ELSEVIER

Thermochimica Acta 262 (1995) 195–207

thermochimica
acta

Synthesis and thermoanalytical characterization of two polymorphs of samarium sulphite trihydrate

T. Leskelä [a,]*, L. Niinistö [a], M. Lippmaa [b]

[a] *Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, FIN-02150 Espoo, Finland*

[b] *Department of Technical Physics, Helsinki University of Technology, FIN-02150 Espoo, Finland*

Received 25 January 1995; accepted 24 February 1995

Abstract

A new polymorph of $Sm_2(SO_3)_3 \cdot 3H_2O$ (β-form) has been synthesized and its properties are compared to those of the previously known α-form. The polymorphs have been characterized by X-ray diffractometry, FTIR spectroscopy and thermal analysis. The thermoanalytical studies, particularly by simultaneous TG and DTA, as well as by EGA with both MS and FTIR detection, show distinct differences between the two phases.

Keywords: EGA; FTIR; Polymorphism; Samarium sulphite trihydrate; TG–DTA; TG–MS; XRD

1. Introduction

Two different series of rare earth sulphite hydrates, $Ln_2(SO_3)_3 \cdot nH_2O$, are known which differ in their water content, n being 3 or 6 [1–4]. In addition, a sulphite dihydrate phase has been reported [4, 5] but its existence has been questioned [6]. The trihydrate series exhibits two structure types, one for the heavy rare earth metals (Ho–Lu) [3] and the other for the middle of the series (Pr–Dy) [2]. Hexahydrates are known only for the middle of the series. In this paper, we report a new form of samarium sulphite trihydrate which has a structure different from the earlier known polymorph. In addition to the crystal structure, we have compared the thermal behaviour and IR spectra of the two forms.

---

* Corresponding author.

SSDI 0040-6031(95)02329-1

2. Experimental

2.1. Preparation of the compounds

Samarium sulphite trihydrate (α-form) was prepared in a slightly different way than previously [1]. A slow stream of nitrogen was first passed through a suspension of 1 g Sm_2O_3 (99% purity from Kemira Oy, Oulu, Finland) in 50 ml of water for 30 min in a three-necked bottle. Then a slow stream of sulphur dioxide was passed through the suspension for approximately 2 h at room temperature. During this time the oxide gradually dissolved. The clear solution was poured into two big test tubes which were first filled with nitrogen. The test tubes were covered with a paraffin layer of approximately 1.5 cm and kept overnight at 70°C to precipitate the samarium sulphite trihydrate. If the precipitation time was longer (2–5 days), samarium sulphite sulphate hydrate [6] was likely to form. The precipitate was filtered, washed with small amounts of water, ethanol and ether and dried over calcium chloride. The β-form was prepared as follows. Samarium oxide was dissolved as in the preparation of the α-form. The clear solution was kept in a water bath at 70°C for two days while a slow stream of nitrogen was passed through the solution. During this time, the β-samarium sulphite trihydrate precipitated. The precipitate was filtered, washed and dried as in case of the α-form.

2.2. Chemical analysis

The samarium content was determined by complexometric titration and sulphite was determined gravimetrically as barium sulphate.

2.3. X-ray diffraction

X-ray powder diffraction diagrams were recorded at 25°C with a Philips MPD 1880 diffractometer using Cu Kα radiation ($\lambda = 0.15406$ nm).

2.4. Infrared absorption spectra

IR spectra were recorded for both samples in the region 4000–400 cm^{-1}, using a Nicolet Magna-FTIR spectrometer 750 and the KBr technique.

2.5. Thermal analysis

TG measurements were carried out in a Seiko Instruments TG/DTA 320 analyser, equipped with a SSC/5200 disc station. Measuring conditions were the following: heating rate, 10 and 2 K min^{-1}; sample weight, 15–20 mg; atmosphere, dynamic air, argon and hydrogen–argon with a flow rate of 80 ml min^{-1}; temperature range, 25–1300°C. Standard platinum crucibles were employed and aluminium oxide was used as a reference material. TG–EGA measurements were carried out in a Perkin-Elmer TGA 7 instrument which was connected to the Leybold-Heraeus IQ 200 quadrupole mass spectrometer (mass range 1–200 amu), which can scan up to 10 preselected *m*/*z* values. Details of the TG–EGA system have been described elsewhere [7]. TG–FTIR measurements were carried out in a Bomem TG/Plus system consisting of a DuPont 951 thermobalance and a Bomem MB 102 FTIR spectrometer.

3. Results and discussion

3.1. Chemical analysis

Within the limits of accuracy, the analytical data for both forms were the same. Thus, the Sm contents were found to be 49.5 and 49.4% while SO_3 contents were 40.8 and 40.7% for the α- and β-forms, respectively. The calculated values for $Sm_2(SO_3)_3 \cdot 3H_2O$ are 50.5% (Sm) and 40.4% (SO_3).

3.2. X-ray diffraction

From the X-ray powder diffraction data (Table 1), it can be seen that the crystal structures of the α- and β-forms are clearly different. The powder diffraction data of the

Table 1
X-ray powder diffraction patterns of α-$Sm_2(SO_3)_3 \cdot 3H_2O$ and β-$Sm_2(SO_3)_3 \cdot 3H_2O$

α-$Sm_2(SO_3)_3 \cdot 3H_2O$		β-$Sm_2(SO_3)_3 \cdot 3H_2O$	
d/nm	I/I_0	*d*/nm	I/I_0
0.621	30	1.022	50
0.588	100	0.651	80
0.510	25	0.607	20
0.478	9	0.590	10
0.372	6	0.482	45
0.343	15	0.351	15
0.323	9	0.343	100
0.317	8	0.338	25
0.312	10	0.326	30
0.304	10	0.307	80
0.295	40	0.304	75
0.294	25	0.294	10
0.277	6	0.285	10
0.268	7	0.278	55
0.247	7	0.267	35
0.217	6	0.213	25
0.208	7	0.208	15
0.206	7	0.203	15
0.188	7	0.200	20
		0.1894	15
		0.1874	10
		0.1727	9
		0.1698	8
		0.1663	15

α-form correspond to those of a gadolinium sulphite trihydrate made earlier which is isomorphous with samarium sulphite trihydrate [2]. The crystal structure of $Gd_2(SO_3)_3 \cdot 3H_2O$ (isostructural with the α-form of $Sm_2(SO_3)_3 \cdot 3H_2O$) has recently been reported. It shows that the crystallographically independent gadolinium ions are octa-coordinated by oxygens from bridging sulphite ligands and water molecules [8]. The crystal symmetry of the β-form appears to be low. Unfortunately, the crystal structure of the latter has not been solved because it was not possible for us to grow single crystals of sufficient size.

3.3. *Infrared spectra*

The infrared spectra of the two forms are very similar in the S–O region as regards the number, intensity and position of the vibrational bands (Fig. 1). For instance, the symmetric stretching mode ν_1 is situated at 1008 and 1011 cm^{-1} in the α- and β-forms, respectively. These values are the same as found in $Gd_2(SO_3)_3 \cdot 3H_2O$ [2] and coincide with that (1010 cm^{-1}) found for Na_2SO_3 in the solid state [9].

The OH bending mode at 1617 and 1619 cm^{-1} is not split, indicating that all the water molecules probably have a similar structural environment. The X-ray structure determination of $Gd_2(SO_3)_3 \cdot 3H_2O$ (isostructural with α-$Sm_2(SO_3)_3 \cdot 3H_2O$) has

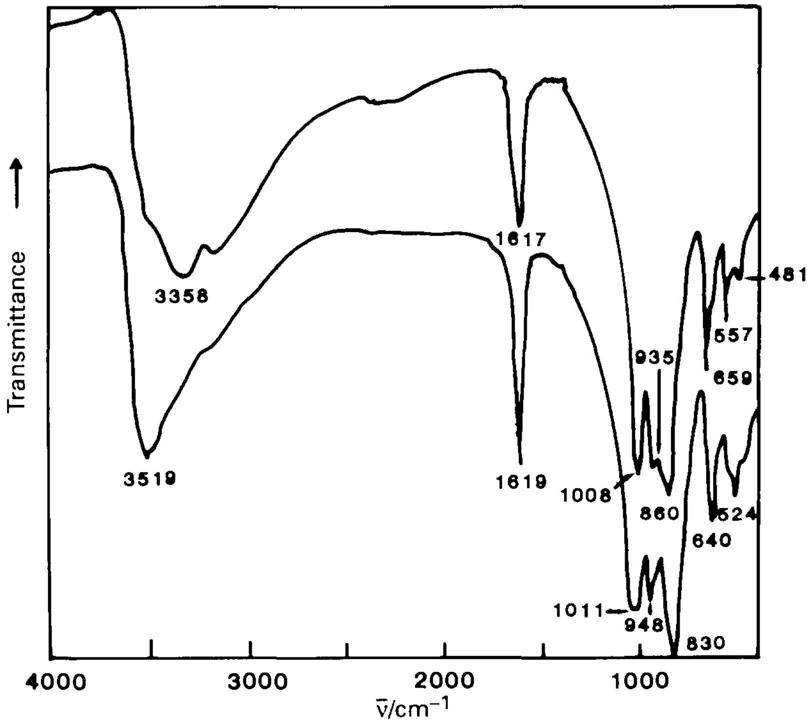

Fig. 1. FTIR spectra for α-$Sm_2(SO_3)_3 \cdot 3H_2O$ (upper curve) and β-$Sm_2(SO_3)_3 \cdot 3H_2O$ (lower curve).

shown that all water molecules are coordinated to the central atom [8]; this could also be the case in the β-form. However, the OH stretching region shows differences. When comparing our spectra with those presented by Moskalenko et al. [4], differences are obvious. It seems that the sulphites of Moskalenko et al. may also contain sulphate. In fact the published spectra [4] closely resemble those which we have obtained for the sulphite sulphates [6].

3.4. Thermal analysis

3.4.1. Air atmosphere

Samples of α- and β-forms behave in a different way upon heating in air with a heating rate of 10 K min^{-1} (Fig. 2). The first step, dehydration, is already different. The α sample is stable up to 150°C and the water release process, according to the DTG curve, occurs in two steps. The first step is larger which may indicate the release of two water molecules. However, the β sample begins to loose weight immediately heating is started. The water-releasing reaction is slow and DTG does not show any clear maximum. The DTA curves resemble the DTG curves, i.e. in sample α there are two endothermic peaks while in sample β there is only one shallow peak.

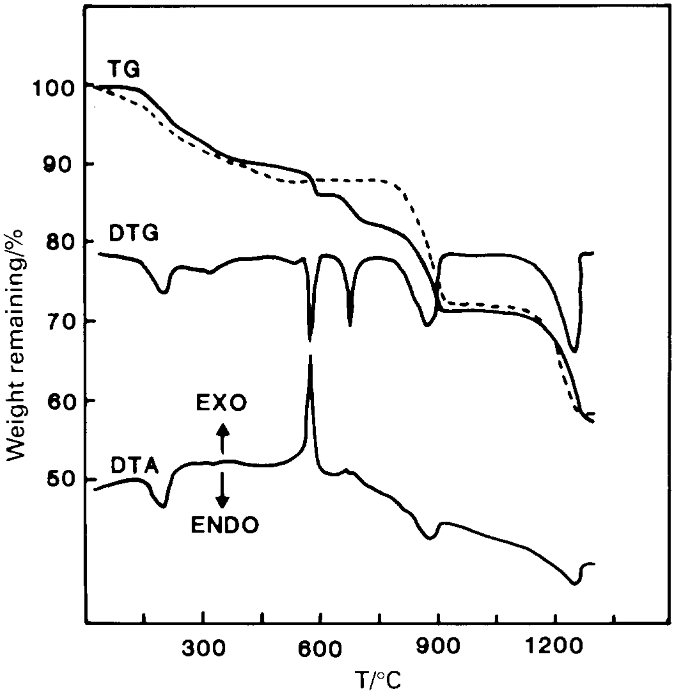

Fig. 2. TG, DTG and DTA curves for α-$Sm_2(SO_3)_3\cdot 3H_2O$ in air (heating rate 10 K min^{-1}) and the TG-curve for the β-form (dotted line).

The dehydration is complete in both cases above 350°C but no clear plateau corresponding to $Sm_2(SO_3)_3$ can be seen. In sample α, the weight continues to decrease slowly but in sample β a constant weight is reached. The level (88.4%) does not, however, correspond to anhydrous sulphite (calculated weight 91.0%). The weight remains constant up to 800°C but according to the DTA curve the composition does not remain constant, some oxidation taking place at around 580 and 700°C. This means that sulphite is partly oxidized to sulphate but simultaneously partial decomposition and release of gaseous species must occur. The reactions are in balance so that no weight change can be seen. The α-form of the anhydrous sulphite, after decomposing slowly, has a fast weight loss at around 580°C. There is also an additional weight loss at 700°C. The plateaus obtained again do not correspond to any stoichiometric composition which is in agreement with our earlier results with other rare earth sulphites [10].

The DTA curves of both samples between 500 and 800°C are almost similar, having exothermic peaks. In the case of sample α, two small peaks can be seen around 700°C in addition to the major peak at 580°C. The oxidation of sulphur is an exothermic process but the decomposition is usually endothermic. It is obvious that the two reactions also occur simultaneously in the α sample: oxidation of sulphite and release of sulphur oxides. The DTA peaks observed are sums of the thermal effects in the reactions.

Around 900°C, both samples decompose to a distinct phase, oxosulphate, $Sm_2O_2SO_4$. The decomposition is endothermic. Systematic studies on the thermal decomposition of rare earth sulphates show that the decomposition of sulphate to oxosulphate is an endothermic process which occurs at 800–1150°C depending on the rare earth and experimental conditions [11]. Thus it is obvious that both samples contain mainly sulphate before the decomposition reaction at 900°C. The oxosulphate phase is stable up to approx. 1150°C and decomposes above that to oxide. The total weight loss from the starting material to oxide is almost the same for both samples, confirming similar initial compositions, $Sm_2(SO_3)_3 \cdot 3H_2O$.

The thermal behaviour of rare earth sulphites depends on the experimental conditions [12]. This is also seen in Fig. 3 which shows the TG curves for α and β samples heated at a rate of 2 K min^{-1} in air. The dehydration is similar with both heating rates. The effect of the heating rate appears in the decomposition of sulphite. In sample α, only one intermediate level can be seen between the sulphite and oxosulphate phases. The weight at this intermediate level between 600 and 750°C, 85.2%, corresponds quite well to the formula $Sm_2O(SO_4)_2$. The oxidation occurring at 550°C can be seen from the exothermic peak in the DTA curve. The existence of this oxodisulphate phase has not been clearly detected in our earlier thermal studies on rare earth sulphites. The oxosulphate phase is formed at 850°C and then decomposes to oxide at the expected temperature of approx. 1150°C.

With the slow heating rate, sample β shows a totally different behaviour. The anhydrous sulphite first decomposes slowly and loses sulphur oxides but at 550°C, an oxidation process begins. In this case the oxidation does not show the release of sulphur oxides but sulphite oxidizes to sulphate in the solid state and the weight increases. In the case of europium sulphite, a similar weight increase has been seen

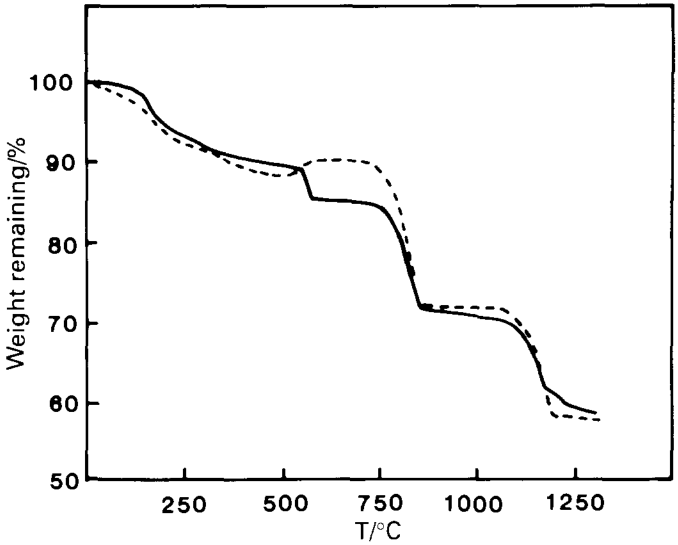

Fig. 3. TG curves for α-$Sm_2(SO_3)_3 \cdot 3H_2O$ and β-$Sm_2(SO_3)_3 \cdot 3H_2O$ (dotted line) in air (heating rate 2 K min^{-1}).

and the formation of a stoichiometric sulphite sulphate $Eu_2(SO_3)_2SO_4$ has been confirmed [13]. With cerium sulphite, even a stoichiometry of $Ce_2SO_3(SO_4)_2$ has been recorded [10]. In the present case the weight gain is smaller than calculated for $Sm_2(SO_3)_2SO_4$, however. The weight remains constant between 550 and 750°C. Above 750°C, the decomposition to oxosulphate takes place. A small exothermic peak is involved with this reaction step indicating that the phase at 550–750°C contained sulphite.

In contrast to heating rate, the sample weight affects the TG curves only slightly. The effect can mainly be seen in the decomposition temperatures, which with smaller amounts of sample are somewhat lower.

3.4.2. Argon atmosphere

In an inert atmosphere, the first decomposition step, the release of water, is closely similar to that found in air atmosphere for both samples, α and β (Fig. 4).

The decomposition of the anhydrous sulphite in an inert atmosphere is a very complicated process. The final product is oxosulphate at 800°C in both cases. The TG curves of both samples are somewhat similar, i.e. no clear plateaus exist between the sulphite and oxosulphate phases. Also the DTG and DTA curves show that many steps and reactions occur simultaneously and successively. Despite the inert atmosphere, partial oxidation of sulphite to sulphate takes place because oxosulphate is formed. The oxidation is corroborated by the DTA curve. In an inert atmosphere, oxidation is possible only if reduction is simultaneously taking place. Decomposition via a disproportionation reaction is an obvious explanation for the behaviour recorded. The oxosulphate phase then decomposes to oxide in argon atmosphere above 1000°C.

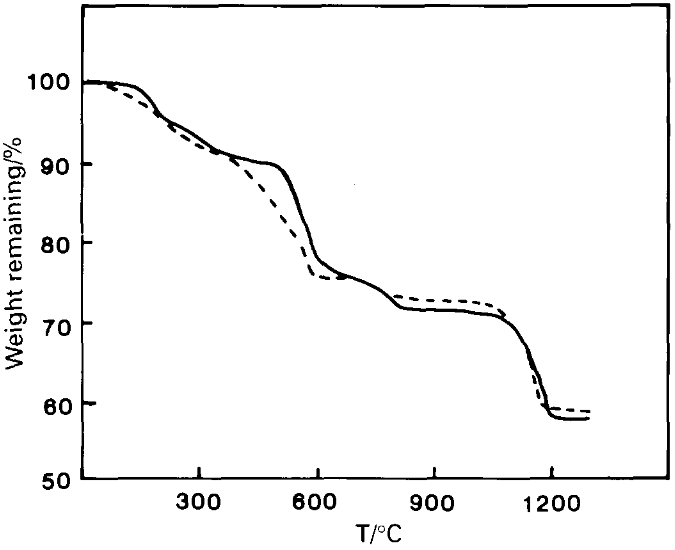

Fig. 4. TG curves for α-$Sm_2(SO_3)_3 \cdot 3H_2O$ and β-$Sm_2(SO_3)_3 \cdot 3H_2O$ (dotted line) in argon (heating rate 10 K min^{-1}).

3.4.3. *Reductive atmosphere*

TG curves for samples α and β measured in flowing H_2/Ar (5% H_2) atmosphere are presented in Fig. 5. The curves are closely similar between room temperature and 350°C to those obtained in air and argon atmospheres. The decomposition of sulphite occurs between 400 and 800°C in both samples. According to the DTG curves, the decomposition rates vary and the curves have 4–5 maxima. The decomposition is at first fast but after a turning point around the remaining weight of 72–75%, the decomposition rate becomes somewhat slower. The mass corresponding to the turning point is quite close to that of $Sm_2O_2SO_4$. The disproportionation of sulphite also seems to be effective to some extent in a reductive atmosphere. Obviously the reduction reaction is relatively slow and above 480°C both the reduction and decomposition of sulphite take place, and above 600°C the partly formed $Sm_2O_2SO_4$ is reduced. The several maxima in the DTG curves and the exothermic peak in DTA support this explanation.

The weight remaining at 750–800°C (around 61%) corresponds closely to oxosulphide, Sm_2O_2S, although according to the weight loss the formation of SmS cannot be excluded. XRD measurements carried out from the residue showed that the end product is, in fact, oxosulphide. In this respect, samarium behaves similarly to most of the rare earth sulphites [14]. Under the same conditions, however, europium forms EuS [15, 16].

The weight of oxosulphide is not far from that of oxide. However, oxosulphide and oxide can easily be distinguished by heating the reduced sample again in air. The present sample begins to oxidize to oxosulphate above 600°C (DTG maximum at 750°C). Almost constant weight is reached above 800°C. The weight increase is about

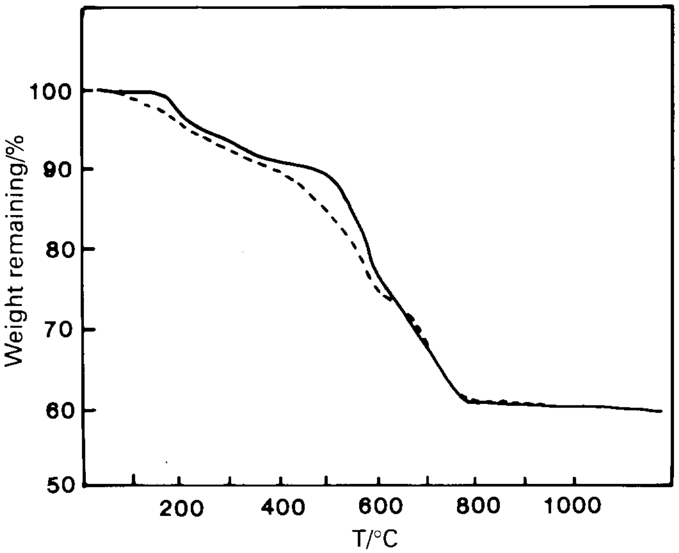

Fig. 5. TG curves for α-$Sm_2(SO_3)_3 \cdot 3H_2O$ and β-$Sm_2(SO_3)_3 \cdot 3H_2O$ (dotted line) in hydrogen–argon (5% H_2) (heating rate 10 K min^{-1}).

12% while the theoretical value for oxidation to oxosulphate is 17.5%. This is in agreement with our earlier results [17] which showed that oxidation and decomposition of oxosulphate occur simultaneously, that the theoretical weight increase is obtained only with lanthanum, and that the weight gain decreases along the lanthanide series [18].

3.4.4. TG–MS measurements

For TG–MS measurements, the samples were heated in helium atmosphere up to 1000°C with a heating rate of 10 K min^{-1}. The evolved gases were carried to the mass spectrometer by a slow helium flow. The TG curves (Figs. 6 and 7) of the α and β samples are closely similar to those recorded with the Seiko instrument in an inert atmosphere, i.e. in sample α the steps are steep and the intermediate plateaus are clear, while sample β decomposes slowly and gradually without clear plateaus before 875°C ($Sm_2O_2SO_4$).

When recording the mass spectra the mass numbers of oxygen (16, 32), water (18), sulphur oxide (48) and sulphur dioxide (64) were monitored; the presence of sulphur oxide, SO, is due to decomposition of SO_2 in the ionization chamber of the mass spectrometer, however [7]. The mass spectra also showed the different behaviour of the samples. Sample α loses water between 150 and 500°C in a two-step process with relatively sharp peaks at 280 and 330°C (Fig. 6). The first peak is bigger than the second indicating that two water molecules are released first and then the third. In sample β the dehydration is also a two-step process but the maxima in the curve are broad and water is released over a wide temperature range (150–600°C) (Fig. 7).

In the decomposition of sulphite, the release of oxygen at 610°C (α) and 590°C (β) is clear. The release of sulphur oxide and dioxide is quite different in samples α and β. The

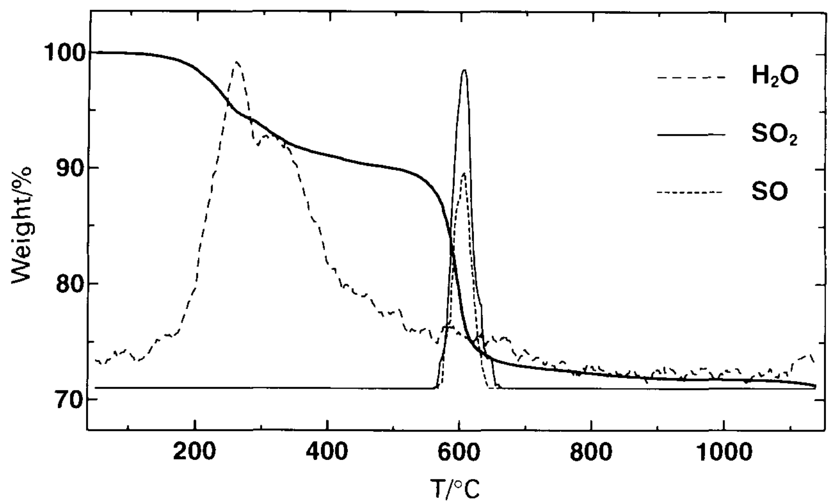

Fig. 6. TG and EGA–MS curves of α-$Sm_2(SO_3)_3 \cdot 3H_2O$.

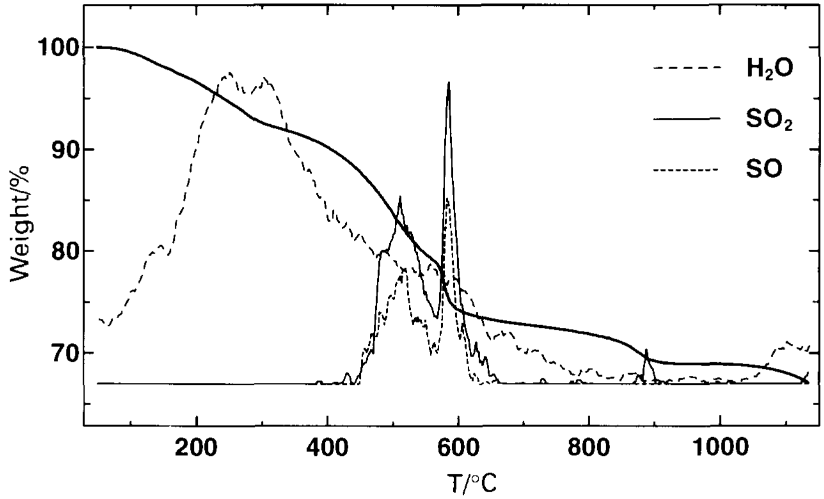

Fig. 7. TG and EGA–MS curves of β-$Sm_2(SO_3)_3 \cdot 3H_2O$.

release of sulphur oxides in sample β is a two-step process and it occurs over a wide temperature range (380–700°C) while in α there is only one sharp peak at 600°C. This can also be seen in the TG curves. The phase formed in sample β is not stable but sulphur oxides are still releasing between750 and 950°C. The oxygen peaks here follow, of course, those of sulphur oxides. The last decomposition step from oxosulphate to oxide simply shows the release of sulphur oxides.

3.4.5. *TG–FTIR measurements*

In TG–FTIR experiments, 60 mg samples were heated at 10 K min^{-1} in flowing helium up to 1100°C and the IR spectra were recorded every 30 s. During measurements, H_2O and SO_2 evolutions were followed. The release of water and that of sulphur dioxide from samples α and β as a function of temperature are presented in Figs. 8 and 9. Sample α (Fig. 8) loses water between 150 and 500°C in a two-step process with distinct peaks at 225 and 340°C; the first peak is about twice the size of the second. This may indicate that two water molecules are first released and then the third. Sample β (Fig. 9) loses water over a wide temperature range, 60–600°C, indicated by several more or less distinct peaks. If these results are compared to the TG and TG–MS measurements, they are very similar indicating that possibly water is bound in a different way in samples α and β.

The release of sulphur dioxide is also different in samples α and β according to the TG–IR measurements. The release of SO_2 in sample β occurs in a wide temperature range between 300 and 800°C with two main peaks at 520 and 660°C. This is quite consistent with the results of TG–MS measurements. The release of SO_2 in sample α occurs between 500 and 800°C with three main peaks at 550, 600 and 675°C. The three

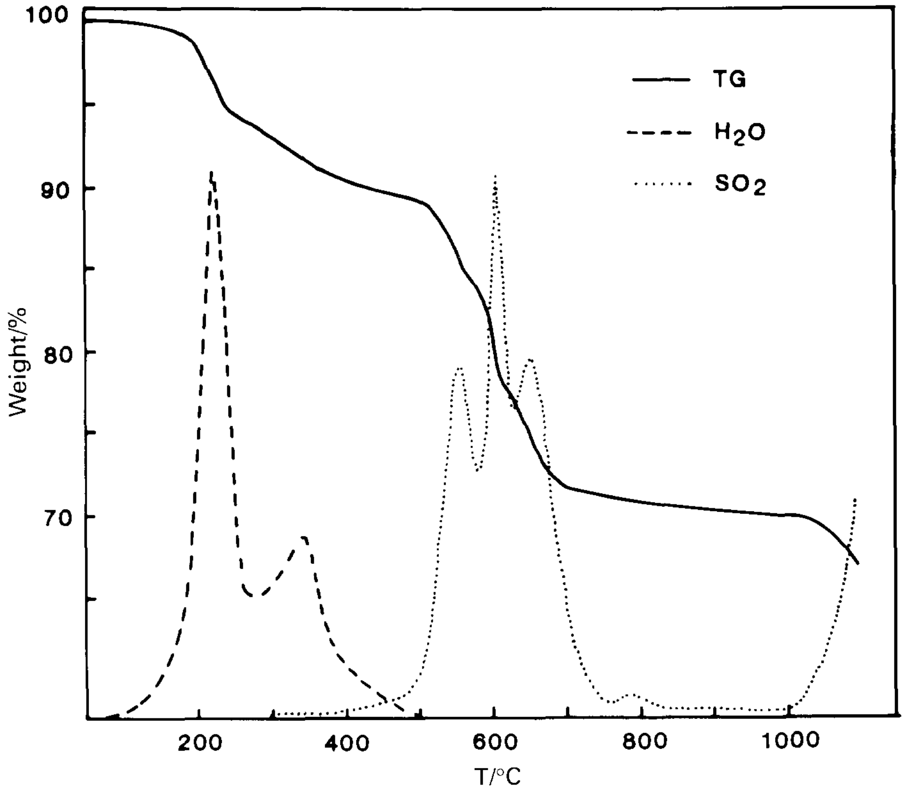

Fig. 8. TG and EGA–FTIR curves of α-$Sm_2(SO_3)_3 \cdot 3H_2O$.

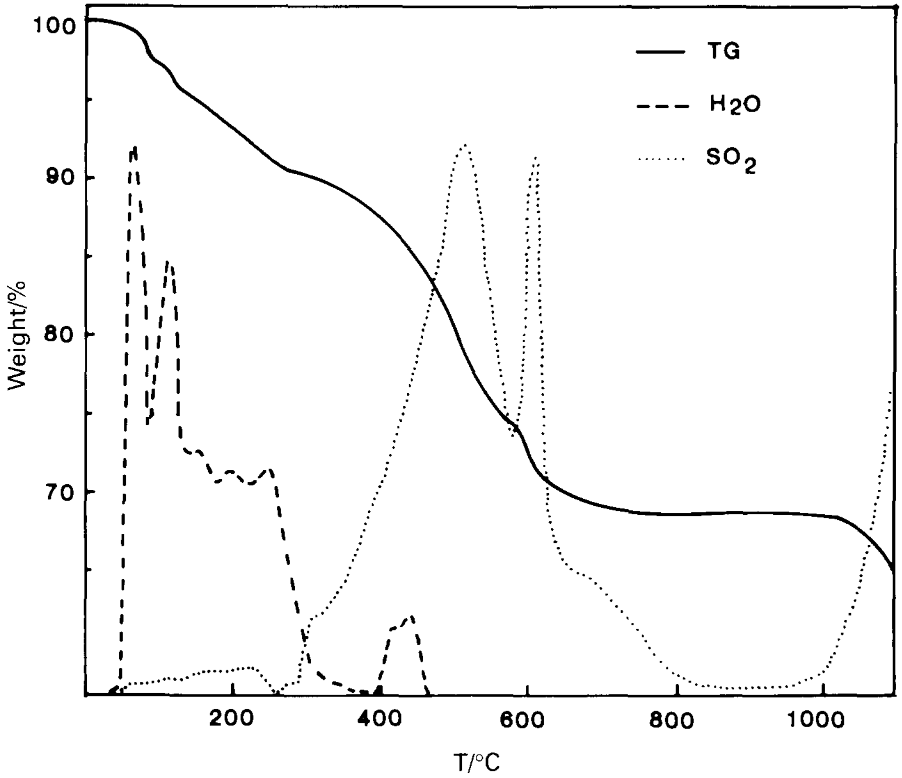

Fig. 9. TG and EGA-FTIR curves of β-$Sm_2(SO_3)_3 \cdot 3H_2O$.

steps can also be seen in the TG curve which is quite similar to the TG curve measured with the Seiko instrument in similar conditions. This result differs from that of TG-MS where the release of sulphur oxides seems to happen in one step. The apparently different decomposition mechanisms of sulphites in TG-IR and TG-MS systems are obviously due to the different thermobalances used in these measurements.

4. Conclusions

The two polymorphs of $Sm_2(SO_3)_3 \cdot 3H_2O$ showed quite different thermal behaviour which was established by using several thermoanalytical techniques and experimental conditions. The differences in crystal structures are probably the main factors contributing to the thermal processes; in particular, the temperatures for the dehydration reaction and for the decomposition of the anhydrous sulphite are different. The degree of crystallinity may also play a role. Sample α was crystallized at a slower rate and consequently its diffraction pattern shows a higher peak-to-background ratio and sharper maxima than that of the β-form. As the crystal structure of the β-form is not known, further conclusions based on structure are not possible.

The present study shows, however, that the various thermoanalytical techniques yield consistent data in detecting different dehydration and decomposition behaviours.

Acknowledgement

The authors wish to thank Ms. Maarit Järvinen for TG–FTIR measurements.

References

[1] L. Niinistö and M. Koskenlinna, Suom. Kemistil. B, 46 (1973) 245.
[2] M. Koskenlinna and L. Niinistö, Finn. Chem. Lett., (1975) 83.
[3] V.I. Moskalenko, M.B. Varfolomeev, K.I. Petrov and A.K. Molodkin, Russ. J. Inorg. Chem., 20 (1975) 46.
[4] V.I. Moskalenko, M.B. Varfolomeev, A.K. Molodkin and K.I. Petrov, Russ. J. Inorg. Chem., 22 (1977) 1641.
[5] H.-U. Hummel, P. Joerg and G. Pezzei, Z. Naturforsch. Teil B, 48 (1993) 82.
[6] T. Leskelä, M. Leskelä and L. Niinistö, Thermochim. Acta, 256 (1995) 67.
[7] T. Leskelä, M. Lippmaa, L. Niinistö and P. Soininen, Thermochim. Acta, 214 (1993) 9.
[8] H.-U. Hummel, P. Joerg, G. Pezzei and A. Wolski, Z. Naturforsch. Teil B, 49 (1994) 60.
[9] B. Nyberg and R. Larsson, Acta Chem. Scand., 27 (1973) 63.
[10] M. Leskelä, J.E.X. de Matos and L. Niinistö, Thermochim. Acta, 95 (1985) 407.
[11] L. Niinistö and M. Leskelä, in K.A. Gschneidner and L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 9, North-Holland, Amsterdam, 1987, p. 91.
[12] M. Koskenlinna, M. Leskelä, J.E.X. de Matos and L. Niinistö, Thermochim. Acta, 95 (1985) 401.
[13] M. Karppinen, M. Leskelä and L. Niinistö, J. Therm. Anal., 35 (1989) 355.
[14] M. Koskenlinna and L. Niinistö, Suom. Kemistil. B, 46 (1973) 326.
[15] M. Leskelä and L. Niinistö, Thermochim. Acta, 37 (1980) 125.
[16] M. Leskelä and L. Niinistö, J. Electrochem. Soc., 123 (1976) 75.
[17] M. Leskelä and T. Leskelä, Thermochim. Acta, 48 (1981) 43.
[18] M. Leskelä and L. Niinistö, J. Therm. Anal., 18 (1980) 307.