THERMAL STABILITY OF RARE EARTH OXYSULFIDE SOLID SOLUTIONS IN AIR

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ABSTRACT

The thermal stability of rare earth oxysulfide solid solutions has been studied in dynamic air atmosphere. Two pseudobinary systems, Eu_2O_2S—Y_2O_2S and La_2O_2S—Y_2O_2S, were included in the study. In the europium—yttrium system, where no two-phase region exists, the thermal behavior was identical to that observed for pure rare earth oxysulfides. The temperatures at which the oxysulfide oxidizes to the oxysulfate and the oxysulfate decomposes to the oxide depend on the molar ratio of the cations in the solution. In the La_2O_2S—Y_2O_2S system, where the existence of two phases was detected, the decomposition reaction of the oxidized phase consisted of two stages. In the DTG and DTA curves two peaks could sometimes be observed for the oxidation reaction, too, the two stage process being clearer the larger the difference in the unit cell sizes.

INTRODUCTION

In earlier studies concerning the solid solution formation of rare earth oxysulfides we noted that the solubility depends on the difference in ionic radius of the cations [1]. If the difference is less than 9—10% solid solutions are formed in all cation proportions, but when the difference exceeds 10% there exists a two-phase region, i.e. incomplete solubility. For instance, in the lanthanum—yttrium system there are two different hexagonal phases in the two-phase region: lanthanum oxysulfide rich in yttrium and yttrium oxysulfide rich in lanthanum. Besides X-ray powder diffraction, fluorescence spectroscopy and high resolution electron microscopy have been used to study the solid solubility of rare earth oxysulfides [2,3].

The rare earth oxysulfides are unstable when heated in air and they oxidize to oxysulfates. The temperature at which the oxidation begins, completeness of the oxidation reaction and the stability range of the oxysulfate phase depend on the rare earth and on the particle size of the starting material [4,5].

The aim of the present study was to investigate the thermal behavior of

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solid solutions of rare earth oxysulfides in air. Two series, one with complete (Eu_2O_2S—Y_2O_2S) and the other with incomplete solubility (La_2O_2S—Y_2O_2S), as established by X-ray diffraction, were chosen for the investigation. A further goal of the work was to determine whether or not the existence of structurally closely related separate phases can be detected by thermoanalytical methods.

EXPERIMENTAL

The rare earth oxysulfides were prepared by reducing the corresponding sulfites in carbon monoxide, as described earlier [6]. This method has been found very satisfactory for the preparation of oxysulfide solid solutions [2]. In the present case, however, firing in inert atmosphere after reduction was not carried out and thus the particle size of the compounds was very small. The rare earth oxides used for the synthesis were products of Kemira Oy, Oulu, Finland, with a minimum purity of 99%.

The thermal decomposition of the rare earth oxysulfides was studied on a Mettler thermoanalyzer TA-1, recording simultaneously the TG, DTG and DTA curves. The flow rate of air was 95 cm^3 min^{-1} and the heating rate was 10°C min^{-1}. Standard platinum crucibles (7 mm diameter and 19 mm depth) were used, and in DTA measurements aluminum oxide was the reference material. Sample weights were about 30 mg in all measurements.

RESULTS AND DISCUSSION

Eu_2O_2S—Y_2O_2S system

The TG, DTG and DTA curves for the decomposition of the pure Eu_2O_2S phase are presented in Fig. 1. As can be seen, the oxidation of the oxysulfide

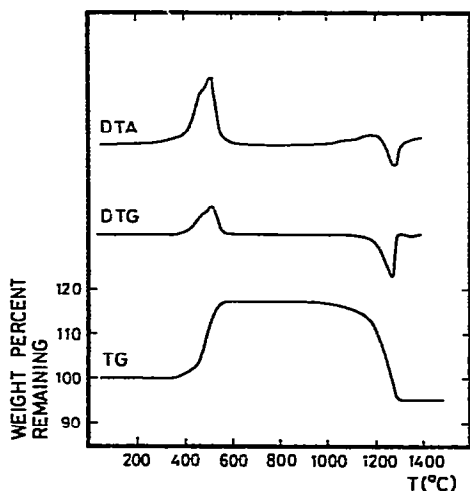Fig. 1. TG, DTG and DTA curves for the thermal decomposition of Eu_2O_2S in dynamic air atmosphere. Heating rate: 10°C min^{-1}.

begins at 380°C and the DTG maximum lies at 510°C. The strongly exo-
thermic oxidation reaction is complete at 580°C. The observed weight
increase is 17.0% against the calculated value of 17.4%. This means that the
oxidized phase consists of other phases (oxysulfide and oxide) in addition to
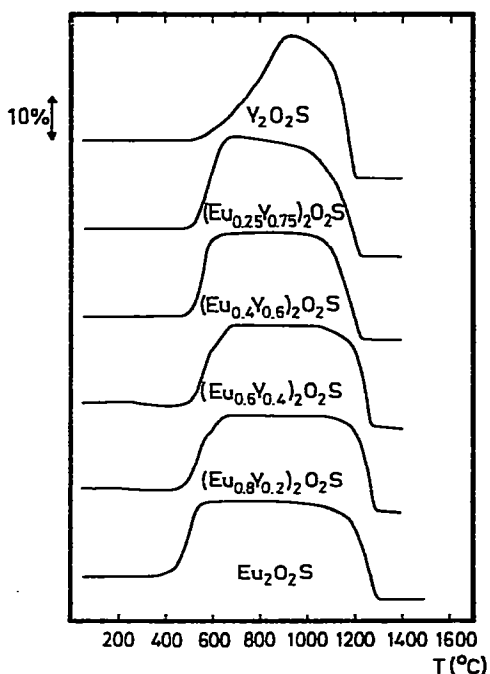

Fig. 2. TG curves for the decomposition of Eu_2O_2S, Y_2O_2S and their solid solutions.
Heating rate: $10°C \ min^{-1}$.

the main phase oxysulfate [4]. The oxidized phase decomposes to the oxide
between 1000 and 1300°C, with a DTG peak maximum at 1280°C. A com-
parison of our present and earlier results shows the oxidation to begin at a
lower temperature and occur faster here [4]. The reason for this behavior is
the smaller crystallite size of the oxysulfide: the only difference between

TABLE 1

DTG peaks (°C) for the decomposition of europium—yttrium oxysulfide solid solutions
in air (heating rate: $10°C \ min^{-1}$)

Phase	DTG peak of the oxidation reaction	DTG peak of the decomposition reaction
Eu_2O_2S	510	1280
$(Eu_{0.8}Y_{0.2})_2O_2S$	535	1270
$(Eu_{0.6}Y_{0.4})_2O_2S$	550	1255
$(Eu_{0.4}Y_{0.6})_2O_2S$	560	1200
$(Eu_{0.25}Y_{0.75})_2O_2S$	585	1185
Y_2O_2S	720	1170

this and previous experiments is that the present oxysulfide was not fired in an inert atmosphere after the reduction. The oxysulfate phase, on the other hand, decomposes in the same temperature range regardless of the crystallinity of the oxysulfide.

Figure 2 shows the TG curves for some solid solutions of europium and yttrium oxysulfides, and the DTG maxima obtained from the curves are listed in Table 1. The addition of yttrium to the europium oxysulfide lattice causes an increase in the oxidation temperatures and a decrease in the decomposition temperatures. Thus the stability range of the oxysulfate phase decreases significantly. The difference between the DTG peak temperatures decreases from $770°$ $(510—1280°C)$ for Eu_2O_2S to $450°$ $(720—1170°C)$ for Y_2O_2S. All TG curves of the Eu—Y oxysulfide solid solutions are closely related to those obtained for pure rare earth oxysulfides. All reactions proceed in a single step and the single peaks indicate that compounds are homogeneous and contain only one phase.

$La_2O_2S—Y_2O_2S$ system

The TG, DTG and DTA curves for $(La_{0.6}Y_{0.4})_2O_2S$ are depicted in Fig. 3, as an example of the second series of rare earth oxysulfide solid solutions. The oxidation of the compound begins at $550°C$. According to the TG curve, the reaction occurs in one step and is complete by $860°C$. However, the DTG and DTA curves display two peaks at 710 and $790°C$. The oxidized phase has a plateau between 860 and $1050°C$ in the TG curve. The decomposition reaction is likewise a two-stage process. This is obvious even from the TG curve, which shows the reactions to take place over the ranges $1050—1390$ and $1390—1470°C$. However, no clear plateau is reached at $1390°C$. The corresponding DTG maxima are at 1250 and $1430°C$. A combination of the TG curves for the pure phases presented in Fig. 4 would give a similar result.

Figure 4 also shows the TG curves for some solid solutions in the $La_2O_2S—$

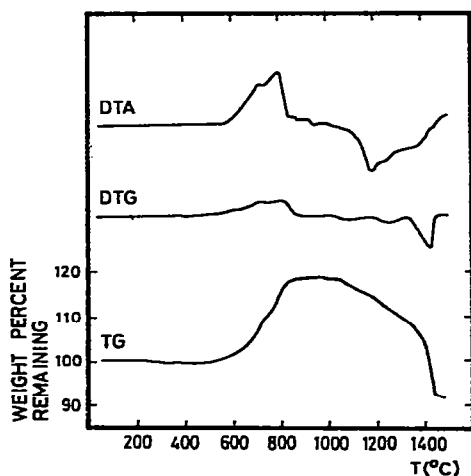Fig. 3. TG, DTG and DTA curves for the thermal decomposition of $(La_{0.6}Y_{0.4})_2O_2S$ in air. Heating rate: $10°C$ min^{-1}.

Y_2O_2S system. The corresponding DTG maximum values are collected in Table 2. When the cation concentrations in the solid solutions are in the 40—60% range all decomposition reactions have two stages. For smaller concentrations and for pure compounds this two-stage effect cannot be detected.
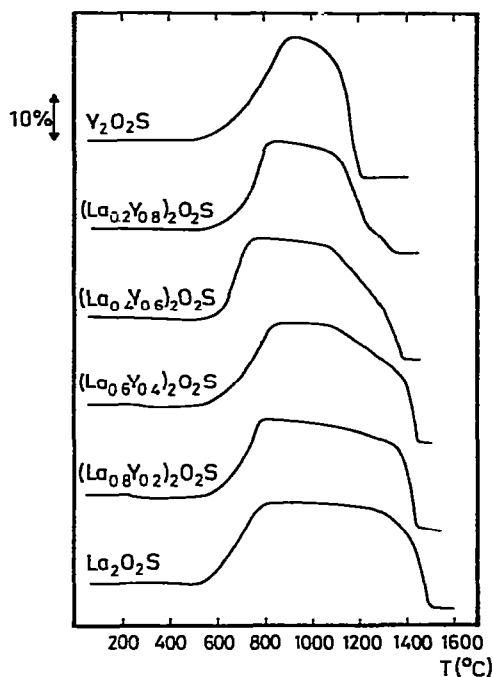

Fig. 4. TG curves for the decomposition of La_2O_2S, Y_2O_2S and their solid solutions. Heating rate: $10°C\ min^{-1}$.

The results obtained for the thermal behavior of the lanthanum—yttrium oxysulfide system indicate that the number of phases present affects the curves. When the solid solubility is complete and the compound homogeneous, the oxidation and decomposition reactions occur in one stage and the temperatures of the reactions depend on the rare earths and on their concen-

TABLE 2

DTG peaks (°C) for the decomposition of lanthanum—yttrium oxysulfide solid solutions in air (heating rate: $10°C\ min^{-1}$)

Phase	DTG peak of the oxidation reaction	DTG peak of the decomposition reaction
La_2O_2S	640	1470
$(La_{0.8}Y_{0.2})_2O_2S$	705	1445
$(La_{0.6}Y_{0.4})_2O_2S$	710, 790	1250, 1430
$(La_{0.4}Y_{0.6})_2O_2S$	660, 720	1220, 1350
$(La_{0.2}Y_{0.8})_2O_2S$	780	1190
Y_2O_2S	720	1170

trations. On the other hand, when solid solubility is incomplete and two hexagonal phases exist, the DTG and DTA curves show two peaks for each reaction. In the TG curves the existence of the two phases is more difficult to detect and is generally possible only for the decomposition of the oxidized phase. This behavior can be understood from a study of the TG curves of the pure oxysulfides. There are no large differences in the oxidation temperatures, but for the decomposition reactions of the oxidized phase the temperature difference between pure La_2O_2S and Y_2O_2S is 300°C [4]. Therefore the solid solutions consisting of two phases show clearly distinguishable two-step decomposition reactions.

Other systems

To confirm the conclusions drawn for the thermal behavior of the oxysulfide solid solutions, additional solutions were studied: $(La_{0.7}Lu_{0.3})_2O_2S$, $(La_{0.4}Yb_{0.6})_2O_2S$, $(La_{0.55}Dy_{0.45})_2O_2S$, $(La_{0.4}Gd_{0.6})_2O_2S$ and $(Nd_{0.6}Y_{0.4})_2O_2S$. Their behavior was identical to that found in the Eu_2O_2S—Y_2O_2S and La_2O_2S—Y_2O_2S series. For systems where X-ray diffraction revealed incomplete solubility, the thermoanalytical curves showed two separate decomposition reactions. The existence of the separate reactions was more pronounced when the difference in the ionic radii of the cations was increased. DTG curves were generally more informative than the TG curves, as in the case of La_2O_2S—Gd_2O_2S where the ionic radii difference is only 10%.

From the calculated and theoretical weight changes in the TG curves similar conclusions may be drawn as in our earlier study [4]. Thus, the oxidation reaction to the oxysulfate is always incomplete except for pure La_2O_2S, and the incompleteness increases with the concentration of heavier rare earth ions. However, for the total weight decrease from the oxysulfide to the oxide the theoretical and experimental values are in good agreement.
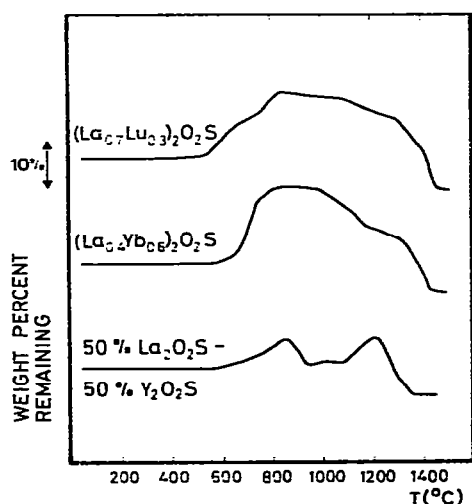

Fig. 5. TG curves for solid solutions with formula $(La_{0.7}Lu_{0.3})_2O_2S$, $(La_{0.4}Yb_{0.6})_2O_2S$ and for a mixture of 50% La_2O_2S—50% Y_2O_2S prepared by mixing and firing the pure compounds in an inert atmosphere. Heating rate: 10°C min^{-1}.

Figure 5 presents TG curves for some oxysulfide solid solutions having two phases. The first two phases, $(La_{0.7}Lu_{0.3})_2O_2S$ and $(La_{0.4}Yb_{0.6})_2O_2S$, have been prepared as described in the Experimental section and they are true solid solutions. Both oxidation and decomposition reactions of these compounds have two stages. The third curve in Fig. 5 shows the thermogravimetric behavior of a mixture prepared by heating 50% La_2O_2S and 50% Y_2O_2S in an inert atmosphere at $1500°C$ for 3 h. The product made in this way remains inhomogeneous and consists only partially of solid solutions. The TG curve obtained from this mixture differs from those of all other systems investigated in this work. It has two maxima which correspond well to the values of pure oxysulfides. This result indicates that the mixing of the cations before the preparation is a pre-requisite for the production of good oxysulfide solid solutions.

The effect of heating rate

A sample of composition $(La_{0.5}Y_{0.5})_2O_2S$ was also heated with a slower heating rate ($2°C$ min^{-1}). The reaction temperatures decreased, as could be expected, relative to those obtained with the rate $10°C$ min^{-1}. The oxidation began at $440°C$ and the decomposition was complete at $1370°C$. In spite of the slow heating rate, it was difficult to observe the presence of two phases from the shape of the TG curve. However, the observed weight increase (11.2%) was only half of the calculated value. The obvious explanation is that there were two phases, one of which was not yet fully oxidized before the other started to decompose. The DTA curve also verified that two reactions were occurring simultaneously: a broad exothermic peak was observed in the DTA curve although the weight was decreasing slowly. This shows that in the beginning, the enthalpy contribution from the exothermic oxidation dominates over the endothermic decomposition of the oxysulfate. A clear endothermic peak exists only above $1250°C$ where the weight decrease is faster.

CONCLUSION

The present work demonstrates that thermoanalytical techniques can be used to detect the existence of different phases. When the phases are structurally and chemically closely related the DTG and DTA curves are more informative than the TG curve. The homogeneity of the product and the existence of pure compounds in solid solutions can also be detected by thermal analysis. The curves of the rare earth oxysulfides, which display only two reactions, are relatively simple and observations are not difficult to interpret. However, with a more complex system of reactions and phases, an additional technique such as electron microscopy would probably need to be combined with thermoanalytical methods in order to obtain reliable results.

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