

SYNTHESIS, IDENTIFICATION AND THERMAL DECOMPOSITION OF DOUBLE SULFATES OF La, Ce, Pr OR Nd WITH ETHANOLAMMONIUM

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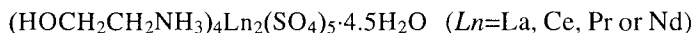
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Abstract

On evaporation at room temperature of an aqueous reaction mixture of Ln(III) sulfate and ethanolammonium sulfate in a molar ratio higher than 1:16, crystal products with a waxy feel were obtained. They were identified by means of the X-ray powder diffraction patterns and it was concluded that they are isostructural. The results of elemental analysis and the mass losses by TG analysis indicated the formation of double sulfates with general formula:



Their thermal decompositions in static atmosphere in the temperature range from ambient up to 1173 K took place in a similar way, and mainly $\text{Ln}_2\text{O}_2\text{SO}_4$ was obtained as final product. The exception was the Ce compound, which decomposed to CeO_2 . The double sulfates decomposed in many not well-differentiated steps. From the mass losses occurring during thermal decomposition, the mode of thermal decomposition was presumed. The X-ray powder diffraction patterns of $\text{Ln}_2\text{O}_2\text{SO}_4$ ($\text{Ln}=\text{La, Pr and Nd}$) show that they are also isostructural.

Keywords: double sulfates, lanthanides, synthesis, thermal studies

Introduction

There are many data on the double sulfates of rare earths(III) with monovalent cations with empirical formula $\text{MLn}(\text{SO}_4)_4 \cdot x\text{H}_2\text{O}$ [1], but few data as concerns double sulfates of Ln(III) and M(I) with other stoichiometry. Investigations have been reported on the syntheses and crystal structures of anhydrous double sulfates of potassium with rare earths, e.g. $\text{K}_3\text{Ln}(\text{SO}_4)_3$, $\text{K}_7\text{Ln}_3(\text{SO}_4)_8$, $\text{K}_4\text{Ln}_2(\text{SO}_4)_5$, $\text{K}_6\text{Ln}_4(\text{SO}_4)_9$, $\text{K}_5\text{Ln}(\text{SO}_4)_4$, and $\text{K}_8\text{Ln}_2(\text{SO}_4)_7$; of ammonium, e.g. $(\text{NH}_4)_3\text{Ln}(\text{SO}_4)_3$ and $(\text{NH}_4)_5\text{La}(\text{SO}_4)_4$; of rubidium; e.g. $\text{Rb}_3\text{Ln}(\text{SO}_4)_3$, $\text{Rb}_4\text{Ln}_2(\text{SO}_4)_5$ and $\text{Rb}_3\text{Ln}_3(\text{SO}_4)_7$; and of cesium; e.g. $\text{Cs}_3\text{Ln}(\text{SO}_4)_3$. The above

compounds were obtained by isothermal evaporation of aqueous solutions, dehydration of crystallohydrates, solid–solid hydrothermal reactions, or syntheses in the presence of sulfuric acid [2].

Data are also available on the dehydration of double sulfate crystallohydrates with general formula $K_3Ln_4(SO_4)_9 \cdot 8H_2O$ [2]. Results on the syntheses and thermal decompositions of double sulfates of some rare earths with dimethylammonium, with general formula $[(CH_3)_2NH_2]_3Ln(SO_4)_3 \cdot 3H_2O$ [3], or with trimethylammonium, with general formula $[(CH_3)_3NH]_3Ln(SO_4)_3 \cdot 4.5H_2O$, were recently reported [4]. It was found that these compounds were obtained only at a high molar ratio. The double sulfates of Pr and Ce with tetramethylammonium, with empirical formula $[(CH_3)_4NH]_4Ln_2(SO_4)_5 \cdot 10H_2O$, have also been synthesized and identified through methods of thermal decomposition, X-ray powder diffraction patterns and elemental analysis [5]. Double sulfate crystallohydrates of Al(III) and Fe(III) with ethanolammonium, with general formula $HOCH_2CH_2NH_3M(SO_4)_2 \cdot xH_2O$, have been synthesized and characterized *via* the X-ray powder diffraction patterns, TG and DTA analysis [6].

Continuing our work on double sulfates of M(III) with different nonclassical monovalent cations, in the present paper we report results on the synthesis, identification and thermal behavior of double sulfates of La, Ce, Pr and Nd with ethanolammonium, as part of our investigations of double sulfates of lanthanides and yttrium with this monovalent cation, for which we have found no data in the literature.

These investigations were performed to confirm the possibility of synthesis of double sulfates of Ln(III) with large monovalent cations and to detect some differences in behavior of the lighter and heavier lanthanides.

Experimental

Chemicals

2-Ethanolamine (purum, Merck); $Ln_2(SO_4)_3 \cdot 8H_2O$; sulfuric acid (p.a. Merck).

Procedure for synthesis

Double sulfates of Ln (La, Ce, Pr and Nd) were obtained by evaporation at ambient temperature of a concentrated aqueous solution of lanthanide(III) sulfate and ethanolammonium sulfate in a molar ratio higher than 1:16. The products were characterized by elemental analysis and *via* the X-ray powder diffraction patterns. The residues of thermal decomposition were also determined *via* the X-ray powder diffraction patterns.

Ethanolammonium sulfate solution was obtained by neutralization of 2-ethanolamine with 1:1 sulfuric acid to *pH* 3–4, with constant external cooling in an ice-water bath.

Analytical methods

X-Ray powder diffraction patterns were recorded on a Philips PW 1050 vertical goniometer with monochromatized $\text{CuK}\alpha$ 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 crucibles.

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 analyses of carbon and hydrogen were carried out on a Coleman model 33 instrument by Liebig's method, and nitrogen was determined by the Dumas method.

X-ray powder diffraction patterns were recorded on a Philips PW 1050 vertical goniometer with a proportional counter, using graphite-monochromatized $\text{CuK}\alpha$ radiation.

Results and discussion

The crystal products obtained were colourless of La and Ce, or were lighter in colour than the starting lanthanide sulfates for Pr and Nd, e.g. light-green or light-violet. The crystal products have a waxy feel. Their X-ray powder diffraction patterns (Figs 1 and 2) demonstrated that the double sulfates were isostruc-

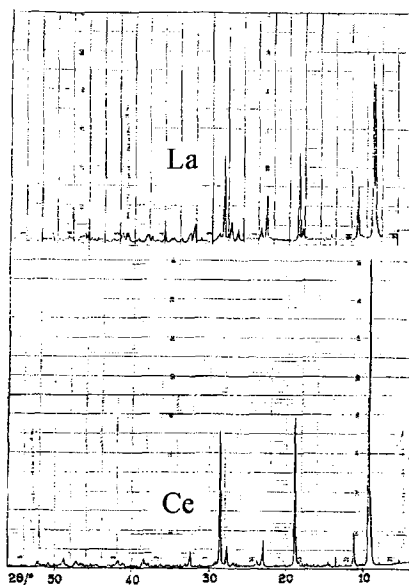


Fig. 1 X-ray powder diffraction patterns of $(\text{HOCH}_2\text{CH}_2\text{NH}_3)_4\text{Ln}_2(\text{SO}_4)_5 \cdot 4.5\text{H}_2\text{O}$

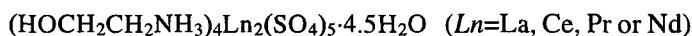
Table 1 Results of elemental analysis of C, H, N and determination of H₂O and Ln₂O₂SO₄ or CeO₂ from TG curves for compounds with general formula (HOCH₂CH₂NH₃)₄Ln₂(SO₄)₅·4.5H₂O

Ln	C	H	N	H ₂ O	Ln ₂ O ₂ SO ₄
La	8.45	3.75	4.27	7.18	38.49
	8.82	3.80	5.15	7.45	37.32
Ce	8.72	3.57	4.94	7.16	29.74
	8.81	3.79	5.14	7.44	31.58*
Pr	8.50	3.35	4.55	7.95	33.30 (35.5)**
	8.78	3.78	5.12	7.43	37.47
Nd	9.41	3.60	5.03	7.16	36.00
	8.75	3.76	5.10	7.38	37.93

* calculated value for CeO₂

**in brackets is found value at 1073 K

tural. Their crystal structure differed from that of double sulfates of other rare earths with the same monovalent cation [7]. The results of elemental analysis (Table 1) and the mass losses (TG curves) indicated the following general formula:



X-ray powder diffraction patterns of the residues of thermal decomposition of the La, Pr and Nd compounds showed that mainly Ln₂O₂SO₄ (X-ray powder diffraction pattern of La₂O₂SO₄ File No. 16-501 [8]) were obtained as final products at about 1173 K and that they were isostructural (Fig. 5), but in the case of the Ce compound, CeO₂ was obtained: X-ray powder diffraction pattern, File No. 4-593 [8].

Thermal studies

The main feature of this investigation was the thermal decomposition of the investigated compounds in static air atmosphere. The thermal decomposition up to 1173 K took place without clearly differentiated steps (Figs 3 and 4), but they were resolved by means of inflection points. This sometimes influences the exact determination of the mass losses in each step of thermal decomposition. Generally, the first step (up to about 473 K) involved dehydration of the compounds, and the second and third steps (from 473 up to about 973 K) decomposition of the anhydrous sulfates to Ln₂O₂SO₄ (for La to La₂O(SO₄)₂ and in a fourth step to dylanthanum dioxysulfate). For the Ce compound, the thermal decomposition continued to CeO₂, in a fourth step. The residues of the thermal decomposition were identified *via* their X-ray powder diffraction patterns. It could be observed that

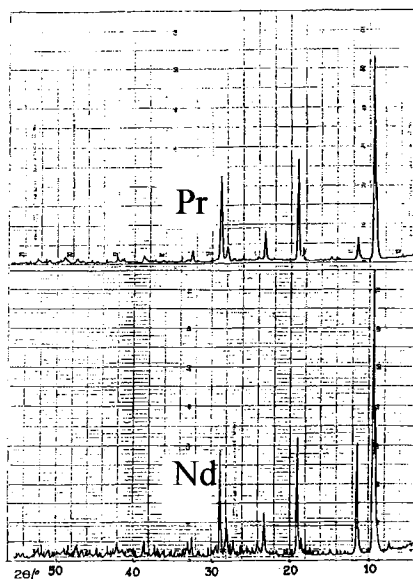


Fig. 2 X-ray powder diffraction patterns of $(\text{HOCH}_2\text{CH}_2\text{NH}_3)_4\text{Ln}_2(\text{SO}_4)_5 \cdot 4.5\text{H}_2\text{O}$

the oxysulfates of La, Pr and Nd were isostructural. As may be seen from Table 1, the lower mass of the residue of thermal decomposition of the Pr compound (33.3%) than that calculated for $\text{Pr}_2\text{O}_2\text{SO}_4$ (37.7%) could be attributed to the further decomposition of part of the oxysulfate to the oxide (the mass of the residue at 1073 K is closer to the theoretical value, 35.5%). In Fig. 4 (for the Pr compound), at higher temperature than the above, a decrease in the TG curve is noticeable. The level in the TG curve (Fig. 3) at about 973 K is probably related to CeOSO_4 , as could be concluded from the calculated value 46.27% (found from the TG curve: 47.0% at 973 K). This probably means that the Ce is oxidized from the (III) to the (IV) state in the third step. In the case of thermal decomposition of the La compound, the level from about 1000 K to about 1130 K (Fig. 3) corresponds to $\text{La}_2\text{O}(\text{SO}_4)_2$ (found 47% at 1140 K, calculated value 44.63%). In the same temperature range in the thermal decompositions of the Nd and Pr compounds (Fig. 4, TG curves), the levels correspond to the existence of $\text{Ln}_2\text{O}_2\text{SO}_4$ the calculated value for the Pr compound is 37.27%, and for the Nd compound is 37.76%; the found values from the TG curves are 36.0% at 1100 K for the Pr, and 38.0% at 1140 K for the Nd compound). The third step is associated with exothermic effects. This leads to the conclusion that the formation of oxysulfates is not the only process of dissociation of the lanthanide sulfates; other processes take place at the same time. It is also possible that at temperatures higher than 780 K a redox process takes place with carbon liberated from the dissociation of ethanolanmonium cation, as supposed for double sulfates with other monovalent organic cations [9]. This may be the reason why the formation of lanthanide

oxysulfates in the thermal decomposition of double sulfates with organic cations generally takes place at much lower temperature than for pure lanthanide sulfates [10], or for double sulfates with alkali metal sulfates [2].

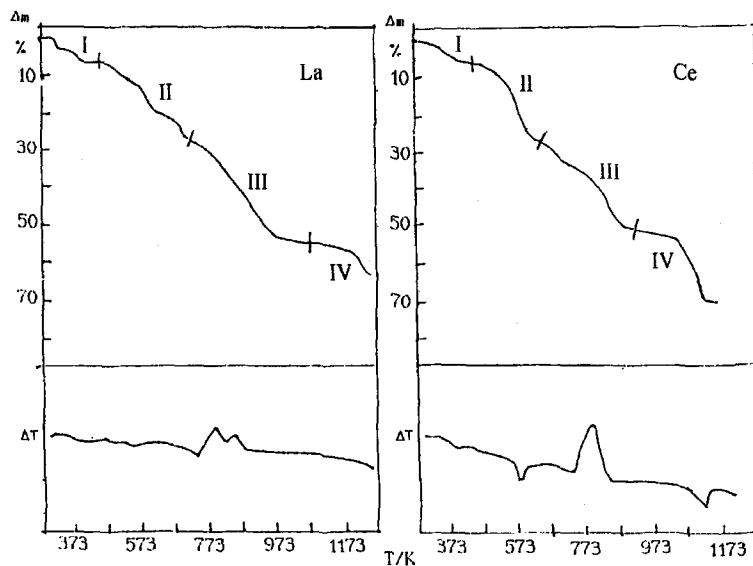


Fig. 3 TG and TA curves of thermal decomposition of $(\text{HOCH}_2\text{CH}_2\text{NH}_3)_4\text{Ln}_2(\text{SO}_4)_5 \cdot 4.5\text{H}_2\text{O}$

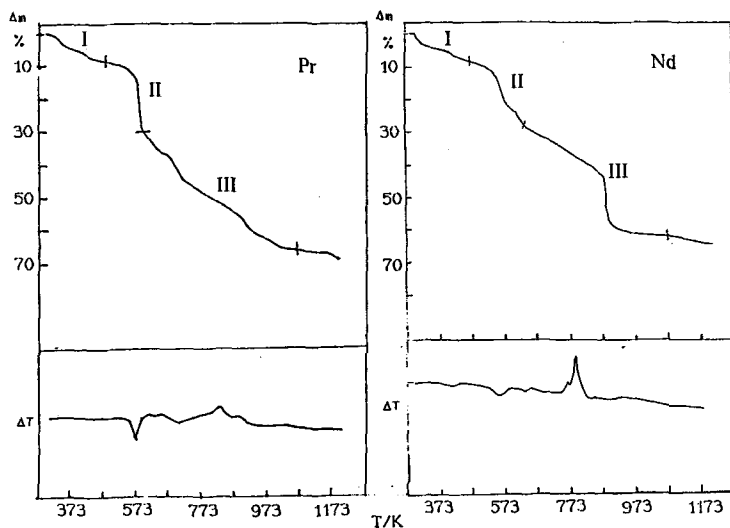


Fig. 4 TG and TA curves of thermal decomposition of $(\text{HOCH}_2\text{CH}_2\text{NH}_3)_4\text{Ln}_2(\text{SO}_4)_5 \cdot 4.5\text{H}_2\text{O}$

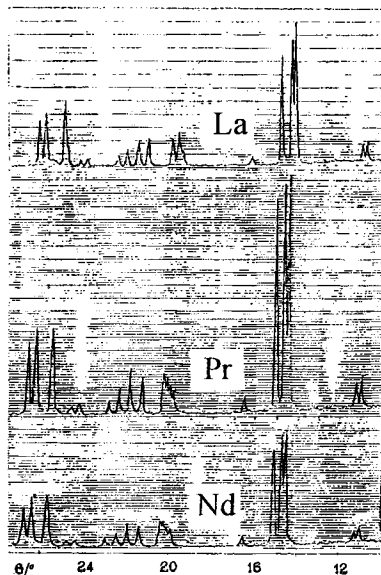
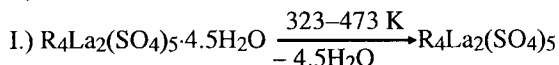


Fig. 5 X-ray powder diffraction patterns of the residues at about 1173 K of thermal decomposition of $(\text{HOCH}_2\text{CH}_2\text{NH}_3)_4\text{Ln}_2(\text{SO}_4)_5 \cdot 4.5\text{H}_2\text{O}$

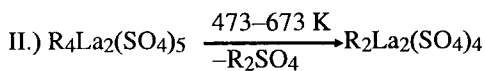
The TG and DTA curves, demonstrated that $(\text{HOCH}_2\text{CH}_2\text{NH}_3)_4\text{Ln}_2(\text{SO}_4)_5 \cdot 4.5\text{H}_2\text{O}$ undergoes thermal decomposition as follows:



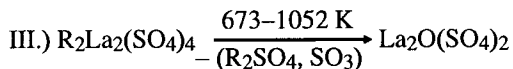
1) $\text{Ln} = \text{La}$:



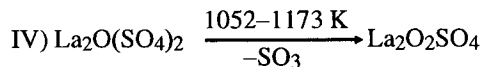
mass loss: found 7.18%, calculated 7.45%



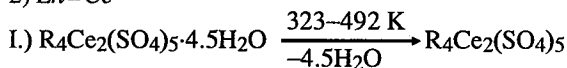
found 19.82%, calculated 20.25%



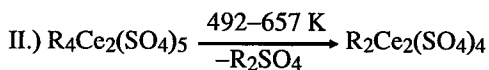
found 27.03%, calculated 27.61%



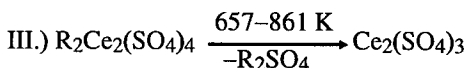
found 7.24%, calculated 7.36%

2) $Ln=Ce$ 

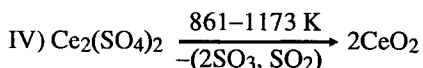
mass loss: found 7.16%, calculated 7.44%



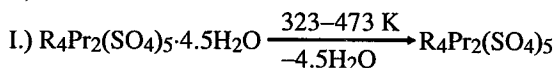
found 19.94%, calculated 20.20%



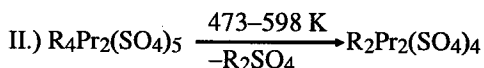
found 20.86%, calculated 20.20%



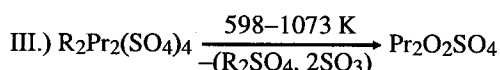
found 22.30%, calculated 20.58%

3) $Ln=Pr$ 

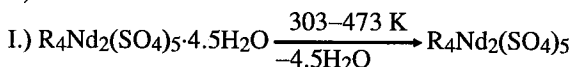
mass loss: found 7.95%, calculated 7.43%



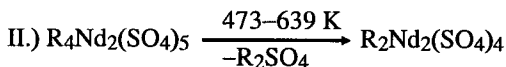
found 22.05%, calculated 20.17%



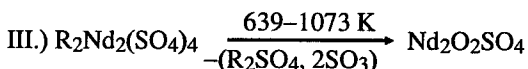
found 34.5%, calculated 34.83%

4) $Ln=Nd$ 

mass loss: found 7.5%, calculated 7.38%



found 20.00%, calculated 20.05%



found 34.5%, calculated 34.63%

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