

Hydrothermal Syntheses, Structures, and Characterizations of Two Lanthanide Sulfate Hydrates Materials, $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$

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Two- or three-dimensional framework materials containing rich structural diversities are of continuous interest attributable to their technologically important properties and potential applications such as catalysis, ion-exchange, adsorption, intercalation, and radioactive waste remediation.¹⁻⁴ Materials showing these functional features are normally composed of structurally versatile cations. Heavier metal cations with larger coordination spheres and cations exhibiting ability to accommodate other polyhedral units could be excellent candidates for materials with rich structural variations. Among many, lanthanide cations have been used widely, since they could create higher coordination numbers as well as easily adopt other metal polyhedra to generate the full range of topological diversity in the frameworks.⁵⁻⁷ Meanwhile, one of the most effective synthetic methods for the preparations of these versatile framework materials is a hydrothermal (or solvothermal) reaction technique.⁸⁻¹³ In this synthetic method, mineralizers such as acids or bases are introduced to increase the solubility and reactivity of the reagents.^{14,15} And also, organic or inorganic templates are used to direct the framework structures and the subsequent physical properties of the products.^{1,8,9} Thus, we have utilized hydrothermal reactions with two lanthanide cations (La^{3+} and Eu^{3+}) and sulfate anions to prepare higher dimensional framework materials. A number of lanthanide sulfate hydrate materials with general formula of $\text{Ln}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ have been reported ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$ and Yb).¹⁶⁻³⁹ The number of hydration, x varies from 1 to 9 for most of lanthanide cations. Until now, approximately nine different phases including one orthorhombic, two triclinic, five monoclinic, and one hexagonal structure have been reported.¹⁶⁻³⁹ However, any systematic approaches to understand the factors affecting on the formation of different polymorphs are rarely observed. It would be very important to understand the relationships between the reaction conditions employed and the product obtained in any hydrothermal reaction. In this paper, we report on the hydrothermal syntheses, full structural descriptions, and characterizations of two lanthanide sulfate hydrate materials, $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$. With the lanthanum (III) cation, a systematic synthetic study to reveal the origin of the formation of different polymorphs with different hydration number is also discussed.

Experimental Section

Synthesis. $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Aldrich, 99.9%), $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$

(Aldrich, 99.9%), and H_2SO_4 (Duksan, 95.0%) were used as received. For $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, 0.562 g (1.73×10^{-3} mol) of $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and 2.0 mL of concentrated H_2SO_4 were combined with 5.0 mL of H_2O . For $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, 0.772 g (1.73×10^{-3} mol) of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.6 mL of concentrated H_2SO_4 were combined with 1.0 mL of H_2O . Each solution was placed in a 23 mL Teflon-lined autoclave that was subsequently sealed. The autoclaves were gradually heated to 150 °C, held for 2 days, and cooled slowly down to room temperature at a rate of 6 °C h^{-1} . The products were recovered by filtration and washed with water. Pure crystals, the only product from each reaction, of $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ were obtained in 80 ~ 90% yield, on the basis of the corresponding lanthanide nitrates. The crystal structure of $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ has been reported recently.³⁵ The material has been prepared at 180 °C for 7 days using $\text{LaCl}_3 \cdot 2\text{H}_2\text{O}$ and sulfuric acid. And also, the authors argued that 1,2-diaminopropane is necessary as a structure directing agent in order to form the $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$. However, we have prepared phase pure $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ in high yield at lower temperature in much shorter period of time without any organic structure directing agent.

Crystallographic determination. A colorless block ($0.12 \times 0.15 \times 0.22 \text{ mm}^3$) for $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and a colorless block ($0.10 \times 0.14 \times 0.18 \text{ mm}^3$) for $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ were used for single crystal data analyses. The data were collected using a Bruker SMART APEX CCD X-ray diffractometer at 173 K using graphite monochromated $\text{Mo K}\alpha$ radiation at the Korea Basic Science Institute. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30° in omega, and an exposure time of 5 s/frame. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability. The maximum correction applied to the intensities was < 1%. The data were integrated using the SAINT program,⁴⁰ with the intensities corrected for Lorentz, polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. A semiempirical absorption correction was made on the hemisphere of data with the SADABS program.⁴¹ The data were solved and refined using SHELXS-97 and SHELXL-97, respectively.^{42,43} All of the metal atoms were refined with anisotropic thermal parameters and converged for $I > 2\sigma(I)$. With the $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, the displacement parameters for oxygen atoms were refined isotropically attributable to the much larger X-ray absorption of the heavy La cations. All calculations were performed using the WinGX-98 crystallographic software pack-

Table 1. Crystallographic data for $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$

Empirical formula	$\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	$\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$
Formula weight	584.02	664.16
Crystal system	Orthorhombic	Monoclinic
space group	$Pccn$ (No. 56)	$P2_1/n$ (No. 14)
Z	4	4
a (Å)	17.3110(18)	12.8680(9)
b (Å)	6.8594(7)	7.1379(5)
c (Å)	8.5355(9)	13.1741(9)
α (°)	90	90
β (°)	90	92.091(3)
γ (°)	90	90
V (Å ³)	1013.53(18)	1209.24(15)
T (K)	173.0(2)	173.0(2)
ρ_{calcd} (g cm ⁻³)	3.814	3.648
μ (mm ⁻¹)	9.006	10.890
λ (Å)	0.71073	0.71073
$R(F)^a$	0.0265	0.0243
$R_w(F_o^2)^b$	0.0585	0.0599

$$^a R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b R_w(F_o^2) = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}$$

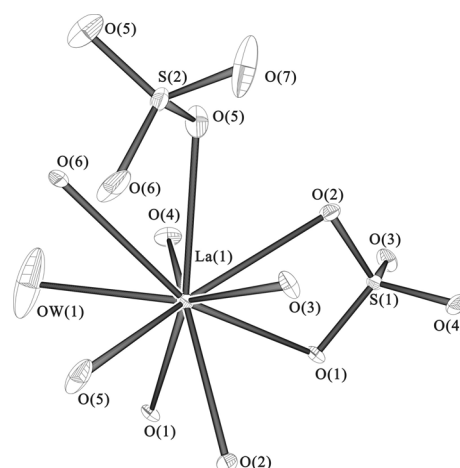
Table 2. Selected bond distances (Å) for $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$

$\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$		$\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$	
La(1)-O(1)	2.558(4)	Eu(1)-O(1)	2.460(6)
La(1)-O(1)	2.592(4)	Eu(1)-O(1)	2.589(6)
La(1)-O(2)	2.588(4)	Eu(1)-O(2)	2.438(7)
La(1)-O(2)	2.709(4)	Eu(1)-O(2)	2.666(6)
La(1)-O(3)	2.468(5)	Eu(1)-O(7)	2.393(6)
La(1)-O(4)	2.458(4)	Eu(1)-O(9)	2.376(6)
La(1)-O(5)	2.564(4)	Eu(1)-O(10)	2.389(7)
La(1)-O(5)	2.731(5)	Eu(1)-Ow(1)	2.507(7)
La(1)-O(6)	2.725(12)	Eu(1)-Ow(2)	2.450(7)
La(1)-O(6) ^a	2.863(17)	Eu(2)-O(4)	2.384(7)
La(1)-O(7) ^b	2.709(4)	Eu(2)-O(5)	2.587(6)
La(1)-Ow(1)	2.554(13)	Eu(2)-O(6)	2.450(7)
		Eu(2)-O(8)	2.391(7)
		Eu(2)-O(11)	2.273(6)
		Eu(2)-O(12)	2.354(6)
		Eu(2)-Ow(3)	2.423(7)
		Eu(2)-Ow(4)	2.414(6)

^{a,b}O(6) and O(7) are disordered.

age.⁴⁴ Crystallographic data and selected bond distances for all the reported materials are given in Tables 1 and 2. In examining the thermal ellipsoid for S(2) in $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, we determined that the atom is split over two sites with 50% occupancy on each site. During the further refinement for $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, we also determined that partial occupancy must occur in some oxygen atoms such as O(6) and O(7) in order to retain charge balance. The amount of water molecule was confirmed by thermal analysis (see the thermogravimetric analysis section). In doing so, set occupancies of 50% on O(6), O(7), and Ow(1) were fixed. Bond valence calculations support the results (see Results and Discussion).

Powder X-ray diffraction was used to confirm the phase

**Figure 1.** ORTEP (50% probability ellipsoids) drawing for the LaO_{10} polyhedra and SO_4 tetrahedra in $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$.

purity for each product. The X-ray powder diffraction data were collected on a Scintag XDS2000 diffractometer at room temperature (Cu K α radiation, θ - θ mode, flat plate geometry) equipped with Peltier germanium solid state detector with 35 kV and 30 mA in the 2θ range $5 \sim 70^\circ$ with a step size of 0.02° , and a step time of 1 s.

Characterization. Infrared spectra were recorded on a Varian 1000 FT-IR spectrometer in the $400 \sim 4000 \text{ cm}^{-1}$ range, with the sample intimately pressed between two KBr pellets. IR for $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ (KBr, cm^{-1}): La-O, 598, 620, 655; S-O, 1054, 1097, 1124, 1159; O-H, 1614, 3345. IR for $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ (KBr, cm^{-1}): Eu-O, 598, 620, 651, 669; S-O, 1014, 1059, 1102, 1120, 1163; O-H, 1614, 3371. Thermogravimetric analyses were carried out on a Setaram LABSYS TG-DTA/DSC Thermogravimetric Analyzer. The polycrystalline samples were contained within alumina crucibles and heated to 800°C at a rate of $10^\circ\text{C min}^{-1}$ under flowing argon.

Results and Discussion

The space group of previously reported $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ crystal was noncentrosymmetric $P2_12_12_1$.³⁵ However, upon examining the unit-cell, one can find that the structure contains a center of symmetry. And also, one of the reported unit-cell parameters is approximately twice to that of our determination. Thus, we think that the reported structure is based on a twinned crystal. Our structural determination suggests that $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ crystallizes in the centrosymmetric space group, $Pccn$ (No. 56). Any missing symmetry and selection of the space group were checked and confirmed using the ADDSYM command in PLATON.⁴⁵ $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ has a three-dimensional crystal structure consisting of LaO_{10} polyhedra and SO_4 tetrahedra excluding all the disordered atoms (see Figure 1). The unique La^{3+} cation is linked to ten oxygen atoms with bond distances ranging from 2.458(4) to 2.863(17) Å. These bond distances are consistent with previously reported La-O bonds.^{16,20,25,28,35} While nine oxygen atoms around La are linked to the sulfate groups, one oxygen atom in the water molecule does not have any further connection. The two four-coordinate S^{6+} cations are

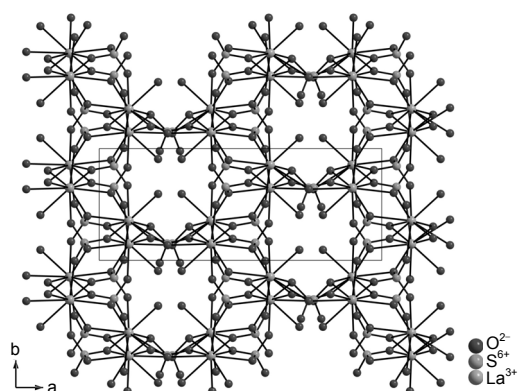


Figure 2. Ball-and-stick representation of $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ in the ab -plane. For clarity, only one of the disordered sulfur and oxygen atoms is shown.

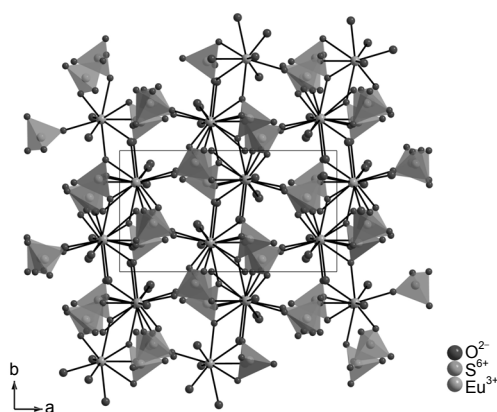


Figure 3. Ball-and-stick and polyhedral representation of $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ in the ab -plane.

in tetrahedral environment with S-O bond distances ranging from 1.420(6) to 1.499(6) Å. As seen in Figure 2, each LaO_{10} group is sharing their edges through O(1) and corners through O(2) and O(5), which generate helical bands along the [010] direction. The helical bands are further sharing their corners through O(6) and produce a three-dimensional lanthanum oxide framework. Finally, the 3D-framework of LaO_{10} group is connected by SO_4 tetrahedra through O(1), O(2), O(3), O(4), and O(5). Thus, a complete three-dimensional framework of $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ consisting of LaO_{10} polyhedra and SO_4 tetrahedra is formed (see Figure 2). The only terminal La-O bonds are observed from the bonding between La^{3+} and water molecules, of which the bond distance is 2.554(13) Å. Along the [001] direction, infinite channels are observed, where the approximate dimensions of the channel is 4.686(13) Å × 5.310(7) Å if excluding the water molecules. Bond valence calculations^{46,47} resulted in values of 3.38 for La^{3+} and 6.00 ~ 6.30 for S^{6+} .

$\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ exhibits another three-dimensional framework with a structure similar to those of $\text{Ln}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ (Ln = Nd or Ce).^{25,39} There are two unique Eu^{3+} cations in the framework. The $\text{Eu}(1)^{3+}$ is bonded to nine oxygen atoms with bond distances ranging from 2.376(6) to 2.666(6) Å. However, the $\text{Eu}(2)^{3+}$ is coordinated by eight oxygen ligands with bond lengths

ranging from 2.273(6) to 2.587(6) Å. Both of the Eu^{3+} cations have two terminal oxygen atoms that are water molecules. The bond distances of Eu-OH_2 range from 2.414(6) to 2.507(7) Å. The other oxygen atoms in the Eu^{3+} cations are further bonded to S^{6+} cations. The three unique S^{6+} cations are linked to four oxygen atoms, resulting in a tetrahedral environment. The bond distances for the S-O bonds range from 1.451(7) to 1.496(6) Å. While the $\text{Eu}(1)^{3+}\text{O}_9$ polyhedra are sharing their edges through O(1), the $\text{Eu}(2)^{3+}\text{O}_8$ polyhedra do not show any sharing with other Eu^{3+} cations. Along the [010] direction, infinite helical chains of $\text{Eu}(1)^{3+}\text{O}_9$ polyhedra are observed (see Figure 3). The europium oxide, $\text{Eu}(2)^{3+}\text{O}_8$ monomers and helical chains of edge-sharing $\text{Eu}(1)^{3+}\text{O}_9$ polyhedra are further connected by SO_4 groups to complete a three-dimensional framework structure. In connectivity terms, the structure of $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ can be written as a neutral framework of $\{[\text{Eu}(1)(\text{OH})_2\text{O}_{3/2}\text{O}_{4/3}]^{2.6667-} [\text{Eu}(2)(\text{OH})_2\text{O}_{6/2}]^{3-} [\text{S}(1)\text{O}_{1/1}\text{O}_{1/2}\text{O}_{2/3}]^{1.6667+} [\text{S}(2)\text{O}_{4/2}]^{2+} [\text{S}(3)\text{O}_{4/2}]^{2+}\}^0$. Bond valence calculations^{45, 46} resulted in values of 3.14-3.31 for Eu^{3+} and 5.94 ~ 6.00 for S^{6+} .

The infrared spectra of $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ compounds reveal S-O vibrations in the region *ca.* 1050 ~ 1160 cm^{-1} . The broad stretches centered at *ca.* 3340 ~ 3430 and 1610 ~ 1620 cm^{-1} are observed, which can be assigned to stretching and bending modes of water molecules, respectively. The La-O and Eu-O vibrations are observed around 598 ~ 655 and 598 ~ 669 cm^{-1} , respectively. The infrared vibrations and assignments are consistent with those previously reported.^{35,37}

The thermal behavior of $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ was investigated using thermogravimetric analysis. $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ shows a weight loss of 3.32% between room temperature and 260 °C, that is attributed to the loss of the water molecule from the material (calc.: 3.08%). $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ similarly revealed weight losses of 10.21% (calc.: 10.85%) between room temperature and *ca.* 280 °C, which are consistent with the loss of four water molecules from the framework structure.

Since many polymorphs of lanthanum sulfates with a variety of water contents have been known, we have performed a series of experiments in order to understand any dependence on some specific conditions for the formation of different polymorphs. We used La^{3+} cation for the systematic syntheses: the amount of $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and water was fixed and the reaction temperature and time were kept at 150 °C for two days. However, the volume of concentrated H_2SO_4 was varied from 0.3 to 2.0 mL. Interestingly, when least amount of sulfuric acid (0.3 mL), i.e., lower concentration of sulfuric acid, was used, the most hydrated product, $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ^{20,28} was obtained based on the powder X-ray diffraction pattern. As we increase the amount of H_2SO_4 to 1 mL, the product was subsequently changed to $\text{La}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$.²⁵ Pure $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ was obtained when 2 mL of concentrated sulfuric acid was used. Thus, the product formations with different water contents and structures clearly depend on the concentration of sulfuric acid. The experimental conditions and results are tabulated in the Table 3.

We have successfully synthesized two lanthanide sulfate hydrates materials, $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ through hydrothermal reaction techniques. Full structural analyses by single crystal X-ray diffraction reveal that the lanthanide sulfate hydrates exhibit 3D-framework structures containing both

Table 3. Acid concentration dependence for the formation of different polymorphs of $\text{La}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$

$\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (g)	H_2SO_4 (mL)	H_2O (mL)	Temperature (°C)	Products
0.562	0.3	5	150	$\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$
0.562	1.0	5	150	$\text{La}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$
0.562	2.0	5	150	$\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$

corresponding lanthanide oxide polyhedra and SO_4 tetrahedra. A systematic synthetic approach suggests that the formation of different polymorphs with variable water contents depends on the concentration of sulfuric acid. We are in the process of exploring further polymorphs of lanthanide sulfate hydrates materials and will report them shortly.

Supplementary Material. The crystallographic files in CIF format for $\text{La}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and $\text{Eu}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ have been deposited with FIZ Karlsruhe as CSD numbers 420714 and 420715, respectively. Copies of the data may be obtained free of charge by contacting FIZ Karlsruhe at +497247808 666 (fax) or crysdata@fiz-karlsruhe.de (e-mail). Detailed experimental data for the reported materials are available from the authors upon request.

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