

Local structure of cerium in fluoride or oxyfluoride at high temperature

Haruaki MATSUURA*¹, Kosuke HIGAKI¹, Takafumi UCHIYAMA¹, Masahide MIYOSHI¹,
Kyoko IZAKI¹, Atsushi NEZU²

¹Dept.Nucl. Safety Eng., Tokyo City University, Tamazutsumi, Setagaya-ku, Tokyo 158-8557, Japan

²Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152-8550, Japan

Introduction

Some of the light rare earth fluorides and oxyfluorides have the feature of superionic conductance at high temperature. To design the functional ceramics with fluorine conductance, the in-situ evaluation of local structure would be important. To obtain supercooling phase at ambient temperature effectively, the composition of the compounds and its ratio with inert matrix material are key parameters. In this report, the local structure of cerium in CeF_3 or CeO_2 , and their mixtures with LiF with boron nitride at various temperatures have been evaluated.

Experimental

Mixtures of LiF, CeF_3 , Li_2O , CeO_2 at various weight ratio were mixed with boron nitride powder, and pressed into pellets. The mixing ratio is fixed to be 1 to 2.5 weight times of BN. To prevent from the chemical reaction during heating process in EXAFS measurements, these pellets were installed in a cell made with pyrolytic boron nitride and the electric furnace was filled with He gas under 30 kPa. EXAFS spectra of Ce L_{III}-edge (5.727keV) were collected with a fixed time scan method by using Si (111) double crystal monochromator in transmission mode. EXAFS data were analysed by using the WinXAS ver.3.1.

Results and discussion

Figure 1 shows the Fourier transformed structure functions of one of the samples at various temperatures. On the contrary to the normal behavior of shorten trend of the 1st neighbor distance between Ce and F or O with increasing temperature due to an unharmonic oscillation effect, this mixture is not in the case. This fact would be affected to the local structure around cerium by the chemical characteristics of dissolution of oxides into molten fluorides. When we focus on the variation trend of the absorption energy edges depending on temperature, CeO_2 containing samples had large edge energy shift before and after heating treatment, which is shown in Fig.2. This fact is due to the variation of valence of cerium, i.e. Ce^{3+} in fluorides, Ce^{4+} in oxides. Since the edge energy of Ce^{4+} is larger than that of Ce^{3+} , initial Ce^{4+} is considered to be transferred to Ce^{3+} after heating treatment. However, in the case of Fig.1, the 1st neighbor structure after heating treatment is not so much different

from CeO_2 . Therefore, this fact implies the most of CeO_2 would be dissolved into LiF and transform to CeOF at molten phase.

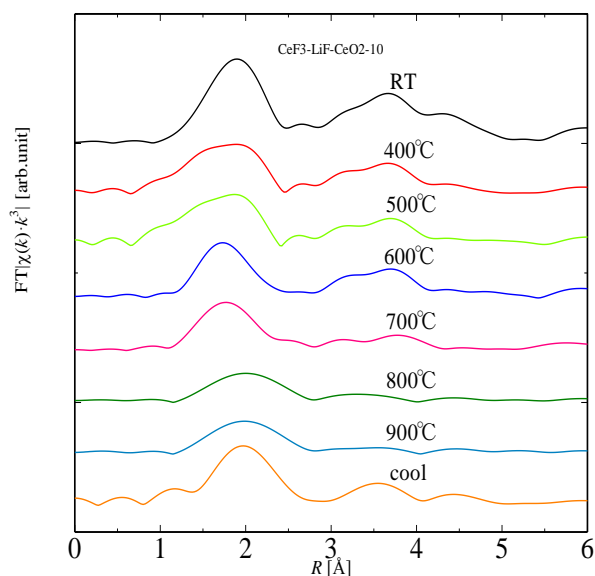


Fig. 1 EXAFS structure functions of 79LiF-11CeF₃-10CeO₂ at various temperatures upto 900 °C.

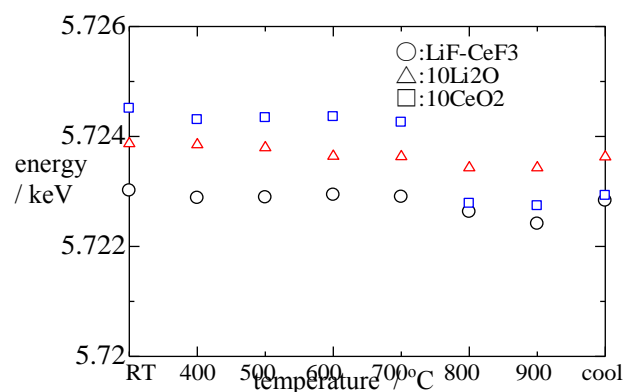


Fig. 2 Absorption energy edges of 9LiF-CeF₃, 8LiF-CeF₃-Li₂O, 10CeO₂ depending on temperatures.

*hmatuura@tcu.ac.jp