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THERMAL DECOMPOSITION OF EUROPIUM SULFITE TRIHYDRATE IN CARBON MONOXIDE

MARKKU LESKELÄ and LAURI NIINISTÖ

Department of Chemistry, Helsinki University of Technology, Otaniemi, SF-02150 Espoo 15 (Finland)

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ABSTRACT

Thermal decomposition of $Eu_2(SO_3)_3 \cdot 3\ H_2O$ in carbon monoxide at temperatures up to 900°C has been studied by thermoanalytical methods. Mössbauer and IR spectroscopy and X-ray diffraction methods were used in the identification of reaction products and intermediates. The end products of the reduction process are europium(II) sulfide, EuS, and europium oxysulfide, Eu_2O_2S. The optimum temperature range for Eu_2O_2S production is 700—850°C.

INTRODUCTION

Rare earth oxysulfides, which are important luminescent materials, can be prepared by several methods including carbon monoxide reduction of the corresponding sulfites [1,2]. Thermoanalytical studies have established that in this process a complete dehydration takes place, after which the anhydrous sulfite is reduced in a single step to the oxysulfide [1—3].

Europium sulfite appears to be reduced differently from the other rare earths, probably because, under certain conditions, divalent europium compounds are easily formed [1]. They are known to form in the reduction of europium hydrogen selenite, for example [4]. When europium-activated phosphors, e.g. Eu : Y_2O_2S [2], are produced by the reduction of sulfites; however, it is economically important that nearly all the europium remains in the trivalent state and is transformed as completely as possible into the end product in the form of an oxysulfide.

In order to clarify the thermal decomposition mechanism of europium sulfite and to optimize the reaction conditions with respect to maximum yield of Eu_2O_2S, we have carried out a series of thermoanalytical experiments for $Eu_2(SO_3)_3 \cdot 3\ H_2O$. The chemically quite difficult task of analyzing Eu^{2+} and Eu^{3+}, present simultaneously in the reaction products and intermediates, was solved by recording the Mössbauer spectra where the two oxidation states are readily distinguishable on the basis of their isomer shifts [5].

EXPERIMENTAL

Europium sulfite trihydrate was prepared as described earlier [3,6]. The starting material was Eu_2O_3 of 99.9% purity from Kemira Oy, Oulu, Finland.

TG, DTG and DTA curves up to 900°C were recorded simultaneously with a Mettler Thermoanalyzer TA-1 in a dynamic carbon monoxide atmosphere (95 cm^3 min^{-1}). Standard platinum crucibles (diam. 7 mm, depth 19 mm) were used. The sample weight was approximately 50 mg and alumina was the reference material in DTA.

In batch experiments, 400 mg samples were heated in an 80 cm^3 quartz reactor vessel in carbon monoxide with a flow rate of 100 cm^3 min^{-1}. The temperature range in the batch experiments was 550—900°C. As the crystallinity and luminescence properties of phosphors are significantly improved by firing in an inert atmosphere [7], a portion of the product obtained was afterwards heated at 900°C for one hour in a nitrogen atmosphere.

Mössbauer spectra were recorded for selected samples from both batch and thermoanalyzer experiments. ^{151}Sm in Sm_2O_3, with an activity of 100 mCi, was used as source and absolute calibration of the velocity scale was achieved by the use of ^{57}Fe. Measurements were carried out at room temperature. The source was moved relative to the absorber with a sinusoidal drive. The spectra were detected with a scintillation counter using an energy of 21.6 keV and recorded on a 1024-channel analyzer.

X-Ray diffraction patterns were recorded at 25°C with an Enraf-Nonius FR 552 Guinier camera of 114.6 mm diameter and monochromatized $CuK\alpha_1$ radiation.

IR spectra were measured on a Perkin-Elmer 521 instrument using the KBr pellet technique.

RESULTS AND DISCUSSION

In the first stage of the thermal decomposition of $Eu_2(SO_3)_3 \cdot 3\ H_2O$, the water molecules are expelled and an anhydrous sulfite is formed, as was found earlier [1—3]. According to the DTG and DTA curves, the dehydration takes place in two steps and is complete at 270°C (cf. Fig. 1). The observed weight loss of 9.1% agrees well with the calculated value (9.0%).

The anhydrous phase is not stable and begins to decompose immediately. The decomposition is first endothermic and slow but above 400°C turns into an exothermic and rapid process. The weight loss involved in the slow phase (270—400°C) is only 1.6%. It seems reasonable to assume that the slow endothermic reaction is due to the disproportionation of anhydrous sulfite to sulfide and sulfate. The sulfate is probably in the form of the oxydisulfate, $Eu_2O(SO_4)_2$ [8], but its presence could not be confirmed by X-ray diffraction because of the small concentration and low crystallinity. The sulfide formed is europium(II) monosulfide, EuS. The observed loss of 1.6% would correspond to an 8.4% disproportionation of the sulfite to oxysulfate and monosulfide. Further support for the disproportionation was obtained from the experiments carried out at slower rates; the amount of weight loss increased accordingly.

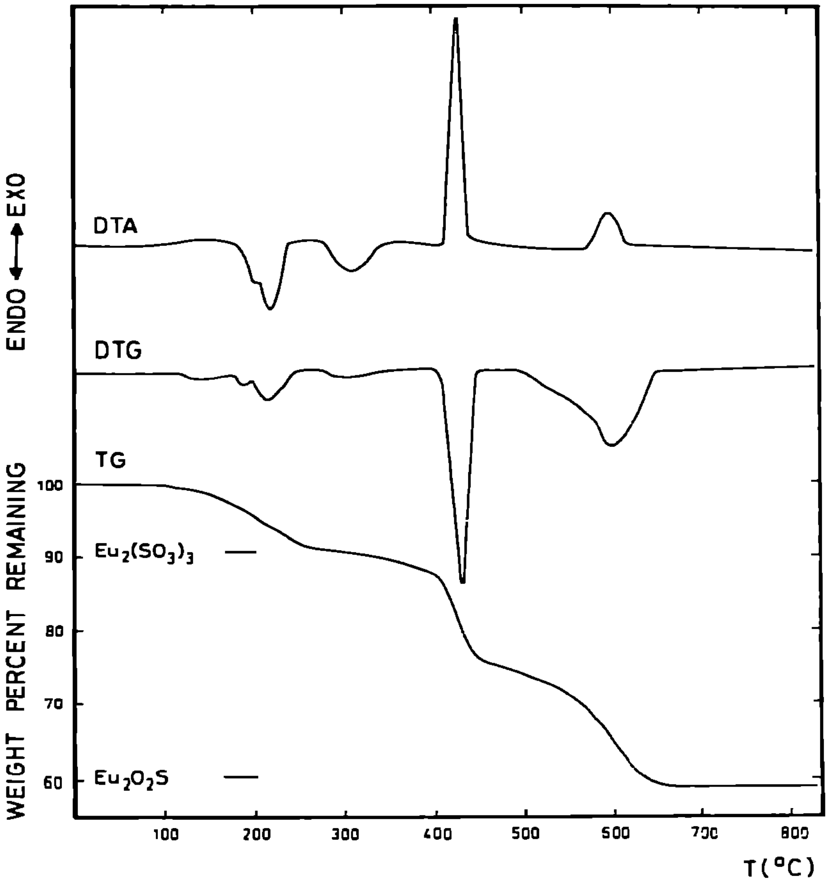

Fig. 1. Thermal decomposition of $Eu_2(SO_3)_3 \cdot 3\ H_2O$ in carbon monoxide. Heating rate 6°C min^{-1}.

After the dehydration and disproportionation reactions, the next change represents the reduction of the sulfite. This step is strongly exothermic and takes place in a relatively narrow temperature range of 410—440°C. The total weight loss of the sample up to the plateau at 450°C is 24.3%. At this stage, the sample contained EuS, $Eu_2O_2SO_4$, and Eu_2O_2S (cf. Table 1). This plateau is not a very distinct one, however, and the decomposition proceeds slowly until 550°C where it is again accelerated and exothermic in nature. The change at 550°C is obviously due to the reduction of $Eu_2O_2SO_4$.

Constant weight of the sample is achieved first at 650°C where 40.2% of the original weight is lost. The reduction goes further than oxysulfide, since the calculated weight loss from $Eu_2(SO_3)_3 \cdot 3\ H_2O$ to Eu_2O_2S is only 38.8%. According to the IR, X-ray diffraction and Mössbauer results, the sample at 650°C contained Eu_2O_2S and some EuS. The presence of EuS was also visible in the purple color of the sample, which disappeared when the EuS was dissolved in acetic acid.

Mössbauer spectra further indicate that the amount of divalent europium almost doubles during the second reduction stage from 450 to 650°C (cf. Fig. 2); at the latter temperature, approximately half of the europium is in

TABLE 1

X-Ray diffraction data for the intermediate and end-products obtained in the thermoanalytic experiments

Heating rate 6° min^{-1}.

Intermediate product at 450°C						End-product at 650°C					
d_{obs} (Å)	I_{obs} [a]	Assignment [b]				d_{obs} (Å)	I_{obs}	Assignment			
		h	k	l	Phase			h	k	l	Phase
6.52	m	0	0	2	A	6.70	vw	0	0	1	C
4.19	w	1	0	1	A	3.47	w	1	1	1	B
3.82	m	0	1	1	A	3.36	m	1	0	0	C
3.45	w	1	1	1	B	3.34	m	0	0	2	C
2.99	m	1	0	3	A	3.00	vs	1	0	1	C
		1	0	1	C	2.96	m	2	0	0	B
2.96	w	0	1	3	A	2.37	m	1	0	2	C
		2	0	0	B	1.94	s	1	1	0	C
2.92	m	1	1	0	A	1.86	s	1	0	3	C
2.69	m	1	1	2	A	1.78	vw	3	1	1	B
2.22	w	0	1	5	A	1.70	w	2	0	0	C
2.17	w	1	1	4	A	1.68	w	1	1	2	C
2.03	w	0	2	0	A	1.63	m	2	0	1	C
1.84	w	2	1	1	A	1.53	vw	4	0	0	B
1.74	vw	1	1	6	A	1.50	m	1	0	4	C
		3	3	1	B	1.46	m	1	1	3	C
1.66	vw	1	2	3	A	1.34	m	2	0	3	C
		1	1	2	C	1.33	m	4	2	0	B
1.61	vw	2	0	1	C	1.27	m	1	1	4	C
1 37	w	0	1	9	A	1.24	m	2	1	1	C
1.33	w	4	2	0	B	1.21	vw	4	2	2	B
		2	0	3	C			2	1	2	C
1.32	vw	2	1	7	A	1.18	w	5	1	1	B
1.28	vw	0	3	3	A						
		1	1	4	C						
1.22	vw	4	2	2	B						

[a] Estimated relative intensities are: vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

[b] A, B and C indicate the phases $Eu_2O_2SO_4$, EuS, and Eu_2O_2S, respectively The indexing is based on lattice parameters determined for the pure compounds [9—11].

the divalent form. In isothermal batch experiments, however, the results were quite different and showed decreasing Eu(II) content with increasing temperature between 550 and 700°C (Table 2). The difference may be due to kinetic factors as the heating rate has an appreciable effect on the decomposition and reduction mechanisms of the europium sulfite (Fig. 2). When the heating rate is slow (2° min^{-1}), an oxysulfate, $Eu_2O(SO_4)_2$, phase is formed after the dehydration. Approximately 20% of this phase decomposes at 480°C to $Eu_2O_2SO_4$ and EuS. The existence of EuS may be observed from the darkening of the material.

There are no great differences between the heating rates of 4 and 6°

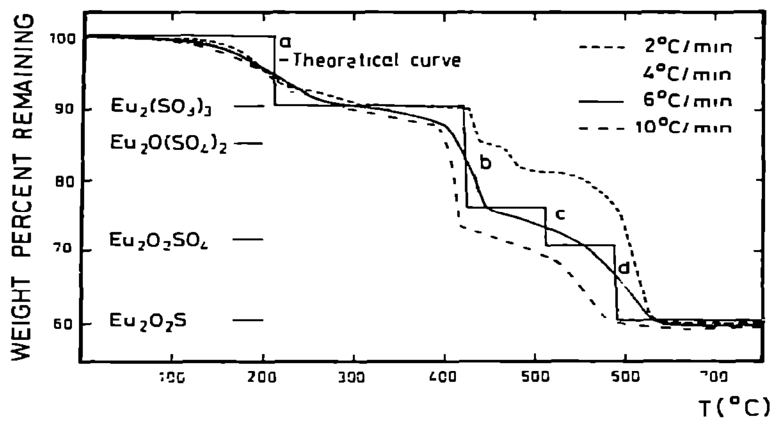

Fig. 2. The effect of heating rate on the decomposition of europium sulfite trihydrate. The theoretical curve has been drawn according to eqn. (1).

min^{-1}, but generally the disproportionation of anhydrous sulfite increases with increasing heating rate; the results obtained with a 10° min^{-1} heating rate are in agreement with this (Fig. 2). As expected, all reactions occur at lower temperature ranges when the heating rate increases. The overall weight losses are not, however, significantly different and the end-products always contain both EuS and Eu$_2$O$_2$S. Greater solubility in acetic acid was observed with faster heating rate, which may be due to either poorer crystallinity of the oxysulfide or to increasing concentration of monosulfide.

CONCLUSIONS

The thermoanalytical results from non-isothermal runs show that the decomposition is a complicated process which is also greatly influenced by the heating rate. The main intermediate products after the anhydrous sulfite

TABLE 2

The amount of Eu^{2+} as analyzed by Mossbauer spectroscopy

Thermoanalyzer [a]		Batch	
T (°C)	Eu^{2+} (%)	*T* (°C)	Eu^{2+} (%)
250		550	33
450	33	600	30
650	>50	650	28
		700	
		750	
		800	
		850	
		900	8

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[a] Heating rate 6° min^{-1}

are $Eu_2O(SO_4)_2$ and $Eu_2O_2SO_4$, but divalent sulfide EuS may be formed, too. The end-product Eu_2O_2S may also contain appreciable amounts of EuS.

When the heating rate is 6° C min^{-1}, the decomposition may be best described by the scheme

$$Eu_2(SO_3)_3 \cdot 3H_2O \xrightarrow{(a)} Eu_2(SO_3)_3 \xrightarrow{(b)} 1/2\ Eu_2O(SO_4)_2 + 1/4\ Eu_2O_2SO_4$$

$$+ 1/2\ EuS \xrightarrow{(c)} 1/4\ Eu_2O(SO_4)_2 + 1/4\ Eu_2O_2SO_4 + 1/6\ Eu_2O_2S$$

$$+ 2/3\ EuS \xrightarrow{(d)} 1/2\ Eu_2O_2S + EuS \qquad (1)$$

The theoretical weight change according to this reaction scheme is shown in Fig. 2. As can be seen from the figure, the decomposition mechanism changes with the heating rates of 2 and 10° C min^{-1}, however. The formation of $Eu_2O(SO_4)_2$ as an intermediate is particularly evident at the low heating rate, whereas at 10° C min^{-1} its presence cannot be verified from the curves.

In the isothermal batch reactions, the reduction scheme changes into the simpler scheme

$$Eu_2(SO_3)_3 \cdot 3H_2O \xrightarrow{-3H_2O} Eu_2(SO_3)_3 \xrightarrow{-SO_3} Eu_2O_2SO_4 \xrightarrow{-2O_2} Eu_2O_2S \qquad (2)$$

Divalent europium does not appear here at all and, indeed, the Mössbauer spectra indicate its absence in the samples when the reduction temperature is in the range 650—850° C.

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