Chemistry

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

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Introduction

Solid rare earth metal fluorides (LnF_x) are known to be useful materials in industrial applications (e.g. solid electrolytes and optical lens). Moreover, the development of pyrochemical reprocessing of spent nuclear fuels in molten fluorides or the molten salt nuclear reactor in nuclear engineering requires a better knowledge of their structural and physico-chemical properties at high temperature. In a recent study, it has been reported that the LiF-CaF_2 eutectic melt can be used as solvent for the electrodeposition of Nd and Th, while LiF-NaF and LiF-KF eutectic melts cannot be used for the same purpose theoretically. However, the structure of LnF_x and actinide fluorides (AnF_x) in LiF-CaF_2 eutectic melt has not been clarified yet. In this study, 0.20TbF_3-0.80LiF, 0.20TbF_3-0.62LiF-0.18CaF_2, 0.20TbF_3-0.48LiF-0.32CaF_2, 0.50TbF_3-0.50LiF, and 0.50TbF_3-0.38LiF-0.12CaF_2 mixtures are specially focused for the structural investigation.

Experimental

XAFS measurements in transmission mode were performed. Tb L_{III}-edge (7.519 keV) XAFS spectra were collected with a fixed time scan method by using Si (111) double crystal monochromator. Mixtures of TbF_3, LiF and CaF_2 in various compositions were melted once in a glassy carbon crucible at 1123 K in a glove box filled with an argon atmosphere in high purity. Then, they were mixed with boron nitride powder (BN), and pressed into pellets in 0.7-1.0 mm diameter and 1 mm thickness. It has been found that if the source of oxidation (e.g. moisture) as impurity exists in an electric furnace, TbF_3 reacts with BN to be $TbBO_3$ at ca. 1073 K. Therefore, to prevent chemical reaction during heating process in XAFS measurements, these pellets were installed in a cell made with pyrolytic boron nitride and the electric furnace was filled with He gas. 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.

Results and discussion

The experimental data on molten 0.20TbF_3-aLiF-$b$$CaF_2$, mixtures are shown in Fig. 1. In molten 0.20TbF_3-0.62LiF-0.18CaF_2 mixture, coordination number of terbium (N_i) and inter ionic distance between terbium and fluorine first neighbour (r_i) were quite similar to those in 0.20TbF_3-0.80LiF mixture, thus the similar octahedral configuration was formed. On the other hand, in ternary 0.20TbF_3-0.48LiF-0.32CaF_2 mixtures, N_i decreased from 8 to 6.8 and r_i did not change on melting. In addition, the Debye-Waller factor was relatively larger than those of the rest of the mixtures investigated. Therefore, the local structure around Tb^{3+} tends to be varied with depending on concentration of CaF_2. It is conjectured that the difference among structural variation in molten phase relates to the amount of F^- supplied by solvent melts. In 0.20TbF_3-0.48LiF-0.32CaF_2 mixture, the largest amount of F^- is supplied by the solvent melts among all mixtures investigated, i.e. Tb^{3+}: F^-=1.8.6. Thus N_i would indicate slightly larger than 6. In ternary 0.50TbF_3-aLiF-$b$$CaF_2$ mixtures, the effect of CaF_2 would appear more strongly. Since only 4 times amount of F^- can exist around a Tb^{3+} in 0.50TbF_3-0.50LiF mixture, the octahedral configurations should be connected by the edge or corner sharing. Some part of networking structure would be broken by addition of even small amount of CaF_2 ($b$$CaF_2$=0.12), and local structure around Tb^{3+} would be distorted from octahedral configuration.

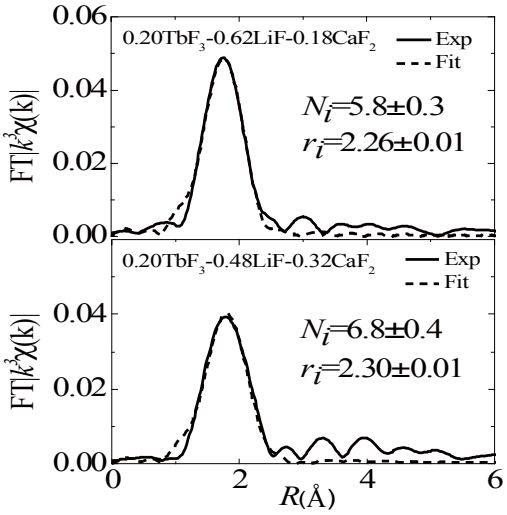

Fig. 1 radial structure functions of experiment and curve fitting of the 0.20TbF_3–aLiF–$b$$CaF_2$ mixtures at molten states

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