Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Solid State Chemistry 178 (2005) 3046–3054

JOURNAL OF
SOLID STATE
CHEMISTRY

www.elsevier.com/locate/jssc

U(IV)/*Ln*(III) unexpected mixed site in polymetallic oxalato complexes. Part I. Substitution of *Ln*(III) for U(IV) from the new oxalate $(NH_4)_2U_2(C_2O_4)_5 \cdot 0.7H_2O$

Benedicte Chapelet-Arab[a,b], Guy Nowogrocki[a], Francis Abraham[a,*], Stephane Grandjean[b]

[a]*Laboratoire de Cristallochimie et Physicochimie du Solide, UMR CNRS 8012, ENSCL-USTL, B.P. 90108, 59652 Villeneuve d'Ascq Cedex, France*
[b]*Laboratoire de Chimie des Actinides, CEA VALRHO/DRCP/SCPS, Bât 399 BP 17171, 30208 Bagnols sur Ceze Cedex*

Received 8 April 2005; received in revised form 24 June 2005; accepted 26 June 2005
Available online 29 August 2005

Abstract

A new ammonium uranium (IV) oxalate $(NH_4)_2U_2(C_2O_4)_5 \cdot 0.7H_2O$ (**1**) and three mixed uranium (IV)–lanthanide (III) oxalates, $(N_2H_5)_{2.6}U_{1.4}M_{0.6}(C_2O_4)_5 \cdot xH_2O$ ($M = \mathrm{Nd}$ (**2**) and $M = \mathrm{Sm}$ (**3**)), $Na_{2.56}U_{1.44}Nd_{0.56}(C_2O_4)_5 \cdot 7.6H_2O$ (**4**) and $Na_3UCe(C_2O_4)_5 \cdot 10.4H_2O$ (**5**), have been prepared. The crystal structures of compounds **1**, **4** and **5** have been determined by single-crystal X-ray diffraction. The crystal structures were solved by the direct methods and Fourier difference techniques, and refined by a least square method on the basis of F^2 for all unique reflections. Compounds **2** and **3** are isotypic with **1**. Crystallographic data: **1**, hexagonal, space group $P6_3/mmc$, $a = 19.177(3)$, $c = 12.728(4)$ Å, $Z = 6$, $R_1 = 0.0575$ for 52 parameters with 1360 reflections with $I \geqslant 2\sigma(I)$; **2**, hexagonal, space group $\mathrm{P}6_3/mmc$, $a = 19.243(4)$, $c = 12.760(5)$ Å, $Z = 6$; **3**, hexagonal, space group $P6_3/mmc$, $a = 19.211(3)$, $c = 12.274(4)$ Å, $Z = 6$; **4**, orthorhombic, space group $Pbcn$, $a = 18.79(3)$, $b = 11.46(1)$, $c = 12.77(2)$ Å, $Z = 4$, $R_1 = 0.0511$ for 183 parameters with 3026 reflections with $I \geqslant 2\sigma(I)$; **5**, monoclinic, space group $C2/c$, $a = 18.878(6)$, $b = 11.684(4)$, $c = 12.932(4)$ Å, $\beta = 95.97(1)^\circ$, $Z = 4$, $R_1 = 0.0416$ for 213 parameters with 4060 reflections with $I \geqslant 2\sigma(I)$. The honeycomb-like structure of the five compounds is built from the same three-dimensional arrangement of metallic and oxalate ions. Similar hexagonal rings of alternating metallic and oxalate ions form layers parallel to the (001) plane that are pillared by another oxalate ion. Indeed, some torsions or rotations of the bridging oxalate ligands led to modifications of the network symmetry. The monovalent cations and the water molecules occupy the hexagonal tunnels running down the [001] direction. Starting from the uranium (IV) compound $A_2U_2(C_2O_4)_5 \cdot 0.7H_2O$ with $A = NH_4^+$ (**1**), the mixed U(IV)/*Ln*(III) oxalates are obtained by partial substitution of U(IV) by *Ln*(III) in a ten-coordinated site, the charge deficit being compensated by intercalation of supplementary monovalent ions within the tunnels. The distortion of the arrangement in the [001] direction for the Na-containing compounds allows the accommodation of a greater number of water molecules that insure an octahedral coordination of the Na atoms.

Keywords: Uranium (IV) oxalates; Uranium (IV)–Lanthanide (III) oxalates; Uranium (IV)–Lanthanide (III) mixed site

1. Introduction

Many publications have been devoted in the last decades to the chemistry of actinides and lanthanides associated with oxalic acid. Indeed, oxalic acid is often used as precipitating agent—in the industrial plutonium conversion process or for waste decontamination purpose—or as complexing agent to adjust extracting characteristics of actinides and lanthanides or redox behavior of actinides. Thus chemical properties of actinide and lanthanide oxalates were often investigated

---

*Corresponding author. Fax: +33 3 20 –43 68 14
E-mail address: francis.abraham@ensc-lille.fr (F. Abraham).

0022-4596/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2005.06.031

in the past, but surprisingly enough, only few crystallographic structures of these compounds have been determined.

Layered lanthanide oxalates $[Ln(H_2O)_3]_2(C_2O_4)_3\cdot xH_2O$ have been obtained for Ln = La, Ce, Pr [1–3], Eu–Dy [4] and Er [5]. In the particular $[Nd(H_2O)_2]_2(C_2O_4)_3$ compound double layers are formed [6]. Structures of monovalent ion–lanthanide oxalates corresponding to $M^+/Ln^{3+} = 1$ (called throughout this paper **112** compounds in relation to the $M/Ln/Ox = 1/1/2$ ratio) have also been established. $M[La(H_2O)_2](C_2O_4)_2\cdot H_2O$, ($M$ = K, NH_4) [7], $(NH_4)[Gd(H_2O)](C_2O_4)_2$ and $(NH_4)La(C_2O_4)_2$ [8] contains lanthanide-oxalate layers, although a three-dimensional framework is built in $M[Ce(H_2O)](C_2O_4)_2\cdot H_2O$, ($M$ = Li, Na) [9]. Only one series of compounds corresponding to $M^+/Ln^{3+}\neq 1$, **313** compounds, has been reported for $K_3[Ln(H_2O)](C_2O_4)_3\cdot 2H_2O$, ($Ln$ = Nd, Sm, Eu, Gd, Tb) in which chains of Ln^{3+} alternating with oxalate ions are formed [10].

The crystal chemistry of actinides oxalates is certainly more rich but less investigated. The only simple actinide (IV) oxalates ($An/Ox = 1/2$) belong to the series $An(C_2O_4)_2\cdot 6H_2O$ (An = Np, U, Pu) [11,12]. Dihydrates $An(C_2O_4)_2\cdot 2H_2O$ (An = Th, U, Pu) have also been reported but without structural study [11]. Plutonium (III) oxalate $Pu_2(C_2O_4)_3\cdot 10H_2O$ [13] is isomorphic with $[Ln(H_2O)_3]_2(C_2O_4)_3\cdot 7H_2O$; Ln = La, Ce, Pr, Nd [1–3]. With monovalent cations, only $K_4An(C_2O_4)_4\cdot 4H_2O$ oxalates (**414** compounds) have been reported for An = Th [14] and U [15]. Two series of oxalates containing both actinide and lanthanide have been reported for composition $MLn^{III}U^{IV}(C_2O_4)_4$ (**124** compounds) for Ln = La, Ce, Pr, Nd, Tb and $M = K^+$ [16] and NH_4^+ [17]. They were characterized by chemical, infrared spectroscopy, powder X-ray diffraction and thermal methods, without any structure determination. While exploiting the $M/Ln/An$ ratio, many new double or triple oxalates should be obtained. In fact, crystal growth of actinide and lanthanide oxalates is not easy at all.

Recently, we have demonstrated the efficiency of crystal growth of oxalate compounds by using the slow diffusion of ions through silica gel impregnated with oxalic acid [18,19]. The use of this crystal growth method from gel for several M^I–U^{IV}–Ln^{III} systems (M^I = Na, NH_4, N_2H_5, Ln^{III} = Ce, Nd, Sm, Gd) enabled us to isolate crystals of a new uranium(IV) oxalate $(NH_4)_2U_2^{IV}(C_2O_4)_5\cdot 0.7H_2O$ (**225** compound) and of double U(IV)–Ln(III) oxalates resulting from the partial substitution of U^{IV} by Ln^{III} up to $M_3ULn(C_2O_4)_5\cdot 10.4H_2O$ (**325** compounds) obtained for M = Na and Ln = Ce. The preparation of single crystals and the X-ray crystal structure study of these new oxalates are reported in the first part of this work.

2. Experimental

2.1. Crystal synthesis

Single crystals of $(NH_4)_2U_2(C_2O_4)_5\cdot 0.7H_2O$ (**1**), $(N_2H_5)_{2.6}U_{1.4}Nd_{0.6}(C_2O_4)_5\cdot xH_2O$ (**2**), $(N_2H_5)_{2.6}U_{1.4}Sm_{0.6}(C_2O_4)_5\cdot xH_2O$ (**3**), $Na_{2.46}U_{1.54}Nd_{0.46}(C_2O_4)_5\cdot 7.6H_2O$ (**4**) and $Na_3UCe(C_2O_4)_5\cdot 10.4H_2O$ (**5**) were obtained by the slow diffusion of the cations U^{4+} and Ln^{3+} (Ln = Ce, Sm or Nd) through silica gel impregnated with oxalic acid [20]. The silica gel is prepared by pouring 1 M sodium metasilicate solution into a mixture of 1 M oxalic acid and 3 M nitric acid so as to get a pH between 3.5 and 4. Nitric acid is used to acidify the medium and oxalic acid as a source of anions. The resulting solution is then allowed to set in tubes of internal diameter 15 mm. To extend the scope of this mean of synthesis, substitution by other monovalent cations like ammonium or hydrazinium cations has been performed by ionic exchange between the silica gel and a nitric solution of oxalic acid 0.2 M and ammonium or hydrazinium nitrate 2 M added on the gel. For each silica gel, several crystal growths were experimented for Ln = Ce, Nd, Sm and Gd. Five single crystals belonging to the family presented in this paper were obtained, only three of them were good enough for a complete structure determination by X-ray diffraction.

Compound **1**. When an aqueous solution of U^{4+} (0.66 M, 1mL) and ammonium cations (2 M, 4 mL), acidified by 3 M nitric acid (4 mL) is slowly added on the set ammonium-exchanged gel, green needle-like shaped crystals with an hexagonal cross section form slowly inside the gel.

Compounds **2** *and* **3**. The addition of a nitric mixture (3 M, 2 mL) of uranium (IV) (0.66 M, 1 mL) neodymium or samarium (0.25 M, 1 mL) and hydrazinium (0.3 M, 10 mL) cations above an hydrazinium-exchanged gel permitted the synthesis of **2** and **3**. Crystals are green and exhibit a needle-like shape with a hexagonal cross section.

Compound **4**. When a mixture of aqueous solutions of U^{4+} (0.5 M, 3 mL) and Nd^{3+} (0.25 M, 6 mL) nitrates, acidified by 3 M nitric acid (3 mL) is slowly added on the set Na^+-gel, prismatic green crystals with an hexagonal section of mixed uranium–neodymium–sodium oxalate **4** form slowly inside the gel.

Compound **5**. The slow addition on the set Na^+-gel of a mixture of aqueous solutions of U^{4+} (0.5 M, 1 mL) and Ce^{3+} (0.25 M, 2 mL) nitrates, acidified by 3 M nitric acid (5 mL) leads to the formation inside the gel of prismatic green crystals with an hexagonal section of **5.**

For all compounds single crystals were isolated after a 2–8 days crystallization process.

Crystal growth in silica gels is a quite particular method because ions diffusion rates, local concentrations and pH cannot be controlled, so the chemical composition of resulting crystals is not always in agreement with the starting stoichiometric ratios of the solutions and can display some variations depending on the position within the gel. So, CHN compositional and TGA analysis cannot be performed. Furthermore, good enough crystals are not always obtained. For example, using hydrazinium exchanged gel and mixtures of U^{4+} and Nd^{3+} or Sm^{3+} cations, crystals of mixed hydrazinium–uranium–neodymium or samarium oxalates **2** and **3** similar to **1** were obtained but the quality of the crystals did not allow a complete structural determination. Finally, for the three used gels containing Na^+, NH_4^+ or $N_2H_5^+$, no single crystal belonging to the hereafter reported family was obtained using Gd^{3+}. On the opposite, with Na^+ and $N_2H_5^+$-gels, by slightly changing synthesis conditions crystals belonging to other families are obtained.

2.2. Single-crystal data collection

The single crystal diffraction intensities for each compound **1**, **4** and **5** were measured on a AXS BRUKER SMART CCD-1 K diffractometer system equipped with a fine-focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power. The detector was placed at a distance of 5.41 cm from the crystal under the conditions given in Table 1 and extracted from the collected frames using the program SaintPlus 6.02 [21]. The structure resolutions and refinements were performed with the SHELXTL software package [22]. The lattice parameters were refined from the complete data set and an empirical absorption correction was performed for all compounds [23]. The heavy atoms were located using the direct methods, while the remaining atoms were found from successive Fourier map analyses. The location of the H atoms of water molecules was not determined because of the presence of very heavy atoms and important thermal agitation of water molecules. The atomic positions for all atoms and the anisotropic displacement parameters for U (compound **1**) and for all the non-water oxygen atoms (compounds **4** and **5**) were included in the last cycles of refinement.

Table 1
Crystal data and structure refinement for the four mixed oxalate compounds

Compound	**1**	**4**	**5**
Empirical formula	$U_2N_2C_{10}O_{20.7}H_{9.4}$	$U_{1.44}Nd_{0.56}Na_{2.56}C_{10}O_{30}H_{20}$	$UCeNa_3C_{10}O_{30.4}H_{20.8}$
Formula weight	964.86	1099.14	1074.32
Crystal size (μm)	100 × 30 × 40	150 × 50 × 60	150 × 40 × 50
Crystal system	Hexagonal	Orthorhombic	Monoclinic
Space group	$P6_3/mmc$	$Pbcn$	$C2/c$
a (Å)	19.177(3)	18.79(3)	18.878(6)
b (Å)		11.46(1)	11.684(4)
c (Å)	12.728(4)	12.77(2)	12.932(4)
β (deg)			95.97(1)
Volume (Å^3)	4054(2)	2752(6)	2838(2)
Z	6	4	4
Density (calculated)	2.371	2.601	2.468
Absorption correction	Empirical	Empirical	Empirical
Absorption coef.(mm^{-1})	12.055	9.648	7.472
$F(000)$	2616	1967	1945
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073 Å	0.71073	0.71073
Theta range for data collection	2.45–25.00	2.17–28.23	2.05–31.03
Index ranges	$-22 \leqslant h \leqslant 22$ $-22 \leqslant k \leqslant 22$ $-15 \leqslant l \leqslant 15$	$-23 \leqslant h \leqslant 24$ $-15 \leqslant k \leqslant 14$ $-16 \leqslant l \leqslant 16$	$-27 \leqslant h \leqslant 26$ $-16 \leqslant k \leqslant 16$ $-18 \leqslant l \leqslant 18$
Reflections collected	14,979	14,205	12,814
Independent reflections	1360 [R(int) = 0.0368]	3026 [R(int) = 0.0535]	4060 [R(int) = 0.0374]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Weighting scheme	Sigma	Sigma	Sigma
Data/restraints/parameters	1360/3/52	3026/0/183	4060/0/213
Final R indices	$R_1 = 0.0575$ w$R_2 = 0.1331$ [$I > 2$sigma(I)]	$R_1 = 0.0511$ w$R_2 = 0.1186$ [$I > 2$sigma(I)]	$R_1 = 0.0416$, w$R_2 = 0.0893$ [$I > 2$sigma(I)]
R indices (all data)	$R_1 = 0.1295$, w$R_2 = 0.1651$	$R_1 = 0.1215$ w$R_2 = 0.1369$	$R_1 = 0.0768$, w$R_2 = 0.0973$
Extinction coefficient	/	/	0.00017(4)
Largest diff. peak/hole (e.Å^{-3})	1.845/−1.237	1.994/−1.014	1.792/−1.362

2.3. Chemical composition analysis

Chemical composition analysis was performed by Energy Dispersive Spectroscopy (EDS) on a JSM 5300 Scanning Electronic Microscope (SEM) equipped with a PGT X-ray microanalysis system (IMIX).

3. Structure solution and refinement

The crystal structure determination of **1** was led in two steps. First the structure was solved in trigonal symmetry, with space group *P*3 and lattice parameters $a \approx 11.10$ and $c \approx 6.38$ Å in agreement with that published by Charushnikova et al. [24] for the mixed oxalate $H_2Np_2(C_2O_4)_5 \cdot 9H_2O$. Unfortunately, the structure solution was chemically unacceptable; indeed an oxalate ion is disordered on three positions related by a three-fold axis passing through the U atom leading to aberrant interatomic distances and angles within non-planar oxalate ions. Finally, considering the weak reflections, the structure was refined in the actual cell with hexagonal symmetry, space group $P6_3/mmc$ and lattice parameters $a = 19.177(3)$ and $c = 12.728(4)$ Å. The localization of water molecules and ammonium ions inside the channels was more laborious. Indeed water O and ammonium N atoms cannot be distinguished and are considered as disordered on four partially occupied sites. In the last stages of the refinement the isotropic displacement parameters for these atoms were fixed to 0.08 Å^2, as usually found in related materials [25].

The crystals of **2** and **3** are not sufficiently good quality to allow a complete structural determination, however, the crystallographic data and the main structural features deduced from a structural approach indicate that these compounds are isotypic with **1**. The hexagonal unit cells are similar, $a = 19.243(4)$, $c = 12.760(5)$ Å for **2**, $a = 19.211(3)$, $c = 12.274(4)$ Å for **3** and metal and oxalate atoms are located in the same positions. The main characteristic of these structures is the substitution of one part of the uranium by neodymium (**2**) or samarium (**3**) without any structural modification of the metal–oxalate framework. For **2**, the structural approach, considering refinement of the U/Nd ratio in the same crystallographic site with equal anisotropic displacement parameters, led to U/Nd $= 0.7(1)/0.3$ in agreement with EDS analysis performed on the same single crystal. EDS analysis of crystal **3** indicates a close value for the U/Sm ratio. Unfortunately, due to the bad quality of the single crystals, the numerous low-intensity reflections, the disorder of both hydazinium ions and water molecules lying in large tunnels and the sensitivity of the water content to both the synthesis conditions and the ambient water-pressure and temperature commonly found in similar compounds [26], it was not possible to satisfactorily refine the tunnels content. The chemical formula of **2** and **3** were established assuming the neutralization of the metal–oxalate framework by hydrazinium ions as confirmed by the structural study of crystals **4** and **5**.

The crystal structure of **4** was solved in the orthorhombic symmetry with space group *Pbcn* with lattice parameters $a = 18.79(3)$, $b = 11.46(1)$, $c = 12.77(2)$ Å. As in the preceding structural resolution, the determination of the crystal chemical composition using EDS spectroscopy led to the introduction of a mixed site uranium(IV)–neodymium(III). Uranium and neodymium atoms were fixed in the same crystallographic site with equal anisotropic displacement parameters. The occupancy of their crystallographic position was refined to U(IV)/Nd(III) ratio equal to 0.77(1)/0.23. The occupancy rate of the sodium atom Na(2) site is also refined and the resulting value (0.46(2)) is in good agreement with the charge neutrality. Finally, the site-occupancy factor of the weakly bonded oxygen–water atoms were refined with displacement parameters fixed to 0.08 Å^2 leading to 7.6(1) water molecules per chemical formula.

Finally, the structure of the mixed oxalate **5** was solved in a monoclinic symmetry in space group $C2/c$ with lattice parameters $a = 18.878(6)$, $b = 11.684(4)$, $c = 12.932(4)$ Å and $\beta = 95.97(1)^\circ$ (Table 1). At first, it was thought that the crystal contained only uranium and sodium as metallic ions: the structure resolution led to the formula $U_2Na_3(C_2O_4)_5(OH) \cdot nH_2O$ which implied that hydroxyl ion was necessary to ensure the charge neutrality. As the pH of the solution used was very low this solution was not very credible. Moreover, distance calculations indicate that this OH^- anion does not belong to the uranium coordination sphere. Then, the analysis by EDS was performed on a number of crystals of this batch and revealed, besides uranium and sodium, the presence of cerium in the entire sample with ratio U/Ce close to unity. Then, in final cycles of refinement, uranium and cerium were introduced in the same crystallographic position with equal anisotropic displacement parameters and the partial occupancy rate of each element was fixed to 0.5. So, the resulting formula $UCeNa_3(C_2O_4)5 \cdot 10.4H_2O$ was in agreement with the experimental conditions. The splitting of U and Ce over two close sites did not improve the results.

The atomic positional parameters and displacement parameters are given in Tables 2–4 for compounds **1**, **4** and **5**, respectively.

4. Results and discussion

The compound $(NH_4)_2U_2(C_2O_4)_5 \cdot 0.7H_2O$ (**1**) exhibits a three-dimensional arrangement of U-centered polyhedra linked through bis–bidentate oxalate groups. The U(IV) atom is ten-fold coordinated by oxygen atoms from five bidentate oxalate groups and the polyhedron can be described as a bi-capped square antiprism (Fig. 1). This coordination of U(IV) by five oxalate ions is similar to that observed in the two forms of $K_4U(C_2O_4)_4 \cdot 4H_2O$ [15]. Although the overall structure has three-dimensional connectivity it may be useful in a first instance to consider layers in the (0 0 1) plane formed by U–Ox–U edge-shared hexagonal six-membered rings $[UOx]_6$ where Ox denotes an oxalate ion (Fig. 2.1a). These layers are similar to those obtained in $(NH_4)_2[(UO_2)_2(C_2O_4)_3] \cdot 3H_2O$ [19] which are formed by uranyl and oxalate ions. In this compound the presence of uranyl bonds perpendicular to the layers precluded their connection; on the opposite, in **1** the layers are further linked in the third direction along c via other bridging oxalate groups (Fig. 2.1b and c) leading to a honeycomb-like structure. The large one-dimensional tunnels running down the [001] direction are occupied by NH_4^+ ions and water molecules distributed over several sites.

Selected interatomic distances are listed in Table 5. The U–O bond lengths vary in a narrow range from 2.441(14) to 2.507(11) Å with a mean U–O, 2.46(1) Å in agreement with the value calculated in the orthorhombic and triclinic forms of $K_4U(C_2O_4)_4 \cdot 4H_2O$, 2.45(1) and 2.47(1) Å, respectively [15]. Bond valence sum calculations using Brese and O'Keeffe data [27] with $b = 0.37$ Å provide value of 3.9 consistent with formal valence U^{4+}.

The bond lengths and bond angles in the oxalate ligands (distances C–O range from 1.165(16) to 1.300(15) Å and C–C from 1.496(17) to 1.522(18) Å, average angle O–C–O is 126(1)° and O–C–C is 117(1)°) are in good agreement with the mean values reported by Hahn for oxalate compounds, C–O = 1.24 Å, C–C = 1.55 Å, O–C–O = 125°, O–C–C = 117° [28].

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $(NH_4)_2U_2(C_2O_4)_5 \cdot 0.7H_2O$

Atom	Site	Occup.	*x*	*y*	*z*	*U*(eq.)
U(1)	12*i*	1	0.33305(5)	0.33305(5)	1/2	0.0184(3)
O(1)	24*l*	1	0.3280(9)	0.4017(9)	0.6608(11)	0.057(4)
O(2)	24*l*	1	0.2659(7)	0.4157(6)	0.4783(8)	0.026(3)
O(3)	24*l*	1	0.1895(7)	0.2624(7)	0.5431(9)	0.030(3)
O(4)	24*l*	1	0.4130(9)	0.4667(9)	0.4214(11)	0.057(4)
O(5)	24*l*	1	0.3053(8)	0.2565(8)	0.6630(11)	0.051(4)
C(1)	12*j*	1	0.3274(15)	0.3722(12)	3/4	0.026(6)
C(2)	12*j*	1	0.3124(12)	0.2882(11)	3/4	0.009(5)
C(3)	12*k*	1	0.1477(7)	0.2954(14)	0.530(2)	0.047(8)
C(4)	12*k*	1	0.1914(6)	0.3827(13)	0.4940(19)	0.025(5)
C(5)	12*k*	1	0.4837(6)	0.5163(6)	0.4596(16)	0.035(7)
N/O(1)	2*a*	0.63(13)	0	0	1/2	0.08
N/O(2)	12*k*	0.23(5)	0.376(4)	0.624(4)	0.480(10)	0.08
N/O(3)	24*l*	0.31(4)	0.435(4)	0.639(4)	0.659(5)	0.08
N/O(4)	12*j*	0.41(4)	0.342(4)	0.519(4)	1/4	0.08

U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

Table 3
Atomic coordinates and equivalent isotropic displacement parameters for $Na_{2.46}U_{1.54}Nd_{0.46}(C_2O_4)_5 \cdot 7.6H_2O$

Atom	Site	Occup.	*x*	*y*	*z*	*U*(eq.)
U/Nd	8*d*	0.77(1)/0.23	0.67114(2)	0.00223(4)	0.02364(16)	0.0170(2)
C(1)	8*d*	1	0.4977(6)	0.0421(12)	0.0453(1)	0.028(3)
C(2)	8*d*	1	0.7045(7)	0.0354(10)	0.2758(9)	0.024(3)
C(3)	8*d*	1	0.6523(6)	−0.0704(11)	0.2745(10)	0.028(3)
C(4)	8*d*	1	0.7849(6)	0.2198(10)	0.0073(8)	0.018(3)
C(5)	8*d*	1	0.7162(7)	0.2802(11)	0.0439(9)	0.025(3)
O(1)	8*d*	1	0.6616(4)	0.2221(7)	0.0527(7)	0.030(2)
O(2)	8*d*	1	0.6601(4)	−0.2194(7)	0.0037(7)	0.028(2)
O(3)	8*d*	1	0.7783(4)	0.1144(7)	−0.0152(6)	0.026(2)
O(4)	8*d*	1	0.7782(3)	−0.1107(6)	0.0662(6)	0.024(2)
O(5)	8*d*	1	0.7244(4)	0.0740(7)	0.1888(6)	0.030(2)
O(6)	8*d*	1	0.6381(4)	0.1114(7)	−0.1406(6)	0.030(2)
O(7)	8*d*	1	0.6318(4)	−0.1004(7)	0.1856(6)	0.030(2)
O(8)	8*d*	1	0.7241(4)	−0.0707(6)	−0.1373(6)	0.028(2)
O(9)	8*d*	1	0.5540(4)	0.0767(6)	0.0846(6)	0.026(2)
O(10)	8*d*	1	0.4357(4)	0.0767(6)	0.0678(7)	0.034(2)
Na(1)	8*d*	1	0.5519(4)	0.2834(6)	0.1302(6)	0.092(3)
Na(2)	4*a*	0.46(2)	1/2	1/2	0	0.073(7)
O(w11)	8*d*	0.89(2)	0.5890(7)	0.4849(10)	0.1284(11)	0.08
O(w12)	8*d*	0.87(2)	0.5731(6)	0.2924(11)	0.3141(11)	0.08
O(w13)	8*d*	0.69(2)	0.3907(9)	0.5145(13)	0.1298(14)	0.08
O(w14)	8*d*	0.72(2)	0.4940(7)	0.3001(16)	−0.0503(15)	0.08
O(w15)	4*c*	0.56(3)	1/2	0.218(3)	−1/4	0.08
O(w16)	8*d*	0.36(2)	0.3756(16)	0.651(3)	0.258 (2)	0.08

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 4
Atomic coordinates and equivalent isotropic displacement parameters for $Na_3UCe(C_2O_4)_5 \cdot 10.4H_2O$

Atom	Site	Occup.	x	y	z	U(eq.)
U/Ce	8f	0.5/0.5	0.1723(1)	0.5017(1)	−0.0056(1)	0.017(1)
C(1)	8f	1	−0.0038(4)	0.5417(6)	−0.0445(6)	0.025(1)
C(2)	8f	1	0.2058(4)	0.4647(6)	0.2482(5)	0.024(1)
C(3)	8f	1	0.1555(4)	0.5672(6)	0.2403(5)	0.026(1)
C(4)	8f	1	0.2847(4)	0.2800(6)	−0.0111(5)	0.022(1)
C(5)	8f	1	0.2159(3)	0.7793(6)	−0.0248(5)	0.020(1)
O(1)	8f	1	0.1607(2)	0.7186(4)	−0.0356(4)	0.026(1)
O(2)	8f	1	0.1611(2)	0.2807(5)	0.0111(4)	0.027(1)
O(3)	8f	1	0.2803(3)	0.6170(4)	0.0452(4)	0.025(1)
O(4)	8f	1	0.2787(3)	0.3863(4)	−0.0303(4)	0.028(1)
O(5)	8f	1	0.2250(3)	0.4274(4)	0.1652(4)	0.030(1)
O(6)	8f	1	0.1404(3)	0.6112(4)	0.1539(4)	0.033(1)
O(7)	8f	1	0.1328(3)	0.4018(5)	−0.1756(4)	0.034(1)
O(8)	8f	1	0.2249(3)	0.5731(4)	−0.1628(4)	0.031(1)
O(9)	8f	1	0.0523(3)	0.5724(4)	−0.0813(4)	0.029(1)
O(10)	8f	1	0.0657(2)	0.4245(4)	0.0741(4)	0.030(1)
Na(1)	8f	1	0.0494(2)	0.7702(3)	−0.1262(3)	0.047(1)
Na(2)	4a	1	1/2	1/2	0	0.054(1)
Ow(11)	8f	1	0.4161(3)	0.5335(6)	0.1216(6)	0.052(2)
Ow(12)	8f	1	0.0739(4)	0.7741(6)	−0.2970(6)	0.060(2)
Ow(13)	8f	1	0.6056(4)	0.5145(7)	0.1195(6)	0.071(2)
Ow(14)	8f	1	0.4896(4)	0.3004(6)	0.0358(6)	0.058(2)
Ow(15)	4e	0.84(2)	0	0.2962(13)	−1/4	0.079(6)
Ow(16)	8f	0.78(2)	0.6331(5)	0.3515(7)	0.2644(8)	0.064(4)

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

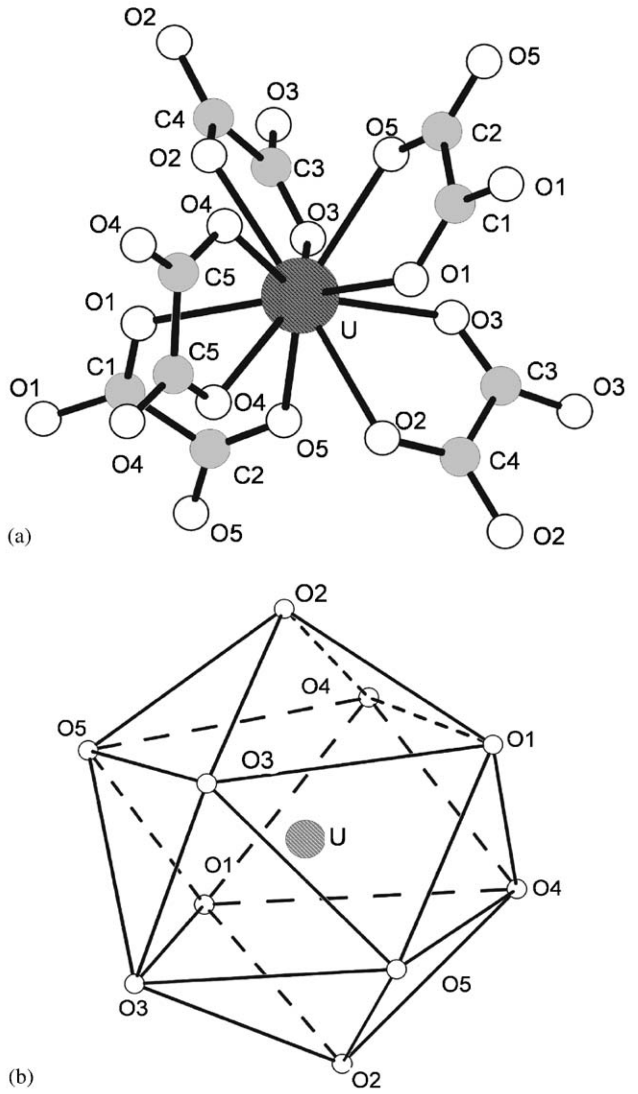

Fig. 1. The coordination of U(IV) ion in $(NH_4)_2U_2(C_2O_4)_5 \cdot 0.7H_2O$ by five oxalate ions and the oxygen polyhedron described as a bi-capped square antiprism.

The compounds $(N_2H_5)_{2.6}U_{1.4}Ln_{0.6}(C_2O_4)_5 \cdot xH_2O$ (Ln = Nd, **2** and Ln = Sm, **3**) are characterized by the same three-dimensional arrangement of U-centered polyhedra linked through bis–bidentate oxalate groups but, astonishingly U(IV) is partially substituted by Ln(III) in the same crystallographic site, the deficit of charge being compensated by additional monovalent ions. In **2** and **3,** there is a great disorder between the water molecules and between the hydrazonium cations, so nitrogen and oxygen atoms are very difficult to localize precisely.

The compound $Na_{2.56}U_{1.44}Nd_{0.56}(C_2O_4)_5 \cdot 7.6H_2O$ **(3)** has practically the same composition as **2** and **3** with Na^+ replacing $N_2H_5^+$. The orthorhombic unit cell is related to the hexagonal cell of **1** by:

$$\begin{bmatrix} a_0 \\ b_0 \\ c_0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ \frac{1}{3} & \frac{1}{3} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} a_h \\ b_h \\ c_h \end{bmatrix}.$$

Selected interatomic distances for **4** and **5** are listed in Table 6. The arrangement of U/Nd and oxalate ions in the (001) plane is very similar (Fig. 2.3a), on the contrary the relative orientations of the oxalate entities connecting the metal ions in the [001] direction are different for the compounds **4** and **1** (Fig. 2.4b and c). The three-dimensional arrangement in **4** allows the accommodation of a greater number of water molecules necessary to the environment of the sodium ions. In fact the two independent Na atoms are coordinated to six oxygen atoms forming distorted octahedra. The Na(1) atom is linked to the oxalate–U/Nd framework by O(1) and O(9) atoms, the octahedron is completed by four water molecules (Table 6). The coordination of Na(2) located on an inversion center is assured by six water molecules with Na(2)–OH_2 distances spread from 2.349(14) to 2.645(18) Å. The water molecules located in the sodium atoms neighborhood are connected to the three-dimensional network by hydrogen bonds. Depending on the occupancy (τ) of the Na(2) site, a domain

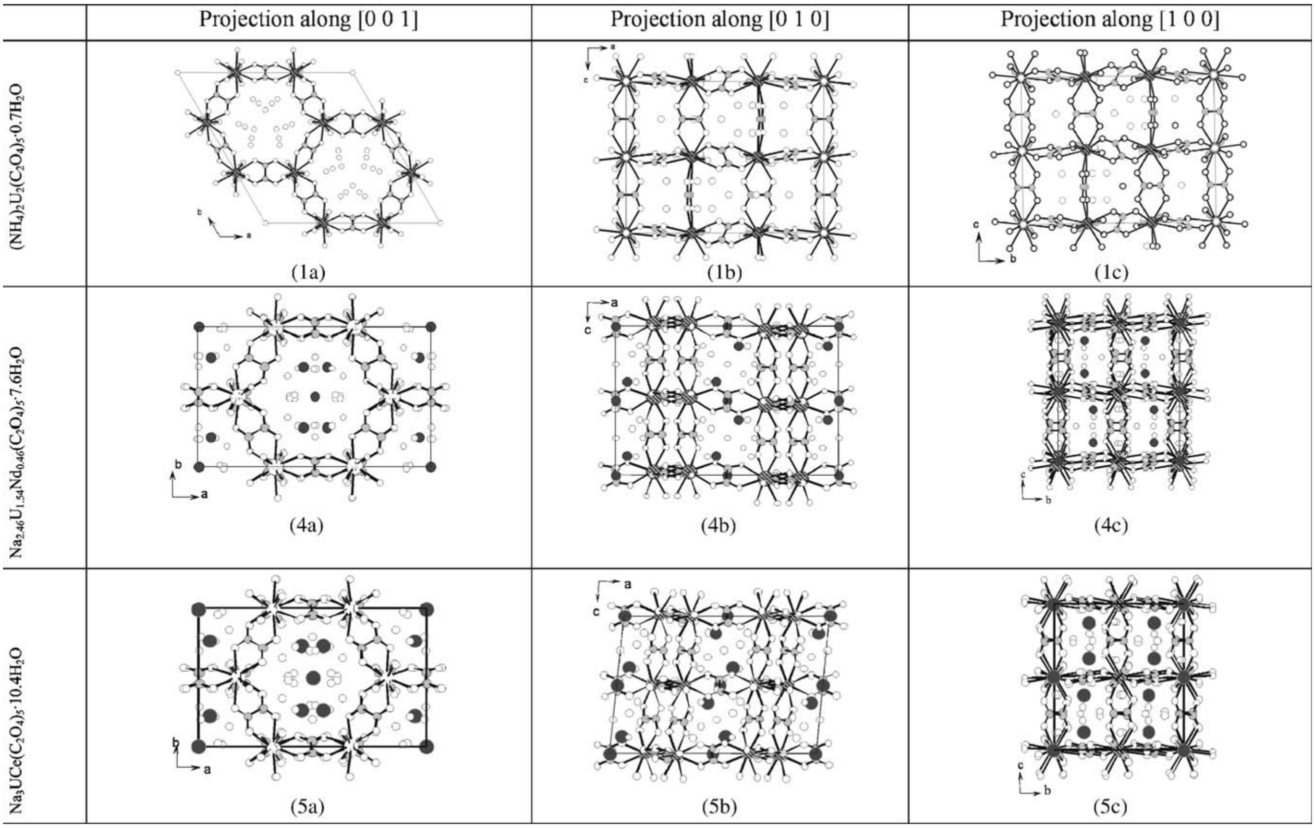

Fig. 2. Comparison of the homeotypic crystal structures of $(NH_4)_2U_2(C_2O_4)_5 \cdot 0.7H_2O$ (first line), $Na_{2.56}U_{1.44}Nd_{0.56}(C_2O_4)_5 \cdot 7.6H_2O$ (second line) and $Na_3UCe(C_2O_4)_5 \cdot 10.4H_2O$ (third line). The projection of the structures along the [001] direction (left column) shows the same layered arrangement of hexagonal rings of metallic ions connected by bis–bidentate oxalate entities and the occupation of the tunnels of the honeycomb like structure by the monovalent ions together with water molecules. The projections along [100] (middle column) and [010] (right column) directions show the role of the oxalates that connect the layers and the distortion of the arrangement leading to various symmetries, hexagonal, orthorhombic and monoclinic from the first line to the third.

Table 5
Significant bond lengths [Å] and angles [°] for $(NH_4)_2U_2(C_2O_4)_5 \cdot 0.7H_2O$

Within the UO₁₀ polyhedron			
U–O(1) (2*x*)	2.462(15)		
U–O(2) (2*x*)	2.507(11)		
U–O(3) (2*x*)	2.447(11)		
U–O(4) (2*x*)	2.448(15)		
U–O(5) (2*x*)	2.441(14)		
Within the oxalate groups			
C(1)–C(2)	1.496(17)	O(1)–C(1)–O(1)	128(2)
C(1)–O(1)	1.165(16)	O(1)–C(1)–C(2)	116.0(13)
C(2)–O(5)	1.235(15)	O(5)–C(2)–O(5)	127(2)
		O(5)–C(2)–C(1)	116.2(10)
C(3)–C(4)	1.522(18)	O(2)–C(4)–O(2)	125(2)
C(3)–O(3)	1.257(15)	O(2)–C(4)–C(3)	117.6(10)
C(4)–O(2)	1.257(14)	O(3)–C(3)–O(3)	126(2)
		O(3)–C(3)–C(4)	117.1(11)
C(5)–C(5)	1.497(19)	O(4)–C(5)–O(4)	125.2(15)
C(5)–O(4)	1.300(15)	O(4)–C(5)–C(5)	116.9(8)

of existence from $Na_2U_2(C_2O_4)_5 \cdot nH_2O$ ($\tau = 0$) to $Na_3UNd(C_2O_4)_5 \cdot nH_2O$ ($\tau = 1$) can be expected.

Whereas $Na_2U_2(C_2O_4)_5 \cdot nH_2O$ single crystals could not be obtained under our experimental conditions, single crystals of the other limit $Na_3ULn(C_2O_4)_5 \cdot nH_2O$ were obtained for $Ln = Ce$ (compound **5**). Once again the network in the (001) plane is very similar with an increase of the translation symmetry to a *C*-centered-base (Fig. 2.5a), but the connection in the [001] direction leads to a distortion of the unit cell to a monoclinic symmetry (Fig. 2.5b and c). In the two Na containing compounds the sites of the water molecules coordinated to Na are fully occupied. The total occupation of the Na(1) site on a inversion center in **5** is accompanied by a very symmetrical environment with Na–OH$_2$ distances varying in a narrow range from 2.378(7) to 2.399(8) Å. The increase of the U/*Ln*–O average distance from **4** to **5** is in agreement with the higher U^{IV}/Ln^{III} substitution rate and with the increase of the Ln^{III} radius from Nd^{III} to Ce^{III} [29].

Table 6
Significant bond lengths [Å] and angles [°] for $Na_{2.46}U_{1.54}Nd_{0.46}(C_2O_4)_5 \cdot 7.6H_2O$ and $Na_3UCe(C_2O_4)_5 \cdot 10.4H_2O$

(U,*Ln*)O_{10} polyhedron	*Ln* = Nd	*Ln* = Ce			
U/*Ln*–O(8)	2.432(8)	2.497(5)			
U/*Ln*–O(3)	2.441(8)	2.476(5)			
U/*Ln*–O(4)	2.454(7)	2.468(5)			
U/*Ln*–O(5)	2.475(8)	2.483(5)			
U/Ln–O(9)	2.486(8)	2.513(5)			
U/*Ln*–O(7)	2.492(8)	2.532(5)			
U/*Ln*–O(10)	2.494(8)	2.521(5)			
U/*Ln*–O(6)	2.520(8)	2.552(5)			
U/*Ln*–O(1)	2.554(9)	2.570(5)			
U/*Ln*–O(2)	2.562(8)	2.601(5)			
Na(1)O_6 polyhedron	*Ln* = Nd	*Ln* = Ce	Na(2)O_6 polyhedra	*Ln* = Nd	*Ln* = Ce
Na(1)–O(w12)	2.385(16)	2.304(8)	Na(2)–Ow(11) (2*x*)	2.349(14)	2.378(7)
Na(1)–O(w11)	2.413(13)	2.383(7)	Na(2)–O(w14) (2*x*)	2.383(19)	2.390(7)
Na(1)–O(w12)	2.456(15)	2.433(8)	Na(2)–O(w13) (2*x*)	2.645(18)	2.399(8)
Na(1)–O(w14)	2.56(2)	2.506(8)			
Na(1)–O(1)	2.393(10)	2.376(6)			
Na(1)–O(9)	2.441(10)	2.382(6)			
Oxalate groups	*Ln* = Nd	*Ln* = Ce		*Ln* = Nd	*Ln* = Ce
C(1)–C(1)	1.51(3)	1.505(15)	O(9)–C(1)–O(10)	126.6(13)	
C(1)–O(9)	1.237(12)	1.257(8)	O(9)–C(1)–C(1)	117.9(13)	
C(1)–O(10)	1.264(12)	1.254(8)	O(10)–C(1)–C(1)	115.3(12)	
C(2)–C(3)	1.561(198)	1.525(10)	O(8)–C(2)–O(5)	126.2(12)	126.0(7)
C(2)–O(5)	1.254(13)	1.246(8)	O(8)–C(2)–C(3)	116.8(11)	117.1(6)
C(2)–O(8)	1.238(12)	1.250(8)	O(5)–C(2)–C(3)	116.9(10)	116.8(6)
C(3)–O(6)	1.212(13)	1.236(8)	O(6)–C(3)–O(7)	129.8(12)	126.3(7)
C(3)–O(7)	1.247(13)	1.263(8)	O(6)–C(3)–C(2)	115.5(11)	118.1(6)
			O(7)–C(3)–C(2)	114.7(11)	115.6(6)
C(4)–C(5)	1.537(16)		O(2)–C(4)–O(3)	127.9(11)	
C(4)–O(2)	1.247(12)		O(2)–C(4)–C(5)	117.0(10)	
C(4)–O(3)	1.248(13)		O(3)–C(4)–C(5)	115.1(10)	
C(5)–O(1)	1.230(13)		O(1)–C(5)–O(4)	125.0(12)	
C(5)–O(4)	1.287(14)		O(1)–C(5)–C(4)	119.0(11)	
			O(4)–C(5)–C(4)	115.9(10)	
C(5)–C(5)		1.537(13)	O(3)–C(5)–O(1)		126.3(6)
C(5)–O(3)		1.244(8)	O(3)–C(5)–C(5)		117.3(7)
C(5)–O(1)		1.255(8)	O(1)–C(5)–C(5)		116.4(8)
C(4)–C(4)		1.539(14)	O(2)–C(4)–O(4)		127.9(7)
C(4)–O(2)		1.245(8)	O(2)–C(4)–C(4)		117.2(8)
C(4)–O(4)		1.270(8)	O(4)–C(4)–C(4)		114.9(8)

5. Conclusion

Single crystals of five new U(IV) containing oxalates have been obtained using a gel method: an U(IV) oxalate and four mixed U(IV)/*Ln*(III) oxalates with *Ln* = Nd, Sm, Ce. The crystal structure determination shows that these compounds are homeotypic and adopt a honeycomb-type structure based on a three-dimensional arrangement of metallic and oxalate ions. Astonishingly in the mixed U(IV)/*Ln*(III) oxalates, U(IV) and *Ln*(III) are disordered on the same crystallographic site and are ten-coordinated by oxygen atoms from five bidentate oxalate ions. The mixed oxalates can be deduced from the only U(IV) containing oxalate by the substitution $U(IV) \rightarrow Ln(III) + A^+$. Thus solid solutions of the type $A^+_{2+x}U_{2-x}{}^{IV}Ln_x{}^{III}(C_2O_4)_5 \cdot nH_2O$ can be expected for $A^+ = Na^+$, NH_4^+, $N_2H_5^+$. Unfortunately, the gel method does not give good enough crystals for X-ray diffraction in all cases. Changing crystal growth conditions other structural family of lanthanide–actinide oxalates are obtained and will be reported in further papers. In addition, preparation of powder samples is in progress and should allow the determination of the solid solution domains for the different systems and chemical compositional analysis together with TGA to determine the water content for each composition. The results will be presented in a forthcoming paper.

Acknowledgments

This research was financially supported by Cogema, France. We thank Jean Luc Emin, Cogema, France, for encouraging this work and for fruitful discussions.

References

[1] W. Ollendorff, F. Weigel, Inorg. Nucl. Chem. Lett. 5 (1969) 263.
[2] A. Michaelides, S. Skoulika, A. Aubry, Mater. Res. Bull. 23 (1988) 579.
[3] K.K. Palkina, N.E. Kuz'mina, O.V. Koval'chukova, S.B. Strashnova, B.E. Zaitsev, Russ. J. Inorg. Chem. 46 (2001) 1348.
[4] D. Trollet, S. Romero, A. Mosset, J.-C. Trombe, CR. Acad. Sci. Paris, Sér. II b. 235 (1997) 663.
[5] I.V. Kalinina, A.L. Guschin, D.G. Samsonenko, A.V. gerasimenko, M.N. Sokolov, V.P. Fredin, Acta Crystallogr. E 59 (2003) 784.
[6] J.-C. Trombe, J. Jaud, J. Chem. Crystallogr. 33 (2003) 19.
[7] T. Bataille, M. Louër, J.-P. Auffredic, D. Louër, J. Solid State Chem. 150 (2000) 81.
[8] J.-C. Trombe, P. Thomas, C. Brouca-Cabarrecq, Solid State Sci. 3 (2001) 309.
[9] S. Romero, A. Mosset, J.-C. Trombe, Eur. J. Solid State Inorg. Chem. 32 (1995) 1053.
[10] I.A. Kahwa, F.R. Fronczeck, J. Selbin, Inorg. Chim. Acta 82 (1984) 161.
[11] I.L. Jenkins, F.H. Moore, J. Inorg. Nucl. Chem. 27 (1965) 81.
[12] M.S. Grigor'ev, I.A. Charushnokova, N.N. Krot, A.I. Yanovskii, Yu.T. Struchkov, Radiochemistry 39 (1997) 420.
[13] I.L. Jenkins, F.H. Moore, J. Inorg. Nucl. Chem. 27 (1965) 77.
[14] M.N. Akhtar, A.J. Smith, Acta Crystallogr. B 31 (1975) 1361.
[15] M.C. Favas, D.L. Kepert, J.M. Patrick, A.H. White, J. Chem. Soc. Dalton Trans. 3 (1983) 571.
[16] A.K. Chadha, K.D. Singh Mudher, K. Krishnan, N.C. Jayadevan, Thermochim. Acta 191 (1991) 323.
[17] K.D. Singh Mudher, K. Krishnan, A.K. Chadha, V. Venugopal, Thermochim. Acta 297 (1997) 169.
[18] B. Chapelet-Arab, G. Nowogrocki, F. Abraham, S. Grandjean, J. Solid State Chem. 177 (2004) 4269.
[19] B. Chapelet-Arab, G. Nowogrocki, F. Abraham, S. Grandjean, Radiochim. Acta (2005) in press.
[20] H.K. Henisch, Crystals in Gels and Liesegangs Rings, The Pennsylvania State University Press, University Park and London, 1988.
[21] Bruker Analytical X-ray system, SAINT + Version 6.22, Madison, USA, 2001.
[22] G.M. Sheldrick, SHELXTL NT, Program Suite for Solution and Refinement of Crystal Structure Version 5.1, Bruker Analytical X-ray Systems, Madison, WI, 1998.
[23] G.M. Scheldrick, SADABS, Bruker-Siemens Area Detector Absorption and Other Correction, Version 2.03″, Goetingen, Germany, 2001.
[24] I.A. Charushnokova, N.N. Krot, S.B. Katser, Radiochemistry 40 (1998) 558.
[25] E. Jeanneau, N. Audebrand, M. Le Floch, B. Bureau, D. Loüer, J. Solid State Chem. 170 (2003) 330.
[26] E. Jeanneau, N. Audebrand, J.-P. Auffrédic, D. Loüer, J. Mater. Chem. 11 (2001) 2545.
[27] N.E. Brese, M. O'Keeffe, Acta Crystallogr. B 47 (1991) 192.
[28] T. Hahn, Z. Anorg. Allg. Chem. 109 (1957) 438.
[29] R.D. Shannon, Acta Crystallogr. A 32 (1976) 751.