

XAFS measurement on molten salts related to pyrochemical treatment of nuclear oxide fuels

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Introduction

During the course of development of pyrochemical reprocessing of oxide nuclear fuels, one of the several critical issues is remained, that is, how to make realization of the uranium-plutonium oxides (MOX) co-electrodeposition process. To find out alternative candidate of melt bath is essential because the current melt bath developed, i.e., 2CsCl-NaCl, contains Cs and un-separable long lived fission products Cs will be build up as fuel treatments repeatedly. Thus we evaluate the local structure around actinides depending upon various melt baths by XAFS to find out the melts containing the uranyl ions closely coordinated to that in molten 2CsCl-NaCl. We have done 'cold tests' using yttrium and lead chlorides and 'hot tests' using uranyl chlorides in various molten alkali chlorides.

Experimental

The UO_2Cl_2 with various melt baths were prepared in a dried argon circulated glove box in Kyoto University Research Reactor Institute. A certain amount of the samples was sealed in a specially designed quartz cell. The electric furnace used was the similar to that originally designed for the laboratory XAFS, but slightly modified to improve thermal homogeneity as well as vacuum tightness. We have carried out the XAFS measurement of hexavalent uranyl chlorides with various alkali chlorides at molten and solid phases, using Si (111) double crystal monochromator at U-L_{III} X-ray absorption edge.

Results and discussion

All quartz cells could successfully confine any samples during performing the experiments at high temperatures. XAFS spectra and radial structure factors of various molten alkali chlorides – UO_2Cl_2 are shown in Fig. 1 and 2, respectively. The spectrum of 2CsCl-NaCl containing melt is obtained by fluorescence mode under the 3 GeV operation, otherwise transmission modes under the 2.5 GeV operations. We note that the quality of the data on 2CsCl-NaCl system is one of the best resolution data and well comparable to the spectra obtained by transmission modes. However the quality of the data on RbCl-NaCl is relatively poor, mainly due to the high X-ray absorption of Rb. In Fig. 2, the peaks at ca 1.3 Å are attributed to the closest U-O contributions, which do not depend on various melts, since $\text{O}=\text{U}=\text{O}^{2-}$ ions are rigid. However, the peaks at between 2 and 2.5 Å are

corresponding to U – Cl coordination, that is, chlorides are expected to be in horizontal plane if $\text{O}=\text{U}=\text{O}^{2-}$ is placed in axial. This second coordination distance in RbCl – NaCl is apparently closest in the spectra obtained, thus $\text{UO}_2\text{Cl}_4^{2-}$ species are well stabilized like in 2CsCl – NaCl. Thus, still we need to obtain the structural parameters to discuss much precise, we can conclude that RbCl – NaCl melt is one of alternative candidates of melt baths suitable for MOX co-electrodeposition process. The variation of 2nd coordination spheres in various conditions is good indication of 'stabilization' of the local environment around uranyl ions, thus we are going to introduce another anionic species to expect much drastic effect on local coordination variation.

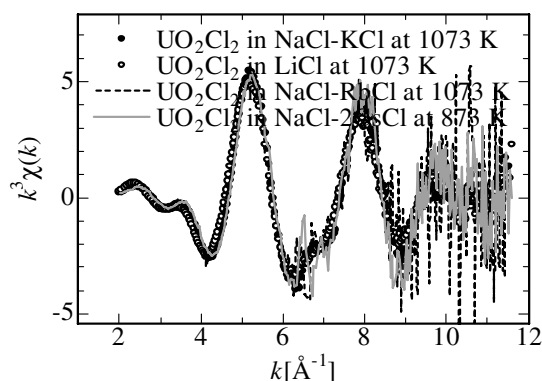


Fig. 1 Extracted oscillation of XAFS of various molten alkali chlorides containing UO_2Cl_2 .

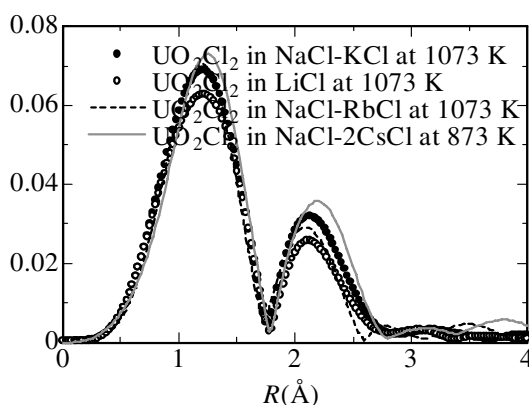


Fig. 2 Fourier transformed radial structure factors of various molten alkali chlorides containing UO_2Cl_2

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