

Thermal and spectroscopic investigation of europium and samarium sulphates hydrates by TG-FTIR and ICP-MS techniques[☆]

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Abstract

The investigation of europium(III) sulphate hydrate and samarium(III) sulphate hydrate was performed by thermal analysis (TG-DTG) and simultaneous infrared evolved gas analysis-Fourier transformed infrared (EGA-FTIR) spectroscopy. The TG, DTG and DTA curves were recorded at the 25–1400 °C in the dynamic air atmosphere by TG/DTA analyser. The infrared evolved gas analysis was obtained on the FTIR spectrometer. $\text{Eu}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ ($n = 3.97$) and $\text{Sm}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ ($n = 8.11$) were analysed, the dehydration and decomposition steps were investigated and the water content was calculated. The formation of different oxysulphates was studied.

The trace rare earth elements in Eu and Sm sulphates were determined by ICP-MS. The concentration of trace Eu, Sm, La, Gd, Y and Ce ranged from 3.9×10^{-6} to $1.5 \times 10^{-4}\%$ (m/m).

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1. Introduction

Rare earth elements compounds (REECs) have a numerous applications in various industrial and technological fields, they are important materials in the synthesis of high-temperature superconductors and luminophors [1,2]. Lanthanide-doped Y_2O_3 is well-known phosphors material used for the lighting and cathode ray tubes and has shown promise in the development of high power lasers [3–5].

Especially, Eu-doped alkaline-earth sulphides such as CaS:Eu and SrS:Eu and considered to be one of the most promising candidates for red phosphor, compared with other sulphides (ZnS:Eu , ZnS:Sm) [6,7]. Calcium sulphide doped with europium and samarium (CaS:Eu , Sm) has been found

to be one of important matrix for electron trapping optical memory materials (ETOMs) [8].

The research on rare earth sulphites has been focused on their complex thermal degradation in various atmospheres is shown in a review of Niinistö and Leskelä [9]. The thermal analysis of Er, Ce, Nd and Sc sulphites has been studied in detail [10–12]. Thermogravimetric study of europium sulphite trihydrate $\text{Eu}_2(\text{SO}_3)_3 \cdot 3\text{H}_2\text{O}$ was performed in dynamic air and nitrogen atmosphere in temperature range 25–1250 °C [13]. The thermal behaviours of samarium sulphite sulphate hydrate were examined by X-ray powder diffraction, thermal analysis and IR spectroscopy by Leskelä et al. [14]. The trends in the thermal dehydration and decomposition reactions of rare earth sulphates hydrates has been studied in air by TG and DTA/DSC techniques by Niinistö et al. [15]. The thermal decomposition of hydrated europium sulphate has been studied by high-resolution luminescence spectroscopy and thermal analysis by Lunch et al. [16]. The synthesis and thermal decomposition of some rare earth(III) dimethylammonium

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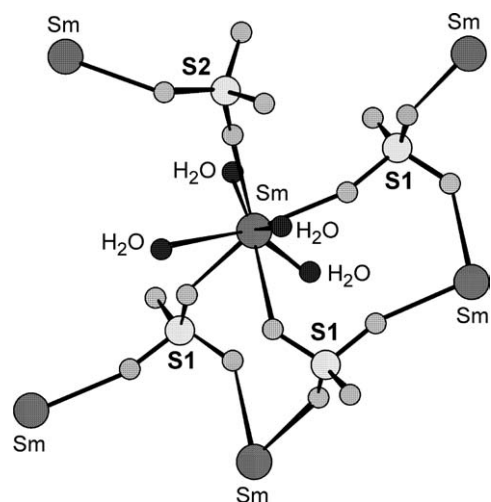


Fig. 1. Structure of Sm coordination in $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. Structural information of Podbereskaya and Borissov [28].

sulphate crystallohydrates have also been investigated [17].

As the demand for rare earth elements compounds is increasing, the development of analytical methods for the determination of trace impurities in those materials is required. It is well known that inductively coupled plasma atomic emission spectrometry (ICP-AES) and ICP-MS have been widely applied to determination of trace amounts of rare earth elements, because of its high sensitivity, wider linear dynamic range, relative freedom from interferences and low detection limits [18–25]. Developments and summary of analysis of advanced materials by ICP-AES and ICP-MS presented by Fisher et al. [26].

In earlier reports, we studied thermal investigation of rare earth carbonates [27] and the determination of activators in cathodoluminophors [2]. The aim of the present study is to characterise the thermal decomposition of europium and samarium sulphates by thermal analysis (TG-DTG) and simultaneous infrared evolved gas analysis-Fourier transform infrared (EGA-FTIR) spectroscopy. Another aim of this work is to develop an effective method for the determination of trace rare earth impurities in Sm and Eu sulphates.

The crystal structure of $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ was refined from X-ray diffraction data. The crystals are monoclinic, space group $C2/c$ [28]. The structure of Sm coordination in $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ is shown in Fig. 1. The central Sm atom are surrounded by four aquo ligands, and the four oxygen atoms forming the bridge between the Sm and sulphur. The sulphur atoms are present in two special positions S1 and S2. The sulphur atoms S1 are bounded with tree Sm atoms and the sulphur atoms S2 are bounded with two Sm atoms.

The recent crystal structure of dieuropium trisulphate octahydrate $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ was presented by Wey and Zeng [29].

Table 1

The operating conditions for ICP-MS

Inductively coupled plasma	
RF power	1.320 kW
Reflected power	5.0 W
Plasma gas flow	13.3 l min ⁻¹
Auxiliary gas flow	0.72 l min ⁻¹
Nebuliser gas flow	0.93 l min ⁻¹
Sample uptake	1.0 ml min ⁻¹
Nebuliser	Concentric nebuliser
Spray chamber	Double-pass (cyclonic chamber)
Observation height	15 mm
Data acquisition parameters	
Scanning mode	Peak hopping
Dwell time	30 ms
Sweeps	100
Number of replicates	3
Read delay time	25 s
Ion lens system	Optimised by ¹¹⁵ In

2. Experimental

2.1. Equipments and procedures for thermal and infrared spectroscopic analysis

The TG-DTG curves were obtained using Pyris Diamond TG/DTA (2002 Seiko Instruments, Inc) thermal analyser in the temperature range 25–1400 °C. The dynamic experiment was carried out in air atmosphere with a flow rate 100 ml min⁻¹ and a heating rate 10 °C min⁻¹. The Pt cups were used and the samples mass was varied between 8 and 12 mg.

The TG-FTIR analysis was carried out by Perkin Elmer PC series TGA-7 thermogravimetric analyser in the temperature range 25–900 °C in air atmosphere with a flow rate 80 ml min⁻¹ and a heating rate 10 °C min⁻¹. Samples mass was varied between 10 and 20 mg and the samples were weighed in platinum pans. The infrared evolved gas analysis was performed on a FTIR spectrometer Perkin-Elmer System 2000 with KBr optics, in a dynamic air atmosphere. The TG analyser was coupled to FTIR by a heated transfer line and a heated 10 cm³ gas cell was used in FTIR [27,30].

2.2. Apparatus and operating conditions for ICP-MS

A quadrupole ICP-MS instrument Thermo Elemental X Series (Winsford, Cheshire, UK) was used in analyses. Sample introduction was made with a conventional pneumatic concentric nebuliser (Meinhard type A1) and the instrument was equipped with CETAC-500 autosampler. The ICP operating conditions and data acquisition parameters are given in Table 1.

2.3. Materials

The analysed REE sulphates:

- *Europium(III) sulphate hydrate*, $\text{Eu}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, 99.9%, Aldrich Chemical Company Inc., Milwaukee, USA;

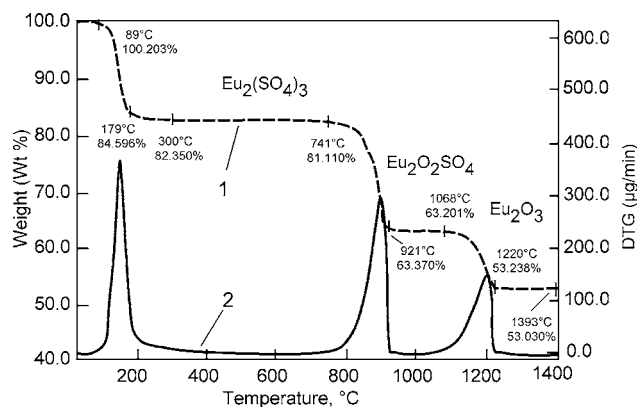


Fig. 2. TG-DTG analysis of europium(III) sulphate hydrate in dynamic air atmosphere: (1) TG curve and (2) DTG curve.

- *Samarium(III) sulphate hydrate*, $\text{Sm}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, 99.9%, Aldrich Chemical Company Inc., Milwaukee, USA.

2.4. Reagents and standards for ICP-MS analysis

Stock solutions, containing 1000 mg l^{-1} of Eu, Sm, Gd, Y, Ce and La were prepared using 99.99% purity oxides: Eu_2O_3 , Sm_2O_3 , Gd_2O_3 , Y_2O_3 , Ce_2O_3 and La_2O_3 (Aldrich Chemical Company Inc., Milwaukee, USA). The calibration standards were prepared by serial dilution of the stock solution with $18 \Omega \text{ cm}^{-1}$ deionised water, and concentrated nitric acid (Suprapur, Merck, Darmstadt, Germany) was added to standard solution (5% HNO_3 , v/v). Six multi-element calibration standards were used in following range: 0.02, 0.05, 0.50, 1.0, 5.0, 20.0 ng ml^{-1} (ppb) of Eu, Sm, Gd, Y, Ce and La. The samples of Eu and Sm sulphates ($0.2 \pm 0.0002 \text{ g}$) were dissolved in deionised water and 2.5 ml nitric acid, Suprapur, Merck was added and the samples were transferred into 50 ml volumetric flask. All standard solutions and samples were prepared by dilution by mass in polyethylene flasks previously cleaned according to a procedure for trace element analysis [31].

3. Results and discussion

3.1. TG-DTG analysis of europium and samarium sulphates hydrates

The TG and DTG curves were recorded at the $25\text{--}1400^\circ\text{C}$ in the dynamic air atmosphere (Pyris Diamond TG/DTA thermal analyser) and are shown in Figs. 2 and 3. The weight loss peak around $110\text{--}190^\circ\text{C}$ is indicated by hygroscopic water, where those appearing at $190\text{--}400^\circ\text{C}$ are attributed to bound water. The complete dehydration of Eu and Sm sulphates hydrates occurring around $230\text{--}400^\circ\text{C}$. The weight loss (%) estimated from TG and DTG curves of analysed samples in the different temperature range selected is presented in

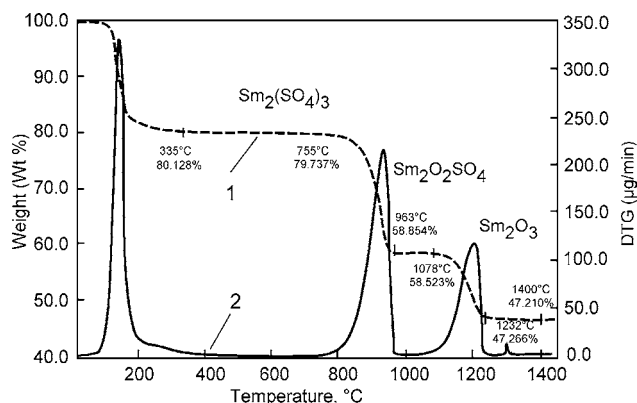
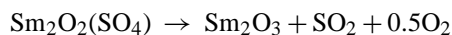
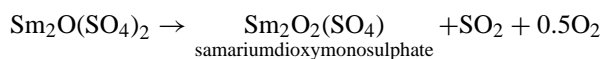
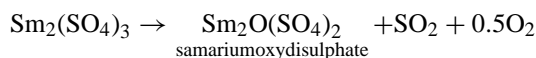
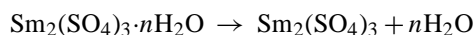


Fig. 3. TG-DTG analysis of samarium(III) sulphate hydrate in dynamic air atmosphere: (1) TG curve and (2) DTG curve.

Table 2. The europium sulphate hydrate is hygroscopic and containing the adsorbed water.

According to opinion of authors and previously cited works of Niinistö et al. [14,15] and Lurch et al. [16] a two different oxysulphates must exist and the decomposition mechanism is:



Anhydrous $\text{Eu}_2(\text{SO}_4)_3$ begins to decompose at 741°C and $\text{Sm}_2(\text{SO}_4)_3$ at 755°C . The formation of unstable Eu and Sm oxydisulphate associates at $780\text{--}850^\circ\text{C}$. The complete decomposition to more stable Eu-dioxymonosulphate occurs at $920\text{--}1070^\circ\text{C}$ and Sm-dioxymonosulphate at $965\text{--}1080^\circ\text{C}$, finally to Eu_2O_3 at 1220°C and to Sm_2O_3 at 1235°C .

3.2. FTIR evolved gas analysis

The evolved gases from the TG ($25\text{--}900^\circ\text{C}$) were analysed by FTIR. The same major decomposition products are observed in all samples including water and SO_2 .

In the course of the dehydration steps $100\text{--}186^\circ\text{C}$ and $186\text{--}400^\circ\text{C}$ the characteristic water peaks at $1700\text{--}1500 \text{ cm}^{-1}$ and at $3740\text{--}3500 \text{ cm}^{-1}$ can clearly be seen. SO_2 gives two strong absorption peaks at 616 and 1104 cm^{-1} and weak peaks at $3850\text{--}3650 \text{ cm}^{-1}$ (Table 3).

Stacked plot FTIR gas spectra from the thermal decomposition of Eu and Sm sulphates hydrates are presented in Figs. 4 and 5.

The decomposition of Eu and Sm sulphates hydrates clearly proceeds via several stages and these results confirm

Table 2
Results of TG-DTG analysis of europium and samarium sulphates hydrates

Sample	Temperature range (°C)						
	25–200	200–400	400–700	700–960	960–1160	1160–1400	25–1400
Weight loss (%)							
Eu ₂ (SO ₄) ₃ · <i>n</i> H ₂ O ^a , <i>n</i> = 3.97, MW = 663.58	16.95	0.70	0.74	18.23	10.14	0.21	46.97
Sm ₂ (SO ₄) ₃ · <i>n</i> H ₂ O ^b , <i>n</i> = 8.11, MW = 734.90	18.20	1.67	0.40	21.21	10.72	0.60	52.79

MW: molecular weight.

^a Expected SO₂ wt.% of Eu₂(SO₄)₃ → Eu₂O₃: 40.56%.

^b Expected SO₂ wt.% of Sm₂(SO₄)₃ → Sm₂O₃: 40.79%.

Table 3
Decomposition products of Eu and Sm sulphates and major peaks of FTIR gas spectra

Sample	Decomposition gases (wavenumber, cm ⁻¹)	
	H ₂ O	SO ₂
Eu ₂ (SO ₄) ₃ ·3.97H ₂ O	186 °C: 1542.0, 1508.3, 1716.3, 3736.1, 3649.8, 3567.6, 3588.0	900 °C: 616.2, 1104.4, 1340.5, 1374.0, 1508.0, 3649.7, 3751.0
Sm ₂ (SO ₄) ₃ ·8.11H ₂ O	185 °C: 1457.3, 1508.3, 1647.9, 1698.5, 1716.3, 3503.5, 3525.7, 3649.8, 3712.0, 3736.1	900 °C: 616.2, 1104.4, 1339.8, 1374.3, 1507.8, 3649.6, 3675.8, 3853.6, 3750.5

that intermediate oxysulphates are formed during heat treatment.

3.3. Determination and calculation of water content in analysed sulphates hydrates

The number of water molecules was calculated by using thermoanalytical calculations. The molecular weight of compounds was calculated by using weight % in the TG curves (Figs. 2 and 3, Table 2). The weight % for Eu₂O₃ at 1400 °C was 53.03% and for Sm₂O₃ at 1400 °C was 47.21%. The molecular weight of Eu₂(SO₄)₃·*n*H₂O was 663.58 g mol⁻¹ and *n* = 3.97, the molecular weight of Sm₂(SO₄)₃·*n*H₂O was 734.90 g mol⁻¹ and the number of water molecule *n* = 8.11 (Table 2).

The ratio of central atoms (Eu, Sm) was determined by complexometric titration at pH 3.9–4.0 (acetate buffer), using 1-(2-Pyridylazo)-2-Naphthol (PAN) (pro Analysi, Merck) as an indicator [32,33]. The number of water molecules cal-

culated by complexometric titration were for europium sulphate hydrate (*n* = 4.09) and for samarium sulphate hydrate (*n* = 8.05).

The results of analysis of water content showed no significant differences between the results of TG analysis and chemical method of analysis.

3.4. Determination of trace impurities rare earth elements by ICP-MS

The analysis of individual rare earth elements (REEs) are usually very difficult because the chemical properties of REEs are similar. To users of REEs compounds it is critically important to be able to determine trace levels of impurities REEs in high-purity REEs products. Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful method and its fields of application are rapidly developing because of extremely high sensitivity and interference free analysis. The combination of extraction chromatography with high perfor-

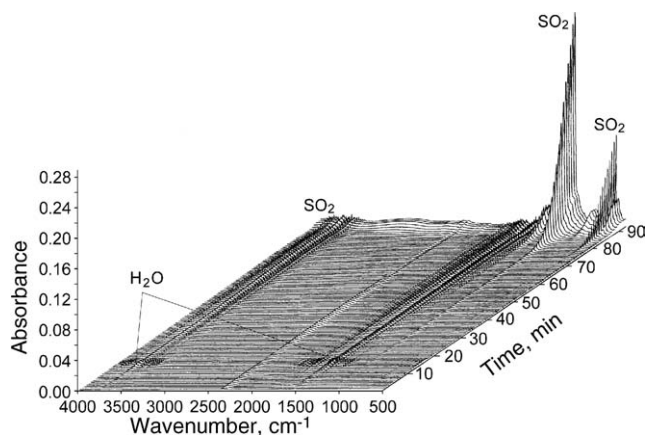


Fig. 4. Stacked plot FTIR gas spectrum of Eu₂(SO₄)₃·3.97H₂O in air.

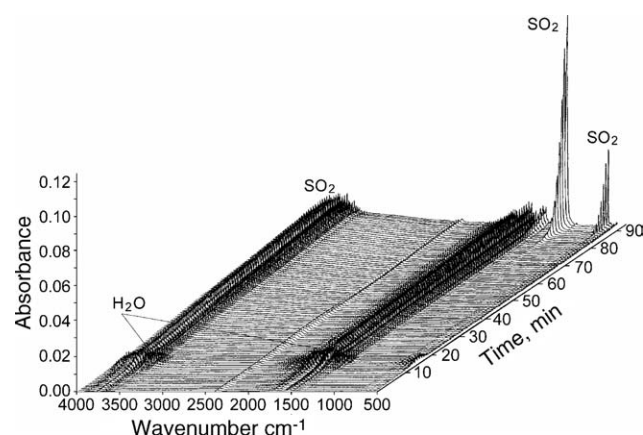


Fig. 5. Stacked plot FTIR gas spectrum of Sm₂(SO₄)₃·8.11H₂O in air.

Table 4
Isotopes and precision (R.S.D., %) of analysis reference standard solution (2.0 ng ml⁻¹) detection limits of elements

Element	Isotope (abundance %)	Concentration (ng ml ⁻¹)			
		Expected	Found ^a		Detection limit (ng ml ⁻¹)
			$\bar{c} \pm s$	R.S.D. ^b (%)	
Eu	151 (47.8)	2.0	1.96 ± 0.05	2.4	0.007
Sm	152 (26.7)	2.0	2.03 ± 0.04	2.0	0.009
La	139 (99.9)	2.0	1.95 ± 0.03	1.8	0.005
Gd	158 (24.84)	2.0	1.93 ± 0.04	2.2	0.009
Y	89 (100)	2.0	2.02 ± 0.03	1.3	0.008
Ce	140 (88.48)	2.0	2.04 ± 0.04	1.9	0.006

^a Six replicates.

^b R.S.D., relative standard deviation.

mance ICP-MS was used for the determination of REEs in high-purity gadolinium and lanthanum oxides [22,23]. The trace REEs in high-purity Y₂O₃ and G₂O₃ (grade of 99.99% purity) were determined using high-resolutions ICP-MS [34]. The concentration of different REEs in gadolinium and yttrium oxides ranged from 3.9 to 2900 ng g⁻¹ (3.9×10^{-7} to 2.9×10^{-4} %, m/m).

The ICP-MS determination of trace elements Y, La, Eu, Sm, Gd and Ce in europium and samarium sulphates (Aldrich, grade of 99.9% purity) were performed. The detection limits (3 σ , blanks prepared as samples) were in the range 0.005–0.009 ng ml⁻¹. The validity of the analytical method was tested by analysing the reference standard solution (Table 4). The results obtained were in good agreement of the recommended values. The precision of the determination (relative standard deviation, R.S.D.) ranged from 1.3 to 2.2%.

The trace impurities of Y, La; Eu, Sm, Gd and Ce were determined in Eu and Sm sulphates and the results obtained are shown in Table 5. The concentration of REEs in analysed sulphates was from 3.9×10^{-6} to 1.5×10^{-4} % (m/m) or from 0.039 to 1.45 μ g g⁻¹. The practical detection limits (PDL) of the elements varied between 1.5×10^{-7} to 2.25×10^{-7} % (m/m).

Table 5
ICP-MS analysis of europium and samarium sulphates (five replicates)

Element (isotope)	Concentration (% m/m)				PDL ^a
	Sm ₂ (SO ₄) ₃ · 8.11H ₂ O		Eu ₂ (SO ₄) ₃ · 3.97H ₂ O		
	\bar{c}	R.S.D. (%)	\bar{c}	R.S.D. (%)	
Eu (151)	1.2×10^{-4}	2.6	—	—	1.75×10^{-7}
Sm (152)	—	—	1.5×10^{-4}	2.7	2.25×10^{-7}
La (139)	3.3×10^{-5}	2.1	6.3×10^{-5}	1.9	1.25×10^{-7}
Gd (158)	1.7×10^{-5}	2.6	9.1×10^{-5}	2.8	2.25×10^{-7}
Y (89)	4.8×10^{-6}	1.8	3.9×10^{-6}	1.7	2.00×10^{-7}
Ce (140)	5.1×10^{-5}	2.0	7.9×10^{-5}	2.1	1.50×10^{-7}

^a PDL (practical detection limit) calculated: sample weight 0.2 ± 0.0002 g, volume 50 ml.

4. Conclusion

The production processes of materials involving heat are well suited for study by methods of thermal analysis, where physical and chemical properties of materials are measured during a controlled temperature programme. The dehydration and decomposition schemes of REE sulphates were investigated. The decomposition of R₂(SO₄)₃ to R₂O₃ clearly proceeds via several stages. The results obtained demonstrate that TG-DTG and FTIR spectroscopic techniques are indispensable tool in order to study rare earth materials. ICP-MS is an excellent capability for trace elements analysis in solid samples in the sub-nano-gram per gram range with a minimum of sample preparation. The results of this study place important implications on the synthesis of cathodoluminophors (CaS:Eu, Sm; SrS:Eu), electron trapping memory materials and in material science.

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