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THERMAL DECOMPOSITION OF RARE EARTH OXYSULFIDES IN AIR

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The thermal decomposition of rare earth oxysulfides (excluding Sc, Ce and Pm) has been studied in air. The oxysulfides are oxidized to oxysulfates between 600 and 900° and the oxysulfate phase, which is unstable at higher temperatures, decomposes to oxide. The stability of the oxysulfate and its decomposition temperature decreases with decreasing radius of the rare earth ion. For the heavier rare earths the oxidation to oxysulfate takes place only partially before the decomposition to oxide begins.

Although the rare earth oxysulfides are widely used as phosphor materials, no systematic study has been made of their thermal behaviour. There are some thermoanalytical data available in the literature for individual rare earths. Eick [1] reported in 1958 that samarium oxysulfide oxidizes in one step to oxysulfate, $Sm_2O_2SO_4$. This exothermic reaction occurs with a weight increase at 630–930° and the new oxysulfate phase decomposes when heated to 1000°. More recently, Hale [2] reported that at 600–1000° neodymium oxysulfate oxidizes similarly to oxysulfate, which then decomposes to oxide at temperatures over 1200°.

Haynes and Brown [3] have published thermogravimetric data in air for rare earth oxysulfides used as phosphor host materials, *viz.* lanthanum, gadolinium, lutetium and yttrium oxysulfides. The oxidation occurs at 510–910° for lanthanum, 470–815° for gadolinium, 635–850° for lutetium and 595–950° for yttrium. The oxysulfates then decompose to oxides and the decomposition is complete above 1400, 1305, 965 and 1095°, respectively. Haynes and Brown [3] as well as Baybarz *et al.* [4] noted that the oxidation is not completed before decomposition begins.

Ozawa [5] has made a detailed study of the stability of Y_2O_2S in air. His X-ray diffraction results indicate that Y_2O_2S is stable below 700°. The oxidation begins at 750°, and between 750 and 950° Y_2O_2S and $Y_2O_2SO_4$ coexist. Above 950° a third phase, Y_2O_3, appears. The three-phase region extends to 1050°, by 1075° the oxysulfide phase has disappeared, and above 1100° only the oxide is present.

In the present study thermogravimetric data for all rare earth oxysulfides, except the Sc, Ce and Pm compounds, were measured in a dynamic air atmosphere under nonisothermal conditions.

Experimental

Sample preparation

The rare earth oxysulfides were prepared by reducing the corresponding sulfites in carbon monoxide as described earlier [6]. After reduction the samples were fired in nitrogen to improve the crystallinity. Rare earth oxides of 99.9% purity (from Kemira Oy, Oulu, Finland) were used. The purity of the oxysulfides was checked and the decomposition products were identified by X-ray powder diffraction.

Thermal analysis

The thermal decomposition of oxysulfides was investigated in a dynamic atmosphere on a Mettler Thermoanalyzer TA-1 by simultaneously recording the TG, DTG and DTA curves. Samples were heated in a high-temperature furnace (max. 1600°) at a heating rate of 10°/min, and in two cases also at 1 and 6°/min. The flow rate of air was 95 cm^3/min and the sample weights were 31.0 – 33.0 mg. The sample holder was a standard platinum crucible (diam. 7 mm, depth 20 mm) and in DTA measurements alumina was the reference material.

Results and discussion

As a typical example of the thermal decomposition of rare earth oxysulfides in air, the TG, DTG and DTA diagrams for dysprosium oxysulfide are shown in Fig. 1. The oxysulfide is stable up to 500°, after which the weight begins to increase,

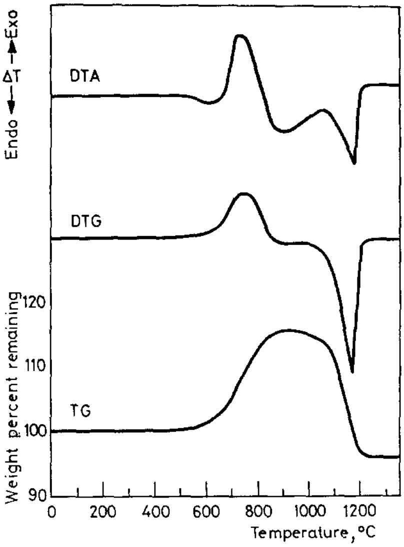

Fig. 1. TG, DTG and DTA curves of Dy_2O_2S in air atmosphere. Heating rate 10°/min

first slowly to 650° and then at a higher rate up to 880°. The oxidation is strongly exothermic but slow, so that the maxima in the DTA and DTG curves are broad. The oxysulfate phase formed is stable up to 1020°, where it begins to decompose to an oxide. The endothermic decomposition is very fast above 1100° and reaches a maximum at 1160°. The observed weight increase in the oxidation is 15.30%, as against a calculated value of 16.45%. This result indicates that, under these experimental conditions, about 5% of the dysprosium oxysulfide decomposes to oxide even before the oxidation is completed. That the original oxysulfide sample did not contain any oxide is verified by the total weight loss of 4.28%, which corresponds well to the calculated value of 4.32%.

TG curves for the other rare earth oxysulfides are presented in Fig. 2. The stability range of the oxysulfate phase is clearly broader for the lighter rare earths, and decreases more or less regularly with increasing atomic number down to only 20°

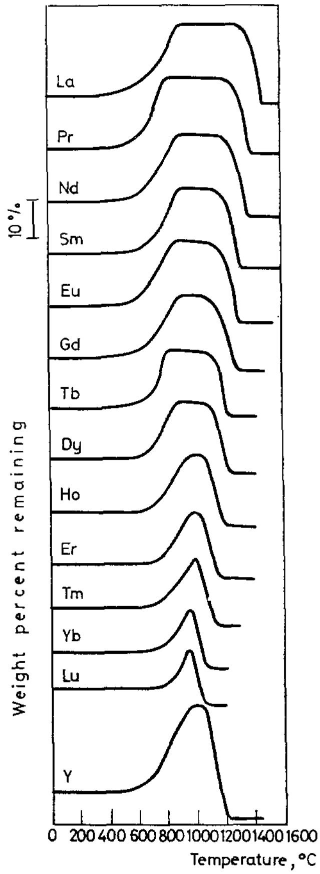

Fig. 2. TG curves for the decomposition of rare earth oxysulfides when heated at 10°/min

Table 1

Selected temperatures (°C) from the TG and DTG curves of the rare earth oxysulfides
Heating rate 10°/min

Ln	Temperature at which 50% of the oxysulfide is oxidized	Stability range of the oxysulfate	DTG peak temperature for the decomposition of oxysulfates
La	765	950–1310	1470
Pr	715	790–1170	1375
Nd	720	890–1170	1355
Sm	800	890–1140	1310
Eu	750	860–1090	1280
Gd	800	880–1070	1250
Tb	710	785–1035	1210
Dy	740	880–1020	1160
Ho	800	935–1005	1140
Er	835	960–995	1115
Tm	840	960–985	1080
Yb	790	930–950	1020
Lu	770	915–935	1005
Y	790	960–1030	1170

for lutetium (Table 1). Praseodymium and neodymium behave slightly differently than the other oxysulfates. From the Figure it can also be seen that the oxidation occurs slowly. Praseodymium and terbium behave exceptionally in this respect, as their oxysulfides oxidize faster and at lower temperature than those of the adjacent rare earths. This results in a broader stability range for praseodymium (380°) than for lanthanum oxysulfate (360°).

The oxidation reactions are so slow that it is very difficult to find any clear maxima in the DTG curves. Accordingly, the temperatures at which 50% oxidation has taken place are presented in Table 1. There seems to be clear correlation between these temperatures and the atomic numbers, a finding which is in agreement with the results of Haynes and Brown [3]. On the other hand, the decomposition temperatures of the oxysulfates do depend on the atomic number. The DTG maxima presented in Table 1 show a linear decrease from lanthanum (1470°) to lutetium (1005°). These observations are in agreement with those of Bukovec *et al.* [7], Pokrosvkii and Kovba [8], as well as those of Niinistö and Saikkonen [9] who studied the thermal decomposition of rare earth sulfate hydrates. The temperature values reported in the literature differ slightly from ours, but no doubt because of the different experimental conditions.

The observed values for the weight change during oxidation are presented in Table 2. The experimental and calculated values are nearly equal for lanthanum, but for all the other rare earths observed values are smaller. The difference between the values increases systematically with the atomic number, reaching about 4% for lutetium. Hence, the oxidation to oxysulfate is nearly complete for La_2O_2S, but for

Table 2

Weight changes (%) in the oxidation of oxysulfides to oxysulfates
Heating rate 10°/min

Ln	Experimental value	Calculated value
La	18.80	18.72
Pr	18.45	18.50
Nd	17.80	18.16
Sm	17.25	17.45
Eu	17.05	17.39
Gd	16.10	16.90
Tb	15.95	16.76
Dy	15.30	16.45
Ho	14.15	16.25
Er	13.35	16.06
Tm	12.35	15.92
Yb	11.35	15.61
Lu	11.30	15.46
Y	23.70	26.46
Y (with 6 mole % Eu)	22.85	25.65

lutetium 22% of the oxysulfide has decomposed to oxide at the temperature corresponding to the maximum of the TG curve. In spite of these differences, the total experimental weight loss on going from oxysulfide to oxide is in close agreement with the calculated loss in all cases.

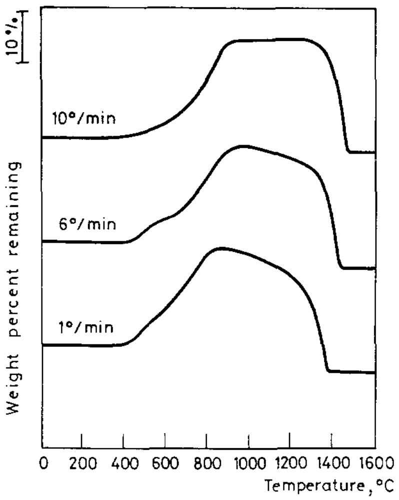

Fig. 3. The effect of the heating rate on the decomposition of La_2O_2S

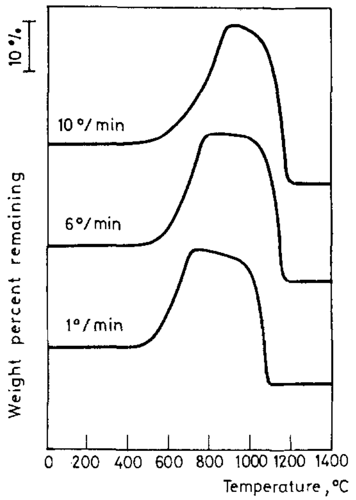

Fig. 4. The effect of the heating rate on the decomposition of Eu-activated (6 mole%) Y_2O_2S

The effect of the heating rate on the decomposition was investigated in two cases: *viz.* La_2O_2S and Eu-activated (6 mole%) Y_2O_2S. The heating rates used were 1, 6 and 10°/min. As expected, all reactions occurred at lower temperatures when lower heating rates were used (Figs 3 and 4). The stability range of the lanthanum oxysulfate decreased markedly when the heating rate was lower. With yttrium oxysulfate the effect was not observed as clearly, because the stability range of $Y_2O_2SO_4$ is much smaller than those of the oxysulfates of lighter lanthanoids. The weight

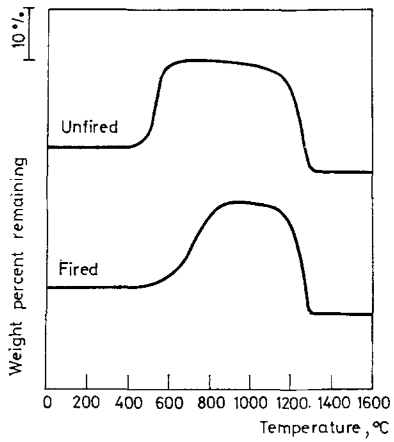

Fig. 5. The decomposition curves of two europium oxysulfide samples of different crystallinity. The lower curve was obtained for a sample fired in an inert atmosphere after reduction, and the upper curve for an unfired sample. Heating rate 10°/min

Table 3

The effect of the heating rate on the decomposition temperatures and weight changes of La_2O_2S and Eu: Y_2O_2S

Heating rate (°/min)	Temperature at which 50% of the oxysulfide is oxidized	DTG peak temperature for the decomposition of the oxysulfate	Experimental weight increases in the oxidation of the oxysulfides (%)
La_2O_2S			
10	765	1470	18.80
6	730	1430	18.52
1	640	1360	18.40
Eu: Y_2O_2S			
10	770	1190	22.83
6	680	1165	21.91
1	620	1090	19.22

gain during the oxidation also decreased when the heating rate was lower (Table 3), probably because the decomposition of the oxysulfate had more time to proceed.

The crystallinity of the oxysulfide also has a considerable effect on the thermal behaviour. This effect was studied with two europium oxysulfide samples, one of which was prepared as described above by firing in nitrogen to improve the crystallinity, while the other was left unfired. The results show that the oxidation begins at a much lower temperature and occurs faster in the unfired sample. The difference in the starting temperatures was about 200°. These results indicate that the stability of the rare earth oxysulfide phosphors in air and at high temperatures cannot be predicted until their particle size is known. On the other hand, the method of preparing the oxysulfide seems to have no effect on the later stages of the decomposition, i.e. the stability of the oxysulfate phase.

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Zusammenfassung — Die thermische Zersetzung der Oxysulfide der seltenen Erden (mit Ausnahme von Sc, Ce und Pm) wurde in Luft untersucht. Die Oxysulfide werden zwischen 600 und 900° zu Oxysulfaten oxidiert und die Oxysulfatphase, welche bei höheren Temperaturen instabil ist, wird zu Oxid zersetzt. Die Stabilität des Oxysulfats und seine Zersetzungstemperatur nehmen mit abnehmendem Radius des seltenen Erden-Ions ab. Bei den schwereren seltenen Erden erfolgt die Oxysulfatbildung nur teilweise vor den Einsetzen des Abbaus zu Oxid.

Резюме — Было изучено термическое разложение в атмосфере воздуха оксисульфидов щелочно-земельных металлов, исключая Sc, Ce и Pm. Оксисульфиды между 600 и 900° окисляются до оксисульфатов и эта фаза, будучи нестабильной при высоких температурах, разлагается до оксидов. Устойчивости оксисульфатов и температура их разложения уменьшается с уменьшением радиуса щелочно-земельного иона. В случае более тяжелых щелочно-земельных металлов, имеет место только часточное окисление до оксисульфатов и которое происходит перед началом разложения до оксида.