XAFS analysis on molten multivalent metal fluorides

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Introduction
The available structural data of molten multivalent metal chlorides along with other relevant information on thermodynamic, electrochemical, physico-chemical properties, etc. can be used for nuclear engineering applications based on pyrochemistry. We have already successfully evaluated the structures of some molten pure multivalent metal fluorides using X-ray absorption fine structure (XAFS) technique [1], [2]. Following the similar strategy, local structures of molten multivalent fluorides in alkali metal fluorides are also expected to be revealed by this technique. In this report, we have summarized the variation in local structures of molten divalent metal fluorides MIIIF2 (MII = Sr, Ba, Pb), trivalent metal fluorides MIIIF3 (MIII = Gd, Dy, Ho, Er, Y, Lu, Yb) and their mixtures with alkali metal fluorides MIF (MI = Li, Na, K; MII = Sr, Pb; MIII = La, Ce, Nd, Sm, Gd, Dy, Ho, Er, Yb, Lu, Y; the molar ratio MIIF2 or MIIIF3:MIF being 20:80 mole %) around the multivalent metal ions.

Experimental
Mixtures of chemicals were pre-melted in glassy carbon crucibles inside a glove box. These reagents were then mixed with boron nitride matrix powder homogeneously, and pressed into pellets. A pellet was installed in an electric furnace located between ionization chambers. Transmitted XAFS spectra have been collected, using Si (111) double crystal monochromator at Ln-LIII X-ray absorption edges.

Results and discussion
The inter-ionic distances and coordination numbers around MII2+ or MIII3+ ions in pure melts and their mixtures with alkali metal fluorides are plotted versus the elements in Figs. 1 (a) and (b), respectively [3]. Figure 1 (a) indicates perfectly the “lanthanide contraction”. The nearest-neighbour MII2+-F or MIII3+-F distances have values almost similar to the sum of the ionic radii, σMII + σF, for 4-coordinated structures, σMIII + σF, for 6-coordinated structures, σMIII + σF. Nevertheless, the trends in the coordination numbers of all the investigated systems seem to be much complicated, especially for the lanthanide fluorides and their mixtures (Fig. 1(b)). Although only heavier rare-earth fluorides’ data for pure melts are available, local minima in the coordination numbers occur throughout the pure rare-earth fluoride series. These changes seem to be correlated to the variation in crystal structures at high temperatures. In the mixtures with alkali metal fluorides, coordination numbers decrease in mixtures than those in pure melts. Another observation that can be clearly made is that with decreasing ionic radius, the coordination number decreases with the exception of some elements. The dependencies on the type of alkali metal cannot be observed clearly in the case of mixtures with MIF. Thus, in the investigated concentration region (0.2 MIF + 0.8 MIIIF), the local environment around lanthanide ion is determined mainly by their own characteristics, i.e., the strong coulombic interactions between MIII3+ and F, providing an ideal test case to perform MD simulations.

References

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