Chemistry

NW10A/2006G319

XAFS analysis on molten lithium - lanthanum fluorides containing lithium oxides

Haruaki MATSUURA*[1], Hiroki ICHII[1], Jun MIZUOCHI[1],
Catherine BESSADA[2], Anne-Laure ROLLET[2], Didier ZANGHI[2]
[1]Res. Lab. for Nucl. Reactors, Tokyo Tech., Ookayama, Meguro-ku, Tokyo, 152-8550, Japan
[2]CRMHT, CNRS, 1D, Avenue de la Recherche Scientifique, 45071 Orléans cedex 2, France

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]. Very recently, we have launched the joint project of studying on oxide dissolution behaviour in molten fluorides by using multispectroscopic techniques, NMR and EXAFS. The EXAFS spectra of LiF-LaF_3-Li_2O system (x_{LaF3}=0.2, x_{Li2O}=0, 0.15, 0.25, 0.32) at various temperatures have been measured to investigate oxide additional effect on LiF-LiF_3 mixture.

Experimental

Variety ratios of chemicals were mixed with boron nitride matrix powder homogeneously, pressed into pellets, and inserted inbetween the boron nitride holders hermetically sealed under argon circulated glove box. A sample was installed in an electric furnace located between ionization chambers. During 48 hours beamtime, transmitted XAFS spectra have been collected, using Si (311) single crystal monochromator at La-K X-ray absorption edge.

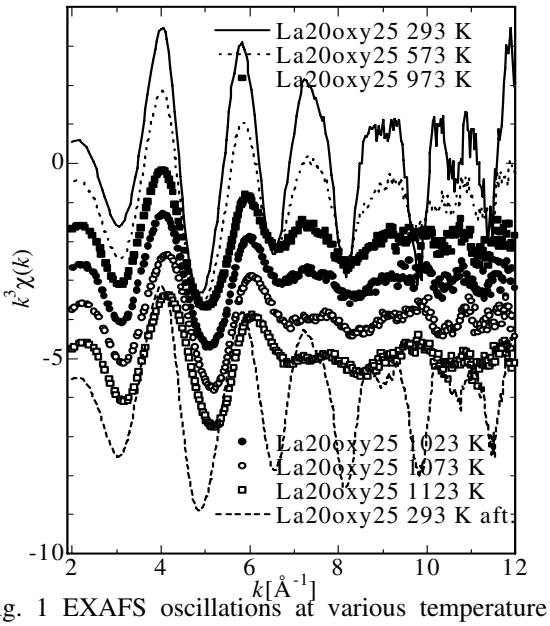

Fig. 1 EXAFS oscillations at various temperature equilibrated.

Results and discussion

Using NW10A, we have obtained EXAFS spectra of La-K edge in high resolution, which is well comparable to the data collected at SPring-8. EXAFS oscillations of LiF-LaF_3-Li_2O (x_{LaF3}=0.2, x_{Li2O}=0.25) at various equilibrated temperatures are shown in Fig. 1. Clear phase shift occurs between 1023 K and 1073 K, which is good indication of the sample to be in molten state. However, this temperature is slightly higher than those observed at the EXAFS of lower contents of Li_2O, thus oxide may affect on melting behaviour of LiF-LaF_3 mixture. EXAFS oscillations of all samples after cooled down are shown in Fig. 2. We found some 'threshold' composition of oxide amount, i.e., 15-25mol% of Li_2O for LiF-LaF_3 (x_{LaF3}=0.2). However, this discrepancy is very small, otherwise these phases are nearly the same each other, more strikingly, gone back to initial spectra unheated. Local environment around lanthanum doesn't change after cooled down, that is, lanthanum is surrounded by fluorides as like in LaF_3. By NMR experiments, we found both lanthanum and fluoride local environments are modified even in the less amount of addition of Li_2O which we have done in EXAFS experiments, thus, we are planning to measure other compositions of this system to fill the discussion gaps.

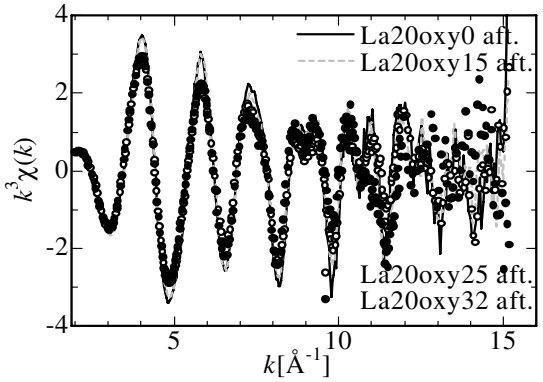

Fig. 2 EXAFS oscillations of various oxide contents after colled down.

References

[1] S. Watanabe et al., J. Phys. Chem. Solids, 66, 402 (2005).
[2] S. Watanabe et al, Electrochemistry, 73, 612 (2005).
* hmatsuur@nr.titech.ac.jp