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XAFS analysis on lead-lithium fluoride at various compositions and temperatures

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Introduction

Molten PbF_2 - LiF is one of candidate materials for a fusion blanket, and we have evaluated various properties so far. We reported a significant change in the EXAFS pattern in solid PbF_2 at high temperature caused by the transition to the superionic phase along with the local structures of liquid phases [1]. The interpretation of the structural change is important not only for designing superionic conductors but also for optimizing the inter-ionic potential between Pb^{2+} and F^-. In this study, we have obtained the new EXAFS results of molten x PbF_2 - (1-x)LiF systems (x_{PbF2}= 0.2, 0.4, 0.6, 0.8, 1.0), and discuss the composition dependence of the local structure around the lead ion.

Experimental

Samples are subdivided into micrometric sized particles and mixed with BN matrix powder homogeneously in the glove box filled with dried Ar gas. These powders were pressed into pellets, and installed into an electric furnace located between two ionization chambers. The electric furnace heated the sample up to 50 K above the melting point at each composition. The sample environment was He gas throughout the EXAFS experiments. During 132 hours of beamtime, transmitted XAFS spectra have been collected, using Si (311) channel-cut monochromator at Pb-L_{III} X-ray absorption edge (13.04keV).

Results and discussion

EXAFS oscillations $\chi(k)\cdot k^3$ of molten xLiF-(1-x)PbF_2 are shown in Fig. 1. The single electron excitation probability S_0^2 is found to be 0.389 by the curve fitting of β-PbF_2 at 573 K. Although S_0^2 = 0.8 - 1.0 is general for EXAFS analysis, this value might be reasonable, because double-electron excitation and triple-electron excitation, which reduce the S_0^2 value, are reported at about 180 eV and 410 eV above the L_{III} threshold energy, respectively. The coordination number and inter-ionic distances of these molten salts show similar values in different mixtures except at the eutectic composition, *i.e.* N_{PbF} = 5.39 and R_{PbF} = 2.39 Å for the eutectic composition but N_{PbF} = 3.76 - 4.58, R_{PbF} = 2.35 - 2.36 Å for others. Although the coordination number and inter-ionic distance are evaluated as the average value of various clusters PbF_n existing in the molten salts, 4-coodinated tetrahedral PbF_4^{2-} geometry seems to be predominant both in molten pure PbF_2 and in LiF-PbF_2 mixtures, except at around the eutectic composition. The 6-coordinated octahedral PbF_6^{4-} geometry seems to be the most stable at the eutectic composition. These results suggest that the addition of Li^+ hardly affects the local structure around Pb^{2+} except at the eutectic composition. This unique structural property at the eutectic composition may be caused by specific characteristics of the molten salt at this composition, although the lower temperature at which the eutectic mixtures is studied might also be considered to be one of the reasons for the observation of a higher coordination number and inter ionic distance.

We have also carried out molecular dynamics simulations on PbF_2 at various temperatures by using a polarizable ion model. The changes observed in the EXAFS signals of solid PbF_2 at α, β, superionic phases are reasonably reproduced but not at molten phase [2]. MD simulation on the LiF-PbF_2 system is going underway. The work was financially supported by JSPS No. 99GC0006.

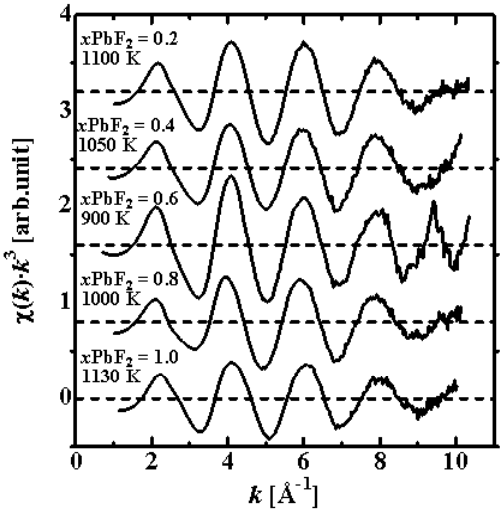

Fig. 1 EXAFS oscillations of molten xLiF-(1-x)PbF_2.

References

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