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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. $Eu_2(SO_4)_3{\cdot}nH_2O$ ($n = 3.97$) and $Sm_2(SO_4)_3{\cdot}nH_2O$ ($n = 8.11$) 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 1.5×10^{-4}% (m/m).

Keywords: Eu and Sm sulphates hydrates; TG; DTG analysis; FTIR spectroscopy; ICP-MS

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 $Eu_2(SO_3)_3{\cdot}3H_2O$ 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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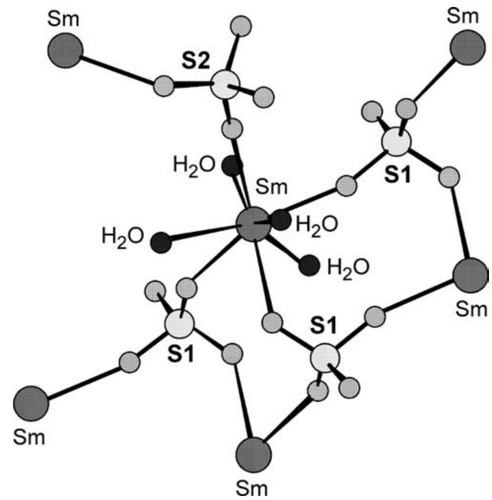

Fig. 1. Structure of Sm coordination in $Sm_2(SO_4)\cdot 8H_2O$. Structural information of Podberezskaya and Borissov [28].

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 $Sm_2(SO_4)_3\cdot 8H_2O$ was refined from X-ray diffraction data. The crystals are monoclinic, space group $C2/c$ [28]. The structure of Sm coordination in $Sm_2(SO_4)_3\cdot 8H_2O$ 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 $Eu_2(SO_4)\cdot 8H_2O$ 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 cm^3 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*, $Eu_2(SO_4)_3\cdot nH_2O$, 99.9%, Aldrich Chemical Company Inc., Milwaukee, USA;