

TABLE I
CRYSTAL STRUCTURES OF RARE EARTH SESQUICHALCOGENIDES^a

		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc	
R_2S_3	γ	—————						////////////////////////////////////										
	β	—————						////////////////////////////////////										
	α	—————						////////////////////////////////////										
	δ	—————						////////////////////////////////////										
	ϵ	—————						////////////////////////////////////										
R_2Se_3	γ	—————						////////////////////////////////////										
	η	—————						////////////////////////////////////										
	ζ	—————						////////////////////////////////////										
R_2Te_3	γ	—————			////////////////////////////////////			////////////////////////////////////										
	η	—————						////////////////////////////////////										
	ζ	—————						////////////////////////////////////										
	?	—————						////////////////////////////////////										

————— Known compound^{b-c}
 ////////////////////////////////// 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
 ////////////////////////////////// High-pressure form predicted
 ϵ Rhombohedral $\alpha-Al_2O_3$
 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. ^bJ. Flahaut, L. Domange, M. Guittard, and M. P. Pardo, *Bull. Soc. Chim. France*, 326 (1965). ^cReference 4. ^dJ. P. Dismukes and J. G. White, *Inorg. Chem.*, 4, 970 (1965). ^eA. W. Sleight and C. T. Prewitt, *ibid.*, 7, 2282 (1968). ^fC. T. Prewitt and A. W. Sleight, *ibid.*, 7, 1090 (1968). ^gJ. 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 $\pm 2\sigma$, Å	Compound	Cell parameter $\pm 2\sigma$, 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 sesquiseelenide 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 Tecotzky¹¹ and Iandelli.¹²

The synthesis of these new compounds suggests that

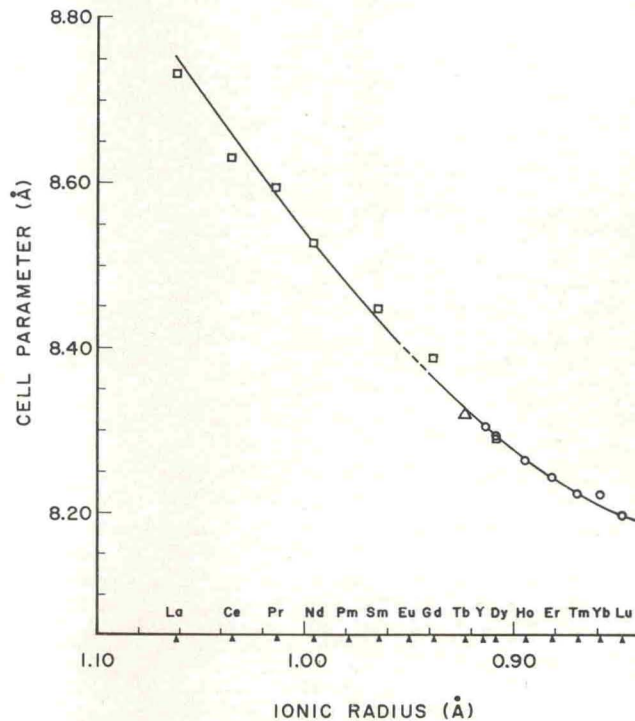


Figure 3.—Variation of cell parameters with ionic radius of the cubic rare earth sesquisulfides: \square , Picon, *et al.*;³ Δ , Collins and Loriers;⁵ \circ , present work.

the Th_3P_4 forms of the sesquiseelenides 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.

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(10) M. Guittard, A. Benacerraf, and J. Flahaut, *Ann. Chim. (Paris)*, 9, 25 (1964).

(11) S. A. Ring and M. Tecotzky, *Inorg. Chem.*, 3, 182 (1964).

(12) A. Iandelli in "Rare Earth Research," E. V. Kelber, Ed., The Macmillan Co., New York, N. Y., 1961, pp 135-141.