



Infrared evolved gas analysis during thermal investigation of lanthanum, europium and samarium carbonates

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Abstract

The characterisation of rare earth elements carbonates (REECs) was performed by thermal analysis (TG–DTG) combined with simultaneous infrared evolved gas analysis–Fourier transform infrared (EGA–FTIR) spectroscopy. The TG–DTG curves were obtained using the Perkin-Elmer PC series TGA-7 thermogravimetric analyser in the temperature range 25–800 °C both in dynamic air and nitrogen atmosphere.

$\text{La}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$, $\text{Eu}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ and $\text{Sm}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ were analysed, the dehydration and decarbonation steps were investigated and the water content was calculated. The trace rare earth elements in lanthanum, europium and samarium carbonates were determined by Philips PU 7000 inductively coupled plasma atomic emission spectrometry (ICP-AES) and the concentration of REE ranged from 6.2×10^{-5} to $4.2 \times 10^{-4}\%$ (w/w).

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Keywords: REE carbonates (R = La, Eu, Sm); TG–DTG analysis; FTIR spectroscopy; ICP-AES

1. Introduction

The requirement of high-purity rare earth elements carbonates (REECs) in a many industrial fields as semiconductors, high temperature superconductors, luminophors and optic–electronics areas is increasing rapidly [1,2]. REECs and oxides are very important materials in the synthesis of high-temperature superconductors $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ (R: rare earth element and Y) [3,4]. Lanthanide-doped Y_2O_3 is well-known phosphors material used for lighting and cathode ray tubes and has shown promise in the development of high power lasers [5–7]. The luminescence properties of

alkaline-earth sulphides with rare earth activator have drawn considerable attention due to their potential use for electro- and cathodo-luminescence display [7].

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 application of coupled thermal and gas analysis methods provides information on type and quantity of gases evolved during technical production processes [8,9].

There are many published studies on the thermal decomposition of Ln(III) oxalates [10–12]. Using a combination of various techniques as high-resolution TGA, TG–FTIR, HT-DRIF and HT-XRD the more intermediate products could be detected during the thermal decomposition of lanthanum oxalate by

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Vanhoyland et al. [13]. A comparative TG and DTG study of the preparation and thermal stability of lanthanum and gadolinium oxycarbonates was published by Hölsä and Turkki [14]. The stability of the carbonates of rare earth elements (Ce, Pr, Gd, Tb, Dy, Ho, Er) was investigated by thermogravimetry to determination of solid-state basicity of rare earth oxides [15].

In the present study we extend the investigations of dehydration and decomposition of lanthanum, europium and samarium carbonates to observe the reactions associated with the controlled heating procedure at 25–800 °C in dynamic air and nitrogen atmosphere. The characterisation of REECs is performed by thermal analysis (TG–DTG) and simultaneous TG–FTIR. For the determination of trace impurities of rare earth elements the inductively coupled plasma atomic emission spectrometry (ICP–AES) technique was used [16].

2. Experimental

2.1. Equipments and procedure

The TG–DTG curves were obtained using a Perkin-Elmer PC series TGA-7 thermogravimetric analyser in the temperature range 25–800 °C. The sample mass was varied between 10 and 20 mg and the samples were weighed in the platinum pans [17]. The dynamic experiment were carried out both in air and nitrogen atmosphere with a flow rate 80 ml min⁻¹ and a heating rates 2 and 10 °C min⁻¹. The infrared evolved gas analysis was performed on a FTIR spectrometer Perkin-Elmer System 2000 with KBr optics, in a dynamic air and nitrogen atmosphere.

The trace element analysis of REECs was obtained by use a PU 7000 Philips sequential ICP–AES. The spectrometer is equipped with a Gilson 221 autosampler and Philips P3230 computer. The ICP operation parameters and optimal conditions of analysis are summarised in the earlier publication of the present authors [16].

2.2. Materials

The analysed REE carbonates:

- lanthanum(III) carbonate hydrate (La₂(CO₃)₃·nH₂O), 99.9%, Fluka, Switzerland;

- europium(III) carbonate hydrate (Eu₂(CO₃)₃·nH₂O), 99.9%, Reak. Khim, Sverdlovsk, Russia;
- europium(III) carbonate hydrate ((Eu₂(CO₃)₃·nH₂O), 99.9%, Aldrich Chemical Company Inc., Milwaukee, USA;
- samarium(III) carbonate hydrate (Sm₂(CO₃)₃·nH₂O), 99.99%, Aldrich Chemical Company Inc., Milwaukee, USA.

The analysed carbonates were an orthorhombic lanthanite-type REE carbonates and one-phase materials by using single-crystal X-ray diffraction techniques.

2.3. Reagents and standards for ICP–AES analysis

Stock solutions, containing 1000 mg l⁻¹ of Eu, Sm, Gd, Y and La, were prepared using 99.99% purity oxides: Eu₂O₃, Sm₂O₃, Gd₂O₃, Y₂O₃, and La₂O₃ (Aldrich Chemical Company Inc., Milwaukee, USA). The calibration standards were prepared by serial dilution of the stock solution with 18 Ω cm⁻¹ deionized water, and concentrated nitric acid (Suprapur, Merck, Darmstadt, Germany) was added to standard solution (5% HNO₃, (v/v)). Five multi-element calibration standards were used in following range: 0.02–5.0 mg l⁻¹ of Eu, Sm, Gd, Y, and La.

All samples of REECs (0.5 ± 0.0002 g) were dissolved in 6 M nitric acid, Suprapur, Merck (10 ml). The dissolved samples were transferred into 100 ml volumetric flask and diluted to volume with deionized water. The blank samples were also prepared following the instructions described above.

3. Results and discussion

3.1. TG–DTG and EGA–FTIR analysis

The thermal analysis (TG–DTG) and EGA–FTIR can be used to identify various components of REECs and observe the reactions associated with a controlled heating process in the dynamic air and nitrogen atmosphere. The TG and DTG curves were recorded in the 25–800 °C range both in air and nitrogen atmosphere and are shown in Figs. 1a–4a. The weight loss peak around 100 °C is induced by hygroscopic water (i.e. physically absorbed water),

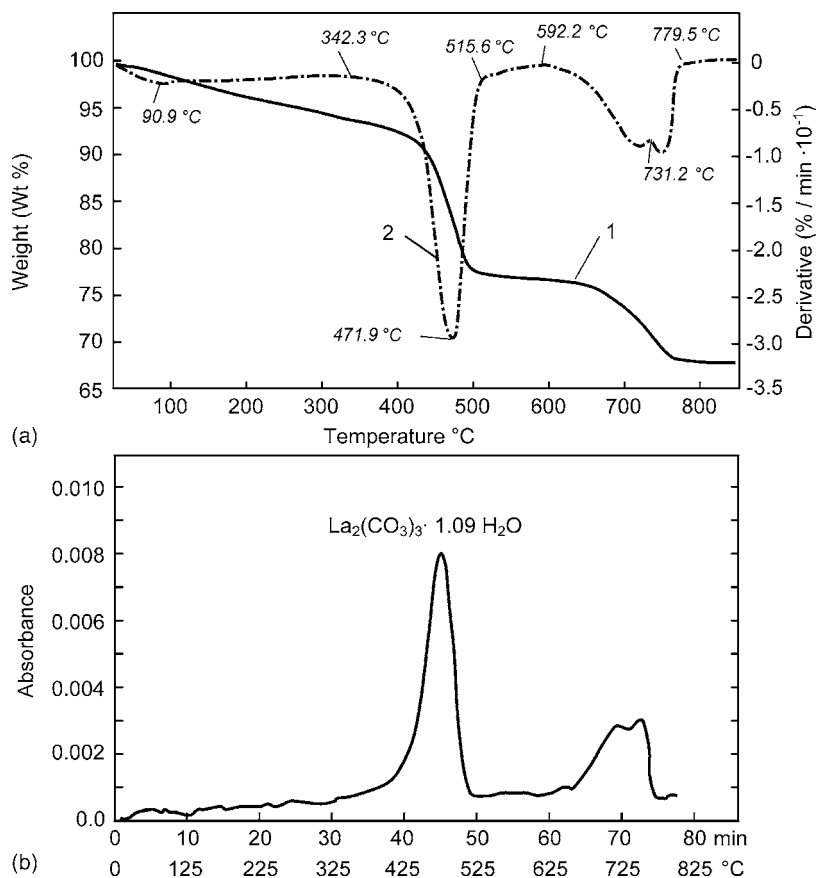


Fig. 1. (a) TG–DTG analysis of lanthanum carbonate (Fluka) in dynamic nitrogen atmosphere: 1—TG curve, 2—DTG curve; (b) RMS intensity profile of evolved gases at 25–825 °C in nitrogen.

whereas those, appearing at 170–300 °C are attributed to bound water. The complete dehydration of rare earth carbonates occurring around 280–380 °C. The weight loss (%) estimated from TG and DTG curves of analysed REECs in the different tempera-

ture range selected is presented in Table 1. From the observed decomposition curves in dry air and nitrogen, it was apparent that the decomposition mechanism of REE carbonates was not sensitive to the atmosphere.

Table 1
TG–DTG analysis of REECs

Sample	Atmosphere	Weight loss (%)					
		25–125 °C	125–300 °C	300–480 °C	480–570 °C	570–800 °C	25–800 °C
La ₂ (CO ₃) ₃ ·nH ₂ O (99.9%, Fluka) ^a	N ₂	1.28	3.89	11.83	5.46	9.31	31.77
Eu ₂ (CO ₃) ₃ ·nH ₂ O (99.9%, Reak. Khim.) ^b	N ₂	1.22	5.80	9.48	9.57	7.36	33.43
Eu ₂ (CO ₃) ₃ ·nH ₂ O (99.9%, Aldrich) ^b	Air	0.75	2.05	9.80	14.08	6.34	33.02
Sm ₂ (CO ₃) ₃ ·nH ₂ O (99.99%, Aldrich) ^c	Air	13.02	2.88	8.12	8.36	7.46	39.94

^a Expected CO₂ wt.% of R₂(CO₃)₃ → R₂O₃: 28.83%.

^b Expected CO₂ wt.% of R₂(CO₃)₃ → R₂O₃: 27.28%.

^c Expected CO₂ wt.% of R₂(CO₃)₃ → R₂O₃: 27.46%.

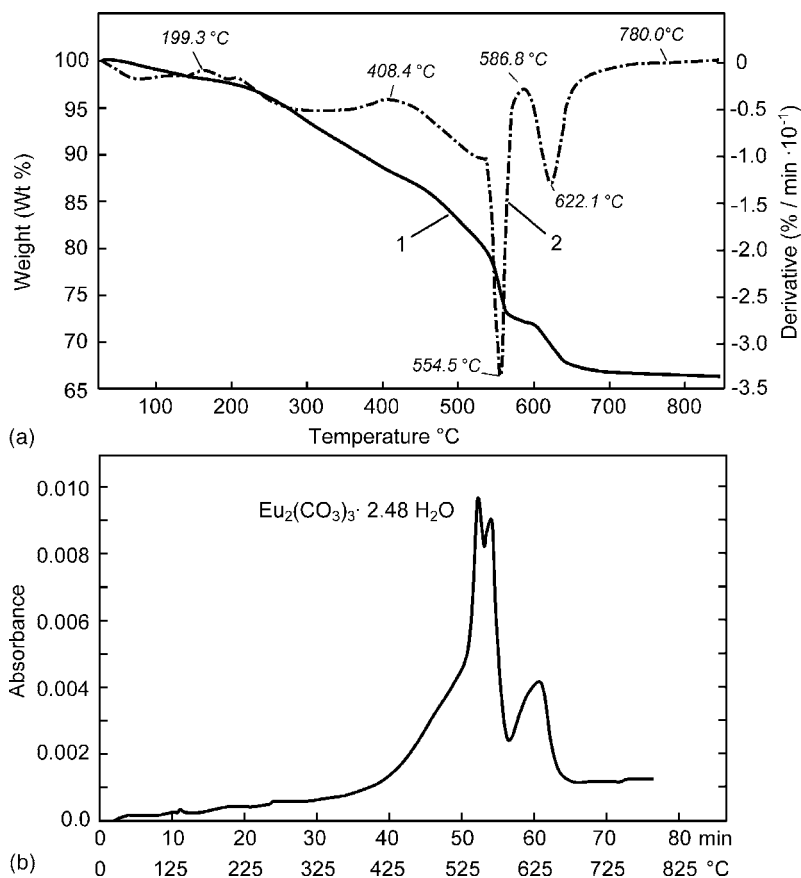
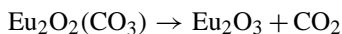


Fig. 2. (a) TG–DTG analysis of europium carbonate (Reak. Khim.) in dynamic nitrogen atmosphere: 1—TG curve, 2—DTG curve; (b) RMS intensity profile of evolved gases at 25–825 °C in nitrogen.

According to opinion of authors and previously cited work of Vanhoyland et al. [13] a two different oxycarbonates must exist and the decarbonisation mechanism is:



The reaction temperatures which are indicated the loss of CO₂ are shown in Table 2. The evolved gas from the TG was analysed by FTIR. The TG was coupled to the FTIR by heated transfer line and a heated 10 cm gas cell was used in the FTIR analysis. The temperature of the transfer line and gas cell was

adjusted to 200 °C. Scanning and data collection parameters were: resolution, 8 or 4 cm⁻¹; scan speed, 0.2 cm s⁻¹; detector, DTGS. The detected peaks of the root-mean-square (RMS) or Gram–Schmidt (GS) intensity profiles of the total evolved gases were successfully used in the FTIR experiment in parallel the TG curves, as shown in Figs. 1b–4b. The evolved gases mostly consist of the CO₂ and water. The infrared spectra show the water peaks at 1628–1541 and 3735–3526 cm⁻¹. CO₂ gives two strong absorption peaks at 670 and 2359–2311 cm⁻¹. Stacked plot FTIR gas spectra from the thermal decomposition of REECs are presented in Figs. 5–8. The decomposition of REE carbonates clearly proceeds via several stages and these results confirm that intermediate oxycarbonates is formed during the heat treatment.

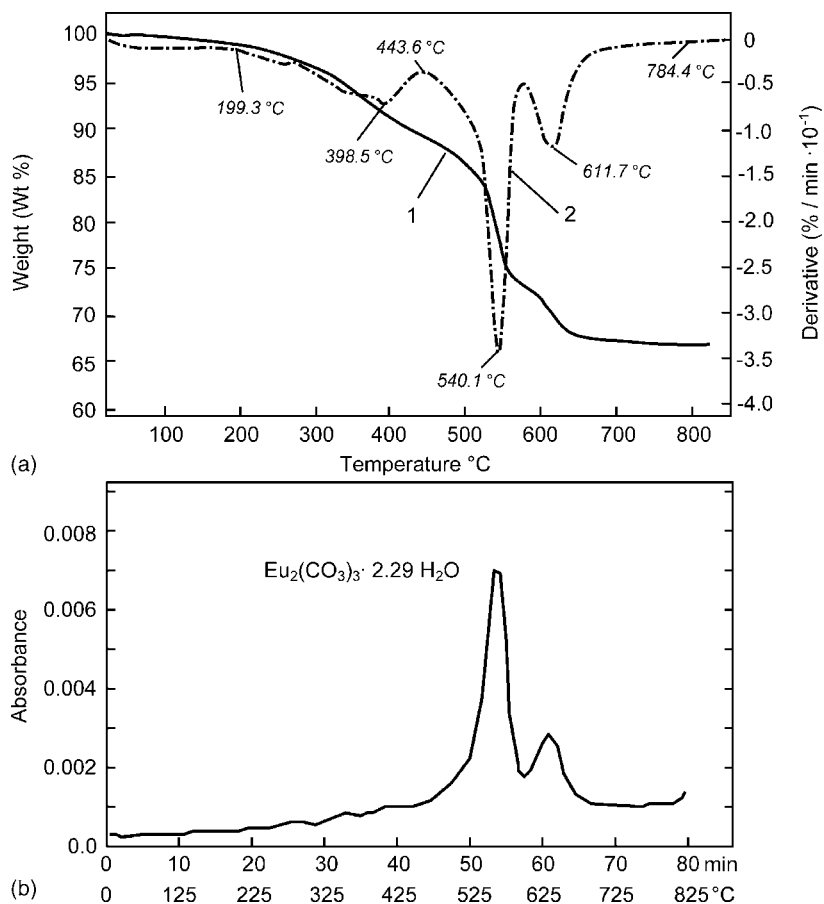


Fig. 3. (a) TG–DTG analysis of europium carbonate (Aldrich) in dynamic air atmosphere: 1—TG curve, 2—DTG curve; (b) RMS intensity profile of evolved gases at 25–825 °C in air.

Table 2
Dehydration and decarbonisation temperatures of REECs

Compounds	Temperature (°C)			
	La ₂ (CO ₃) ₃ ·1.09H ₂ O (Fluka)	Eu ₂ (CO ₃) ₃ ·2.48H ₂ O (Reak. Khim.)	Eu ₂ (CO ₃) ₃ ·2.29H ₂ O (Aldrich)	Sm ₂ (CO ₃) ₃ ·5.54H ₂ O (Aldrich)
R ₂ (CO ₃) ₃ · <i>n</i> H ₂ O	25–280	25–325	25–380	25–300
R ₂ (CO ₃) ₃	280	325	380	300
R ₂ O(CO ₃) ₂	480	480–490	530	480
R ₂ O ₂ CO ₃	525	560	560	540–550
R ₂ O ₃	770	800	770	780
H ₂ O% (w/w)	4.13	8.44	7.90	17.21
CO ₂ % (w/w)	27.64	24.99	25.12	22.73

R = La, Eu, Sm.

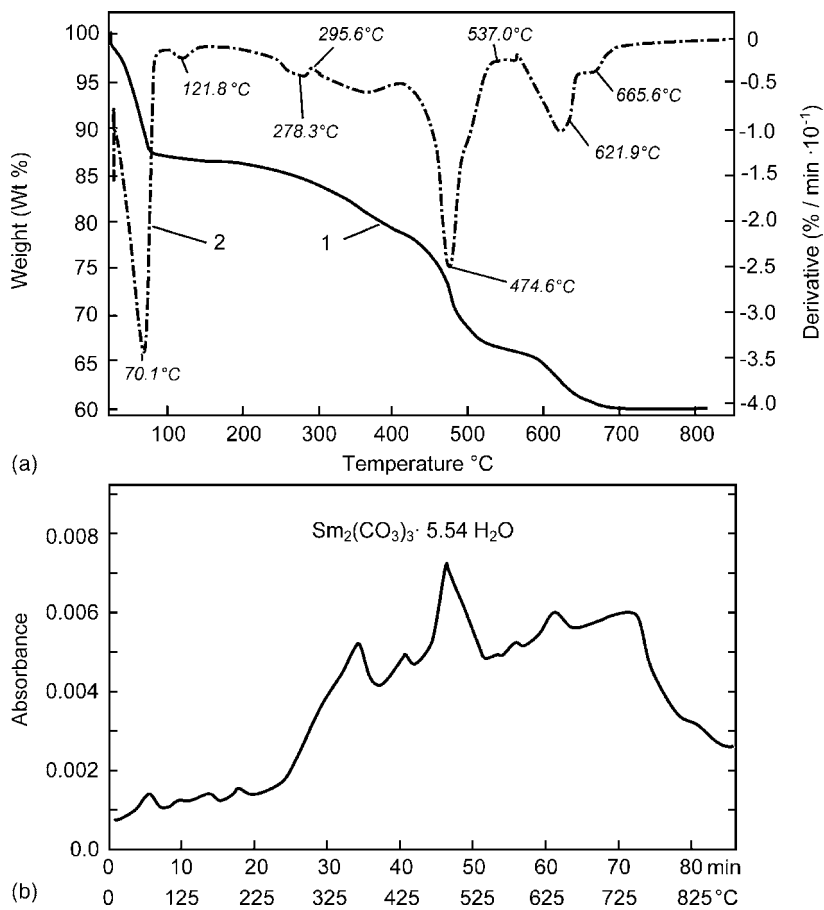


Fig. 4. (a) TG–DTG analysis of samarium carbonate (Aldrich) in dynamic air atmosphere: 1—TG curve, 2—DTG curve; (b) RMS intensity profile of evolved gases at 25–825 °C in air.

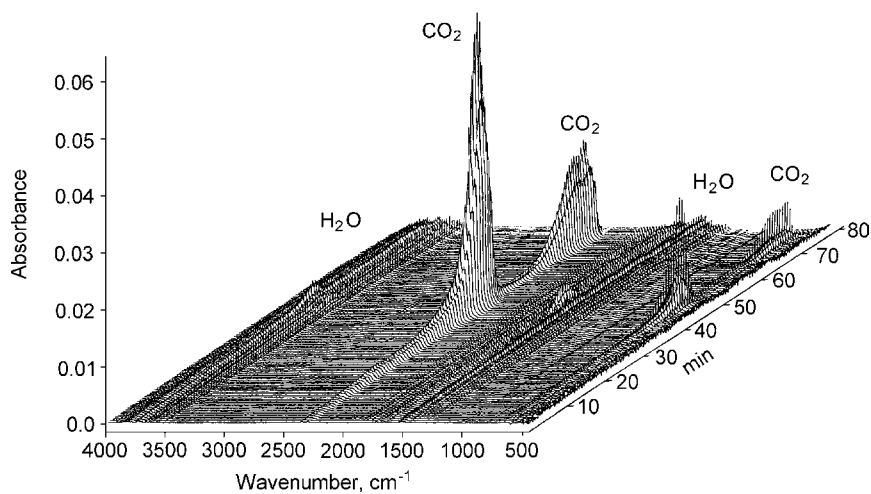


Fig. 5. Stacked plot FTIR gas spectrum of $\text{La}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ in nitrogen.

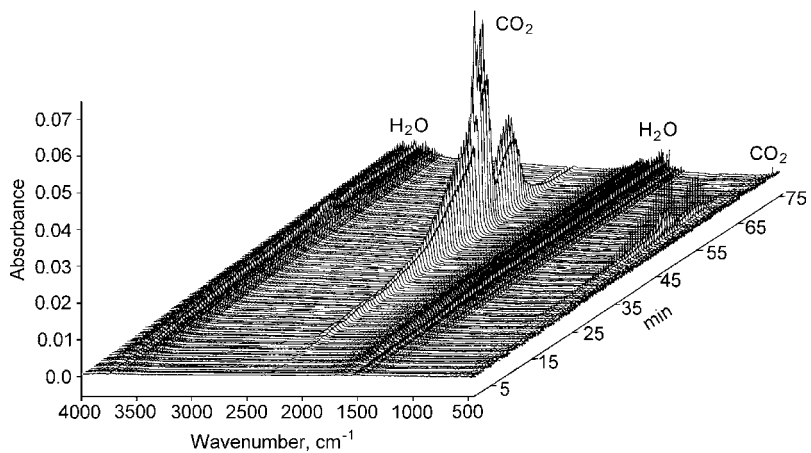


Fig. 6. Stacked plot FTIR gas spectrum of $\text{Eu}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ (Reak. Khim.) in nitrogen.

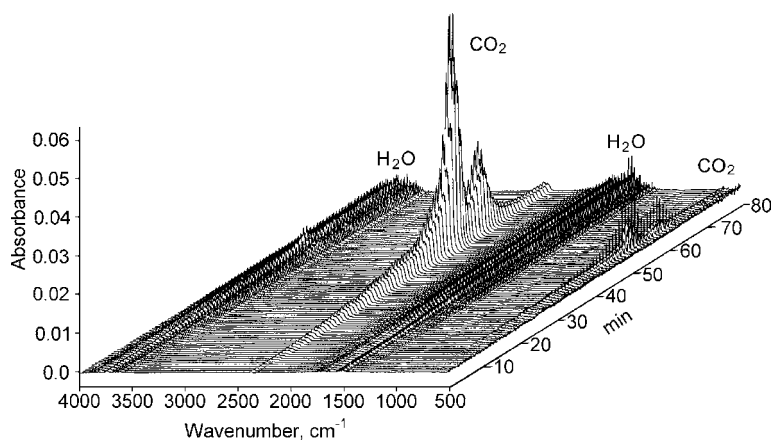


Fig. 7. Stacked plot FTIR gas spectrum of $\text{Eu}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ (Aldrich) in air.

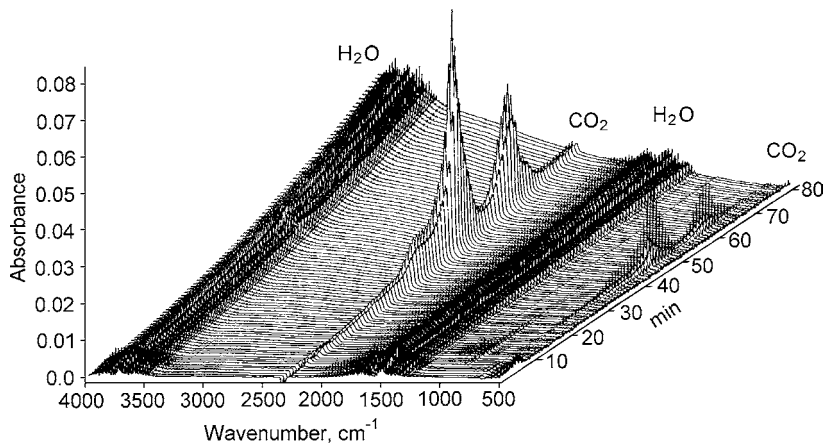


Fig. 8. Stacked plot FTIR gas spectrum of $\text{Sm}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ (Aldrich) in air.

Table 3
Results of ICP-AES analysis of REECs, detection limits (DLs) and practical detection limits (PDLs)

Samples	Concentration (% , w/w) ^a									
	Sm (359.260 nm)		Eu (381.967 nm)		Gd (342.247 nm)		Y (371.030 nm)		La (333.749 nm)	
	\bar{c}	R.S.D. (%)	\bar{c}	R.S.D. (%)	\bar{c}	R.S.D. (%)	\bar{c}	R.S.D. (%)	\bar{c}	R.S.D. (%)
La ₂ (CO ₃) ₃ ·1.09H ₂ O (99.9%, Fluka)	3.2×10^{-4}	1.6	1.8×10^{-4}	1.3	1.5×10^{-4}	1.7	4.2×10^{-4}	1.4	–	–
Eu ₂ (CO ₃) ₃ ·2.48H ₂ O (99.9%, Aldrich)	1.5×10^{-4}	2.2	–	–	4.0×10^{-4}	2.8	9.2×10^{-5}	1.8	8.3×10^{-5}	1.5
Eu ₂ (CO ₃) ₃ ·2.29H ₂ O (99.9%, Reak. Khim.)	1.8×10^{-4}	2.4	–	–	2.2×10^{-4}	3.1	3.6×10^{-4}	1.1	4.1×10^{-4}	1.4
Sm ₂ (CO ₃) ₃ ·5.54H ₂ O (99.99%, Aldrich)	–	–	1.3×10^{-4}	1.9	1.2×10^{-4}	2.6	8.0×10^{-5}	2.0	6.2×10^{-5}	1.8
DLs (mg l ⁻¹)	0.004	–	0.002	–	0.006	–	0.004	–	0.003	–
PDLs (% , w/w) ^b	8.0×10^{-5}	–	4.0×10^{-5}	–	1.2×10^{-4}	–	8.0×10^{-5}	–	6.0×10^{-5}	–

^a Four replicates.

^b PDLs calculated: sample weight, 0.5 ± 0.0002 g; volume, 100 ml.

The weight losses of the TG curves and FTIR spectroscopic analysis make possible to calculate the water and CO₂ contents in the analysed REE carbonates: La₂(CO₃)₃·1.09H₂O, (99.9%, Fluka), Eu₂(CO₃)₃·2.48H₂O, (99.9%, Reak. Khim), Eu₂(CO₃)₃·2.29H₂O, (99.9%, Aldrich), and Sm₂(CO₃)₃·5.54H₂O, (99.99%, Aldrich). The content of water in different samples, calculated in the 25–380 °C range, varies between 4.13 and 17.21% (w/w). The percent of adsorbed water (25–125 °C) was between 0.75 and 1.28% for La and Eu carbonates and 13.02% for Sm carbonate. The content of CO₂ was 22.73–27.64% (Table 2).

3.2. Trace element analysis of REE carbonates by ICP-AES

To supply high-purity REE carbonates to users, it is critically important to be able to determine trace levels of impurity REE in the high-purity rare earth compounds. Traditionally, ICP-AES had been utilised for REE determinations [2,16,18]. Spectral lines for ICP-AES measurements were selected on the basis of minimum spectral line interferences and maximum sensitivity. The lanthanum emission line La(II) at 333.749 nm was used for source peaking (to find an optimum viewing position in the ICP discharge) and satisfactory results were obtained for determination of La, Eu, Sm, Y and Gd. The emission lines La(II) at 333.749 nm, Sm(II) at 359.260 nm, Eu(II) at 381.967 nm, Gd(II) at 342.247 nm and Y(II) at 371.030 nm were used for analysis of REE carbonates. The studied lines were all ion lines (II).

The matrix effects can be substantially reduced by using the operation conditions that lead to an efficient energy transfer between the plasma and the sample. With a high radio frequency power level (≥ 1200 W), a low nebuliser gas flow rate (≤ 0.61 min⁻¹) and a wide injector inner diameter (≥ 2 mm), all ionic lines having an energy sum between 8 and 16 eV are suppressed by more or less the same amount in the presence of the matrix as compared to the matrix free situation. The optimal plasma power was 1200 W, the coolant argon flow rate was 15.01 min⁻¹ and the detection limits (3 S.D. of the blank prepared as sample) were all in the 0.002–0.006 mg l⁻¹ range in the determination of REE. The matrix effects and spectral interferences were studied by scanning of different emission lines by using the standard solutions

containing high concentrations (1000–2000 mg l⁻¹) of matrix elements. The spectral interferences were found on the determination of trace impurities of Gd and Sm in Eu₂(CO₃)₃ and inter-element correction (IEC) technique was performed. The spectral interferences were not encountered on the analysis of La and Sm carbonates. The trace impurities of La, Eu, Sm, Gd and Y were determined in the REE carbonates and the results obtained are shown in Table 3. The concentration of REE in analysed carbonates was from 6.2×10^{-5} to 4.2×10^{-4} % (w/w) and precision of the determination (R.S.D.) ranged from 1.2 to 3.1%.

4. Conclusion

The dehydration and decarbonation schemes of REE carbonates were investigated. The decomposition of R₂(CO₃)₃ to R₂O₃ clearly proceeds via several stages. The results obtained demonstrate that TG–DTG and FTIR spectroscopic techniques are an indispensable tool in order to study features of rare earth materials. The direct ICP-AES method is well suited to the determination of trace level REE impurities in lanthanum, europium and samarium carbonates. The principal advantage of ICP-AES are a low instrumental detection limits, wide dynamic range and good precision. The combination of thermal analysis and spectroscopic methods allows us to present a possibility characterising the thermal properties and chemical quality of different REECs. The results of this study place important implications on the synthesis of cathodoluminophors. Especially, Eu, Sm-doped alkaline-earth sulphides such as CaS: Eu, Sm, and SrS: Eu are considered to be one of the most promising candidates for red phosphors.

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