

According to Gschneidner and Valletta⁸ 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 GdSb₂, TbSb₂, and DySb₂, 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.

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High-Pressure Th₃P₄-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 Th₃P₄-type cubic structure by high-pressure-high-temperature techniques.² Also, the Th₃P₄ forms of Ho₂Se₃ and Er₂Se₃ have been synthesized from the elements using high-pressure techniques.² We have now succeeded in preparing Tm₂Se₃, Yb₂Se₃, Lu₂Se₃, and Y₂Se₃ in the Th₃P₄-type structure by applying high pressure-high temperature to a stoichiometric mixture of the elements. Consequently, all the rare earth sesquiselenides except Eu₂Se₃ are now known in the Th₃P₄ 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 Th₃P₄-type polymorphs of Y₂Se₃, Tm₂Se₃, Yb₂Se₃, and Lu₂Se₃ have been synthesized from stoichiometric mixtures of the elements using the conditions

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TABLE I

CUBIC RARE EARTH SESQUISSELENIDES

	Pressure, kbars	Temp, °C	Lattice parameter, Å
Y ₂ Se ₃	70	1800	8.6626 ± 0.0008
Tm ₂ Se ₃	70	1800	8.5992 ± 0.0007
Yb ₂ Se ₃	80	1800	8.615 ± 0.002
Lu ₂ Se ₃	90	1800	8.570 ± 0.003

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.

Guittard, *et al.*,⁵ found the sesquiselenide series from Gd₂Se₃ to Dy₂Se₃ 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 Y₂Se₃ fits well

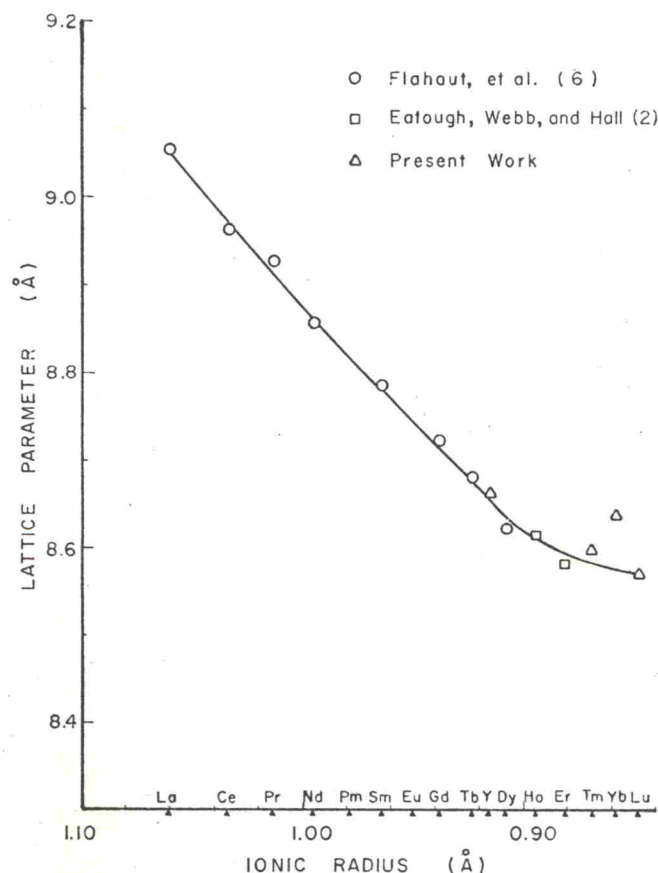


Figure 1.—Variation of lattice parameter with ionic radius of the Th₃P₄-type rare earth sesquiselenides.

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

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