cedure consisting of adding the alkylaluminum compound in a chosen solvent to the metal salt in the same solvent at 0–25° under dry nitrogen, followed by transferring the reaction mixture to an autoclave, pressurizing with carbon monoxide and heating to the desired reaction temperature; B—a sealed ampoule procedure consisting of adding the metal salt in a sealed ampoule to a 100-ml. Magne–Dash autoclave containing the alkylaluminum compound in a chosen solvent, pressurizing with carbon monoxide, breaking the ampoule at room temperature and heating to a desired temperature; C—a simultaneous contact procedure consisting of gradually adding the alkylaluminum compound in a chosen solvent to the metal salt in the same solvent in the presence of carbon monoxide at the desired temperature. When superatmospheric pressures of carbon monoxide were employed in conjunction with procedure C, the alkylaluminum solution was pumped in under dry nitrogen pressure.

Procedure B was generally employed for the reaction variable study. For preparative purposes, procedures A or C are best for preparing manganese carbonyl in ethers, procedure C for preparing manganese carbonyl in benzene, procedure A or C for preparing chromium carbonyl and procedure C for preparing molybdenum or tungsten carbonyl.

Preparation of Manganese Carbonyl.—A typical procedure is described: to 34.6 g. (0.20 mole) of anhydrous manganese acetate suspended in 150 ml. of dry isopropyl ether was added dropwise with stirring a solution consisting of 120 ml. (0.80 mole) of triethylaluminum and 290 ml. of isopropyl ether at 0° under a dry nitrogen atmosphere. The addition time was about 2.5 hr. With the aid of 40 ml. of isopropyl ether, the mixture then was transferred (in a nitrogen dry box) to a one-liter Magne–Dash autoclave. After assembly, the autoclave was purged twice with 600 p.s.i.g. of C.P. carbon monoxide. The autoclave then was pressured with 3000 p.s.i.g. of CO and heated by means of a steam-bath (with an alternate cold water supply) to 80–85° with stirring. It is important to maintain this temperature constant during the initial stage of the reaction to prevent a violent reaction between the manganese acetate and triethylaluminum. After the initial reaction occurred, the autoclave was heated to and maintained at 100° for 5 hr.

After the autoclave cooled to room temperature, it was carefully vented and the reaction mixture was transferred to a 2-liter three-neck flask equipped with a Dry Ice condenser, dropping funnel, and stirrer and was kept under a dry nitrogen blanket. The mixture then was carefully quenched by dropwise addition of 400 ml. of water and 100 ml. of concentrated hydrochloric acid at 0°. The mixture was distilled at atmospheric pressure into a three-neck round-bottomed flask which had an outlet at the bottom and condensers at the receiving and exit necks of the flask. This receiver was cooled in an ice-bath throughout the distillation. A forecut, mainly solvent, was taken at 92° and the manganese carbonyl steam distilled (static) at 92–100°. The product was filtered and allowed to dry in air for several hours (preferably in the dark under nitrogen). The yield was 21.0 g. (54% conversion) of yellow solid, m.p. 153–155°.

At 1000 p.s.i.g. of CO pressure under otherwise comparable conditions a 33% conversion to manganese carbonyl was obtained.

Preparation of Chromium Carbonyl.—Into a 250-ml. Magne–Dash autoclave in a dry nitrogen box was added 73 ml. of anhydrous diethyl ether, 67 ml. (0.45 mole) of triethylaluminum and 11.9 g. (0.075 mole) of chromic chloride. After assembly, the autoclave was purged twice with 600 p.s.i.g. CO and pressurized to 1000 p.s.i.g. The autoclave then was heated with stirring to 115° and maintained there for 7 hr.

After the autoclave had cooled to room temperature, it was vented slowly and the reaction mixture was carefully quenched with 20 ml. of 1:1 methanol–benzene, 100 ml. of water and 100 ml. of 1:1 water:concentrated hydrochloric acid. An additional 100 ml. of water was added and the reaction mixture then was distilled under nitrogen. The chromium carbonyl steam distilled (static) at 90–100°. The product then was filtered and allowed to dry in air. Yield was 15.2 g. (92%) of white crystalline product, m.p. 154–155°.

Preparation of Molybdenum Carbonyl.—To a 1-liter autoclave (Autoclave Engineers) fitted with stainless steel baffles and a turbine-type stirrer was added 54.8 g. (0.20 moles) of molybdenum pentachloride and 100 ml. of dry benzene. To a 700-ml. capacity reservoir (50 mm. diameter Pyrex tube) was added 200 ml. of benzene and 120 ml. (0.80 moles) of triethylaluminum under dry nitrogen. The autoclave was purged twice with 600 p.s.i.g. of CO, pressurized to 1000 p.s.i.g. of CO and heated with stirring to 50°. The triethylaluminum solution then was pumped in under slight nitrogen pressure *via* a Lapp Microflow Pulsafeeder in the course of about 1 hr. The reaction was exothermic and heating was not required during the addition of the triethylaluminum solution (maximum temperature was 68°). The mixture then was maintained at 65° an additional 2 hr.

The reaction mixture was worked up by the procedure described for the preparation of manganese carbonyl. The yield of snow-white crystalline molybdenum carbonyl was 40 g. (76% yield), m.p. 150–151° dec.

Preparation of Tungsten Carbonyl.—The same procedure as described for molybdenum carbonyl was used. The charge to the autoclave consisted of 79.4 g. (0.20 mole) of tungsten hexachloride and 100 ml. of benzene. The reservoir was charged with 200 ml. of benzene and 89.4 ml. (0.60 mole) of triethylaluminum. The initial reaction temperature was 50° and the temperature rose to 94° during the addition of the triethylaluminum solution. The mixture then was stirred an additional 2 hr. at 50°. Yield of snow-white crystalline tungsten carbonyl was 65 g. (92% yield), m.p. 169.5–170°.

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BATON ROUGE, LOUISIANA

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY]

The Preparation and Properties of Boron Phosphides and Arsenides[1]

BY FORREST V. WILLIAMS AND ROBERT A. RUEHRWEIN

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Four methods of preparation of cubic boron phosphide, BP, are described. The chemical and physical properties of BP and BAs are reported. The formation of lower phosphides and arsenides is noted.

Introduction

The semiconducting properties of silicon and germanium have generated considerable interest in the Group III-A-Group V-A compounds. The antimonides, arsenides and phosphides of indium, gallium and aluminum crystallize in the cubic zinc-blende structure, which is closely related to the diamond structure of the Group IV-A elements. Welker[2] was the first to show that these compounds

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[1] Presented in part at the 135th meeting of the American Chemical Society, Boston, Mass., April 7, 1959.

[2] H. Welker, *Naturforsch.*, **7a**, 744 (1952).

have a variety of interesting semiconducting properties. The nitrides of the Group III-A elements have the hexagonal wurtzite structure. The cubic form of boron nitride has been prepared by the application of high pressures at elevated temperatures.[3] The arsenides and phosphides have received less attention than the more easily prepared antimonides.

The literature on boron phosphide and boron arsenide is scanty. At the end of the last century, preparations of boron phosphide were reported by two routes.[4]

$$BI_3 + P_4 \xrightarrow{CS_2} BPI_2 \xrightarrow{500°} BP + I_2 \qquad (1)$$

$$BBr_3 + PH_3 \xrightarrow{25°} BBr_3{\cdot}PH_3 \qquad (2)$$

$$BBr_3{\cdot}PH_3 \xrightarrow{300°} BP + 3HBr$$

While the structure of the material prepared by these two routes naturally was unknown, work in this Laboratory showed that boron phosphide prepared by the second method is amorphous. The chemical properties of this amorphous material are vastly different from those of crystalline BP prepared by methods described later in this paper. The properties described for BP by standard references are those of the amorphous material.

It has been reported recently that products of unspecified stoichiometry with zinc-blende structures can be prepared by reaction of boron and phosphorus or arsenic at high temperatures.[5]

In the present paper some general methods of preparation and the physical and chemical properties of cubic boron phosphide and arsenide are described. The electrical and some optical properties of these materials will be discussed elsewhere.

Experimental

1. Preparative. a. From the Elements.—Weighed amounts of amorphous boron, in graphite boats, and reagent grade red phosphorus or arsenic were sealed in evacuated fused silica tubes. The boron, 99.6%, was purchased from Cooper Metallurgical Associates, Cleveland, Ohio. The phosphorus and arsenic were reagent grade. The end of the tube containing the boron was heated to 1000–1100° and the other end of the tube, containing the phosphorus or arsenic, was heated in a separate furnace to provide the desired pressure of phosphorus or arsenic. Temperatures were determined by chromel–alumel thermocouples. The boron charges were reweighed after exposure to the phosphorus or arsenic. This gave the compositions of the products.

In a typical experiment, 3.1095 g. (0.287 g. atom) of boron were heated for 50 hr. at 1100–1120° under a phosphorus pressure of 1.2 atm. The boron increased in weight by 7.69 g. (0.278 g. atom phosphorus), corresponding to a 71.2 wt. % phosphorus product. When the product was analyzed by wet chemical techniques (see below), the phosphorus content was found to be 71.2 wt. % calcd. for BP: P, 74.1%.

b. From a Metal Phosphide and Boron Trichloride.—Comparison of the heats of formation of various metal chlorides and BCl_3 suggested the possibility of preparing boron phosphide by reaction of metal phosphides with BCl_3. The volatility of $AlCl_3$ suggested AlP as a first choice. AlP was prepared by the method of White and Bushey.[6] 74.3 g. of BCl_3 was passed over 7.44 g. of crude AlP at 975°. After 3.5 hr., the AlP had decreased in weight by 1.75 g. This represented a 84.5% yield of BP, assuming a pure sample of AlP. X-Ray powder diagrams of the product showed only BP and α-Al_2O_3.

c. From BCl_3 and PH_3 or P_4 and H_2.—In a preliminary experiment, 10 g. of AlP was partially hydrolyzed with dil. H_2SO_4. The PH_3 resulting from the hydrolysis was mixed with BCl_3 and the gas stream was passed through a fused silica tube heated to 1000°; 0.54 g. of a shiny black film was recovered from the walls of the silica reactor.

Anal. Calcd. for BP: B, 25.9; P, 74.1. Found: B, P, 25.3; B, 73.7.

Owing to the inconvenience of handling PH_3 and to the fact that PH_3 dissociates into its elements above about 400–500°, the reaction of BCl_3 with P_4 and H_2 is a more convenient synthesis route for BP. Mixtures of BCl_3 and H_2 (excess) are simply passed over red phosphorus which is heated to a temperature necessary to provide a convenient pressure of phosphorus vapor. The resulting gas mixture is then passed into a reactor heated to about 1000°.

2. Analytical.—These compounds of boron resist decomposition but can be decomposed completely by a fusion (sodium peroxide) technique. Details of this fusion as applied to refractory materials will be published elsewhere by Mr. John Fairing of this Laboratory.

After fusion was complete, the phosphorus was determined gravimetrically as magnesium pyrophosphate following a molybdate and double magnesia precipitation. After removal of the phosphorus using $BaCO_3$, the boron was determined by potentiometric titration with NaOH using mannitol. The boron determination was performed on a separate aliquot of the fused sample.

Results and Discussion

The methods of preparation of BP investigated were

$$4B + P_4 \xrightarrow{1000°} 4BP \qquad (3)$$

$$AlP + BCl_3 \xrightarrow{1000°} BP + AlCl_3 \qquad (4)$$

$$BCl_3 + PH_3\ (\text{or } P_4 + H_2) \xrightarrow{1000°} BP + 3HCl \qquad (5)$$

The products obtained were analyzed by wet chemical methods and boron to phosphorus atom ratios of very nearly unity were obtained. Some typical results are shown in Table I. Analysis by X-ray diffraction of all the products showed zinc-blende structures with a lattice parameter value $a_0 = 4.537$ Å., in excellent agreement with the published value.[5]

TABLE I

ANALYSES OF REACTION PRODUCTS

Reaction	B	P	Atoms, B/P
$B + P$	27.92	71.04	1.13
$BCl_3 + PH_3$	25.33	73.74	0.983
$BCl_3 + P_4 + H_2$	25.88	74.12	1.00

Reaction 3 is slow and several days time is required for completion. The product from reaction 4 is generally contaminated (up to 5–10%) with alumina which is present in the reagent AlP. The products from reaction 5 are usually obtained as shiny black films on the walls of the reactor. In some preparations (using phosphorus and hydrogen) *via* reaction 5 translucent red films have been obtained in the down stream portion of the reactor. Impurities in the reagents are probably deposited initially.

The minimum temperature for BP formation at a significant rate *via* reaction 5, using P_4 and H_2, is in the range 700–800°. Duplicating the ex-

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(3) R. H. Wentorf, Jr., *J. Chem. Phys.*, **26**, 956 (1957).

(4) (a) H. Moissan, *Compt. rend.*, **113**, 726 (1891); (b) M. Besson, *ibid.*, **113**, 78 (1891).

(5) (a) P. Popper and T. A. Ingles. *Nature*, **179**, 1075 (1957); (b) S. Rundqvist, Abstracts of Papers presented at the Division of Inorganic Chemistry. International Union of Pure and Applied Chemistry, Paris, France, July 1957, p. 162; (c) J. A. Perri, S. La Placa and B. Post, *Acta Cryst.*, **11**, 310 (1958).

(6) W. E. White and A. H. Bushey, THIS JOURNAL, **66**, 1666 (1944).

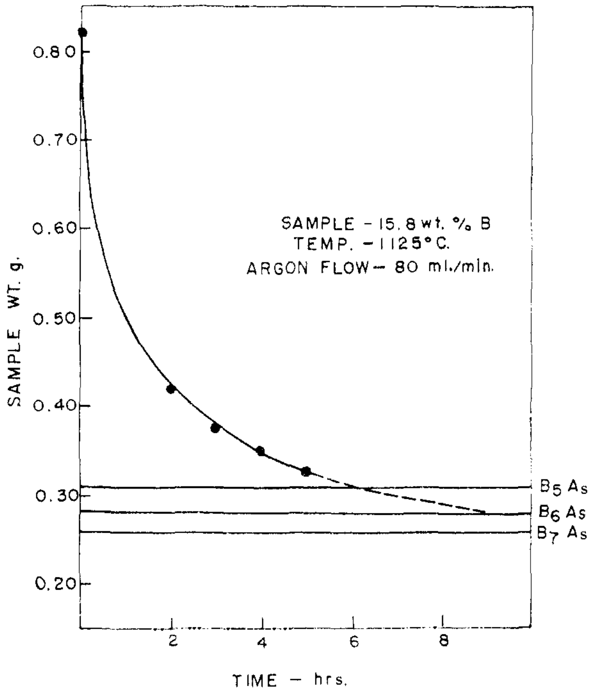

Fig. 1.

periments and excluding phosphorus showed that no boron is formed at 900°, indicating that BP formation does not proceed through a reduction of BCl_3 to boron. Neither was it possible to prepare BP from only BCl_3 and P_4. The reaction intermediate may be a species such as $BPCl_2$ (eq. 1).

Two products can be prepared from boron and arsenic, depending upon the temperature and arsenic pressure. At 700–800° and arsenic pressures greater than one atmosphere a cubic material with a boron to arsenic atom ratio approaching unity is obtained. The lattice constant of this cubic material is 4.777 Å. At 1000–1100° and arsenic pressures less than one atmosphere compositions of boron to arsenic of 5–7 to 1 are obtained which have an orthorhombic structure. These compositions did not show the cubic phase by X-ray diffraction. This orthorhombic structure also was obtained by Post[5c] by evaporation of arsenic from the cubic material.

When BP is heated at elevated temperatures (above 1100°) under reduced pressure (less than about 1 mm.), phosphorus is lost. The composition of the light grey residue has been tentatively established as B_6P,[7] *via* a thermogravimetric technique. In addition, crystals analyzing as B_6P by wet chemical methods have been prepared *via* eq. 5. No evidence for the phosphide, B_5P_3, described by Moissan,[4a] has been detected in the present investigation.

The equilibrium dissociation pressure of BP

$$6BP \longrightarrow B_6P + 5/2P_2 \qquad (6)$$

was measured in a semi-quantitative fashion by a gas saturation method and was 6.3, 12.6 and 24.2 mm. at 1200, 1250 and 1300°, respectively. Owing to the low accommodation coefficient of phosphorus, these data may be in error by an order of magnitude. These data can be expressed as

$$\log P(\text{mm.})_{\text{diss.}} = \frac{-13.7 \times 10^3}{T} + 10.1 \qquad (7)$$

In a similar fashion. BAs loses arsenic but at much lower temperatures. Again. a more stable lower arsenide with an orthorhombic structure is formed. The results of a thermogravimetric study are shown in Fig. 1. This result together with the preparative results, suggests a composition of $B_{6-7}As$.

It has been reported also that silicon forms an orthorhombic boride, B_6Si.[8] Hexaborides of the alkaline earth and rare earth metals are well known.

All of the above compounds of boron are extremely inert to corrosive reagents. From their position in the periodic classification, they might be expected to possess refractory-like properties, especially the phosphides.

BP, B_6P and B_6As are not attacked by boiling concentrated mineral acids. BAs is decomposed by hot, concentrated HNO_3. BP can be refluxed in aqua regia without detectable weight change. These compounds are resistant to boiling aqueous alkali solution and elevated temperatures are necessary before attack by molten NaOH is evident. BP is resistant to oxidation in air up to about 800–1000°. The product of oxidation (as shown by X-ray diffraction) is BPO_4, which is nonvolatile to about 1500°. BAs can be recovered from reaction mixtures of BAs and B_6As, prepared from the elements, by treatment with hot, concentrated HNO_3. The phosphides of boron can be chlorinated at about 500°.

By analogy with diamond, and cubic boron nitride, which are harder than diamond, cubic boron phosphide might be expected to be harder than silicon carbide. Experimentally, quartz, agate, cemented tungsten carbide, and possibly, sapphire were definitely abraded by BP. Abrasion of SiC was not completely verified since the specimens of BP available were somewhat porous in structure.

Preliminary measurements on the optical transmission of thin films of BP indicate a forbidden energy gap of about 5.9 electron-volts. It can, thus, be predicted that pure boron phosphide should be colorless, much like diamond.

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[7] Personal communication from B. A. Gruber, this Laboratory.

[8] C. F. Cline, *Nature*, **181**, 476 (1958).