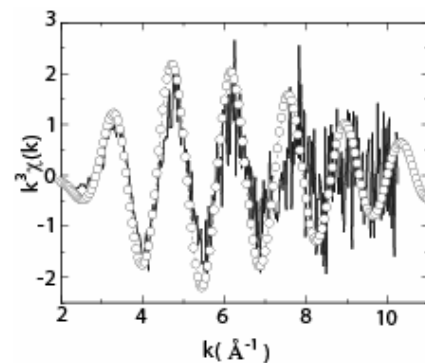


Fig.2 XAFS function of molten 5% UCl_3 in LiCl-KCl eutectic.
(Solid : experimental, open circle : simulation)

References

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