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SYNTHESIS, IDENTIFICATION AND THERMAL DECOMPOSITION OF DOUBLE SULPHATES OF SOME LANTHANIDES AND Y WITH ETHANOLAMMONIUM CATION

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Abstract

On evaporation at room temperature of an aqueous mixture of Ln(III) sulphate and ethanolammonium sulphate in a molar ratio higher than 1:12, in the presence of sulphuric acid, double sulphates of Sm, Eu, Ho, Tm, Yb and Y with a waxy feel were obtained. The stoichiometry of the obtained compounds was determined by means of elemental and TG analysis. On the basis of X-ray powder diffraction patterns it was concluded that an isostructural group with a general formula: $Ln_2(HOCH_2CH_2NH_3)_8(SO_4)_7 \cdot 8H_2O$ was obtained. The above compounds have a stoichiometry and a crystal structure different from those of the double sulphates of La, Ce, Pr and Nd with the same monovalent cation, as presented earlier.

The thermal decomposition of the investigated compounds in the temperature range from ambient temperature up to 1173 K occurred in a similar way, mainly in three not well-differentiated steps. Lanthanide oxysulphates were obtained as final products.

Keywords: double sulphates, ethanolammonium, lanthanides, thermal decomposition

Introduction

Many data are available on the double sulphates of rare earths(III) with mono valent cations with the general formula $MLn(SO_4)_2 \cdot xH_2O$ where M=alkali metal, NH_4, N_2H_5 or Tl(I) and x=0–4.

The crystal structure and thermal behaviour of these compounds have been investigated by many authors [1]. Data have also been reported on the double sulphates of rare earths(III) with monovalent aliphatic ammonium cations. The synthesis, thermal decomposition and crystal structure of lanthanides and Al(III), Cr(III) and Fe(III) with monomethyl- [2, 3], dimethyl- [4–8], trimethyl- [9, 10], tetramethyl- [11–13], diethyl- [14], ethanol- [15], diethanol- and triethanolammonium [16] have been the subject of our investigations for a long time. It was also found that neither of the double sulphates of lanthanides, not even those with

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monomethylammonium ion, belong to the well known alums. It was also found that because of the presence of the organic cation their thermal decomposition is very complex.

As a continuation of our work on the double sulphates of rare earths with various nonclassical monovalent cations, we have presented recently the results of our investigations of double sulphates of trivalent La, Ce, Pr or Nd with the monovalent ethanolammonium cation [17].

This paper presents the results of our investigations on the synthesis, identification and thermal decomposition in static air atmosphere of the double sulphates of trivalent Sm, Eu, Ho, Tm, Yb and Y with the monovalent ethanolammonium cation. Yttrium is included in these investigations because it very often forms double salts identical with those of the heavier lanthanides.

The X-ray powder diffraction patterns which were used only for the identification of the products of synthesis, are presented to demonstrate the isostructurality of the obtained double sulphates.

Experimental

Chemicals

2-ethanolamine(purum Merck), $Ln_2(SO_4)_3 \cdot 8H_2O$ sulphuric acid (p.a. Merck).

Synthesis

The double sulphates of Ln(III) and Y(III) with ethanolammonium were obtained by evaporation at room temperature of a concentrated aqueous solution of Ln(III)- or Y(III) sulphate (0.001 mol) and ethanolammonium sulphate in a molar ratio higher than 1:12 with addition of sulphuric acid (0.008 mol). The crystalline products with a waxy feel were filtered off, washed with ethanol and dried in an exiccator. For the determination of their formula, elemental and thermogravimetrc (TG) analyses were performed.

The concentrated solution of ethanolammonium sulphate was obtained by stepwise neutralization of 2-ethanolamine with dilute sulphuric acid to pH 3–4 with external cooling in an ice-water bath.

Analytical methods

X-ray powder diffraction patterns were obtained on a Philips PW 1050 Vertical Goniometer with monochromatized CuK_α radiation.

TG measurements were performed on a Cahn RG Electrobalance in static air atmosphere at a heating rate of 5 K min^{-1} on samples of about 10 mg, in quartz crucible.

DTA curves were recorded on a Netzsch differential thermoanalyser in static air atmosphere, on samples of about 100 mg, at a heating rate of 5 K min^{-1}. The reference substance was pure alumina.

Elemental analysis for carbon and hydrogen was carried out on a Coleman Model 33 instrumented by Liebig's method, and nitrogen was determined by the Dumas method.

Results and discussion

As can be seen from the X-ray powder diffraction patterns of the products (Figs 1–3), an isostructural group of crystalline compounds of Sm, Eu, Ho, Tm, Yb and Y was obtained. From the results of elemental analysis (Table 1) and the mass losses (TG curves), their general formula, closest to $Ln_2(HOCH_2CH_2NH_3)_8(SO_4)_7 \cdot 8H_2O$ was determined.

Their general formula and their crystal structure are different from the general formula and crystal structure of the La, Ce, Pr, or Nd compounds presented recently [17]. From our investigations on the double salts of Ln(III) and from many other investigations of Ln(III) double salts it could be concluded that there

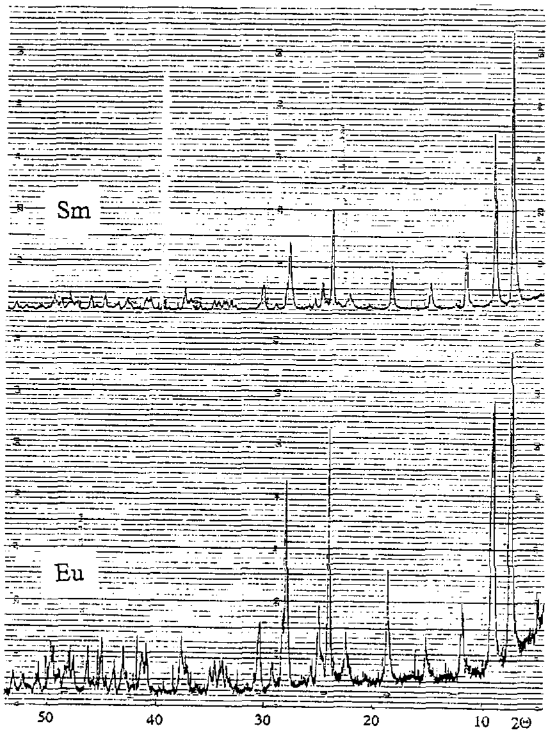

Fig. 1 X-ray powder diffraction patterns of $Ln_2(HOCH_2CH_2NH_3)_8(SO_4)_7 \cdot 8H_2O$

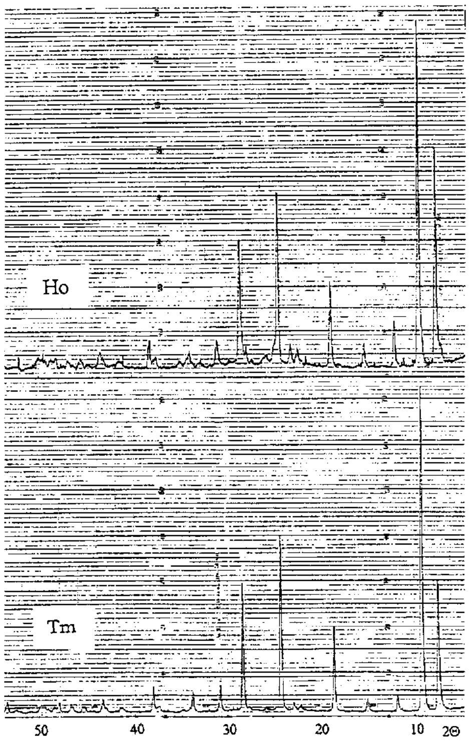

Fig. 2 X-ray powder diffraction patterns of $Ln_2(HOCH_2CH_2NH_3)_8(SO_4)_7{\cdot}8H_2O$

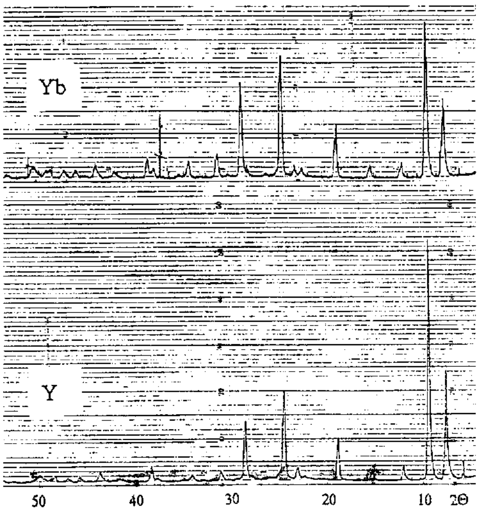

Fig. 3 X-ray powder diffraction patterns of $Ln_2(HOCH_2CH_2NH_3)_8(SO_4)_7{\cdot}8H_2O$

is a difference in the behaviour of lighter and heavier lanthanides. The complicated general formula for double sulphates of trivalent and monovalent ions is not unusual for the double sulphates of lanthanides with larger monovalent cations, such as K^+ [1]. Besides the above general formula, many other complicated stoichiometries for double sulphates of Ln(III) with different, mainly large monovalent cations have also been investigated [1].

Table 1 Results of elemental analysis of $Ln_2(HOCH_2CH_2NH_3)_8(SO_4)_7 \cdot 8H_2O$ and determination of H_2O and $Ln_2O_2SO_4$ from TG curves

Ln	C	H	N	H_2O (1st step)	$Ln_2O_2SO_4$ (after the 3rd step)
	%, found/calc.				
Sm	12.1/11.9	4.4/5.0	6.4/6.9	10.0/8.9	25.0/26.6
Eu	11.4/11.9	4.6/5.0	6.2/6.9	8.5/8.9	26.0/26.7
Ho	12.2/11.7	4.4/4.9	6.4/6.8	8.1/8.8	26.0/27.9
Tm	11.5/11.7	5.6/4.9	6.3/6.8	12.0/8.7	22.0/28.9
Yb	12.1/11.6	5.5/4.9	6.4/6.7	12.0/8.7	22.0/28.6
Y	13.4/12.9	4.8/5.4	6.9/7.5	10.5/9.7	19.0/20.5

As can be seen from the TG curves in Figs 4–6, the thermal decomposition of the double sulphates occurs in a very similar manner. It takes place mainly in three steps. The second and third step are not well differentiated and the mass loss in each step is determined by means of an inflection point at about 740 K. In the first step up to 473 K dehydration of crystal hydrates takes place. Under the conditions given in the experimental section, this process is associated with weakly expressed endothermic peaks in the DTA curves. For the Tm and Yb com-

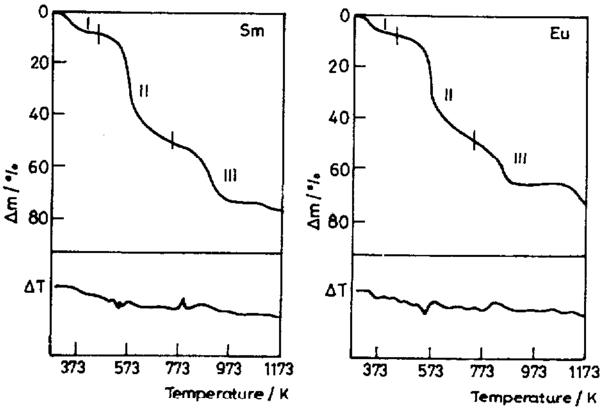

Fig. 4 TG and DTA curves of $Ln_2(HOCH_2CH_2NH_3)_8(SO_4)_7 \cdot 8H_2O$

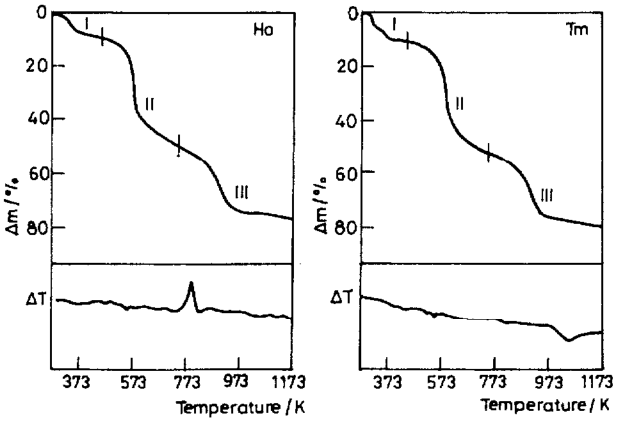

Fig. 5 TG and DTA curves of $Ln_2(HOCH_2CH_2NH_3)_8(SO_4)_7 \cdot 8H_2O$

pound (Table 1), the mass losses in the first step determined from the TG curves (Figs 4 and 5) are larger than the theoretical values. This could be explained by the fact that the compounds contain hygroscopic water which is also released in the first step. In the second (above 473 K) and third step (above 740 K) the thermal decomposition of anhydrous double sulphates occurs. First, three moles of ethanolammonium sulphate are released (in the second step) and after that the remaining one mole of ethanolammonium sulphate and two moles of SO_3 (in the third step) leave. The release of three moles of ethanolammonium sulphate was confirmed by the agreement of the experimental and calculated (in parentheses): mass losses in the second step up to 740 K: Sm, 40% (40.9); Eu, 40% (40.8); Ho, 40% (40.2); Tm, 40% (40.0); Yb, 44% (39.81); Y, 44% (44.3).

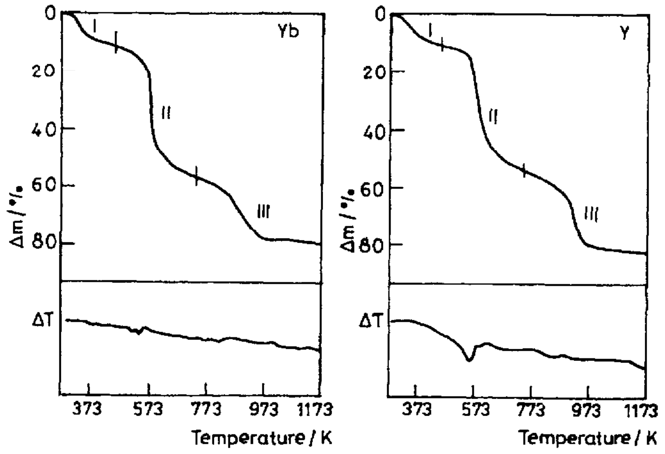

Fig. 6 TG and DTA curves of $Ln_2(HOCH_2CH_2NH_3)_8(SO_4)_7 \cdot 8H_2O$

It is evident that the simple double sulphates of Ln(III) are more stable than those with complex stoichiometry. Above 1073 K the decomposition of $Ln_2O_2SO_4$ to Ln_2O_3 begins. So, in the X-ray powder diffraction patterns of the residues obtained at 1223 K, a mixture of characteristic bands of the oxysulphates and oxides of the lanthanides were observed. The calculated masses for $Ln_2O_2SO_4$ are very close to the masses of the residues obtained at 1023 K.

An exception is the Eu compound which decomposes in four steps (Fig. 4). Namely, the decomposition of Eu sulphate to $Eu_2O_2SO_4$ takes place in two steps, as it can be seen from the good agreement of the calculated 31.7% for $Eu_2O(SO_4)_2$ and the value found at 973 K (third step), 33.0%.

Generally, the thermal decomposition of the investigated compounds can be described by the following equations:

Below 473 K

$$Ln_2(RH)_8(SO_4)_7\cdot 8H_2O \xrightarrow[-8H_2O]{} Ln_2(RH)_8(SO_4)_7 \qquad (1)$$

473–740 K

$$Ln_2(RH)_8(SO_4)_7 \xrightarrow[-3(RH)_2SO_4]{} (RH)_2\,Ln_2(SO_4)_4 \qquad (2)$$

Above 740 K

$$(RH)_2\,Ln_2(SO_4)_4 \xrightarrow[-2SO_3-(RH)_2SO_4]{} Ln_2O_2SO_4 \qquad (3)$$

Partially above 1073 K

$$Ln_2O_2SO_4 \xrightarrow[-SO_3]{} Ln_2O_3 \qquad (4)$$

$^*R$=$HOCH_2CH_2NH_2$

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