U-induced changes in crystal-field of Th^{4+} in $Th_{1-x}U_xO_2$ mixed oxides

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Thorium-uranium mixed oxides exist in different stages of the thorium fuel cycle. Knowledge of the Th local structure is a prerequisite for a better understanding of the physicochemical properties of $Th_{1-x}U_xO_2$ mixed oxides involved in Th-based nuclear fuel cycle.

The crystalline electric field (CEF) splitting of 6*d* shell in $Th_{1-x}U_xO_2$ (x=0.25, 0.5, 0.75) solid solution were probed by using the X-ray absorption near edge spectroscopy (XANES) at the Th L_3-edge measured in the high energy-resolution fluorescence detection (HERFD) mode of an X-ray emission spectrometer by monitoring the maximum of the $L_{\beta 5}$ ($5d_{5/}2–2p_{3/2}$) emission line, which can not be obtained by conventional X-ray absorption methods.

The detected CEF splitting between the 6*d* e_g and t_{2g} orbitals in ThO_2 consisting of ordered Th-O_8 cubes with cubic symmetry for the Th^{4+} ion is ~3.5eV. Because the split peaks of white line corresponding to the crystal-field splitting of the unoccupied 6*d* states were resolved in the HERFD-XANES spectra, the analysis of these split peaks revealed that an increase of the U content involves the distortion of the Th-O_8 cubes in the $Th_{1-x}U_xO_2$ mixed oxides.

The lower symmetry of the Th-O_8 cube induced by the incorporated U trends to reduce the crystal-field effect.

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