Chemistry

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EXAFS on molten terbium fluoride in mono- and divalent fluoride mixtures

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Introduction

Solid rare earth fluorides (LnF_x) are known to be useful materials in various industrial applications (e.g. solid electrolytes and optical lens). Moreover, the development of pyrochemical reprocessing of spent nuclear fuels using 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. Especially, terbium has been recently used for application to one of the essential additives for neodymium magnet of hybrid vehicles, but the price of terbium increased rapidly mainly because of the control of export amount. Thus the development of recycle technology of rare earths becomes more important nowadays. In this study, TbF_3-LiF-CaF_2 and TbF_3-LiF-MgF_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, CaF_2, and MgF_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 BF_2 (B = Ca, Mg) concentration dependence of local structural parameters derived from EXAFS of the constant concentration of $x_{TbF3} = 0.20$ are shown in Fig. 1. Although inter-ionic distance is 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 Tb^{3+} than CaF_2 does. The similar tendency is also confirmed at the ThF_4 – 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 Tb^{3+}. Therefore, Mg^{2+} makes un-stabilised local structure around Tb^{3+}.

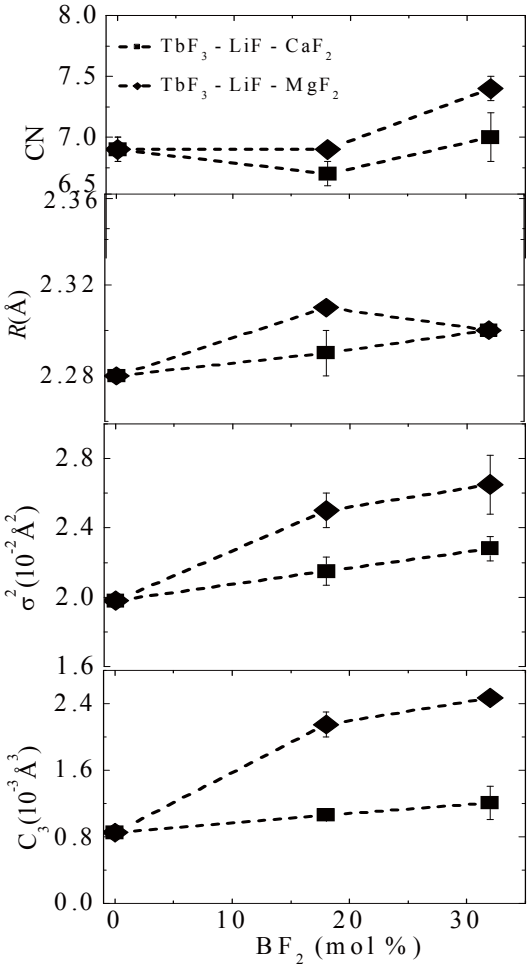

Fig. 1 Structural paramenters obtained by EXAFS of molten 0.20TbF_3 – (0.80-x)LiF - x CaF_2 or MgF_2 mixtures (0<x<1), from the top, coordination number, inter-ionic distance, Debye-Waller factor and C_3 cumulant.

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