

Uranium-induced changes in crystal-field and covalency effects of Th⁴⁺ in Th_{1-x}U_xO₂ mixed oxides probed by high energy resolution fluorescence detected X-ray absorption spectroscopy

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Synchrotron radiation X-ray absorption spectrum (XAS) and X-ray emission spectrum (XES) are important spectroscopy techniques based on the synchrotron radiation light source to research the material structure information, which could be used to acquire the valence state and electronic state of the goal atom, the species, numbers of the atoms around the selected atoms and the information about the local structure. The broadening of XAS and XES are decided by the lifetime of the core hole. The shorter lifetime of the core hole results in the increased broadening of the XAS and XES. Because of the short lifetime of the inner core hole, the conventional XAS and XES have large broadening which results in some information will be covered. Based on the conventional XAS and XES, the high energy resolution fluorescence detected XAS have the high energy resolution, which are the advanced spectroscopy techniques for Actinide elements local structural analysis [1-3].

Understanding of the local structure of thorium is a prerequisite for a better understanding of the physicochemical properties of the thorium-based mixed oxides involved in the Th-based nuclear fuel cycle. The crystalline electric field (CEF) splitting of the 6d shell in Th_{1-x}U_xO₂ solid solution was probed by the Th L₃ edge high-energy-resolution fluorescence-detected (HERFD) X-ray absorption near-edge spectroscopy (XANES) collected at the Lβ₅ emission line at 14W1 beamline of SSRF, which cannot be obtained by conventional X-ray absorption methods [4-6]. Because the split peaks of the white line corresponding to the crystal-field splitting of the unoccupied 6d states were resolved in the HERFD-XANES spectra, the analysis of these split peaks combined with first-principles calculations revealed that an increase of the U content involves the distortion of the Th-O₈ cubes in the Th_{1-x}U_xO₂ mixed oxides. The lower symmetry of the Th-O₈ cube induced by the incorporated U tends to reduce the local crystal-field around Th⁴⁺ as well as the hybridization of Th 6t_{2g}-O 2p which is mainly responsible for the covalent property of the Th-O bond.

References

- [1] - S.M. Butorin et al., *Chemistry*, 22, 9693, (2016).
- [2] - S.M. Butorin et al., *Proceedings of the National Academy of Sciences of the United States of America*, 113, 8093 (2016).
- [3] - R. Bes et al., *Inorganic Chemistry* 55, 4260(2016).
- [4] - H.S. Yu et al., *Nuclear science and techniques*, 26,050102 (2015).
- [5] - P.Q. Duan et al., *X-ray Spectrometry*, 46, 12 (2017).
- [6] - H. Bao et al., *Inorg.Chem.*, 57, 11404 (2018).