Chemistry

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EXAFS on molten thorium fluoride in alkali fluoride mixtures

Masahiko NUMAKURA[1], Yasuaki SHIMOHARA[1], Keisuke TAJIMA[1], Hirokazu KAWANO[1], Takeshi NAKAHAGI[1], Atsushi NEZU[1], Hiroshi AKATSUKA[1], Catherine BESSADA[2], Nobuaki SATO[3], Haruaki MATSUURA*[1]

[1]Res. Lab. for Nucl. Reactors, Tokyo Tech., Ookayama, Meguro-ku, Tokyo, 152-8550, Japan
[2]CEMHTI, CNRS, 1D avenue de la recherche scientifique, 45071 Orléans cedex 2, France
[3]Inst. of Multidisc. Res. for Adv. Mater., Tohoku Univ., Katahira, Aoba-ku, Sendai, 980-8577, Japan

Introduction

Thorium has been recently focused by the environmental problem on extracting rare earths from ores, such as monazite. Actually thorium can be utilized for nuclear fertile material, thus the electrochemical process is one of promising techniques of separation from rare earth elements. One of the systematic studies on the chemistry of the compounds containing thorium was the development of molten salt reactors. To investigate the relationship between electrochemical behaviour and physico - chemical properties of thorium is important for process design, but structural information of the related materials are still limited. Thus, EXAFS analysis of molten thorium fluoride in alkali fluoride mixtures have been systematically carried out to elucidate the variation of local structure of thorium cation in various melts.

Experimental

XAFS measurements in transmission mode were performed. Th L_{III}-edge XAFS spectra were collected with a fixed time scan method by using Si (111) double crystal monochromator. Mixtures of ThF_4, LiF and NaF in various compositions were melted once in a glassy carbon crucible at 1073 K in a glove box filled with an argon atmosphere in high purity. Then, they were mixed with boron nitride powder (BN), and pressed into pellets in 7 mm diameter and 1 mm thickness. The mixing weight ratio of ThF_4 to BN was ca. 1: 2.5. To prevent chemical reaction of sample and contamination of ThF_4 to outside during heating process in XAFS measurements, these pellets were installed in a double barrier cell. 1st barrier is made with pyrolytic boron nitride and 2nd barrier is made with boron nitride (HIP). The electric furnace was filled with He gas at 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 their large anharmonic effect.

Results and discussion

The structural parameters obtained by the curve fitting analysis of EXAFS spectra of $xThF_4 - (1\text{-}x)$ MF (M = Li and Na, $0<x<1$) are shown in Fig. 1. With decreasing the concentration of ThF_4, coordination number tends to decrease upto ca. 7 in both systems. This tendency of the variation of coordination number of local structure depending on the concentration of ThF_4 has been also confirmed by NMR and Raman spectroscopic studies in ThF_4 mixtures as well as ZrF_4 mixtures which can be sometimes used as a simulated material for ThF_4. The most striking feature can be found in the tendency of σ and C_3 cumulant. With decreasing the concentration of ThF_4, both σ and C_3 decrease, and the values in ThF_4-NaF system are smaller than those in ThF_4-LiF system in general. These features have been also confirmed in the mixture systems including TbF_3.

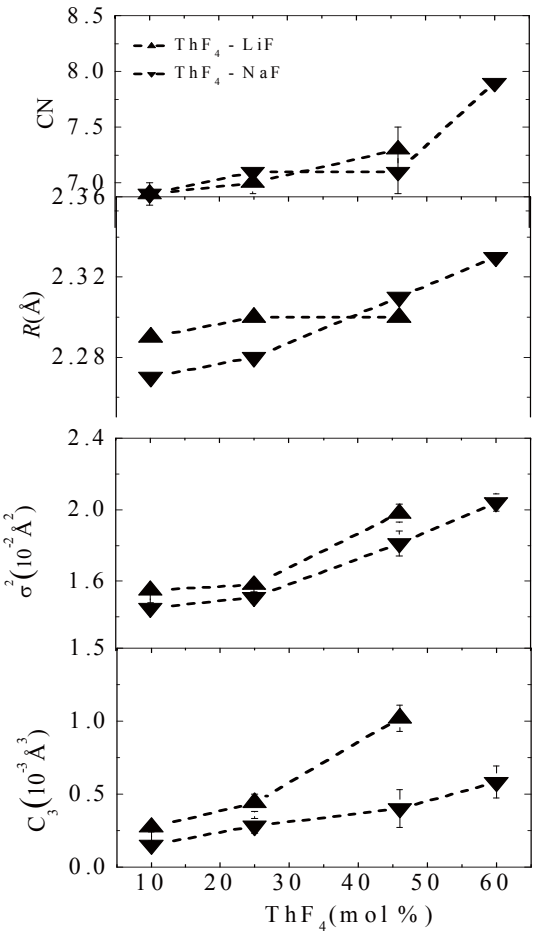

Fig. 1 Structural paramenters obtained by EXAFS of molten $xThF_4$ –(1-x)MF (M=Li and Na, $0<x<1$) mixtures, from the top, coordination number, inter-ionic distance, Debye-Waller factor and C_3 cumulant.

*hmatsuur@nr.titech.ac.jp