

Synthesis of new mixed actinides oxalates as precursors of actinides oxide solid solutions

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Abstract

In an integrated fuel cycle such as considered for generation IV nuclear systems, actinides co-conversion processes play an important role by producing mixed actinides compounds used as starting materials for fuel re-fabrication. Among the different co-conversion routes considered, oxalic co-precipitation is one of the investigated ways to synthesised actinides mixed oxides. Oxalic co-conversion of a solution containing a tetravalent actinide An(IV) and a trivalent actinide An(III) under controlled conditions leads to the precipitation of two original series of mixed An(IV)–An(III) oxalate compounds (An(IV) = Th, Np, U or Pu and An(III) = Pu or Am) characterized by an unexpected An(IV)–An(III) crystallographic mixed site which induces a local homogeneity of the composition at a molecular scale. These families of mixed oxalates correspond to two solid solutions of type $M_{2+x}An^{IV}_{2-x}An^{III}_x(C_2O_4)_5 \cdot nH_2O$ and $M_{1-x}[An^{III}_{1-x}An^{IV}_x(C_2O_4)_2 \cdot H_2O] \cdot nH_2O$ (M = single charged cation), with hexagonal or tetragonal symmetry, respectively.

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1. Introduction

The main objectives of the development of innovative fuel cycles such as those conceived in the Generation IV forum, are an efficient use of energetic resources by recycling together the major and valuable actinides such as uranium and plutonium, and a drastic decrease of the radiotoxicity of the ultimate wastes by partitioning and transmutating the minor ones such as americium, curium or neptunium. Whatever the choice of management in the present or future, innovative synthesis methods are studied to elaborate new mixed actinides based materials [1]. For their synthesis, wet methods fulfill very valuable requirements such as flexibility, compatibility with a hydrometallurgical fuel processing, less dissemination of highly radioactive dusts during processing, and above all a better accessibility to very homogeneous polymetallic compounds and interesting nanostructures [2]. Moreover these homogeneous solids may improve

the proliferation resistance by diluting plutonium with other actinides.

The oxalic precipitation of plutonium is used at an industrial scale during the reprocessing of the nuclear fuel, e.g. by the PUREX process [3], in order to convert into oxide this energetically valuable actinide. Oxalic acid is also a very common reagent to recover actinides from liquid waste using precipitation methods because of the very low solubility of An(IV) or An(III) oxalate compounds in acidic solutions [4,5]. The flexibility of the oxalate ligand leads to actinides-based solid compounds, which are particularly suitable precursors of actinides oxide solid solutions.

The present work deals with the thorough investigation of the mixed An(IV)–An(III) oxalic co-conversion (An(IV) = Th, U, Np or Pu and An(III) = Pu or Am) and aims at (i) identifying and characterizing the An(IV)–An(III) co-precipitated oxalates; (ii) underlining the quantitative transfer of metallic cations initially in solution to the co-precipitated solid, without modification of their oxidation state; (iii) clarifying the role of monovalent cations taking part in the charge compensation in the structure.

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2. Experimental

2.1. Reagents

Actinide(IV) or actinide(III) solutions were prepared using specific procedures, either from purified monometallic solutions or by dissolving monometallic oxides or hydroxides. Hydrazinium nitrate (N_2H_5^+ , NO_3^-) was used as an anti-nitrous agent to stabilize the lowest oxidation states (typically IV for U and Np, and III for Pu).

2.2. Oxalate co-precipitation experiments

The oxalate co-precipitates were prepared by mixing a solution of An(IV) and An(III) (An(IV)=Th, U, Np, Pu; An(III)=Pu, Am) and a concentrated $\text{H}_2\text{C}_2\text{O}_4$ solution (with a slight excess of oxalic acid) in nitric medium. The resulting crystallized powders were filtered off and dried at room temperature. For these An(IV)–An(III) mixtures, different molar ratios were studied in order to investigate the influence of the actinide(IV) and actinide(III) nature and of the An(III)/(An(IV) + An(III)) molar ratio on the co-precipitate structure.

2.3. Apparatus

- *X-ray powder diffraction data* for oxalate and oxide compounds were obtained with an INEL CPS 120 diffractometer (curved position sensitive detector) using $\text{Cu K}\alpha 1$ radiation isolated by a germanium monochromator. Silicon was used as an internal standard. Actinides oxalates diffraction patterns were compared with the recently built $M^+ \text{–U(IV)–Ln(III)}$ oxalate structures database [6–8] in order to detect isomorphic similitudes.
- *UV-visible spectroscopy*: actinides concentrations in solution were determined by UV-visible spectroscopy using a CINTRA 10e GBC UV spectrophotometer between 350 and 900 nm. Actinides oxidation states in the co-precipitates were investigated using a HITACHI U-3000 spectrophotometer equipped with an integration sphere for reflexion measurements in glove-box.
- *Infra-red spectra* of all samples were recorded with the NICOLET MAGNA IR 550 series II. A spectral range from 400 to 4000 cm^{-1} was typically used.
- *Thermogravimetric analyses* were carried out with a NETZSCH STA 409C thermal analysis system with an alumina crucible up to 950°C , under argon flow and with a heating rate of $10^\circ\text{C min}^{-1}$, in order to determine the water content of the precipitates.

3. Results and discussion

The new mixed An(IV)–An(III) (An(IV) = Th, U, Np or Pu, and An(III) = Pu or Am) single-phase co-precipitates obtained by oxalic co-conversion, were characterized from powder diffraction patterns by analogy to uranium(IV)–lanthanide(III) oxalates whose structures were solved recently from single-crystal X-ray diffraction data [6–8] (Fig. 1). By varying the (An^{IV}, An^{III}) pair and depending on the An^{IV}/An^{III} ratio, two original series were identified, $M_{2+x}\text{An}^{\text{IV}}_{2-x}\text{An}^{\text{III}}_x(\text{C}_2\text{O}_4)_5 \cdot n\text{H}_2\text{O}$ (1) and $M_{1-x}[\text{An}^{\text{III}}_{1-x}\text{An}^{\text{IV}}_x(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}] \cdot n\text{H}_2\text{O}$ (2) (M = single charged cation), with hexagonal or tetragonal symmetry, respectively. Thus, considering the An(IV)–Pu(III) pairs (An(IV) = Th, U, Np, Pu) and a Pu(III)/(An(IV) + Pu(III)) ratio close to 0.5, an evolution of the structure of the precipitate is observed along the actinides series. For An(IV) = Th or U, the precipitate is characterized by an hexagonal structure whereas for An(IV) = Np or Pu, the solid compound crystallizes in the tetragonal system.

At the same time, the influence of the An(III) nature (An(III) = Pu or Am) on An(III)–U(IV) precipitates structure

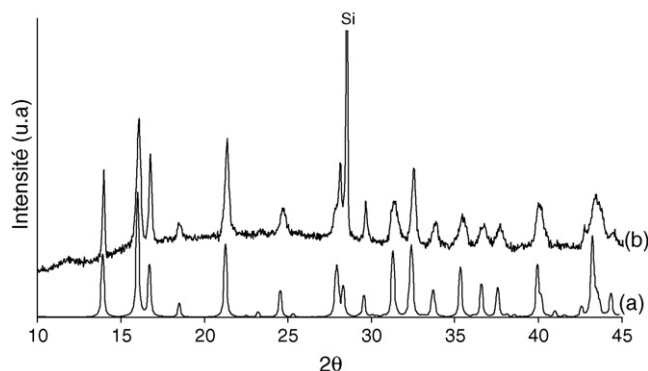


Fig. 1. Theoretical X-ray diffraction pattern of An(IV)–An(III) hexagonal mixed oxalate (a); experimental X-ray diffraction pattern of $\text{U}_{0.725}\text{Pu}_{0.275}$ oxalate (b).

was investigated. For a ratio An(III)/(U(IV) + An(III)) close to 10%, whatever the actinide(III) considered, the An(III)–U(IV) mixed oxalate adopts an hexagonal structure.

The sample preparation and the partial radiolysis induced by some isotopes are responsible for the low signal–background ratio which makes the lattice parameters refinement difficult. However, the lattice parameters of An(IV)₅₀–Pu(III)₅₀ mixed oxalate compounds were quite accurately refined by pattern matching using the Fullprof software [9]. The decrease of the lattice parameters from Th(IV) to U(IV) for the hexagonal structure and from Np(IV) to Pu(IV) for the tetragonal one is in agreement with the decrease of the ionic radii along the actinides series [10] (Table 1).

The originality of both structures is based on a mixed crystallographic site, which can accept either a tetravalent actinide or a trivalent one, the charge balance being ensured by the adjustment of the single-charged ions within the structure. The main difference between the hexagonal structure (1) and the tetragonal one (2) is that actinides are ten-coordinated in (1) and nine-coordinated in (2) (Fig. 2). The honeycomb-like structure of the hexagonal compound is based on a three-dimensional network of metallic and oxalate ions creating parallel tunnels. For the tetragonal series, the metallic ions are linked through oxalate ions to build a bi-dimensional arrangement of squared cycles stacked along the third direction.

The An(IV)–An(III) crystallographic mixed site is responsible for the homogeneous distribution of actinides (solid solution) in the precipitates which are thus, relevant mixed oxide precursors.

Complementary investigations by UV–visible spectroscopy confirm the simultaneous co-precipitation of An(III) and An(IV) without modification neither of the ratio between An(IV) and An(III) nor of the oxidation state (Fig. 3) Oxalic co-precipitation

Table 1
Lattice parameters of An(IV)₅₀–Pu(III)₅₀ mixed oxalate compounds

System	Structure	a (Å)	c (Å)
Th(IV)–Pu(III)	Hexagonal	19.176(4)	12.735(5)
U(IV)–Pu(III)	Hexagonal	19.115(7)	12.664(5)
Np(IV)–Pu(III)	Tetragonal	8.792(2)	8.018(3)
Pu(IV)–Pu(III)	Tetragonal	8.813(7)	7.97(1)

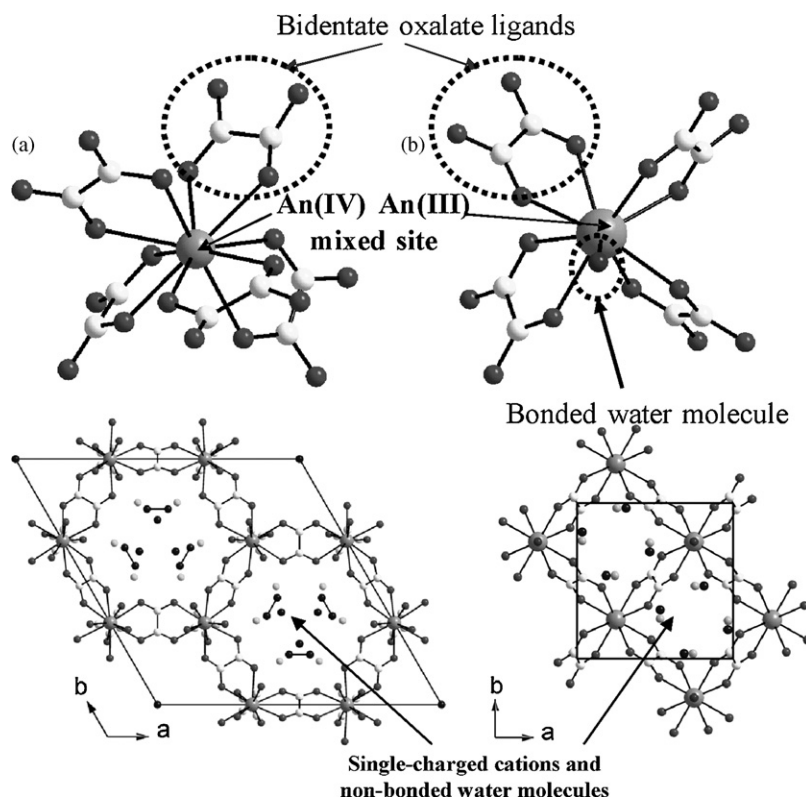


Fig. 2. Environment of An(IV)–An(III) crystallographic mixed site and structural arrangement in: the hexagonal mixed oxalate (a) and the tetragonal one (b).

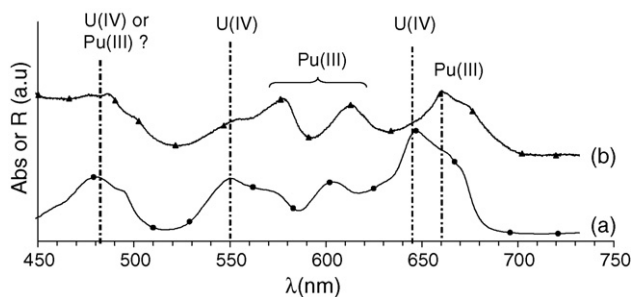


Fig. 3. UV-vis spectra of U(IV)–Pu(III) 50/50 nitric solution (a); and U(IV)–Pu(III) solid co-precipitate; (b) showing the invariability of oxidation state during experiment.

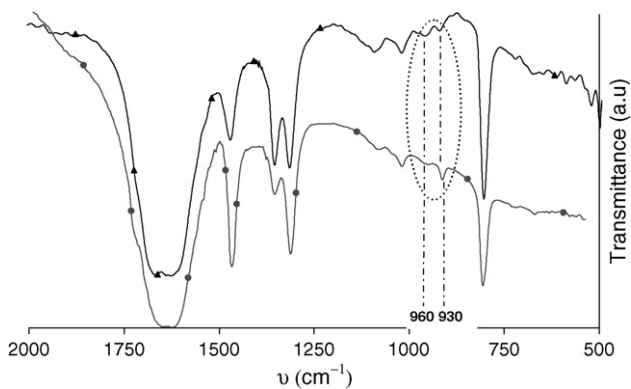


Fig. 4. Infrared spectra of An(IV)–An(III) oxalic co-precipitates: (▲) An(IV)–An(III) hexagonal mixed oxalate; (●) An(IV)–An(III) tetragonal mixed oxalate.

yields are higher than 99% using the experimental method described above.

Infrared spectra of An(IV)–An(III) coprecipitates are characteristics of oxalate compounds but exhibit two additional bands at 960 and 930 cm^{-1} which could be assigned to N–N stretching vibrations in N_2H_5^+ hydrazinium cation (Fig. 4). Then, hydrazinium cations located in the cavities of the crystal network take partially part to the charge balance in the structure. Chemical composition analysis and thermogravimetric experiments highlight the nature of single-charged cation and the water molecule content in the precipitate (Fig. 5).

So, in reducing conditions, the co-conversion of U(IV), Pu(III), Np(IV), Am(III) and Cm(III) by oxalic co-precipitation in a single step could be envisaged to elaborate particularly

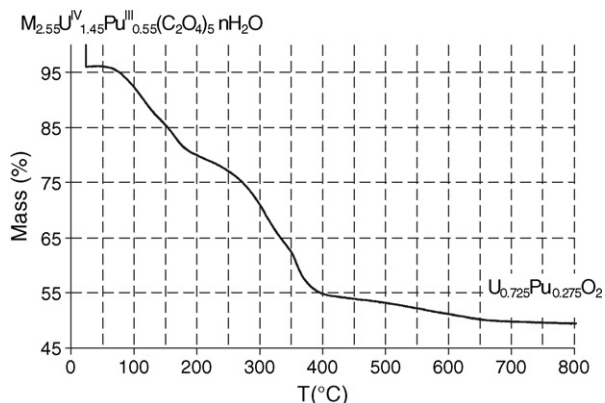


Fig. 5. TG plot starting from a mixed U(IV)/Pu(III) 72.5/27.5 hexagonal oxalate under Ar.

homogeneous solid compounds with the desired composition. The scientific feasibility was recently assessed in the ATALANTE facility at a laboratory scale: (U, Np, Pu, Am) O₂ solid solution powder was obtained at a gram level after a controlled oxalic co-precipitation of the actinides in nitric/oxalic medium and a thermal treatment of the co-precipitate under an inert atmosphere.

4. Conclusion

In these oxalic co-precipitation experiments dedicated to actinides co-management using oxalic co-conversion, the simultaneous co-precipitation of the involved actinides is an important first achievement considering the specific chemical and redox properties of each actinide.

The resulting solid compounds are characterized by an original crystallographic mixed site, which can accept either a tetravalent actinide or a trivalent one, which explains the homogeneous distribution of the different actinides inside the precipitate.

Thus, innovative mixed actinides solids exhibiting a controlled composition can be obtained by oxalic co-conversion and used as mixed oxides precursors in order to synthesize starting materials for the re-fabrication of advanced fuels [11].

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