

XAFS analysis on molten rare earth alkali metal fluoride systems

Haruaki MATSUURA*¹, Sou WATANABE¹, Takeshi SAKAMOTO¹, Koichi NAOI¹, Toshiaki KANUMA¹, Masahiko HATCHO¹, Naohisa KITAMURA¹, Hiroshi AKATSUKA¹, Yoshihiro OKAMOTO², Kuniyuki SUZUKI³, Yasuhiko IWADATE³

¹Res. Lab. for Nucl. Reactors, Tokyo Tech., Ookayama, Meguro-ku, Tokyo, 152-8550, Japan

²Dept. of Material Science, JAERI, Tokai-mura, Naka-gun, Ibaraki, 319-1195, Japan

³Graduate Sch. of Sci. and Technol., Chiba Univ., Inage-ku, Chiba, 263-8522, Japan

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 by using molten fluoride baths, structural information of these molten salts must first be elucidated systematically. In this study, the local structures of molten lanthanide-alkali metal fluoride systems (0.2 LnF₃-0.8 MF; Ln = La, Ce, Nd, Sm; M = Li, Na, K) around lanthanide ions have been investigated at the room temperature and at a higher temperature above their melting points by XAFS.

Experimental

Both, the rare earth fluorides, LnF₃, and the alkali metal fluorides, MF (*x*LnF₃ = 0.2), were melted in a glassy carbon crucible at 1173 K, and known amounts of these salts 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 1173 K. During 192 hours of beamtime, transmitted XAFS spectra have been collected, using Si (111) double crystal monochromator at Ln-L_{III} X-ray absorption edges, with mirrors for higher order X-ray rejection.

Results and discussion

EXAFS oscillations, $\chi(k) \cdot k^3$, obtained from the Nd and Sm L_{III} X-ray absorption spectra are shown in Fig. 1. The curve-fitting analysis was carried out on a predominant peak of the radial structure factors at ca. $R = 2 \text{ \AA}$, which is considered to be the Ln³⁺-F⁻ nearest-neighbour distance. The resulting structural parameters between the Ln³⁺ ion and the nearest-neighbouring F⁻ ions are reported in detail [2]. R_{LnF} and N_{LnF} at 300 K were evaluated as average values of the 1st coordination shell around Ln³⁺ ion. A comparison of these values with both the evaluated, N_{LnF} and R_{LnF} , values at 300 K shows that the current values are slightly underestimated by a few percent. This underestimation may be caused by the fact that the EXAFS signal is not sensitive to farther atoms when the atomic geometry around the X-ray absorption atom is asymmetric. Both, the inter-ionic distance, R_{LnF} , and the coordination number, N_{LnF} , of the molten salts do not change drastically on varying the alkali metal, and these

values seem to depend mainly on the lanthanide ion species; NdF₃ system: $R_{\text{NdF}} = 2.39\text{-}2.40 \text{ \AA}$, $N_{\text{NdF}} = 6.7\text{-}6.9$, SmF₃ system: $R_{\text{SmF}} = 2.35 \text{ \AA}$, $N_{\text{SmF}} = 3.9\text{-}4.6$, i.e., NdF₃ systems are 6-coordinated, and SmF₃ system is 4-coordinated. Thus, it is reasonable to suggest that the main factor that dominates the local structure around a given Ln³⁺ ion is the Ln³⁺-F⁻ interaction due to its strong coulombic attraction. Also, the structural difference observed between the SmF₃ and NdF₃ arises from the difference in the Ln³⁺-F⁻ interactions resulting from the structural differences in the LnF₃ crystals at the room temperature (NdF₃: tysonite, SmF₃: orthorhombic). In spite of difficulties in analysis of LaF₃ and CeF₃ systems due to short gap between L_{III}-L_{II} absorption energies, we have also obtained valuable spectra for elucidating mechanism of multi-electron excitation by comparison with Ln K XAFS spectra in SPring-8.

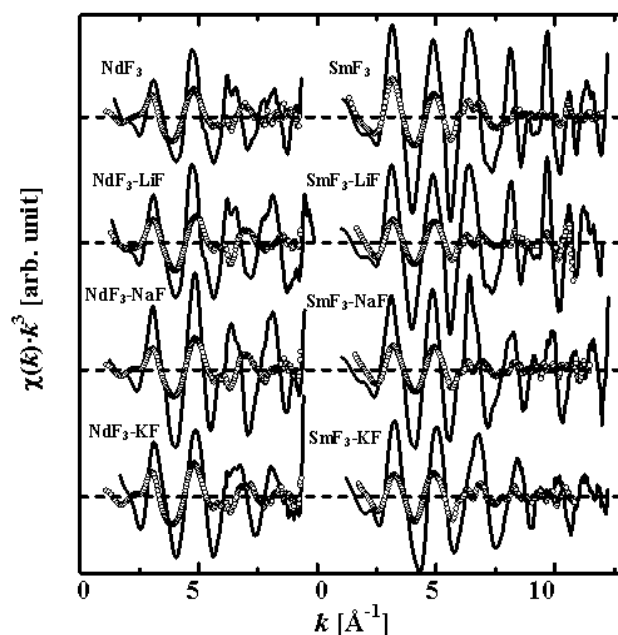


Fig. 1 EXAFS oscillations of NdF₃ and SmF₃ systems.

References

- [1] e.g. S. Watanabe et al., Physica Scripta, T115, 297 (2005).
- [2] S. Watanabe et al, J. Alloys Compd, in press (2005).

* hmatsuur@nr.titech.ac.jp