

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 $M_{II}F_2$ ($M_{II} = \text{Sr, Ba, Pb}$), trivalent metal fluorides $M_{III}F_3$ ($M_{III} = \text{Gd, Dy, Ho, Er, Yb, Lu, Y}$) and their mixtures with alkali metal fluorides $M_I F$ ($M_I = \text{Li, Na, K}$; $M_{II} = \text{Sr, Pb}$; $M_{III} = \text{La, Ce, Nd, Sm, Gd, Dy, Ho, Er, Yb, Lu, Y}$; the molar ratio $M_{II}F_2$ or $M_{III}F_3:M_I F$ 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- L_{III} X-ray absorption edges.

Results and discussion

The inter-ionic distances and coordination numbers around M_{II}^{2+} or M_{III}^{3+} 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 $M_{II}^{2+}-F^-$ and $M_{III}^{3+}-F^-$ distances have values almost similar to the sum of the ionic radii, M_{II}^{2+} for 4-coordinated structures, $\sigma_{M_{III}} + \sigma_F$, and M_{III}^{3+} for 6-coordinated structures, $\sigma_{M_{III}} + \sigma_F$. 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 $M_I F$. Thus, in the investigated concentration region (0.2 $M_I F$ + 0.8 $M_{III} F$), the local environment around lanthanide ion is determined mainly by their own characteristics, *i.e.*, the strong coulombic interactions between M_{III}^{3+} and F^- , providing an ideal test case to perform MD simulations.

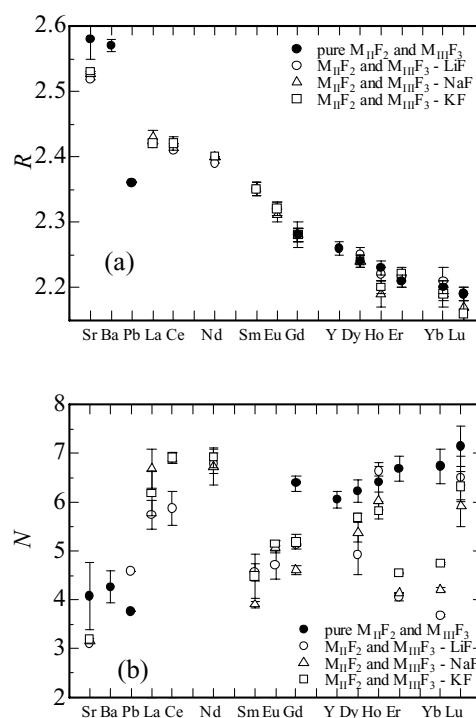


Fig. 1(a), (b) Interionic distances and coordination numbers of 1st coordination shell in various molten fluoride melts.

References

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