[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KENTUCKY]

The Preparation, Lattice Parameters and Some Chemical Properties of the Rare Earth Mono-thio Oxides

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A method of preparation and the unit cell dimensions are given for the mono-thio oxides of lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. The space group is $D_{3d}^3 - P\bar{3}m$, with the atomic positions being two metal atoms in $\pm(1/3, 2/3, u_1)$, $u_1 \approx 0.29$, two oxygen atoms in $\pm$ $(1/3, 2/3, u_2)$, $u_2 \approx 0.64$, and one sulfur atom in (0, 0, 0). Evidence is presented for a new isostructural series of rare earth compounds having the formula $M_2O_2SO_4$. These compounds are very easily reduced to the mono-thio oxides.

Introduction

Mono-thio oxides of lanthanum and cerium and some of the 5-f series elements have been prepared and their crystal structures reported previously.[2] Although this previous report postulated a series of isostructural compounds, their preparation was not reported. A different and much simpler method of preparation of the mono-thio oxides from that previously reported was devised. This, together with a second method, is presented.

Experimental

Materials.—The oxides of lanthanum, praseodymium, neodymium, samarium and lutetium, greater than 99.9% pure, were obtained from Ames Laboratories, Ames, Iowa. Europium sesquioxide, labeled 99.8% Eu_2O_3, was obtained from Lindsay Chemical Company, West Chicago, Illinois. The remainder of the rare earth sesquioxides were obtained from Mitten Chemical Company, Alma, Michigan, and were found to be greater than 99.9% pure by spectroscopic analysis.

Apparatus.—Two apparati were used. The first consisted of a 30-ml. Pyrex round bottom flask whose neck had been elongated about 10 inches, terminating with a 19/38 ₸ joint. One inch below this joint a side arm was sealed into a 10 inch Pyrex condenser which was equipped with a very small drip tip. This drip tip was connected by a ring seal into a larger piece of glass which was sealed in turn into the bottom of the flask. The closed system was opened to the atmosphere at the drip tip. Silicone stopcock grease was used in the ₸ joint whose upper member held a small Vycor crucible (1″ × 0.5″ o.d.) suspended about 6 inches above the bottom of the flask. An iron-constantan thermocouple touched the external side of the Pyrex glass at this point. The elongated neck was wrapped with asbestos and wound with B. & S. 26 gage nichrome wire. A second heater wound with B. & S. 32 gage wire warmed the 30-ml. flask which contained CS_2. Both of these heaters were controlled by Variacs. Temperature was measured by means of a Leeds and Northrup portable potentiometer.

The second system consisted of a Vycor tube furnace which could be either sealed off or swept with various gases as the reactants were being heated.

Procedure.—The sesquioxide of lanthanum, neodymium, samarium or europium was placed in the crucible of the first apparatus described above and heated to between 750 and 800° while the CS_2 was boiled vigorously. The time of heating varied from 1 hr. and 50 minutes to 8 hr. X-Ray power diffraction diagrams were taken of the product to confirm the completion of the reaction. The carbon-contaminated reaction product was placed in a vacuum desiccator for 1 hr. to remove traces of CS_2; then it was heated in a stream of oxygen for 1 hr. to between 800 and 1200°, depending upon the oxide involved. After cooling, the sample was heated in a stream of hydrogen to between 1200 and 1300° for varying lengths of time, depending upon whether precision lattice measurements were to be made or whether it was to be used only for analysis or other experimentation. Praseodymium sesquioxide was formed from the $PrO_{1.83}$ before using this procedure.

The remainder of the sesquioxides was mixed with reagent grade thioacetamide and heated in the closed furnace tube to 1200° for 4–6 hr. Excess thioacetamide was contained in the tube which was slowly moved into the furnace so that fresh vapors would strike the hot sample. After cooling to 800° air was forced through the tube to burn out the impurities and oxidize the sample. The oxidized sample was then reduced to the thio-oxide in a stream of hydrogen.

Analysis and X-Ray Data.—Purified samples of Nd_2O_2S and Sm_2O_2S were analyzed for sulfur content. The agreement was good: % S in Nd_2O_2S—9.09 expected, 9.01 observed; in Sm_2O_2S-8.79 expected, 8.78 observed.

Intensity calculations made on the first few lines of an X-ray powder diagram of Sm_2O_2S confirmed that the structure was identical with that reported for Ce_2O_2S[2] and was therefore isostructural. Intensity was calculated according to the formula $I \propto LPjF^2$. The space group is $D_{3d}^3 - P\bar{3}m$, with the atomic positions being two metal atoms in $\pm$ $(^1/_3, {}^2/_3, u_1)$, $u_1 \approx 0.29$, two oxygen atoms in $\pm$ $(^1/_3, {}^2/_3, u_2)$, $u_2 \approx 0.64$, and one sulfur atom in (0, 0, 0). The observed intensity was obtained on a General Electric XRD-5 diffractometer. Visual comparison of the diagrams of the rest of the series indicated that all were isostructural. Iron radiation (λ_{α_1} = 1.93597 Å, λ_{α_2} = 1.93991 Å, and λ_β = 1.75654 Å.) was used exclusively because reflections from planes (303), (214) and (205) which were among the few reflections caused by only one plane were thus put in the back reflection region and the data were therefore suitable for precision treatment. Additional reflections which became resolved on most of the diagrams were used to increase the precision. A Norelco 114.6 mm. Debye–Scherrer powder camera was used. The data were fit by Cohen's[3] least squares treatment using an IBM 650 digital computer. The error reported is that obtained from the least squares equations and is the standard error.

Weight uptake measurements were made on the oxidation of the mono-thio oxides of samarium and erbium. X-Ray diffraction powder diagrams taken of the oxidized products were found to be similar. Qualitative tests for the $SO_4^=$ on the oxidized product were positive. A differential thermal-thermogravimetric curve of the oxidation of Sm_2O_2S was obtained.

Discussion

Table I lists the observed and calculated *d* values and the observed and calculated intensity for a Sm_2O_2S sample. Table II lists the hexagonal lattice parameters and calculated densities of the various mono-thio oxides. A plot of volume *versus* atomic number gives a smooth curve with a slight cusp at gadolinium, and a plot of volume *versus* crystal radius[4] gives a relatively smooth, but not straight, line.

The differential thermal-thermogravimetric analysis indicated that Sm_2O_2S oxidized in one step to $Sm_2O_2SO_4$. This exothermic reaction along with a weight increase began at about 620°. The sample continued to gain weight until about 930°

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[2] W. H. Zachariasen, *Acta Cryst.*, **2**, 60 (1949).

[3] M. U. Cohen, *Rev. Sci. Instr.*, **6**, 68 (1935).

[4] D. H. Templeton and C. H. Dauben, THIS JOURNAL, **76**, 5237 (1954).

TABLE I

hkl	*d* value (Å.) Obsd.	*d* value (Å.) Calcd.	Intensity Obsd.	Intensity Calcd.
001		6.716		23
100	3.362	3.372	117	108
002		3.356		
101	3.008	3.012	298	255
102	2.379	2.378	72	83
003	2.238	2.238	27	21
110	1.946	1.947	70	77
111	1.864	1.870	50	54
103		1.864		
200		1.686		
112	1.684	1.688	45	53
004		1.678		
201	1.636	1.635	30	42
202	1.506	1.506	33	46
104		1.502		
113	1.470	1.467	25	32
203	1.347	1.346		23
005		1.343		

TABLE II

	a (Å.)	*c* (Å.)	Calcd. dens., g./cm.^{3}
La	4.0509 ± 0.0007	6.943 ± 0.003	5.73
	(4.04 ± .02)[a]	(6.89 ± .04)[a]	(5.81)[a]
Ce	(4.01 ± .02)[a]	(6.83 ± .03)[a]	(5.99)[a]
Pr	3.9737 ± .0009	6.825 ± .003	6.16
Nd	3.946 ± .001	6.790 ± .003	6.40
Sm	3.8934 ± .0003	6.717 ± .001	6.87
Eu	3.8716 ± .0002	6.6856 ± .0007	7.04
Gd	3.8514 ± .0005	6.667 ± .002	7.34
Tb	3.8249 ± .0005	6.6260 ± .0008	7.56
Dy	3.8029 ± .0008	6.603 ± .001	7.81
Ho	3.7816 ± .0004	6.5800 ± .0004	8.02
Er	3.7601 ± .0006	6.5521 ± .0005	8.25
Tm	3.747 ± .006	6.538 ± .009	8.39
Yb	3.7233 ± .0008	6.5031 ± .0007	8.72
Lu	3.7093 ± .0008	6.486 ± .001	8.89

[a] W. H. Zachariasen (from kX. units).

had been reached, at which point the reaction ended and the weight, now corresponding to the formula $Sm_2O_2SO_4$, became constant. The $Sm_2O_2SO_4$ did not decompose when heated to 1000°. $Er_2O_2SO_4$ slowly decomposed on extended heating in an oxygen atmosphere at temperatures of 1100–1200°. All evidence points to a sulfate which can be easily reduced with hydrogen.

Although the reduction to the thio-oxide was complete within 1 hr., extremely sharp powder diagrams could be obtained only by heating the samples for 8–12 hr. in a hydrogen atmosphere at temperatures of 1100–1200°. This extended heating apparently allowed the micro crystals to grow. Sharp powder diagrams of dysprosium, holmium and thulium were not obtained at these temperatures but probably could be obtained by extended heating at higher temperatures. Neither CeO_2 nor $PrO_{1.83}$ would react with CS_2. However, since the Pr_2O_3 reacted readily, it may be assumed that Ce_2O_3 would do likewise. Y_2O_3 could not be made to react with CS_2 at these temperatures.

An additional phase was observed in some of the Sm_2O_2S samples when the time of the reaction was from 6–8 hr. On oxidation and reduction this phase disappeared. The scant lines could not be intensified appreciably by extended heating. They did not seem to correspond either to any expected sulfur or any Sm_2S_3 lines and it was hypothesized that they might belong to a Sm_2OS_2 phase which was less stable than the Sm_2O_2S and which reverted to the latter when the samples were heated in air. Other attempts to prepare this samarium(III) dithio-oxide have thus far been unsuccessful.

Nomenclature.—Eastman, *et al.*,[5] called Ce_2O_2S a mono-thio-oxide since the crystal structure of the oxide was the same as that of the oxide-sulfide. The oxide crystal structure changes to body centered cubic beyond praseodymium sesquioxide; however, the oxide-sulfide remains isostructural. According to this method of nomenclature the compounds should be called either oxy-sulfides (if crystal structure is the same as the sulfides) or sulfoxides (if crystal structure is different from the sulfides). This would mean that this series of isostructural compounds having the same general formula would be called by two names. To avoid this confusion, the name mono-thio-oxide was used exclusively.

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[5] E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, THIS JOURNAL, **73**, 3896 (1951).