XAFS analysis on molten rare earth alkali metal fluoride systems

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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 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 (xLnF3 = 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-LⅢ X-ray absorption edges, with mirrors for higher order X-ray rejection.

Results and discussion
EXAFS oscillations, \( \chi(k)k^2 \), obtained from the Nd and Sm Lm 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. \( R = 2 \) Å, which is considered to be the Ln- F nearest-neighbour distance. The resulting structural parameters between the Ln ion and the nearest-neighbouring F ions are reported in detail [2]. \( R_{\text{at}} \) and \( N_{\text{at}} \) at 300 K were evaluated as average values of the 1st coordination shell around Ln ion. A comparison of these values with both the evaluated, \( N_{\text{at}} \), and \( R_{\text{at}} \), 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, \( R_{\text{at}} \), and the coordination number, \( N_{\text{at}} \), 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: \( R_{\text{at}} = 2.39-2.40 \) Å, \( N_{\text{at}} = 6.7-6.9 \), SmF3 system: \( R_{\text{at}} = 2.35 \) Å, \( N_{\text{at}} = 3.9-4.6 \), 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 Ln ion is the Ln-F interaction due to its strong coulombic attraction. Also, the structural difference observed between the SmF3 and NdF3 arises from the difference in the Ln-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 LⅢ-LⅡ 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.

References

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