Chemistry

27B/2009G544

EXAFS on thorium fluoride in molten lithium fluoride and lithium-calcium fluoride mixtures

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

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

Introduction

For the development of the molten salt reactor, it is important to establish the separation technique of actinides (An) and lanthanides (Ln) by electrochemical methods. The lithium fluoride-calcium fluoride (LiF-CaF_2) eutectic melt can be used as the solvent for the electrodeposition of Nd and Th, while LiF-NaF and LiF-KF eutectic melts cannot be used for the same purpose theoretically. To find better electrolysis conditions to improve the efficiency of the pyrochemical reprocessing, clarification of the correlation between structures of molten An (Ln)F_n and their physico-chemical properties is useful. However, structural information of the ternary $x$$ThF_4$-$a$LiF-$b$$CaF_2$ mixtures has not been reported yet.

Experimental

XAFS measurements in transmission modes have been performed. The Th L_{III}-edge XAFS spectra have been collected with fixed time scan method by the X-ray from a double Si (111) crystals monochromator. ThF_4 was synthesized by ThO_2 under fluorine gas (40 ml/min) at 650 °C for 4 h. Mixtures made by ThF_4, LiF and CaF_2 were melted once in a glassy carbon crucible at 1073 K in a quartz tube filled with an argon atmosphere in high purity. Then, they were mixed with boron nitride powder, 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.

Results and discussion

The CaF_2 concentration dependence of local structural parameters derived from EXAFS of the constant concentration of x_{ThF4} = 0.25 are shown in Fig. 1. Although inter-ionic distance is independent from the concentration of CaF_2, coordination number, Debye-Waller factor and C_3 cumulant parameter increase once until the concentration of x_{CaF2} = 0.17, but these values decrease with increasing at x_{CaF2} > 0.17. The local structure of thorium cation has been un - stabilized until certain concentration of calcium fluoride and then going to be stabilized by further addition of calcium fluoride. To confirm this complicated tendency, the MD simulation of molten 0.25ThF_4-LiF-CaF_2 has also been performed. The distribution of coordination number is getting wider until x_{CaF2} = 0.25, but at x_{CaF2} > 0.25, even getting sharper. This complicated feature depending on the concentration of CaF_2 is also identified in the cage correlation functions around Th^{4+}. The diminishing rate of the function is once getting larger, but going back to smaller. These tendencies by the MD are quite consistent to these derived from the structural parameters by EXAFS.

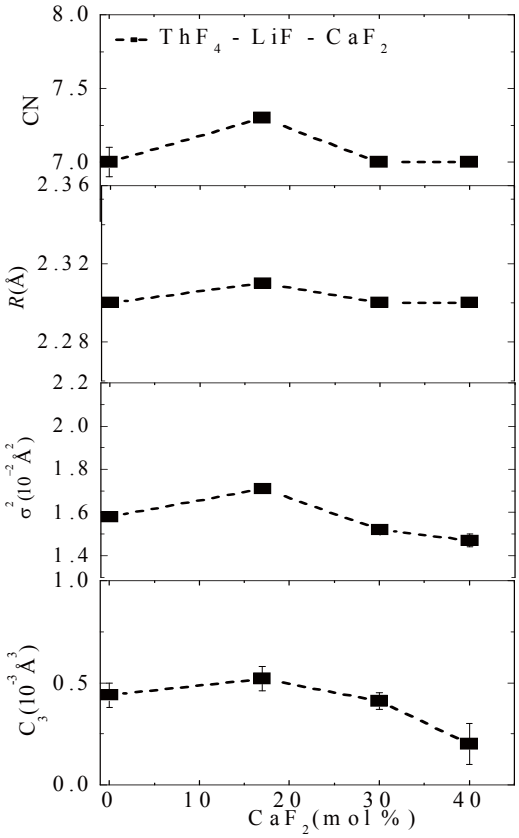

Fig. 1 Structural paramenters obtained by EXAFS of molten 0.25ThF_4 – (0.75-x) LiF - xCaF_2 mixtures (0<x<1), from the top, coordination number, inter-ionic distance, Debye-Waller factor and C_3 cumulant.

*hmatsuur@nr.titech.ac.jp