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Dedicated to Corresponding Member of the Academy of Sciences of the Estonian SSR Oskar Kirret on the occasion of his 75th birthday.

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## TRENDS IN THE THERMAL DEHYDRATION AND DECOMPOSITION REACTIONS OF RARE EARTH SULFATES

(Presented by M. Veiderma)

Thermal degradation of rare earth sulfate hydrates  $Ln_2(SO_4)_3 \cdot nH_2O$  ( $n=5,8$ ;  $Ln=Sc, Y, La-Lu$  excl. Pm) has been studied in air by TG and DTA/DSC techniques. The trends observed in the dehydration temperatures and enthalpies as well as in the formation temperatures of the oxysulfate and oxide phases are discussed.

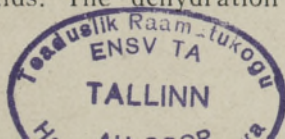
### Introduction

Rare earth compounds represent an interesting case for thermoanalytical studies because their decomposition reactions usually occur in a wide temperature range from room temperature up to 2000 K. Furthermore, due to the existence of isostructural series in the lanthanoid compounds, the thermoanalytical investigations can be usually extended to cover several lanthanoids including yttrium, making the conclusions more reliable.

The octahydrated sulfates of trivalent rare earths have been frequently studied by thermoanalytical methods. The early comprehensive studies by W. W. Wendlandt et al. using TG and DTA techniques [1-3] have been complemented by a simultaneous TG/DTA study by N. Bukovec et al.; the latter authors have also used DSC to determine the dehydration enthalpies [4]. Individual rare earth sulfate hydrates have been frequently investigated, too. For example, the most recent study employs high resolution luminescence spectroscopy to monitor the decomposition products of  $Eu_2(SO_4)_3 \cdot 8H_2O$  during the TG experiments [5].

The decomposition schemes and trends observed in the studies involving all lanthanoids have been discussed to some extent in [1-4]. In addition, A. N. Pokrovski and L. M. Kovba have given experimental data for the decomposition temperatures when anhydrous sulfates were used as starting materials [6].

In order to get a more complete picture of the structure — thermal stability relationships for the rare earth sulfate and selenate hydrates, the present authors have undertaken a systematic study of the decomposition temperatures and trends. The dehydration reactions have been





recently discussed in relation to the crystal structures [7]. Here we present the results concerning overall decomposition schemes and temperatures for the penta- and octahydrated sulfates.

### Experimental

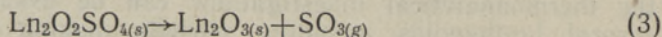
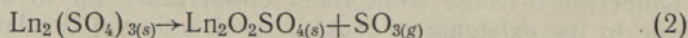
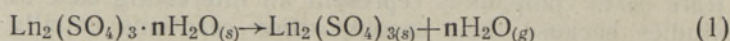
Rare earth sulfate penta- and octahydrates were crystallized from strong and medium sulfuric acid solutions, respectively; the crystals were characterized by X-ray diffraction. Samples ground to uniform grain size (100 mesh) were packed by a vibrating spatula into standard platinum crucibles (diam. 7 mm, depth 19 mm).

Simultaneous TG, TDG and DTA curves were recorded in the temperature range 300—1900 K on a Mettler TA-1 Thermoanalyzer using dynamic air atmosphere (90 cm<sup>3</sup> min<sup>-1</sup>). Generally two sample weight/heating rate combinations were used: 200 mg/10 K min<sup>-1</sup> (I) and 20 mg/2 K min<sup>-1</sup> (II). The effect of sample holder geometry was studied in a third series of the experiments (III) by using the 20 mg/2 K min<sup>-1</sup> sample rate combination but smaller crucibles (diam. 5 mm, depth 5 mm). All obtained curves were redrawn by the use of a computer programme taking care of buoyancy etc. corrections. In DTA measurements alumina was used as reference material and the calibrations were performed from 400 to 700 K with high-purity In, Sn, Cd and Zn metals.

Dehydration mechanism and enthalpy determinations were further checked by the use quasi-isothermal (MOM Derivatograph) and DSC (Perkin-Elmer DSC-1B and DSC-4) techniques, respectively.

### Results and discussion

Thermal degradation in air consists of three main steps, viz. (1) dehydration, followed by formation of (2) oxysulfate and (3) oxide:



As a representative example, the behaviour of  $\text{Ho}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  upon heating is depicted in Fig. 1.

Generally the observed decomposition temperatures in the penta- and octahydrate series depend on the structure type and, within the isostructural compounds, on the rare earth ionic radii. Only cerium and scandium deviate slightly from this overall scheme; the trends and deviations thereof will be discussed in greater detail below.

**Dehydration.** The dehydration of the octahydrates proceeds in a single step with smaller samples (II), but when larger samples and higher heating rate (I) are employed, dehydration becomes a 2—3 step process (cf. Fig. 1). The stability of the intermediate hydrates is obviously low because the plateaus do not correspond to phases of well-defined composition. This is in agreement with the report of T. Spasibenko who found by tensimetric studies several intermediate sulfate hydrates for trivalent cerium [8].

The starting temperatures in the dehydration process seem to be rather uniformly around 380 K, but the completion temperatures show descending trend as the size of the rare earth ion decreases (cf. Fig. 2).



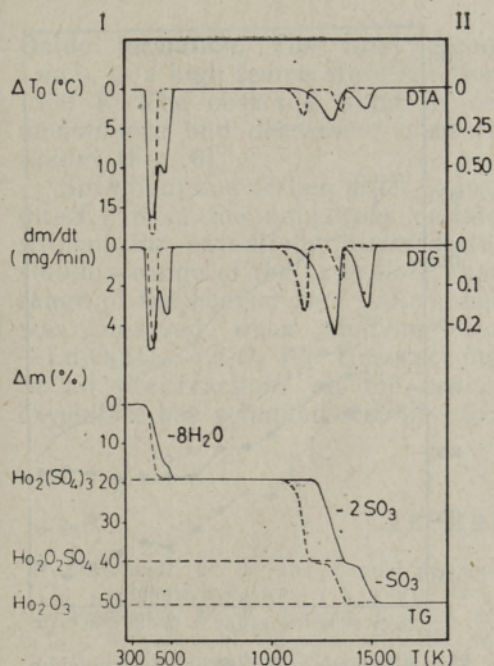


Fig. 1. TG, DTG and DTA curves for  $\text{Ho}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  recorded in air under two different conditions I (—) and II (---). For experimental details, see the text.

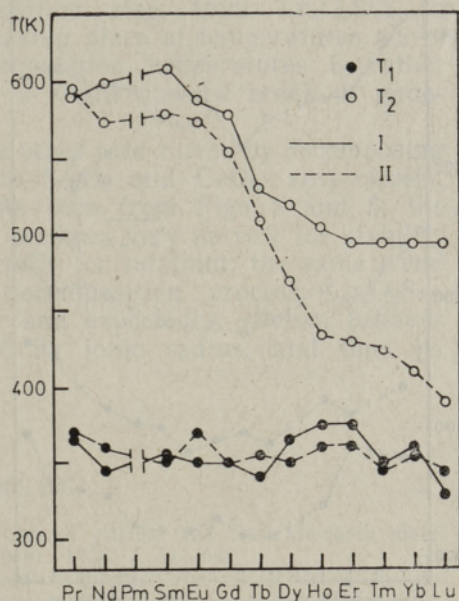


Fig. 2. Starting  $T_1$  (●) and completion  $T_2$  (○) temperatures, measured in air under two conditions, for the dehydration reaction  $\text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O} \rightarrow \text{Ln}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}(\text{g})$  in the isostructural series Pr—Lu.

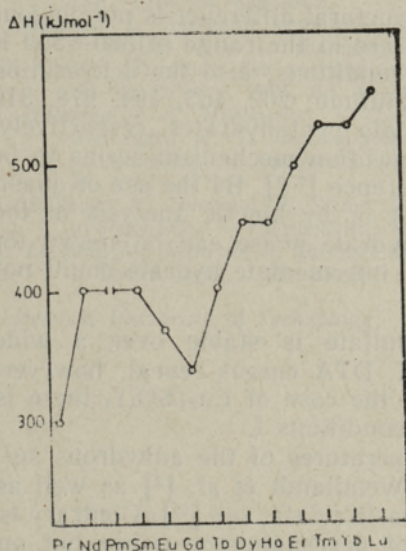


Fig. 3. Dehydration enthalpies ( $\text{kJ/mol}$ ) for the octahydrates  $\text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  ( $\text{Ln} = \text{Pr} - \text{Lu}$ ) measured under conditions II.

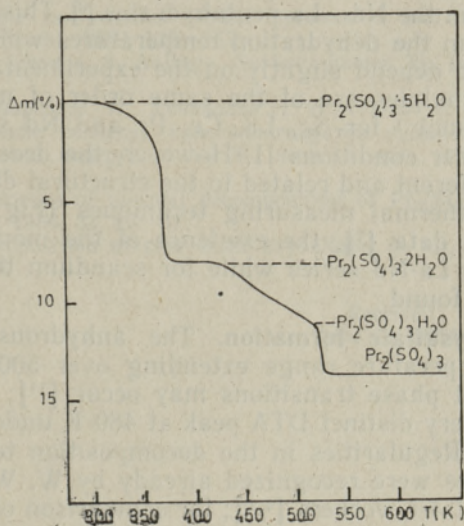


Fig. 4. Dehydration reactions of  $\text{Pr}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  measured in air under quasi-isothermal conditions with a Q-Derivatograph. Sample size is 200 mg.



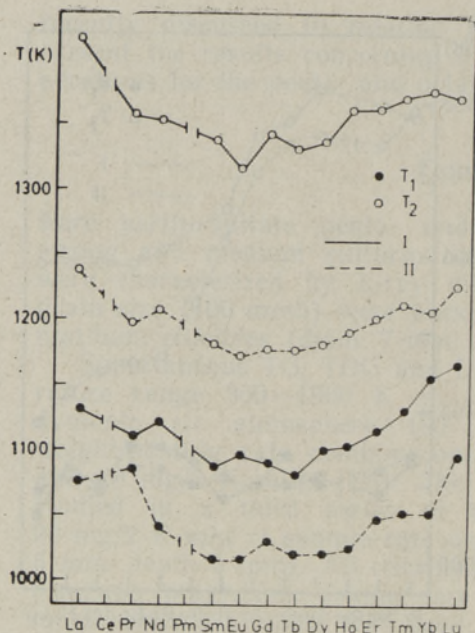


Fig. 5. Starting  $T_1$  (●) and completion temperatures  $T_2$  (○) for the reaction  $\text{Ln}_2(\text{SO}_4)_3(\text{s}) \rightarrow \text{Ln}_2\text{O}_2\text{SO}_3(\text{s}) + 2\text{SO}_3(\text{g})$  in the lanthanoid series (La—Lu). Experimental conditions: I —, II — —.

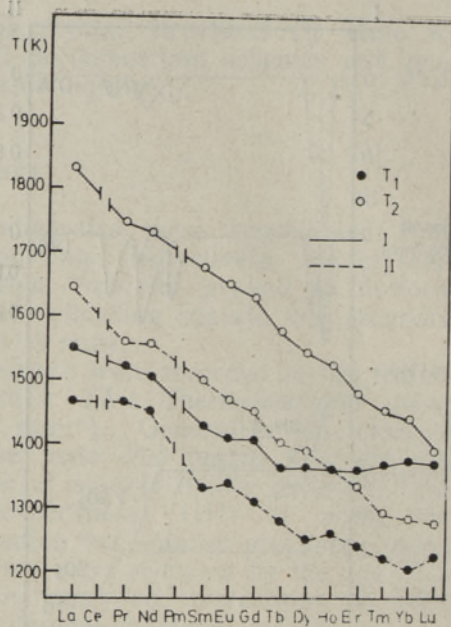


Fig. 6. Starting  $T_1$  (●) and completion temperatures  $T_2$  (○) for the reaction  $\text{Ln}_2\text{O}_2\text{SO}_4 \rightarrow \text{Ln}_2\text{O}_3$  in the lanthanoid series (La—Lu). Experimental conditions: I —, II — —.

Lanthanum and cerium sulfates deviate slightly from this general trend; this is obviously due to their different structure [9]. The dehydration enthalpies given in Fig. 3 show the opposite tendency with a maximum value for lutetium and a distinct break at gadolinium.

In the case of pentahydrates, scandium sulfate has a different structure than the Nd—La pentahydrates [9]. This structural difference is not obvious from the dehydration temperatures which are in the range of 380—550 K and depend slightly on the experimental conditions; also the dehydration enthalpies are of the same order of magnitude: 202, 163, 194, 278, 310 kJ/mol<sup>-1</sup> for Sc, La, Ce, Pr and Nd sulfate pentahydrates, respectively, under conditions II. However, the decomposition mechanism seems to be different and related to the structural difference [7, 9]. By the use of quasi-isothermal measuring techniques (Fig. 4) or by kinetic analysis of the TG data [7], the existence of the monohydrate phase can be shown for the La—Nd series while for scandium this intermediate hydrate could not be found.

**Oxysulfate formation.** The anhydrous sulfate is stable over a wide temperature range extending over 500 K. DTA curves reveal, however, that phase transitions may occur [11]; in the case of  $\text{Eu}_2(\text{SO}_4)_3$  there is a very distinct DTA peak at 480 K under conditions I.

Regularities in the decomposition temperatures of the anhydrous sulfates were recognized already by W. W. Wendlandt et al. [2] as well as by later workers [4, 6]; for comparison of earlier data, see [10]. Contrary to the dehydration trend, the curves are not descending or rising but on the basis of present results they could be best described as U-shape curves (Fig. 5). Kinetic calculations for  $\text{Pr}_2(\text{SO}_4)_3$  have indicated the decomposition to follow a linear law until  $\alpha=0.5$  [12].



**Oxide formation.** The final decomposition step, from  $\text{Ln}_2\text{O}_2\text{SO}_4$  to  $\text{Ln}_2\text{O}_3$ , is a high temperature reaction taking place at temperatures above 1200 K. The observed trend in decomposition temperatures is rather monotonous and decreasing one, with a slight upward break at gadolinium (Fig. 6).

Scandium and cerium differ from the other rare earths by decomposing directly from the anhydrous sulfate to  $\text{Sc}_2\text{O}_3$  and  $\text{CeO}_2$ , respectively, without the oxysulfate intermediate. As seen from Figs 1 and 6, the stability range of the oxysulfate phase becomes very narrow for stability range of the heavier rare earths, especially for lutetium; the same trend was observed when studying the decomposition process  $\text{Ln}_2\text{O}_2\text{S} - \text{Ln}_2\text{O}_2\text{SO}_4 - \text{Ln}_2\text{O}_3$  [13]. Unsurprisingly and expectedly, yttrium behaves in all the reactions on the basis of its ionic radius, and thus its oxysulfate has a limited stability, too.

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**HARULDASTE MULDMETALLIDE SULFAATIDE  
TERMILISEST DEHÜDRATATSIOONIST JA LAGUNEMISREAKTSIOONIDEST**

On uuritud haruldaste muldmetallide sulfaatide hüdraatide  $\text{Ln}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$  ( $n=5,8$ ;  $\text{Ln}=\text{Sc}, \text{Y}, \text{La}-\text{Lu}$ , välja arvatud  $\text{Pm}$ ) termilist degradatsiooni õhus TG ja DTA/DSC meetodiga ja analüüsitud dehüdratiseerimistemperatuuride ja -entalpiate ning oksiid-sulfaatide ja oksiide sisaldavate faaside tekketemperatuuride määramise tulemusi.

Л. НИИНИСТЁ, П. САЙККОЕН, Р. СОННИНЕН

**О ТЕРМИЧЕСКОЙ ДЕГИДРАТАЦИИ И РЕАКЦИЯХ РАЗЛОЖЕНИЯ  
СУЛЬФАТОВ РЕДКИХ ЗЕМЕЛЬ**

Исследована термическая деградация гидратов сульфатов редких земель  $\text{Ln}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$  ( $n=5,8$ ;  $\text{Ln}=\text{Sc}, \text{Y}, \text{La}-\text{Lu}$  за исключением  $\text{Pm}$ ) в воздухе методами TG и DTA/DSC. Обсуждены результаты определения температур и энтальпий их дегидратации, температур образования оксисульфатов и оксидсодержащих фаз.