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# Group IV Analogs and High Pressure, High Temperature Synthesis of B$_2$O[1]

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An "unsymmetrical" analog of graphite, B$_2$O, has been synthesized by reduction of B$_2$O with B and Li and also be the oxidation of B with KClO$_3$. Application of pressures ranging from about 50,000 to 75,000 atm. combined with temperatures from about 1200 to 1800° is required for these syntheses. The new B$_2$O compound has hexagonal crystal symmetry with $a = 7.98$ and $c = 9.09$ Å. and has a density of about 2.24 g./cm.$^3$. The synthesis of this new material points up the possibility of synthesizing a host of other unsymmetrical group IV analogs that have heretofore been overlooked. These analogs have the following unit formulas when two kinds of atoms are involved: I-V$_3$, I$_2$-VI$_3$, II-V$_2$, II$_3$-VII$_2$, III$_2$-VI, and III$_3$-VII. The well-known symmetrical group IV analogs, of course, have the unit formulas I-VII, II-VI, and III-V.

## Introduction

The elements with principal quantum number $n = 2$ (Li, Be, B, C, N, O, F) exhibit a tendency to form strongly directed bonds, particularly tetrahedral bonds, when the electronegativity difference $\Delta X$ between combining atoms is not too large. Diamond is the foremost example of a tetrahedrally-bonded, crystalline structure, and, after about 125 years of scientific effort, was finally synthesized in the year 1954.[2] The first synthesis utilized a catalyst together with high pressure and temperature to convert graphite to diamond. Several years later, graphite was converted directly to diamond without the aid of a catalyst by dynamic pressure[3] and also by static pressure[4] at high temperature. Much higher pressure and temperatures were required in the direct conversion than when a catalyst was present.

The compound BN ($\Delta X = 1.0$) has long been known in a hexagonal, layer-lattice form related to graphite. This material was converted to a diamond-like form by means of high pressure and high temperature in the presence of a catalyst just a few years ago.[5] Still more recently the diamond-like form of BN was prepared directly from the hexagonal form by utilizing higher pressures and temperatures than were needed when a catalyst was used.[6]

The compound BeO ($\Delta X = 2.0$) is only known in one crystalline form—a hexagonal wurtzite structure in which tetrahedral bonding prevails. It is likely, however, that the bonding in BeO is somewhat more ionic than covalent. The compound LiF ($\Delta X = 3.0$) is known only in an octahedrally coordinated rock salt structure in which the bonding is essentially ionic.

The three compounds BN, BeO, and LiF are composed of elements symmetrically arranged each side of carbon in the periodic table. These compounds are isoelectronic with carbon; *i.e.*, the average number of valence electrons per atom is four. Consequently, they tend to simulate the properties of carbon. The compound BN, being closest to carbon, and having the smallest $\Delta X$, imitates the properties of carbon quite well. Some properties of carbon (in the diamond form) are moderately well-displayed in BeO, while LiF bears very little resemblance to either the graphite or diamond forms of carbon.

In recent years, silicon and germanium have assumed great importance because of their semiconducting properties. These properties are intimately dependent upon the tetrahedral bonding that exists in crystals of these elements. To obtain other semiconducting materials that simulate the properties of silicon and germanium of other group IV elements, such tetrahedrally bonded substances as AlP, GaAs, ZnS, CdTe, InSb, and AgI have been prepared. High pressure is not needed to synthesize any of the known I-VII, II-VI, and III-V compounds (group IV analogs) other than diamond-like BN.

## Unsymmetrical Carbon Analogs

The above "symmetrical" group IV analogs are a relatively obvious type of compound and much work has been done on their synthesis and properties. The less obvious, "unsymmetrical" group IV analogs, however, have apparently never before been considered. The unsymmetrical carbon analogs are listed in Table I together with $\Delta X$. the symmetrical isoelectronic analogs are also listed for comparison.

Table I
Isoelectronic, Two-Atom Analogs of Carbon
Listed with $\Delta X$

| Symmetrical | Unsymmetrical | |
|---|---|---|
| BN (1.0) | $B_2O$ (1.5) | $B_3F$ (2.0) |
| BeO (2.0) | $BeN_2$ (1.5) | $Be_3F_2$ (2.5) |
| LiF (3.0) | $LiN_3$ (2.0) | $Li_2O_3$ (2.5) |

## Synthesis of $B_2O$

The authors have succeeded in preparing the unsymmetrical compound $B_2O$ as a graphite analog by high pressure, high temperature methods. Attempts to make this new material at 1 atm. have not met with success. The high pressure, high temperature synthesis has been accomplished by reducing $B_2O_3$ with B or Li and also by oxidizing B with $KClO_3$. A convenient synthesis utilizes a mixture of B and $B_2O_3$ powders in the reaction $4B + B_2O_3 \rightarrow 3B_2O$. The reacting powders are ground together for 24 hr. in a ball mill and are then compressed into a small cylindrical specimen for use in the Tetrahedral Press.[7,8] The specimen is contained
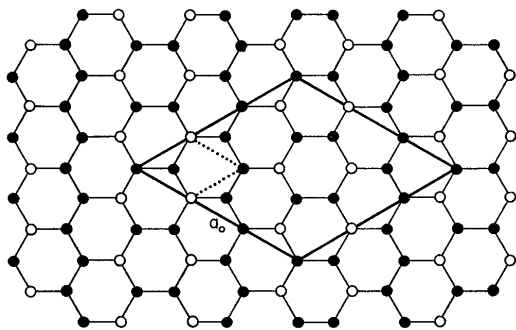


Figure 1.—A possible hexagonal lattice for $B_2O$. Open circles represent the centers of oxygen atoms; solid circles the centers for boron.

in a hexagonal BN capsule and is indirectly heated. The pyrophyllite tetrahedral cell geometry and resistance strip-heater arrangement have been described elsewhere.[9] Pressure from

about 50,000 to 75,000 atm. are used at temperatures from about 1200 to 1800°. After pressure has been applied, the temperature is increased to the desired value in about 5 sec. Temperature is held for about 3 min. and then the heating current is switched off to quench the product to room temperature. The product is light reddish brown in color and has a measured density of 2.24 ± 0.04 g./cm.[3] Powder X-ray diffraction patterns indicate hexagonal crystal symmetry with unit cell dimensions $a = 7.98$ and $c = 9.09$ Å. This, together with the density, suggests a layer-lattice structure related to graphite.

A hexagonal layer of a possible $B_2O$ lattice is shown in Figure 1. A second identical layer could be located above the first layer a distance of $c/3$ but shifted along the a axis by the distance $a/3$. A third layer could similarly spaced and shifted above the second layer to give an . . . ABCABC . . . layer repeat. The theoretical density of this structure would be 2.24 g./cm.[3], which agrees with the measured $B_2O$ density. The suggested unit cell contains 36 boron and 18 oxygen atoms. In this structure, $a$ for $B_2O$ is 8% long that $3a$ for graphite and $c$ for $B_2O$ is 10% shorter than the value for $c$ for "rhombohedral" graphite. In moving along the a direction of the hexagonal layer lattice depicted in Figure 1, it is noted that the linear atom sequence is . . . BOBBOBBOB . . . , which corresponds to the unit formula $B_2O$ and gives a sequential repeat after every third atom. In graphite, the corresponding sequence is . . . CCCCCCCCC . . . , which, of course, gives a repeat after very carbon atom. Consequently, the $a$ axis repeat distance in graphite is only about one-third of that for $B_2O$ and the graphite layer cell (completed by the dotted lines) has only about one-ninth the area of the $B_2O$ layer cell. For comparison, structural data for "rhombohedral" graphite, hexagonal BN, and hexagonal $B_2O$ are given in Table II.

Table II
Structural Data for Rhombohedral Graphite and
Hexagonal BN and $B_2O$

| Substance | $a$, Å. | $c$, Å. | Inter-planer spacing ,Å | Av. atom—atom dist. in plane, Å |
|---|---|---|---|---|
| Rhombohedral graphite | 2.45 | 10.05 | 3.35 | 1.42 |
| Hexagonal BN | 2.50 | 6.66 | 3.33 | 1.45 |
| Hexagonal $B_2O$ | 7.98 | 9.09 | 3.03 | 1.54 |

Pressures of about 120,000 atm. have been utilized in attempts to synthesize a diamond-like form of $B_2O$. So far, faint indications of a diamond-like form have been evident in some powder X-ray diffraction patterns and in scratch tests. Although this evidence is quite inconclusive, a final, clean-cut synthesis of diamond-like $B_2O$ is expected to be achieved. It is also contemplated that graphite and diamond-like forms of $BeN_2$, which is symmetrically related to $B_2O$, will eventually be synthesized. For the compounds $LiN_3$ and $B_3F$, $\Delta X = 2$, the same value for BeO. Therefore, tetrahedral bonding may be possible in these compounds. As is the case with BeO, however, the bonding would probably be more ionic than covalent. In $Li_2O_3$ and $Be_3F_2$, $\Delta X = 2.5$. This large difference in electronegativity may preclude the formation of diamond-like or graphite-like bonds under ordinary circumstances. However, high pressure tends to decrease and level electronegativities and consequently lowers $\Delta X$ values. This lowering of $\Delta X$ would favor the formation of covalent bonds at a sufficiently high pressure. Thus, if diamond- or graphite-like bonds were formed at high pressure and temperature, they might survive a return to room temperature and pressure. At a sufficiently high pressure, even LiF, with $\Delta X = 3$, might assume appreciable covalent bonding. However, covalently-bonded LiF could probably not remain as a metastable entity at atmospheric pressure.

### Silicon Analogs

What has been said above, in a general way, for carbon analogs also holds for silicon and for other group IV elements. For reference, the silicon analogs, together with $\Delta X$, are listed in Table III. The symmetrical compounds AlP (tetrahedrally-bonded, sphalerite structure), MgS (rock salt structure), and NaCl (rock salt) are all well-known. However, none of the unsymmetrical compounds is known. With the increased metallicity of the $n = 2$ period, the tendency to form strong, directed bonds probably disappears when $\Delta X$ exceeds 1.5. An increase in principal quantum number increases the degree of metallization of a bond and decreases bond directionality.[10] The compounds $MgP_2$, $NaP_3$, $Al_2S$, MgS, and $Al_3Cl$ should be capable of forming covalent, directionally-bonded structures. Attempts to prepare them from stoichiometric mixtures of the elements under high pressure, high temperature conditions

would certainly be worthwhile. It might be noted here that catalysts might be efficacious in these syntheses. This is certainly true in the synthesis of diamond and of diamond-like BN. However, experience with catalysts in high pressure synthesis is very limited and no guidelines can be offered to the interested researcher. Suffice it to say that molted transition metals aid diamond synthesis from graphite, alkali and alkaline earth metals and nitrides aid the synthesis of diamond-like BN from hexagonal BN, and water and a host of low

Table III
Isoelectronic, Two-Atom Analogs of Silicon
Listed with $\Delta X$

| | | |
|---|---|---|
| AlP (0.6) | $Al_2S$ (1.0) | $Al_3Cl$ (1.5) |
| $MgP_2$ (0.9) | MgS (1.3) | $Mg_3Cl_2$ (1.8) |
| $NaP_3$ (1.3) | $Na_2S_3$ (1.6) | NaCl (2.1) |

melting salts and oxides assist in the formation of dense forms of $SiO_2$ and silicate minerals from less dense reactants. The remaining compounds of Table III, $Mg_3Cl_2$ and $Na_2S_3$, night form strong directed bonds under sufficiently high pressure but would not likely survive a return to atmospheric pressure.

### Cross Compounds

There is, of course, a possible series of group IV "cross compound" analogs between the elements of $n = 2$ and $n = 3$, between those of $n = 2$ and $n = 4$, and so on. An average principal quantum number $\bar{n}$ for cross compounds, where $n_i$ is the principal quantum number of an atom of kind $i$ and $c_i$ is the number, per formula unit, of atoms of this kind, can be assigned as follows: $\bar{n} = \Sigma c_i n_i / \Sigma c_i$.[10] Cross compounds of $n = 2$ and $n = 3$ atoms, together with $\bar{n}$ and $\Delta X$, are listed in Table IV.

The symmetrical compounds SiC, BP, AlN, and BeS and the unsymmetrical compound NaN3 are all known in structures possessing tetrahedral bonding. These can all be prepared at atmospheric pressure. However, some of them can be prepared more conveniently under high pressure, high temperature conditions. The high pressure product is usually more crystalline and the macroscopic density more nearly approaches the theoretical (X-ray) density than products formed at 1 atm. Crystalline BP, for example, is easily synthesized from the intimately mixed elements at about 10,000 atm. at temperatures around 1500°. These conditions are very easily

achieved in an internally heated Tetrahedral Press, Belt, or Piston-Cylinder apparatus.

Table IV
Cross Compounds, Composed of Elements with
$n = 2$ and $n = 3$

| Compd. | $\Delta X$ | $\bar{n}$ | Compd. | $\Delta X$ | $\bar{n}$ |
|---|---|---|---|---|---|
| LiCl | 2.0 | 2.5 | NaF | 3.1 | 2.5 |
| $Li_2S_3$ | 1.5 | 2.6 | $Na_2O_3$ | 2.6 | 2.4 |
| $LiP_3$ | 1.1 | 2.8 | $NaN_3$ | 2.1 | 2.2 |
| $Be_3Cl_2$ | 1.5 | 2.4 | $Mg_3F_2$ | 2.8 | 2.6 |
| BeS | 1.0 | 2.5 | MgO | 2.3 | 2.5 |
| $BeP_2$ | 0.6 | 2.7 | $MgN_2$ | 1.8 | 2.3 |
| $B_3Cl$ | 1.0 | 2.2 | $Al_3F$ | 2.5 | 2.8 |
| $B_2S$ | 0.5 | 2.3 | $Al_2O$ | 2.0 | 2.7 |
| BP | 0.1 | 2.5 | AlN | 1.5 | 2.5 |
| CSi | 0.7 | 2.5 | SiC | 0.7 | 2.5 |

The well-known compounds MgO, LiCl, and NaF crystallize in the rock salt structure. None of the remaining compounds in Table IV is presently known. Other things being equal, the strongest directed bonds would be expected to form in cross compounds having small values of both $\bar{n}$ and $\Delta X$. Consequently $B_2S$ and $B_3Cl$ (Table IV) are particularly good candidates for attempted synthesis in graphite or diamond-like forms. The compounds $Be_3Cl_2$, $MgN_2$, and $BeP_2$ would be expected to form reasonably strong directed bonds, while $Li_2S_3$, $LiP_3$, and perhaps $Al_2O$ would form weaker directed bonds. The remaining compounds would be poor candidates for possible synthesis as group IV analogs.

**Conclusions**

The proposed, directionally-bonded compounds discussed above would have relatively high melting or sublimation temperatures, high hardness and high thermal conductivity (in tetrahedrally bonded structures), and good semiconducting properties. Additional tables of group IV analogs (similar to Tables I, III, and IV) can be constructed by involving $n = 4, 5, 6$, and $7$ atoms and by considering the "B" periodic grouping of elements as well as the "A." The above ideas can also be extended to include more than two kinds of atoms in a compound. This greatly increases the number of isoelectronic types. For example, if three different kinds of atoms with $n = 2$ are used to make carbon analogs there are 27 possible compounds. (With two kinds of atoms there are only 9 possible compounds.)

The above group IV analogs should prove to be of interest to the high pressure researcher for a number of reasons: (1) Only a limited number of these compounds are known. Conventional synthesis techniques have not produced them. Therefore, it would seem worthwhile to utilize the newly available tool of high pressure, high temperature to attempt their synthesis. (2) Diamond and diamond-like BN and probably hexagonal $B_2O$ are thermodynamically stable only at high pressure. Consequently, high pressure is required for their synthesis. Rate considerations allow these materials to remain in a metastable state under room conditions when once formed. It is anticipated that many of the proposed compounds will also only be stable while under high pressure. High temperature is also required because the breaking and forming of strong, directed bonds is involved. Such bonds are only mobile at high temperature and, in addition, often require the presence of a catalyst to orient atoms for bond formation properly. (3) Regardless of the thermodynamic requirements for the synthesis of a given group IV analog, high pressure is often required just to "contain" reactants which may be quite volatile at the required temperature. Today's high pressure, high temperature equipment is admirably capable of doing this job. Substances such as sulfur are easily contained at temperatures of 1500°.

It is hoped that this paper, in calling attention to the unsymmetrical group IV analogs, will incite inorganic chemists to attempt their synthesis. These compounds far outnumber the symmetrical analogs and should be very important to solid state technology.

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