

XAFS analysis on molten lithium - yttrium fluorides containing lithium oxides

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Introduction

Molten fluorides have still fascinating features to be applied in pyro-metallurgical processing as well as nuclear engineering fields, however, the material limitation for surviving long period is the most crucial disadvantage. Generally, molten fluorides can dissolve 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 research project focused on the dissolution behaviour of oxide into lanthanide fluorides containing melts. We are planning to elucidate the variation of the local structures of these melts by multi-spectroscopic methods, e.g. NMR and EXAFS. EXAFS spectra of LiF-YF₃-Li₂O systems ($x_{\text{LaF}_3}=0.2, 0.5$, $x_{\text{Li}_2\text{O}}=0, 0.02, 0.05, 0.1, 0.18, 0.28, 0.50$) at various temperatures have been collected to investigate oxide additional effect on LiF-YF₃ mixture.

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 Y-K X-ray absorption edge.

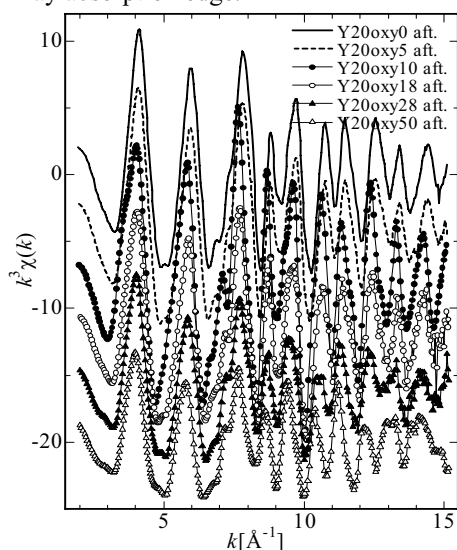


Fig. 1 EXAFS oscillations of various oxide contents after cooled down.

Results and discussion

EXAFS oscillations of LiF-YF₃-Li₂O ($x_{\text{LaF}_3}=0.2$, $x_{\text{Li}_2\text{O}}=0, 0.05, 0.1, 0.18, 0.28, 0.5$) at room temperatures after heating until 1073 K to 1173 K are shown in Fig. 1. These samples were definitely once molten, since we confirmed clear phase shifts between the spectra obtained under elevating temperature very slowly around the melting point. On the contrary to the results of LiF-LaF₃ system, a clear phase shift can be identified between $x_{\text{Li}_2\text{O}}=0.05$ and 0.1, and the variation is larger than that in LiF-LaF₃ system. This feature is much clarified in Fig. 2, which is depicted Fourier transformed structure functions of these spectra. With increasing oxide contents, the first coordination shell (close to ca. 2 \AA), dominantly attributed to Y-F contribution decreases, and 2nd coordination shell relatively increases. We have to evaluate the 'inhomogeneous sample' effect on all the samples after solidified, but the EXAFS oscillation of the largest amount of Li₂O is somewhat close to the one of oxide compounds. Thus we conclude in LiF-YF₃ system, oxides are likely to be dissolved into the melts than that in LiF-LaF₃ system, and oxide ion can coordinate to Y in local environment. NMR experiments will be performed on these samples systematically to understand much profoundly oxide dilution behaviour in the near future.

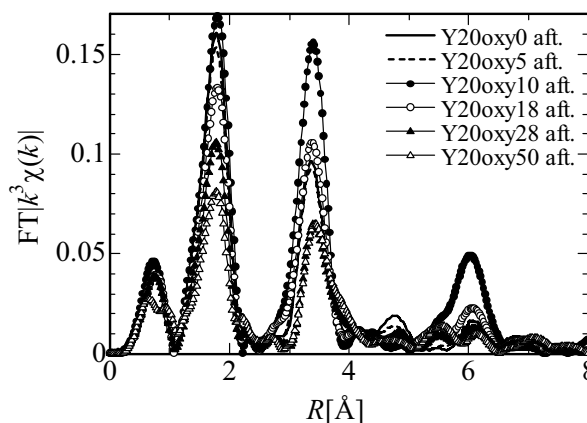


Fig. 2 Structure functions of various oxide contents after cooled down.

References

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

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