THERMAL DECOMPOSITION OF DOUBLE RARE EARTH(III) MONOMETHYLAMMONIUM SULFATES WITH GENERAL EMPIRICAL FORMULA $CH_3NH_3Ln(SO_4)_2 \cdot 3H_2O$ (*Ln* = La-Er AND Y)

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Double rare earth(III) monomethylammonium sulfates with general empirical formula $CH_3NH_3Ln(SO_4)_2 \cdot 3H_2O$ (*Ln* = La-Er and Y) were synthesized and examined by X-ray powder diffraction, TG, DTG and DTA in the temperature range from 25° to 700°C, and chemical analysis. It was found that these compounds are isomorphous and decompose to rare earth sulfate at 700°C.

Introduction

Many data are available on double salts of rare earths(III) with monovalent cations with general empirical formula $MLn(SO_4)_2 \cdot xH_2O$, where M = alkali metal, NH_4, NH_3NH_2 or $Tl(I)$ and $x = 0-4$. The thermal behavior and crystal structure of these compounds have been subjected to investigation by many authors.

Data have also been reported on double salts of rare earths(III) with aliphatic ammoniums. Results on the synthesis, thermal decomposition and crystal structure investigations of isomorphous dimethylammonium rare earth(III) sulfate tetrahydrates [1, 2] and the crystal structure of tetramethylammonium cerium(III) sulfate trihydrate [3] were recently reported.

Investigations have been carried out on the difference in thermal decomposition of some aliphatic ammonium double sulfates of rare earths(III) in air and argon under dynamic conditions [4]. In argon, the anhydrous double salts decompose at lower temperature than in air.

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Besides the known double sulfates of some trivalent metals with monomethylammonium (e.g. the alums of trivalent Al, Cr and Fe) we have found no data (with the exception of some results on Er and Sm [4]) for rare earths with this monovalent cation. Continuing our work on double salts of rare earths(III), in the present paper we report results on the synthesis, thermal decomposition under dynamic conditions in the temperature interval $20^{\circ}-700^{\circ}C$, and chemical analysis of an isomorphous group of double sulfates with general empirical formula $CH_3NH_3Ln(SO_4)_2 \cdot 3H_2O$ (where Ln = La-Er and Y).

Table 1 Results of chemical and thermal analysis of rare earth(III) sulfate trihydrates-$CH_3NH_3Ln(SO_4)_2 \cdot 3H_2O$

Ln(Mr)	%H$_2$O	%Ln	%SO$_4$	%Ln$_2$(SO)$_2$	%(CH$_3$NH$_3$)$_2$SO$_4$
La(417.14)	12.96	33.30	46.06	67.84	19.20
	12.90			68.70	18.93
Ce(418.35)	12.92	33.49	45.92	67.94	19.15
	13.00	33.18	46.02	68.60	18.40
Pr(419.14)	12.89	33.62	45.84	67.80	19.11
	12.70			66.80	20.50
Nd(422.47)	12.79	34.14	45.47	68.25	18.96
	12.68			67.68	19.64
Sm(428.63)	12.61	35.09	44.82	68.70	18.69
	12.40			69.07	18.53
Eu(430.19)	12.56	35.32	44.66	68.82	18.62
	12.15			66.16	21.69
Gd(435.48)	12.41	36.11	44.12	69.20	18.39
	11.85			69.16	18.99
Tb(437.15)	12.36	36.35	43.95	69.31	18.32
	12.50			68.60	18.90
Dy(440.73)	12.26	36.87	43.59	69.56	18.17
	12.25			69.15	18.60
Ho(443.16)	12.20	37.22	43.35	69.73	18.07
	12.09			68.87	19.04
Er(445.49)	12.13	37.55	43.12	69.89	17.98
	12.37			68.92	18.71
Y(367.13)	14.72	24.22	52.33	63.46	21.82
	14.82			59.80	25.38

The second line of every element refers to the experimental values.
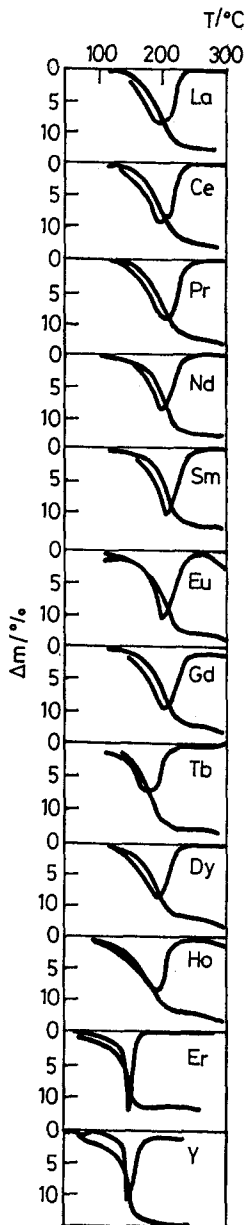
Fig. 1 TG and DTG curves of dehydratation of $CH_3NH_3Ln(SO_4)_2 \cdot 3H_2O$

Experimental

Procedure

Double sulfates of rare earths(III) with monomethylammonium were obtained by evaporation at room temperature of an aqueous mixture of monomethylammonium sulfate and rare earth(III) sulfate in a molar ratio of from 1:2 to 1:10. The crystal products were filtered off, washed with ethanol and dried in air. These products were identified by X-ray powder diffraction, chemical analysis for rare earth and sulfate, and TG, DTG and DTA analysis. The results of chemical and TG analyses are given in Table 1.

Methods

TG, DTG and DTA curves were recorded on a Mettler thermoanalyser in dynamic dry air: flow velocity 5 L/h, Pt/Pt-Rh thermocouple, Pt crucibles(TD1), sample mass about 100 mg, heating rate 6 deg/min; the reference substance for DTA determination was α-Al$_2$O$_3$.

X-ray powder diffraction patterns were obtained on a Guinier de Wolff camera with CuK$_\alpha$ radiation.

Rare earth and sulfate were determined with classical gravimetric methods, as rare earth oxide and barium sulfate.

Table 2 DTG maxima of thermal decomposition of CH$_3$NH$_3$Ln(SO$_4$)$_2$·3H$_2$O, from 25° to 700°C

Ln			Temperature /°C		
La	195, 208		350	465	542
Ce	194, 212		365	465	532
Pr	202		370	470	527
Nd	199		370	453	547
Sm	200		360	415, 465	549
Eu	199	317		407, 456	
Gd	200			432, 456	557
Tb	187			405, 423	
Dy	194			427	
Ho	193			418, 446	
Er	154			417	
Y	147, 153	312	377	420	

Results and discussion

The X-ray powder diffraction patterns of the rare earth double salts with monomethylammonium revealed that two isomorphous groups with different structures were obtained. The first isomorphous group involves the compounds from La to Er and Y, and the second isomorphous group the compounds from Tm to Lu. The structure of the double sulfates of the first group has been solved [5], and thus these sulfates crystallize in monoclinic space group $P2_1$ with $z = 2$, and empirical formula $CH_3NH_3Ln(SO_4)_2 \cdot 3H_2O$. The results of chemical and thermal
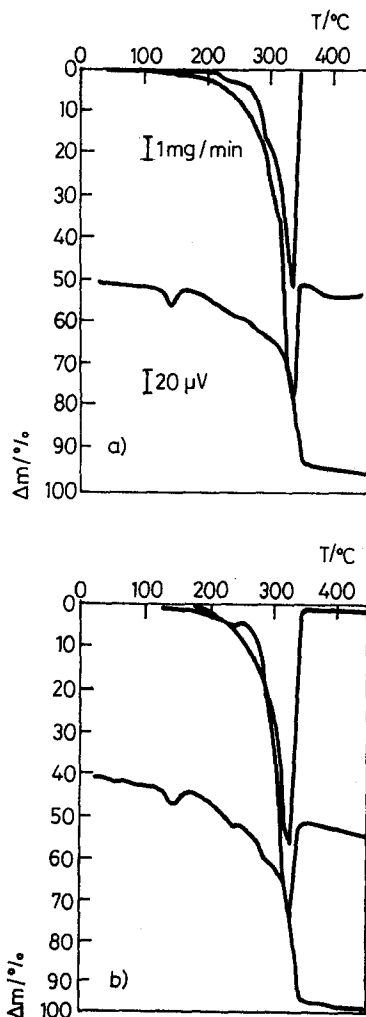

Fig. 2 TG, DTG and DTA curves of the thermal decomposition of Monomethyl ammonium sulfate: *a*) in air, *b*) in argon

analyses gave the empirical formula $CH_3NH_3Ln(SO_4)_2 \cdot 3H_2O$ for the second group (where Ln = Tm-Lu). The results of the investigations of the second group are already in press (in this Journal). For this reason, the present paper gives only the results of the investigations of the double sulfates of the first group. As can be seen from Fig. 2, the thermal decomposition of the investigated double sulfates is very complicated, but two stages of decomposition can be distinguished. In the first stage, dehydration takes place (Fig. 1). It begins at a temperature higher than 100°C and ends at about 250°C. The DTG maxima are at about 200°C for all compounds, with the exceptions of Er and Y, where the DTG maxima are at 154° and 147°C (Table 2). The second stage of thermal decomposition begins at a temperature higher than 300°C and in most cases involves several steps which are not well resolved. At a temperature higher than 527°C, there is one well-resolved step, with an associated exothermic effect. This can be attributed to the oxidation of liberated carbon, because there is good agreement between the theoretical and
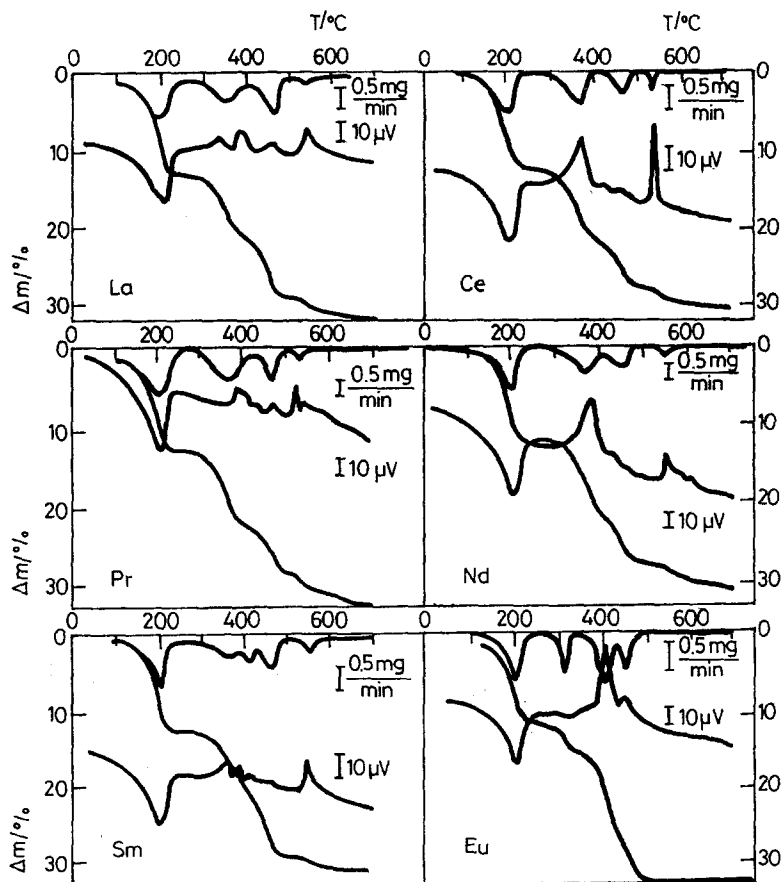

Fig. 3/1 TG, DTG and DTA curves of thermal decomposition of $CH_3NH_3Ln(SO_4)_2 \cdot 3H_2O$

experimental values for $Ln_2(SO_4)_3$. It is not clear why this step does not appear for the thermal decomposition of the anhydrous Eu, Tb, Dy, Ho and Er double sulfates, or why the thermal decomposition to $Ln_2(SO_4)_3$ ends at a much lower temperature than 500°C.

For the Eu and Y double salts, some difference of the experimental results from the theoretical values can be attributed to the fact that these compounds are not easily isolated and some free monomethylammonium sulfate is present. This is indicated by the fact that one more step appears on thermal decomposition at 317°C for the Eu and at 312°C for the Y compound, which may be ascribed to the thermal decomposition of free monomethylammonium sulfate (compare Fig. 3, Eu and Y, and Fig. 2).
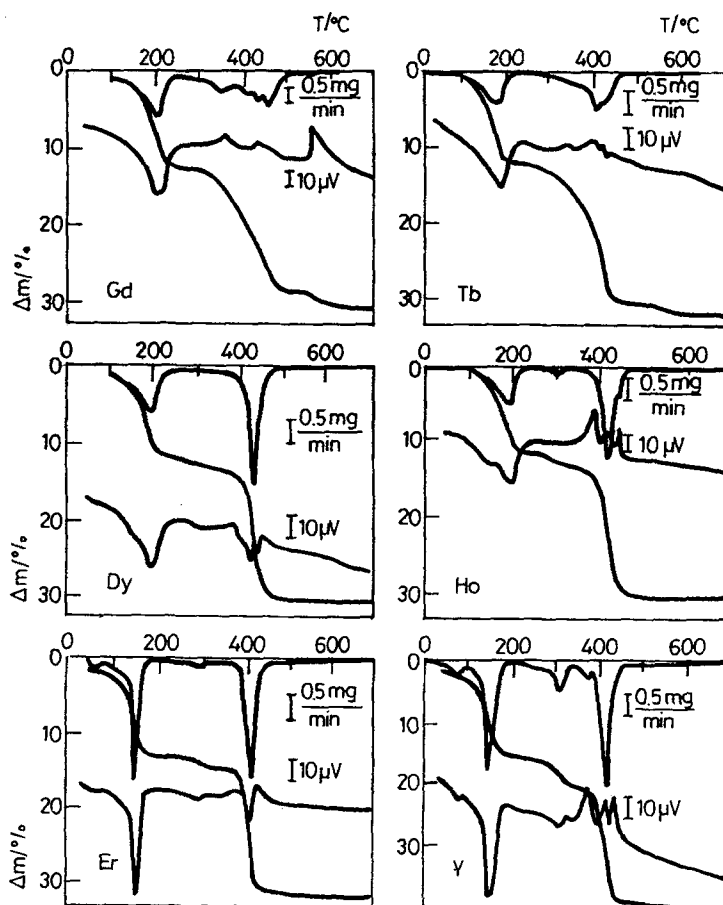

Fig. 3/2 TG, DTG and DTA curves of thermal decomposition of $CH_3NH_3Ln(SO_4)_2 \cdot 3H_2O$

The stoichiometry of the obtained double sulfates was determined from the TG stages in the thermal decomposition and from the fact that the final product at 700°C was rare earth(III) sulfate, according to the relationship:

$$x H_2O \cdot y \, (CH_3NH_3)_2 \cdot z Ln_2 \, (SO_4)_2$$

where x, y and z are whole numbers.

The percentage of water was determined from the mass loss in the first stage of thermal decomposition of the double sulfates, that of monomethylammonium sulfate from the mass loss in the second stage, and that of rare earth sulfate from the residue at 700°C.

The thermal decomposition of monomethylammonium sulfate in vacuum takes place as in air (Fig. 2, a and b). Monomethylammonium sulfate decomposes without exothermic effects (see DTA curves). In contrast, exothermic effects appear in the second stage of thermal decomposition of the double sulfates (Fig. 3, DTA curves). This can be attributed to the formation of rare earth intermediates with products of monomethylammonium sulfate decomposition, which decompose in steps.

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References

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Zusammenfassung — Seltenerden(III)-monomethylammoniumdoppelsulfate mit der allgemeinen empirischen Formel $CH_3NH_3Ln(SO_4)_2 \cdot 3H_2O$ ($Ln=$ La-Er und Y) wurden dargestellt und mit Hilfe des Debeye-Scherrer-Verfahrens, mittels TG, DTG und DTA im Temperaturbereich 25°–700°C sowie durch Elementaranalyse untersucht. Man fand, daß es sich dabei um isoamorphe Verbindungen handelt, die sich bei 700°C in Seltenerdensulfate zersetzen.