BL-27B/2015G084

XAFS study of uranium oxides for evaluation of simulated debris

Yoshihiro Okamoto* Masahide Takano and Mitsuo Akabori
Japan Atomic Energy Agency, 2-4 Shirakata, Tokai-mura, Naka-gun, 319-1195, Japan

1 Introduction

The XAFS analysis of simulated debris containing uranium is very useful to evaluate chemical state of uranium in the Fukushima Daiichi Nuclear Power Station (1F). The valence of uranium is estimated by an energy shift of white line in the L_3-edge XANES measurement. In addition, the 1st U-O distance and an appearance of the 2nd peak corresponding to the U-U pair are known from the EXAFS analysis. In the present study, L_3-edge XAFS measurement of some standard uranium compounds were performed to confirm the above analytical points and obtain fundamental information as a pre-stage of the XAFS analysis of simulated debris.

2 Experiment

The XAFS measurements were performed at the BL-27B station in the Photon Factory. A transmission geometry XAFS measurement system was used to obtain the U L_3-edge (E_0=17.167keV) XAFS data. The amorphous and crystalline UO_3, U_3O_8, $UO_{2.00}$ and UCl_3 were selected as standard samples. The $UO_{2.00}$ sample was adjusted to O/U ratio by heating under reduction atmosphere. The EXAFS data was analyzed using WinXAS Ver.3.2[1]. The correction parameter in the curve fitting analysis of EXAFS function was calculated from FEFF Ver.8.40[2].

3 Results and Discussion

The U L_3-edge XANES spectra after normalization are shown in Fig.1. An energy shift of white line position is clearly observed in the figure. In the amorphous and crystalline UO_3, the peak positions of their white lines are located at the highest energy. It shows a valence of uranium atom in them is hexavalent. On the other hand, that of UCl_3 having trivalent uranium was observed at lower energy. The difference of the peak position of the white line between crystalline UO_3 and UCl_3 reached 8eV. The peak position of $UO_{2.00}$, in which a valence of uranium must be tetravalent, is located slightly higher than that of UCl_3. The U_3O_8 is considered to be a mixed valence compound containing tetravalent and hexavalent uranium. Therefore the peak position is located between those of UO_3 and $UO_{2.00}$. These results suggests that a valence of uranium can be evaluated by comparing peak positions of white line.

Fig.2 shows radial structure functions $|FT(k^3\chi(k))|$ obtained from fourier transform of the EXAFS functions. The results correspond to tendency expected naturally by the difference of valence, attraction of U-O pair and repulsion of U-U pair. The 1st U-O distance of amorphous UO_3 is the shortest, while that of $UO_{2.00}$ is the longest among oxides. On the other hand, the 1st U-U distance of crystalline UO_3 is the longest, while that of $UO_{2.00}$ is the shortest. In the amorphous UO_3, the 2nd peak corresponding to the 1st U-U was not detected in the radial structure function. It can be concluded that the XANES and EXAFS analysis in the present work can be used in the chemical analysis of uranium element in the simulated debris.

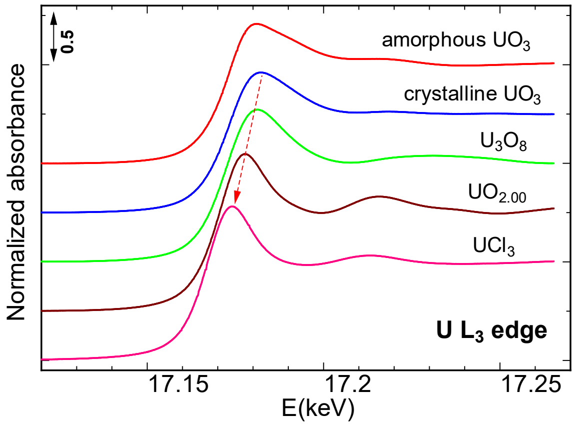

Fig. 1: The U L_3-edge XANES spectra of standard uranium compounds

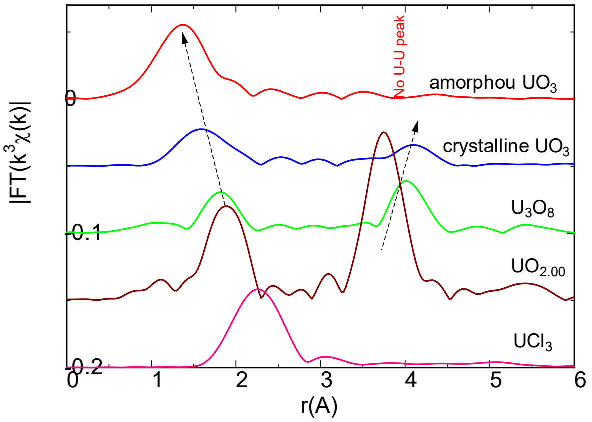

Fig. 2: The radial structure function of standard uranium compounds obtained from the U L_3-edge EXAFS functions

References

[1] T. Ressler, *J. Synch. Rad.*, **5**, 118-122 (1998)
[2] A.L. Ankudinov et al., *Phys. Rev. B* **58**, 7565-7576 (1998).

* okamoto.yoshihiro@jaea.go.jp