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Structural study of $(N_2H_5,H)_{2.9}U_{1.1}Ce_{0.9}(C_2O_4)_5 \cdot 10H_2O$ from a conventional X-ray diffraction diagram obtained on a powder synthesized by a fast vortex process

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ABSTRACT

In the context of research on U/minor actinides for nuclear fuel reprocessing in the transmutation process, developments are first studied with surrogates containing uranium and lanthanides to facilitate testing. The tests consist of precipitating and calcining a hydrazinium uranium/cerium oxalate. The structure of this oxalate had not been previously determined, but was necessary to validate the physicochemical mechanisms involved.

The present study, firstly demonstrates the structural similarity of the U/Ce oxalate phase $(N_2H_5,H)_{2.9}U_{1.1}Ce_{0.9}(C_2O_4)_5 \cdot 10H_2O$, synthesized using a vortex precipitator for continuous synthesis of actinide oxalates, with previously known oxalates, crystallizing in $P6_3/mmc$ symmetry, obtained by more classical methods.

This fast precipitation process induces massive nucleation of fine powders. Their structural and microstructural determination confirms that the raw and dried phases belong to the same structural family as $(NH_4)_2U_2(C_2O_4)_5 \cdot 0.7H_2O$ whose structure was described by Chapelet-Arab in $P6_3/mmc$ symmetry, using single crystal data. However, they present an extended disorder inside the tunnels of the structure, even after drying at 100 °C, between water and hydrazinium ions. This disorder is directly related to the fast vortex method.

This structure determination can be used as a basis for further semi-quantitative analysis on the U/minor actinides products formed under various experimental conditions.

1. Introduction

The oxalic conversion of U/minor actinide is a subject of research for nuclear fuel in the goal of the transmutation and reprocessing minor actinide.

Because of the radiotoxicity of actinides [1], process development involves preliminary studies with inactive surrogates containing uranium and a lanthanide. In order to be a representative surrogate, the uranium/lanthanide oxalate must have a structure similar to $(NH_4)_2U_2(C_2O_4)_5 \cdot 0.7H_2$, oxalate of hexagonal symmetry investigated by Chapelet-Arab [1].

The most widely used surrogate for analytical assessment of actinide conversion studies is U/Nd oxalate, whose structure was also investigated by Chapelet-Arab [2]. Another surrogate, U/Ce, is also used in the development of conversion processes. Cerium has the advantage that its valence state changes from III to IV during calcination, whereas Nd remains at valence III during the conversion.

The structure of U/Ce oxalate must be determined to understand the precipitation mechanisms in order to determine and quantify the phases formed (cerium oxalate, uranium oxalate, uranium–cerium oxalate). Although structural determination is generally carried out optimally from X-ray diffraction data obtained with a perfect single crystal, actinide oxalate crystals are difficult to grow. The detailed structural study of $(NH_4)_2U_2(C_2O_4)_5 \cdot 0.7H_2O$ was performed by Chapelet-Arab [2] by growing crystals by ion diffusion through a silicate gel impregnated with oxalic acid. The objective of the present work is to verify the structural similarity of U/minor's actinide oxalates with the $(N_2H_5,H)_{2.9}U_{1.1}Ce_{0.9}(C_2O_4)_5 \cdot 10H_2O$ phase obtained with a Ce/(U+Ce) ratio of 0.45 using a vortex precipitator for continuous synthesis of actinide oxalates.

Vortex precipitation induces massive nucleation which limits crystal growth, leading to the formation of small crystallites, and is

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thus unsuitable for producing single crystals. Using methods specific to X-ray powder diffraction (Rietveld refinement, peak profile analysis), we therefore attempted to obtain crystallographic and structural data on this phase. The positions of the water molecules in the structure were fitted from a heat treated powder sample.

The structural determination of $(N_2H_5,H)_{2.9}U_{1.1}Ce_{0.9}(C_2O_4)_5 \cdot 10H_2O$ is necessary for the quantification of the phases formed by precipitation. Indeed, the precipitated solid is sometimes not a monophasic compound (mixed U/Ce oxalate) but can include some other oxalate phases $U(C_2O_4)_2 \cdot 6H_2O$ and $Ce_2(C_2O_4)10H_2O$ in the case of incomplete synthesis.

2. Experimental

2.1. Reagents

U(IV) nitrate solution is prepared by catalytic reduction of U(VI) nitrate (natural uranium) by H_2 on a Pt/Si backing. The concentration, purity and oxidation state of the uranium(IV) solution were essentially determined by UV-vis spectroscopy. Cerium nitrate (Aldrich, 99.9% Reagent Grade $Ce(NO_3)_3 \cdot 6H_2O$) was used to prepare Ce(III) solution.

Hydrazinium ion ($N_2H_5^+$) was used to control the nitrous acid concentration to stabilize uranium at oxidation state (IV), which exhibits very low solubility in the presence of oxalic acid. In addition to its reductive properties, it also contributes to balancing the charges in the resulting mixed precipitate.

2.2. Synthesis

Hydrazinium oxalate precipitate $(N_2H_5,H)_{2.9}U_{1.1}Ce_{0.9}(C_2O_4)_5 \cdot 10H_2O$ was prepared by blending a solution of uranium(IV) nitrate and cerium(III) nitrate and a concentrated $H_2C_2O_4$ solution (with a slight excess of oxalic acid) in a nitric medium ($pH < 1$) in a vortex reactor.

This vortex reactor is characterized by two macromixing zones: in the center of the vortex. The nucleation is massive which limits crystal growth whereas outside, the crystal growth is favored and nucleation is limited [3].

The vortex formation and the position of the reagents introduction in the reactor has a significant effect on the mixing process and then on particles nucleation and crystal growth.

The solid product was recovered by vacuum filtration, then rinsed with ethanol 90% to stabilize it without dehydrating the molecule prior to X-ray diffraction analysis. SEM observation of the solid precipitate indicated that it consisted of particles with hexagonal morphology (Fig. 1).

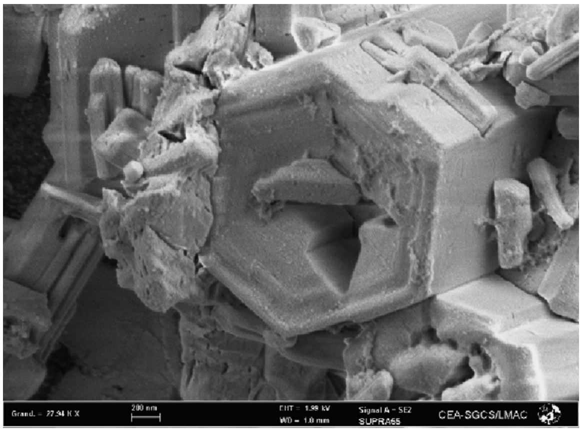

Fig. 1. SEM image of a $(N_2H_5,H)_{2.9}U_{1.1}Ce_{0.9}(C_2O_4)_5 \cdot 10H_2O$ crystal.

Table 1
Data recording conditions.

Radiation	CuKα
Operating parameters	40 kV, 40 mA
Data range (° 2θ)	12–140
Counting step (° 2θ)	0.007
Counting time (s/step)	10

2.3. Solid composition

Uranium and cerium cations inserted in the solid were quantified after dissolution of the oxalate compounds in nitric/hydrochloric acid media ($[HNO_3]=8$ M) by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) with a Thermo Scientific "Iris intrepid" system. The concentrations measured were 25.78 for U wt% and 12.30 for Ce wt% so the elemental ratio of U/Ce is near to (1.1/0.9).

2.4. XRD data collection

The sample X-ray powder diffraction diagram was obtained using a Bruker-AXS D8 Advance diffractometer with CuKα radiation and a LynxEye fast linear detector (2θ angular range: 4°). The data recording conditions are indicated in Table 1.

Two samples were recorded to determine the positions of the water molecules and hydrazinium ions in the structure. The first sample (1) corresponded to the phase at room temperature, with the nominal composition, directly filtered, as described above; the second (2) was the same phase heated for 10 min at 100 °C in atmosphere for comparison.

2.5. SEM characterization

The observations were performed on a CARL ZEISS SUPRA 55 scanning electron microscope (SEM FEG) at 2 kV without metal-coated.

3. Results

3.1. Structure characterization

3.1.1. Unit cell refinement

The reference parent structure $(NH_4)_2U_2(C_2O_4)_5 \cdot 0.7H_2O$, precisely resolved and described by Chapelet-Arab [2], exhibits hexagonal symmetry (space group $P6_3/mmc$) with lattice parameters $a=19.177$ Å and $c=12.728$ Å. A related phase with a similar formulation, $(N_2H_5)_2U_{1.4}Nd_{0.6}(C_2O_4)_5 \cdot xH_2O$, was indexed in the same space group with $a=19.243$ Å and $c=12.760$ Å, but the poor quality of the monocrystals obtained did not permit complete structural determination [2].

Both $(N_2H_5,H)_{2.9}U_{1.1}Ce_{0.9}(C_2O_4)_5 \cdot 10H_2O$ raw and dried phases were analyzed by Rietveld refinement, using TOPAS 4.2 software and Le Bail pattern matching [4]. The profile parameters (cell dimensions; peak shape, background, sample displacement correction and asymmetry) were refined. The peak shape was described by a pseudo-Voigt function with the formulation of Caglioti [5]. The two refinements could be indexed with the same hexagonal symmetry and the same space group as the previous phases (Fig. 2 and Table 2) with the following lattice parameters: $a=19.452$ (1) Å and $c=12.9036$ (9) Å for the oxalate phase obtained at room temperature (1); $a=19.394(2)$ Å and $c=12.883(1)$ Å for the same oxalate phase heated at 100 °C (2). These values, slightly higher than for $(N_2H_5)_2U_{1.4}Nd_{0.6}(C_2O_4)_5 \cdot xH_2O$, are