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Thermogravimetric study of reduction and sulfurization of $Y_2(SO_4)_3$ using carbon disulfide

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Abstract

The reaction of $Y_2(SO_4)_3$ with CS_2 was studied using thermogravimetry. Anhydrous yttrium sulfate $Y_2(SO_4)_3$ first decomposes to $Y_2O_2SO_4$ at temperatures which depend upon the heating rate, namely 550-650°C at 1 K min^{-1} and 550-750°C at 5 K min^{-1}. With increasing temperature, $Y_2O_2SO_4$ is further deoxidized to Y_2O_2S, and in this step the heating rate exerts a larger effect than in the first step. This reaction is complete at 700 and 875°C at heating rates of 1 and 5 K min^{-1}, respectively. The last step involves the reaction of Y_2O_2S to form δ-Y_2S_3. Single phase Y_2S_3 was formed at ≈ 950°C when the heating rate was as low as 1 K min^{-1}. When the heating rate was increased to 5 K min^{-1}, a small amount of unreacted Y_2O_2S was found in the Y_2S_3 product. The compound YS_{2-x}, which was determined as $YS_{1.85}$, was stable below ≈ 600°C and decomposed to Y_2S_3 at higher temperatures. The difference of the present reaction from the reaction of $Nd_2(SO_4)_3$ with CS_2 lies mainly in the decomposition of sulfate to oxysulfate and the sulfurization of oxysulfide to sesquisulfide.

Keywords: Carbon disulphide; TG; Yttrium disulphide; Yttrium oxysulphate; Yttrium oxysulphide; Yttrium sesquisulphide; Yttrium sulphate

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1. Introduction

Rare-earth (RE) sulfides are used for various electronic devices which utilize their semiconductive, electroluminescent or magneto-optical properties. For the study and/or application of such sulfides, the method for synthesis of the RE sulfides should desirably be simple, easy and inexpensive. In our work to develop synthetic methods for neodymium sulfides [1,2], we noticed the high reactivity of $Nd_2(SO_4)_3$ with CS_2, and efforts were made to clarify the reaction mechanism. By analogy with this, attempts were made to form Y_2S_3 from $Y_2(SO_4)_3$. However, it was found that the optimum reaction conditions for the preparation of a single phase of Nd_2S_3 [1,2] did not give pure Y_2S_3 free from Y_2O_2S. This difference was thought to stem from the instability of Y_2S_3. In fact, although both are rare-earth elements, there are significant differences between the properties of their sulfides as reported in the literature. Stoichiometric NdS_2 has been prepared by the direct reaction of Nd_2S_3 with excess sulfur in vacuum-sealed ampoules at 600°C [2]. By contrast, stoichiometric YS_2 can only be prepared under high pressures [3]: yttrium disulfide is hypostoichiometric at ambient pressure. Also, the crystal structures of Nd_2S_3 and Y_2S_3 are different: Nd_2S_3 is orthorhombic (A- or α-form [4,5]) but Y_2S_3 is monoclinic (D- or δ-form [4]). Cubic Nd_2S_{3-x} (C or γ-Nd_2S_3) forms easily at temperatures above 1000°C under low sulfur pressures [1,2]. This compound was observed to form even at a temperature as low as 650°C in our previous study [1], and it is stable at an oxygen pressure below 10^{-15} Pa in the temperature range 500-1000°C [6]. However, cubic Y_2S_{3-x} (C- or γ-Y_2S_3, $0 \leqslant x \leqslant 1/3$) is formed only by high pressure synthesis [7]. The stability of yttrium sulfides has not been reported, although a further compound, Y_5S_7, is known to exist [8].

Before forming Y_2S_3, the successive deoxygenation/sulfurization reactions occur starting from the decomposition of $Y_2(SO_4)_3$. The purpose of this work is to clarify these reaction mechanisms by means of thermogravimetry. The result is compared with that for the formation of Nd_2S_3 from $Nd_2(SO_4)_3$.

2. Experimental

2.1. Materials

Yttrium sulfate hydrate was prepared by dissolving Y_2O_3 (99.9%, Nippon Yttrium Co., Ltd.) in sulfuric acid solution. The anhydrous sulfate $Y_2(SO_4)_3$ was obtained by heating the hydrate in air (muffle furnace) at 450°C for 1 h.

Yttrium disulfide YS_2 (or more exactly YS_{2-x}) was prepared by heating Y_2S_3 with an excess of sulfur in a vacuum-sealed ampoule at 600°C for 1 day. The same hypostoichiometric YS_{2-x}, as determined by X-ray diffraction analysis, was obtained by the reaction of Y_2S_3 and excess sulfur at 600°C for 1 day followed by annealing at 500°C for 7 days. The YS_{2-x} samples contained a small amount of free sulfur (2-3 wt%) deposited in the disulfide powder during cooling.

Analytical grade CS_2 of boiling point 46–47°C and maximum impurity water content 0.02 wt% was obtained from Wako Pure Chemicals Industries, Ltd., and used as received. Nitrogen gas of 99.99% purity from Nippon Sanso Co., Ltd. was used as carrier gas for the CS_2.

2.2. *Thermogravimetry*

The procedure for the thermogravimetric measurements was essentially the same as described elsewhere [2]. The quartz cylindrical crucible (8 mm diameter × 10 mm high) containing a weighed sample was suspended from a quartz spring of sensitivity 12.76 mg mm^{-1}. After evacuating the system, CS_2 in N_2 carrier gas was passed through the reaction tube. The CS_2 was handled with care considering its inflammability. The furnace temperature was raised at a constant rate, and the weight change was measured by a levelmeter. The weight of samples was 150–200 mg. Preliminary experiments were carried out with heating rates of 1 and 5 K min^{-1} and with CS_2/N_2 gas flow rates of 50/100, 100/200 and 200/400 ml min^{-1}. The result showed that the heating rate plays an important role, whereas the effect of the flow rate was negligibly small on the reaction of $Y_2(SO_4)_3$ with CS_2. On this basis, the reactions were studied with the CS_2/N_2 gas flow rate fixed at 100/200 ml min^{-1} for most experiments but with two heating rates of 1 and 5 K min^{-1}.

2.3. *X-ray diffraction analysis*

The X-ray diffraction analysis was carried out with a Rigaku Type RAD-IC diffractometer using CuKα radiation (40 kV, 20 mA) monochromatized by curved pyrolytic graphite. The least-squares calculation of lattice parameters was carried out using the LCR2 program [9].

3. Results and discussion

3.1. *Formation of* $Y_2O_2SO_4$

On heating, $Y_2(SO_4)_3$ changes to a mixture of $Y_2O_2SO_4$ and Y_2O_3 at 900–1000°C [10,11]. However, according to the present results the product was all Y_2O_3 after prolonged heating (7 days) at 900°C. The $Y_2O_2SO_4$ was therefore prepared at 800°C. Although the decomposition of $Y_2(SO_4)_3$ was slow (about one sixth of total weight loss per day), a single phase of $Y_2O_2SO_4$ was obtained after 7 days. The observed weight loss of 34.31 wt% was in good agreement with the theoretical value of 34.36 wt% for the change of $Y_2(SO_4)_3$ into $Y_2O_2SO_4$. X-ray diffraction analysis confirmed the formation of $Y_2O_2SO_4$ without any trace of other phases. The decomposition temperatures for $Y_2(SO_4)_3$ and $Y_2O_2SO_4$ in Refs. [10,11] seem to be significantly higher than those in this work: anhydrous yttrium sulfate $Y_2(SO_4)_3$ did not lose weight at 700°C even after 7 days. $Y_2O_2SO_4$ began to decompose at 900°C. The preparation of $Y_2O_2SO_4$ was successful only in a narrow range of temperature around 800°C. The difference of the temperature from the literature value [10,11] may arise because those TG or DTA experiments were made at high heating rates.

3.2. Formation of Y_2O_2S in H_2

When $Y_2O_2SO_4$ was reduced in a stream of H_2 at 850°C for 1 h, a weight loss of 21.62 wt% was observed. This value is a little larger than the theoretical weight change of 20.92 wt% from $Y_2O_2SO_4$ to Y_2O_2S. The difference of 0.7 wt% corresponds to the formation of 13.3 mol% of Y_2O_3, and the peaks of Y_2O_3 were actually detected in the X-ray diffraction pattern. The sample prepared at 650°C for 3 h showed a weight decrease of 21.02 wt%, and the X-ray diffraction analysis confirmed the formation of Y_2O_2S as a single phase. Thus the heating temperature of 800°C suggested by Laptev et al. [12] for the preparation of RE oxysulfides (RE is La–Tb) by reduction of their sulfates in a stream of the gas mixture H_2/N_2 (20 vol% H_2) seems to be a little higher for the formation of Y_2O_2S. This is because of the lower stability of $Y_2O_2SO_4$ at higher temperatures.

3.3. Reaction of $Y_2(SO_4)_3$ with CS_2

The TG curves for the reaction of $Y_2(SO_4)_3$ with CS_2 are shown in Fig. 1. After $Y_2(SO_4)_3$ has decomposed to $Y_2O_2SO_4$, the subsequent reduction of $Y_2O_2SO_4$ to Y_2O_2S is seen to occur without interruption, giving weight changes close to the theoretical value. The decomposition of $Y_2(SO_4)_3$ begins at around 550°C, which is

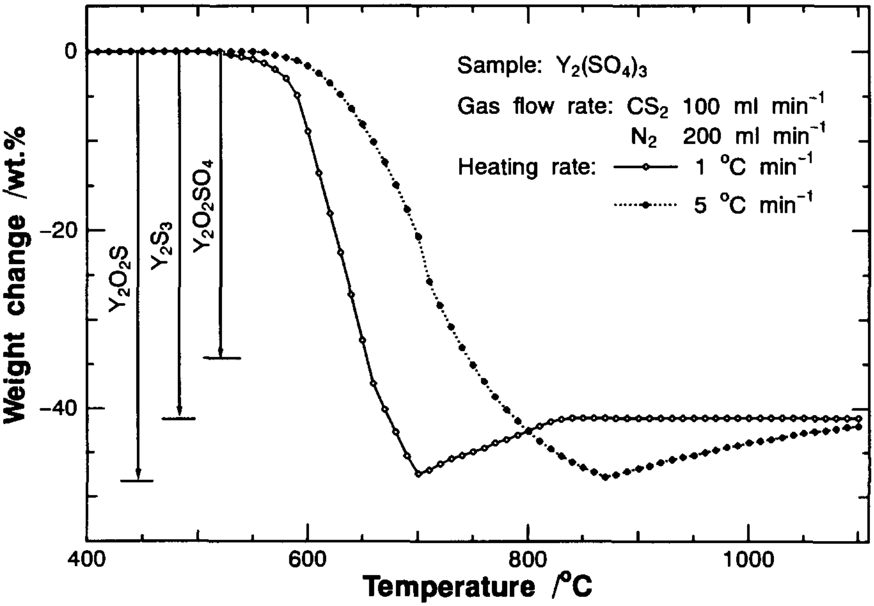

Fig. 1. TG curves of reaction of $Y_2(SO_4)_3$ with CS_2.

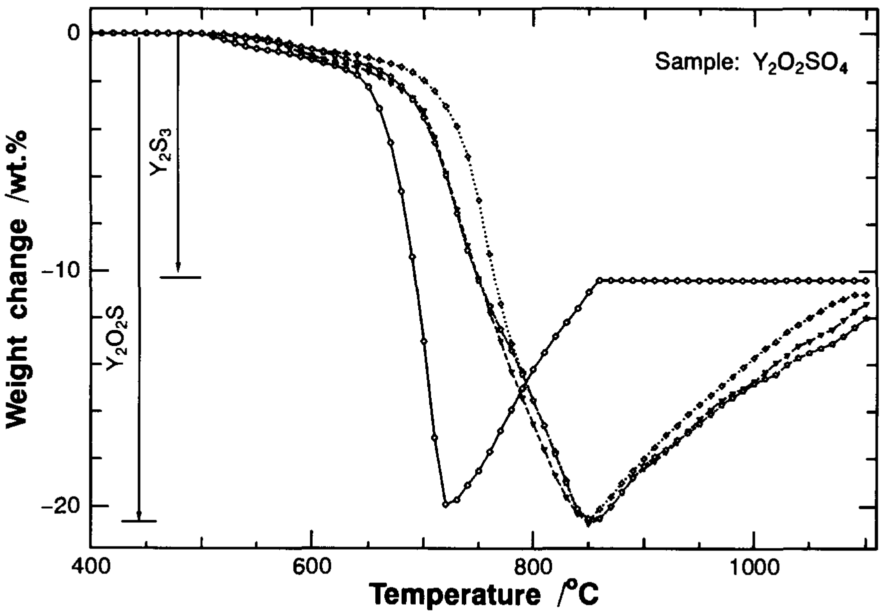

Fig. 2. TG curves of reaction of $Y_2O_2SO_4$ with CS_2. (○) 1 K min^{-1}, CS_2/N_2 = 100/200 ml min^{-1}; (◇) 5 K min^{-1}, CS_2/N_2 = 50/100 ml min^{-1}; (▽) 5 K min^{-1}, CS_2/N_2 = 100/200 ml min^{-1}; 5 K min^{-1}, CS_2/N_2 = 200/400 ml min^{-1}.

a little higher than that of $Nd_2(SO_4)_3$ [2]. It is seen from the present TG curves that the reaction rate of Y_2O_2S formation largely depends on the heating rate. The sulfurization reaction of Y_2O_2S to Y_2S_3 is slow and begins after the formation of Y_2O_2S has been completed. This behavior is different from that in the case of neodymium, where Nd_2O_2S was quickly converted to NdS_2 at the lower temperature of ≈ 600°C. The formation of Y_2S_3 was complete at 850°C if the heating rate was 1 K min^{-1}, but only at 1100°C if the heating rate was 5 K min^{-1}.

3.4. *Reaction of $Y_2O_2SO_4$ with CS_2*

The starting material $Y_2O_2SO_4$ was that prepared by heating $Y_2(SO_4)_3$ in air at 800°C for 10 days. The TG curves of the reaction of $Y_2O_2SO_4$ with CS_2 are shown in Fig. 2. It is seen that, although the gas flow rate has a fairly small effect, a heating rate change from 1 to 5 K min^{-1} causes a temperature shift of nearly 150°C. There are no significant differences in the weight change between the CS_2/N_2 gas flow rates of 100/200 and 200/400 ml min^{-1} at low temperatures. However, a gas flow rate of 50/100 ml min^{-1} was too low. It is possible that the flow rate might be correlated with the evolution and removal of the reaction gases. The reaction with CS_2 is considered to proceed in the following two steps at different temperatures

$$Y_2O_2SO_4 + CS_2 = Y_2O_2S + (CO,\ CO_2,\ COS,\ S_2\ ...) \quad (1)$$

$$Y_2O_2S + CS_2 = Y_2S_3 + (CO,\ CO_2,\ COS,\ S_2\ ...) \quad (2)$$

In the case of neodymium, however, not only did the above two step reactions overlap but also the formation reaction of NdS_2 was included in reaction (2). The formation of Nd_2S_3 was complete at ≈750°C when the heating rate was 1 K min^{-1}.

3.5. Reaction of Y_2O_2S with CS_2

The starting material Y_2O_2S was that prepared by reducing $Y_2O_2SO_4$ in a stream of H_2 at 650°C for 3 h. The weight change during the reaction of Y_2O_2S with CS_2 is shown in Fig. 3. The heating rate of 5 K min^{-1} is seen to be too high to complete the reduction and sulfurization of Y_2O_2S below 1100°C. When the heating rate was 1 K min^{-1}, however, the reaction was finished at 920°C. Extrapolation of the slope in the high temperature range to zero weight change gives 700°C as the starting temperature of the reaction forming Y_2S_3. This temperature was the same for the lines of both 1 and 5 K min^{-1} heating rates. The starting temperature of 700°C is in accordance with that of the 1 K min^{-1} curves in Figs. 1 and 2.

In order to investigate the reason for the fluctuations in Fig. 3, another experiment was carried out in which the Y_2O_2S sample was heated to 650°C at a heating rate of 20 K min^{-1} and thereafter it was maintained at this temperature for ≈ 12 h. The rate of the reaction changed only very slightly in this period, suggesting that a surface reaction was rate determining. X-ray diffraction analysis revealed that the sample after heating was a mixture of Y_2S_3 and Y_2O_2S. No other phases could be detected.

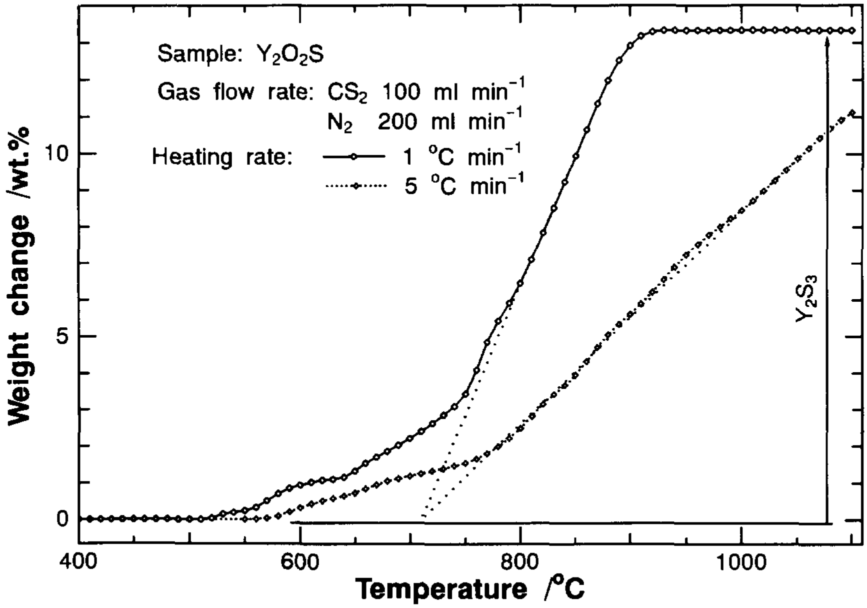

Fig. 3. TG curves of the reaction of Y_2O_2S with CS_2.

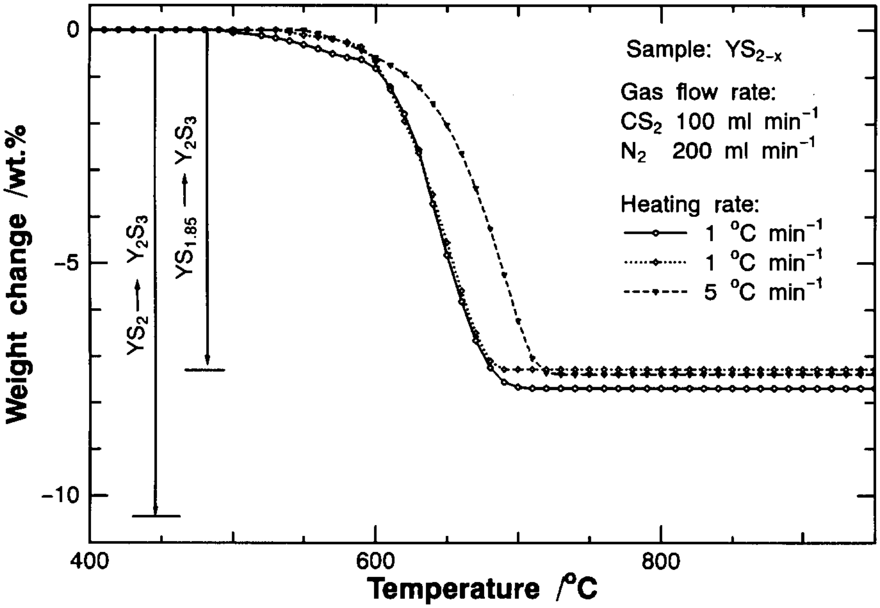

Fig. 4. TG curves of the thermal decomposition of YS_{2-x} in a stream of CS_2/N_2 gas mixture. (○) YS_{2-x} prepared at 500°C; (◇, ▲) YS_{2-x} prepared at 600°C.

Under these circumstances, YS_{2-x} was heated in a stream of CS_2/N_2. The weight changes are given in Fig. 4. The weight change of the specimen prepared at 500°C is a little larger than that of material prepared at 600°C, which might be ascribed to the larger amount of the free sulfur in admixture with YS_{2-x} formed on prolonged heating at the lower temperature of 500°C. The curves in the figure show that the composition of the present disulfide is $YS_{1.85}$. This value is close to that we obtained for neodymium disulfide, i.e. $NdS_{1.88}$ [2], taking into account the ± 0.01 error margin of the measurements of chemical formulae. The curves in Fig. 4 show that YS_{2-x} has already decomposed below 700°C.

From the above results, it is considered that the reaction causing the fluctuations shown in Fig. 3 in the temperature range 550–750°C might be the formation of YS_{2-x}. The starting temperature of the reaction of Y_2O_2S with CS_2 coincides with the decomposition temperature of YS_{2-x} (Fig. 4). Therefore it seems probable that the formed YS_{2-x} decomposed competitively to Y_2S_3. In Fig. 3, a reaction temperature of 900°C was needed for the complete change to Y_2S_3 at a heating rate of 1 K min^{-1}. The lower reaction rates than those of Figs. 1 and 2 are considered to be attributable solely to the starting material (different gaseous species being evolved).

The oxidation of Y_2S_3 in air was studied at 600°C. The phases and weight changes were examined by X-ray diffraction analysis and TG, respectively. The results are listed in Table 1. It is seen that YS_{2-x} is formed during oxidation, but

Table 1
Products after oxidation of Y_2S_3 in air at 600°C (minor phases in parentheses)

Time/h	$YS_{(2-x)}$ lattice parameters		Phases	Weight loss/wt%
	a/nm	c/nm		
1	0.3845(1)	0.7876(2)	Y_2S_3, Y_2O_2S, $YS_{(2-x)}$	−3.1
10	0.3847(1)	0.7871(2)	Y_2O_2S, $YS_{(2-x)}$	−2.1
50	0.3848(1)	0.7873(2)	Y_2O_2S, $YS_{(2-x)}$	−2.6
100	−	−	Y_2O_2S, ($YS_{(2-x)}$), ($Y_2O_2SO_4$)	−2.6
200	−	−	Y_2O_2S, ($Y_2O_2SO_4$)	−0.8

on prolonged heating it disappears, forming a mixture of Y_2O_2S and $Y_2O_2SO_4$. This result indicates the stability of YS_{2-x} at lower temperatures.

The present reduction/sulfurization reaction can be compared with that of $Nd_2(SO_4)_3$. In the case of neodymium, stoichiometric NdS_2 was formed first, and changed to nonstoichiometric NdS_{2-x} at 500–600°C. The NdS_{2-x} was then converted to Nd_2S_3 at 630–800°C, liberating sulfur. On the other hand, since yttrium disulfide is less stable than neodymium disulfide, as seen in Fig. 4, only nonstoichiometric YS_{2-x} has been obtained at sulfur pressures of 0.21 and 0.684 MPa at 500–600°C [13]. Therefore YS_{2-x} was not formed in any large amount as an intermediate phase during the formation reaction of Y_2S_3 from Y_2O_2S, although YS_{2-x} does contribute to the reaction.

4. Conclusions

(1) The decomposition of $Y_2(SO_4)_3$ in CS_2 was slower than the subsequent reduction of $Y_2O_2SO_4$. The two reactions appeared to proceed simultaneously. This behavior is different from that in the decomposition of $Nd_2(SO_4)_3$ and reduction of $Nd_2O_2SO_4$.

(2) Yttrium oxysulfate $Y_2O_2SO_4$ changes to Y_2O_2S in CS_2. The reduction of Y_2O_2S and the formation of Y_2S_3 proceed with an enhanced reaction rate above 700°C. The formation of YS_{2-x} at temperatures lower than 700°C during this reaction was not significant.

(3) Yttrium disulfide YS_{2-x} was stable below ≈600°C but decomposed to Y_2S_3 at higher temperatures.

(4) Monoclinic Y_2S_3 was formed in a single phase at ≈950°C with a reaction rate slower than that of the formation of orthorhombic Nd_2S_3.

(5) The oxidation of Y_2S_3 in air at 600°C resulted in the formation of Y_2O_2S, $Y_2O_2SO_4$ and YS_{2-x}.

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