beginning at $X = 0.45$. The rate of rise is less pronounced for the diethylamine adduct, but this is to be expected, since the equilibrium vapor pressures of the two amines at 0° are quite different (700 Torr for trimethylamine *vs.* 90 Torr for diethylamine). The plots also show pressure decreases from $X = 0$ to a low at $X = 0.33$. Thus, there is a minimum in the equilibrium pressure extending from $X = 0.33$ to $X = 0.45$. The existence of the pressure minimum and the fact that the equilibrium pressure begins to rise before the $X = 0.5$ point are significant when one considers the method used to prepare the adducts (trap-to-trap distillation). Because substances volatile at the chosen trap temperature are removed during the distillation, the product obtained with this technique would be the least volatile one. Since an excess of amine was used in every case and more and more amine is removed as the distillation progresses, the concentration of amine in the trap decreases. One can visualize the system as moving toward greater concentrations of hydroxylamine, approaching the least volatile composition as amine is removed. The formation of the 1:1 adduct is precluded since the pressure minimum lies at $X < 0.5$, and, therefore, amine will continue to be removed when the $X = 0.5$ point is reached. The system would follow the mole fraction plot along the pressure minimum from $X = 0.45$ to $X = 0.33$.

No chemical evidence can be cited to explain the formation of the 2:1 adducts. Formation of the 2:1 adducts cannot be correlated with the structure of the amine with the least crowded electron pair on the nitrogen showing the greatest tendency to form a 2:1 adduct. Since both $(CH_3)_3N$ and $(C_2H_5)_2NH$ possess an electron pair on the nitrogen surrounded by bulky groups, they should show less tendency to form a 2:1 adduct than CH_3NH_2, $(CH_3)_2NH$, or $C_2H_5NH_2$. Thus, if the availability of the electron pair was the determining factor, there would be a larger number of 2:1 adducts.

Acknowledgments.—This work was supported in part through a contract with the Office of Naval Research. We are indebted to the National Science and the Max C. Fleischmann Foundations for grants to purchase the HA-100 nmr spectrometer. The authors wish to thank Mr. L. M. Zaborowski for the ^{19}F nmr spectra and Mr. R. L. Boyd for the mass spectra.

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High-Pressure Th_3P_4-Type Polymorphs of Rare Earth Sesquichalcogenides[1]

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Recieved December 4, 1968

Th_3P_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 Th_3P_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.[3-5] 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[6] 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[7] and Sawyer, Hyde, and Eyring[8] 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 Sc_2S_3 type to either the Th_3P_4 type or the U_2S_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.[9] 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.

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[1] This research was supported by the National Science Foundation and the Army Research Office, Durham, N. C.

[2] NSF traineeship recipient.

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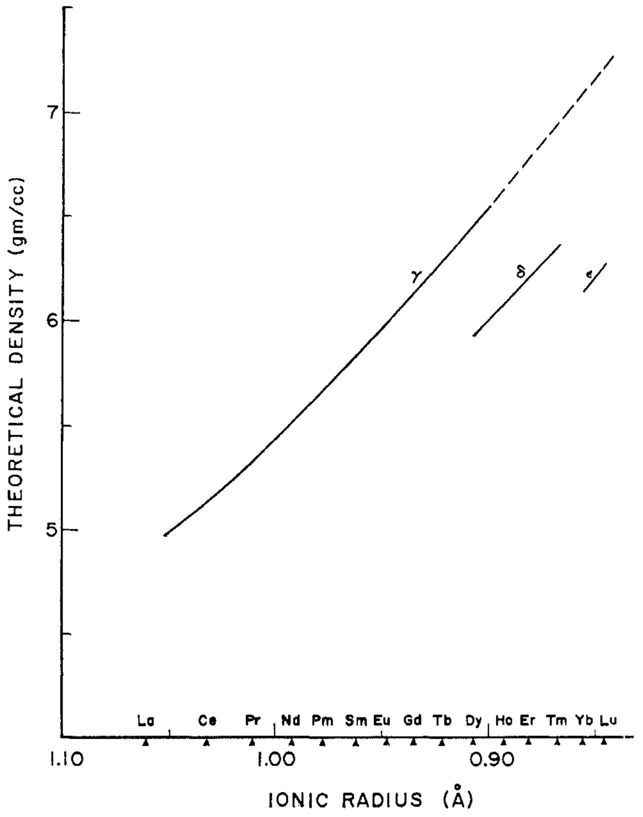


Figure 1.—Theoretical densities of rare earth sesquisulfides as a function of ionic radius.

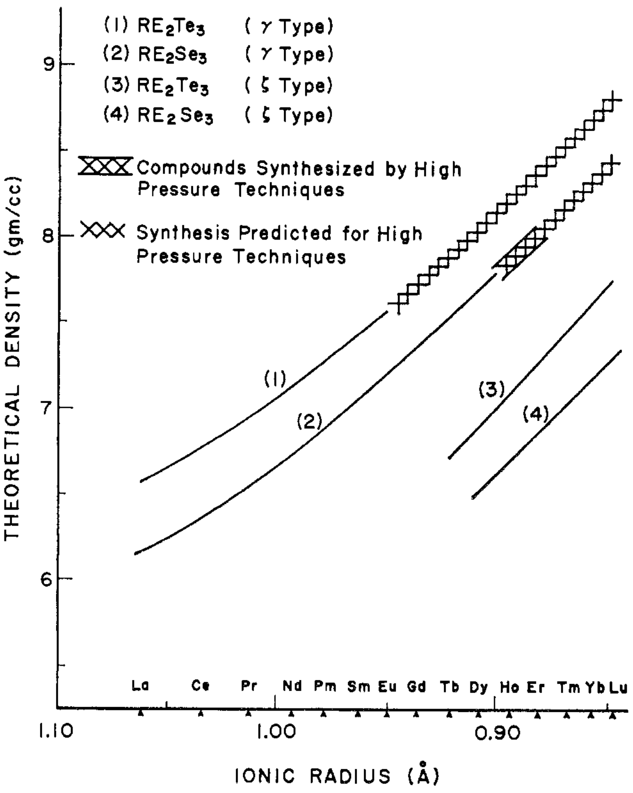


Figure 2.—Theoretical densities of rare earth sesquiselenides and sesquitellurides as a function of ionic radius.

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

The monoclinic forms of Dy_2S_3, Ho_2S_3, Er_2S_3, Tm_2S_3, and Y_2S_3 and rhombohedral Yb_2S_3 and Lu_2S_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° 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 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 $\lambda(K\alpha)$ 1.5418 and $\lambda(K\alpha_1)$ 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% Rh thermocouples. The procedure followed with the tetrahedral cells was similar to that for the cubic.

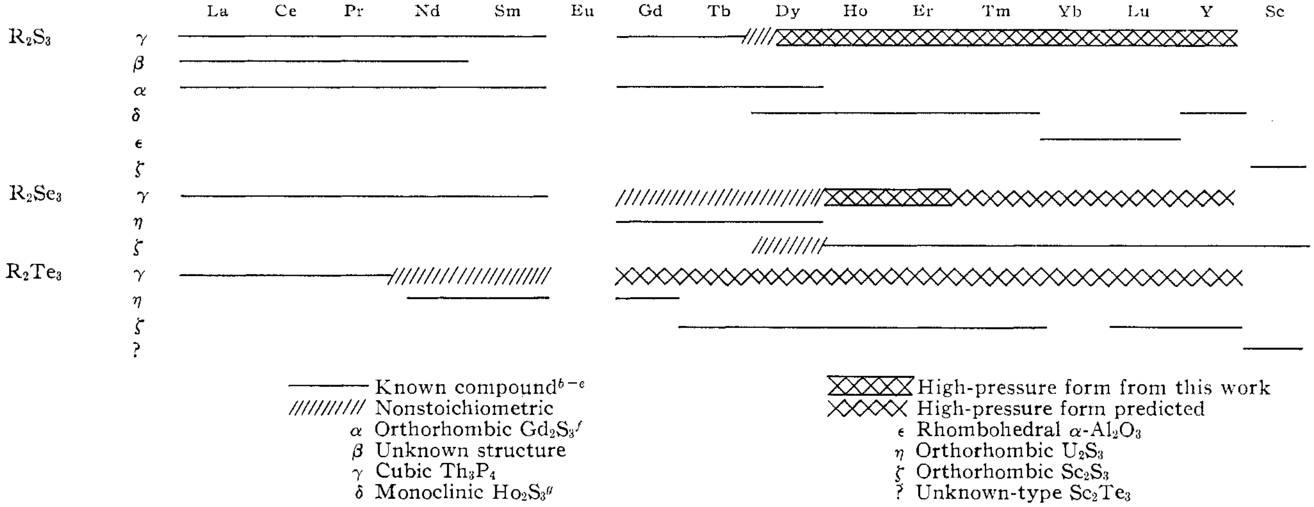
Results

Monoclinic Dy_2S_3 was completely converted to the Th_3P_4-type cubic form at 70 kbars and 1200°; however, monoclinic Ho_2S_3 and Er_2S_3 did not undergo this conversion at 70 kbars and 1700°. Subsequent runs at 77 kbars and 2000° resulted in complete transition to the Th_3P_4-type cubic structure for Ho_2S_3, Er_2S_3, Tm_2S_3, Tb_2S_3, Yb_2S_3, and Y_2S_3 in 3 min. Lu_2S_3 was about 50% converted to the cubic form under these conditions.

Ho_2S_3 of the cubic Th_3P_4 type was also obtained from the elements at pressures above 50 kbars and temperatures above 1500°. Cubic Yb_2S_3 was obtained from the elements at pressures 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.

TABLE I

CRYSTAL STRUCTURES OF RARE EARTH SESQUICHALCOGENIDES[a]



——— Known compound[b–e]
////////// Nonstoichiometric
α Orthorhombic Gd_2S_3[f]
β Unknown structure
γ Cubic Th_3P_4
δ Monoclinic Ho_2S_3[g]
▨ High-pressure form from this work
XXXXX High-pressure form predicted
ε Rhombohedral α-Al_2O_3
η Orthorhombic U_2S_3
ζ Orthorhombic Sc_2S_3
? Unknown-type Sc_2Te_3

[a] Recent works[d,f,g] 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. [b] J. Flahaut, L. Domange, M. Guittard, and M. P. Pardo, *Bull. Soc. Chim. France*, 326 (1965). [c] Reference 4. [d] J. P. Dismukes and J. G. White, *Inorg. Chem.*, **4**, 970 (1965). [e] A. W. Sleight and C. T. Prewitt, *ibid.*, **7**, 2282 (1968). [f] C. T. Prewitt and A. W. Sleight, *ibid.*, **7**, 1090 (1968). [g] J. G. White, P. N. Yocom, and S. Lerner, *ibid.*, **6**, 1872 (1967).

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

Discussion

Picon, *et al.*,[3] found cubic Dy_2S_3 to be nonstoichiometric with a sulfur deficiency. Guittard, *et al.*,[10] 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.

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 Y_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[11] and Iandelli.[12]

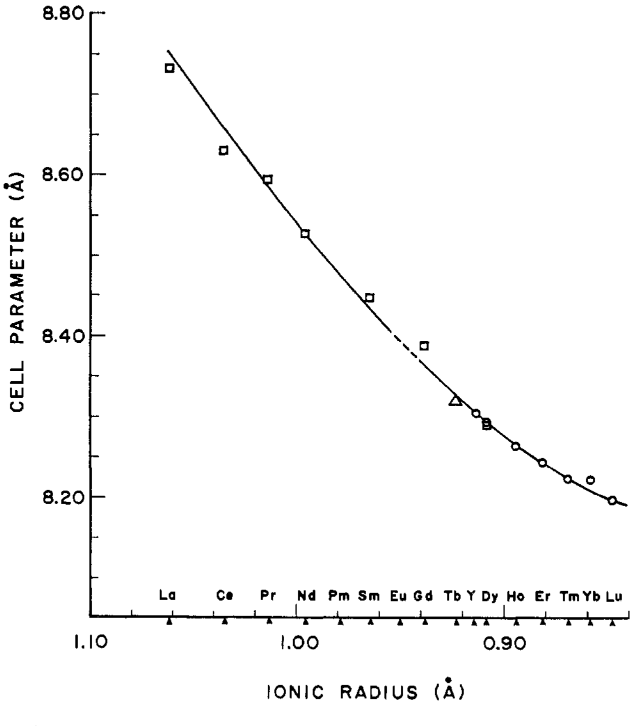


Figure 3.—Variation of cell parameters with ionic radius of the cubic rare earth sesquisulfides: □, Picon, *et al.*;[3] △, Collins and Loriers;[5] ○, present work.

The synthesis of these new compounds suggests that the Th_3P_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.

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