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High-Pressure Synthesis of Rare Earth Diantimonides¹

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New rare earth diantimonides of orthorhombic (LaSb₂ type) crystal structures were prepared for Pr, Gd, and Tb. Also, new diantimonides of Gd, Tb, Dy, Ho, Er, Tm, Yb, and Y indexed as orthorhombic with two molecules per unit cell were made. Pressures to 70 kbars with simultaneous temperatures to 1800° were employed in the work.

Introduction

In a series of rare earth compounds R₂B₃ where the rare element R is varied, it is common to find that the compounds have been prepared for only a certain range of R. For example, rare earth diantimonides, RSb₂, have previously been known only for the lighter rare earths. Efforts to synthesize diantimonides for Gd and heavier rare earths by ordinary techniques have not been successful (except for Yb, which often displays exceptional behavior).³ In this and similar situations it has been reasoned that size differences between atoms R and B, due to the lanthanide contraction, lead to instability of the crystal structures thus limiting the range of R.

High pressure is capable of altering the relative sizes of atoms and has been used in the present work, simultaneously with high temperature, to provide a favorable thermodynamic and kinetic situation for the synthesis of diantimonides of the heavier rare earth elements. Once formed, the compounds remain stable (or metastable) on return to normal room conditions.

Previous Work

Earlier studies of rare earth-antimony systems include those of Vogel and Klose,⁴ who in 1954 reported the compounds La₂Sb, La₃Sb₂, LaSb, and LaSb₂. The latter compound, LaSb₂, was the first rare earth dianti-

monide discovered. In 1966, Olcese⁵ reported the formation of Ce₂Sb, Ce₃Sb₂, CeSb, and CeSb₂. Bodnar and Steinfink in 1967 reported the discovery of the ytterbium compounds YbSb₂, YbSb, Yb₅Sb₄, Yb₄Sb₃, Yb₅Sb₃, and Yb₅Sb₂.⁶ The first specific study on the diantimonides was reported by Wang and Steinfink in 1967.³ They prepared LaSb₂, CeSb₂, NdSb₂, SmSb₂, and YbSb₂. They attempted the synthesis of the diantimonides of Gd, Dy, Ho, and Er but were not able to make them. They did not work with Pr, Eu, Tb, Tm, or Lu. By single-crystal X-ray diffraction techniques the diantimonides of La, Ce, Nd, and Sm were found to have an orthorhombic structure which Wang and Steinfink designated as the LaSb₂-type structure. YbSb₂ was shown to have a ZrSi₂-type structure. They found the Sb-Sb bond distance to be very short in the LaSb₂-type structure and postulated that as the rare earth size decreases the Sb-Sb repulsion from increasingly shorter Sb-Sb bonds causes the structure to become unstable at Gd. A summary of the known rare earth-antimony compounds is given in Table I.

Experimental Section

Our high-pressure, high-temperature studies of the rare earth diantimonides were carried out in a tetrahedral anvil apparatus equipped with anvil guide.^{7,8} The triangular faces of the tungsten carbide were 19 mm on an edge.

The rare earth metals were obtained from Research Chemicals,

(1) This research supported by the National Science Foundation and the Army Research Office, Durham, N. C.

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(5) G. L. Olcese, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **40**, 629 (1966); *Chem. Abstr.*, **65**, 17877 (1966).

(6) R. E. Bodnar and H. Steinfink, *Inorg. Chem.*, **6**, 327 (1967).

(7) H. T. Hall, *Rev. Sci. Instr.*, **33**, 237 (1953).

(8) H. T. Hall, *ibid.*, **33**, 1278 (1952).

TABLE I
A SUMMARY OF RARE EARTH-ANTIMONY COMPOUNDS

	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
RSb ₂ (LaSb ₂ Type)			X	X	X	X	X	X	X	X	X	X	X	X	X	X
RSb ₂ (HPO)**		X							X	X	X	X	X	X	X	X
RSb ₂ (ZrSi ₂ Type)																X
RSb (NaCl Type)	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
R ₅ Sb ₄ (Tetragonal)																
R ₄ Sb ₃ (Th ₃ P ₄ Type)			X	X	X	X	X	X	X	X	X	X	X	X	X	X
R ₃ Sb ₂			X	X	X	X	X	X	X	X	X	X	X	X	X	X
R ₅ Sb ₃ (Hexagonal)																X
R ₂ Sb			X	X	X	X	X	X	X	X	X	X	X	X	X	X
R ₅ Sb ₂ (Orthorhombic)																X

* New compounds synthesized in the present work

** High Pressure Orthorhombic Type

Phoenix, Ariz., and Alfa Inorganics, Beverly, Mass., and were 99.9% pure. The antimony was obtained from Mallinckrodt Chemical Works, New York, N. Y., and was 99.8% pure, reagent grade metal. The rare earths were filed, sieved through a 100 mesh nylon sieve, and used immediately. The antimony was ground with a mortar and pestle and sieved through a 200 mesh nylon sieve. Mixtures of 1 g-atom of rare earth and 2 g-atoms of antimony were prepared and hand mixed for several minutes in a plastic vial.

The tetrahedral cells used in the apparatus were constructed as shown in cross section in Figure 1. The tetrahedrons were made of pyrophyllite (available as Grade A lava from the American Lava Corp., Chattanooga, Tenn.) and had 25-mm edges and a 3.18-mm sample hole. The electrical leads were made from strips of molybdenum 12.7 × 5.6 × 0.13 mm. The graphite heater consisted of a tube 3.18 mm in o.d., 2.16 mm in i.d., and 3.80 mm long and two end caps 3.18 mm in diameter and 1.27 mm thick. The boron nitride liner fit inside the graphite tube and was made of a tube 1.27 mm in i.d. and 2.54 mm long and two end caps 2.16 mm in diameter and 0.51 mm thick. The reagents for synthesis were placed inside the BN tube, and the completed tetrahedron was painted with a slurry of rouge in methanol, dried at 110° for at least 1 hr, and allowed to cool in a desiccator. The tetrahedron was then placed in the press, compressed to the desired pressure, heated for 3 min, and quenched. The pressure was released and the product was removed from the BN tube.

To provide a larger sample volume for metallographic studies and density determinations, the BN liner was replaced by a molybdenum tube 0.076 mm thick with 0.127 mm thick end caps.

Runs were made at pressures of 15–70 kbars. Temperatures of 600–1000° were used at the lower pressures and 600–1800° at the higher pressures. Enough runs were made for each system to define the reaction product boundaries. Boundaries were specified within ±3 kbars and about ±100°.

Pressure was calibrated as a function of hydraulic ram load by use of fixed-point electrical resistance transitions. The following transitions were used: cerium at 8.1 kbars, Hg at 12.2 kbars, Bi(I) and Bi(II) at 26.5 kbars, Tl(II) and Tl(III) at 35.4 kbars, Yb(I) and Yb(II) at 38.2 kbars, and Ba(I) and Ba(II) at 54.6 kbars.

Heating power input (volts × amperes) was recorded for each run and was related to the temperature by making several runs containing Pt–Pt–10% Rh thermocouples. Standard deviation of the measured temperature as a function of heating power for the thermocouple runs was about 5%. No correction for the pressure effect on the emf of the thermocouples was applied. Neither was the effect of temperature on the pressure taken into account.

All runs in the reaction product studies were analyzed by the Debye–Scherrer powder diffraction method. The samples were ground between two polished tungsten carbide surfaces and loaded into a 0.5-mm glass capillary. Diffraction patterns were

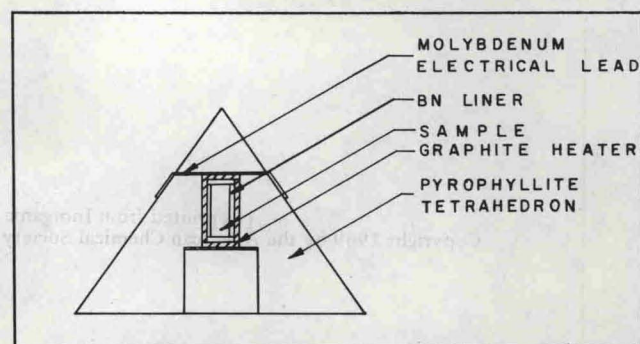


Figure 1.—Cross section of tetrahedral sample geometry.

obtained on a 143-mm Debye–Scherrer camera with a General Electric CA-7 copper X-ray tube using a nickel filter. The best films were read and d values were calculated using $\lambda(K\alpha)$ 1.5418 Å and $\lambda(K\alpha_1)$ 1.54050 Å.

The LaSb₂-type patterns were indexed by comparing them to the NdSb₂ indexing given by Wang.⁹ All lines of the new high-pressure structure were indexed orthorhombic with two molecules per unit cell. Lattice parameters were determined by the least-squares method.

Results

Synthesis studies on mixtures of RE–2Sb (RE = rare earth) were carried out on all of the lanthanides except Pm and also on Sc and Y. The known LaSb₂-type structure for rare earth diantimonides was extended through GdSb₂ and TbSb₂. PrSb₂ of this structure was also made. The new orthorhombic structure with two molecules per cell was found for GdSb₂, TbSb₂, DySb₂, HoSb₂, ErSb₂, TmSb₂, and YSb₂.

In the case of La, Ce, and Eu no compounds with antimony formed. Only the rare earth oxides were obtained from all pressures from 15 to 70 kbars and temperatures from 600 to 1500°. The oxygen apparently migrated into the sample from the pyrophyllite. The La and Ce diantimonides of LaSb₂ type had, of course, been previously prepared by high-temperature vacuum techniques.^{4,5} Above 600° at pressures from 15 to 70 kbars the previously known diantimonides of Yb, Nd, and Sm were formed.

The only phase found in the Sc–2Sb system was ScSb–Sb over the entire range of pressure and temperature to 70 kbars and 1800°, respectively.

Reaction product diagrams on a pressure–temperature field are shown for some of the systems studied in Figures 2–8. These are not to be regarded as equilibrium phase diagrams but merely represent the products obtained by quenching from the pressure–temperature region indicated. Pressure, as previously indicated, was maintained during quenching. A discussion of specific results for some of the rare earths follows.

Gadolinium (Figure 2).—Several different reaction products were obtained in this case. At pressures between 10 and 50 kbars and temperatures above 1000° an X-ray diffraction pattern matching that of NdSb₂ was obtained which verified the synthesis of LaSb₂-type GdSb₂. At lower temperatures and pressures below 20 kbars cubic GdSb and also Sb were obtained. At tem-

(9) R. Wang, Ph.D. Dissertation, Department of Chemical Engineering, University of Texas, 1967.