

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 ₂ S ₃	γ	—————					—————									
	β	—————					—————									
	α	—————					—————									
	δ	—————					—————									
	ε	—————					—————									
R ₂ Se ₃	γ	—————					—————									
	η	—————					—————									
	ξ	—————					—————									
R ₂ Te ₃	γ	—————					—————									
	η	—————					—————									
	ξ	—————					—————									
	?	—————					—————									

————— Known compound^{b-c}
 ////////////// Nonstoichiometric
 α Orthorhombic Gd₂S₃^f
 β Unknown structure
 γ Cubic Th₃P₄
 δ Monoclinic Ho₂S₃^g
 ⊗⊗⊗⊗⊗ High-pressure form from this work
 ⊗⊗⊗⊗⊗ High-pressure form predicted
 ε Rhombohedral α-Al₂O₃
 η Orthorhombic U₂S₃
 ξ Orthorhombic Sc₂S₃
 ? Unknown-type Sc₂Te₃

^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. ^b J. Flahaut, L. Domange, M. Guittard, and M. P. Pardo, *Bull. Soc. Chim. France*, 326 (1965). ^c Reference 4. ^d J. P. Dismukes and J. G. White, *Inorg. Chem.*, 4, 970 (1965). ^e A. W. Sleight and C. T. Prewitt, *ibid.*, 7, 2282 (1968). ^f C. T. Prewitt and A. W. Sleight, *ibid.*, 7, 1090 (1968). ^g J. 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 Lu₂S₃ for which 17 lines were measured.

 TABLE II
 CELL PARAMETERS OF SOME RARE
 EARTH SESQUICHALCOGENIDES

Compound	Cell parameter ± 2σ, Å	Compound	Cell parameter ± 2σ, Å
Ho ₂ S ₃	8.265 ± 0.001	Lu ₂ S ₃	8.198 ± 0.005
Er ₂ S ₃	8.244 ± 0.001	Y ₂ S ₃	8.306 ± 0.002
Tm ₂ S ₃	8.225 ± 0.002	Ho ₂ Se ₃	8.614 ± 0.006
Yb ₂ S ₃	8.224 ± 0.001	Er ₂ Se ₃	8.581 ± 0.006

Discussion

Picon, *et al.*,³ found cubic Dy₂S₃ to be nonstoichiometric with a sulfur deficiency. Guittard, *et al.*,¹⁰ found a similar nonstoichiometry in the sesquiselenide series from Gd₂Se₃ through Dy₂Se₃. 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 Yb₂S₃ indicates some Yb²⁺ character. The lattice parameter of Y₂S₃ indicates that Y³⁺ 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

(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.

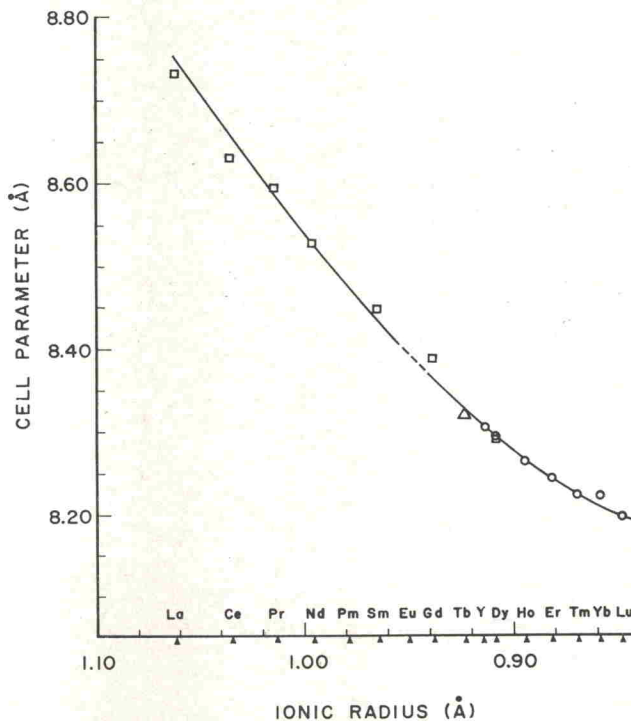


Figure 3.—Variation of cell parameters with ionic radius of the cubic rare earth sesquisulfides: □, Picon, *et al.*;³ △, Collins and Lorjers;⁵ ○, present work.

the Th₃P₄ forms of the sesquiselenides 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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