PHYSICAL REVIEW B **82**, 094119 (2010)

Design of three-dimensional solid-state boron oxide networks: *Ab initio* calculations using density functional theory

Frederik Claeyssens[*,†]
Engineering Materials Department, Biomaterials and Tissue Engineering Group, Kroto Research Institute, University of Sheffield, Broad Lane, Sheffield S3 7HQ, United Kingdom

Neil L. Allan,[*,‡] Nicholas C. Norman, and Christopher A. Russell
School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, United Kingdom

(Received 18 August 2010; published 30 September 2010)

Most binary oxides are classic examples of densely packed systems; a given compound generally adopts only a small number of structures. Here for boron monoxide (BO) in contrast we demonstrate the existence of many low, equienergetic forms, consistent with the limited experimental NMR data. All are dominated by six-membered rings connected in various ways; there is considerable variation in B-O-B angles and torsion angles but not in bond lengths. The volume per formula unit of a less dense nanoporous phase is twice that of other denser forms.

DOI: 10.1103/PhysRevB.82.094119 PACS number(s): 61.50.Ah, 61.66.Fn, 62.20.−x, 71.15.Mb

I. INTRODUCTION

Numerous bulk polymorphs of binary oxides have been studied theoretically, concentrating chiefly on prototypical dense crystal phases with structures adopted also by other systems.[1] Pressure-induced phase transitions, in particular, provide a well-established route to new denser polymorphs. Detailed examination of energy landscapes have also yielded predictions of alternative phases for the bulk[1] and for conditions of reduced dimensionality, such as various reconstructed and strained nanostructures and thin films. One recent example is a planar graphene (or *h*-BN) form[2] of ZnO, subsequently confirmed experimentally.[3] More recently attention has also been drawn to the possibility of nanoporous polymorphic phases with densities not higher but lower than the ambient form.[4] A*b initio* calculations have suggested new low-density nanoporous crystalline phases of MgO and ZnO may be accessible through the coalescence of nanocluster building blocks. Postulated polymorphs have unit-cell volumes 20–110 % larger than the binary oxides under ambient conditions, and the suggestions are similar topologically to known SiO_2 nanoporous crystals. Nanoporous phases of alkali-metal halides have also been proposed,[5] and breathing and gate-opening structural transitions in metal-organic frameworks are known.[6]

Here we report results of calculations on a binary oxide, demonstrating the stability and energetic feasibility of new low-density nanoporous oxide structures containing boron and oxygen. We chose to search for a boron-related material since novel boron oxides have received considerable attention,[7] and a wide range of structural possibilities (such as B-O-B angles) is well established for borate glasses.[8] We investigate possible structures for boron monoxide $(BO)_x$ rather than the trioxide and borate glasses (B_2O_3), in view of the already extensive literature on borate glasses (B_2O_3) and in order to investigate the likely effects of lower oxygen content on cross linking of polyatomic boron-oxygen building blocks. There is a long history[9–14] of reports of a solid material formulated as boron monoxide, BO or $\{BO\}_x$, formed by reduction in B_2O_3 or dehydration of diboronic acid, $B_2(OH)_4$. B-B bonds[15,16] are undoubtedly present but there remains considerable uncertainty as to its structure. The solid-state ^{11}B NMR spectrum of BO (Ref. 16) is complex, but shows a broad shoulder at ca 25 ppm, also observed in the NMR spectra of trigonal bonded boron compounds containing one B-B bond per boron atom, i.e., BBO_2, but not observed in materials containing trigonal BO_3 units.

II. METHODS

We carried out periodic *ab initio* calculations using plane-wave density functional theory (DFT) calculations in the generalized gradient approximation (GGA) as implemented in the CASTEP code[17] with the Perdew-Wang exchange-correlation functional.[18] Only valence electrons were considered, with core electrons replaced by ultrasoft Vanderbilt potentials[19] and energy cutoff for plane waves of 380 eV. Reciprocal space integration utilized the Monkhorst-Pack sampling scheme[20] and convergence of the energy with the number of k points checked carefully. Cell parameters and atomic positions were relaxed and optimized by energy minimization using a conjugate-gradient algorithm with maximum force tolerance 0.05 eV Å^{-1} and maximum stress component 0.1 GPa. Optimizations relaxed all degrees of freedom.

III. RESULTS

We have considered a large number of possible *AB* binary structures for solid BO, including all those in Ref. 21 and the framework structures of Ref. 4. Full details are given in Ref. 27 and here we concentrate only on those lowest in energy (within a 20 kJ mol^{-1} range), with the exception of one previous suggestion.[22] All these lowest energy structures contain B-B bonds as suggested by NMR.[16]

We start with a chain form, periodic in one dimension, based on motif **A** (Fig. 1). We also calculated the energy of a

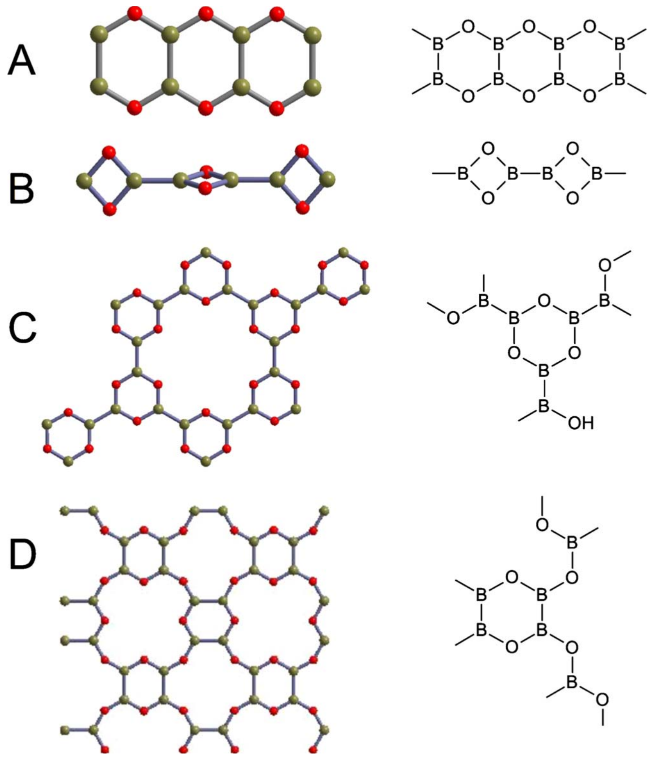

FIG. 1. (Color online) Calculated optimized chain and layer structures for solid boron monoxide (boron green/grey, oxygen red/dark grey) and their chemical formulas.

TABLE I. Calculated energies and unit-cell volumes of possible BO structures. Energies relative to that of the lowest energy structure (A), for which the calculated absolute energy is −518.211 eV (per formula unit). Optimized structures are available as in Ref. 27.

	Relative energy (per formula unit) (kJ/mol)	Volume (per formula unit) (Å^3)
A	0.0[a]	21.7
B	85	
C	*AA* stacking: 14	*AA*: 31.7
	AB: 11	*AB*: 28.4
D	*AA*: 15	*AA*: 29.1
	AB: 13	*AB*: 26.9
E	14	30.9
F	8	53[b]
G	9	33[b]
H	9	14.5

[a] Chains packed giving a 3D structure with $P2/m$ symmetry. Isolated chains have same energy as F. Other packing possibilities at most 35 kJ mol^{-1} higher in energy.

[b] Very small variation in energy with volume around the equilibrium volume.

chain structure **B** based on four-membered rings B_2O_2, suggested as a possibility at low temperature,[22] analogous to the Al_2O_2 units in some Al_nO_m compounds[23] and the N_2B_2 rings in some aminoboranes.[24] This structure is very high in energy, by over 85 kJ mol^{-1} (per mole formula unit), and so is not considered further. We then turned our attention to two possible layer structures [periodic in two dimensions (2D)] containing six-membered rings derived from motifs **C** and **D**, respectively. Structure **C** contains B_3O_3 rings linked by B-B bonds, whereas in **D** B_4O_2 rings are connected together by O atoms.

The optimized structures are shown in Fig. 1 with results of calculations summarized in Table I. Structures **A**, **C**, and **D** are comparable in energy while clearly **A** has a much higher density. We have investigated two possible stackings of layers made up of units **C** and **D**. In the first, the layers are stacked directly above each other (*AA* stacking) while in the second, the six-membered rings of one layer lie above the large holes in the adjacent layer formed by the larger $B_{12}O_6$ (**C**) or B_8O_4/B_8O_8 (**D**) rings (*AB* stacking). While the *AA* arrangements are highest in energy, consistent with the unfavorable electrostatic repulsions between adjacent layers present in this stacking, the differences in energy between stackings are only a few kilojoule per mole.

Calculated B-B bond distances (1.716 Å, 1.694 Å, and 1.717–1.720 Å in **A**, **C**, and **D**, respectively) are all in the range encountered for B-B bonds in diborane(4) compounds.[25,26] B-O bond distances for **A**, **C**, and **D** are 1.368 Å, 1.372 Å, and 1.352–1.372 Å, respectively, which compare well with such bonds in, for example, diborane(4) diolates. In **D**, B-O bonds linking the six-membered rings are shorter (1.352 Å) than those within the B_4O_2 rings themselves (1.372 Å). Linking oxygen atoms are coplanar with the B_4O_2 rings, with an associated B-O-B angle of 150° while the B-O-B angle within the six-membered ring is much smaller (120°). We have already drawn attention to the B-O-B angles in borate glasses,[8] with which these values are consistent.

We started our search for three-dimensional (3D) network structures from layer motif **D** since unlike **C**, the six-membered rings are connected by B-O-B bridges. An extreme adaptation of **D**, still not yet a 3D network, is shown by another essentially equienergetic local minimum in the energy landscape, structure **E** (Fig. 2) in which every layer is folded such that adjacent six-membered rings are all perpendicular to each other. Whereas in (optimized) **D** the BOB angle is 150°, the B-O-B angles are 129° and 141° in **E**, respectively, with corresponding BBBB torsion angles 70° and 55°.

In **E** the B-O-B linkages only connect rings in the same 2D sheet. We can readily connect six-membered B_3O_3 rings in different layers with B-O-B bridges, thus forming our first 3D network. Figures 3(b) and 3(c) show one resulting optimized structure **F** which we denote colloquially as the “wine-rack” structure. The local molecular environment in **F** of an individual six-membered ring is shown in Fig. 3(a) which highlights the connections between the different rings. The blue rings (top right and bottom left) lie above the plane of the central six ring, while the two red rings (bottom right and top left) lie below. The B-O-B bridge angle connecting the rings is 145°. The energy of **F** is 5 kJ mol^{-1} lower than structure **D**.

Structures **A**-**F** include both dense and nanoporous forms, with a striking variation in density with equilibrium volumes

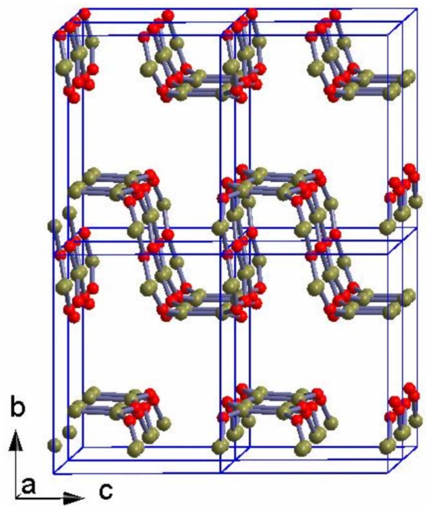

FIG. 2. (Color online) Layered structure (local minimum) **E**. The BOB angles are 129° and 141°, and associated BBBB torsions 70° and 55°, respectively.

(per formula unit) varying from 25 to 55 Å^3. Structure **F** has the optimized structure shown in Fig. 3(b) corresponding to a volume of 53 Å^3 which compares with 27 Å^3 for **D**. Figure 3(c) is a structure **G** with the same topological connectivity as **F** but at higher densities (33 Å^3/f.u.). The orientations of Figs. 3(b) and 3(c) are identical. **G** and **F** have very similar B-O bond lengths (1.35 Å for the B-O bonds connecting the rings and 1.37 Å for the B-O within the ring) even though the unit-cell volumes are markedly dissimilar; the change in volume is reflected in the inter-ring B-O-B angles and the torsion angles which determine the relative orientations of these rings.

On compression of structure **A** we obtained a third 3D structure **H**, equivalent in energy to **F** (within 1 kJ/mol) and similar in structure to β-InS. This is the densest of all calculated low-energy structures with a volume per formula unit of 14.5 Å^3. In this low-volume structure,[27] illustrated in Fig. 4, there is a key change in coordination number—the boron atoms are fourfold coordinate, forming one bond to boron and three to oxygen while the oxygen atoms are three-coordinate to B.[27] Similar changes in coordination numbers of boron and oxygen have recently been observed in B_2O_3 glasses at high pressure (4–20 GPa).[28]

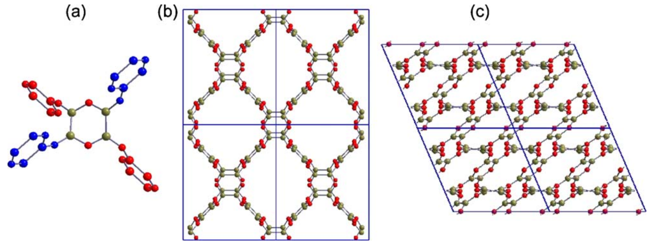

FIG. 3. (Color online) (a) Relative positions of six-membered rings in structure **F** (b) 3D structure (V=53 Å^3) viewed along the b axis. BOB bond angles are 131° and 136°, with associated BBBB torsion angles 120° and 63°, respectively. (c) Higher density 3D structure **G** (V=33 Å^3) (with the same connectivity as **F**) viewed along the b axis, respectively. BOB bond angles are 143° and 146°, with associated BBBB torsion angles 103° and −117°, respectively. Note (b) and (c) are viewed along the same direction.

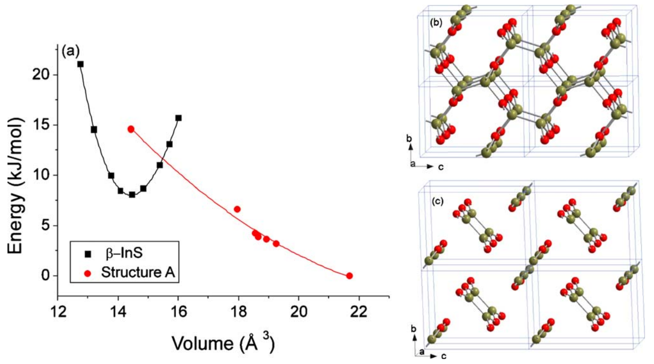

FIG. 4. (Color online) The structural transformation from structure **A** (assuming stacking of chains with $P2/m$ symmetry) to a high-pressure form structure **H** containing four-coordinate boron. The thermodynamic transition pressure for $\mathbf{A} \rightarrow \mathbf{H}$ is ~10 GPa. (a) Energy (per formula unit) vs volume for **A** and **H**. All energies relative to that of the lowest energy structure (a) at zero pressure. (b) High-pressure β-InS form **H** (c) Structure **A**.

Finally we estimate the relative thermodynamic stability of boron monoxide with respect to other boron oxides. Calculated heats of formation of B_6O, BO, and B_2O_3 are −520 kJ mol^{-1}, −365 kJ mol^{-1}, and −1210 kJ mol^{-1}, respectively. Disproportionation of BO to B and B_2O_3 is slightly exothermic (≈45 kJ mol^{-1}). This of course ignores the entropic contribution to the Gibbs energy of formation, and the likely accuracies of the DFT calculated energies are such that the formation of boron monoxide cannot therefore be ruled out on thermodynamic grounds. Slow kinetics associated with first-row elements may also help.

IV. CONCLUSIONS

In summary, we find many structures low in energy for boron monoxide, dominated by six-membered rings connected in various ways. There is a striking flexibility which leads to an unprecedented wide range of possible densities,[29] as shown by the very similar energies of **F** and **G**. Overall we have demonstrated the stability and energetic feasibility of low-density nanoporous oxide structures containing B and O. The ability to modify the B-O-B angle offers in principle a wide range of structural, and thus chemical and electronic possibilities. Experimental data are limited but it is encouraging that our calculated low-energy structures are consistent with the bonding pattern suggested by the NMR. Encouraged by reports of synthesis of a compound with stoichiometry BO, we hope this study will encourage experimental efforts toward the synthesis and characterization of such materials.

ACKNOWLEDGMENTS

This work was supported by time on the Mott2 cluster at RAL. F.C. thanks EPSRC (Grant No. EP/C532066/1).

*Corresponding author.

†f.claeyssens@sheffield.ac.uk
‡n.l.allan@bris.ac.uk

[1] J. C. Schön, Z. Anorg. Allg. Chem. **630**, 2354 (2004).

[2] C. L. Freeman, F. Claeyssens, N. L. Allan, and J. H. Harding, Phys. Rev. Lett. **96**, 066102 (2006).

[3] C. Tusche, H. L. Meyerheim, and J. Kirschner, Phys. Rev. Lett. **99**, 026102 (2007).

[4] J. Carrasco, F. Illas, and S. T. Bromley, Phys. Rev. Lett. **99**, 235502 (2007).

[5] W. Sangthong J. Limtrakul, F. Illas, and S. T. Bromley, J. Mater. Chem. **18**, 5871 (2008).

[6] F.-X. Coudert, C. Mellot-Draznieks, A. H. Fuchs, and A. Boutin, J. Am. Chem. Soc. **131**, 11329 (2009)..

[7] For example, H. Hubert, B. Devouard, L. A. J. Garvie, M. O'Keeffe, P. R. Buseck, W. T. Petuskey, and P. F. McMillan, Nature (London) **391**, 376 (1998).

[8] N. Umesaki, Y. Kita, T. Kirihara, T. Iida, T. Fukunaga, and M. Misawa, J. Non-Cryst. Solids **177**, 200 (1994).

[9] F. A. Kanda, A. J. King, V. A. Russell, and W. Katz, J. Am. Chem. Soc. **78**, 1509 (1956).

[10] D. J. Nicholls, J. Chem. Soc. **1965**, 6644.

[11] E. Zintl, W. Morawietz, and E. Z. Gastinger, Z. Anorg. Allg. Chem. **245**, 8 (1940).

[12] A. K. Holliday and A. G. Massey, Chem. Rev. **62**, 303 (1962).

[13] T. Wartik and E. F. Apple, J. Am. Chem. Soc. **77**, 6400 (1955).

[14] R. J. Brotherton, in *Progress in Boron Chemistry*, edited by H. Steinberg and A. L. McCloskey (Pergamon Press, Oxford, 1964).

[15] R. J. Brotherton, A. L. McCloskey, and H. M. Manasevit, Inorg. Chem. **2**, 41 (1963).

[16] N. C. Norman (unpublished).

[17] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, and M. C. Payne Z. Kristallogr. **220**, 567 (2005).; Rev. Mod. Phys. **64**, 1045 (1992).

[18] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[19] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[20] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[21] F. Claeyssens, J. N. Hart, N. L. Allan, and J. M. Oliva, Phys. Rev. B **79**, 134115 (2009).

[22] A. L. McCloskey, R. J. Brotherton, and J. L. Boone, J. Am. Chem. Soc. **83**, 4750 (1961).

[23] A. V. Nemukhin and F. Weinhold, J. Chem. Phys. **98**, 1329 (1993).

[24] C. A. Jaska, K. Temple, A. J. Lough, and I. Manners, J. Am. Chem. Soc. **125**, 9424 (2003).

[25] F. J. Lawlor, N. C. Norman, N. L. Pickett, E. G. Robins, P. Nguyen, G. Lesley, T. B. Marder, J. A. Ashmore, and J. C. Green, Inorg. Chem. **37**, 5282 (1998).

[26] W. Clegg, M. R. J. Elsegood, F. J. Lawlor, N. C. Norman, N. L. Pickett, E. G. Robins, A. J. Scott, P. Nguyen, N. J. Taylor, and T. B. Marder, Inorg. Chem. **37**, 5289 (1998).

[27] See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevB.82.094119 for details of the optimized geometries of the structures in this paper.

[28] S. K. Lee, P. J. Eng, H. K. Mao, Y. Meng, M. Newville, M. Y. Hu, and J. F. Shu, Nature Mater. **4**, 851 (2005).

[29] The existence of very low density forms of B_2O_3 with open structures at high temperatures [L. Huang and J. Kieffer, Phys. Rev. B **74**, 224107 (2006)] have been proposed on the basis of classical molecular-dynamics simulations.