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Properties of B_2O: An unsymmetrical analog of carbon

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The compound B_2O has been proposed to be an isoelectronic analog of carbon. The high-temperature, high-pressure syntheses of both "graphitelike" and "diamondlike" phases of B_2O have been reported, although the material has not been well characterized. We have applied the density-functional total-energy method to two candidate structures for this material. Both structures are based on a diamond lattice, but differ in the direction of stacking of the boron and oxygen planes. In order to find the equilibrium structures, we have relaxed both the internal coordinates and the unit-cell parameters. We find that one structure, proposed previously, is unstable, while the other has a bulk modulus of approximately 2 Mbar, comparable to SiC.

I. INTRODUCTION

Diamond has long been valued for its superlative properties. Its bulk modulus and mechanical hardness are the largest of any known materials. Other important properties include high thermal conductivity, low mass density, large electronic band gap, and high breakdown voltage.[1] Diamond surfaces are chemically stable and also have very low friction. There has been a continuing search for materials with similarly optimal properties. The best known of these is cubic BN, which has a bulk modulus and mechanical hardness second only to diamond.

Diamond was first synthesized from graphite in 1955 by applying high pressure and high temperature in the presence of a liquid-metal catalyst.[2] This has lead to commercially viable processes for manufacturing abrasive grits containing diamond grains up to 1 mm. The direct synthesis without the need for catalysts has also been reported,[3] as well as similar processes for cubic BN.[4,5] In the 1980's vapor deposition methods for diamond were perfected,[6,7] leading to a variety of new diamondlike carbon materials, such as amorphous carbon and hydrogenated amorphous carbon.[7] This has given further impetus for the search for related compounds having similar properties.

Hall and Compton[8] have suggested that materials such as BN and BeO be classified as "symmetrical" analogs of carbon, since they are composed of elements symmetrically disposed around carbon in the Periodic Table. They have also pointed out that there exists a class of "unsymmetrical" analogs of carbon. Of these B_2O and BeN_2 are the most likely to form tetrahedral crystals, since they are composed of elements with a comparatively small difference in electronegativities, thus favoring covalent bonding. The authors attempted a high pressure high temperature synthesis of B_2O from B and B_2O_3 powders, based on the reaction $4B + B_2O_3 \rightarrow 3B_2O$. The powders are compressed to a pressure of 50–75 kbar in a tetrahedral press, and then heated to 1200–1800 °C. They obtain a reddish-brown sample having

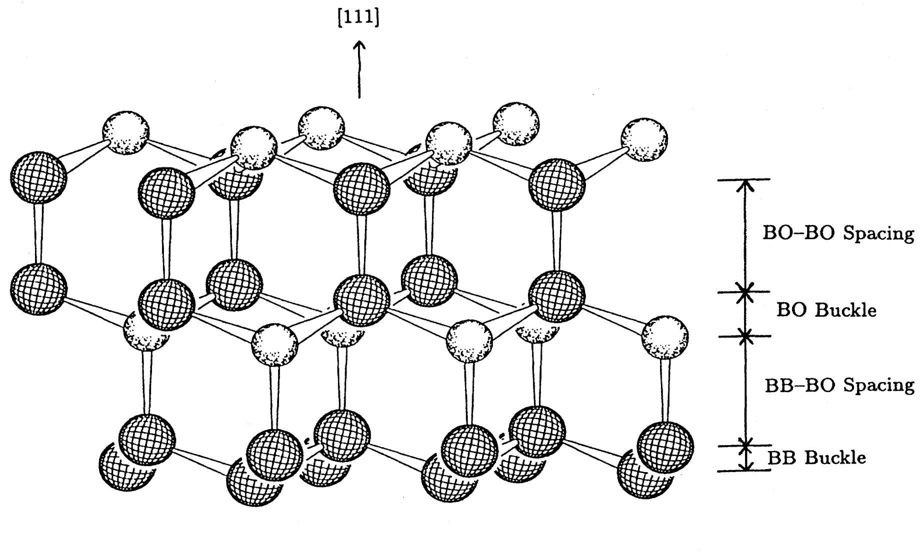

FIG. 1. 111 structure proposed by Endo *et al.* (Ref. 9).

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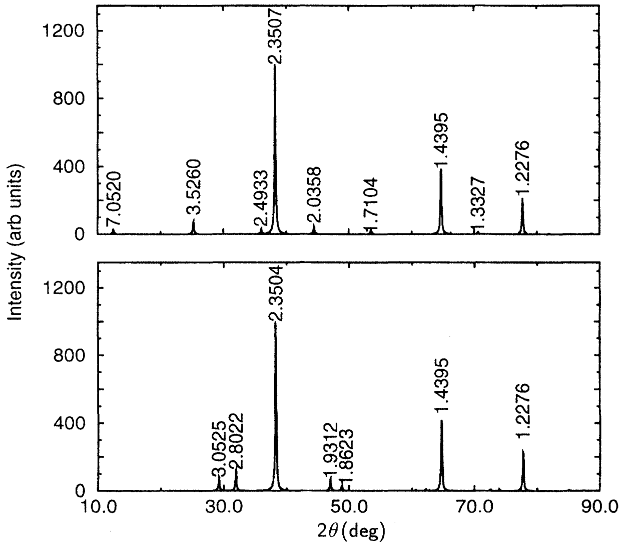

FIG. 2. Computed x-ray-diffraction powder pattern for the ideal forms of the 111 structure (upper panel) and the 100 structure (lower panel). *d* spacings (Å) are indicated above each peak.

a mass density of 2.24 g/cm^3. The x-ray powder diffraction indicates hexagonal crystal symmetry with $a = 7.98$ Å and $c = 9.09$ Å. They conjecture that the material has a layered structure similar to graphite. In an attempt to obtain a diamondlike modification, they repeated the synthesis to pressures up to 120 kbar, but were able to find only trace evidence for a second phase.

Endo *et al.*[9,10] have attempted a different synthesis, based on the oxidation of BP by CrO_3. In this work, the precursors were separated by a Zr foil within a gold capsule, then compressed to 40 kbar and heated to 1000 to 1300 °C. They obtain dark brown crystals, 50–110 μm in length, having a density of 2.48 g/cm^3. A powder x-ray-diffraction pattern is reported, although a full structural refinement was not carried out. They have proposed a possible crystal structure consisting of diamond lattice sites with planes of O alternating with two planes of B along the [111] crystallographic direction. When the trigonal lattice parameters are chosen to be $a = 2.879$ Å and $c = 7.052$ Å, the peaks in the predicted x-ray powder pattern match some of the peaks seen in the experimental pattern.[9]

In this paper we present a theoretical investigation of this material. We use the density-functional total energy method to study two possible diamondlike structures for B_2O. The first structure we examine is the one proposed by Endo *et al.*, while the second is also based on a diamond lattice, but with stacking of the B and O planes in a different crystallographic direction. For a particular choice of lattice constants, this structure also exhibits a theoretical powder pattern with peaks matching some of the ones seen experimentally. We determine the stability of both structures, and also compute the electronic structure and bulk modulus.

TABLE I. Dependence of total energy on sampling of the Brillouin zone. The 111 structure with lattice constants as reported by Endo *et al.*[10] is used for this test.

Sampling of the irreducible BZ	*E* eV/B_2O
Γ only	-573.972
$(0,0,\frac{1}{2})$ only	-588.117
2 special points	-585.346
10 special points	-585.255

II. METHODS

The total energy of the system of interacting ions and electronic wave functions is evaluated using density functional theory[11] with the local density approximation[12] for the exchange and correlation energies. The wave functions were expanded in a basis set of plane waves with kinetic energies up to 50 Ry. The interaction between the ionic cores and the valence electrons is modeled using the pseudopotential approximation.[13,14] The nonlocal part of the pseudopotential is evaluated using a fully separable form.[15] Summations over the Brillouin zone are approximated by sampling at special points.[16] The variational minimum of the total energy is found by a preconditioned conjugate gradient method.[17] Forces on the atoms are obtained from the Hellman Feynman theorem, and these are relaxed using a damped molecular dynamics.

A separate method was used to compute the electronic band structure. This method is also a self-consistent implementation of density functional theory with the local density approximation, but the basis consists of localized atomic orbitals. For the calculations reported here, we used *s* and *p* orbitals for each atom. The matrix elements are computed using fast Fourier transform (FFT) methods, and the Kohn-Sham equations are solved by direct diagonalization.

III. 111 STRUCTURE

A possible structure for B_2O was proposed by Endo *et al.*[10] This structure can be constructed by considering the atomic planes along the [111] direction in a diamond lattice, as shown in Fig. 1. The structure for B_2O consists of three double layers: one double layer is composed entirely of B, while the other two are composed of equal numbers of B and

TABLE II. Relaxation of the 111 structure proposed by Endo *et al.*[10]

Cell/Basis	*a* (Å)	*c* (Å)	*E*/B_2O (eV)	BB Buckle	BO Buckle	BB-BO Spacing	BO-BO Spacing
Ideal/Ideal	2.879	7.052	-585.310	0.5876	0.5876	1.7630	1.7630
Ideal/Relaxed	2.879	7.052	-585.368	0.3182	0.5260	1.9959	1.6895
Relaxed/Relaxed	2.609	∞	-586.707	0.3784	0.5583	∞	1.7427

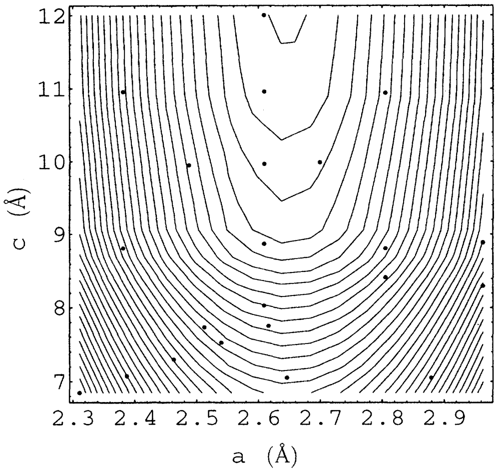

FIG. 3. Energy surface as a function of a and c for the 111 structure. Dots indicate points sampled. The contours were obtained by interpolation.

O atoms. The unit cell is hexagonal, and the space group is $P\bar{3}m1$. Two of the boron atoms occupy the $2d$ position, $(2/3,1/3,+z_1)$ and $(1/3,2/3,-z_1)$, the remaining two boron atoms occupy the $2c$ position, $(0,0,+/-z_2)$, and the oxygen atoms occupy another $2d$ position, $(2/3,1/3,+z_3)$ and $(1/3,2/3,-z_3)$. Ideal values for the internal coordinates ($z_1=1/24=0.042$, $z_2=3/8=0.375$, $z_3=7/24=0.292$) and an ideal aspect ratio for the cell ($c/a=\sqrt{6}$) results in a diamondlike lattice. Endo *et al.* reported lattice constants of $a=2.879$ Å and $c=7.052$ Å for their sample. Using these, a theoretical powder pattern can be generated, shown in Fig. 2. The three major peaks of this pattern match three peaks in the pattern reported by Endo *et al.*,[9] both in position and intensity.

We begin by examining the crystal with the structural parameters reported by Endo *et al.* We have determined the number of points that are needed to sample the Brillouin zone by computing the total energy for several different levels of sampling. As shown in Table I, we find the two special k points in the irreducible Brillouin zone are sufficient to obtain an accuracy of 0.1 eV/B_2O for the total energy, which we consider adequate for this initial study. We use this sampling to perform the relaxation of the structure, although as we will see below a more accurate sampling is needed in order to compare to the other proposed structure. To test the accuracy of the 50 Ry basis set, we have repeated the calculation using a 90 Ry basis set, which is known to give well-converged results for oxides.[14] We find that the forces on the atoms change by less than 5%.

TABLE III. Relaxation of the 100 structure proposed here.

Cell/Basis	a (Å)	c (Å)	E/B_2O (eV)
Ideal/Ideal	2.879	12.215	-585.474
Relaxed/Ideal	2.845	10.934	-585.878
Relaxed/Relaxed	2.845	10.934	-585.882

Upon examining the forces on the atoms in this configuration we find that the system is not relaxed. If we allow the forces to relax the atoms we find that the layers move relative to each other. The forces and resulting relaxation are entirely along the z axis. The mixed boron-oxygen layers move closer together, and away from the pure boron layer, which becomes isolated. The new internal coordinates are $z_1=0.023$, $z_2=0.380$, and $z_3=0.306$. The change in structure is summarized in Table II.

In order to find the equilibrium values for the lattice constants, we have computed total energy of the crystal for a number of values of a and c, maintaining constant cutoff energy for the basis set. For each pair of a and c we allow the atomic positions to relax within the cell. The results are shown in Fig. 3. We find that the energy of the system can be systematically lowered by increasing c. As the c axis is lengthened, we find that the atoms segregate into a B layer and a BO double layer, as shown in Fig. 4. At the largest

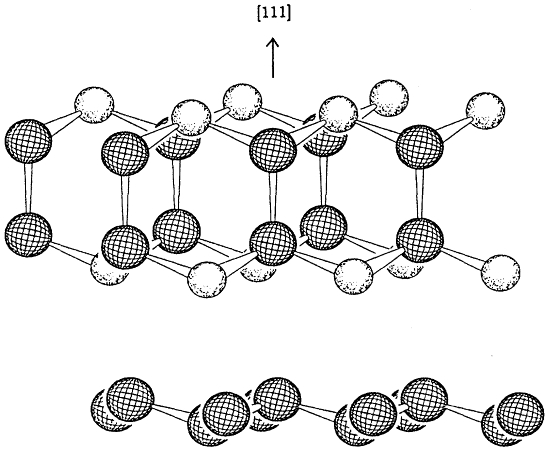

FIG. 4. Internal relaxation of the 111 structure for $c=12.00$ Å.

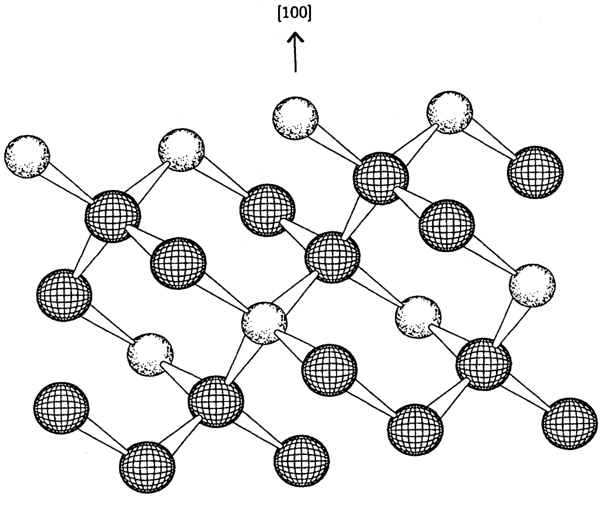

FIG. 5. 100 structure proposed here.

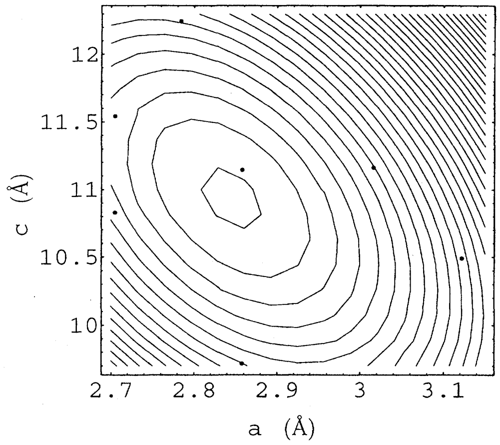

FIG. 6. Energy surface as a function of a and c for the 100 structure. Dots indicate points sampled. The contours were obtained by fitting the data to Eq. (4.1).

value of c investigated (12.00 Å), the layers are separated by 4.38 Å, which is much larger than the interlayer separation (3.35 Å) in graphite. Since we do not find any bonding out to such a large distance, we conclude that the system is unstable towards decomposition. The structures of the segregated layers, however, are well defined at this large separation, and are summarized in Table II. There does not appear to be a simple chemical explanation for this behavior. Although several oxides of boron do exist (B_2O_3, B_6O), there are none with stoichiometry BO. The structure of the pure boron layer does not resemble any known phases of boron.

IV. 100 STRUCTURE

It is possible to construct another diamondlike lattice by stacking the B and O planes in the [100] direction, as shown in Fig. 5. This structure has a body-centered tetragonal unit cell, with space group $I\bar{4}m2$. Initially we choose lattice constants $a=2.879$ Å and $c=3\sqrt{2}a=12.215$ Å, so that all the bond lengths are 1.763 Å, equal to the average value reported by Endo *et al.* The theoretical powder x-ray-diffraction pattern for this choice is shown in Fig. 2. The three major peaks in this pattern are also seen in the theoretical pattern for the 111 structure (Fig. 2), as well as in the experimental pattern reported by Endo *et al.*[9]

We have computed the total energy for several values of a and c, keeping the ideal basis fixed. The energies obtained are plotted in Fig. 6. We assume that near the minimum the energy surface can be approximated as quadratic in a and c:

$$E(a,c)=E_0+h_{11}(a-a_0)^2+2h_{12}(a-a_0)(c-c_0)+h_{22}(c-c_0)^2. \tag{4.1}$$

The function that results from fitting the coefficients to our data is shown by the contours in Fig. 6. We find that the equilibrium lattice constants are $a=2.845$ Å and $c=10.934$ Å, showing a significant decrease in the c/a ratio from the ideal value. The cohesive energy at the minimum is 19.95 eV/B_2O.

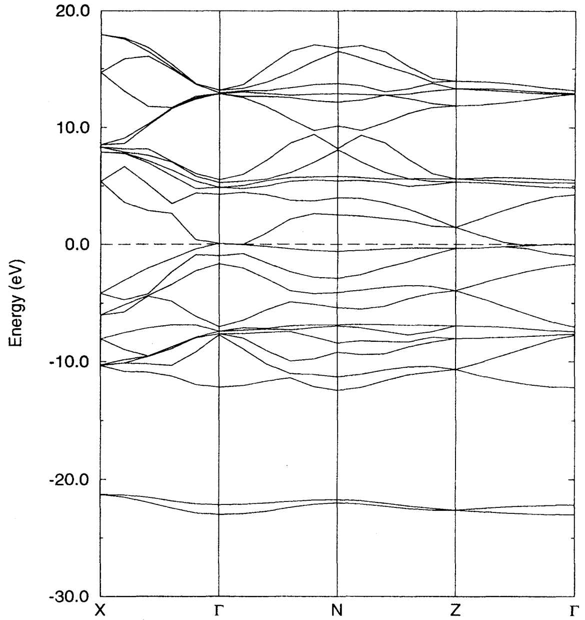

FIG. 7. Computed electronic band structure for the 100 structure with optimized lattice constants and ideal internal coordinates.

From the energy expression, Eq. (4.1), we can derive an equation of state. For a tetragonal system, pressure can be defined by requiring

$$P=\frac{F_{aa}}{a^2}=\frac{F_{ac}}{ac}, \tag{4.2}$$

where $F_{aa}=-\partial E/\partial c$ is the force on the basal plane of the cell and $F_{ac}=-\frac{1}{2}\partial E/\partial a$ is the force on a lateral plane. This can be solved to obtain the equilibrium value for c as a function of a under conditions of constant pressure. Thus we can compute both P and V as function of the parameter a. A quadratic fit of the resulting parametric curve gives $B=2.05881$ Mbar.

We have also computed the band structure, shown in Fig. 7, for the cell with optimal lattice constants. We find that the valence and conduction bands are degenerate at the Γ point.

The results reported thus far have been obtained with the internal parameters of the structure held fixed at ideal values. If we remove this restriction by allowing the internal degrees of freedom to relax, we find that each of the four B atoms distorts by 0.01 Å away from ideal diamondlike positions, while the two O atoms remain stationary. The motion of each B atom is entirely along the z axis, and in the direction of the nearest B neighbor. This results in a drop in total energy of 0.004 eV/B_2O. The band structure remains essentially identical to Fig. 7, with the exception of the Fermi level which drops by 0.26 eV, causing two small pockets of holes to appear at Γ. Thus we conclude that this structure is semimetallic.

If we compare the total energy of the segregated 111 structure to that of the 100 structure (with ideal basis) we find that the first structure is more stable by 0.825 eV/B_2O. Since comparisons of energies of different structures is particularly sensitive to Brillouin zone sampling, we have recomputed the total energies using a denser sampling. Using 16 special points in the irreducible wedge for the segregated 111 structure, we obtain a total energy of -586.099 eV/B_2O, and using 13 points in the irreducible wedge for the 100 structure, we obtain -586.435 eV/B_2O. We therefore conclude that the 100 structure is energetically favored by 0.336 eV/B_2O.

V. CONCLUSIONS

We have examined a candidate structure for B_2O (the 111 structure) that was previously proposed to be consistent with an experimental powder diffraction pattern. We find that this structure is not stable. In particular, we find that as the structure relaxes (allowing for relaxation of both the unit cell parameters and the internal coordinates), the material segregates into layers of BO and B. Thus it is unlikely that this structure is the one synthesized experimentally.

We have proposed a second tetrahedral phase for B_2O (the 100 structure) and examined its properties. Using $a=2.879$ and the ideal $c/a=3\sqrt{2}$ we find a theoretical powder pattern that is also consistent with the experimental pattern. When we relax the cell parameters, we find the equilibrium lattice constants to be $a=2.845$ and $c=10.934$. Since the c axis contraction (10%) is greater than the error typically associated with this kind of calculation, we cannot positively identify this structure as the one seen experimentally. We also find that the internal coordinates do not relax significantly from their ideal values, and that the bulk modulus is 2.1 Mbar, comparable to that of SiC. The band structure indicates semimetallic character. Finally, we find that this structure is energetically more stable than the segregated 111 structure.

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