

Study of Thorium-Uranium (IV) oxalate dihydrate phase transition through coupled XRD / μ -Raman

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The co-precipitation of tetravalent actinides as an oxalate single phase is currently considered as a promising option to improve the homogeneity as well as the sinterability of mixed oxides fuels envisaged in several concepts of Gen-IV nuclear reactors [1]. Even if actinides oxalates are studied since several decades in this purpose, some uncertainties remain about the associated crystallographic data. In this frame, the crystal structure of $\text{Th}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ solid solutions was first elucidated at room temperature. While these compounds are usually reported as orthorhombic [2,3], all the samples studied during this study were found to crystallize at ambient temperature with a monoclinic (pseudo-orthorhombic) lattice (space group $C 2/c$). The structure determined from twinned single crystals consists in a two-dimensional metal organic framework formed by metallic centers connected through bis-bidentate oxalate ions (fig. 1a). The stability is then ensured through two kinds of hydrogen bonds achieved with the coordinated water molecules (fig. 1b).

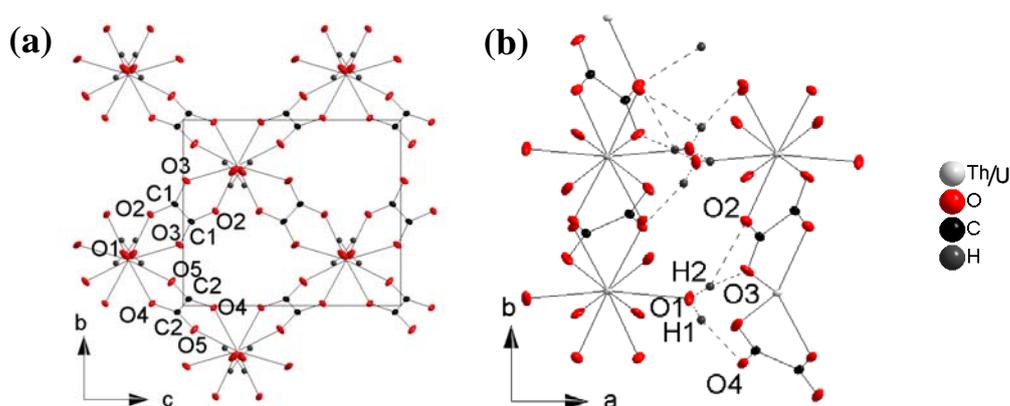


Fig. 1. Projection along a axis $\text{Th}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ metal-organic framework (a) and scheme of hydrogen bonding between the layers (b).

The variation of unit cell parameters *versus* the thorium substitution rate showed that only the c axis was significantly modified while the β angle was found to tend to 90° when increasing the uranium amount in the sample. This slight structural variation observed between thorium and uranium(IV) end-members was also evidenced through μ -Raman spectroscopy analysis since the double band associated to the $\nu_s(\text{C}-\text{O})$ vibration (around $1470\text{-}1490\text{ cm}^{-1}$) was found to be highly sensitive to the cationic environment.

In a second step, *in situ* HT-XRD and HT-Raman experiments allowed to point out a phase transition leading to an orthorhombic variety of $\text{Th}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ solid solutions. The structure was solved for $x = 0.5$ from single crystal data collected at 90°C in the space group $Ccca$. The transformation mainly consists in a rearrangement of the oxalate entities leading to a unique carbon site and a reduction from 4 to 2 oxygen atomic positions. In this form, all the hydrogen bonds became equivalent. Moreover, the ferroelastic-paraelastic type transition between the monoclinic and orthorhombic forms is accompanied by few differences

in the structural arrangement and the reverse transition led to systematically twinned crystals. Finally, μ -Raman spectrometry allowed to point out the phase transition through the observation of the $\nu_s(\text{C-O})$ vibration bands, that turned as a single band due to the symmetrisation of the oxalate group (fig. 2). This study also led to determine the temperature of transition which was found to decrease linearly with the increase of uranium amount in the solid, leading to a strong difference between thorium (around 116°C) and uranium (IV) (42°C) end-members.

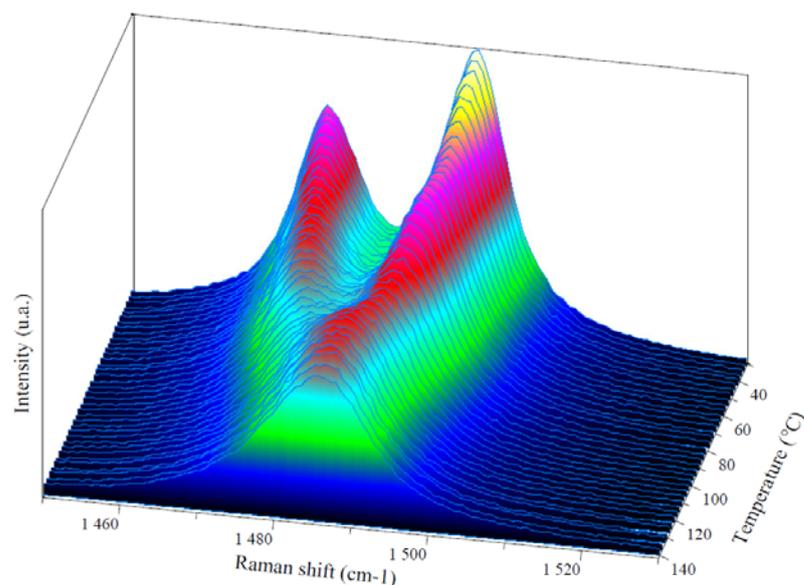


Fig. 2. Variation of the *in situ* HT-Raman spectrum through the monoclinic \rightarrow orthorhombic transition of $\text{Th}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ solid solutions.

References

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