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EXAFS on thorium compounds in molten 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 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 mode. ThF_4 was synthesized from ThO_2 under fluorine gas (40 ml/min) at 650 ^oC for 4 h. Mixtures of ThF_4 and LiF 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 temperature dependence of EXAFS structure functions of certain sample is shown in Fig. 1. Unfortunately, this sample contains few percent of thoria identified by powder X-ray diffraction analysis. With increasing temperature, the intensity of the 1st neighbour contribution which is mainly attributed to Th – F correlation has been reduced. This fact is typical behaviour of temperature effect caused by an anharmonic oscillation. Over the melting point, the spectra at 600^{o}C and 800^{o}C are similar to each other. It means that the most of the part of sample had been already molten below 600^{o}C. The most striking fact is the spectra of before heating and after cooling down are nearly similar to each other. The small peak at ca. 4 Å is corresponding to multiple scattering caused by thoria, since the spectra of thoria indicates that even larger contribution exists in 2nd coordination than that in 1st coordination. The ratio of the intensity of 1st and 2nd coordination peak is constant before and after heating, therefore, molten fluoride can stably co-exist with thoria. The behaviour of oxide species should be clarified to make realization of the molten salt reactor concept, and this study would provide the first information for the future study.

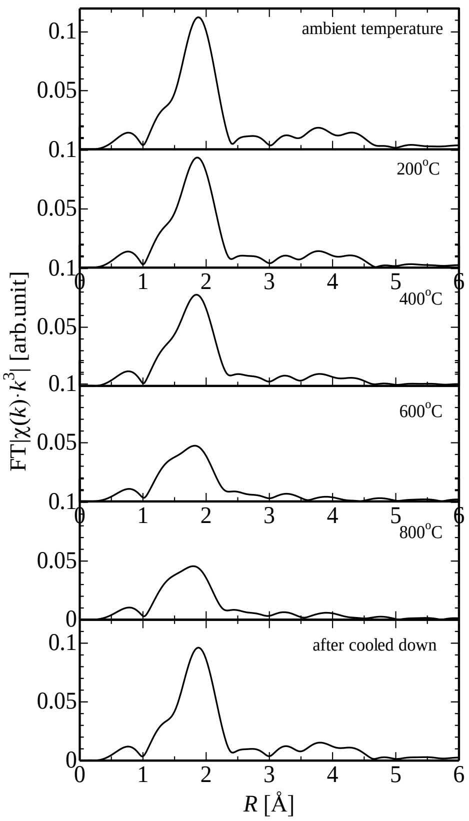

Fig. 1 Structure functions of LiF-ThF_4 (x_{ThF4} = 0.25) at various temperatures.

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