

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

Masahiko NUMAKURA¹, Nobuaki SATO², Catherine BESSADA³, Olivier PAUVERT³,
Didier ZANGHI³, Pierre CHAMELOT⁴, Yasuaki SHIMOHARA¹, Keisuke TAJIMA¹,
Atsushi NEZU¹, Hiroshi AKATSUKA¹, Haruaki MATSUURA*^{1,3}

¹Res. Lab. for Nucl. Reactors, Tokyo Tech., Ookayama, Meguro-ku, Tokyo, 152-8550, Japan

²Inst. of Multidisc. Res. for Adv. Mater., Tohoku Univ., Katahira, Aoba-ku, Sendai, 980-8577, Japan

³CEMHTI, CNRS, 1D avenue de la recherche scientifique, 45071 Orléans cedex 2, France

⁴LGC, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex 4, 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-CaF₂) 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 clarify the correlation between structures of molten An (Ln)F_n and their physico-chemical properties, it would be useful to find better electrolysis conditions to improve the efficiency of the pyrochemical reprocessing. However, structural information of the ternary $x\text{ThF}_4-a\text{LiF}-b\text{CaF}_2$ mixtures has not been reported yet. In this study, molten 0.25ThF₄-0.75LiF, 0.25ThF₄-58LiF-0.17CaF₂ and 0.25ThF₄-0.45LiF-0.30CaF₂ are specially focused for the structural investigation.

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. ThF₄ was synthesized by ThO₂ under fluorine gas (40 ml/min) at 650 °C for 4 h. Mixtures made by ThF₄, LiF (Soekawa Co. 4N) and CaF₂ (Soekawa Co. 4N) 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 (BN, Showa Denko Co. ltd), and pressed into pellets in 7 mm diameter and 1 mm thickness. The mixing weight ratio of ThF₄ to BN was ca. 1: 2.5. To prevent chemical reaction of sample and contamination of ThF₄ to outside during heating process in XAFS measurements, these pellets were installed in a double barrier cell. 1st barrier is made with pyrolitic boron nitride and 2nd barrier is made with boron nitride (HIP). The electric furnace was filled with He gas at ca. 30 kPa.

Results and discussion

In the solid state of 0.25ThF₄-0.75LiF, the coordination number of thorium (N_i) and inter ionic distance between thorium and fluorine first neighbour (r_i) were 9 and 2.35Å, respectively. These structural parameters correspond to the structure of Li₃ThF₇ reported in the literature. N_i 's

and r_i 's in all solid states were almost constant among the mixtures investigated. Radial structure functions of molten 0.25ThF₄- a LiF- b CaF₂ are shown in Fig. 1. In the molten states, N_i 's decreased from 9 to ca. 7.5 and r_i 's also decreased from 2.35 to ca. 2.30Å, thus the similar local structure around thorium was preserved. On the other hand, in the case of 0.20TbF₃- a LiF- b CaF₂ mixtures, N_i and r_i tend to be varied with depending on concentration of CaF₂. It is conjectured that this fact relates to the amount of F⁻ supplied by solvent melts. In the molten TbF₃- a LiF- b CaF₂, structural variation appears at $b > 0.32$ and N_i is slightly larger than 6 (Tb³⁺:F=1:8.6). While in the case of 0.25ThF₄-0.45LiF-0.30CaF₂, the ratio of Th⁴⁺: F⁻ is 1:8.2. Compared to the TbF₃ mixtures, larger amount of F⁻ is required for the modification of the local structure in the ThF₄ mixtures. Therefore the local structure of Th⁴⁺ would not be varied considerably by the addition of CaF₂.

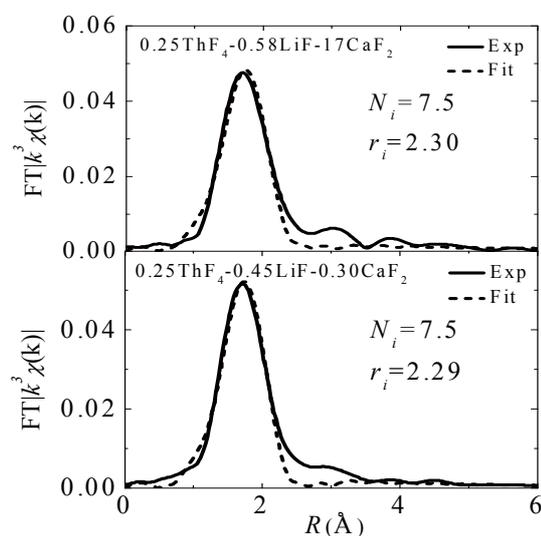


Fig 1 radial structure functions of experiment and curve fitting of the 0.25ThF₄- a LiF- b CaF₂ mixtures at molten states

*hmatuur@nr.titech.ac.jp