# New Structure Type among Octahydrated Rare-Earth Sulfates, $\beta$ -Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O, and a new Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·4H<sub>2</sub>O Polymorph

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Abstract. Syntheses, crystal structures and thermal behavior of two new hydrated cerium(III) sulfates are reported,  $Ce_2(SO_4)_3 \cdot 4H_2O(I)$ and  $\beta$ - $Ce_2(SO_4)_3 \cdot 8H_2O(II)$ , both forming three-dimensional networks. Compound I crystallizes in the space group  $P2_1/n$ . There are two non-equivalent cerium atoms in the structure of I, one nineand one ten-fold coordinated to oxygen atoms. The cerium polyhedra are edge sharing, forming helically propagating chains, held together by sulfate groups. The structure is compact, all the sulfate groups are edge-sharing with cerium polyhedra and one third of the oxygen atoms, belonging to sulfate groups, are in the S $-O\mu_3-Ce_2$ bonding mode. Compound II constitutes a new structure type among the octahydrated rare-earth sulfates which belongs to the space group *Pn*. Each cerium atom is in contact with nine oxygen atoms, these belong to four water molecules, three corner sharing and one edge sharing sulfate groups. The crystal structure is built up by layers of  $[Ce(H_2O)_4(SO_4)]_n^{n+}$  held together by doubly edge sharing sulfate groups. The dehydration of **II** is a three step process, forming  $Ce_2(SO_4)_3$ ·5H<sub>2</sub>O,  $Ce_2(SO_4)_3$ ·4H<sub>2</sub>O and  $Ce_2(SO_4)_3$ , respectively. During the oxidative decomposition of the anhydrous form,  $Ce_2(SO_4)_3$ , into the final product  $CeO_2$ , small amount of  $CeO(SO_4)$  as an intermediate species was detected.

Keywords: Hydrated rare-earth sulfate; Cerium sulfate; Lanthanides; Thermal behaviour; X-ray diffraction

# Introduction

In the chemistry of the rare-earth compounds, complex anions play an important role. Research interest in the area of rare-earth sulfates derives from their application in the separation of rare-earth elements and a large number of complexes and salts have been described. A comprehensive review of the lanthanide compounds with complex anions was presented in 2002 by *Wickleder* [1] covering all data of structurally characterized compounds known to that date. Recently, during investigations of rare-earth frameworks, advances in the synthesis of new inorganic materials [2] with interesting applications [3] have been achieved. Although a great number of complexes and salts have been reported, the structural information on the rare-earth sulfates is still limited [1].

The sulfates decompose at elevated temperatures and cannot be obtained from their melt [1, 4, 5]. Thus, due to the use of water as solvent, most of the known crystal struc-

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tures are those of hydrated binary and ternary sulfates [1]. The most common hydrated binary rare-earth sulfates are the octahydrates,  $M_2(SO_4)_3 \cdot 8H_2O$ , and many of them are described structurally (M = Y [6], Ce [8], Pr [9], Nd [10], Sm [11], Eu [7], Gd [12], Tb [13], Dy [8,13], Er [14], Yb [8], Lu [8]). Binary sulfates with lower water content are uncommon, the crystal structure have been determined for  $M_2(SO_4)_3 \cdot 5H_2O$  (M = Ce [8], Nd [15]),  $M_2(SO_4)_3 \cdot 4H_2O$ (M = La [16], Ce [17], Nd [16], Er [14]) and  $Lu_2(SO_4)_3 \cdot 3H_2O$  [8]. Sulfates with higher water content, M<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O, have been characterized for the larger lanthanide ions only, La [8] and Ce [18]. Structural information on anhydrous binary rare-earth sulfates is limited and only four compounds  $(M_2(SO_4)_3, \text{ where } M = Y [5], Sc [5], Nd$ [19], Er [4]) have been reported. Among the rare-earth salts, the cerium(III) sulfate displays the greatest diversity in the hydrate number. Within the binary system Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O, solid phases with x = 2 [20], 4, 5, 8, 9, 12 [20] and 14 [21] were reported.

The thermal behavior of hydrated binary rare-earth sulfates have been studied several times [20-26], mainly for the octahydrates. According to these investigations, at first an endothermic dehydration of  $M_2(SO_4)_3 \cdot xH_2O$  takes place resulting in the anhydrous form,  $M_2(SO_4)_3$ . During the decomposition of the anhydrous form into the final product  $M_2O_3$ , an intermediate  $M_2O_2(SO_4)$  species is formed [1], except for cerium(III) sulfate. The description of the thermal behavior of  $Ce_2(SO_4)_3$  is ambiguous. Investigations on its thermal decomposition have revealed several disagreements [20-26]. Early studies [22-24] reported that  $Ce_2(SO_4)_3$  like

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other rare-earth sulfates first decomposed into  $Ce_2O_2(SO_4)$ which, during further heating, in the final stage gave  $Ce_2O_3$ . Udupa [21] made a thermal decomposition study on Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·14H<sub>2</sub>O pointing out two dehydration steps involving nine and five water molecules, respectively. On cooling,  $Ce_2(SO_4)_3$  rehydrates to give  $Ce_2(SO_4)_3$ ·5H<sub>2</sub>O which slowly converted into Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·14H<sub>2</sub>O on exposure to open atmosphere for several days [21]. The studies made by Udupa [21] showed that the anhydrous Ce<sup>III</sup> sulfate is very stable and undergoes oxidative decomposition in one single step giving CeO<sub>2</sub>. Tagawa [25] confirmed the same final product, CeO<sub>2</sub>. Recent research by Poston et al. [26] proposes that the decomposition environment of air or nitrogen has an effect on the decomposition process of Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Poston et al. [26] detected, in ambient atmosphere, many intermediate phases, various oxysulfides, oxides and one oxysulfate. On further heating these converted into CeO<sub>2</sub>. In nitrogen environment, the decomposition end-product was identified as Ce<sub>2</sub>O<sub>3</sub> [26].

The thermal behavior of Ce(SO<sub>4</sub>)<sub>2</sub> is ambiguous as well. *Udupa* [21] showed that anhydrous cerium(IV) sulfate converts into CeO<sub>2</sub>·2Ce(SO<sub>4</sub>)<sub>2</sub> which in the final stage loses sulfur dioxide and oxygen to give CeO<sub>2</sub>. *Tagawa* [25] suggested one single decomposition step from Ce(SO<sub>4</sub>)<sub>2</sub> to the final stage: CeO<sub>2</sub>. *Ying and Rudong* [27] showed evidence that the observed weight lost in the temperature range 450–495 °C corresponds to the reduction of anhydrous cerium(IV) sulfate, giving Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. This reduction process has also been noticed by *Zhao* [28] and confirmed by *Poston* et al. [26] Our studies [29] did not show any evidence for a reductive decomposition step and proposes that only intermediate Ce<sup>IV</sup> species, xCeO<sub>2</sub>·yCe(SO<sub>4</sub>)<sub>2</sub>, are formed during the decomposition of Ce(SO<sub>4</sub>)<sub>2</sub> into the final product CeO<sub>2</sub>.

In this work two new polymorphic forms of hydrated rare-earth sulfates,  $Ce_2(SO_4)_3 \cdot 4H_2O$  and  $Ce_2(SO_4)_3 \cdot 8H_2O$ , have been structurally characterized and the thermal behaviour of  $Ce_2(SO_4)_3 \cdot 8H_2O$  has been examined.

#### **Result and Discussion**

#### Structural description of Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·4H<sub>2</sub>O (I)

The tetrahydrated cerium(III) sulfate (I) crystallizes in the space group  $P2_1/n$  with a = 12.3119(2), b = 7.1368(1), c = 14.2321(3) Å,  $\beta$  = 90.629(1) and Z = 4. There are two cerium atoms, three sulfate groups and four water molecules in each asymmetric unit. The Ce1 atom is in contact with ten oxygen atoms: they belong to one water molecule, three corner sharing and three edge sharing sulfate groups (Fig. 1). For Ce2 the coordination sphere consists of nine oxygen atoms from three water molecules, four corner sharing and one edge sharing sulfate groups (Fig. 1). Coordination numbers such as ten (Ce1) and nine (Ce2) are expected for the large Ce<sup>3+</sup> ion. The Ce1–O and Ce2–O distances average to 2.60(14) and 2.54(7) Å, respectively (Table 1). The bond-valence sums are 2.90 and 2.94 v.u. for Ce1 and Ce2, respectively (using parameter from *Trzesowska* et al. [30]).



Fig. 1 Coordination geometry for Ce1 and Ce2 in I. The displacement ellipsoids are drawn at 50 % probability level.

Table 1 Bond lengths /Å for I.

Ce1-011	2.582(2)	S3-O31	1.461(2)
Ce1-O31 <sup>ii</sup>	2.456(2)	S3-O32	1.504(2)
Ce1-O32	2.542(2)	S3-O33	1.490(2)
Ce1-O33	2.787(2)	S3-O34	1.458(2)
Ce1-O34 <sup>iii</sup>	2.561(2)	S4-O41	1.491(2)
Ce1-O41	2.879(2)	S4-O42	1.473(2)
Ce1-O44	2.551(2)	S4-O43	1.485(2)
Ce1-O51 <sup>i</sup>	2.447(2)	S4-O44	1.476(2)
Ce1-O52	2.618(2)	S5-O51	1.466(2)
Ce1-O53	2.563(2)	S5-O52	1.480(2)
Ce2-O21	2.506(2)	S5-O53	1.513(2)
Ce2-O22	2.490(3)	S5-O54	1.457(2)
Ce2-O23	2.478(2)		
Ce2-O32 <sup>v</sup>	2.585(2)		
Ce2-O33 <sup>iv</sup>	2.599(2)		
Ce2-O41 <sup>v</sup>	2.504(2)		
Ce2-O42	2.683(2)		
Ce2-O43	2.551(2)		
Ce2-O53 <sup>iv</sup>	2.465(2)		

Symmetry transformations for equivalent atoms:

(i): -x+1, -y+2, -z (ii): -x+1/2, y-1/2, -z+1/2

(iii): -x+1/2, y+1/2, -z+1/2 (iv): x-1/2, -y+3/2, z-1/2

(v): -x, -y+1, -z

The three sulfate groups show a small departure from the ideal tetrahedral symmetry and the S-O distances (Table 1) average to 1.48(2) A. There is only one terminal oxygen atom (O54) within the sulfate groups, all other sulfate oxygen atoms are bridging to one or two cerium atoms. The S3-group is edge sharing with the Ce1-polyhedron, with the edge sharing oxygen atoms (O32, O33) in the  $\mu_3$  bonding mode and the other two oxygen atoms in the  $\mu_2$  bonding mode. The S4-group is edge sharing with both the Ce1and the Ce2-polyhedra, with one oxygen atom (O41) in the  $\mu_3$  bonding mode and three oxygen atoms in the  $\mu_2$ bonding mode. The S5-group, with one terminal, one  $\mu_3$ bonding (O53) and two  $\mu_2$  bonding oxygen atoms, is edge sharing with the Ce2 polyhedron. As expected, the S-O distances (average: 1.47(1) A) within the S–O $\mu_2$ –Ce bonds are slightly shorter than S-O distances (average: 1.50(1) Å) within the  $S-O\mu_3-Ce_2$  bonds. This compound forms an intricate three dimensional network (Fig. 2a), each Cel atom is connected through sulfate bridges to five Ce1 and six Ce2 atoms and each Ce2 atom is bridging through sul-



Fig. 2 Packing diagrams, views along  $2_1$  axes. a) Compound I (type A) showing the three dimensional network. b) Structure of  $Ce_2(SO_4)_3$ ·4H<sub>2</sub>O, type B [17].

fate groups to six Ce1 and three Ce2 atoms. The cerium polyhedra are edge sharing as well, each Ce1 polyhedron shares two edges with two Ce2 polyhedra and vice versa, shown in Figure 2a as groups of four cerium polyhedra in the **ac** plane. The edge sharing cerium polyhedra form chains propagating helically in the **b** direction, shown in Figure 3. The S3 sulfate groups are binding within those chains only, while the S4 and S5 sulfate groups are connecting each chain to neighboring chains. In structure of **I** most of the hydrogen bonding contacts are connecting chains. The O11–H11A–O22 and O22–H22B–O11 hydrogen bonds are acting within the chains while the all the remaining contacts are found to the  $\mu_3$  bonding oxygen atoms.



Fig. 3 Helical strings of edge sharing cerium polyhedra intra connected by the S3 sulfate groups, within structure I.

Table 2 Hydrogen bonds for I/Å and °.

D-H···A	d(D-H)	d(H···A)	d(D…A)	<(DHA)
011-H11A…O22 <sup>i</sup>	0.76(2)	2.31(3)	3.055(4)	166(5)
O11-H11B…O42 <sup>ii</sup>	0.76(2)	2.05(3)	2.737(3)	151(5)
O21-H21A…O54 <sup>iii</sup>	0.76(2)	2.03(3)	2.759(3)	162(5)
O21-H21B····O44 <sup>iv</sup>	0.78(2)	2.31(3)	3.076(3)	171(5)
O22-H22A…O11 <sup>v</sup>	0.77(2)	1.99(3)	2.705(4)	154(5)
O22-H22B···O43v	0.76(2)	2.24(5)	2.758(3)	126(5)
O23-H23A…O52 <sup>iv</sup>	0.78(2)	1.97(3)	2.741(3)	172(5)
O23-H23BO54vi	0.77(2)	1.94(3)	2.699(3)	169(6)

Symmetry transformations used to generate equivalent atoms: (i): -x, -y+1, -z (ii): x, y+1, z (iii): -x+1, -y+1, -z

(iv): -x+1/2,y-1/2,-z-1/2 (v): x,y-1,z (vi): x-1/2,-y+1/2,z-1/2

The crystal structure for one polymorph and three chemical analogues to I have been described earlier:  $M_2(SO_4)_3 \cdot 4H_2O$  (M = Ce [17], La [16], Nd [16], Er [14]). These compounds, except for the erbium [14] salt, all crystallizes in the same space group ( $P2_1/n$ ) but they belong to two different structure types. The structure of I and the lanthanum salt are isomorphic (structure type A). The cerium polymorph described by *Deregine* et al. [17] is isomorphic with the neodymium [16] salt (structure type B). All these  $M_2(SO_4)_3 \cdot 4H_2O$  compounds form three dimensional networks.

The structure of  $\text{Er}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$  [14] (space group  $P\overline{1}$ ) differs essentially from the other structures, it is less compact and does not show any edge sharing between the metal polyhedra. There are two nonequivalent erbium ions, one with seven-fold coordination binding to six sulfate groups and one water molecule and one with eight-fold coordination binding to five sulfate groups and three water molecules. The three sulfate groups are bridging by corner sharing only.



**Fig. 4** Coordination geometry for Ce1 and Ce2 in **II**. The displacement ellipsoids are drawn at 50 % probability level.

The structure type A shows many similarities with the structure type B. Both these structure types are rather compact and contain edge sharing metal polyhedra. They both also contain edge sharing sulfate groups, but the structure of type B does not contain any doubly edge sharing sulfate group as the structure of type A. These structures also differ in the coordination geometry of the metal ions: they are ten and nine coordinated in the structure type A, while both non-equivalent metal ions are nine coordinated in the structure type B. One metal ion is binding to five sulfur groups (one is bidentate) and two water molecules, the other metal ion is binding to six sulfate groups (one is bidentate) and one water molecule, both ions are also sharing one water molecule. These differences result in different packing features for these two structure types, compare Figure 2a (type A) and Figure 2b (type B).

# Structural description of Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O (II)

The octahydrated cerium(III) sulfate, (II) crystallizes in the space group Pn with a = 6.8502(2), b = 17.2693(5), c = 6.8747(2) Å,  $\beta = 92.587(1)$  and Z = 2. There are two cerium atoms, three sulfate groups and eight water molecules in each asymmetric unit. Each cerium atom is in contact with nine oxygen atoms, these belong to four water molecules, three corner sharing and one edge sharing sulfate groups (Fig. 4). Nine-fold coordination is the most common coordination for Ce<sup>3+</sup> ions. The Ce–O distances average to 2.54(10) Å, see Table 3. The bond-valence sums are 2.97 and 2.98 v.u. for Ce1 and Ce2, respectively (using parameter from Trzesowska et al. [30]). The S-O distances within the three sulfate groups (Table 3) average to 1.475(5) A. The S3-group is edge sharing both with the Ce1 and with the Ce2 polyhedra. The S4- and S5-groups are corner sharing to three Ce1 and three Ce2 polyhedra, respectively. Two of the sulfates (S4, S5) show almost ideal tetrahedral symmetry while the S3-group shows smaller angles  $105.04(17)^{\circ}$  and  $106.00(18)^{\circ}$  towards the edge sharing Ce1- and Ce2 polyhedra, respectively. The crystal structure is built up by layers of [Ce1(H<sub>2</sub>O)<sub>4</sub>(S5O<sub>4</sub>)]<sub>n</sub><sup>n+</sup> alternating with layers of [Ce2(H<sub>2</sub>O)<sub>4</sub>(S4O<sub>4</sub>)]<sub>n</sub><sup>n+</sup>, parallel to the ac plane, see Figure 5. These layers are held together,

Table 3 Bond lengths /Å for II.

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Ce1-O14         2.653(3)         S3-O34         1.475(3)           Ce1-O31         2.540(3)         S4-O41         1.477(3)           Ce1-O32         2.767(3)         S4-O42         1.470(3)	)
Ce1-O31         2.540(3)         S4-O41         1.477(3)           Ce1-O32         2.767(3)         S4-O42         1.470(3)	)
Ce1-O32 2.767(3) S4-O42 1.470(3	)
	)
Ce1-O51 2.437(3) S4-O43 1.468(3	)
Ce1-O52 <sup>i</sup> 2.423(3) S4-O44 <sup>iv</sup> 1.473(3	)
Ce1-O54 2.506(3) S5-O51 1.471(3	)
Ce2-O21 2.463(3) S5-O52 1.470(3	)
Ce2-O22 2.524(3) S5-O53 1.475(3	)
Ce2-O23 2.695(3) S5-O54 <sup>v</sup> 1.479(3	)
Ce2-O24 2.595(3)	
Ce2-O33 <sup>iii</sup> 2.669(3)	
Ce2-O34 <sup>iii</sup> 2.555(3)	
Ce2-O41 2.498(3)	
Ce2-O43 <sup>ii</sup> 2.427(3)	
Ce2-O44 2.432(3)	

Symmetry transformations for equivalent atoms: (i): x+1/2, -y+1, z+1/2 (ii): x-1, y, z (iii): x+1, y, z+1(iv): x+1/2, -y+2, z-1/2 (v): x-1/2, -y+1, z+1/2

Table 4Hydrogen bonds for II/Å and °.

D-H…A	d(D-H)	d(H···A)	d(D…A)	<(DHA)
011-H11A…053 <sup>vi</sup>	0.80(3)	2.14(5)	2.789(5)	138(7)
O11-H11A-031 <sup>iv</sup>	0.80(3)	2.35(6)	2.886(5)	125(6)
O11-H11B…O14 <sup>iv</sup>	0.80(3)	2.12(3)	2.881(5)	159(6)
O12-H12A…O22	0.81(2)	2.08(3)	2.871(5)	163(7)
O12-H12B…O42 <sup>ii</sup>	0.81(2)	1.93(3)	2.724(4)	169(6)
O13-H13A-054i	0.83(3)	2.06(4)	2.830(4)	156(7)
O13-H13BO53	0.82(3)	1.90(3)	2.672(4)	156(6)
O14-H14A····O33vii	0.82(3)	1.97(3)	2.785(4)	171(7)
O14-H14B…O13 <sup>iii</sup>	0.84(3)	2.15(3)	2.971(5)	165(7)
O21-H21A…O42	0.81(3)	2.07(4)	2.782(5)	146(6)
O21-H21B····O23viii	0.80(3)	2.03(3)	2.806(5)	165(8)
O22-H22A···O32 <sup>vii</sup>	0.82(3)	1.91(3)	2.727(5)	172(7)
O22-H22BO53i	0.82(2)	1.89(3)	2.681(4)	162(6)
O23-H23A…O24 <sup>v</sup>	0.81(3)	2.13(4)	2.911(5)	161(6)
O23-H23B····O32 <sup>vii</sup>	0.82(3)	2.02(3)	2.816(4)	163(7)
O24-H24A···O41 <sup>ix</sup>	0.82(2)	2.04(3)	2.827(4)	163(7)
O24-H24B…O42 <sup>v</sup>	0.80(2)	1.96(3)	2.729(4)	163(6)

Symmetry transformations used for equivalent atoms:

(i): x+1/2, -y+1,z+1/2 (ii): x-1,y,z (iii): x-1/2, -y+1,z+1/2 (iv): x+1,y,z (v): x-1/2, -y+2,z+1/2 (vi): x+1/2, -y+1,z-1/2 (vii): x,y,z+1 (viii): x,y,z-1 (ix): x-1/2, -y+2,z-1/2

in the **b** direction, by the doubly edge sharing S3-groups, forming together the three dimensional network (Fig. 6). There are sixteen different hydrogen bonding contacts within the network (Table 4, Fig. 7), ten of them acting within the layers while the rest of them are acting between the layers.

The octahydrates prevail in the system of  $M_2(SO_4)_3 \cdot xH_2O$ and many octahydrated rare-earth sulfates have been structurally characterized [6–14]. The previously reported compounds are all isostructural members of the well known rare-earth octahydrates sulfate structure type (type  $\alpha$ ) and they all crystallizes in space group *C2/c*. Temporary interest in these compounds was inspired by the supposed existence of pyroelectricity in crystals of rare-earth octahydrates, indicating that some crystals may belong to a non-centrosymmetric space group [6, 31] The structure of **II** is non-centro-



Fig. 5 Layers of  $[Ce2(H_2O)_4(S4O_4)]_n^{n+1}$ 



**Fig. 6** Packing diagram of compound **II** showing the three dimensional network, from the top layers of:  $[Ce2(H_2O)_4(S4O_4)]_n^{n+}$ ,  $[Ce1(H_2O)_4(S5O_4)]_n^{n+}$  and  $[Ce2(H_2O)_4(S4O_4)]_n^{n+}$ , held together by  $(S3O_4)^{2^-}$  groups.

symmetric (space group *Pn*), and represents a new structure type among the rare-earth octahydrates, type  $\beta$ . The structure types  $\alpha$  and  $\beta$  differ significantly. In the structure type  $\alpha$ , the metal atoms have eight-fold coordination while the



Fig. 7 Packing diagram, showing part of the hydrogen bonding network. There are sixteen different hydrogen bonding contacts within compound II most of them are contacts toward terminal sulfate oxygen atoms or to water molecules.



Fig. 8 Packing diagram, structure of  $\alpha$ -Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O [8].

cerium atoms in **II** are in contact with nine oxygen atoms. The sulfate groups in structure type  $\alpha$  are all linking by corner sharing, while one of the sulfate groups is doubly edge sharing with two metal polyhedra in structure type  $\beta$ . As a consequence, two very different structural packing are featured. The structure type  $\alpha$  forms layers of



Fig. 9 TG and DSC curves for 29 mg sample of  $\beta$ -Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O, in flowing high purity N<sub>2</sub> at a heating rate of 10 °C min<sup>-1</sup>

Table 5 Thermal behaviour

TG-DSC	Weight	Temperature	Peak max	Peak area
reaction	loss	range /°C	°C	kJ/g
1a	7.8 %	50-100	105	0.17
1b	2.6 %	105-150	135	_
1c	9.7 %	150-270	250	0.19
2a and 2b	31.4 %	730-920	890	1.4
Ex situ reactio	n	Temperature range	/°C	
1a and 2b		22		
1c		150-250		
3		350-480		
4 and/or 5		480-		

 $M_2(SO_4)_3 \cdot 8H_2O$  connected by hydrogen bonds (Fig. 9), while the structure of II forms a three-dimensional network, Figures 6 and 7. Compound II has a slightly higher density than  $\alpha$ -Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> \cdot 8H<sub>2</sub>O.

The diffractogram on the bulk material of **II** was compared with the calculated powder pattern from the structure solution of **II** and the agreement was perfect, an evidence of a pure material. The best fit matching the experimental peaks was achieved with a powder pattern reference [32a] of an assumed orthorhombic modification, indexed by *Pannetier* and *Dereigne* [33] (space group *Cmca*); we believe that this compound is the same as **II**.

#### Thermal behaviour

The thermal behaviour of  $\beta$ -Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O (II) has been studied by thermogravimetry (TG), differential scanning calorimetry (DSC) and X-ray powder thermodiffractometry, *in situ* and *ex situ*.

The TG and DSC analysis showed that the endothermic dehydration of **II** takes place in three steps, on heating up to 300 °C, giving approximately 7.8 %, 2.6 % and 9.7 % weight loss, corresponding to three, one and four water of hydration, respectively (Fig. 9, Table 5). However, we know from our earlier work with the  $\alpha$ - and the  $\beta$ -Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, that the dehydrations steps may be different for the  $\alpha$ - and  $\beta$ -forms [29]. After the dehydration

process the heat capacity increases, possibly to give crystalline Ce<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>, up to 450 °C, then the heat capacity decreases. At 730 °C the decomposition process starts, proceeding to 920 °C. During this distinct oxidative decomposition step, 31.4 % of the weight is lost, see Figure 9 and Table 5. The end product, CeO<sub>2</sub>, was confirmed by X-ray powder diffraction [32b]. On the basis of TG results the thermal decomposition of **II** proceeds by the following reactions:

 $Ce_2(SO_4)_3 \cdot 8H_2O \rightarrow Ce_2(SO_4)_3 + 3H_2O + H_2O + 4H_2O$  (1)

$$\operatorname{Ce}_2(\operatorname{SO}_4)_3 \to 2\operatorname{CeO}_2 + 2\operatorname{SO}_3 + \operatorname{SO}_2 \tag{2a}$$

$$SO_3 \rightarrow SO_2 + \frac{1}{2}O_2 \tag{2b}$$

The *ex situ* X-ray powder thermodiffractometry (by heating in furnace with N<sub>2</sub> flush, Table 5) showed traces of CeO(SO<sub>4</sub>) [32c, 34] (also observed by *Poston* et al. [26]) already at 350 °C and traces of CeO<sub>2</sub> [32b] at 480 °C. An oxidation encountered at lower temperature in the furnace experiment may be due to the lower heating rate or to the more oxidizing environment of the furnace. On the other hand, the presence of SO<sub>3</sub> itself might be enough to contribute to the Ce<sup>III</sup> oxidation in both cases. Based on results from the furnace experiments and X-ray powder diffraction, the thermal decomposition of **II** may proceed by the following reactions:

$$Ce_2(SO_4)_3 \rightarrow 2CeO(SO_4) + SO_2$$
 (3)

$$\operatorname{Ce}_2(\operatorname{SO}_4)_3 \to 2\operatorname{CeO}_2 + 2\operatorname{SO}_3 + \operatorname{SO}_2 \tag{4}$$

$$\operatorname{CeO}(\operatorname{SO}_4) \to \operatorname{CeO}_2 + \operatorname{SO}_3$$
 (5)

According to these experiments,  $Ce_2(SO_4)_3$  [32d] undergoes an oxidative decomposition and no other crystalline compounds than traces of  $CeO(SO_4)$  as an intermediate, and  $CeO_2$  as the only final product, were detected. Since there were indication on that the decomposition of  $Ce(SO_4)_2$  could take place through a reductive step, forming  $Ce_2(SO_4)_3$  as an intermediate [27, 28], we also studied and compared the thermal decompositions of  $Ce_2(SO_4)_3$  and  $Ce(SO_4)_2$  by TG and DSC. The DSC curves as well as the enthalpy changes differ and the end product,  $CeO_2$ , is formed at a lower temperature for the tetravalent cerium sulfate.

The thermodiffractometry *in situ* (evacuated sample chamber) on compound **II** showed some traces of its polymorphic form  $\alpha$ -Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O [32e, 8] at 70 °C. Small amounts of Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O [32f, 8] started to form at 80 °C and traces of Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·4H<sub>2</sub>O [32g, 17] (type B) was detectable at 85 °C, together with the former hydrates. The hydrates turned into amorphous phases on slow heating up to 100 °C. Due to the detection of the polymorphic form, several experiments were carried out to obtain a  $\beta \rightarrow \alpha$  phase transition, but all of them resulted in a Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·4H<sub>2</sub>O [32g, 17] (type B) + 4H<sub>2</sub>O. At ambient

temperature and humidity,  $\beta$ -Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O easily dehydrates to form Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·4H<sub>2</sub>O [32g, 17] (type B).

## **Experimental Section**

## Sample preparations

 $Ce_2(SO_4)_3 \cdot 4H_2O$ , space group  $P2_1/n$ : Single crystals of  $Ce_2(SO_4)_3 \cdot 4H_2O$  were achieved during studies on the  $Ce^{IV}/Ce^{III} - Cr^{VI}/Cr^{III}$  redox system [35, 36].  $Ce(SO_4)_2 \cdot 4H_2O$  (3.0 g, 7.5 mmol) was dissolved in water (20 mL) and  $Ce(OH)_4$  was precipitated with 15 M ammonia. Dried  $Ce(OH)_4$  (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). Sulfuric acid was added until the solid residue was dissolved. After a month many small corn-formed and light-yellow colored single crystals of  $Ce(SO_4)_2 \cdot 4H_2O$  (*Pnma*) were obtained [29]. This sample was then left covered and unguarded and after a long period many very many small (0.08 × 0.06 × 0.02 mm) rhombic-formed and uncolored single crystals were obtained.

 $Ce_2(SO_4)_3 \cdot 8H_2O$ , space group Pn: Recrystallization at ambient atmosphere and temperature of  $Ce_2(SO_4)_3 \cdot xH_2O$  (P.A. quality, manufactured by Aldrich).

## Single crystal X-ray analysis

Data were collected using a Siemens SMART CCD diffractometer equipped with a Siemens LT-2A low temperature device, at -100 °C. Full spheres of the reciprocal space were scanned by  $0.3^{\circ}$ steps in  $\omega$  with a crystal-to-detector distance of 3.97 cm and exposure time per frame, being 15 s. Preliminary orientation matrices were obtained using SMART (Siemens,1995) [37]. The collected frames were integrated with the orientation matrices updated every 100 frames. Final cell parameters were obtained by refinement on

Table 6 Crystal data and structure refinement for I and II.

the position of 8192 reflections with I >  $10\sigma(I)$  after integration of all the data using SAINT (Siemens, 1995) [37]. The data were corrected empirically for absorption and other effects using SADABS (Sheldrick, 2002) [38]. The structures were solved by direct methods and refined by full-matrix least squares on all F<sup>2</sup> data using SHELXTL (Bruker, 2001) [39]. The non hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps and refined isotropically with restrained common O-H distances and a common temperature factor. The crystal of compound (II) was twinned, twin law: [(0 0 1) (0 -1 0) (1 0 0)], and the twin volume ratio was refined to 0.9046(6) / 0.0954(6).

Details on data collections and refinements are given in Table 6. Further details of the crystal structures may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopold-shafen, Germany, on quoting the depository number CSD-417417 for I and CSD-417418 for II. Molecular graphics: DIAMOND (Brandenburg, 2001) [40].

#### *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 10 °C min<sup>-1</sup>, kept at 1000 °C for 60 min and finally cooled down at 10 °C min<sup>-1</sup>. The sample was measured in a dynamic nitrogen atmosphere (gas flow rate 20 ml min<sup>-1</sup>).

# X-ray powder diffraction

X-ray powder diffraction was made using a Siemens D 5000 diffractometer in parallel beam geometry, with X-ray source and

Empirical formula	$Ce_2(SO_4)_3$ ·4H <sub>2</sub> O	$Ce_2(SO_4)_3:8H_2O$
Formula weight	640.48	712.55
Temperature	-100 °C	-100 °C
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	$P2_{1}/n$	Pn
Unit cell dimensions	a = 12.3119(2)  Å	a = 6.8502(2)  Å
	b = 7.1368(1)  Å	b = 17.2693(5)  Å
	c = 14.2321(3)  Å	c = 6.8747(2)  Å
	$\beta = 90.629(1)^{\circ}$	$\beta = 92.587(1)^{\circ}$
Volume	1250.46(4) Å <sup>3</sup>	812.44(4) Å <sup>3</sup>
Z	4	2
Density (calculated)	$3.402 \text{ Mg/m}^3$	2.913 Mg/m <sup>3</sup>
Absorption coefficient	$7.780 \text{ mm}^{-1}$	$6.020 \text{ mm}^{-1}$
F(000)	1200	680
Crystal size	$0.08 \times 0.06 \times 0.02 \text{ mm}^3$	$0.06 \times 0.04 \times 0.02 \text{ mm}^3$
$\theta$ range for data collection	2.18 to 32.00°.	1.18 to 33.10°.
Index ranges	$-18 \le h \le 18, -10 \le k \le 10, -21 \le 1 \le 21$	$-10 \le h \le 10, -26 \le k \le 25, -10 \le l \le 10$
Reflections collected	20400	14756
Independent reflections	4329 [R(int) = 0.0370]	5764 [R(int) = 0.0294]
Completeness to $\theta = 32.00^{\circ}$	99.7 %	100.0 %
Max. and min. transmission	0.8599 and 0.5749	0.8891 and 0.7140
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	4329 / 12 / 217	5764 / 26 / 278
Goodness-of-fit on F <sup>2</sup>	0.999	1.017
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0236, wR2 = 0.0491	R1 = 0.0236, wR2 = 0.0580
R indices (alldata)	R1 = 0.0361, wR2 = 0.0538	R1 = 0.0249, wR2 = 0.0588
Largest diff. peak and hole	$0.763 \text{ and } -1.009 \text{ e.} \text{\AA}^{-3}$	$0.682 \text{ and } -1.898 \text{ e.} \text{\AA}^{-3}$
Absolute structure parameter		-0.052(13), 2823 Friedel pairs

sample in fixed position and a moving detector  $(2\theta - scan)$  in order to identify material during thermodiffractometry both, *in situ* and *ex situ*.

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