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ScienceDirect
Journal of Nuclear Materials 373 (2008) 259–268
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Synthesis and characterization of mixed An(IV)An(III) oxalates (An(IV) = Th, Np, U or Pu and An(III) = Pu or Am)

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Received 29 January 2007; accepted 7 June 2007

Abstract

The reaction of a solution containing a tetravalent actinide An(IV), a trivalent actinide An(III) and a single-charged cation such as hydrazinium in the presence of oxalic acid in an acidic medium under controlled conditions leads to the precipitation of mixed An(IV)–An(III) oxalate compounds never discussed elsewhere. Two original series were obtained by varying the (An^{IV},An^{III}) pair and the An^{IV}/An^{III} ratio, $(N_2H_5,H_3O)_{2+x}An^{IV}_{2-x}An^{III}_x(C_2O_4)_5 \cdot 4H_2O$(**1**) and $(N_2H_5,H_3O)_{1-x}[An^{III}_{1-x}An^{IV}_x(C_2O_4)_2 \cdot H_2O] \cdot 4H_2O$(**2**). The crystal structures were identified from powder diffraction patterns by analogy with hydrazinium uranium (IV) lanthanide (III) oxalates whose structures were solved recently by single crystal X-ray diffraction. Complementary investigations by UV–vis and infra-red spectroscopy and thermogravimetric analysis confirm the presence of both tetravalent and trivalent states of actinides in structures (**1**) and (**2**) and the role of single-charged cation and water molecules. The originality of both structures consists in the existence of a mixed crystallographic site for the tetravalent actinide and the trivalent one, the charge balance being ensured by the adjustment of the single-charged ions within the structure. The main difference is that actinides are tenfold coordinated in (**1**) and ninefold coordinated in (**2**). This is the first evidence of a mixed actinide(IV)–actinide(III) site in the same oxalate structure.

1. Introduction

Oxalic precipitation of plutonium(IV) is used at an industrial scale during reprocessing of nuclear fuel by the PUREX process to convert this energetically valuable actinide into oxide form suitable for future use, e.g. as raw material for MOX production. Oxalic acid is also a very common reagent to recover actinides from liquid waste by using precipitation methods because of the very low solubility of An(IV) or An(III) oxalate compounds in acidic solutions. The chemical properties of actinide oxalates have often been investigated but, surprisingly, only few detailed structural determinations are dedicated to such compounds [1]. Previous studies have been devoted to crystallographic structures of simple oxalates of actinide(IV) $An^{IV}(C_2O_4)_2 \cdot 6H_2O$ [2,3] and actinide(III) $An^{III}_2(C_2O_4)_3 \cdot 10H_2O$ [3] (isomorphic with $Ln_2(C_2O_4)_3 \cdot 10H_2O$; Ln = La, Ce, Pr, Nd [4–6]) and of double M^+–An(IV) ($M = K^+$, H^+, An = Th [7], U [8], Np [9]) oxalates. However, mixed An(IV)–An(III) oxalate structures have never been described to date. Recently we published the crystal structure of new mixed M^+–U(IV)–Ln(III) [10–12] oxalate compounds ($M^+ = Na^+$, NH_4^+, $N_2H_5^+$, Ln = Ce, Nd, Sm, Gd) synthesized using a crystal growth method based on slow diffusion of metallic cations through silica gel impregnated with oxalic acid. Single crystal data acquisition led to elucidate new original mixed structures that belong to three series called triclinic, hexagonal and tetragonal. These three families of mixed U(IV)–Ln(III) oxalates are characterized by an unexpected mixed U(IV)–Ln(III) crystallographic site, where U(IV) and Ln(III) are 10-fold coordinated in the hexagonal structure and 9-fold coordinated in the triclinic and tetragonal ones. Monovalent cations equilibrate the charge in these structures depending on the Ln(III)/(U(IV)+Ln(III)) mole

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doi:10.1016/j.jnucmat.2007.06.004

ratio. The hexagonal and triclinic compounds adopt a honeycomb type structure based on a three-dimensional network of metallic and oxalate ions, while the tetragonal structure is built from a two-dimensional arrangement of squared metal-oxalate cycles.

5f-Actinides are known to exhibit structural behavior similar to that of 4f-lanthanides in many cases. The most obvious analogy is the similar cation size of An^{3+} and Ln^{3+} at a given coordination number [13]: Ce^{3+} and Nd^{3+}correspond to Pu^{3+} and Am^{3+}, respectively. Considering this analogy between An^{3+} and Ln^{3+} in coordination chemistry, structural data recently published about U(IV)–Ln(III) oxalates can be used to identify An(IV)–An(III) co-precipitated compounds.

The silica gel method is a convenient means of promoting crystal growth of oxalate compounds [14,15] but it exhibits major drawbacks: (i) the chemical composition of the resulting crystals cannot be controlled; (ii) only few crystals are synthesized, so full characterization of the resulting compounds using various and often destructive techniques is not possible and (iii) this method is complex to implement in confined environments such as glove-boxes: alpha self-irradiation may induce damage to the crystals during their slow growth; isolation and conservation of sub-millimeter single crystals from the silica gel are moreover a particularly uneasy task.

The present work deals with a thorough investigation of the mixed U(IV)–Ln(III) oxalates synthesized by co-precipitation methods and aims at (i) specifying the solid solution domains; (ii) investigating the transfer of metallic cations initially in solution to the co-precipitated solid, with particular attention to their redox behavior and (iii) clarifying the role of monovalent cations taking part in the charge compensation in the structure. Finally, these co-precipitation experiments were extended to An(IV)–An(III) mixtures (An(IV) = Th, U, Np or Pu and An(III) = Pu or Am) in order to identify and structurally characterize co-precipitated An(IV)–An(III) oxalates.

2. Experimental section

2.1. Reagents

Actinide(IV) and actinide(III) solutions were prepared using specific procedures, either from purified mono-metallic solutions or by dissolving mono-metallic 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) and as source of monocharged cations. The concentration, purity and oxidation state were essentially determined by UV–vis spectroscopy. Lanthanide nitrate salts (Aldrich, 99.9% Reagent Grade $Ln(NO_3)_3 \cdot 6H_2O$) were used when appropriate to prepare Ln(III) solutions to simulate An(III) solutions in pseudo-active experiments, considering the similarities between Ln(III) and An(III) ions [13].

2.2. Oxalate co-precipitation experiments

The oxalate co-precipitates were prepared by mixing a solution of An(IV) and An(III) or Ln(III) (An(IV) = Th, U, Np, Pu; An(III) = Pu, Am; and Ln(III) = Nd, Sm) and a concentrated $H_2C_2O_4$ solution (with a slight excess of oxalic acid) in a nitric medium [16]. The selected lanthanides for this work were Nd(III) and Sm(III) which both exhibit UV–vis peaks in the 350–900 nm domain.

The resulting crystallized powders, whose color depends on the elements involved, were filtered off and dried at room temperature. A series of lanthanide–uranium co-precipitates were prepared with Ln/Ln + U mole ratios equal to 0%, 10%, 20%, 30%, 40%, 50%, 60% and 70% (Ln = Nd, Sm). Above 70%, the co-precipitated powder is a polyphase system based on the well-known lanthanide oxalate $Ln_2(C_2O_4)_3 \cdot 10H_2O$ [4–6].

For An(IV)–An(III) mixtures, two mole ratios: (10% and 50%) were studied to investigate the influence of the actinide(IV) and actinide(III) nature and the An(III)/(An(IV) + An(III)) mole ratio on the co-precipitate structure.

2.3. XRD acquisition

X-ray powder diffraction data for all mixed oxalates were obtained with an INEL CPS 120 diffractometer (curved position-sensitive detector) using Cu Kα1 radiation isolated by a germanium monochromator. Silicon was added to all samples as an internal standard to calibrate the angular positions of the observed XRD lines. Actinide oxalates were mixed with an epoxy resin to prevent contamination spreading and their diffraction patterns were compared with the recently built M^+–U(IV)–Ln(III) oxalate structures database [10–12] to detect isomorphic similitude. The lattice parameters of the mixed oxalates were refined by pattern matching using the Fullprof software [17].

2.4. UV–vis spectroscopic analysis

Actinide and lanthanide concentrations in solution were determined by UV–vis spectroscopy using a CINTRA 10e GBC UV spectrophotometer between 350 and 900 nm. Actinide oxidation states in the co-precipitates were investigated in a glove-box using a HITACHI U-3000 spectrophotometer equipped with an integration sphere for reflection measurements.

Hydrazinium cations were quantified by colorimetric analysis: in a 1 M nitric medium, hydrazinium cation reacts with dimethylamino-4-benzaldehyde to form a yellow complex that presents a peak around 455 nm.

2.5. Infrared spectroscopic analyses

Infrared spectra of all samples were recorded with the NICOLET MAGNA IR 550 series II between 400 and 4000 cm^{-1}.