

XAFS analysis on molten rare earth fluorides

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Introduction

We have proposed molten alkali metal fluorides as melt baths for the pyrochemical reprocessing of nuclear fuels, and investigated the structural characteristics of some molten fluorides [1]. In order to develop the pyrochemical process using molten fluoride baths, structural information of these molten salts must first be elucidated systematically. In this study, we chose orthorhombic LnF₃ (Ln = Gd, Dy, Ho, Er, Yb, Lu) salts, and investigated the local structures in liquid states by XAFS.

Experimental

The known amounts of rare earth fluorides, LnF₃, were homogeneously dispersed in dried boron nitride powder, and pressed into pellets. For each measurement, a pellet was installed in an electric furnace located between the ionization chambers, and the sample was heated from 300 to 1473 K, except Gd and Yb to 1523 K. During 144 hours of beamtime, transmitted XAFS spectra have been collected, using Si (111) double crystal monochromator at Ln-L_{III} X-ray absorption edges, with detuning for higher order X-ray rejection.

Results and discussion

The extracted XAFS oscillations $\chi(k) \cdot k^3$ are shown in Fig. 1, where solid lines and circles show solid and liquid states, respectively. For all the spectra, one can notice slight phase shifts in the XAFS oscillation upon heating, which is the typical tendency observed in molten halides. Since any irregular or distinct oscillation can not be observed in these spectra both in the solid and liquid phases, multiple electron excitation effects, which are reported to be observed often at the Ln-L edge and result in ghost peak appearance in $FT|\chi(k) \cdot k^3|$ or drastic decrease of S_0^2 , can be neglected in these molten fluoride cases. Predominant peaks of Fourier transformed radial structure functions at ca. 2.0 Å are attributed to the Ln³⁺-F⁻ correlation. The curve fitting analyses to obtain structural parameters are carried out by using these Ln³⁺-F⁻ correlation peaks. The resulting structural parameters between the Ln³⁺ ion and the nearest-neighbouring F⁻ ions are reported in detail [2]. Coordination numbers of all the investigated LnF₃ molten samples fall in the range 6-7. Various structural investigations of rare earth halides by Raman spectroscopy, XAFS, diffraction measurements, and molecular dynamics simulations conclude that

relatively heavier rare earth (Z > 66) trihalides, which take AlCl₃- (chlorides) or FeCl₃- (bromides) like structure in the solid state, form 6-coordinated octahedra in melts, while LnX₃ (Ln = La, Ce, Nd, X = Cl, Br) which take UCl₃-like structure in the solid state are suggested to be in somewhat higher coordination than 6 in the liquid phase. Similar to the suggestions on chloride and bromide melts, structures of molten fluorides are also expected to vary depending on their crystal structures. However, structural differences between the three groups (Gd, Dy + Ho and Er + Yb + Lu) could not be unambiguously confirmed by the present XAFS measurements, although coordination numbers of the group (Er, Yb, and Lu) show slightly higher values than the other systems. This implies that some higher coordinated units other than 6-coordinated octahedra can also exist in these three melts belonging to the third group.

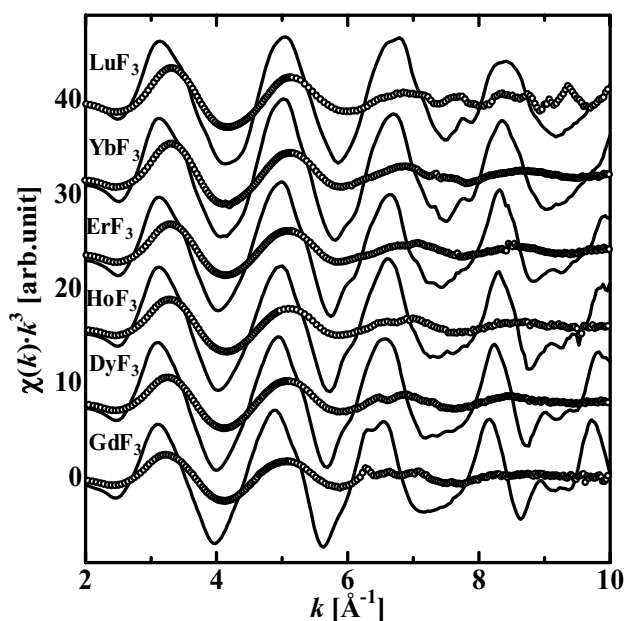


Fig. 1 EXAFS oscillations of LnF₃.

References

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