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## High-Pressure $\text{Th}_3\text{P}_4$ -Type Polymorphs of Rare Earth Sesquiselenides

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Received September 3, 1969

Previous work has shown that the normal monoclinic and rhombohedral forms of rare earth sesquisulfides could be converted to the more dense  $\text{Th}_3\text{P}_4$ -type cubic structure by high-pressure-high-temperature techniques.<sup>2</sup> Also, the  $\text{Th}_3\text{P}_4$  forms of  $\text{Ho}_2\text{Se}_3$  and  $\text{Er}_2\text{Se}_3$  have been synthesized from the elements using high-pressure techniques.<sup>2</sup> We have now succeeded in preparing  $\text{Tm}_2\text{Se}_3$ ,  $\text{Yb}_2\text{Se}_3$ ,  $\text{Lu}_2\text{Se}_3$ , and  $\text{Y}_2\text{Se}_3$  in the  $\text{Th}_3\text{P}_4$ -type structure by applying high pressure-high temperature to a stoichiometric mixture of the elements. Consequently, all the rare earth sesquiselenides except  $\text{Eu}_2\text{Se}_3$  are now known in the  $\text{Th}_3\text{P}_4$  structure.

### Experimental Section

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

### Results and Discussion

The  $\text{Th}_3\text{P}_4$ -type polymorphs of  $\text{Y}_2\text{Se}_3$ ,  $\text{Tm}_2\text{Se}_3$ ,  $\text{Yb}_2\text{Se}_3$ , and  $\text{Lu}_2\text{Se}_3$  have been synthesized from stoichiometric mixtures of the elements using the conditions

TABLE I  
 CUBIC RARE EARTH SESQUISELENIDES

	Pressure, kbars	Temp, °C	Lattice param- eter, Å
$\text{Y}_2\text{Se}_3$	70	1800	$8.6626 \pm 0.0008$
$\text{Tm}_2\text{Se}_3$	70	1800	$8.5992 \pm 0.0007$
$\text{Yb}_2\text{Se}_3$	80	1800	$8.615 \pm 0.002$
$\text{Lu}_2\text{Se}_3$	90	1800	$8.570 \pm 0.003$

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.*,<sup>5</sup> found the sesquiselenide series from  $\text{Gd}_2\text{Se}_3$  to  $\text{Dy}_2\text{Se}_3$  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.<sup>6</sup> It can be seen that  $\text{Y}_2\text{Se}_3$  fits well

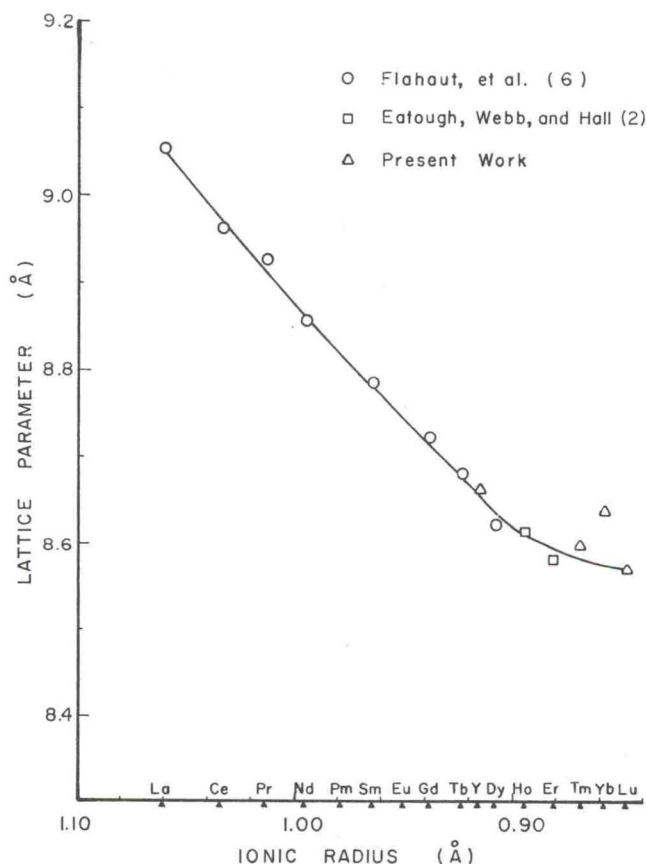


Figure 1.—Variation of lattice parameter with ionic radius of the  $\text{Th}_3\text{P}_4$ -type rare earth sesquiselenides.

at an ionic radius of  $0.915 \text{ \AA}$  which is the same value as previously obtained for the sesquisulfide.<sup>2</sup> Ionic radii for the other rare earths were taken from Templeton and

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 (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).

Dauben.<sup>7</sup> The lattice parameters of  $\text{Tm}_2\text{Se}_3$  and  $\text{Lu}_2\text{Se}_3$  are somewhat larger than would be predicted from a straight-line extrapolation of the lighter rare earths, and this same effect has been previously observed for the sesquisulfides. The lattice parameter of  $\text{Yb}_2\text{Se}_3$  is somewhat greater than its neighbors which indicates some  $\text{Yb}^{2+}$  character in  $\text{Yb}_2\text{Se}_3$ . This same effect was also observed in  $\text{Yb}_2\text{S}_3$ .<sup>2</sup> A graph of the minimum pressure for synthesis of the cubic polymorphs as a function of ionic radius of the rare earth is shown in Figure 2. Values for  $\text{Ho}_2\text{Se}_3$  and  $\text{Er}_2\text{Se}_3$  were taken from Eatough, Webb, and Hall.<sup>2</sup> The synthesis of  $\text{Ho}_2\text{Se}_3$ ,  $\text{Er}_2\text{Se}_3$ , and  $\text{Tm}_2\text{Se}_3$  takes place at about the same pressure. According to Gschneidner and Valletta<sup>8</sup> if the pressure required for synthesis increases with atomic number of the rare earth, there is 4f-electron participation in the chemical bonding. If the pressure required decreases with increasing atomic number, the crystal structure of the compound is determined by size effects only. In the sesquiselenide series there seems to be a combination of size effect and 4f-electron bonding determining the structure for the cubic polymorphs of Ho, Er, and Tm. For Yb and Lu the 4f bonding becomes increasingly important.

**Acknowledgments.**—Thanks are extended to the Army Research Office (Durham) for financial support during this research.

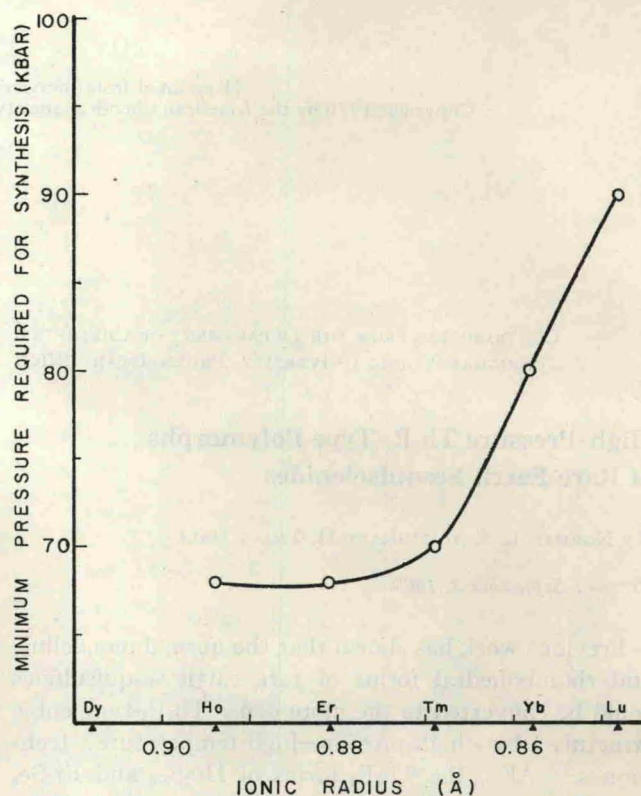


Figure 2.—Minimum pressure required for synthesis of cubic rare earth sesquiselenides.

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

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