

## XAFS measurement on molten chlorides containing yttrium chloride

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### Introduction

During the course of development of pyrochemical reprocessing of oxide nuclear fuels, one of the several critical issues is how to make realization of the uranium-plutonium oxides (MOX) co-electrodeposition process. To electrodeposit MOX fuel effectively, one has to clarify the relationship between local structure around actinide species and electrochemical behaviour depending upon chlorine – oxygen gas ratio, melt bath composition, temperature, co-existing fission and cladding elements etc. In a real process, these materials are usually diluted in molten chloride baths. In such condition, the local structure around rare earths depending upon various melt baths should be much importantly evaluated. First, we have targeted yttrium in molten alkali chlorides before using actinide compounds because rare earths have been utilized as prototypes of actinides in some cases of electrochemical studies.

### Experimental

The  $YCl_3$  with various melt baths were prepared in a dried argon circulated glove box. A certain amount of the samples were sealed in specially designed quartz cells. The electric furnace used was the similar to that originally designed for the laboratory XAFS equipment, but slightly modifying to improve thermal homogeneity as well as vacuum tightness. We have carried out the XAFS measurement of yttrium chlorides and mixture with alkali chlorides at molten and solid phases, using Si (111) double crystal monochromator at Y-K X-ray absorption edge.

### Results and discussion

These quartz cells have successfully sealed the samples during performing the experiments at high temperatures in whole experiments, thus this type of confinement would be transferable to perform XAFS measurement on actinide compounds in molten state. XAFS spectra of both molten and solidified NaCl-KCl (1:1 molar ratio) –  $YCl_3$  ( $x_{YCl_3}=0.5, 0.1, \text{ and } 0.01$ ) have been obtained using transmission mode. Similar to the results on pure  $YCl_3$  and LiCl-KCl (eutectic)- $YCl_3$  [1], phase shift in XAFS spectra between solid and molten phases are relatively small, as compared to  $LaCl_3$  and its alkali chloride mixtures cases. These facts imply that the local environment around a yttrium ion in molten states does not drastically change from that in solid phases, i.e., 6-coordinated structure. The most striking result is performing SSD fluorescence XAFS measurement for molten NaCl-CsCl (1:2 molar ratio) –  $YCl_3$  mixture

( $x_{YCl_3}=0.1$ ). Due to large amount of co-existence of high X-ray absorbing atom, i.e. Cs, we have only choice of fluorescence mode. Figure 1(a) and (b) show extracted  $\chi(k)$  XAFS spectra of solid and molten samples, respectively. We have tested fluorescence measurement using yttrium water solution with quartz containers and the same furnace several times beforehand, but luckily, even in molten phase at high temperature, we have obtained one of the best spectra ever. As shown in Fig. 1 (a), we have obtained well recognizable oscillation until  $15 \text{ \AA}^{-1}$ . Probably this would be the first time of obtaining excellent resolution data of fluorescence XAFS spectra in molten phase at high temperature. The local environment around a rare earth ion in various melt composition and elements can be evaluated by this way, thus these techniques are applicable to arrange new processes in pyrochemical treatment for not only oxide fuels but also another compound types of nuclear fuels.

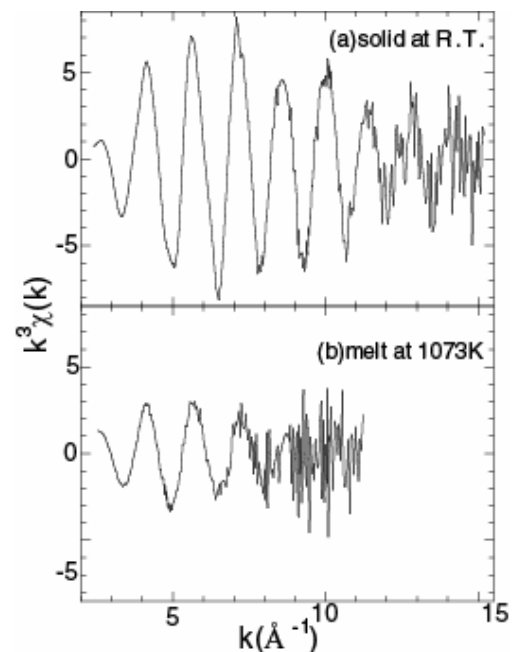


Fig. 1(a), (b) Extracted oscillation of fluorescence XAFS of NaCl-CsCl (1:2 molar ratio) –  $YCl_3$  mixture.

### References

[1] Y. Okamoto et al., J. Synchr. Rad. 8, 1191 (2001).

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