

## Synthesis and dehydration of double sulfates of some rare earths (lanthanons) with silver

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### Abstract

The synthesis of double sulfates of rare earths(III) and silver with empirical formula  $\text{AgLn}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  ( $\text{Ln} = \text{La} - \text{Gd}$ ) is presented. TG and DTG curves from 20 to 500°C show that the dehydration process takes place in a large temperature interval and, in some cases, with formation of intermediate products. By means of X-ray powder diffraction patterns, it is concluded that the compounds studied are isomorphous.

### INTRODUCTION

There are many data about double sulfates of rare earths with different monovalent cations. They are obtained as crystallohydrates with different amounts of water of crystallization or as anhydrous salts. It is also known that double sulfates of rare earths with monovalent cations with empirical formula  $\text{MTr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  have been subject of many investigations: the synthesis, thermal decomposition and structural investigations of double sulfates with sodium [1–5, 8, 12, 20], potassium [6, 9–12, 14, 18, 20], rubidium [14, 16, 17], as well as with lithium [7] have been reported.

There is no evidence about the double sulfates of silver with rare earths(III), whereas the anhydrous double sulfates with other M(III), such as chromium, vanadium, iron, rhodium and gallium, have been synthesized and studied crystallographically [15]. Considering the possibility of obtaining double salts of silver with other trivalent cations, we have tried to obtain double sulfates with rare earths, as a continuation of our investigations of double salts of rare earths with different monovalent cations.

In this paper, the results of the synthesis, identification, thermogravimetric and derivative thermogravimetric analysis of double sulfate

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monohydrates of some rare earths(III) with monovalent silver, are presented.

## EXPERIMENTAL

### *Reagents and methods*

Starting substances for the synthesis of double sulfates were rare earth(III) sulfate and silver sulfate (p.a., Merck). The rare earth(III) sulfates were obtained from rare earth oxides by dissolving them in an equivalent amount of 1 M sulfuric acid and adding of 0.05 mol of sulfuric acid in excess. A saturated solution of silver sulfate was prepared by dissolving the corresponding amount of silver sulfate in water at room temperature (0.78 g per 100 g H<sub>2</sub>O, at 20°C).

The rare earth was determined by gravimetry as rare earth oxide after precipitation as rare earth oxalate and ignition. The sulfate group was also determined gravimetrically as barium sulfate, and silver was determined volumetrically by titration with a standard solution of ammonium rhodanide in the presence of a saturated solution of ammonium iron(III) sulfate as indicator.

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were obtained on a Mettler Thermoanalyzer in dynamic dry air: flow velocity 5 l h<sup>-1</sup>, Pt/Pt–Rh thermocouple, Pt crucibles (TD1 and TDMa), samples mass about 100 mg, heating rate 6 deg min<sup>-1</sup>. The temperature range was 20–500°C.

For identification and comparison of the crystal structure of the obtained compounds, X-ray powder diffraction patterns were obtained using a Guinier de Wolff camera, with Cu K $\alpha$  radiation. The X-ray powder diffraction patterns are not presented.

### *Procedure*

The double sulfate monohydrates of rare earths with monovalent silver were prepared by evaporation of an aqueous mixture of silver sulfate and the corresponding rare earth sulfate in a molar ratio from 1:1 to 1:4 over a water bath or at room temperature. The crystal products obtained were filtered off, washed with water and dried in a dark place in air.

## RESULTS AND DISCUSSION

The procedure described in the Experimental section gave double sulfates as very fine monocrystals with a color lighter than that of the corresponding rare earth sulfate, from lanthanum to gadolinium, in molar ratio 1:1 (for gadolinium compound, 1:2), at room temperature and over a steam bath. In the higher molar ratio the mixture of double salt and

TABLE 1

Results of elemental and thermal analyses for  $\text{AgLn}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ 

| Ln | Relative molecular mass $M_r$ | $\text{H}_2\text{O}$ (%) | Ln (%)             | $\text{SO}_4$ (%) | Ag (%)             |
|----|-------------------------------|--------------------------|--------------------|-------------------|--------------------|
| La | 456.909                       | 3.94                     | 30.40              | 42.05             | 23.61              |
|    |                               | 3.80 <sup>a</sup>        | 30.12 <sup>a</sup> |                   | 23.63 <sup>a</sup> |
| Ce | 458.119                       | 3.93                     | 30.59              | 41.94             | 23.55              |
|    |                               | 4.03 <sup>a</sup>        | 29.87 <sup>a</sup> |                   | 23.49 <sup>a</sup> |
| Pr | 458.909                       | 3.92                     | 30.71              | 41.86             | 23.51              |
|    |                               | 3.79 <sup>a</sup>        |                    |                   |                    |
| Nd | 462.239                       | 3.90                     | 31.20              | 41.66             | 23.34              |
|    |                               | 3.73 <sup>a</sup>        | 30.88 <sup>a</sup> |                   | 23.15 <sup>a</sup> |
| Sm | 468.399                       | 3.85                     | 32.11              | 41.02             | 23.03              |
|    |                               | 3.73 <sup>a</sup>        |                    |                   |                    |
| Eu | 469.959                       | 3.83                     | 32.33              | 40.88             | 22.95              |
|    |                               | 3.95 <sup>a</sup>        |                    |                   |                    |
| Gd | 475.249                       | 3.79                     | 33.09              | 40.42             | 22.70              |
|    |                               | 4.00 <sup>a</sup>        |                    |                   |                    |

<sup>a</sup> Experimental result.

silver sulfate was obtained. In the case of heavier lanthanides, after many attempts, only starting sulfates were obtained.

The X-ray powder diffraction patterns showed that the double sulfates obtained are isomorphous. That is confirmed by solving the crystal structure on neodymium double sulfate and determination of the unit cell parameters of the other double sulfates. It was found that they crystallize in the hexagonal  $P3_21$  space group with  $Z = 3$ . By means of elemental and TG analyses (Table 1), the empirical formula  $\text{AgLn}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  ( $\text{Ln} = \text{La} - \text{Gd}$ ) was established, and this was confirmed by the crystal structure determination.

TG and DTG curves (Fig. 1) of double salts show that dehydration takes place in the temperature interval 200–400°C with different velocities. An exception is the double salt of lanthanum where the water molecule goes out in one step. This suggests formation of intermediate products in a rather large temperature interval. The high temperature of dehydration confirmed strong bonding of the water molecule to rare earth; this can be seen from the crystal structure determination [19] where the  $\text{M}-\text{O}(\text{w})$  bond length of 2.503 Å is similar to that of other  $\text{M}-\text{O}$  bonds (where O belongs to sulfate group) which have an average length of 2.495 Å. Such high temperature of dehydration appears in the double sulfate monohydrates of rare earths with sodium as monovalent cation [3, 20], which has an ionic radius somewhat smaller than that of monovalent silver [13].

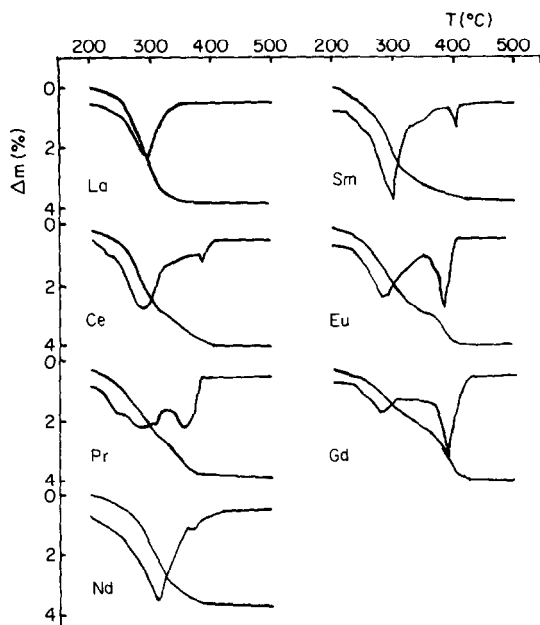


Fig. 1. TG and DTG curves of dehydration of  $\text{AgLn}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ .

Isomorphous lanthanum and cerium double sulfates with sodium crystallize in the  $P3_121$  space group [8] and are enantiomorphs of the compounds presented in this paper. It was found that they are isomorphous with the other rare earths from praseodymium to gadolinium [1]. It can be seen from Fig. 1 that there is no regularity of the temperature of the dehydration versus the ionic radius as in sodium double salts [3], where the temperature of dehydration increases with decrease of ionic radius of rare earth.

From the X-ray powder diffraction patterns of the residue, it was concluded that at  $500^\circ\text{C}$ , anhydrous double salts were obtained as final products; these are also isomorphous, as are anhydrous double rare earth sulfates with sodium, obtained by thermal decomposition of isomorphous monohydrates [3].

Since there are no remarkable changes on the TG and DTG curves in the temperature interval  $20\text{--}200^\circ\text{C}$ , only the  $200\text{--}500^\circ\text{C}$  temperature interval is presented in Fig. 1.

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