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Thermochimica Acta 256 (1995) 67–73
thermochimica acta

Thermoanalytical studies on samarium sulfite sulfate hydrate ☆

Tuula Leskelä, Markku Leskelä [1], Lauri Niinistö

Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, FIN-02150 Espoo, Finland

Abstract

A prolonged crystallization of samarium sulfite solution at 70°C yields a disulfite sulfate hydrate precipitate $Sm_2(SO_3)_2SO_4 \cdot nH_2O$, where n is ≈ 2.5. The solid phase was characterized by X-ray powder diffraction, thermal analysis (TG, DTG and DTA) and IR spectroscopy. TG measurements revealed dehydration at 150–300°C and then a complex decomposition between 300 and 900°C leading in both air and argon to oxosulfate $Sm_2O_2SO_4$.

Keywords: FTIR; Samarium sulphite; Sulphate hydrate; TG–DTA

1. Introduction

Interest in the rare earth sulfite sulfate hydrates stems from the suggested use of the cerium compound in thermochemical cycles [1–3]. Two methods have been presented for the synthesis of rare earth sulfite sulfate hydrates. The first method consists of the reaction of rare earth oxosulfate with sulfur dioxide in aqueous media. The water content of the compounds depends on the rare earth and on the crystallization temperature [4]. Depending on the experimental conditions, the compounds may exhibit non-stoichiometry of the sulfite/sulfate ratio and water

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☆ Presented at the 14th Symposium on Thermal Analysis and Calorimetry, Oslo, Norway, 15–17 June 1994.

[1] Permanent address: Department of Chemistry, University of Helsinki, P.O. Box 6, FIN-00014 Helsinki, Finland.

SSDI 0040-6031(94)02170-8

content. In the other method, rare earth oxides were dissolved in sulfuric acid ($RE^{3+}:SO_4^{2-}$ ratio 2:1) and the solution was saturated with sulfur dioxide. The sulfite sulfate hydrates were crystallized at 90°C [4]. In these compounds the sulfite/sulfate ratio was always stoichiometric, namely 2, but the water content varied between 2 and 3 molecules.

The present work is a continuation of our studies on rare earth sulfites [5,6]. The earlier studies on rare earth sulfites have been reviewed with an emphasis on structural and thermal data [7]. Recently we have studied samarium sulfite hydrate in more detail [8], and as a part of that investigation the present study was initiated.

2. Experimental

2.1. Preparation of the compound

A slow stream of nitrogen was first passed for 30 min through a suspension of 1 g of Sm_2O_3 (99% purity, from Kemira Oy, Oulu, Finland) in 70 ml of water placed in a three-neck bottle at room temperature. Then a slow stream of sulfur dioxide was passed through the suspension for 3 h. During this time the oxide dissolved. The clear solution was poured into two large test tubes and covered with a paraffin layer ≈ 1.5 cm thick, and kept at 70°C for 2–5 days. During that time white samarium sulfite sulfate hydrate polycrystalline powder precipitated. If the solution was kept only overnight at 70°C, samarium sulfite trihydrate was formed [9]. The precipitate was filtered off, washed with water, ethanol and ether and dried over calcium chloride.

2.2. Chemical analysis

The samarium content was determined by complexometric titration and sulfite and sulfate were together determined gravimetrically as barium sulfate. The results from the chemical analyses were as follows: Sm, found 49.2%, calculated for $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$ 50.0% (for $Sm_2(SO_3)_3 \cdot 3H_2O$, 50.5%); total S, found 16.3%, calculated for $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$ 16.0% (for $Sm_2(SO_3)_3 \cdot 3H_2O$, 16.2%).

2.3. X-ray diffraction

X-ray powder diffraction data were recorded at 25°C with a Philips MPD 1880 diffractometer using Cu Kα radiation ($\lambda = 154.060$ pm).

2.4. Infra-red absorption spectrum

The IR spectrum in the region 4000–400 cm^{-1} was recorded with a Nicolet Magna-FTIR spectrometer 750 using the KBr technique.

2.5. Thermal analysis

TG measurements were carried out in a Seiko Instruments TG/DTA 320 analyzer equipped with a SSC/5200 disk station. A heating rate of 10°C min^{-1}, sample size ≈ 13 mg and dynamic air and argon atmospheres were applied. The temperature range covered was 25–1300°C and standard platinum crucibles were employed. Aluminium oxide was used as reference material.

3. Results and discussion

Based on chemical analyses only, it is difficult to tell whether the material is a pure sulfite hydrate or a sulfite sulfate hydrate. Therefore the identity of the phase was established by X-ray diffraction and IR spectroscopy and its stoichiometry and stability were studied by thermal analysis.

3.1. XRD and IR studies

The X-ray powder diffraction data are presented in Table 1. As can be seen, the XRD patterns for $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$ and for $Sm_2(SO_3)_3 \cdot 3H_2O$ are different. The powder diffraction data published for $Sm_2(SO_3)_3 \cdot 2H_2O$ [10] and $Eu_2(SO_3)_3 \cdot 2H_2O$ [11] are, however, similar to those presented in this work for $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$. It is therefore probable that these sulfite dihydrates are in fact sulfite sulfates. The difference would not show up in normal chemical analysis. Also, the data we published earlier for disulfite sulfate hydrates are similar to those presented in Table 1 for $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$ [4]. As the sulfite sulfates are highly microcrystalline, and because of their low crystal symmetry, the XRD patterns are weak and complex. Because of the availability of reference data, however, the XRD technique can be used to characterize the $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$ phase.

The FTIR spectrum of $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$ also differs from that of $Sm_2(SO_3)_3 \cdot 3H_2O$ (Fig. 1). The absorption frequencies between 1100 and 1200 cm^{-1} clearly show the presence of sulfate ions in $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$. The spectra published for $Sm_2(SO_3)_3 \cdot 2H_2O$ and $Eu_2(SO_3)_3 \cdot 2H_2O$ [10] also show absorption bands at 1100–1200 cm^{-1}, which gives further evidence for the presence of sulfate in those phases.

3.2. Thermal analysis

According to the TG curve, the water content of the compound corresponded exactly to 2.4 molecules when the measurement was made in an argon atmosphere and to 2.5 molecules in an air atmosphere (Figs. 2 and 3). The water content in the crystal lattice cannot be found by TG measurements alone. Because the accuracy of chemical analysis is not sufficient either, and because we have not been able to grow single crystals of the compound to solve the crystal structure, we have assumed,

Table 1

X-ray powder diffraction data of $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$ ($d > 200$ pm). The data for $Sm_2(SO_3)_3 \cdot 3H_2O$ [7] have been presented for comparison

$Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$		$Sm_2(SO_3)_3 \cdot 3H_2O$	
d/pm	I/I_0	d/pm	I/I_0
629	70	621	30
590	30	588	100
576	100	510	25
482	30	478	10
458	30	372	5
409	25	343	15
407	25	323	10
385	10	317	5
343	50	312	10
336	35	304	10
331	10	295.1	40
324	10	294.2	25
316	10	276.7	5
295.2	80	268.3	5
292.5	90	247.2	5
288.1	40	237.1	5
280.1	20	217.5	5
279.5	20	208.1	5
274.9	15	206.2	5
265.8	30	205.6	5
256.7	10		
253.7	10		
242.6	5		
220.7	20		
218.9	20		
214.9	5		
213.7	10		
210.5	20		
209.0	15		
205.9	10		
204.2	5		

based on the TG measurement, that the amount of crystal water is two and a half molecules. The probable error in the determination is ± 0.2. According to the literature, the number of water molecules varies in rare earth disulfite sulfate hydrates from 2.8 to 6.8 [3] and from 2.2 to 3.0 [4] depending on the rare earth.

The thermal decomposition of $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$ was found to be somewhat different in air and in argon atmospheres. The release of water molecules (between ≈ 200 and 300°C) is very similar in both atmospheres. No clear plateau of the anhydrous compound can be seen but the weight continues to decrease slowly. It is probable that the partial release of sulfur oxides begins simultaneously with that of water. The effect of the atmosphere on the decomposition is clear

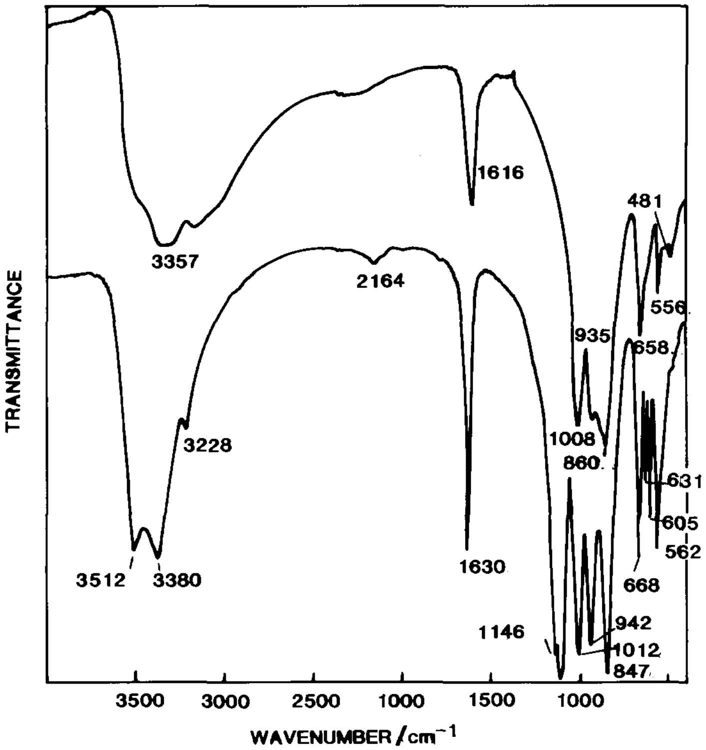

Fig. 1. FTIR spectra for $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$ (lower curve) and $Sm_2(SO_3)_3 \cdot 3H_2O$ (upper curve).

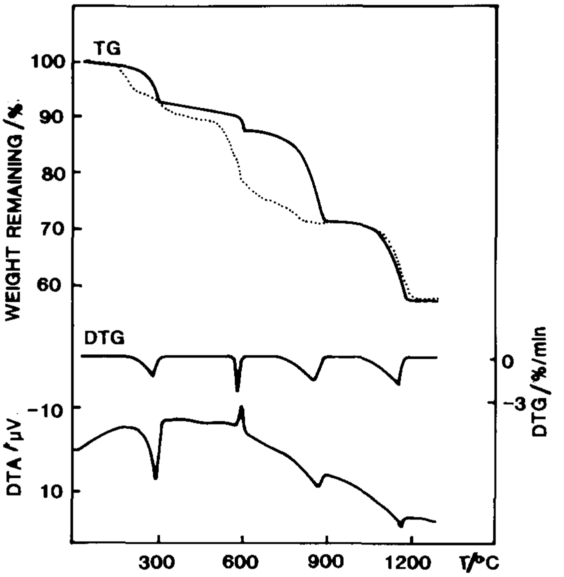

Fig. 2. TG, DTG and DTA curves for $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$ in argon. The TG curve for $Sm_2(SO_3)_3 \cdot 3H_2O$ (dotted line) is presented for comparison.

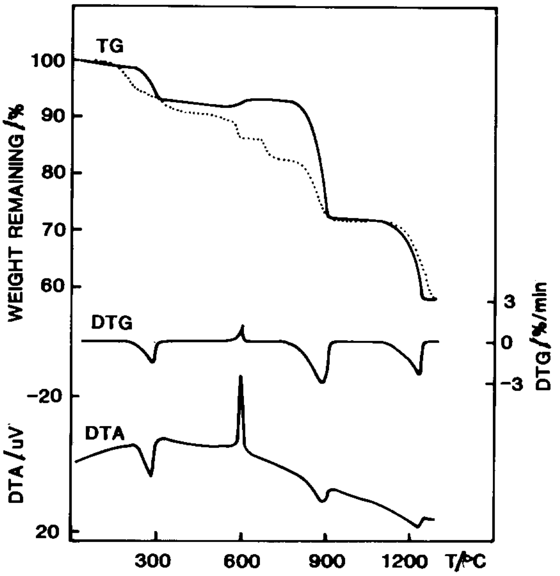

Fig. 3. TG, DTG and DTA curves for $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$ in air. The TG curve for $Sm_2(SO_3)_3 \cdot 3H_2O$ (dotted line) is presented for comparison.

between 550 and 900°C. In air a distinct increase of weight can be seen at 600°C due to the oxidation of sulfite ion to sulfate. The oxidation can also be seen in the DTA curve, where an exothermic peak exists at this temperature. The oxidation product does not correspond to any stoichiometric product, in contrast to the Eu^{3+}- and Ce^{3+}-containing phases, which oxidize via the $Ln_2(SO_3)(SO_4)_2$ phase to $Ln_2O_2SO_4$ [6,12]. In air at ≈ 750°C the decomposition of the sulfate groups starts and at 900°C a clear plateau is reached which corresponds to $Sm_2O_2SO_4$. Then at ≈ 1100°C $Sm_2O_2SO_4$ starts to decompose and one mole of SO_3 is released, leaving Sm_2O_3 as final product.

In an argon atmosphere between 550 and 900°C the decomposition is a two-step process. Again the product after the first small step at 600°C does not correspond to any stoichiometric compound. The exothermic peak in DTA indicates that oxidation takes place also in an inert atmosphere. Because oxygen is not present a disproportionation reaction must occur. The intermediate product between 900 and 1050°C is $Sm_2O_2SO_4$, as in an air atmosphere, but this starts to decompose at somewhat lower temperature and reaches constant weight ≈ 50°C earlier than in air. The end product is also Sm_2O_3 in an argon atmosphere.

The TG curves for $Sm_2(SO_3)_3 \cdot 3H_2O$, recorded for comparison under the same conditions as those for the present compound, are quite different (Figs. 2 and 3). The decomposition processes of $Sm_2(SO_3)_3 \cdot 3H_2O$ are more complicated, involving several steps. Only the last decomposition step from $Sm_2O_2SO_4$ to Sm_2O_3 around 1200°C is the same in both compounds. A detailed interpretation of the thermal decomposition of $Sm_2(SO_3)_3 \cdot 3H_2O$ has been reported elsewhere [8]. Qualitatively the measurements show that TG curves may also be used to distinguish between rare earth sulfite and sulfite sulfate hydrate phases.

4. Conclusions

The present work shows that the rare earth sulfite solution is unstable towards oxidation when kept at elevated temperature for prolonged periods. In the resulting sulfite sulfate system the 2:1 phase is stable, and the solid phase which is precipitated always has the composition $Sm_2(SO_3)_2SO_4 \cdot 2.5H_2O$, even after a crystallization period of 10 days.

The characterization of the samarium sulfite sulfate hydrate demonstrates how necessary it is to employ several complementary methods (XRD, TA and IR). It is difficult to distinguish between the sulfite sulfate and sulfite phases on the basis of chemical analysis or by thermoanalytical methods alone. IR spectroscopy is probably the most sensitive method to detect the sulfate ion in a sulfite matrix.

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