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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] We have now succeeded in preparing Tm_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 knows 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 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

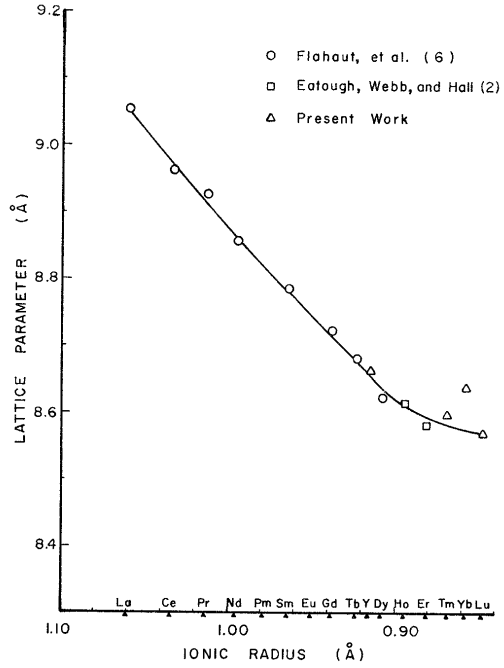

Figure 1.—Variation of lattice parameter with ionic radius of the Th_3P_4-type rare earth sesquiselenides.

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 Dauben.[7] The lattice parameters of Tm_2Se_3 and Lu_2Se_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 Yb_2Se_3 is somewhat greater than its neighbors which indicates some Yb^{2+} character in Yb_2Se_3. This same effect was also observed in Yb_2S_3.[2] A graph of the minimum

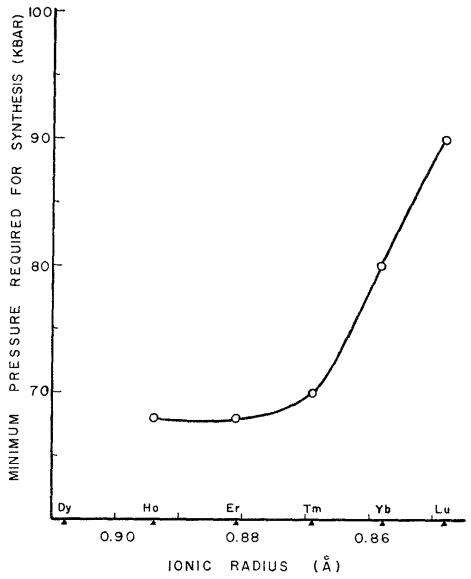

Figure 2.—Minimum pressure required for synthesis of cubic rare earth sesquiselenides.

pressure for synthesis of the cubic polymorphs as a function of ionic radius of the rare earth is shown in Figure 2. Values for Ho_2Se_3, and Er_2Se_3 were taken from Eatough, Webb, and Hall.[2] The synthesis of Ho_2Se_3, Er_2Se_3, and Tm_2Se_3 takes place at about the same pressure. According to Gschneidner and Valletta[8] if the pressure required for synthesis increases with atomic number of the rare earth, there is 4f-elctron participation in the chemical bonding. If the pressure required decreases with increasing atomic number, the crystal structure of the compound in 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.

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