

Two $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ polymorphs: Crystal structure and thermal behavior

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Received 27 November 2006; received in revised form 15 February 2007; accepted 18 February 2007

Available online 28 February 2007

Abstract

Syntheses, crystal structures and thermal behavior of two polymorphic forms of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ are reported. The first modification, $\alpha\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (I), crystallizes in the orthorhombic space group $Fddd$, with $a = 5.6587(1)$, $b = 12.0469(2)$, $c = 26.7201(3)$ Å and $Z = 8$. The second modification, $\beta\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (II), crystallizes in the orthorhombic space group $Pnma$, with $a = 14.6019(2)$, $b = 11.0546(2)$, $c = 5.6340(1)$ Å and $Z = 4$. In both structures, the cerium atoms have eight ligands: four water molecules and four sulfate groups. The mutual position of the ligands differs in (I) and (II), resulting in geometrical isomerism. Both these structures are built up by layers of $\text{Ce}(\text{H}_2\text{O})_4(\text{SO}_4)_2$ held together by a hydrogen bonding network. The dehydration of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is a two step (I) and one step (II) process, respectively, forming $\text{Ce}(\text{SO}_4)_2$ in both cases. During the decomposition of the anhydrous form, $\text{Ce}(\text{SO}_4)_2$, into the final product CeO_2 , intermediate $x\text{CeO}_2 \cdot y\text{Ce}(\text{SO}_4)_2$ species are formed.

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Keywords: $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$; Tetrahydrated ceric sulfate; Cerium sulfate; Sulfate decomposition; Thermogravimetry; Differential scanning calorimetry; X-ray diffraction

1. Introduction

Complex anions play an important role in the chemistry of the lanthanide compounds. A comprehensive review of the rare-earth compounds with complex anions was presented in 2002 by Wickleder [1] covering all data of structurally characterized compounds known so far. Due to the use of complex anions in the separation of rare earth elements, the lanthanide sulfates have been intensively studied and a great number of complexes and salts have been described. The sulfates decompose at elevated temperature and cannot be obtained from their melt. Thus, due to the use of solvent, usually water, most of the known structures are those of hydrated binary and ternary sulfates [1]. The most common hydrated binary lanthanide sulfates are the octahydrates, $M_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. Among the lanthanide salts, the cerium(III) sulfate displays the greatest diversity in the hydrate number. Within the binary

system $\text{Ce}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ hydrate numbers from 4 up to 16 are reported [1,2]. Udupa [3] made a thermal decomposition study on $\text{Ce}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ pointing out two dehydration steps involving nine and five water molecules, respectively. On cooling, $\text{Ce}_2(\text{SO}_4)_3$ rehydrates to give $\text{Ce}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ which slowly converted into $\text{Ce}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ on exposure to open atmosphere for several days [3].

Cerium(IV) sulfate does not show the same diversity as cerium(III) sulfate regarding the hydration grade and only two modifications of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ has been structurally characterized. However, the description of the thermal behavior of tetrahydrated ceric sulfate is ambiguous even in the authoritative handbook [4]. Investigations on the thermal decomposition of tetrahydrated ceric sulfate have revealed obvious disagreement among different references. An early study [5] reported that $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ decomposed into $3\text{CeO}_2 \cdot 4\text{SO}_3$ already at 195 °C, while studies made by Udupa showed [3] that $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ decomposes in four stages, losing two molecules of water in the first stage and in second stage, resulting in the formation of

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anhydrous cerium(IV) sulfate at 340 °C, then $\text{Ce}(\text{SO}_4)_2$ converts into $\text{CeO}_2 \cdot 2\text{Ce}(\text{SO}_4)_2$ which in the final stage, between 700 and 940 °C loses sulfur dioxide and oxygen to give CeO_2 . Tagawa confirmed [6] the same initial decomposition temperature but suggested one single decomposition step from $\text{Ce}(\text{SO}_4)_2$ to the final stage: CeO_2 and SO_3 . Ying and Rudong [7] showed evidence that the dehydration of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ starts at 98 °C and proceeds in two steps up to 322 °C. Further, they suggested [7] that the observed weight lost and endothermic peak in the temperature range 450–495 °C corresponds to the reduction of anhydrous cerium(IV) sulfate, giving $\text{Ce}_2(\text{SO}_4)_3$, SO_2 and O_2 . This reduction process has also been noticed by Zhao [8]. Recent research [9] proposes that the dehydration of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ occurs between 75 and 500 °C and that the initial decomposition temperature is around 600 °C. The weight loss and temperature range observed during the dehydration process does not correlate with the ones reported by other researchers [3–8]. Furthermore, if the dehydration process is assumed to be through the 400 °C range, this would correspond to the starting material $\text{Ce}(\text{SO}_4)_2 \cdot 14\text{H}_2\text{O}$, while if dehydration has been assumed to be completed at approximately 300 °C, this would closely correlate to a starting material of $\text{Ce}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. On cooling, $\text{Ce}(\text{SO}_4)_2$ rehydrates to give $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [3].

Two polymorphic forms of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ have been structurally characterized: one orthorhombic, space group *Pnma* [10] (called the β -form), and one monoclinic, space group *C2/c* [11]. An additional orthorhombic modification, space group *Fddd* (called the α -form) has been known to exist for decades [10,12a] and has been discussed [13,14], but its crystal structure is first reported here.

2. Experimental

2.1. Sample preparations

Single crystals of both the orthorhombic modifications of the $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ product were achieved during studies on the Ce(IV)/Ce(III)–Cr(VI)/Cr(III) redox system [15,16].

Ce(SO₄)₂ · 4H₂O, space group Fddd: A solution of $\text{Ce}(\text{OH})_4$ (probably containing some CeO_2) in concentrated sulfuric acid, intended for synthetic use, was prepared. After several months few rather big ($2.0 \times 0.18 \times 0.14 \text{ mm}^3$) orange-yellow single crystals were formed.

Ce(SO₄)₂ · 4H₂O, space group Pnma: Dried $\text{Ce}(\text{OH})_4$ (0.83 g, 4.00 mmol), probably containing some CeO_2 , and CrO_3 (0.80 g, 8.00 mmol) was dissolved in water (4.0 ml). The solid residue was dissolved in a minimum amount of sulfuric acid solution. After a month, many small ($0.32 \times 0.06 \times 0.06 \text{ mm}^3$) corn-formed and light-yellow colored single crystals were obtained. Crystals of the *Pnma* modification can also be achieved by hydrothermal treatment of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ dissolved in sulfuric

acid solution according to the method described by Lindgren [10].

2.2. Single crystal X-ray analysis

Data were collected using a Siemens SMART CCD diffractometer equipped with a Siemens LT–2A low temperature device, at 22 °C (I) and –90 °C (II). A full sphere of the reciprocal space was scanned by 0.3° steps in ω with a crystal-to-detector distance of 3.97 cm and exposure time per frame, being 1 s for (I) and 20 s for (II). Preliminary orientation matrices were obtained using SMART (Siemens, 1995) [17]. The collected frames were integrated with the orientation matrix updated every 100 frames. Final cell parameters were obtained by refinement on the position of 6440 (I) and 8192 (II) reflections, respectively, with $I > 10\sigma(I)$ after integration of all the data using SAINT (Siemens, 1995) [17]. The data were corrected empirically for absorption and other effects using SADABS [18]. The structures were solved by direct methods and refined by full-matrix least squares on all F^2 data using SHELXTL (Bruker, 2001) [19]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms included in the water molecules were located from difference Fourier maps and refined isotropically with no restraints for (I) and with restrained O–H distances to 0.84 Å and a common temperature factor in case of (II). Details on data collections and refinements are given in Table 1. Further details of the crystal structures may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD–417358 for (I) and CSD–417357 for (II). Molecular graphics: DIAMOND [20].

2.3. Thermogravimetry

The thermogravimetry and differential scanning calorimetry (TG–DSC) measurement was performed by a NETZSCH STA 409 PC Luxx simultaneous thermal analyzer. The samples were heated from room temperature to 1000 °C at a heating rate of 5 °C min^{–1}, kept at 1000 °C for 60 min and finally cooled down at 5 °C min^{–1}. The sample was measured in a dynamic nitrogen atmosphere (gas flow rate 20 mL min^{–1}).

3. Result and discussion

3.1. Structural description

Here we present the crystal structure of two orthorhombic polymorphs of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The first modification of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (I) crystallizes in the space group *Fddd*, with $a = 5.6587(1)$, $b = 12.0469(2)$, $c = 26.7201(3)$ Å and $Z = 8$. The second modification (II), earlier described by Lindgren [10] but without location of the hydrogen atoms, crystallizes in the space group *Pnma*, with $a = 14.6019(2)$, $b = 11.0546(2)$, $c = 5.6340(1)$ Å and $Z = 4$.

Table 1
Crystal data and structure refinement for the two orthorhombic modifications (I) and (II)

Identification code	(I)	(II)
Empirical formula	Ce(SO ₄) ₂ · 4H ₂ O	Ce(SO ₄) ₂ · 4H ₂ O
Formula weight	404.30	404.30
Temperature	22(2) °C	−90(2) °C
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Fddd</i>	<i>Pnma</i>
Unit cell dimensions	<i>a</i> = 5.6587(1) Å <i>b</i> = 12.0469(2) Å <i>c</i> = 26.7201(3) Å	<i>a</i> = 14.6019(2) Å <i>b</i> = 11.0546(2) Å <i>c</i> = 5.6340(1) Å
Volume	1821.50(5) Å ³	909.43(3) Å ³
Z	8	4
Density (calculated)	2.949 Mg/m ³	2.953 Mg/m ³
Absorption coefficient	5.516 mm ^{−1}	5.524 mm ^{−1}
<i>F</i> (0 0 0)	1552	776
Crystal size	2.00 × 0.18 × 0.14 mm ³	0.32 × 0.06 × 0.06 mm ³
θ range for data collection	3.05–32.94°	2.79–32.83°
Index ranges	−8 ≤ <i>h</i> ≤ 8, −18 ≤ <i>k</i> ≤ 18, −40 ≤ <i>l</i> ≤ 40	−22 ≤ <i>h</i> ≤ 22, −16 ≤ <i>k</i> ≤ 16, −8 ≤ <i>l</i> ≤ 8
Reflections collected	7079	15220
Independent reflections	837 [<i>R</i> (int) = 0.0314]	1731 [<i>R</i> (int) = 0.0380]
Completeness to $\theta = 30.50^\circ$	99.7%	99.9%
Max. and min. transmission	0.5123 and 0.0320	0.7328 and 0.2709
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	837/0/45	1731/7/88
Goodness-of-fit on <i>F</i> ²	1.001	1.000
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0186, <i>wR</i> ₂ = 0.0482	<i>R</i> ₁ = 0.0335, <i>wR</i> ₂ = 0.0895
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0203, <i>wR</i> ₂ = 0.0493	<i>R</i> ₁ = 0.0404, <i>wR</i> ₂ = 0.0944
Extinction coefficient	0.00194(12)	0
Largest diff. peak and hole	1.206 and −1.064 e.Å ^{−3}	3.618 and −2.490 e.Å ^{−3}

In both orthorhombic modifications the cerium atoms are surrounded by eight oxygen atoms, a coordination which is expected for Ce(IV), see Fig. 1. In both structures every cerium ion is in contact with four water molecules and four sulfate groups and every sulfate group is in contact with two cerium ions, the bonding distances are given in Table 2. The Ce–O distances average to 2.33(3) Å, the Ce–O(water) are slightly longer, 0.05(1) Å, than the Ce–O(sulfur). The sulfate groups show a very small departure from the ideal tetrahedral symmetry, the bridging oxygen bonds are 0.03(1) Å longer than the terminal oxygen bonds.

The cerium coordination polyhedra within (I) and (II) are both forming slightly distorted square Archimedean

antiprisms, shown in Fig. 2. The angles within the tetragonal and triangular faces of (I) are ranging between 89.02(7)–90.94(7)° and 55.88(6)–66.42(6)°, respectively. In modification (II), the angles within the tetragonal and triangular faces are ranging between 84.58(7)–92.00(11)° and 54.99(8)–65.14(9)°, respectively. Comparing the coordination environment of the Ce ions within the two structures, one can see that they show geometrical isomerism, given by the orientation of the water and sulfate ligands with respect to the central cerium ion, as shown in Figs. 1 and 2. In modification (I) the sulfate ligands lie *trans* to each other in both the tetragonal faces, while in modification (II) the sulfate ligands lie *trans* to each other in one tetragonal face and *cis* in the other.

Both structures are build up by layers of Ce(H₂O)₄(SO₄)₂, where the cerium ions are linked by sulfate bridges. These layers are normal to the *c*-axis for (I) and normal to the *a*-axis for (II), see Fig. 3. The layers are held together by a hydrogen-bonding network (Table 3) between the water molecules in one layer and the sulfate terminal oxygen atoms in an adjacent layer, shown in Fig. 4. In structure (I) half of the hydrogen bonds (O10–H11...O2) are acting within the layers while the other half (O10–H12...O2) are acting between the layers. In structure (II) the O10–H11...O4, O30–H31...O3 and the O20–H21...O4 hydrogen bonds are all layer-connecting while only the O20–H22...O3 hydrogen bond is an inter layer linkage.

3.2. Structurally related compounds

Three polymorphic forms of Ce(SO₄)₂ · 4H₂O have been structurally characterized: two orthorhombic modifications, reported in this work, and one monoclinic. The two orthorhombic modifications are called the α -form (I) and the β -form (II) and they crystallize in space group *Fddd* and *Pnma*, respectively. The crystal structure of the monoclinic modification (space group *C2/c*) has been solved and discussed by Filipenko et al. [11]. The structure of the monoclinic polymorph Ce(SO₄)₂ · 4H₂O [11] is very similar to the structure of the α -modification, structure (I). Within the monoclinic modification the coordination geometry about the two non-equivalent cerium ions is square antiprismatic, the same conformation as the cerium polyhedron in the α -form has (see Fig. 5) and the Ce–O bonding distances average to 2.31(4) Å.

All three polymorphs are built up by layers of Ce(H₂O)₄(SO₄)₂ held together by a hydrogen bonding network between the water molecules that are bound to the central cerium ion and the sulfate group terminal oxygen atoms. The packing features adopted by the monoclinic form are very similar to the one adopted by the α -form (I), while in the β -form (II), both the layers and the packing of the layers are essentially different, see Fig. 6.

The Ce(SO₄)₂ · 4H₂O (I) bulk sample, (space group *Fddd*) was analyzed by X-ray powder diffraction. The diffractogram was compared to the only reference powder pattern

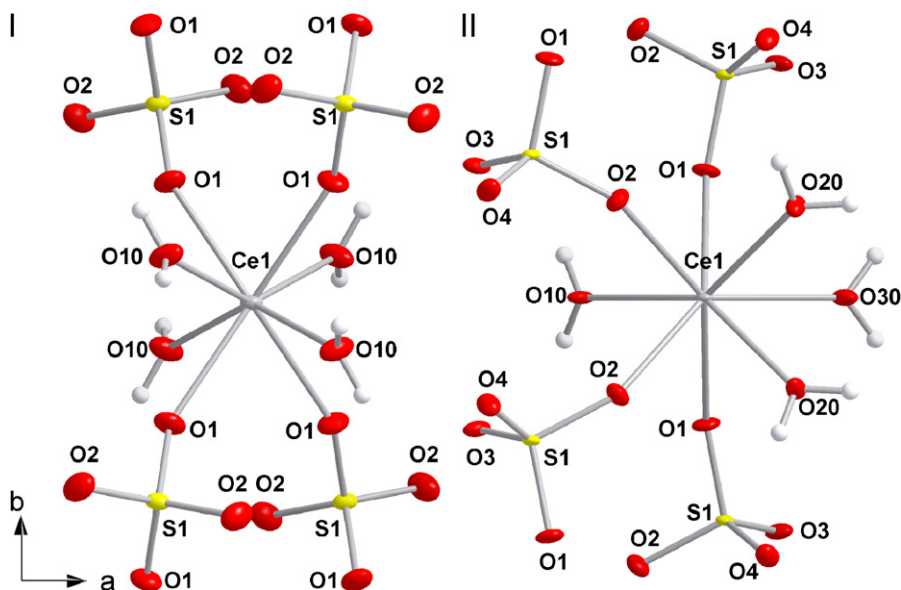


Fig. 1. Coordination geometry for the orthorhombic modifications (I) and (II). The displacement ellipsoids are drawn at 50% probability level.

Table 2
Bond lengths [\AA] for the two orthorhombic modifications

(I)		(II)	
Ce(1)–O(1) ($\times 4$)	2.2969(16)	Ce(1)–O(1) ($\times 2$)	2.312(3)
Ce(1)–O(10) ($\times 4$)	2.3533(16)	Ce(1)–O(2) ($\times 2$)	2.299(2)
		Ce(1)–O(10)	2.335(4)
		Ce(1)–O(20) ($\times 2$)	2.356(2)
		Ce(1)–O(30)	2.375(4)
S(1)–O(1) ($\times 2$)	1.4881(16)	S(1)–O(1)	1.486(3)
S(1)–O(2) ($\times 2$)	1.4620(18)	S(1)–O(2)	1.491(3)
		S(1)–O(3)	1.458(2)
		S(1)–O(4)	1.461(3)

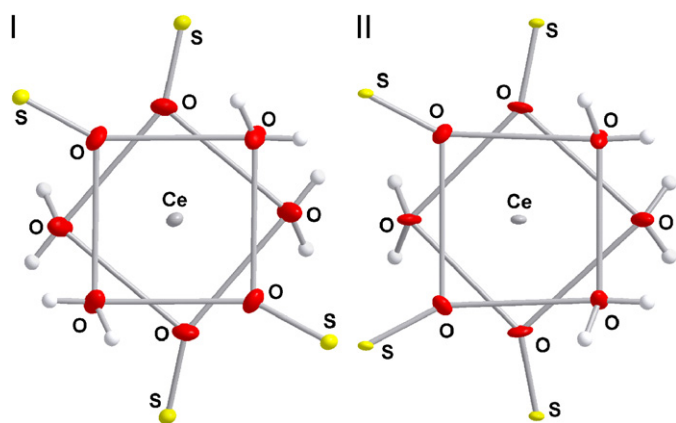


Fig. 2. Square antiprismatic coordination geometry about the Ce ions for the orthorhombic modifications (I) and (II), respectively.

in the database [12a] on the $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ with space group $Fddd$, but there was not a good agreement as several peaks in the reference were missing. The diffractogram was then compared with the calculated powder pattern from the structure solution of (I) and the agreement was perfect,

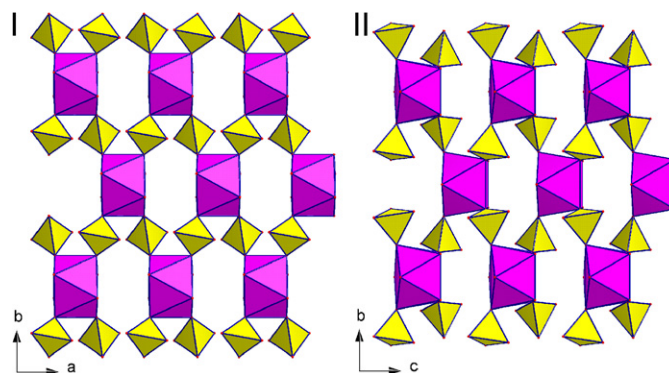


Fig. 3. The cerium polyhedra together with the bridging sulfate ligands are forming layers parallel to the ab plane for the orthorhombic modification (I) and parallel to the bc plane for (II).

Table 3
Hydrogen bonds length in [\AA] and angles [$^\circ$] for compound (I) and (II)

Compound	D–H...A	d(D–H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
(I)	O(10)–H(11)...O(2) ⁱ	0.80(4)	2.02(4)	2.776(2)	158(4)
(I)	O(10)–H(12)...O(2) ⁱⁱ	0.77(5)	1.93(5)	2.692(2)	170(6)
(II)	O(10)–H(11)...O(4) ⁱⁱⁱ	0.80(3)	1.97(3)	2.716(4)	156(4)
(II)	O(20)–H(21)...O(4) ^{iv}	0.82(3)	1.87(3)	2.688(4)	173(5)
(II)	O(20)–H(22)...O(3) ^v	0.81(3)	1.97(3)	2.742(4)	159(5)
(II)	O(30)–H(31)...O(3) ^{vi}	0.82(3)	1.88(3)	2.692(4)	168(4)

Symmetry transformations used to generate equivalent atoms: (i) $x-1, -y+5/4, -z+5/4$ (ii) $x-3/4, -y+3/2, z-1/4$ (iii) $x, y, z-1$ (iv) $x+1/2, y, -z+3/2$ (v) $-x+3/2, -y, z+1/2$ (vi) $x+1/2, y, -z+1/2$.

an evidence of a pure material. The best fit matching all experimental peaks was achieved with Ref. [12b], which is a calculated pattern of the monoclinic modification of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [11]; this is further stressing the similarity among the two structures and also that there is a possibility

that the monoclinic modification may be a result of an overlooked higher symmetry.

Another five heavy quadrivalent ions forming chemical analogous orthorhombic compounds exist: $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Hf}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Np}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. Zirconium and hafnium disulfate tetrahydrate both crystallize in space group $Fddd$. The structure of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ has been published [13] and it is isomorphic with the structure of $\alpha\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. Indexed powder data

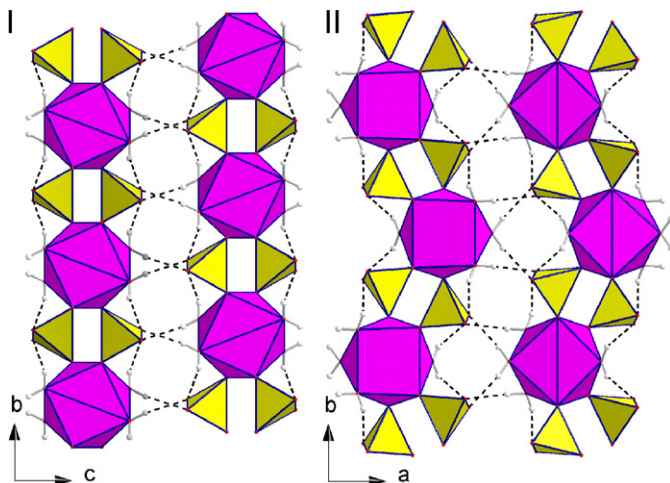


Fig. 4. Hydrogen bonding contacts within (I) and (II) mediated by the cerium coordinating water molecules and the terminal sulfate oxygen atoms.

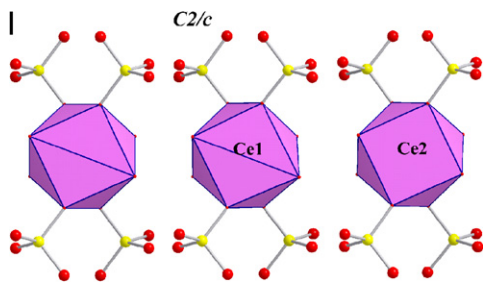


Fig. 5. Comparison of the coordination polyhedra within the orthorhombic α -modification (I) and the monoclinic modification, space group $C2/c$.

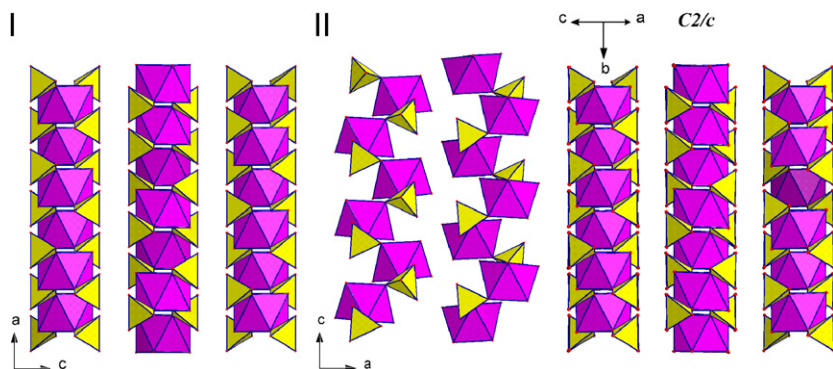


Fig. 6. View of adjacent layers within: the α -form (I), the β -form (II) and the monoclinic modification, space group $C2/c$ [11]. The β -form displays pucker layers while the α -form and the monoclinic modification both have more compact and flatter layers.

[12c,21] show the same space group for $\text{Hf}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The structure of $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ was the first of these structures solved by X-ray single crystal diffraction [22] and it crystallizes in space group $Pnma$ as well as the structure of $\text{Np}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, solved recently [23]. $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is the only compound apart from $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ that has proven to crystallize in both the orthorhombic space groups, $Fddd$ and $Pnma$. The structure of $\beta\text{-Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, space group $Pnma$, has been determined [24] and it is isomorphic with the structure of $\beta\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and even the hydrogen bonding patterns are the same within these two structures. Indexed powder data [12d,24] confirm the existence of the orthorhombic modification with space group $Fddd$, which is isomorphic with the structure of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, as shown by Jayadevan et al. [24], and to the structure of $\alpha\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. As expected, the infrared spectra of the α - and $\beta\text{-Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ did not exhibit substantial differences [24]. The differences between the α - and β -structure have been discussed by Singer and Cromer [13] and by Jayadevan et al. [24]. Singer and Cromer [13] have suggested the operation necessary to relate the $Fddd$ structure of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ to the $Pnma$ structure of $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, resulting in a puckering of the flat layers of the $Fddd$ -structure, shown in Figs. 4 and 6, and as a consequence, the hydrogen bonding contacts being also altered, see Fig. 4.

The $\beta\text{-Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ can be obtained by very slow heating of the $\alpha\text{-Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ to 120°C [24]. This $\alpha \rightarrow \beta$ transformation can also be achieved by hydrothermal equilibration [24] similarly to the $\alpha \rightarrow \beta$ transformation of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$.

3.3. Thermal behavior

The thermal behavior of the two orthorhombic modifications of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, the α -form (I) and the β -form (II), have been studied by thermogravimetry (TG), differential scanning calorimetry (DSC) and X-ray powder thermodiffraction, *in situ* and *ex situ*.

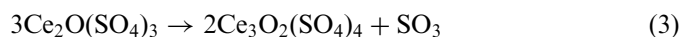
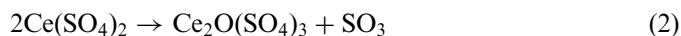
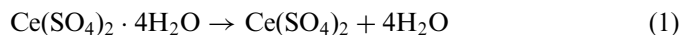
Both the modifications of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ were heated up to 140°C , in sealed autoclaves, in an attempt to obtain a transformation between the two modifications, $\alpha \leftrightarrow \beta$, similar

to the $\alpha \rightarrow \beta$ transformation observed for $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ at 120°C [24]. This transformation was not observed, but a $\alpha \rightarrow \beta$ transformation was achieved by hydrothermal equilibration at 100°C . Both the α - and the β -form can be gently heated up to 90°C to lose water giving crystalline $\text{Ce}(\text{SO}_4)_2$ (space group *Pbca*) [12e] on cooling. After exposure to open atmosphere for several days $\text{Ce}(\text{SO}_4)_2$ turns into β - $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. In the structure of $\text{Ce}(\text{SO}_4)_2$ each cerium atoms is attached to eight sulfate groups and each sulfate group is bridging to four cerium atoms [25]. Then it is not surprising that $\text{Ce}(\text{SO}_4)_2$ is easily hydrated, considering the reluctance of the sulfate group towards a four fold bridging position [1,25].

The thermodiffractionometry *in situ* showed that both the α - and the β -forms turned into amorphous phases on slow heating up to 300°C . On cooling and exposure to open atmosphere also these phases slowly turned into β - $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The preference to form the β -phase upon hydration of the $\text{Ce}(\text{SO}_4)_2$ (*Pbca*) [12e,25] may arise from the breaking of the four weakest Ce–O–S bonds forming four new Ce–OH₂ bonds. Then an adjustment of the coordination polyhedron will result in the antiprismatic geometry found for cerium in β - $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$.

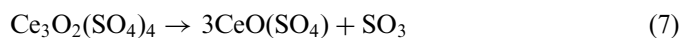
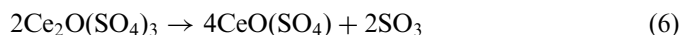
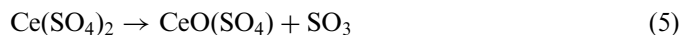
The thermal behaviors of both modifications were also studied by TG and DCS. The endothermic dehydration of α - $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ takes place in two steps giving approximately 13.5% and 4% weight loss, corresponding to three and one water of hydration, respectively (Fig. 7). This differs from the dehydration of β - $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, which takes place in one single step with about 19% lost of its weight. After the dehydration process the heat capacity for both the α - and β -forms increase, giving crystalline $\text{Ce}(\text{SO}_4)_2$. On further heating (from 380°C up to 510°C), a two step endothermic process takes place where 8% plus 5.5% of the weight is lost in the transformation of $\text{Ce}(\text{SO}_4)_2$ into $\text{Ce}_3\text{O}_2(\text{SO}_4)_4$ and SO_3 , with $\text{Ce}_2\text{O}(\text{SO}_4)_3$ as a possible intermediate species. Finally, at 840°C the end products CeO_2 [12f] and SO_3 are formed, see Fig. 7.

On the basis of TG results the thermal decomposition of tetrahydrated cerium sulfate proceeds by the following reactions:



Due to the disagreement among many references on the thermal decomposition of $\text{Ce}(\text{SO}_4)_2$, its thermal behavior was studied by heating in furnace (N_2 gas flow) to different temperatures in the range of 200 – 500°C . The decomposition products were analyzed by X-ray powder diffractometry. These experiments do not reveal any other crystalline decomposition products than $\text{CeO}(\text{SO}_4)$ [12g,26].

The results from the X-ray powder diffraction analysis suggest that also the following thermal decomposition reactions may take place:



Ying and Rudong [7] suggested that the observed weight lost and the endothermic peak in the temperature range 450 – 550°C may correspond to the reduction of anhydrous cerium(IV) sulfate, giving $\text{Ce}_2(\text{SO}_4)_3$, SO_3 and $\frac{1}{2}\text{O}_2$. We also studied and compared the thermal decompositions of $\text{Ce}_2(\text{SO}_4)_3$ and $\text{Ce}(\text{SO}_4)_2$ by TG and DSC. The DSC curves as well as the enthalpy changes differ and the end product, CeO_2 [12f], is formed at a higher temperature for the trivalent cerium sulfate. On the basis of all our experiments, there are no indications that any reduction of the

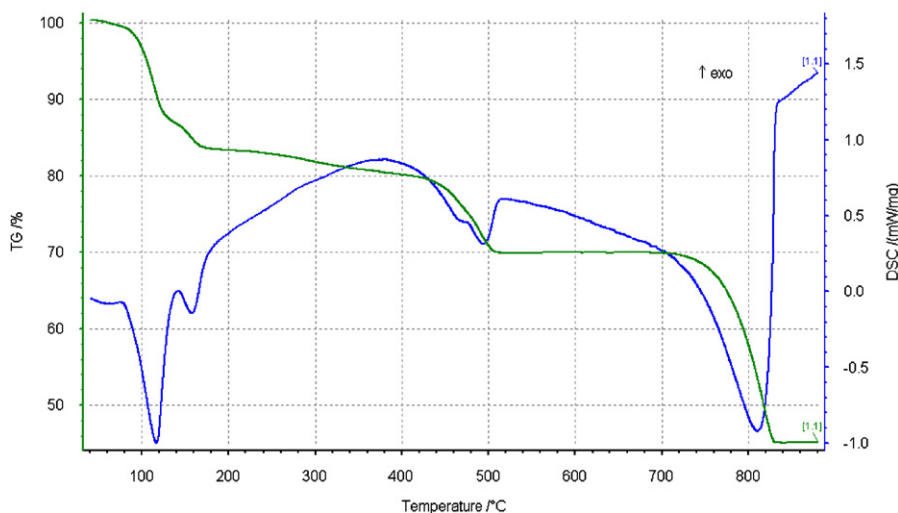


Fig. 7. TG and DSC curves for 15 mg sample of α - $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, in flowing high purity N_2 at a heating rate of 5°C min^{-1} .

Ce(IV) species takes place during the thermal decomposition process.

From a structural point of view the formation of $\text{Ce}_2\text{O}(\text{SO}_4)_3$ during the first decomposition step is reasonable. Within $\text{Ce}(\text{SO}_4)_2$, the cerium atoms are arranged in pairs with a shorter Ce–Ce distance ($< 5 \text{ \AA}$) suitable for the formation of an oxygen bridge between Ce atoms upon losing SO_3 molecules.

Acknowledgment

The authors wish to thank Dr. Christopher S. Knee at the Department of Chemistry, Göteborg University, for valuable supports and assistance with the TG–DSC experiments.

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