

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
BRIGHAM YOUNG UNIVERSITY, PROVO, UTAH 84601

## High-Pressure $\text{Th}_3\text{P}_4$ -Type Polymorphs of Rare Earth Sesquichalcogenides<sup>1</sup>

By Norman L. Eatough,<sup>2</sup> Alan W. Webb, and H. Tracy Hall

*Received December 4, 1968*

$\text{Th}_3\text{P}_4$ -type polymorphs of the sesquisulfides of holmium, erbium, thulium, ytterbium, lutetium, and yttrium were made from the normal forms at 77 kbars and 2000°. Holmium and erbium sesquiselenides of the  $\text{Th}_3\text{P}_4$  type were formed from the elements at 68 kbars and 1800°.

### Introduction

The crystal structures of rare earth sesquisulfides, sesquiselenides, and sesquitellurides, prepared near atmospheric pressure have been systematically investigated by Flahaut and coworkers.<sup>3,4,5</sup> A summary of the polymorphic forms of the sesquichalcogenides is given in Table I. This table is similar to one given by Flahaut but has been expanded and updated.

There is a large density difference between the crystal form of the light rare earth sesquichalcogenides and the modification found in the heavy rare earth compounds. This difference is quite evident when the theoretical densities are plotted against ionic radius of the rare earth elements<sup>6</sup> as in Figure 1. Extrapolation of the densities of the light rare earth compounds suggests that the heavy rare earth chalcogenides might be converted to the crystal form of the lighter compounds by high pressure. This has been found to be true for the sesquioxides by Hoekstra<sup>7</sup> and Sawyer, Hyde and Eyring<sup>8</sup> and has been accomplished in this work for six sesquisulfides and two sesquiselenides.

Theoretical densities of the sesquiselenides and sesquitellurides are shown in Figure 2. They indicate that a transformation from the  $\text{Sc}_2\text{S}_3$  type to either the  $\text{Th}_3\text{P}_4$  type or the  $\text{U}_2\text{S}_3$  type might also be made for the heavy rare earth sesquiselenides and sesquitellurides.

### Experimental Section

The studies on the rare earth sesquisulfides were carried out in a tie-bar type of cubic anvil press equipped with an anvil guide for synchronizing anvil motion.<sup>9</sup> The square faces of the tungsten carbide anvils were 9.9 mm on each edge. Cubes made of pyrophyllite were used to hold the sample and form the compressible gasket. The cubes had 12.0-mm edges and a 4.0-mm sample hole.

Two steel rings, of 7.95-mm o.d., 5.8-mm i.d., and 2.8-mm thickness, served as electrical connectors between the graphite heater, the current disks, and the anvils. The molybdenum current disks were of 7.95-mm diameter and 0.125-mm thickness. The sample was heated by electrical resistance using a graphite tube of 4.0-mm o.d., 2.9-mm i.d., and 5.6-mm length with two end caps 0.75 mm thick and 4.0 mm in diameter. A boron nitride liner fit inside the graphite heater and was made of a tube of 2.9-mm o.d., 1.9 mm i.d., and 4.1-mm length with two end caps 2.9 mm in diameter and 0.75 mm thick. The sample was tamped by hand into the BN liner.

Studies on the rare earth sesquiselenides were carried out in a tie-bar type of tetrahedral anvil press with anvil guide.<sup>10</sup> The triangular faces of the tungsten carbide anvils were 19 mm on an edge. Pyrophyllite tetrahedrons with 24-mm edges were used as sample containers. As

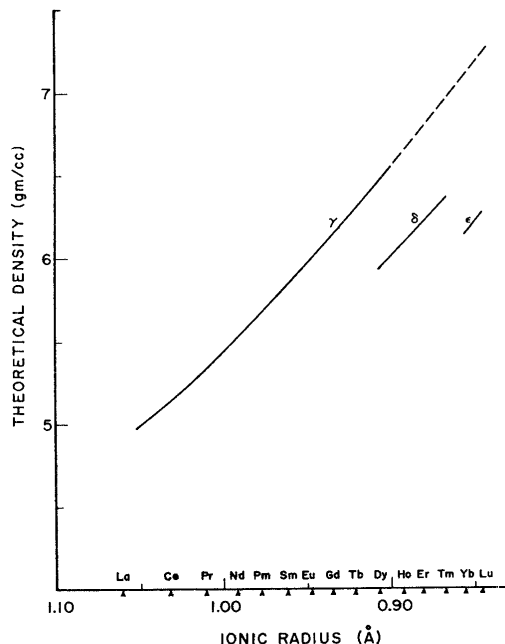


Figure 1.—Theoretical densities of rare earth sesquisulfides as a function of ionic radius.

with the cubic samples a BN liner inside the graphite heater was used to isolate the sample.

The monoclinic forms of  $\text{Dy}_2\text{S}_3$ ,  $\text{Ho}_2\text{S}_3$ ,  $\text{Er}_2\text{S}_3$ ,  $\text{Tm}_2\text{S}_3$ , and  $\text{Y}_2\text{S}_3$  and rhombohedral  $\text{Yb}_2\text{S}_3$  and  $\text{Lu}_2\text{S}_3$  were obtained from K & K Laboratories. Indicated purity was 95-99%.

A stoichiometric mixture of the elements was used for the sesquiselenide studies. The selenium was 99.5% pure powder from Fisher Scientific Co. Erbium and holmium of 99.5% purity were obtained from the Research Chemicals Division of Nuclear Corp. of America. The metals were obtained in ingot form and filed and sieved to -100 mesh before mixing with powdered selenium.

The cubes were assembled and painted with a slurry of rouge in methanol, dried at  $110^\circ$  for 1 hr, and allowed to cool in a desiccator; then the sample was packed in the BN liner with a metal tamp. The completed sample was compressed to pressure, heated to temperature within about 15 sec, and held there for 3 min. Power for heating was supplied from 60-cycle alternating current.

The sample was quenched to room temperature in about 7 sec by abruptly disconnecting the electrical power and was allowed to remain at pressure for 1 min longer. The pressure was then released over about a 30-sec period. The sample was removed from the BN tube, crushed between two polished cemented tungsten carbide surfaces, and loaded

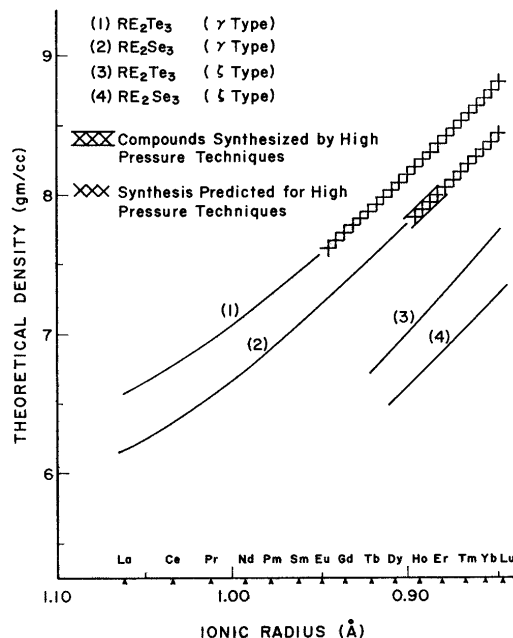


Figure 2.—Theoretical densities of rare earth sesquiselenides and sesquitellurides as a function of ionic radius.

into a 0.5-mm diameter X-ray capillary. A Debye-Scherrer powder diffraction pattern was taken using a 143-mm camera with a copper X-ray tube and nickel filter. The  $d$  values were calculated using  $\lambda(\kappa\alpha)1.5418$  and  $\lambda(\kappa\alpha_1)1.54050$  Å.

Pressure was calibrated as a function of hydraulic ram load by use of fixed-point electrical resistance transitions in Bi and Ba. The Bi I-II transition was taken as 26.5 kbars, the Ba I-II transition as 54.6 kbars, and the Bi III-V transition as 88 kbars. Temperature was estimated by comparing the heating power input to runs of the same geometry which had been calibrated with Pt-Pt-10% Th thermocouples. The procedure followed with the tetrahedral cells was similar to that for the cubic.

### Results

Monoclinic  $\text{Dy}_2\text{S}_3$  was completely converted to the  $\text{Th}_3\text{P}_4$ -type cubic form at 70 kbars and  $1200^\circ$ ; however, monoclinic  $\text{Ho}_2\text{S}_3$  and  $\text{Er}_2\text{S}_3$  did not undergo this conversion at 70 kbars and  $1700^\circ$ . Subsequent runs at 77 kbars and  $2000^\circ$  resulted in complete transition to the  $\text{Th}_3\text{P}_4$ -type cubic structure for  $\text{Ho}_2\text{S}_3$ ,  $\text{Er}_2\text{S}_3$ ,  $\text{Tm}_2\text{S}_3$ ,  $\text{aTb}_2\text{S}_3$ ,  $\text{Yb}_2\text{S}_3$ , and  $\text{Y}_2\text{S}_3$  in 3 min.  $\text{Lu}_2\text{S}_3$  was about 50% converted to the cubic form under these conditions.

$\text{Ho}_2\text{S}_3$  of the cubic  $\text{Th}_3\text{P}_4$  type was also obtained from the elements at pressure above 50

TABLE I  
 CRYSTAL STRUCTURES OF RARE EARTH SESQUICHALCOGENIDES<sup>a</sup>

		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc
$R_2S_3$	$\gamma$									////	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX	
	$\beta$																
	$\alpha$																
	$\delta$																
	$\epsilon$																
$R_2Se_3$	$\gamma$							////////	////////	////////	////////	////////	////////	////////	////////	////////	
	$\eta$																
	$\zeta$																
$R_2Te_3$	$\gamma$				////////	////////		XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX	
	$\eta$																
	$\zeta$																
	?																

— Known compound<sup>b-c</sup>  
 // Nonstoichiometric  
 $\alpha$  Orthorhombic  $Gd_2S_3$ <sup>f</sup>  
 $\beta$  Unknown structure  
 $\gamma$  Cubic  $Th_3P_4$   
 $\delta$  Monoclinic  $Ho_2S_3$ <sup>g</sup>  
 XXXXX High-pressure form from this work  
 XXXXX High-pressure form predicted  
 $\epsilon$  Rhombohedral  $\alpha-Al_2O_3$   
 $\eta$  Orthorhombic  $U_2S_3$   
 $\zeta$  Orthorhombic  $Sc_2S_3$   
 ? Unknown-type  $Sc_2Te_3$

<sup>a</sup> Recent works<sup>d,f,g</sup> have introduced two conflicting sets of English letters for the designation of the sesquichalcogenide structure types. Since polymorphism also exists, we have chosen to follow Flahaut in the use of Greek letters to designate uniquely the different structural modifications and to indicate also the structure types in the series. <sup>b</sup> J. Flahaut, L. Domange, M. Guittard, and M. P. Pardo, *Bull. Soc. Chim. France*, 326 (1965). <sup>c</sup> Reference 4. <sup>d</sup> J. P. Dismukes and J. G. White, *Inorg. Chem.*, **4**, 970 (1965). <sup>e</sup> A. W. Sleight and C. T. Prewitt, *ibid.*, **7**, 2282 (1968). <sup>f</sup> C. T. Prewitt and A. W. Sleight, *ibid.*, **7**, 1090 (1968). <sup>g</sup> J. G. White, P. N. Yocom, and S. Lerner, *ibid.*, **6**, 1872 (1967).

kbars and temperatures above 1500°. Cubic  $Yb_2S_3$  was obtained from the elements at pressure above 35 kbars and temperatures above 1500°. At 70 kbars and 1800°,  $Th_3P_4$ -type  $Ho_2Se_3$  and  $Er_2Se_3$  were formed from a stoichiometric mixture of the elements.

Lattice parameters for the cubic structures are given in Table II. About 30 lines were measured from Debye-Scherrer patterns for each compound except  $Lu_2S_3$  for which 17 lines were measured.

 TABLE II  
 Cell Parameters of Some Rare Earth  
 Sesquichalcogenides

Compound	Cell parameter $\pm$ 2 $\sigma$ , Å	Compound	Cell parameter $\pm$ 2 $\sigma$ , Å
$Ho_2S_3$	8.265 $\pm$ 0.001	$Lu_2S_3$	8.198 $\pm$ 0.005
$Er_2S_3$	8.244 $\pm$ 0.001	$Y_2S_3$	8.306 $\pm$ 0.002
$Tm_2S_3$	8.225 $\pm$ 0.002	$Ho_2Se_3$	8.614 $\pm$ 0.006
$Yb_2S_3$	8.224 $\pm$ 0.001	$Er_2Se_3$	8.581 $\pm$ 0.006

### Discussion

Picon, *et al.*,<sup>3</sup> found cubic  $Dy_2S_3$  to be nonstoichiometric with a sulfur deficiency. Guittard, *et al.*,<sup>10</sup> found a similar nonstoichiometry in the sesquiselenide series from  $Gd_2Se_3$  through  $Dy_2Se_3$ . It is therefore possible that the cubic polymorphs found by this work are also nonstoichiometric. No determination of the actual composition by chemical analysis was made.

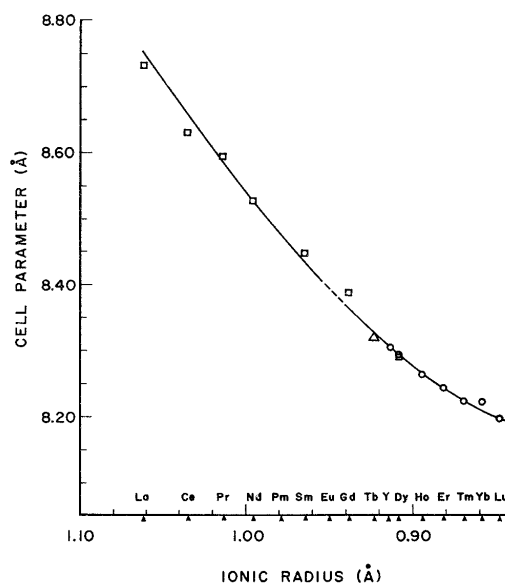


Figure 3.—Variation of cell parameters with ionic radius of the cubic rare earth sesquisulfides: □, Picon, *et al.*;<sup>3</sup> Δ, Collins and Lories;<sup>9</sup> ○, present work.

The lattice parameters of the new cubic rare earth sesquisulfides as shown in Figure 3 form a smooth extension of the previous work with the exception that the lattice parameter for  $Yb_2S_3$  indicates some  $Yb^{2+}$  character. The lattice parameter of  $V_2S_3$  indicates that  $Y^{3+}$  has an ionic radius of about 0.915 Å, compared to 0.910 Å found by Ring and Tecotzky<sup>11</sup> and Iandelli.<sup>12</sup>

The synthesis of these new compounds suggests that the  $\text{Th}_3\text{P}_4$  forms of the sesquiselenides of Tm, Yb, Lu, and Y and the sesquitellurides of Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y can also be made using high-pressure, high-temperature techniques.

**Acknowledgments.**—Assistance rendered by John Cannon, James H. Hoen, M. D. Horton, Fred D. Childs, and Karl Miller is gratefully acknowledged.

---

<sup>1</sup> This research was supported by the National Science Foundation and the Army Research Office, Durham, N. C.

<sup>2</sup> NSF traineeship recipient.

<sup>3</sup> M. Picon, L. Domange, J. Flahaut, M. Guittard, and M. Patrie, *Bull. Soc. Chim. France*, **2**, 221 (1960).

<sup>4</sup> J. Flahaut, P. Laruelle, M. P. Pardo, and M. Guittard, *ibid.*, 1399 (1965).

<sup>5</sup> G. Collin and J. Loriers, *Compt. Rend.*, **260**, 5043 (1965).

<sup>6</sup> D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5327 (1954).

<sup>7</sup> H. R. Hoekstra, *Inorg. Chem.*, **5**, 754 (1966).

<sup>8</sup> J. O. Sawyer, B. G. Hyde and L. Eyring, *ibid.*, **4**, 426 (1965).

<sup>9</sup> H. T. Hall, *Rev. Sci. Instr.*, **33**, 1278 (1962).

<sup>10</sup> M. Guittard, A. Benacerraf, and J. Flahaut, *Ann. Chim. (Paris)*, **9**, 25 (1964).

<sup>11</sup> S.A. Ring and M. Tecotzky, *Inorg. Chem.*, **3**, 182 (1964).

<sup>12</sup> A. Iandelli in "Rare Earth Research," E. V. Kelber, Ed., The Macmillan Co., New York, N. Y., 1961, pp 135-141.