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COMPOUNDS OF DIVALENT LANTHANIDES

PREPARATION, OPTICAL PROPERTIES, AND CRYSTAL STRUCTURE

MASTER

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INTRODUCTION

Although the existence of samarium(II) was first reported in 1906,¹ europium(II) in 1911,² and ytterbium(II) in 1929,³ little is known about their compounds. The only X-ray structure data reported for the sulfates, carbonates, and fluorides of the rare earths is for EuSO_4 ⁴ and EuF_2 .^{5,6}

This paper describes the preparation of the sulfates, carbonates, and fluorides of divalent samarium, europium, and ytterbium. It also includes crystallographic data from both X-ray and optical examination of the compounds. Due to the instability of these plus (II) salts, the precision of the measurements is poor in many cases but is, nevertheless, sufficient for characterization.

A simple and convenient electrolytic method was devised to prepare the divalent sulfates. By metathetical reactions, carbonates and fluorides were then prepared. The X-ray and optical parameters of divalent fluorides formed in this manner were not reproducible, indicating variable compositions. In an attempt to reduce these fluorides all the way to the II state, the molten trifluorides were treated with hydrogen. Analysis of these compounds was carried out using a pyrohydrolytic technique.⁷

EXPERIMENTAL

MATERIALS

The rare earths were of 99% or better purity. All other materials used were of reagent grade. The mercury was triple distilled and used without further purification.

ELECTROLYSIS

Apparatus for the Electrolysis. —A two-compartment cell was used, although a single compartment cell is satisfactory. The cell was constructed from a 15 ml Pyrex cone by sealing a 2 mm capillary U-tube on the bottom of the cone, the capillary arm rising to the level of the top of the cone. Contact with the mercury was made through 30 mil

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tungsten wire immersed in the mercury in the capillary. The anode compartment consisted of a length of 1 cm Pyrex tubing to which was butt-sealed a coarse frit about 1 mm thick. The anode consisted of a 20 mil platinum wire coiled into a flat spiral which was placed in the anode compartment.

Preparation of the Electrolysis Solution. —A 0.1 M solution of rare earth sulfate in 0.1 M acetic acid at a pH of 5.5 was found to be satisfactory. The pH was quite critical for preparation of SmSO_4 but less so for EuSO_4 or YbSO_4 .

Procedure for the Electrolysis. —In practice, 1-2 ml of clean, dry mercury is introduced into the air-dried cell, the solution to be electrolyzed introduced in a volume of 1-2 ml, then the anode tube dipped into the solution. The area of the mercury surface was about 1 cm^2 . The current flow was adjusted only by changing the voltage. With 0.1 M rare earth solutions, the current density varies between 0.02 and 0.06 amp/ cm^2 for a voltage between 6 and 12 volts. Production of the solid sulfates begins within a few minutes.

Separation of the Divalent Rare-Earth Sulfates. —The electrolysis solution containing the solid rare earth(II) sulfate as a suspension was removed from the cell by a pipette. The mother liquor was removed after centrifugation, and the crystals washed with water and then with acetone and dried in air or vacuum. After the above treatment, these sulfates were stable for several days.

Metathetical Reactions for Preparation of Carbonates and Fluorides. —The rare earth(II) sulfate crystals were suspended in water. For preparation of carbonates, concentrated $(\text{NH}_4)_2\text{CO}_3$ or K_2CO_3 solutions were introduced and allowed to contact the sulfate crystals for various lengths of time. Some oxidation of the rare earth was indicated by bubbles arising from the solids. In general, after metathesis was judged to have occurred from the change in appearance of the solids, the compounds were washed with water and then with acetone again and air-dried. Some were examined as a slurry in the carbonate solution.

For preparation of fluorides by metathesis of rare earth(II) sulfates, NH_4F was added to the suspension of sulfate crystals.

PREPARATION OF EuSO_4 BY REDUCTION WITH Zn

A solution of EuCl_3 in dilute HCl was treated with zinc metal for 1 hr. while protected from the atmosphere by argon. To this solution of Eu(II) was added 0.1 M H_2SO_4 . The precipitate was digested at 70°C for ~1 hr. while covered with argon. The solid was washed three times with water and twice with acetone and then air-dried.

HYDROGEN REDUCTIONS

Preparation of Anhydrous Trifluorides for Hydrogen Reductions.

Acid solutions of the appropriate rare earth were made ~1 M in HF, the precipitate washed with water and then with acetone. After air-drying at 110°C, the fluorides were treated with HF (gas) at 1 atm. and 400°C for one hour. Pyrohydrolysis showed that compounds prepared in this way were pure trifluorides within the limit of accuracy of the analysis ~0.5%.

Hydrogen Reduction of Anhydrous Trifluorides. —The anhydrous rare earth trifluoride was placed in either graphite or tantalum crucibles which had previously been outgassed. These were then heated inductively to 900°C under a vacuum of 5×10^{-6} mm of Hg. Hydrogen gas was admitted through a palladium valve to 1/2-1 atmosphere and the temperature raised to ~100°C above the melting point of the trifluoride (1200-1400°C). Periodically the H_2 was removed and fresh H_2 added. Due to the vapor pressure of the trifluorides, the temperature of the crucible was lowered to 700°C during the times the system was not under H_2 pressure. The contents were in the form of a small sphere after cooling and could conveniently be transferred for subsequent analysis.

X-RAY ANALYSIS

The compounds were sealed in conventional thin-walled capillaries. X-ray powder diffraction patterns were made using a 114.6 mm Phillips powder camera. Cu radiation with a nickel filter was used throughout.

OPTICAL ANALYSIS

A petrographic microscope was used to examine the compounds.

RESULTS AND DISCUSSION

SULFATES OF SAMARIUM(II), EUROPIUM(II), AND YTTERBIUM(II).

$SmSO_4$ and $EuSO_4$ are orthorhombic, isostructural with $BaSO_4$ as shown in Table I below. The table lists the observed interplanar spacings and intensities of the first 25 possible reflections of the powder patterns of these compounds. To confirm the isostructuralism of these compounds with $BaSO_4$, the observed intensities of $BaSO_4$ ⁸ are listed for comparison.

In Table II are listed the crystal constants for $SmSO_4$, $EuSO_4$ from present work, and $EuSO_4$ from Pauling's measurement as given by McCoy.⁴

Despite repeated attempts on samples made using different methods of preparation, only one structure was found for $EuSO_4$, although two forms of different density have been reported.⁹

TABLE I
X-ray Data for EuSO_4 and SmSO_4

hkl	Observed Data					
	SmSO_4		EuSO_4		BaSO_4 ⁶	
	d (Å)	I	d (Å)	I	I	
200)					(17	
011)	4.24	S	4.191	M	(36	
111	3.78	S	3.754	M	57	
201	3.60	W	3.562	W	12	
002	3.44	W ⁺	3.422	W ⁺	31	
210	3.31	S ⁺	3.279	S	100	
102	3.19	M	3.171	M ⁺	67	
211	2.99	S ⁺	2.969	S	97	
112	2.74	M	2.727	M	53	
020	2.67	M ⁻	2.667	M	47	
301	2.61	VW	2.582	VW	16	
212	2.39	W	2.378	W	14	
311	--	Nil	--	Nil	2	
220	2.26	W	2.249	W	15	
103	--	Nil	2.212	Nil	6	
302	--	Nil	2.166	Nil	7	
221	2.15	W ⁺	2.137	M	27	
113	2.05	S	2.043	S	80	
312	2.02	S ⁻	2.004	S ⁻	76	
410	1.962	W ⁺	1.947	M	23	
222	--	Nil	--	Nil	< 1	
321	1.866	W	1.858	W	7	
303	1.780	W ⁺	1.768	M	16	
004	--	Nil	--	Nil	3	
031	1.727	W	1.719	W ₋	9	

TABLE II
 SmSO_4 and EuSO_4
Isostructural with BaSO_4
Orthorhombic, Space Group Pnma-D_{2h}^{16}
4 Molecules/Unit Cell

	SmSO_4	EuSO_4 *	EuSO_4 (McCoy) ⁴
a	$8.45 \pm 0.02 \text{ Å}$	$8.382 \pm 0.002 \text{ Å}$	$8.46 \text{ Å} \pm 0.02$
b	5.38 ± 0.02	5.333 ± 0.001	5.37 ± 0.02
c	6.91 ± 0.02	6.870 ± 0.002	6.90 ± 0.02
D _{x-ray}	5.21		5.22

* From $\text{EuCl}_2 + \text{H}_2\text{SO}_4$

In Table III, the calculated and observed intensities of YbSO_4 and also the calculated intensities of CePO_4 ¹⁰ are listed for comparison. The correspondence between the YbSO_4 and CePO_4 values indicates that the two compounds are isostructural. The smaller ionic radius of Yb(II) as compared to Sm(II) or Eu(II) is sufficient explanation for the change from the BaSO_4 structure. Table IV gives lattice constants and other values for YbSO_4 .

Table V summarizes the optical data for the three rare earth sulfates.

TABLE III - - X-ray Data for YbSO_4

hkl	YbSO_4			CePO_4 ¹⁰
	d (Å) obs.	I obs.	I* calc.	I* calc.
100	6.09	M	504	549
101	4.41	S	518	403
110	3.50	M	108	125
111)	3.03	S	(137	149
200)			(432	455
102	2.84	"	439	250
201	2.74	VW	9	11
112	2.36	W ⁺	151	172
210	2.29	W	22	20
202	2.20	VW	7	3
211)	2.15	M	(187	162
003)			(65	64
300)	2.02	VW	(29	29
103)			(29	27
301	1.927	MW	94	98
212	1.862	M	252	230
113	1.826	VW	16	16
220)	1.747	MW	(94	85
203)			(101	83
302	1.708	MW	115	--
221	--	Nil	2	1
310	1.679	MW	22	23
311	1.623	W ⁻	79	68
213	--	Nil	9	10
104	1.552	W	50	77

* Absorption corrections not applied

TABLE IV -- YbSO₄ (0-0.5 H₂O)Isostructural with CePO₄ (0-0.5 H₂O)¹⁰Hexagonal Space Group $P6_222-D_6^4$

3 molecules per unit cell.

$$a = 7.025 \pm 0.003 \text{ \AA}; \quad c = 6.428 \pm 0.003 \text{ \AA}$$

$$7.004 \pm 0.004 \text{ \AA} \quad 6.433 \pm 0.002 \text{ \AA}$$

Calculated density (assuming dry crystal) = 4.90

Atomic Positions (International Tables for X-ray Crystallography)

3 Yb in (c)

3 S in (d)

12 O in (k) where

$$x = 0.446, Y = 0.147, z = 0.360$$

TABLE V

Optical Properties of SmSO₄, EuSO₄, and YbSO₄

SmSO ₄	EuSO ₄	YbSO ₄
Biaxial, positive	Biaxial, sign undetermined	Uniaxial, positive
$N_x = \approx 1.61 \quad N_z = 1.695$	$N_x = 1.666$	$N_o = 1.614 \quad N_e = 1.643$
$2V = 75^\circ \pm 5^\circ$	$N_z = 1.670$	Crude hexagonal prisms
Prismatic grains, parallel extinction	Rough prismatic crystals, parallel extinction, negative elongation.	Colorless
Color: Orange-brown, sharp absorption band at 4710 Å.	Colorless	

CARBONATES OF SAMARIUM(II), EUROPIUM(II), AND YTTERBIUM(II).

Due to instability of the (II) states, it was impossible to obtain pure compounds of good crystalline qualities, and as a result the powder patterns of the (II) carbonates were of poor quality.

Each sample contained large proportions of the respective (III) hydroxides, arising from oxidation of the (II) rare earth. Nevertheless, the data in Table VI are considered satisfactory for establishing that these carbonates are isostructural with BaCO₃¹¹ whose intensities are given for comparison.

The crystal constants for these compounds are listed in Table VII.

TABLE VI

hkl	<u>SmCO₃</u>		<u>EuCO₃</u>		<u>YbCO₃</u>		<u>BaCO₃</u> ¹¹
	<u>d (Å)</u>	<u>I</u>	<u>d (Å)</u>	<u>I</u>	<u>d (Å)</u>	<u>I</u>	<u>I</u>
110)	4.31	VW	--	--	--	--	(9
020)							(4
111	3.52	S	3.52	S	(3.42	(M	(100
021	3.45	M	3.45	M	(	(	(53
002	--	-	--	-	--	-	15
012	--	-	--	-	--	-	4
102	--	-	--	-	--	-	3
200	--	-	--	-	--	-	11
112)	2.46	M	2.47	M	2.391	W	(24
130)							(23
220	--	-	--	-	--	-	6
040	--	-	--	-	--	-	2
221	2.05	MW	2.04	M ⁻	1.986	W	28
041	--	-	1.99	VW	--	-	12
202	--	-	1.95	VW	--	-	10
132	1.91	W	1.90	W	1.846	W	21

TABLE VII

SmCO₃, EuCO₃, and YbCO₃Isostructural with BaCO₃.Orthorhombic, space group Pmcn (Pnma) - $\frac{D_{2h}^{16}}{D_2^{16h}}$

4 molecules per unit cell

	<u>SmCO₃</u>	<u>EuCO₃</u>	<u>YbCO₃</u>
a	5.09 ± 0.02 Å	5.10 ± 0.02 Å	4.98 ± 0.03 Å
b	8.58 ± 0.02	8.45 ± 0.02	8.13 ± 0.04
c	5.97 ± 0.02	6.05 ± 0.02	5.87 ± 0.03
D _x	5.36	5.40	6.51

TABLE VIII
Optical Properties of SmCO_3 , EuCO_3 , and YbCO_3

SmCO_3	EuCO_3	YbCO_3
Biaxial, negative $N_x = 1.64$, $N_z = 1.715$ Anhedral grains Color: green	Biaxial, negative $N_x = 1.610 \pm .002$ N_y near $N_z = 1.738 \pm .004$ $2V = \text{small}$, not estimated Acicular crystals, X parallel to elongation Molar refractivity = 14.94 cm^3 Color:- yellow	Tentative from small specimen $N_x < 1.59$ $N_z > 1.66$

FLUORIDES OF Sm(II) , Eu(II) , AND Yb(II) .

Divalent fluorides of these rare earths were made by metathesis of both the divalent rare earth sulfates and carbonates. Considerable variation was found, both in the refractive index and in the lattice constants of the cubic structures obtained. In an attempt to prepare pure compounds of the stoichiometry MX_2 , the trifluorides were treated with hydrogen at temperatures above their melting point. Since variable parameters were obtained on these preparations also,⁵ several of these compounds were analyzed by a pyrohydrolytic method. This method was chosen due to the refractory nature of the solidified melt. In Table IX are listed the results.

TABLE IX

Analytical Data on H_2 -Reduced Rare Earth Trifluorides

Rare Earth	Refractive Index	Lattice Constant	Density Measured	Composition
Sm	1.63-1.65	5.81 ₅	6.60	$\text{SmF}_{2.29}$
Eu	1.551 (some impurity)	5.84 ₂	6.30	$\text{EuF}_{1.93}$
Yb	1.582 (inclusions)	5.571	8.13	$\text{YbF}_{2.24}$

It would seem that only the Eu compound has a composition with a F:Eu ratio near 2. Repeated cycling of the samarium compound with hydrogen did not reduce the F/Eu ratio below 2.29. The conclusion is reached that mixed fluorides with a cubic structure but with variable compositions are obtained. A solid solution of $\text{CaF}_2\text{-YF}_3$ has been reported¹² which is also cubic. These results may well explain the two different lattice constants reported for EuF_2 .¹³

A similar treatment of TmF_3 resulted in no appreciable reduction of Tm(III) beyond a trace of red coloration in the crystalline mass, possibly due to slight reduction, although no other evidence than the color change was obtained.

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