

Local structure of zirconium in molten lithium – calcium and lithium – magnesium fluoride

Haruaki MATSUURA*¹, Atsushi NEZU¹, Jun TAKEDA¹, Masahiko NUMAKURA¹, Hiroshi AKATSUKA¹

¹Res. Lab. for Nucl. Reactors, Tokyo Tech., Ookayama, Meguro-ku, Tokyo, 152-8550, Japan

Introduction

A molten salt reactor concept contains still fascinating idea from the point of view of its self-sustainability with a closed fuel cycle. In order to develop an on-line recycle process of molten salt fuels, one of promising technologies is an electrochemical separation of actinides (An) from lanthanides (Ln). To find the best electrolysis condition to improve the efficiency of the pyrochemical process, systematic investigations of the correlation between structures of molten An (Ln)F_n and their physico-chemical properties, such as electrochemical behavior are useful. In this report, molten ZrF₄-LiF-CaF₂ and ZrF₄-LiF-MgF₂ mixtures are focused as the structural investigation by EXAFS.

Experimental

Zr K-edge EXAFS spectra have been collected with fixed time scan method by the X-ray from a double Si (111) crystals monochromator in transmission mode. To avoid the contamination by oxygen, premixing treatment was abandoned. Mixtures of ZrF₄, LiF, CaF₂, MgF₂ were weighed then, they were mixed with boron nitride powder, and pressed into pellets in 13 mm diameter and 1 mm thickness. The mixing weight ratio of mixture salt to BN was ca. 1: 2.5. To prevent chemical reaction of sample by atmosphere during performing high temperature EXAFS measurements, these pellets were sanded by pyrolytic boron nitride plates. The electric furnace chamber was filled with He gas under ca. 30 kPa. EXAFS data were analysed by using the WinXAS ver.3.1 and 3rd and 4th cumulants were introduced for the curve fitting analyses of EXAFS data at molten phase due to existence of their large anharmonic effect in some cases.

Results and discussion

By the stepwise-controlled temperature program, the spectra at molten phase were well identified in each sample. The concentration dependence of EXAFS structure functions at molten phase is shown in Fig. 1.

With increasing the ratio of $x_{\text{MgF}_2}/x_{\text{LiF}}$, once interionic distance between Zr⁴⁺ and F⁻ increases, and then decreases, as shown in Fig.1. On the other hand, with increasing the ratio of $x_{\text{CaF}_2}/x_{\text{LiF}}$, interionic distance between Zr⁴⁺ and F⁻ even decreases slightly. Further looking back to previous data of the thorium or terbium mixture systems coexisting divalent cations, by addition of magnesium fluoride, the elongation effect of interionic

distances between Th⁴⁺ and F⁻ or Tb³⁺ and F⁻ were identified. These facts would be explained as follows: the effect of interionic distance elongation by coordinated fluorides removal around a cation with much larger valence and the effect of interionic distance shorten by introduction into network-like structure dominated by magnesium fluoride is complexed depending upon composition and species. Sometimes the only peak fitting procedure of each spectrum tends to mislead the explanation of local structure, thus, a molecular dynamics simulation using well established inter-ionic potential parameters would be required to evaluate proper microscopic structure of these systems.

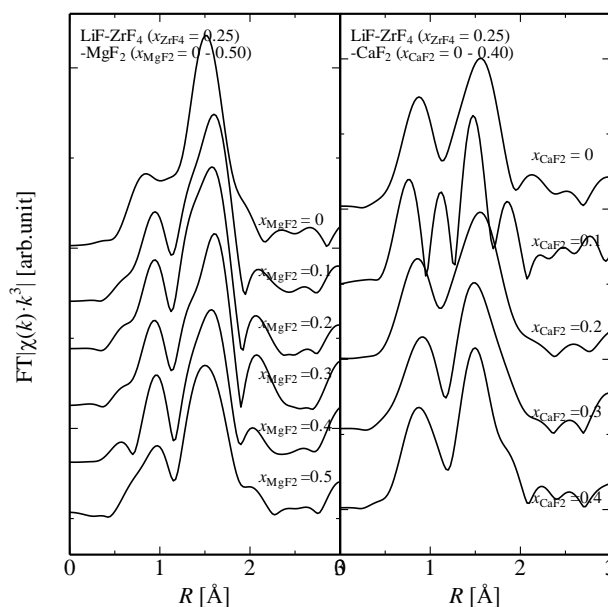


Fig.1 EXAFS structure functions of various compositions of molten ternary systems at 600 °C.

*hmtsuur@nr.titech.ac.jp