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ScienceDirect
Journal of Solid State Chemistry 180 (2007) 2020–2025
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

Hydrothermal synthesis, crystal structure and properties of 2-D and 3-D lanthanide sulfates

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Received 26 January 2007; accepted 13 May 2007
Available online 18 May 2007

Abstract

Two new lanthanum sulfates $DySO_4(OH)$ **1** and $Eu_2(SO_4)_3(H_2O)_8$ **2** have been hydrothermally synthesized. The colorless crystals were characterized by IR, TGA, ICP and XRD. The structure was determined by single-crystal X-ray diffraction. **1** crystallizes with monoclinic symmetry, space group $P2(1)/n$ [$a = 7.995(4)$ Å, $b = 10.945(5)$ Å, $c = 8.164(4)$ Å, $\alpha = 90°$, $\beta = 93.619(6)°$, $\gamma = 90°$, $V = 713.0(5)$ Å^3, $Z = 8$]. It displays a three-dimensional framework, based on the novel Dy–O chains connected by the sulfate groups through helical chains. **2** crystallizes with monoclinic symmetry, space group $C2/c$, [$a = 13.5605(17)$ Å, $b = 6.7676(8)$ Å, $c = 18.318(2)$ Å, $\alpha = 90°$, $\beta = 102.265(2)°$, $\gamma = 90°$, $V = 1642.7$ (4) Å^3, $Z = 4$]. Its layered framework is attained by the europium atoms connected by the sulfate groups arranged in a helical manner.

Keywords: Hydrothermal synthesis; Dysprosium; Europium; Sulfate; Crystal structure

1. Introduction

The significant interest in the crystal engineering of two- and three-dimensional inorganic frameworks reflects their widespread applications in electrical conductivity, catalysis, adsorption, ion-exchange, radioactive waste remediation and optical devices [1–5]. Compared with other transition metals, the rare-earth elements adopt a large range of coordination numbers and long M–O bond lengths to allow the formation of new topological frameworks based on the various polyhedra. One of the strategies used in the synthesis of lanthanide one-, two- or three-dimensional frameworks is to employ hydrothermal technique as the synthesis method [6–10]. Successful examples reported include the preparations of lanthanide sulfates [6–9]. More recently, other topics in three-dimensional materials chemistry are the inorganic materials with helical pores or chains due to their particularly desirable applications in enantiotopic selective separation, optical materials and catalysis. Among a variety of frameworks reported, very limited numbers of germinates [16] and phosphates [11–15] have such chiral structural features. For examples, $[NH_3(C_2H_4)NH_2(C_2H_4)NH_3][Zn_4(PO_4)_3(HPO_4)]\cdot H_2O$ [10] has the intersecting helical chains, UCSB-7 [16] possesses cross-linked helical pores and $[Ln_2(IDC)_2(H_2O)_3]\cdot 1.5H_2O$ [17] (IDC = 4,5-imidazoledicarboxylate). As well, $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7]$ [11] contains interpenetrating double helices. It is therefore vital to design novel rare-earth three-dimensional frameworks with chiral structural features in order to explore their catalytic and optical properties [18,19]. Here we report the hydrothermal synthesis and structural characterization of two lanthanide sulfate inorganic frameworks, designated as **1** and **2**, of particular interest on the helical M–O chains as the building unit of both compounds.

2. Experimental

2.1. Synthesis and characterization of $DySO_4(OH)$

The colorless crystals of $DySO_4(OH)$ or 1 (average sizes: $0.10 \times 0.12 \times 0.14$ mm) were prepared by a hydrothermal

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doi:10.1016/j.jssc.2007.05.005

method from solution consisting of Dy_2O_3 (0.2611 g), H_2O (1.0276 g), tetramethylammoniumhydroxide solution (2.0329 g, 10%) and sulfuric acid (0.3191 g, 98%), in a molar ratio of the 1:81.6:3.2:4.6. The final pH was 1.0–1.5. This gel was sealed in a 24 ml Teflon-lined autoclave and heated at 180 °C for 6 days. The product was washed with deionized water, dried at room temperature for 1 day to give the colorless crystals (0.1126 g, yield 17.4% based on Dy).

2.2. Synthesis and characterization of $Eu_2(SO_4)_3(H_2O)_8$

The colorless crystals of $Eu_2(SO_4)_3(H_2O)_8$ **2** (average sizes: $0.10 \times 0.09 \times 0.08$ mm) were prepared by a hydrothermal method from solution consisting of Eu_2O_3(0.1219 g), H_2O(10.00 ml), tetramethylammonium hydroxide solution (1.0845 g, 10%) and sulfuric acid (0.3201 g, 98%), in a molar ratio of the 1:1604:3.4:9.2. The final pH was 1.0–1.5. This gel was sealed in a 24 ml Teflon-lined autoclave and heated at 180 °C for 6 days. The product was washed with deionized water, dried at room temperature for 1 day to give the colorless crystals (0.0891 g, yield 34.96% based on Eu).

The element analyses were performed on Leeman inductivity coupled plasma (ICP) spectrometer. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Thermogravimetric analyses were carried out in N_2 atmosphere on a diamond thermogravimetric analyzer from 50 to 1200 °C at a heating rate of 10° C/min.

2.3. Determination of crystal structure

Single crystals of two compounds were carefully selected under a microscope and glued at the tip of a thin glass fiber with cyanoacrylate adhesive. Single-crystal structure determination by XRD was performed on a Bruker Apex2 CCD equipped with a normal focus at 273 K, sealed tube X-ray source (Mo KR radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. Both structures were solved by direct

Table 1
Crystal data and structure refinement for **1** and **2**

	$DySO_4(OH)$	$Eu_2(SO_4)_3(H_2O)_8$
Empirical formula	$HDyO_5S$	$H_{16}Eu_2O_{20}S_3$
Formula weight(g/mol)	275.57	736.23
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$C2/c$
Unit cell dimensions	$a = 7.995(4)$ Å	$a = 13.5605(17)$
	$b = 10.945(5)$ Å	$b = 6.7676(8)$
	$c = 8.164(4)$ Å	$c = 18.318(2)$
	$\beta = 93.619(6)^\circ$	$\beta = 102.265(2)^\circ$
Volume	713.0(5) Å^3	1642.7(4) Å^3
Z	8	4
Calculated density	5.135 Mg/m^3	2.977 Mg/m^3
Absorption coefficient	21.427 mm^{-1}	8.049 mm^{-1}
$F(0\,0\,0)$	984	1400
Crystal size	$0.10 \times 0.08 \times 0.07$ mm	$0.10 \times 0.08 \times 0.07$ mm
θ range for data collection	3.12–26.00°	2.28–25.50°
Limiting indices	$-6 \leqslant h \leqslant 9$,	$-12 \leqslant h \leqslant 16$,
	$-13 \leqslant k \leqslant 12$,	$-7 \leqslant k \leqslant 8$,
	$-10 \leqslant l \leqslant 9$	$-22 \leqslant l \leqslant 17$
Reflections collected / unique	3715/1395	4060/1522
	[R(int) = 0.0261]	[R(int) = 0.0234]
Max. and min. transmission	0.3154–0.2232	0.6027–0.4999
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	1395/9/133	1522/12/139
Goodness-of-fit on F^2	1.032	1.085
Final R indices	$R_1 = 0.0283$,	$R1 = 0.0225$,
[$I > 2$sigma(I)]	$wR_2 = 0.0768$	$wR2 = 0.0614$
R indices (all data)	$R_1 = 0.0345$,	$R1 = 0.0228$,
	$wR_2 = 0.0798$	$wR2 = 0.0616$
Largest diff. peak and hole	1.983 and -3.154 e·Å^{-3}	1.803 and -0.594 e·Å^{-3}

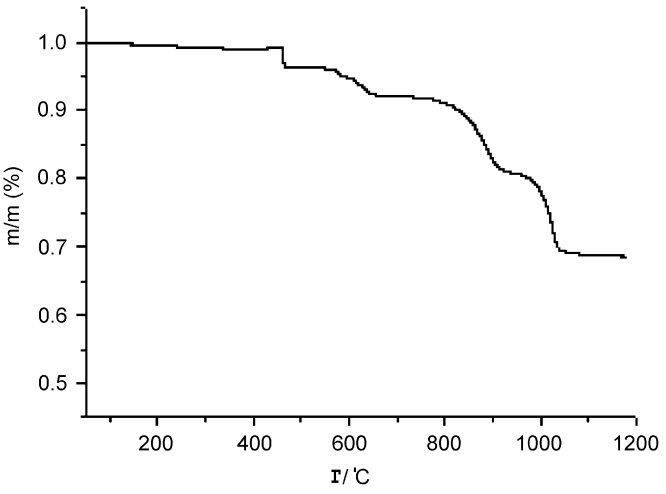

Fig. 1. TG curve of $DySO_4(OH)$ **1**.

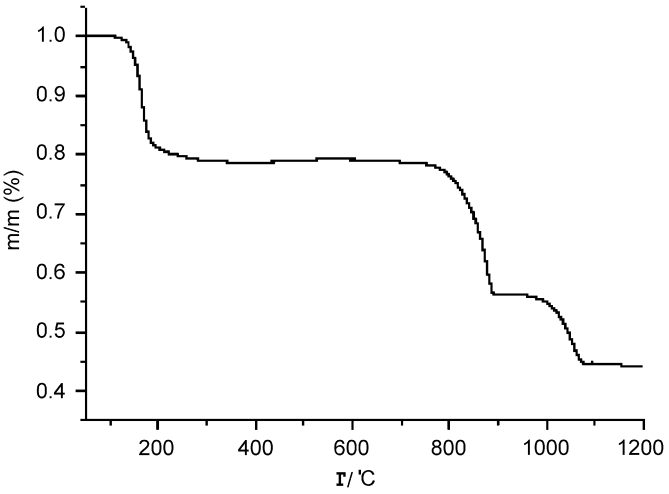

Fig. 2. TG curve of $Eu_2(SO_4)_3(H_2O)_8$ **2**.

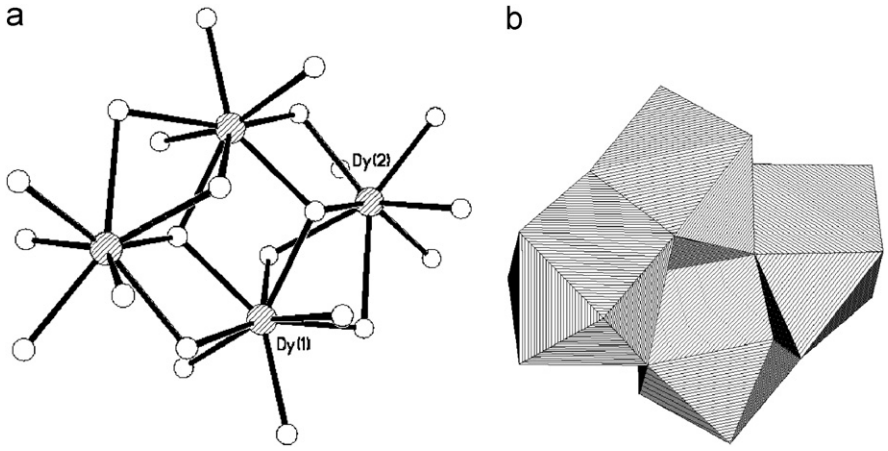

Fig. 3. (a) Building unit $[Dy_4O_{16}(OH)_6]$ of **1**, (b) polyhedral representation of building unit $[Dy_4O_{16}(OH)_6]$.

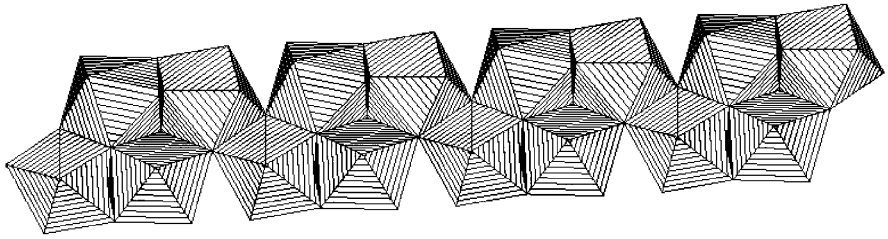

Fig. 4. Polyhedral representation of one-dimensional Dy–O chain by the building units $[Dy_4O_{16}(OH)_6]$.

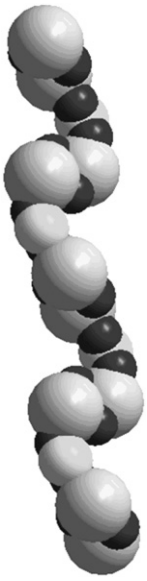

Fig. 5. Helical [Dy–O–Dy–O–S]n chains in **1**.

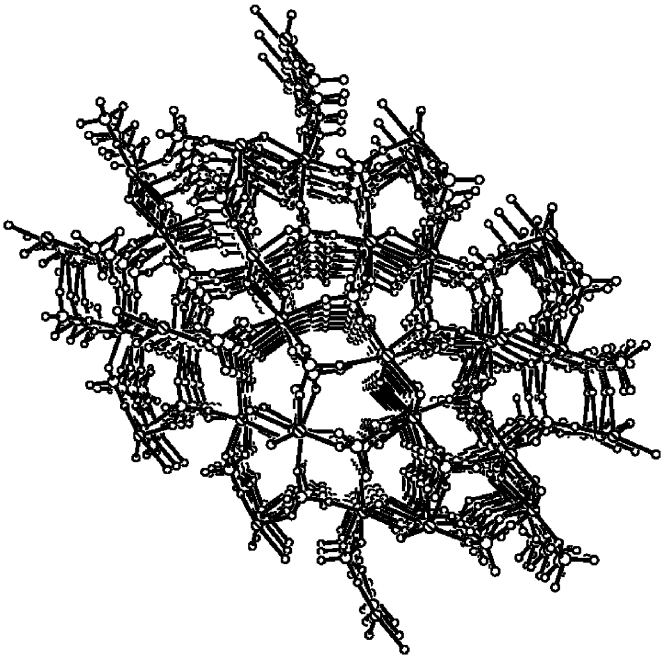

Fig. 6. Three-dimensional framework of $DySO_4(OH)$ **1**.

methods and refined on F^2 by full-matrix least-squares methods using the SHELX97 program package. All non-hydrogen atoms were refined anisotropically. The H atoms of OH and water for both structures were located from difference map. Further details of the X-ray structural analysis for the two compounds are given in Table 1.

3. Results and discussion

3.1. Characterizations

The analysis showed that compound **1** contained Dy 59.14 wt% (calc. 58.98 wt%). The compound **2** contained Eu 36.58 wt% (calc. 36.36 wt%).

IR of **1** (cm^{-1}): 3554.25(s), 3496.65(s), 2361.59(s), 1180.76(m), 751.00(w). IR of **2** (cm^{-1}): 3373.46(w), 1641.06(s), 1140.46(s), 1001.91(s), 601.96(s).

Thermal analysis shows that the total weight loss of **1** is 33.2% (calc.32.31%). As shown in Fig. 1, the weight loss of 4.2% in the range of 50–420° C corresponds to the removal of water (the calculated is 3.27%). The weight loss of 29.0% in the range 420–1100° C due to the loss of SO_3, which is excellent in agreement with calculated value (29.04%). The final product is Dy_2O_3.

As shown in Fig. 2, the weight loss of 20.50% in the range of 50–320° C to the removal of water (calc.19.57%).

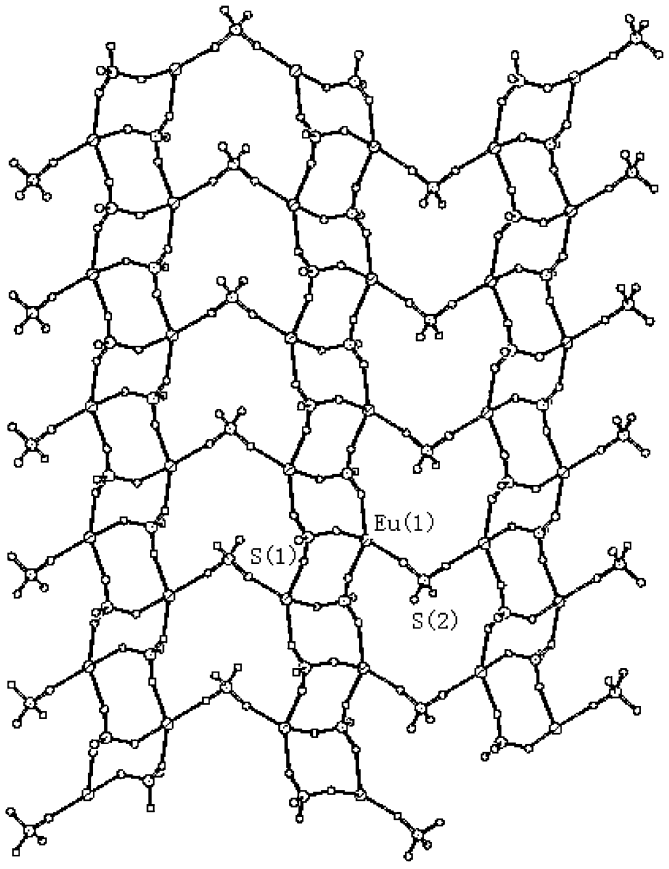

Fig. 7. Layered framework of $Eu_2(SO_4)_3(H_2O)_8$ **2**.

The weight loss of 34.40% in the range 320–1100° C corresponds to the loss of SO_3 (calc. 32.61%). The total weight loss is 54.90%, and the final residual at 1100 °C is Eu_2O_3. The thermal analysis results for both compounds are comparable with other reported rare earth sulfates [20].

3.2. Description of the structures

3.2.1. $DySO_4(OH)$ 1

The XRD analysis of a single crystal of **1** revealed that the 3-D frame-work is DyO_8 and SO_4^{2-} polyhedra. In the structure of **1** there are 20 crystallographically independent non-hydrogen atoms, all of them belong to the framework, including two dysprosium atoms, two sulfate groups and two water molecules. Both Dy atoms are coordinated by eight O atoms from SO_4^{2-} and OH^- groups, while all the S are tetrahedrally coordinated by four O atoms with the S–O distances 1.463(6)–1.497(6), which is comparable with those reported lanthanide sulfates. The O–S–O angles are within the expected range for tetrahedral geometry. The bond distances Dy–O vary from 2.328(6) to 2.678(6) Å, while the angles O–Dy–O are between 64.6(2)° and 144.9(2)°, that were found in other reported Dy compounds [21–23].

The structure of framework **1** can be described from a building unit $[Dy_4O_{16}(OH)_6]$ attached to bridging SO_4^{2-} groups. As shown in Fig. 3, the tetrameric $[Dy_4O_{16}(OH)_6]$ unit is composed of four edge-sharing $DyO_6(OH)_2$ polyhedra. Two adjacent $DyO_6(OH)_2$ polyhedra are sharing bridging atoms to generate a three-membered ring; two three-membered rings are sharing edge to produce a novel moreover SUB $[Dy_4O_{16}(OH)_6]$. The bridging O atoms (O_3 and crystallographic partners) link to adjacent two tetrameric $[Dy_4O_{16}(OH)_6]$ units to generate an interesting one-dimensional chain (Fig. 4). The adjacent [Dy–O] chains are linked by the bridging SO_4^{2-} groups through helical [Dy–O–Dy–O–S]n chains (Fig. 5) to make a three-dimensional framework of $DySO_4(OH)$ (Fig. 6). The central axis for every Dy–O helical chain is a twofold screw axis (symmetry: $0.5-x$, $0.5+y$, $0.5-z$). The OH^- groups are involved strong hydrogen bonding reactions with other O atoms from inorganic framework [O4…O9,

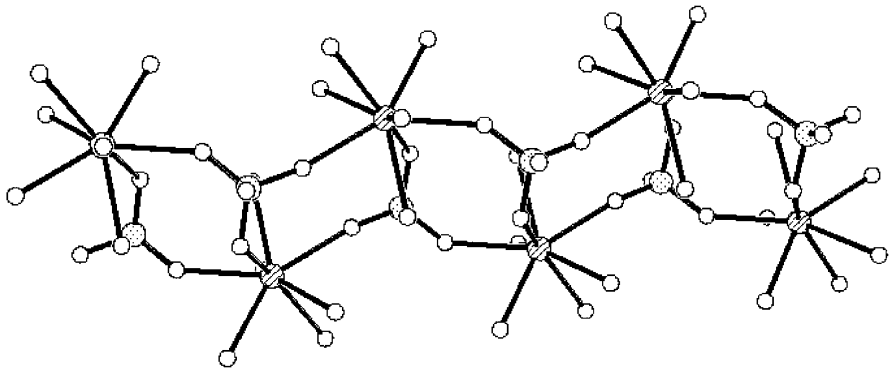

Fig. 8. Double zig-zag chain in **2**.

2.77(2); O4…O3a(−0.5+x, 1.5−y, 0.5+z); O9…O9a(−x, 1−y, 1−z), 2.77(2), O9…O6a(1−x, 1−y, 1−z), 2.64(2)].

3.2.2. $Eu_2(SO_4)_3(H_2O)_8$ 2

As shown in Fig. 7, the layered framework of $Eu_2(SO_4)_3(H_2O)_8$ is constructed from double zig-zag [Eu–O–S–O] chains and two-bridging SO_4^{2-} groups. In the structure of **2**, there are two crystallographically independent S atoms, one of them (S_1) makes three S–O–Eu linkages through two-bridging O atoms [S–O–Eu bridges] to generate a double zig-zag chain, in which two zig-zag chains are sharing the bridging O atoms, as shown in Fig. 8. While other S atoms (S_2 and crystallographic partners) marks two S–O–Eu linkages, and connect adjacent double zig-zag chains through helical [Eu–O–S–O] chains (Fig. 9) to produce a layer of $Eu_2(SO_4)_3(H_2O)_8$. The distances between the adjacent layers are 6 Å, approximately. The water molecule of inorganic framework are involved hydrogen bonds with other water molecule from adjacent layers to form a three-dimensional open framework of $Eu_2(SO_4)_3(H_2O)_8$ (Fig. 10). Every Eu atom is coordinated by eight O atoms: four from SO_4^{2-} groups and four from water molecule. The Eu–O distances are between 2.3373(19) and 2.5126(19) Å, while the angles of O–Eu–O vary from 68.48(7)° to 141.02(7)°, which are in agreement with the reported Eu compound [24,25]. Similar to compound **1**, the S atoms are tetrahedrally coordinated by four O atoms with the bond lengths of 1.453(2)–1.4723(19) Å and the angles of 108.62(11)–112.00(12)°.

Fig. 9. Helical [Eu–O–S–O] chains in **2**.

In the synthesis of both compounds, tetramethylammonium hydroxide plays important roles as SDA (structure-directing agent), though it is not included in the final product. Similarly DABCO (1,4-diazabicyclo[2,2,2]octane) was used as SDA in the preparation of borogermanate $KBGe_2O_6$ [26].

3.3. Optical properties of $Eu_2(SO_4)_3(H_2O)_8$

Because of the excellent luminescent properties of Eu^{3+}, the compound $Eu_2(SO_4)_3(H_2O)_8$ was investigated. Compound **2** shows red luminescence. Fig. 11 showed the solid-state emission spectrum of $Eu_2(SO_4)_3(H_2O)_8$ at room temperature. The emission spectrum exhibits the characteristic transition of Eu^{3+} ion. It is attributed to $^5D_0 \rightarrow {}^7F_J (J = 0,1,3,4)$ transitions: 580 nm $^5D_0 \rightarrow {}^7F_0$; 590 nm and 592.5 nm $^5D_0 \rightarrow {}^7F_1$; 614 and 616 nm $^5D_0 \rightarrow {}^7F_2$; 652.5 nm $D_0 \rightarrow {}^7F_3$; 697.5 nm $^5D_0 \rightarrow {}^7F_4$. Above luminescent property is in agreement with the reported Eu compounds [3,17]. It can predict that the five excitation bands are all the effective energy excitation for the luminescence of Eu^{3+} ions.

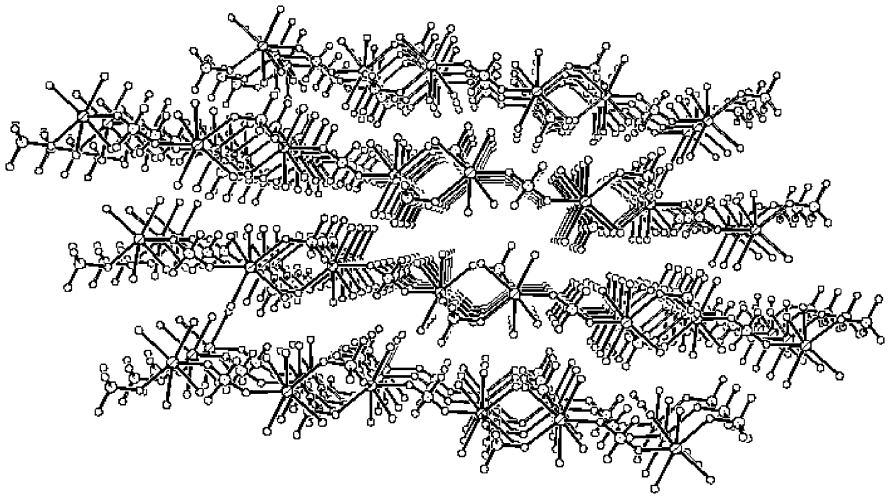

Fig. 10. Three-dimensional open framework of $Eu_2(SO_4)_3(H_2O)_8$ in **2**.

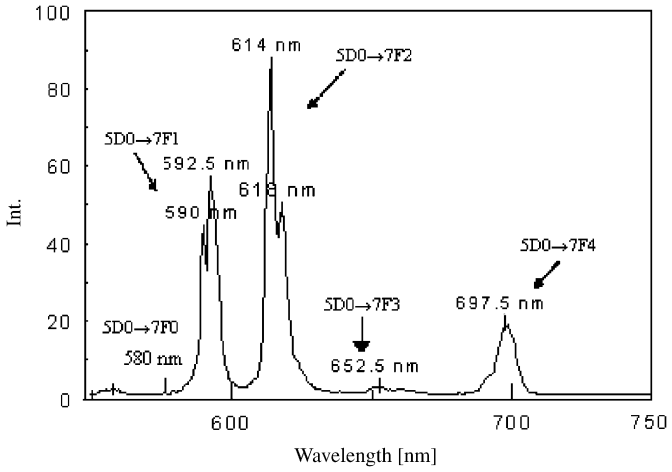

Fig. 11. Solid-state emission spectra of $Eu_2(SO_4)_3(H_2O)_8$ corresponding to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) transition at room temperature (excited at 395 nm).

4. Conclusions

In summary, we have reported two simple, high-yield and pure phase synthesis of 3-D and 2-D framework lanthanide sulfate $DySO_4(OH)$ and $Eu_2(SO_4)_3(H_2O)_8$. The helical chains were found in both frameworks. The ultraviolet absorption spectrum indicate that these Eu compound exhibits luminescence of Eu^{3+}. The synthesis of both compounds has demonstrated that the lanthanide can be designed and prepared by using appropriate solvent and SDAs. The luminescence in the solid state indicates the 2 is an excellent candidate for fluorescent materials.

Acknowledgment

The authors thank the Nature Science Foundation of Liaoning province (20062139) for financial support.

Appendix A. Supplementary material

CC DC CSD-417255 and CSD-417256 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.com.ac.uk/conts/retrieving.html, or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1E2, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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