Chemistry

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XAFS analysis on molten lithium - zirconium fluorides

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Introduction

Molten fluorides have still fascinating features to be applied to pyro-metallurgical processing as well as molten salt reactors, however, the material limitation for resisting long period is the most crucial disadvantage. Generally, molten fluorides can dissolve easily certain amount of oxide, which causes several problems under operation of processes, thus it is very essential to control the oxide contents in the melt. Recently, we have started a joint collaboration research project focused on the local structure around zirconium ions in fluorides, which is one of candidates for melt baths. We are planning to elucidate the variation of the local structures of these melts by multi-spectroscopic techniques, e.g. NMR and EXAFS, complementary. EXAFS spectra of LiF-ZrF_4 systems (x_{ZrF4}=0.15, 0.25, 0.30) at various temperatures have been collected.

Experimental

Various ratios of chemicals were mixed with boron nitride matrix powder homogeneously, pressed into pellets, and inserted inbetween the specially designed boron nitride holders [1] under argon circulated glove box. A sample was installed in an electric furnace located between ionization chambers. Transmitted XAFS spectra have been collected, using Si (111) double crystals monochromator at Zr-K X-ray absorption edge.

Results and discussion

EXAFS oscillations of ZrF_4-LiF (x_{ZrF4}=0.3) at various temperatures equilibrated are shown in Fig. 1. From this figure, even less than 550°C, drastic local structural transformation occurs already, which would be corresponding to the evolution of crystallographic phases of Li_2ZrF_6 and Li_3ZrF_7 compounds. Over this temperature, it seems almost nothing happens from the point of view from Zr local environment even in liquid phase. It means the local structure of solid state is kept in molten phase. This feature is much clarified in Fig. 2, which is depicted Fourier transformed structure functions of the spectra of different composition at highest temperatures. Even the temperatures are different, these functions are very close to each other, that shows the local structures at high temperature are independent from Zr concentration in the range of compositions measured.

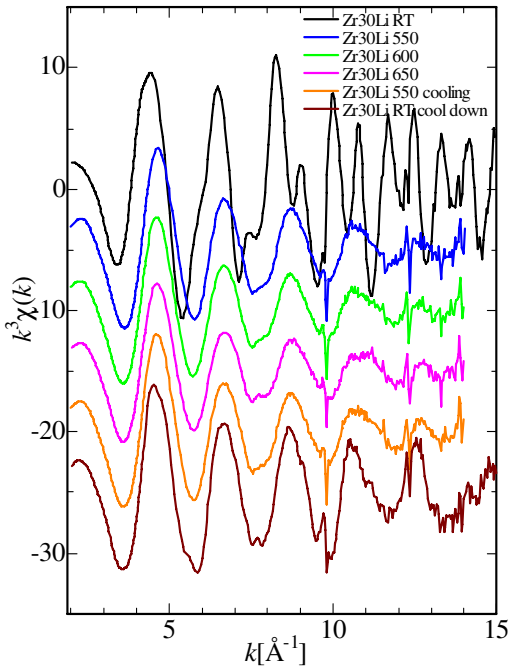

Fig. 1 EXAFS oscillations of ZrF_4-LiF (x_{ZrF4}=0.3) at high temperature

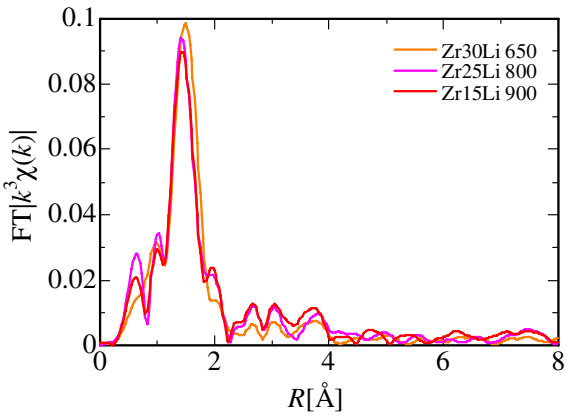

Fig. 2 Structure functions of various ZrF_4 contents at highest temperatures.

References

[1] A. –L. Rollet et al., NIMB, 226, 447 (2004).

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