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Local structural analysis on terbium fluoride at high temperature

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Introduction

Various crystallographic phases exist in the rare earth fluorides depending upon compounds and temperatures. For example, LaF_3-NdF_3 take trigonal structures at room temperature (RT) and transit to superionic conduction phases at high temperature below their melting points, while ErF_3-LuF_3 take orthorhombic structures at RT and transit to trigonal structures at high temperature below their melting points. TbF_3 has somehow the boundary feature of phase transition at high temperature below its melting point. There is a possibility of existence of superionic conduction phase at high temperature, but it has not been clarified yet.

Furthermore, it is considered that there is strong relationship between local structure and physico-chemical properties of molten salts in general. Therefore, to clarify the local structure of the molten salt would contribute to the application of molten salts in nuclear engineering field. Especially, terbium has the characteristics of multi-valence, i.e. trivalent (TbF_3) and tetravalent (TbF_4), which would have some similarity to the case of actinide chemistry. Thus, the information of the local structure and behavior of terbium fluoride would be useful too for development of a molten salt reactor using thorium fluoride as one of the fuel elements.

Experimental

XAFS measurements in transmission modes have been performed at BL27B beamline in Photon Factory. The XAFS spectra using Tb L_{III}-edge have been collected with a fixed time scan method by the X-ray monochromated by double Si (111) crystals. The samples of TbF_3 were mixed with boron nitride (BN) matrix powder, and pressed into pellets in 13 mm diameter and 1 mm thickness. The mixing weight ratio of TbF_3 to BN was ca. 1: 4.5. These pellets were prepared in a glove box filled with an Ar atmosphere in high purity. The temperatures of the samples in XAFS measurements have been calculated by the calibration curve, which had been obtained by the difference between the values of thermocouples at the sample and the sample holder.

Results and discussion

By XAFS measurements of TbF_3 during elevating temperature process, a phase variation to high *k* direction was observed between 785°C and 800°C. It would correspond to the structural change occurred. However, it's unlikely feature of the phase transition and/or melting of TbF_3 at this temperature range according to the literatures. To examine the structural change around this temperature range in detail, XAFS measurements of TbF_3 after heating treatment at varied maximum temperatures were performed, which are shown in Fig. 1. The structural change was not observed until the sample heated upto 600 °C, however, the drastic structural change was identified at the sample upto 800°C. This result indicates that some irreversible reactions would occur at ca. 800°C.

To characterize the sample after heating, the sample of TbF_3 used for XAFS measurement was analyzed by XRD, SEM and EDX. We found that $TbBO_3$ was included in some of the samples as a result. Although, the sample environment was He gas throughout the XAFS measurement, terbium fluoride would react with oxygen and even BN. Thus, to clarify the structure of molten pure TbF_3, we are now going to modify all the procedure of the preparation to prevent from oxidation of the sample.

This research has been done in a collaboration study between JAEA (Dr. Y. Okamoto) and Tokyo Tech.

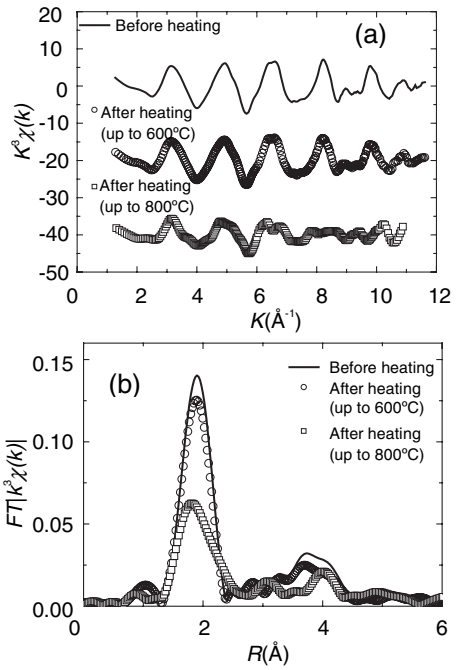

Fig. 1 EXAFS oscillation (a) and radial structure function (b) of TbF_3 at room temperature before and after heating upto 600°C or 800°C.

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