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STUDIES ON LANTHANOID SULFITES. PART VIII.* THERMOGRAVIMETRIC STUDY OF EUROPIUM SULFITE TRIHYDRATE

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When $Eu_2(SO_3)_3 \cdot 3H_2O$ is heated in air it forms after dehydration two sulfite-sulfate phases: $Eu_2(SO_3)_2SO_4$ and $Eu_2SO_3(SO_4)_2$. The latter phase is thermally remarkably stable and decomposes above 700°C via $Eu_2O_2SO_4$ to Eu_2O_3. Anhydrous $Eu_2(SO_3)_3$ and $Eu_2O_2SO_4$ were also found as intermediates before Eu_2O_3 when the TG experiments were carried out in nitrogen but in other details the decomposition mechanism differs from that in air.

Lately the research emphasis on rare earth sulfites has been focused on their complex thermal degradation in various atmospheres as shown by a recent review covering available literature until mid-80ies[1].

In the previous parts of the series, the thermal behaviour of Er, Ce, Nd and Sc sulfites has been studied in detail [2–4]. Under oxidative conditions, cerium forms upon heating the intermediates $Ce_2(SO_3)_2SO_4$ and $Ce_2SO_3(SO_4)_2$ [3]. It has been suggested that $Ce_2(SO_3)_2SO_4$ could be used in a thermochemical cycle for splitting sulfur dioxide into sulfur and oxygen [5]. This interesting property of forming sulfite-sulfate phases seems to be connected with the variable oxidation state of the lanthanoid ion [6], and therefore the present study of europium sulfite trihydrate was initiated.

Experimental

The starting material for thermoanalytical studies, $Eu_2(SO_3)_3 \cdot 3H_2O$, was prepared by precipitation from aqueous solution as described earlier [7]. The TG measurements were carried out in a Perkin-Elmer TGA–7 thermal balance, equipped with the TADS control and computing system, under the following conditions. Heating rate: 2 or 10 deg min^{-1}; sample weight: 10–20 mg; atmosphere: dynamic air or nitrogen; temperature range: 25–1250°. Standard platinum crucibles were employed.

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The starting material and crystalline intermediates ($Eu_2(SO_3)_3$, $Eu_2(SO_3)_2SO_4$, $Eu_2SO_3(SO_4)_2$, $Eu_2O_2SO_4$) were identified by X-ray powder diffractometry (Table 1).

Table 1 X-ray powder diffraction patterns of $Eu_2(SO_3)_3\cdot 3H_2O$, $Eu_2(SO_3)_3$,$Eu_2SO_3(SO_4)_2$ (obtained upon firing at 700°C in air) and $Eu_2O_2SO_4$.

$Eu_2(SO_3)\cdot 3H_2O$		$Eu_2(SO_3)_3$		$Eu_2SO_3(SO_4)_2$		$Eu_2O_2SO_4$	
d, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
6.23	30	6.25	30	6.24	55	6.45	10
5.91	100	5.96	70	5.55	20	4.92	10
5.11	45	3.70	15	5.04	70	3.96	15
4.79	25	3.51	75	4.65	25	3.86	10
4.25	15	3.49	100	4.30	85	3.01	100
3.73	20	3.40	45	4.20	35	2.96	90
3.43	55	3.30	25	3.74	25	2.91	95
3.24	35	3.23	30	3.47	40	2.65	10
3.16	25	3.04	55	3.41	75	2.20	20
3.04	25	2.93	60	3.35	40	2.17	30
2.95	95	2.88	20	3.29	75	2.09	25
2.75	20	2.75	40	3.16	45	1.987	15
2.69	25	2.68	30	3.02	40	1.938	10
2.17	15	2.48	40	2.94	100	1.738	40
2.11	20	2.34	40	2.90	40	1.708	50
2.06	25	2.26	10	2.81	50	1.683	40
1.986	15	2.11	10	2.73	75		
1.871	30			2.40	30		
				2.10	35		
				2.03	35		
				2.00	45		
				1.865	65		

Results and discussion

In air, $Eu_2(SO_3)_3\cdot 3H_2O$ forms after the dehydration the two sulfite-sulfate phases $Eu_2(SO_3)_2SO_4$ and $Eu_2SO_3(SO_4)_2$ (Fig. 1). The stability range of the latter phase is remarkable extending over some 200 degrees, as noted earlier [6]. A change in the heating rate (2 *vs.* 10 deg min^{-1}) appears to influence the curves very slightly. In both cases the dehydration, which takes place in two steps according to the DTG curve, is not complete but oxidation to $Eu_2(SO_3)_2SO_4$ starts before the weight level corresponding to anhydrous $Eu_2(SO_3)_3$ is reached.

Above 750° an abrupt decomposition takes place leading to $Eu_2O_2SO_4$ and finally to Eu_2O_3. The initial and final temperatures (appr. 1100 and

1200°) for the reaction $Eu_2O_2SO_4 \rightarrow Eu_2O_3$ at 10 deg min^{-1} heating rate are approximately same as those observed for $Eu_2(SO_4)_3$ under similar experimental conditions in a comparative study involving all lanthanide sulfates [8].

In nitrogen the formation of sulfite-sulfate phases is excluded but in spite of this the decomposition mechanism is more complicated and more dependent on the heating rate and other experimental conditions. Also in this case the dehydration is a two-step process and not complete before further decomposition occurs (Fig. 2).

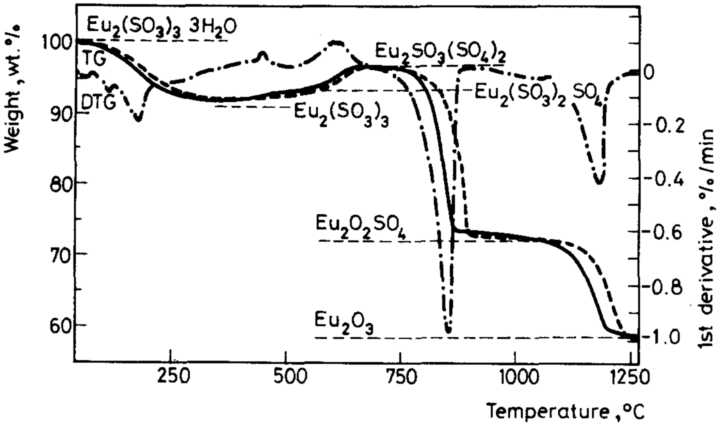

Fig. 1 TG and DTG curves for $Eu_2(SO_3)_3 \cdot 3H_2O$ recorded in air at 2 deg min^{-1}. For comparison, a TG curve recorded at a heating rate of 10 deg min^{-1} is given (broken line). The sample weights are 19.0 and 11.3 mg, respectively. The horizontal lines indicate calculated weight losses which correspond the stoichiometries given with formulas

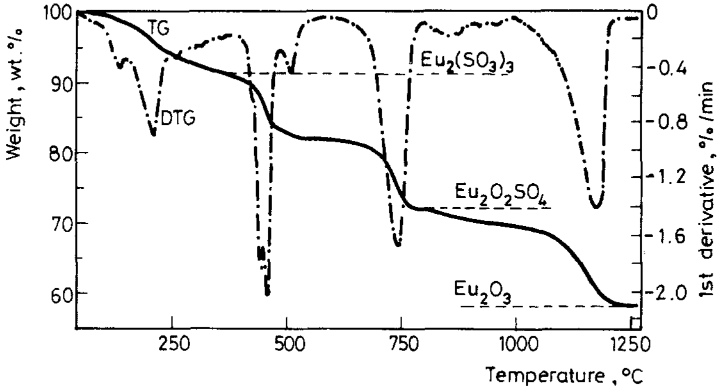

Fig. 2 TG and DTG curves for $Eu_2(SO_3)_3 \cdot 3H_2O$ in nitrogen. Heating rate is 10 deg min^{-1} and sample weight 22.7 mg

The final product in nitrogen is the sesquioxide as in air but the decomposition process $Eu_2(SO_3)_3 \rightarrow Eu_2O_3$ appears to proceed through several steps (Fig. 2). The intermediate phases have low stabilities and do not correspond to stoichiometric compounds with the exception of $Eu_2O_2SO_4$.

The present results may now be compared with the TG data available for other lanthanide sulfites. While all lanthanides may be crystallized from solution as $Ln_2(SO_3)_2SO_4$ hydrates [6], only cerium and europium form the sulfite-sulfate phases when the solid sulfates are slowly heated in air. This behaviour is probably connected with the oxidation-reduction potential of the lanthanides as also the heating curve of $Yb_2(SO_3)_2SO_4$ (and to lesser extent that of Sm) shows a weight increase in air. This weight increase does not correspond to $Yb_2SO_3(SO_4)_2$ before decomposition to oxosulfate begins, however [6].

In other details the decomposition of $Eu_2(SO_3)_3 \cdot 3H_2O$ in air as well as in nitrogen resembles that of the neighbouring lanthanide sulfites, *viz.* Sm and Gd [9]; see also the results obtained for Nd [3]. It may be noted, however, that the degradation in nitrogen (Fig. 2) appears to be more complex for europium than for other lanthanides as the anhydrous $Eu_2(SO_3)_3$ decomposes to $Eu_2O_2SO_4$ in several steps.

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Zusammenfassung – $Eu_2(SO_3)_3 \cdot 3H_2O$ bildet durch Erhitzen in Luft nach Dehydratation zwei Sulfit-Sulfat-Phasen: $Eu_2(SO_3)_2SO_4$ und $Eu_2SO_3(SO_4)_2$. Letztere ist thermisch bedeutend stabiler und zersetzt sich oberhalb 700°C über $Eu_2O_2SO_4$ zu Eu_2O_3. Bei Durchführung der TG-Experimente in Stickstoff wurden als Zwischenprodukte vor Eu_2O_3 auch wasserfreies $Eu_2(SO_3)_3$ und $Eu_2O_2SO_4$ gefunden, in anderen Details weicht jedoch der Mechanismus der Zersetzung von dem der Zersetzung in Luft ab.

Резюме - При нагревании тригидрата сульфита европия в атмосфере воздуха происходит дегидратация его с последующим образованием двух сульфит-сульфатных фаз $Eu/SO_3/_2SO_4$ и $Eu_2SO_3/SO_4/_2$. Последнее соединение термически очень стабильное и разлагается выше 700° до Eu_2O_3 через стадию образования промежуточного соединения $Eu_2O_2SO_4$. При ТГ нагреве тригидрата сульфита европия были также найдены безводные $Eu_2/SO_3/_3$ и $Eu_2O_2SO_4$как промежуточные продукты, но в остальном механизм разложения был отличен от такового в атмосфере воздуха.