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EXAFS on tetravalent uranium cations in molten lithium fluoride

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Introduction

A molten salt reactor concept contains still fascinating idea from the point of view of its self-sustainability constructed by a closed fuel cycle. In order to develop an on-line recycle process of molten salt fuels, one of promising technologies is an electrochemical separation of actinides (An) from lanthanides (Ln). To find the best electrolysis condition to improve the efficiency of the pyrochemical process, systematic investigations of the correlation between structures of molten An (Ln)F_n and their physico-chemical properties, such as electrochemical behavior are useful. In this report, molten UF_4-LiF mixtures are focused as the structural investigation by EXAFS.

Experimental

All UF_4 mixture samples were prepared in France and imported to Japan. To avoid the contamination by oxygen, premixing treatment was abandoned. Mixtures of UF_4 and LiF were weighted then, they were mixed with boron nitride powder, and pressed into pellets in 7 mm diameter and 1 mm thickness. The mixing weight ratio of UF_4 to BN was ca. 1: 2.5. To prevent chemical reaction of sample and contamination of UF_4 by atmosphere during performing high temperature EXAFS measurements, these pellets were installed in a double barrier cell, i.e., the 1st barrier is made with pyrolytic boron nitride and the 2nd barrier is made with boron nitride ceramics. The electric furnace chamber was filled with He gas under ca. 30 kPa. Uranium L_{III}-edge EXAFS spectra have been collected with fixed time scan method by the X-ray from a double Si (111) crystals monochromator in transmission mode. EXAFS data were analysed by using the WinXAS ver.3.1 and 3rd and 4th cumulants were introduced for the curve fitting analyses of EXAFS data at molten phase due to apperance of their large anharmonic effect in some cases.

Results and discussion

By the stepwise-controlled temperature program, the spectra at molten phase were well identified in each sample. The concentration dependence of extracted EXAFS oscillations at molten phase is shown in Fig. 1.

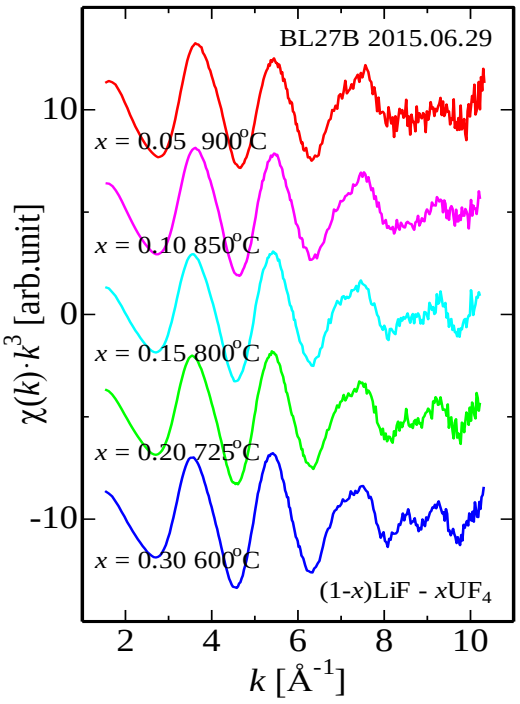

Fig. 1 EXAFS oscillations of LiF-UF_4 (x_{UF4} = 0.05, 0.10, 0.15, 0.20, 0.30) at molten phase.

Temperature of each spectra is varied since its melting temperature is different according to the phase diagram. On the contrary to the case of ThF_4 mixtures, the 1st neighbor contribution which is corresponding to U^{4+} – F^- correlation doesn't seem to be well modified. It is not necessarily to tell that there is no modification of network-like structures depending upon the concentration of UF_4 in LiF. A molecular dynamics simulation using well established inter-ionic potential paramenters would be very helpful to evalute the microscopic structure.

This study has been carried out under collaboration research between French institutes and Japanese universities.

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