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High-Pressure Synthesis of Lutetium Diantimonide

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The synthesis of all the rare earth diantimonides with the exception of $EuSb_2$ and $LuSb_2$ has been reported previously. Diantimonides from $LaSb_2$ to $SmSb_2$ can be prepared by conventional methods[2] while those from $GdSb_2$ to $TmSb_2$ require high-pressure techniques.[3]

In previous work we investigated all of the rare earth–antimony systems at a mixture ratio of 1 mol of rare earth:2 mol of antimony at pressures up to 70 kbars.[3] Since then the Yb + 2Sb and Lu + 2Sb systems have been investigated at higher pressures. No phases other than the $ZrSi_2$ structure of $YbSb_2$[4] were found in the Yb + 2Sb system up to 90 kbars and 1500°. In the Lu + 2Sb system, $LuSb_2$ of the high-pressure orthorhombic type found in $GdSb_2$ through $TmSb_2$ was synthesized at 73 kbars and 1000°. No other phases were found up to 90 kbars and 1500°.

TABLE I

POWDER DIFFRACTION DATA FOR $LuSb_2$

hkl	I_{obsd}	*d*, Å	
		Obsd	Calcd
011	vvw	3.09	3.00
110	vvw	2.85	2.84
111	vvs	2.68	2.67
003	vw	2.58	2.63
112	vvs	2.30	2.30
113	vw	1.918	1.927
020	s	1.618	1.622
114	s	1.606	1.618
021	vvw	1.551	1.588
105	m	1.521	1.522
401	m	1.434	1.434
221	vvw	1.396	1.395
402	w	1.364	1.368
106	vvw	1.294	1.282
024	vs	1.257	1.252
413	vvw	1.180	1.187
025	w	1.134	1.131
421	w	1.075	1.074
422	w	1.046	1.046
316	vw	1.036	1.032
226	w	0.9627	0.9637
034	w	0.9488	0.9480
610	vvw	0.9305	0.9315
522	vw	0.9215	0.9210
523	w	0.8907	0.8911
109, 431	vvw	0.8644	0.8649
417	vw	0.8599	0.8597
209	vw	0.8390	0.8391
621	vw	0.8303	0.8294
622	vw	0.8162	0.8160
530	w	0.7934	0.7931
712	w	0.7908	0.7909
240	w	0.7814	0.7813
241, 532	w	0.7772	0.7775

Experimental Section

Experimental procedure and sample geometry were essentially the same as has already been described elsewhere[3] except that a tetrahedral press with 0.5-in. anvils was used to obtain pressures above 70 kbars.[5,6] Pressures above 70 kbars were calibrated by taking the Bi(III)–Bi(IV) transition pressure to be 77 kbars.

A Debye–Scherrer powder diffraction pattern was taken using a 143-mm camera with 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.

Results

The high-pressure orthorhombic form of $LuSb_2$ was made from the elements at 73 kbars and 1000° or at higher pressures and temperatures. A Debye–Scherrer powder diffraction pattern for $LuSb_2$ is given in Table I. This powder pattern indexed to an orthorhombic structure with lattice constants of $a = 5.935 \pm 0.006$, $b = 3.244 \pm 0.004$, and $c = 7.885 \pm 0.009$ Å.

Using data from this work and the previous investigation[3] a graph of the variation of minimum pressure of formation for the high-pressure orthorhombic form of the rare earth diantimonides of $GdSb_2$ to $LuSb_2$ as a function of ionic radius[7] is shown in Figure 1. It is seen that $GdSb_2$, $TbSb_2$, and $DySb_2$ all require about the same pressure for synthesis but the heavier rare earths require somewhat higher pressures.

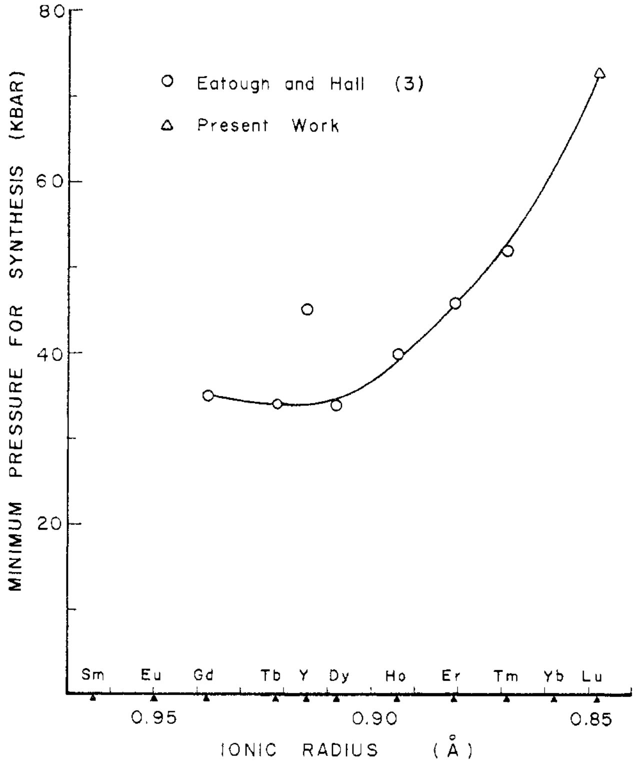

Figure 1.—Minimum pressure required for synthesis of high-pressure orthorhombic type rare earth diantimonides.

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(1) California State Polytechnic College, San Luis Obispo, Calif.

(2) R. Wang and H. Steinfink, *Inorg. Chem.*, **6**, 1685 (1967).

(3) N. L. Eatough and H. T. Hall, *ibid.*, **8**, 1439 (1969).

(4) R. E. Bodnar and H. Steinfink, *ibid.*, **6**, 327 (1967).

(5) H. T. Hall, *Rev. Sci. Instr.*, **29**, 267 (1958).

(6) H. T. Hall, *ibid.*, **33**, 1278 (1962).

(7) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954).

According to Gschneidner and Valletta[8] if the pressure required for synthesis increases with the atomic number of the rare earth, there must be 4f-electron participation in the chemical bonding. If it decreases with increasing atomic number, there is no 4f bonding and crystal structure is determined by size effects only. It appears that in this system both the size effect and 4f bonding are important for $GdSb_2$, $TbSb_2$, and $DySb_2$, but 4f bonding becomes increasingly important for the heavier rare earths.

The diantimonide of yttrium required about 10 kbars higher pressure for synthesis than would be predicted by its ionic radius. This same effect has been observed in other yttrium systems.[8,9] There are, of course, no 4f electrons in yttrium.

Acknowledgment.—Thanks are extended to the Army Research Office (Durham) for financial support of this research.

[8] K. A. Gschneidner, Jr., and R. M. Valletta, *Acta Met.*, **16**. 477 (1968).

[9] A. W. Webb, Ph.D. Dissertation, Brigham Young University, May 1969.

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High-Pressure Th_3P_4-Type Polymorphs of Rare Earth Sesquiselenides

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Previous work has shown that the normal monoclinic and rhombohedral forms of rare earth sesquisulfides could be converted to the more dense Th_3P_4-type cubic structure by high-pressure–high-temperature techniques.[2] Also, the Th_3P_4 forms of Ho_2Se_3 and Er_2Se_3 have been synthesized from the elements using high-pressure techniques.[2] We have now succeeded in preparing Tm_2Se_3, Yb_2Se_3, Lu_2Se_3, and Y_2Se_3 in the Th_3P_4-type structure by applying high pressure–high temperature to a stoichiometric mixture of the elements. Consequently, all the rare earth sesquiselenides except Eu_2Se_3 are now known in the Th_3P_4 structure.

Experimental Section

The studies were carried out in a tetrahedral press with 0.5-in. anvils equipped with an anvil guide.[3,4] Sample geometry and experimental procedure were the same as described previously.[2] Pressures above 70 kbars were calibrated by taking the Bi(III)–Bi(IV) transition pressure to be 77 kbars.

Results and Discussion

The Th_3P_4-type polymorphs of Y_2Se_3, Tm_2Se_3, Yb_2Se_3, and Lu_2Se_3 have been synthesized from stoichiometric mixtures of the elements using the conditions indicated in Table I. No extraneous lines were observed in the X-ray diffraction patterns of the products, showing that the polymorphs were single phase. For runs at temperatures or pressures less than those given in Table I the diselenide was obtained as the major product.

TABLE I

CUBIC RARE EARTH SESQUISELENIDES

	Pressure, kbars	Temp, °C	Lattice parameter, Å
Y_2Se_3	70	1800	8.6626 ± 0.0008
Tm_2Se_3	70	1800	8.5992 ± 0.0007
Yb_2Se_3	80	1800	8.615 ± 0.002
Lu_2Se_3	90	1800	8.570 ± 0.003

Guittard, *et al.*,[5] found the sesquiselenide series from Gd_2Se_3 to Dy_2Se_3 to be nonstoichiometric with a selenium deficiency. It is quite possible that the cubic polymorphs made in this work are also nonstoichiometric; however, facilities were not available to handle the small samples prepared so no chemical analysis of the compounds formed was made.

Lattice parameters of the new cubic sesquiselenides are compared with previously known compounds of this type in Figure 1.[2,6] It can be seen that Y_2Se_3 fits well at an ionic radius of 0.915 Å which is the same value as previously obtained for the sesquisulfide.[2] Ionic radii for the other rare earths were taken from Templeton and

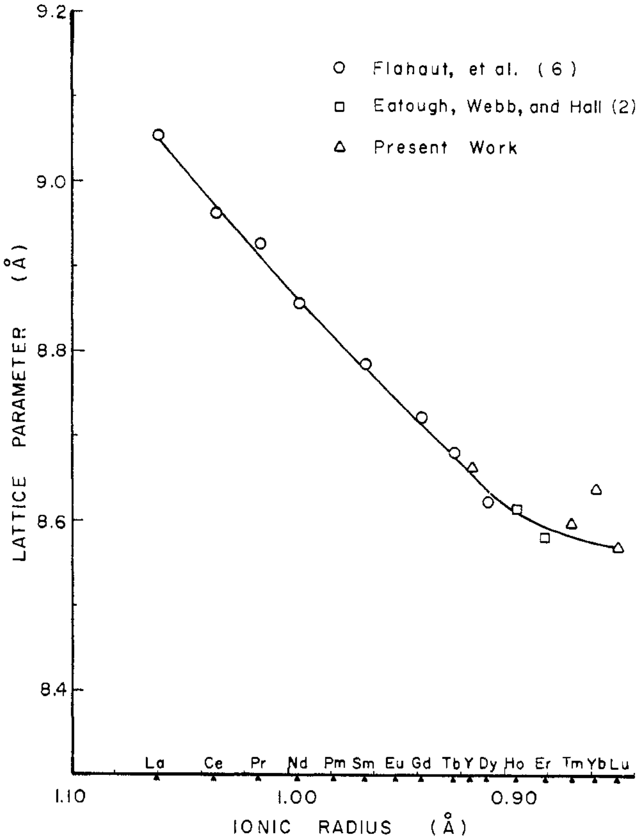

Figure 1.—Variation of lattice parameter with ionic radius of the Th_3P_4-type rare earth sesquiselenides.

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[1] California State Polytechnic College, San Luis Obispo, Calif.

[2] N. L. Eatough, A. W. Webb, and H. T. Hall, *Inorg. Chem.*, **8**, 2069 (1969).

[3] H. T. Hall, *Rev. Sci. Instr.*, **29**, 267 (1958).

[4] H. T. Hall, *ibid.*, **33**, 1278 (1962).

[5] M. Guittard, A. Benacerraf, and J. Flahaut, *Ann. Chim.*, **9**, 25 (1964).

[6] J. Flahaut, P. Laruelle, M. P. Pardo, and M. Guittard, *Bull Soc. Chim. France*, 1399 (1965).