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DOUBLE SULFATES OF SOME RARE EARTHS WITH TETRAMETHYLAMMONIUM

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Double sulfates of rare earths and tetramethylammonium with empirical formula $(CH_3)_4NLn(SO_4)_2 \cdot 3H_2O$ (Ln = Ce, Pr, Nd, Eu, Gd, Tb and Dy) were synthesized and studied by the methods of TG, DTG and DTA in the temperature range from 20 to 500°C, and by X-ray powder diffraction and chemical analysis. Two isostructural groups were obtained: one from Ce to Eu and another from Gd to Dy. It was found that rare earth sulfates are obtained as final products at 500°C. For comparison, TG, DTG and DTA curves of the thermal decomposition of tetramethylammonium sulfate are given.

Introduction

A number of double sulfates are formed from the rare earths and alkali metal, ammonium or Tl(I) ions, and these have been investigated crystallographically. The crystal structure and thermal decomposition of some double sulfates with alkylammonium cations have also been studied [1–3]. There are not many data about the synthesis, crystal structure and thermal behavior of double sulfates of rare earths with tetramethylammonium. Recently, we investigated the crystal structure of tetramethylammonium cesium(III) sulfate trihydrate [4] and found that it belongs to the orthorhombic $Pca2_1$ space group, with $a = 11.670(2)$, $b = 5.440(1)$, $c = 21.841(3)$ Å, $z = 4$, $V = 1386.5$ Å^3 and $\rho = 2.206$ g/cm^3.

As part of our investigations on rare earth compounds, the present paper reports results on the synthesis, and chemical and thermal analysis of double sulfates with general empirical formula $(CH_3)_4NLn(SO_4)_2 \cdot 3H_2O$, where

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Ln = Ce, Pr, Nd, Eu, Gd, Tb, Er and Dy. These form two groups with different crystal structures.

Experimental

Procedure

By evaporation at room temperature and by treatment with ethanol of concentrated aqueous mixed solutions of rare earth(III) sulfate and tetramethylammonium sulfate in molar ratios from 1:4 to 1:10, crystal products were obtained. These products were filtered off, washed with ethanol and dried in the air. The isolated double sulfates were studied by chemical analysis, X-ray powder diffraction and the methods of TG, DTG and DTA analysis. The results of chemical and thermal analyses are given in Table 1.

Table 1 Results of thermal and chemical analysis of $(CH_3)_4(NLn(SO_4)_2 \cdot 3H_2O$

Ln(Mr)		$\%H_2O$	$\%Ln^{3+}$	$\%SO_4^{2-}$	% residue
I group					
Ce(460.44)	calcd.:	11.74	30.43	41.72	61.72
	found:	12.48	29.53	41.24	63.58
Pr(461.23)	calcd.:	11.7	30.55	41.65	62.79
	found:	12.10			66.28
Nd(464.56)	calcd.:	11.63	31.05	41.35	62.06
	found:	11.40			66.53
Eu(472.28)	calcd.:	11.44	32.1	40.68	62.70
	found:	11.73			58.92
II group					
Gd(477.57)	calcd.:	11.32	32.93	40.23	63.09
	found:	11.24			67.72
Tb(479.24)	calcd.:	11.28	33.1	40.09	63.22
	found:	11.10			67.56
Dy(482.82)	calcd.:	11.19	33.66	39.79	63.50
	found:	11.10			68.66

Note: Residue is calculated as $Ln_2(SO_4)_3$
Calculated value for $EuSO_4$ is 55.93%

Methods

The thermoanalytical curves were obtained with a Mettler thermoanalyser in a flow of dry air. Experimental conditions: sample mass about 100 mg; reference subtance for DTA determinations α-Al_2O_3; Pt crucibles; heating rate 6 deg/min; temperature range from 20 to 500°C. X-ray powder diffraction patterns were obtained with a Guinier de Wolff camera with CuK_α radiation. The contents of rare earth and of sulfate were determined by gravimetric methods, as rare earth oxide and barium sulfate.

Results and discussion

From the X-ray powder diffraction patterns of the isolated double sulfates, it was concluded that these compounds can be divided into two isomorphous groups: of from Ce to Eu (the double sulfate of Sm with this structure was not obtained) and another isomorphous group from Gd to Dy. Since the crystal structure of tetramethylammonium cerium sulfate trihydrate has been solved [4], it can be concluded that the first group belongs the orthorhombic

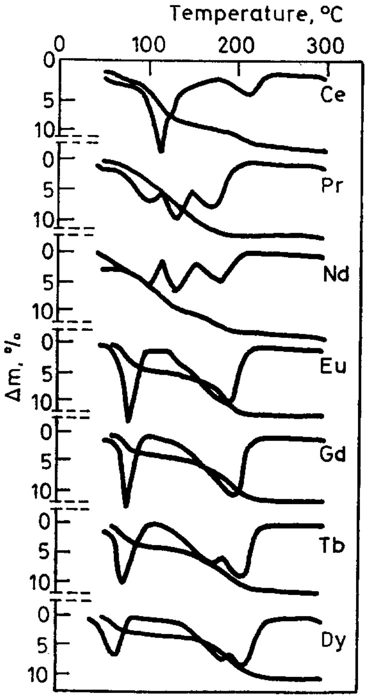

Fig. 1 TG and DTG curves of dehydratation of $(CH_3)_4NLn(SO_4)_2\cdot3H_2O$

$Pca2_1$ space group. The rare earth(III) is coordinated to eight oxygen atoms, of which five belong to sulfate groups and three to water molecules. This means that all the water molecules are in the coordination sphere of Ln(III).

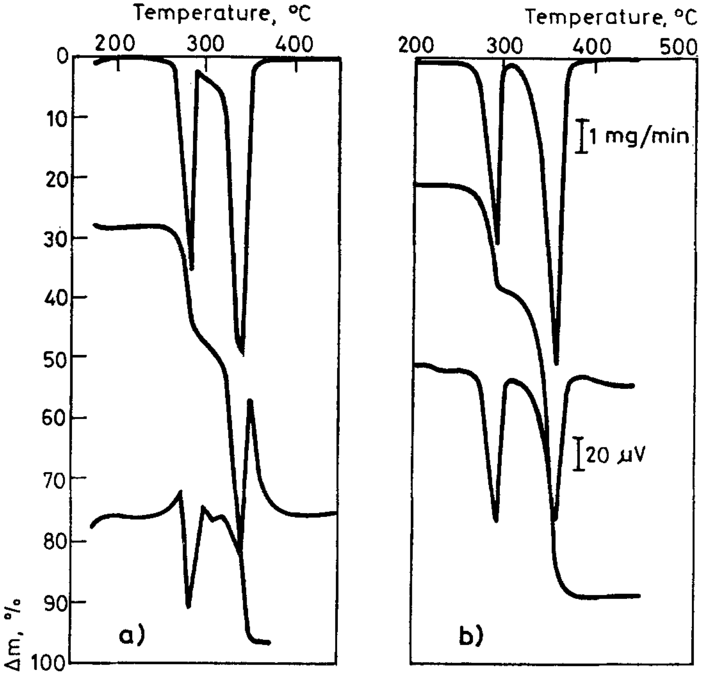

Fig. 2 TG, DTG and DTA curves of thermal decomposition of tetramethylammonium sulfate, a) in air and b) in argon

Table 2 DTG maxima by thermal decomposition of $(CH_3)_4NLn(SO_4)_2 \cdot 3H_2O$ in temperature interval from 20 to 500°C

Double salts of I group	I stage	II stage
Ce	115, 216	370
Pr	100, 140, 166	371
Nd	114, 145, 193	370
Eu	79, 193	409
II group		
Gd	80, 200	409
Tb	75, 175, 210	407
Dy	65, 190, 216	415

It can be seen from Fig. 1 (DTG curves) that the dehydration process for all compounds occurs stepwise. The range of the dehydration moves to higher temperature from Ce to Dy. In the first step, one mole of double sulfate of Ce loses two moles of water (mass loss: found 8.42%, calculated for two moles of water 7.82%) and in the second step loses the remaining mole of water. This means that the monohydrate is more stable than the trihydrate of the Ce(III) double salt. In the case of the dehydration of the double salts of Pr and Nd, three moles of water are lost in three very close steps, at similar temperature

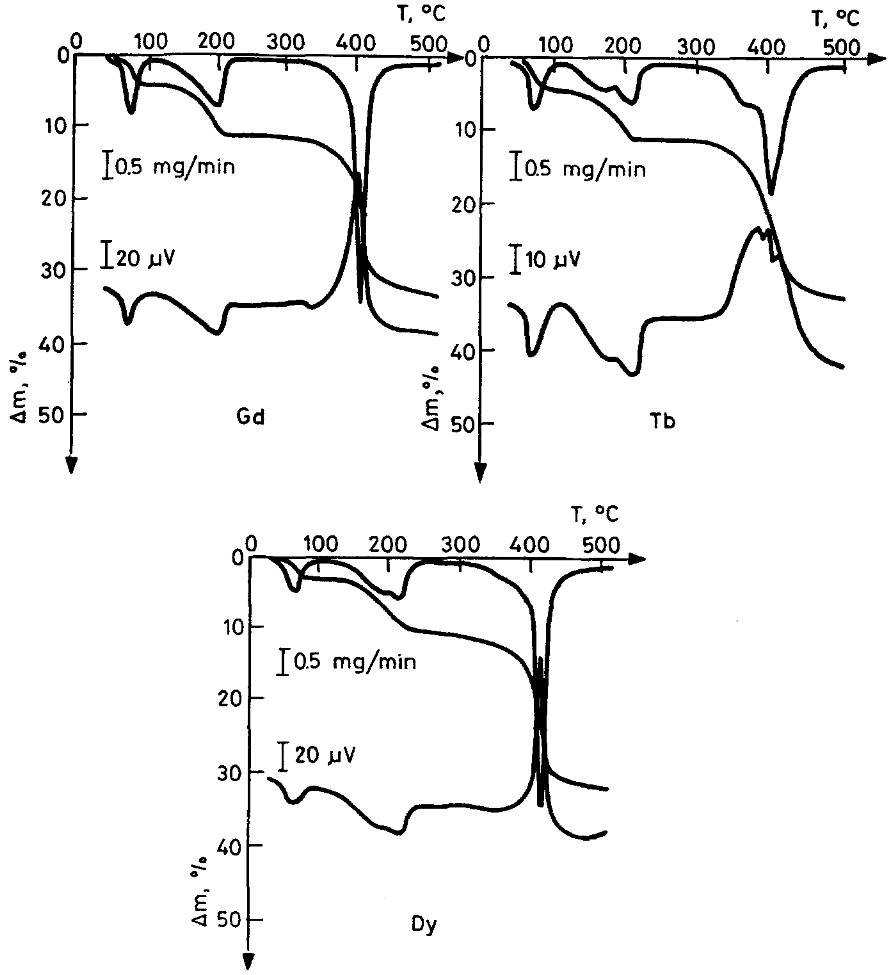

Fig. 3 TG, DTG and DTA curves of thermal decomposition of $(CH_3)_4NLn(SO_4)_2\cdot 3H_2O$

intervals (see Fig. 2). The dehydration of the double salts of the rare earths from Eu to Dy takes place in a similar way. In the first step, one mole of water is lost (mass losses found: Eu, 4.30; Gd, 3.80; Tb, 3.89; and Dy 3.17%; calculated values for one mole of water: Eu, 3.81; Gd, 3.77; Tb, 3.76; and Dy 3.73%). It can be seen from Fig. 1 that the dihydrates of the Eu to Dy double sulfates are more stable than the trihydrates.

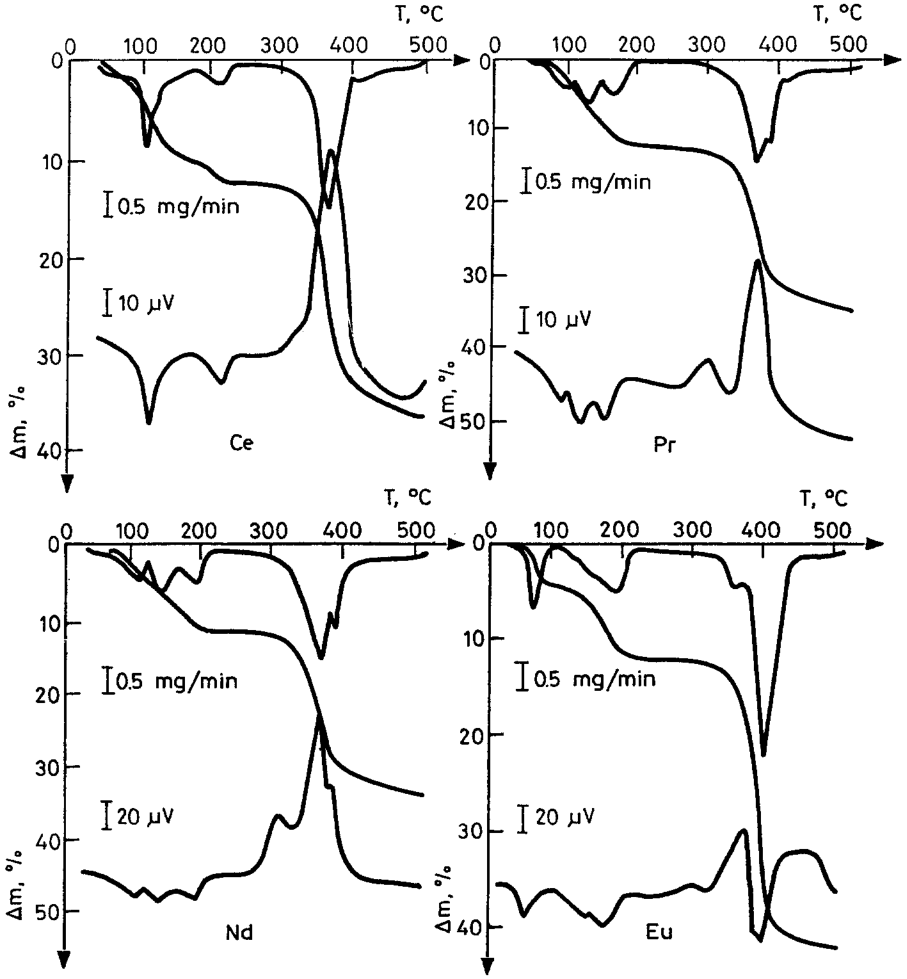

Fig. 3 continue

The thermal decompositions of the anhydrous double sulfates take place at higher temperatures than that for pure tetramethylammonium sulfate (compare Figs 2 and 3). This means that tetramethylammonium sulfate is stabilized in the double sulfates. This is also evident from the thermal decomposition of methylammonium aluminium sulfate [5]. This process of decomposition is followed by exothermic effects. The anhydrous double salts from Eu to Dy decompose at higher temperatures than those of Ce, Pr and Nd (compare the temperatures of the DTG maxima, Table 2). The lower mass loss at 500°C (Table 1) is probably due to liberated carbon, which remains in the residue. The exothermic effects in this stage of thermal decomposition (DTA curves) suggest this possibility. An exception is the double sulfate of Eu. It is possible (according to the lower mass of the residue) that the partial reduction of Eu(III) to Eu(II) takes place in the presence of liberated carbon:

$$Eu_2(SO_4)_3 + C = 2\,EuSO_4 + SO_2 + CO_2$$

The thermal decomposition of tetramethylammonium sulfate takes place in two separate steps. In the first step, at about 270°C, trimethylamine is lost, and in the second step, the obtained methyl ester of tetramethylammonium sulfate decomposes at about 350 [6] with exothermic effects caused by the oxidation process in the presence of oxygen (Fig. 2a). In an inert atmosphere of argon, the second step is not connected with an oxidation process (compare DTG curves in Fig. 2 a and b).

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Zusammenfassung — Doppelsulfate von Seltenerden und Tetramethylammonium der empirischen Formel $(CH_3)_4NLn(SO_4)_2\cdot 3H_2O$ mit Ln = Ce, Pr, Nd, Eu, Gd, Tb und Dy wurden synthetisiert und im Temperaturbereich 20-500°C mittels TG, DTG und DTA, weiterhin mittels Röntgenpulverdiffraktion und chemischer Analyse untersucht. Es wurden zwei isostrukturelle Gruppen erhalten, die eine von Ce bis Eu, die andere von Gd bis Dy. Man fand, daß man bei 500°C als Endprodukt die Seltenerdensulfate erhält. Zum Vergleich wurden die TG-, DTG- und DTA-Kurven der thermischen Zersetzung von Tetramethylammoniumsulfat gegeben.