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EXAFS analysis on molten lithium fluoride-lead fluoride mixture

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Introduction

Molten LiF-PbF_2 has been proposed as a candidate material for fusion reactor blanket using D-T reaction, and its various physico-chemical properties have been reported in literature [1]. However microscopic structural information of molten LiF-PbF_2 will be necessary for practical utilization. Another interest exists in the physico-chemical properties of pure PbF_2. It is well known that PbF_2 undergo phase transition from orthorhombic (α) to cubic (β) at 589 K, and phase transition of superionic conductance at 711K below its melting point (1128 K) [2]. However, the mechanism of these phase transitions is still unexplained precisely. To obtain the short-range structural parameters of molten LiF-PbF_2, we have carried out XAFS measurements both of PbF_2 and LiF-PbF_2 mixture over a wide temperature range from room temperature to above its melting point.

Experimental

The eutectic mixture of lithium and lead fluorides (x_{PbF2}=0.6) were prepared with a glassy carbon crucible in dried argon atmosphere. The chemicals were grinded into a few micrometer particles, mixed with boron nitride powder (10 w/o of matrix powder) and pressed into pellets. The electric furnace available at PF was used. During 84 hours, transmitted XAFS spectra of PbF_2 and LiF-PbF_2 were collected, using Si (311) channel cut monochromator at Pb-LIII X-ray absorption edge (13.04keV).

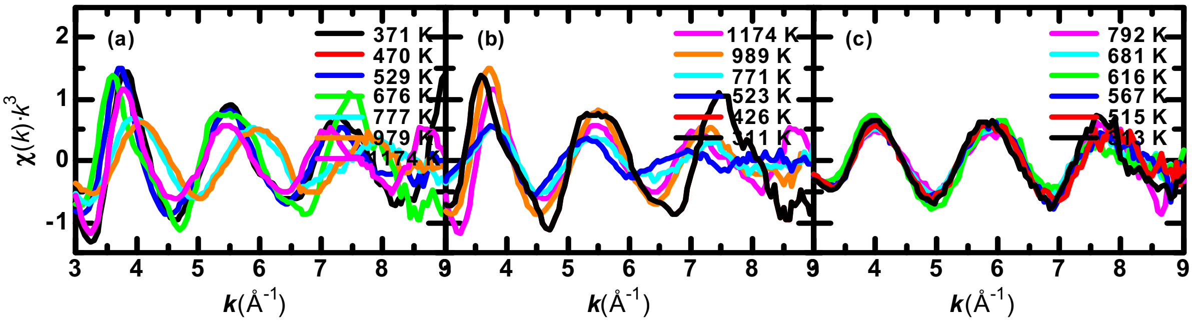

Fig. 1(a, b and c) EXAFS spectra of PbF_2 depending on heating/cooling process.

Results and discussion

Extracted χ(*k*) EXAFS spectra of pure PbF_2 at various temperatures until 1173 K are shown in Fig. 1(a: heating until molten state), (b: cooling from molten state) and (c: cooling without melting), respectively. The distinct phase shifts occur between 680 K and 780 K in the EXAFS spectra during both of the heating and cooling processes when once samples are molten, and these changes correspond to a transition to the super ionic phase. However, as shown in Fig. 1(c), unless the samples are melted, phase shift doesn't occur during cooling process. These facts indicate super ionic phase transition is irreversible change as confirmed by conductance measurements [2]. Pb^{2+}-F^- distance (r_{Pb-F}) is obtained by the curve fitting of the first peak of FT|$k^3\chi(k)$| in *R*-space, including the 3rd and 4th cumulants, and with the number of fluoride ions around a lead ion (N_{Pb-F}) as 4, 6 and 8. In the super ionic phase of PbF_2, the most reasonable N_{Pb-F} is the same as that in its β-phase (N_F=8, r_{Pb-F}=2.49 Å), however the r_{Pb-F} decreases by ca. 0.1 Å during the superionic transition. Above the superionic transition temperature, both N_{Pb-F} and r_{Pb-F} decrease with increasing temperature, and in the liquid phase they become 4 and 2.26 Å, respectively. The structural parameters of LiF-PbF_2 can also be obtained by using the same strategy as that used for PbF_2. The most preferable values for N_{Pb-F} and r_{Pb-F} are thus estimated to be 6 and 2.33 Å, respectively. For a detailed quantitative discussion of the structure of molten lead fluoride systems, further experiments with varying alkali ion concentrations, alkali elements, and with *in-situ* measuring electrochemical properties are planned. This work is financially supported by Grants-in-aid for scientific research from JSPS (Encouragement for young scientists (A) 13740376).

References

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