Contents lists available at ScienceDirect

Journal of Solid State Chemistry
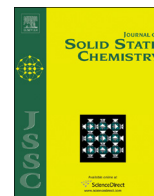
Crystal growth methods dedicated to low solubility actinide oxalates

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ABSTRACT

Two novel crystal growth syntheses dedicated to low solubility actinide-oxalate systems and adapted to glove box handling are described. These methods based on the use of precursors of either actinide metal or oxalic acid have been optimized on lanthanide systems (analogue of actinides(III)) and then assessed on real actinide systems. They allow the synthesis of several actinide oxalate single crystals, $Am_2(C_2O_4)_3(H_2O)_3 \cdot xH_2O$, $Th(C_2O_4)_2 \cdot 6H_2O$, $M_{2+x}[Pu_{2-x}^{IV}Pu_x^{III}(C_2O_4)_5] \cdot nH_2O$ and $M_{1-x}[Pu_{1-x}^{III}Pu_x^{IV}(C_2O_4)_2 \cdot H_2O] \cdot nH_2O$. It is the first time that these well-known compounds are formed by crystal growth methods, thus enabling direct structural studies on transuranic element systems and acquisition of basic data beyond deductions from isomorphic (or not) lanthanide compounds. Characterizations by X-ray diffraction, UV–visible solid spectroscopy, demonstrate the potentialities of these two crystal growth methods to obtain oxalate compounds.

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1. Introduction

Actinide oxalates have been highlighted for use in nuclear industry thanks to their very low solubility leading to a precipitation yield close to 100%. Indeed, the pKs are in the range 25–31 for Ln/An(III) oxalates [1–3] and in the range 21–23 for An(IV) oxalates [4–6]. Oxalic method is found to be a convenient process for conversion of actinides from nitric acid solution to oxides thanks to the formation of intermediate oxalate precursors. The microstructure and properties of the single or mixed oxides largely depend on the oxalate microstructure and, therefore, on their crystal structure [7]. Thus, structural analyses of oxalates are of interest to better characterize these precursors whose solid state chemistry has recently been the subject of a comprehensive review [8]. Up to now, many structural studies were carried out on lanthanide elements or uranium and thorium, which are often considered as good crystallographic analogs of transuranic actinides (IV or III) according to their close ionic radii [9,10]. But their behavior remains quite often different from plutonium or neptunium. There is a huge impact of the An(III)/Ln(III) and An(IV) nature on the solid state structure of the compounds [11]. It is thus recommended to carry out studies directly on systems of interest, *i.e.* with transuranic elements.

The actual lack of structures concerning transuranic oxalates is likely to be due to single crystal growth difficulties. Synthesis routes

dedicated to the growth of high-quality single crystals of actinide oxalates are quite rare and/or not easily controlled. The first family of crystal growth methods dedicated to actinide oxalates is based on solvent diffusion: an "anti-solvent" (a solvent in which the oxalate is particularly insoluble), ethanol, is slowly added to a stable aqueous saturated solution of an oxalate complex. This method was used to synthesize single crystals containing tetravalent actinides, U(IV) [12,13] and Th(IV) [14]. Hydrothermal synthesis allowed the crystal growth of U(IV) [15,16], U(IV)/Th(IV) [17], Pu(III) [18] and Pu(IV) [18] oxalates. The *in situ* generation of oxalic acid in hydrothermal conditions also allowed the synthesis of Th(IV) oxalates [19,20]. The other actinide oxalate crystal growth methods described in literature rely on a slow and controlled diffusion of the different reagents to avoid high supersaturation and uncontrolled precipitation. The slow inter-diffusion of two liquids with different physical properties (*e.g.* density) to avoid a direct complete mixing of the solutions allowed the synthesis of $H_2Np_2(C_2O_4)_5 \cdot nH_2O$ [21]. Another paper reports the single crystals synthesis of $[K_2CdU(C_2O_4)_4 \cdot 5H_2O] \cdot 4H_2O$ [22], using an H-shaped glass tube. An improvement of the previous synthesis consists in the diffusion of a metallic cations solution through a gel impregnated with oxalic acid [23,24]. So, Chapelet et al. synthesized a double ammonium uranium(IV) oxalate, $(NH_4)_2U_2(C_2O_4)_5 \cdot 0.7H_2O$ [25], and mixed U(IV)/Ln(III) oxalates, with formulae $M_{2+x}U_{2-x}^{IV}Ln_x^{III}(C_2O_4)_5 \cdot nH_2O$ [25] and $M_{1-x}[Ln_{1-x}^{III}U_x^{IV}(C_2O_4)_2 \cdot H_2O] \cdot nH_2O$ [26,27]. These mixed oxalates are hereafter called respectively hexagonal and tetragonal phases. Despite the difficulties linked to crystals recovery and gel opacity, Grigor'ev et al. prepared a neptunium(IV) oxalate hexahydrate, $Np(C_2O_4)_2 \cdot 6H_2O$ [28].

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However, due to early hydrolysis and some chemical specifities (*e.g.* redox chemistry) of transuranic actinides, most of the existing single crystal syntheses are unsuitable or adaptable only to a few specific systems. More than their chemical properties, the necessary handling of actinides in glove box does not enable the use of main aforementioned synthesis routes. It is thus necessary to devise new efficient and general crystal growth methods adaptable to specific manipulation conditions and to actinide chemistry. Recently we have developed new crystal growth methods dedicated to actinide oxalates to answer this glove box issues. Still using the diffusion concept, the first one is based on the use of a new designed diffusion triple cell [29]. It has allowed the single crystal growth of plutonium(III) and plutonium(IV) oxalates [30]. The application of this method to mixed actinides and mixed valence systems led to a lot of An(IV)–An(III) oxalate single crystals of composition $(NH_4)_{2+x}An_{2-x}^{IV}An_x^{III}(C_2O_4)_5 \cdot nH_2O$ and $(NH_4)_{1-x}[An_{1-x}^{III}An_x^{IV}(C_2O_4)_2 \cdot H_2O] \cdot nH_2O$ with An^{IV}–$An^{III}=$ U^{IV}–Pu^{III}, Pu^{IV}–Pu^{III}, U^{IV}–Am^{III}, Pu^{IV}–Am^{III} [29–31]. This diffusion triple cell synthesis was also modified to be used with specific oxalate precursors $(An^{IV}(C_2O_4)_3^{2-})$. Crystallization is induced by equilibrium displacement of a solution of soluble anionic complexes $(An^{IV}(C_2O_4)_3^{2-})$ by nitric acid to form the insoluble neutral complex. This special procedure allows the formation of $(NH_4)_2(Pu^{IV}, U^{IV})_2(C_2O_4)_5 \cdot nH_2O$ and $(Pu^{IV}, U^{IV})(C_2O_4)_2 \cdot 6H_2O$ crystals [29] despite the instability of this system in nitric acid solution because of a redox reaction leading to the formation of U(VI) and Pu(III) species. Using this synthesis route two plutonium(IV) oxalate crystals, $(NH_4)_2Pu_2^{IV}(C_2O_4)_5 \cdot nH_2O$ and $Pu^{IV}(C_2O_4)_2 \cdot 6H_2O$, were also synthesized [29,30].

We recently developed new crystal growth syntheses dedicated to actinide oxalates in order to (i) study other systems and (ii) expand the chemical conditions leading to new structures. These new synthesis routes are based on kinetic concepts, the idea being to delay the contact between the actinides and the oxalate ions using precursors of either oxalate ion (synthesis using oxalate ester: **method 1**) or actinide solid compounds (synthesis using actinide oxide: **method 2**). The controlled mixing between species allows limited local supersaturation, thus favoring crystal growth of only a few nuclei. Concerning **method 1**, the use of oxalic acid

2. Experimental section

2.1. Reagents

Because of the radiotoxicity of actinides, especially plutonium and americium, the experiments involving these elements were carried out in glove boxes with very restrictive protocols. Pu(IV) and Am(III) solutions were prepared by dissolving the corresponding oxides, PuO_2 and AmO_2, with concentrated HNO_3. The plutonium(III) solution is prepared by reduction of the plutonium (IV) solution using hydrazinium nitrate $(N_2H_5^+, NO_3^-)$. The concentration of actinides in these primary solutions is close to 1 mol L^{-1}. Hydrazinium nitrate was moreover used as an antinitrous agent to stabilize the plutonium lowest oxidation state, Pu(III). Pu(IV) and Am(III) are stable in nitric acid solutions. The concentration, purity, and oxidation state were essentially determined by UV–vis spectroscopy. The starting material for thorium is thorium nitrate hexahydrate, $Th(NO_3)_4 \cdot 6H_2O$ (prolabo). Lanthanide nitrates $Ln(NO_3)_3 \cdot xH_2O$ (Aldrich, 99.9% Reagent grade) were used to prepare Ln(III) solutions to simulate An(III) solutions in pseudoactive experiments, considering some chemical analogies between Ln(III) and An(III) ions [37]. For some experiments, the lanthanide was introduced as an oxide, Ln_2O_3. Ammonium, sodium, or potassium nitrates were added when appropriate (Aldrich, 99.9% reagent grade). Ethanol, butanol, diethyl ester and dibutyl ester ($>99\%$ purity) were purchased at Sigma Aldrich. Oxalic acid was used in its dihydrate form, $H_2C_2O_4 \cdot 2H_2O$ (VWR).

2.2. **Method 1**: use of oxalate esters

The considered precursor, inert toward actinides, gives oxalic acid by spontaneous and controlled reaction. An appropriate supersaturation is thus gradually met limiting the nucleation process and maintained all along the crystal growth with a regular reagent supply. The oxalate ester family converts to oxalic acid by spontaneous acidic hydrolysis. The reaction can be controlled thanks to various chemical and physical parameters (equilibrium 1 and mechanism).

Equilibrium 1
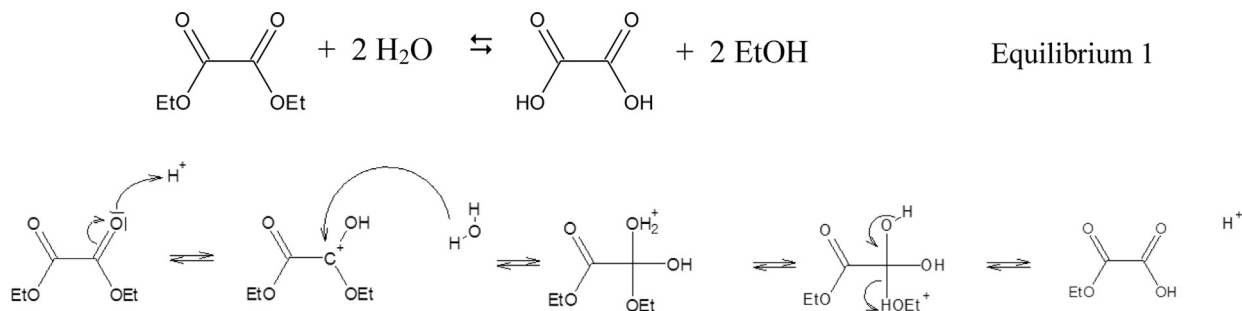
precursors (aside hydrothermal reactions) has already been reported in the literature [32–35], but none of the syntheses can be adapted to f element oxalates because of very specific chemical conditions inadaptable to actinide chemistry. The use of a solid as a starting material, as in **method 2**, and its degradation in the solution containing another reagent has been used once in the literature to synthesize single crystals of $Ba_2U(C_2O_4)_4 \cdot 8H_2O$ [36]. These new synthesis routes were conceived and developed on Ln (III) systems before being specifically applied to actinide systems containing thorium(IV) and transuranic elements such as Am(III) and Pu(III).

One of these esters, diethyloxalate, had already been used for the precipitation of plutonium(III) [38] and americium [39] oxalates but the non-control of the reaction did not allow crystal growth of single crystals. Kustaryono et al. use the dimethyloxalate to grow single crystals of lanthanide oxalate but the biphasic water/benzene medium and specific chemical conditions made this synthesis not so appealing for the target applications [40].

The present crystal growth method was first developed on lanthanide systems with two different esters, diethyloxalate and dibutyloxalate, diluted in ethanol and butanol respectively, before being applied to actinide systems. The chemical conditions are different according to the considered system. Concerning