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SYNTHESIS AND THERMAL DECOMPOSITION OF $CH_3NH_3Ln(SO_4)_2.4H_2O$ (Ln = Tm, Yb OR Lu)

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The double sulfates of Tm, Yb and Lu with monomethylammonium were obtained by evaporation of an aqueous mixture of rare earths(III) sulfate and monomethylammonium sulfate at room temperature and treatment of the concentrated mixture with ethanol. After identification of the double sulfates, they were examined by means of TG, DTG and DTA analysis, from 20 to 700°. Two clearly separated stages of thermal decomposition were evident. It was possible to determine the stoichiometry of the obtained compounds from the TG curves.

As a continuation of work on the synthesis of double sulfates of trivalent and monovalent cations and their characterization, this paper presents results on the synthesis and thermal behavior under dynamic conditions of the double sulfates of Tm(III), Yb(III) and Lu(III) with the monovalent monomethylammonium cation.

Numerous data are available on the double sulfates of rare earths(III) with monovalent cations, but there are not many data on the double sulfates with methylammonium cations. We earlier investigated the crystal structure of $CH_3NH_3Ln(SO_4)_2 \cdot 3H_2O$ and its isomorphism with the Ce and Nd compounds [1]. They crystallize in the monoclinic space group $P2_1$ and $Z = 2$. These compounds belong in a large group of double sulfates with the empirical formula $CH_3NH_3Ln(SO_4) \cdot 3H_2O$, where Ln is one of La to Er or Y [2]. Recently, we also investigated the synthesis and thermal decomposition of the double sulfates of rare earths(III) with dimethylammonium with the empirical formula $(CH_3)_2NH_2Ln(SO_4)_2 \cdot 4H_2O$ (Ln = Tb-Lu or Y) [3]. Their crystal structure was determined and it was found that they are isomorphous and appear in the orthorhombic space group Pnma with 4 formula units in the unit cell [4].

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Experimental

Procedure and methods

The double sulfates of rare earths(III) and monomethylammonium were obtained by evaporation of a mixture of an aqueous solution of the rare earth(III) sulfate and monomethylammonium sulfate in a molar ratio up to 2:20, and subsequent treatment of the concentrated reaction mixture with ethanol. The obtained crystal substances were filtered off, washed with ethanol and dried in air. The crystals were identified as new products via their X-ray powder diffraction patterns. The double sulfates were studied by means of TG, DTG and DTA. The thermoanalytical curves were obtained on a Mettler Thermoanalyser in dynamic dry air: flow velocity 5 L/h, Pt/Pt-Rh thermocouple, Pt crucibles (TD1), sample mass approximately 100 mg, heating rate 6 deg/min, the reference for DTA determinations was α-Al_2O_3, in the temperature range from 20 to 700°.

The X-ray powder diffraction patterns used only for identification of the obtained crystals are not presented.

Results and discussion

From the X-ray powder diffraction patterns of the obtained compounds, it was concluded that there are two structurally different groups, one involving Ln = La-Er and Y and the other Ln = Tm, Yb and Lu. As the results relating to the identification, crystal structure determination and thermal decomposition of the compounds in the first group are already in the press, this paper reports results on the thermal analysis of the double sulfates in the second group. TG, DTG and DTA curves are given in Fig. 1. It is seen that the thermal decomposition of the obtained double sulfates takes place in two clearly separated stages. The first corresponds to dehydration of the double sulfate crystallohydrates. The dehydration begins at a temperature lower than 100°, with varying velocity. The DTG curve of Tm displays three maxima, at 96, 110 and 138°; that of Yb two maxima, at 94 and 110°; and that of Lu one maximum, at 93°. The second stage is connected with the decomposition of the anhydrous double sulfates. This process is very complex. The DTA curves exhibit numerous exothermic peaks, which means that this process is connected with oxidation reactions. The DTA peaks are given in Table 1. Decomposition begins at about 380° and is completed at about 480°. The rare earth(III) sulfate is obtained as final product in all cases.

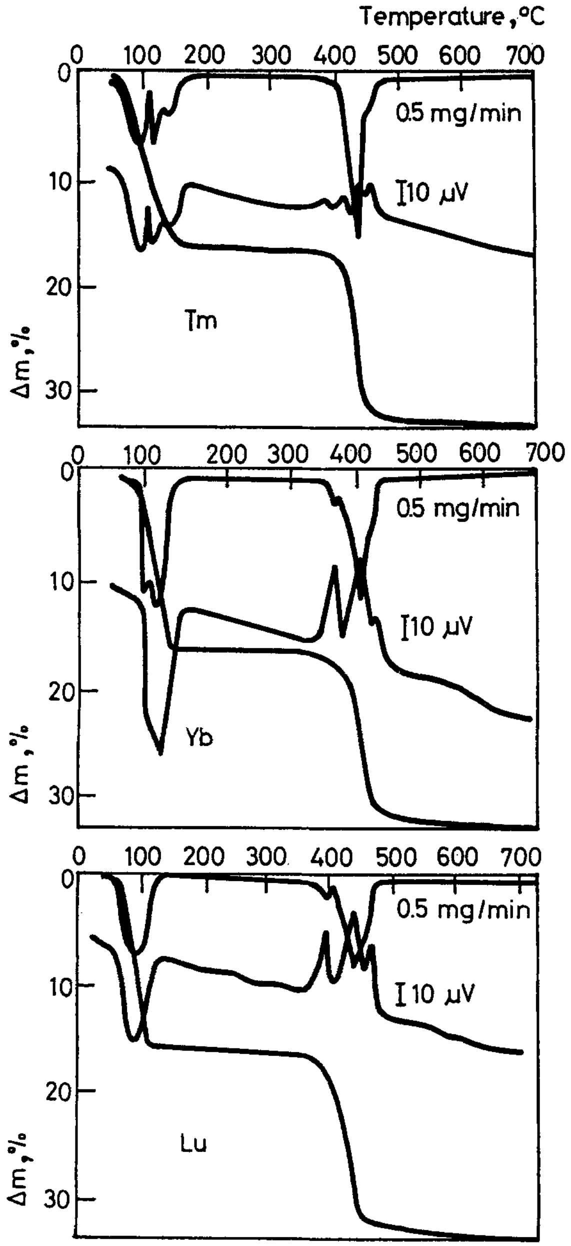

Fig. 1 TG, DTG and DTA curves of thermal decomposition of $CH_3NH_3Ln(SO_4)_2 \cdot 4H_2O$

From the TG curves, it was possible to determine the stoichiometry of the presented compounds; the empirical formula $CH_3NH_3Ln(SO_4)_2\cdot 4H_2O$ was established by starting from the following formula:

$$[(CH_3NH_3)_2SO_4]_x[Ln_2(SO_4)_3]_y(H_2O)_z$$

$$n(H_2O) = \frac{m\,(H_2O)}{M\,(H_2O)}$$

$m(H_2O)$ was found from stage I of the thermal decomposition

$$n(R_2SO_4) = \frac{m\,(R_2SO_4)}{M\,(R_2SO_4)}$$

$m(R_2SO_4)$ was found from stage II of the thermal decomposition

$$n[Ln_2(SO_4)_3] = \frac{m[\,Ln_2\,(SO_4)_2\,]}{M\,[\,Ln_2\,(SO_4)_3\,]}$$

$m[Ln_2(SO_4)_3)]$ was found as the residue of the thermal decomposition.

$$n(R_2SO_4):n[Ln_2(SO_4)_3]:n(H_2O) = x:y:z$$

x, y, z = integers, $R = CH_3NH_3$

Table 1 DTA peaks of thermal decomposition of $CH_3NH_3Ln(SO_4)_2\cdot 4H_2O$

Tm	383	410	434	451
Yb	391		430	456
Lu	390		430	456

The thermal decomposition results are given in Table 2.

The obtained stoichiometry $CH_3NH_3Ln(SO_4)_2\cdot 4H_2O$ is not unusual for double sulfates of rare earths(III) with monovalent cations. There are a number of data on the formation of double sulfates with NH_4^+, Cs^+, and Rb^+ with the above stoichiometry.

It is noteworthy that the thermal decompositions of the Yb and Lu double salts take place in an identical way, but the Tm double salt decomposes in a different way.

Table 2 Results of the thermal decomposition of double sulfates with empirical formula $CH_3NH_3Ln(SO_4)_2\cdot 4H_2O$

Ln(Mr)		%H_2O	%$Ln_2(SO_4)_3$	%$(CH_3NH_3)_2SO_4$
Tm(465.18)	calc.:	15.48	67.84	17.22
	found:	16.11	66.93	16.96
Yb(469.28)	calc.:	15.35	67.58	17.07
	found:	16.01	67.19	16.80
Lu(471.21)	calc.:	15.29	67.71	17.00
	found:	15.92	67.15	16.93

From the X-ray powder diffraction patterns of the above compounds, it was concluded that they are isostructural both with each other, and with the compounds $(CH_3)_2NH_2Ln(SO_4)_2\cdot 4H_2O$.

References

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Zusammenfassung — Die Doppelsulfate von Tm,Yb und Lu mit Monomethylammonium wurden durch Verdampfen eines wäßrigen Gemisches aus Seltenerden(III)-sulfaten und Monomethylammoniumsulfate bei Raumtemperatur und durch Behandlung des konzentrierten Gemisches mit Ethanol erhalten. Nach Identifizierung der Doppelsulfate wurden diese im Temperaturbereich 20 - 700° mittels TG, DTG und DTA- Analyse untersucht. Zwei eindeutig separate thermische Zersetzungsschritte wurden deutlich. Anhand der TG-Kurven war eine Bestimmung der Stöchiometrie der erhaltenen Verbindungen möglich.