27B/2013G233

EXAFS on thorium cations in molten lithium fluoride

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Introduction

A molten salt reactor concept contains still fascinating idea from the point of view of its self-sustainability constructed by 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 ThF_4-LiF mixtures are focused as the structural investigation by EXAFS.

Experimental

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 mode. ThF_4 was synthesized from ThO_2 under fluorine gas (40 ml/min) at 650 ^oC for 4 h and its purity was verified by the powder X-ray analysis. To avoid the contamination by oxygen, premixing treatment was abandoned in this experiment. Mixtures of ThF_4 and LiF were weighted 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 by atmosphere during performing high temperature EXAFS measurements, these pellets were installed in a double barrier cell, i.e., the 1st barrier is made with pyrolytic boron nitride and the 2nd barrier is made with boron nitride ceramics. 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 apperance of their large anharmonic effect in some spectra.

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. Temperature of each spectra is varied since its melting temperature is different according to the phase diagram. Unexpectedly, the 1st neighbor contribution which is corresponding to $Th^{4+} - F^-$ correlation has been modified between x_{ThF4} = 0.35 and 0.46. Especially, the spectra of x_{ThF4} = 0.46 seems to have specific feature, but twice measurements of this composition in different date are well corresponding each other. These facts would be carefully discussed about the modification of network-like structures depending upon the concentration of ThF_4 in LiF. Sometimes the only peak fitting procesure of each spectrum tends to mislead the explanation of local structure, thus, a molecular dynamics simulation using well established inter-ionic potential paramenters are going underway to evalute much properly the microscopic structure of this system.

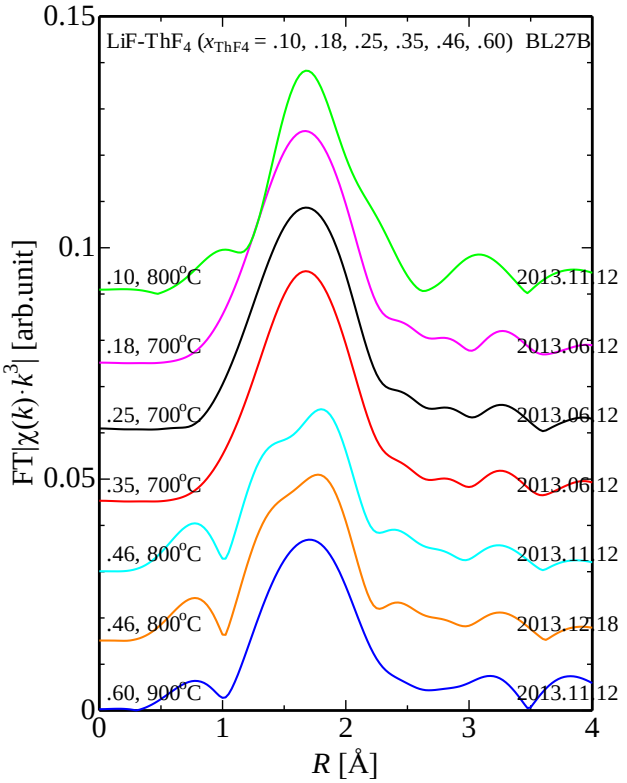

Fig. 1 Structure functions of LiF-ThF_4 (x_{ThF4} = 0.10, 0.18, 0.25, 0.35, 0.46, 0.60) at molten phase.

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