27B/2009G544

EXAFS on thorium fluoride in molten mono- and divalent cationic fluoride mixtures

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Introduction

For the development of the on-line recycling process of molten salt reactor, it is important to establish the separation technique of actinides (An) and lanthanides (Ln) by electrochemical methods. To find better electrolysis conditions to improve the efficiency of the pyrochemical reprocessing, systematic clarification of the correlation between structures of molten An (Ln)F_n and their physico-chemical properties is useful. In this study, ThF_4-LiF-CaF_2 and ThF_4-LiF-MgF_2 mixtures are focused for the structural investigation by EXAFS.

Experimental

The Th L_{III}-edge EXAFS spectra have been collected with fixed time scan method by the X-ray from a double Si (111) crystals monochromator in transmission modes. ThF_4 was synthesized by ThO_2 under fluorine gas (40 ml/min) at 650 ^oC for 4 h. Mixtures made by ThF_4, LiF and CaF_2 or MgF_2 were melted once in a glassy carbon crucible at 1073 K in a quartz chamber 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 EXAFS measurements, these pellets were installed in a double barrier cell. The 1st barrier is made with pyrolytic boron nitride and the 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 in the spectra.

Results and discussion

The BF_2 (B = Ca, Mg) 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 seems to be independent from the both concentration of CaF_2 and MgF_2, coordination number, Debye-Waller factor and C_3 cumulant parameter of MgF_2 mixture are larger than those of CaF_2 in general, and increasing rates depending on the concentration of MgF_2 are also larger than those of CaF_2. These facts imply that MgF_2 makes much un-stabilized local environment around Th^{4+} than CaF_2 does. The similar tendency is also confirmed at the TbF_3 – LiF - BF_2 (M=Ca, Mg) mixtures. This is caused by the difference between the coulombic interaction of Mg^{2+} - F^- and Ca^{2+} - F^-. Ionic radius of Mg^{2+} is smaller than that of Ca^{2+}, thus Mg^{2+} can easily approach to the coordinated F^- around Th^{4+}. Therefore, Mg^{2+} makes un-stabilised local structure around Th^{4+} more strongly.

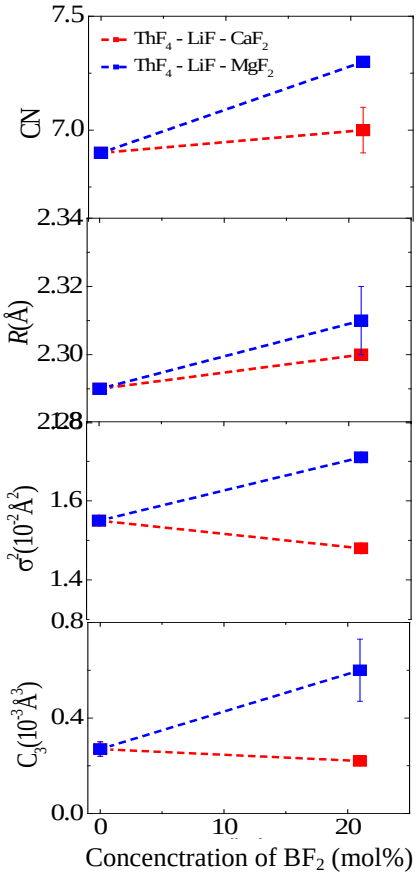

Fig. 1 Structural paramenters obtained by EXAFS of molten 0.25ThF_4 – (0.75-x)LiF - x CaF_2 or MgF_2 mixtures (0<x<1), from the top, coordination number, inter-ionic distance, Debye-Waller factor and C_3 cumulant.

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