Boron oxides under pressure: Prediction of the hardest oxides

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(Received 4 August 2017; revised manuscript received 5 September 2018; published 21 November 2018)

We search for stable compounds of boron and oxygen at pressures from 0 to 500 GPa using the ab initio evolutionary algorithm USPEX. Only two stable stoichiometries of boron oxides, namely, B6O and B2O3, are found to be stable, in good agreement with experiment. A hitherto unknown phase of B6O at ambient pressure, Cmcm-B6O, has recently been predicted by us and observed experimentally. For B2O3, we predict three previously unknown stable high-pressure phases—two of these (Cmc21 and P212121) are dynamically and mechanically stable at ambient pressure, and should be quenchable to ambient conditions. Their predicted hardmesses, reaching 33–35 GPa, make them harder than SiO2-stishovite. These are the hardest known oxides (if one disregards B6O, which is essentially a boron-based insertion compound). Under pressure, the coordination number of boron atoms changes from 3 to 4 to 6, skipping fivefold coordination.

DOI: 10.1103/PhysRevB.98.174109

I. INTRODUCTION

Boron (B) is arguably the most complicated element in the Periodic Table, with as many as 16 allotropes experimentally reported, most of which are probably impurity-stabilized. Well-established α, β, γ, and tetragonal T allotropes are superhard, and have been confirmed to be pure boron allotropes [1]. Recently, yet another pure bulk modification of boron, r-B [2], and two-dimensional (2D) allotropes of boron, borophenes, were identified [3,4]. Boron oxide B2O3 and suboxide B3O are well established, but there are also controversial compounds proposed in the literature [4–15].

To date, two crystalline forms of B2O3 are known: B2O3-I [5] (ambient-pressure form) and B2O3-II [6] (high-pressure form). B2O3-I is composed of BO3 planar triangular units, while B2O3-II is made of BO4 tetrahedra. The change of coordination number from 3 to 4 is similar to the structural transformation in the B2O3 glass under pressure [7]. However, the coordination number change in B2O3 glass under pressure is not without controversy [8–10]. Brazhkin et al. [8] observed the transformation of [3]B→[4]B (the superscript is the coordination number) by x-ray diffraction in B2O3 glass under pressure, and predicted one more transformation to [6]B using first-principles simulations at high pressure. Only four months later, Trachenko et al. [9] reported the transformation BO3 → BO4 → BO3 → BO6 for the local coordination environments in B2O3 glass under pressure; and a similar trend was also observed by Vegiri and Kamitsos [10] in 0.3LiO-B2O3 glass.

Boron suboxides, such as B2O [11], B3O [12], B13O2 [13], B17O [14], and B22O [15], have been reported and, if confirmed, could be promising superhard materials. Among these, B2O (though studied by some theorists [16]), had already been ruled out [17]. B2O, B13O2, B17O, and B22O can be considered as insertion phases based on rhombohedral α-boron structure with icosahedral B12 units and interstitial oxygens. B3O is the most extensively studied phase among them, and it was synthesized at ambient pressure [18], as opposed to diamond [19] and cubic BN [20], which are synthesized at high pressure. Given the numerous controversies in the literature, we decided to perform a thorough study of the structures and stability of B-O compounds at normal and high-pressure conditions by employing a systematic and unbiased first-principles crystal structure and compound prediction method.

II. METHOD OF CALCULATION

We used the ab initio evolutionary algorithm USPEX [21–23], which can simultaneously find the stoichiometry and crystal structures of all stable compounds in a multicomponent system. In our searches at each pressure point, the initial population included 120 structures with up to 32 atoms per primitive cell, with all subsequent generations consisting of 50 structures produced by heredity (30%), transmutation (20%),
softmutation (20%), and random symmetric generator (30%). Structure relaxations and total energy calculations were done within the generalized gradient approximation (GGA) [24] as implemented in the VASP [25] code. We used the PAW [26] method to represent core electrons and their effect on valence electrons, and the kinetic energy cutoff for valence wave functions was set to 600 eV, which gives excellent convergence of energy differences and stress tensors. Brillouin zone sampling was done with uniform Γ-centered \( k \) meshes with the resolution \( 2\pi \times 0.06 \text{ Å}^{-1} \) within USPEX searches and \( 2\pi \times 0.04 \text{ Å}^{-1} \) for further calculations of physical properties. Phonon dispersions were calculated using the finite-displacement method as implemented in the PHONOPY [27] code. Hardness was estimated using the empirical Chen-Niu [28] and Lyakhov-Oganov models [29]. At pressures below 5 GPa we included the van der Waals correction using the DFT-D2 method of Grimme [30].

**III. RESULTS AND DISCUSSION**

Variable-composition calculations were performed at pressures of 0, 20, 50, 100, 150, 200, 300, 400, and 500 GPa. We found that compositions \( \text{B}_2\text{O}_3, \text{B}_3\text{O}_2, \text{BO}, \text{B}_6\text{O}, \text{B}_{12}\text{O}, \text{and} \text{B}_{24}\text{O} \), are stable or close to the convex hull, which can be compared with the reported compositions, such as \( \text{B}_2\text{O}_3 [7], \text{B}_3\text{O}_2 [11], \text{B}_5\text{O} [15], \text{B}_6\text{O} [18], \text{B}_7\text{O} [14], \text{B}_9\text{O} [15], \text{B}_{10}\text{O} [15], \text{and} \text{B}_{22}\text{O} [15] \). For all the found and reported compositions, we carried out fixed-composition evolutionary searches at 0, 20, 40, 60, 80, 100, 150, 200, 250, 300, 350, 400, 450, and 500 GPa (up to 37 atoms per cell) to find the most stable structures. After this, the final pressure-composition phase diagram and convex hulls of the B-O system were constructed (see Fig. 1).

As can be seen from Fig. 1(b) and Fig. S1 in the Supplemental Material [31], \( \text{B}_3\text{O}, \text{B}_5\text{O}, \text{B}_7\text{O}, \text{B}_{11}\text{O}, \text{B}_{12}\text{O}, \text{and} \text{B}_{23}\text{O} \) have enthalpies of formation near (though slightly above) the convex hull. Only \( \text{B}_2\text{O}_3 \) and \( \text{B}_6\text{O} \) lie on the convex hull, indicating stability of only these two compounds, which is in good agreement with the vast majority of experimental results [32,33]. \( \text{B}_2\text{O}_3 \) is stable below 94 GPa; at higher pressures, \( \text{B}_2\text{O}_3 \) remains the only stable boron oxide (see Fig. 1).

Surprisingly, \( \text{Cmcm}-\text{B}_6\text{O} \), rather than the well-known \( \text{R}3\text{m}-\text{B}_6\text{O} \) (Fig. 2) [18], is found to be the stable phase of \( \text{B}_6\text{O} \) in the whole pressure range of 0–94 GPa; see Figs. 1(a) and Fig. S2 in the Supplemental Material online [31]). The enthalpy difference between these two structures is small (at ambient pressure it is only 1.8 meV per formula unit, and increases slightly with pressure). This prediction was published [12] and then our predicted \( \text{Cmcm}-\text{B}_6\text{O} \) phase was experimentally confirmed [34].

Below we focus on \( \text{B}_2\text{O}_3 \). We found the following sequence of pressure-induced phase transitions:

\[
P_{\text{3}121}-\text{B}_2\text{O}_3(\text{I}) \xrightarrow{0.5} \text{Cmcm}-\text{B}_2\text{O}_3(\text{II}) \xrightarrow{46} P_{\text{2}12121}-\text{B}_2\text{O}_3 \xrightarrow{133} P_{\text{mmn}}-\text{B}_2\text{O}_3 \xrightarrow{179} C2/m-\text{B}_2\text{O}_3.
\]

The numbers above the arrows indicate the calculated phase transition pressures in GPa (Table I), at zero Kelvin.

At pressures below 0.5 GPa, \( \text{B}_2\text{O}_3 \) is stable in the \( P_{\text{3}121} \) structure (this is the well-known \( \text{B}_2\text{O}_3\)-I phase). \( \text{B}_2\text{O}_3\)-I is composed of corner-sharing triangular \( \text{BO}_3 \) units; this ultraflexible [36] structure is shown in Fig. 3(a). From 0.5 to 46 GPa, \( \text{Cmcm}-\text{B}_2\text{O}_3 \), i.e., \( \text{B}_2\text{O}_3\)-II [6], is stable. \( \text{B}_2\text{O}_3\)-II is composed of \( \text{BO}_4 \) tetrahedra, as shown in Fig. 3(b). The \( \text{BO}_3 \rightarrow \text{BO}_4 \) coordination number change also occurs in the vitreous \( \text{B}_2\text{O}_3 \) under pressure. The transition pressure point, 0.5 GPa, is consistent with experiments on glassy \( \text{B}_2\text{O}_3 \) [37].

**FIG. 1.** Thermodynamic stability of boron oxides. (a) Pressure-composition phase diagram of the B-O system. (b) Thermodynamic convex hulls of the B-O system at selected pressures. Filled circles represent stable compounds; open circles denote metastable compounds. \( \Delta H \) is the enthalpy of formation per atom (for details of the calculation process, see the Supplemental Material [31]).

**FIG. 2.** Crystal structures of (a) \( \text{R}3\text{m}-\text{B}_6\text{O} \), (b) \( \text{Cmcm}-\text{B}_6\text{O} \). Green (large) and red (small) spheres denote B and O atoms, respectively.
TABLE I. Crystal structures of experimentally known and recently predicted phases of B₆O and B₂O₃.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pressure (GPa)</th>
<th>Volume (Å³/atom)</th>
<th>Cell parameters</th>
<th>Atomic coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>R3m-B₆O (expt. [18])</td>
<td>0</td>
<td>7.376</td>
<td>a = 5.390 Å,  c = 12.313 Å</td>
<td>N/A</td>
</tr>
<tr>
<td>R3m-B₂O₃</td>
<td>0</td>
<td>7.387</td>
<td>a = 5.393 Å,  c = 12.318 Å</td>
<td></td>
</tr>
<tr>
<td>Cmcm-B₆O</td>
<td>0</td>
<td>7.384</td>
<td>a = 5.393 Å,  b = 8.777 Å,  c = 8.736 Å</td>
<td>B1 (0.110,0.221,0.887); B2 (0.317,0.158,0.360) O(0.0,0.0,0.622)</td>
</tr>
<tr>
<td>B₂O₃-I P₃2₁ (expt. [35])</td>
<td>0</td>
<td>9.053</td>
<td>a = b = 4.336 Å,  c = 8.340 Å</td>
<td>B1 (0.395,0.230,0.224); O1 (0.601,0.148,0.128); O2 (0.161,0.0,0.333)</td>
</tr>
<tr>
<td>P₃2₁-B₂O₃</td>
<td>0</td>
<td>9.007</td>
<td>a = b = 4.348 Å,  c = 8.251 Å</td>
<td>B1 (0.395,0.236,0.225); O1 (0.602,0.154,0.128); O2 (0.151,0.0,0.333)</td>
</tr>
<tr>
<td>B₂O₃-II Cmc₂₁ (expt. [6])</td>
<td>7.432</td>
<td>7.462</td>
<td>a = 4.613 Å,  b = 7.803 Å,  c = 4.129 Å</td>
<td>B1 (0.161,0.165,0.434); O1 (0.370,0.291,0.580); O2 (0.248,0.0,0.5)</td>
</tr>
<tr>
<td>Cmc₂₁-B₂O₃</td>
<td>0.5</td>
<td>4.860</td>
<td>a = 6.703 Å,  b = 6.369 Å,  c = 2.277 Å</td>
<td>B1 (0.922,0.827,0.881); B2 (0.078,0.995,0.407) O1 (0.588,0.835,0.996); O2 (0.403,0.022,0.541); O3 (0.066,0.346,0.962)</td>
</tr>
<tr>
<td>Pmmn-B₂O₃</td>
<td>133</td>
<td>4.860</td>
<td>a = 6.703 Å,  b = 6.369 Å,  c = 2.277 Å</td>
<td>B1 (0.5,0.385,0.0); B2 (0.177,0.264,0.5) O1 (0.5,0.995,0.0); O2 (0.5,0.621,0.0) O3 (0.346,0.376,0.5); O4 (0.668,0.869,0.5)</td>
</tr>
<tr>
<td>C₂/m-B₂O₃</td>
<td>179</td>
<td>4.484</td>
<td>a = 9.422 Å,  b = 2.242 Å,  c = 4.358 Å</td>
<td>B1 (0.662,0.0,0.304); B2 (0.916,0.0,0.208) O1 (0.0,0.5,0.253); O2 (0.671,0.5,0.574) O3 (0.833,0.0,0.908)</td>
</tr>
</tbody>
</table>

From 46 to 133 GPa, a previously unknown crystalline phase, P₂₁₂₁₂₁-B₂O₃, is predicted to be stable. Its structure is made of BO₄ tetrahedra, just like Cmc₂₁-B₂O₃; see Fig. 3(c). Between 133 and 179 GPa, another unique structure, Pmmn-B₂O₃, is stable. Its structure contains both BO₄ tetrahedra and BO₆ octahedra. At higher pressures, above 179 GPa, C₂/m-B₂O₃ is stable—and here, we again find both BO₄ tetrahedra and BO₆ octahedra. In addition, we also found an interesting phenomenon: The BO₄ tetrahedra and the BO₆ octahedra in C₂/m-B₂O₃ disappear and convert into BO₃ units when pressure is released down to 0 GPa, as shown in Fig. S3 (Supplemental Material [31]). This is in contrast with Cmc₂₁-B₂O₃ and P₂₁₂₁₂₁-B₂O₃, which maintain their structure with BO₄ tetrahedra on decompression down to ambient pressure (where they are dynamically stable). The latter two phases may retain their original symmetry and dense structural topology under ambient pressure. Cmc₂₁-B₂O₃ has for a long time been known to be quenchable in experiment [6], which is in good agreement with our prediction. The computed hardnesses of Cmc₂₁- and P₂₁₂₁₂₁-phases of B₂O₃ at zero pressure are 35 and 33 GPa from the Chen-Niu model (or 34 and 29 GPa from the Lyakhov-Oganov model) (Table II). Moreover, both structures are dynamically and mechanically stable at ambient pressure (Fig. S4 in the Supplemental Material [31] and Table II). This means that these...
TABLE II. Elastic constants, bulk and shear moduli, and hardnesses of B$_6$O and B$_2$O$_3$ at ambient pressure, in GPa. Pmnn and C2/m phases of B$_2$O$_3$ are mechanically unstable at ambient pressure.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>B$_6$O</th>
<th>B$_6$O</th>
<th>B$_2$O$_3$-I</th>
<th>B$_2$O$_3$-II</th>
<th>B$_2$O$_3$</th>
<th>B$_2$O$_3$</th>
<th>B$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R3m</td>
<td>Cmcm</td>
<td>P3$_1$21</td>
<td>Cm2$_1$</td>
<td>P2$_1$$_2$$_1$2$_1$</td>
<td>Cm2$_1$</td>
<td>P2$_1$$_2$$_1$2$_1$</td>
</tr>
<tr>
<td>c$_{11}$</td>
<td>585</td>
<td>584</td>
<td>175</td>
<td>352</td>
<td>461</td>
<td>376</td>
<td>573</td>
</tr>
<tr>
<td>c$_{22}$</td>
<td>441</td>
<td>354</td>
<td>323</td>
<td>22</td>
<td>6</td>
<td></td>
<td></td>
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<tr>
<td>c$_{33}$</td>
<td>458</td>
<td>563</td>
<td>66</td>
<td>468</td>
<td>396</td>
<td>678</td>
<td>6</td>
</tr>
<tr>
<td>c$_{44}$</td>
<td>178</td>
<td>192</td>
<td>57</td>
<td>148</td>
<td>153</td>
<td>22</td>
<td>3</td>
</tr>
<tr>
<td>c$_{55}$</td>
<td>209</td>
<td>197</td>
<td>66</td>
<td>149</td>
<td>117</td>
<td>26</td>
<td>1</td>
</tr>
<tr>
<td>c$_{66}$</td>
<td>124</td>
<td>75</td>
<td>43</td>
<td>78</td>
<td>73</td>
<td>16</td>
<td>2</td>
</tr>
<tr>
<td>c$_{12}$</td>
<td>50</td>
<td>90</td>
<td>10</td>
<td>40</td>
<td>48</td>
<td>2</td>
<td>2</td>
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<tr>
<td>c$_{14}$</td>
<td>23</td>
<td>18</td>
<td></td>
<td></td>
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<tr>
<td>c$_{36}$</td>
<td>66</td>
<td>40</td>
<td>24</td>
<td>3</td>
<td></td>
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<tr>
<td>c$_{46}$</td>
<td></td>
<td></td>
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<tr>
<td>G (V-R-H)$^a$</td>
<td>208</td>
<td>209</td>
<td>55</td>
<td>158</td>
<td>155</td>
<td>19</td>
<td>21</td>
</tr>
<tr>
<td>B (V-R-H)$^a$</td>
<td>227</td>
<td>226</td>
<td>53</td>
<td>164</td>
<td>161</td>
<td>69</td>
<td>35</td>
</tr>
<tr>
<td>B (expt.)</td>
<td>228$^b$</td>
<td></td>
<td>18.4$^c$</td>
<td>169.9$^d$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hv (Chen)</td>
<td>38$^e$</td>
<td>39$^f$</td>
<td>19</td>
<td>35</td>
<td>33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hv (Lyakhov)</td>
<td>32$^g$</td>
<td>32$^g$</td>
<td>32</td>
<td>34</td>
<td>29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hv (expt.)</td>
<td>33−36$^i$</td>
<td>1.5 ± 5$^f$</td>
<td>16 ± 5$^f$</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

$^a$These were calculated from the elastic constants and Voigt-Reuss-Hill averaging was used [41].
$^b$Reference [42].
$^c$Reference [33].
$^d$Reference [32].
$^e$Reference [12].
$^f$Reference [40].
$^g$Experimental report of hardness of glass-like B$_2$O$_3$ (the local structure of glass-like B$_2$O$_3$ is closest to the structure of B$_2$O$_3$-I) and $\beta$-B$_2$O$_3$ (i.e., B$_2$O$_3$-II), Ref. [43].

Two phases can be synthesized at high pressure (e.g., 5 and 50 GPa for Cmc$_2$$_1$-B$_2$O$_3$ and P2$_1$$_2$$_1$$_2$$_1$B$_2$O$_3$, respectively, with diamond-anvil cells or even a multianvil apparatus) and then may be decompressed to ambient pressure. They may be superior to B$_2$O$_3$, since B$_6$O is usually somewhat oxygen-deficient B$_2$O$_x$$_y$, where $x < 0.9$, and has rather poor crystallinity [39]. Moreover, even though B$_2$O$_3$ when prepared under high pressure, has excellent hardness, its fracture toughness is rather low [40].

For B$_2$O$_3$-I, both elastic moduli and hardness are overestimated (Table II), because B$_2$O$_3$-I has an exotic layered-like structure, as shown in Fig. 3(a), with folded layers bridged by B-O bonds. Such a delicate structure is a difficult case for theory, largely because of the importance of van der Waals interactions, and we see a large difference between theoretical and experimental bulk moduli (Table II). For the other B-O phases, e.g., Cmc$_2$$_1$-B$_2$O$_3$ and P2$_1$$_2$$_1$$_2$$_1$B$_2$O$_3$, as shown in Figs. 3(b) and 3(c), the situation is different. For example, the bulk modulus of Cmc$_2$$_1$-B$_2$O$_3$ calculated by Voigt-Reuss-Hill theory (164 GPa) is in good agreement with the experimental result (169.9 GPa; see Table II) [32]. The empirical Chen-Niu model is presently the most accurate model of hardness and has scored excellent successes, correctly reproducing experimentally measured hardnesses of many materials [28]. Therefore, the moduli and hardness of Cmc$_2$$_1$-B$_2$O$_3$ and P2$_1$$_2$$_1$$_2$$_1$B$_2$O$_3$ predicted by these empirical models are credible.

Glasses with high hardness have been in demand for many years. B$_2$O$_3$ is one of the most common glass materials and the hardness of Cmc$_2$$_1$-B$_2$O$_3$ and P2$_1$$_2$$_1$$_2$$_1$B$_2$O$_3$ crystals is much higher than that of the known oxide glasses. It may be possible to increase the fraction of local environments similar to Cmc$_2$$_1$-B$_2$O$_3$ or even P2$_1$$_2$$_1$$_2$$_1$B$_2$O$_3$ in the glass and enhance the hardness of the glass by applying pressure in the process of glass production.

High-pressure-temperature techniques are very important for the synthesis of novel materials. To further study the high-pressure synthesis conditions, the pressure-temperature phase diagram of B$_2$O$_3$ (Supplemental Material [31], Fig. S5) was constructed within the quasiharmonic approximation as implemented in the PHASEGO code [44] (considering only solid phases). At room temperature, P3$_1$21-B$_2$O$_3$ transforms into Cmc$_2$$_1$-B$_2$O$_3$ at 2.9 GPa, which is consistent with experiment [38], and Cmc$_2$$_1$-B$_2$O$_3$ transforms into P2$_1$$_2$$_1$$_2$$_1$B$_2$O$_3$ at 43 GPa and 300 K.

We analyze the relationship between the volume $V$, density $\rho$, average B-O bond length, coordination number of boron, charge transfer, and band gap as a function of pressure, as shown in Fig. 4. Volume and density as a function of pressure are shown in Figs. 4(a) and 4(b); one can see a series of volume discontinuities corresponding to first-order phase transitions. Bond lengths decrease with pressure for a given crystal structure—but at phase transitions involving increase of coordination number they sharply increase, resulting in a sawtooth-like dependence, and keeping roughly the same average B-O bond length, in the range 1.37–1.46 Å, in the enormous pressure range 0–500 GPa. At the same
FIG. 4. Volume $V$, density $\rho$, average B-O bond length, coordination number (C-N) of boron atoms, Bader charges, and the DFT band gap as a function of pressure in $\text{B}_2\text{O}_3$.

time, atomic charges seem to be not sensitive to structural transitions [Fig. 4(e)]. The DFT band gap [Fig. 4(f)] shows large variations with pressure; the largest values roughly correspond to structures with tetrahedral coordination of boron atoms. For most phases, we see the normal tendency for the band gap to decrease with pressure, but notably, the band gap of $C_{2/m}-\text{B}_2\text{O}_3$ increases with the increase of pressure from 179 GPa to at least 500 GPa.

In the sequence of phase transitions of $\text{B}_2\text{O}_3$, i.e., $P_{\text{3}1\text{2}1}-\text{B}_2\text{O}_3 \rightarrow \text{Cmc}_{\text{2}1}\text{-B}_2\text{O}_3 \rightarrow P_{\text{2}1\text{2}1\text{2}1}\text{-B}_2\text{O}_3 \rightarrow P_{\text{mm}n}\text{-B}_2\text{O}_3 \rightarrow C_{2/m}\text{-B}_2\text{O}_3$, there is a monotonic increase of the coordination number of boron atoms ([3]B $\rightarrow$ [4]B $\rightarrow$ [6]B), corresponding to the evolution BO$_3$ $\rightarrow$ BO$_4$ $\rightarrow$ BO$_6$ of boron coordination polyhedra. Fivefold coordination [5]B is not found in any of the stable phases.

IV. SUMMARY

To summarize, we have searched systematically for stable compounds in the B-O system in the pressure range 0–500 GPa using the ab initio evolutionary algorithm USPEX. We found that there are only two thermodynamically stable oxides, $\text{B}_6\text{O}$ and $\text{B}_2\text{O}_3$. None of the previously discussed $\text{B}_2\text{O}$, $\text{B}_3\text{O}$, $\text{B}_{13}\text{O}_{2}$, or $\text{B}_{22}\text{O}$ are thermodynamically stable. Calculations reveal a theoretical ground state of superhard $\text{B}_6\text{O}$ at ambient conditions and three hitherto unknown stable high-pressure phases of $\text{B}_2\text{O}_3$. Importantly, both of them are dynamically and mechanically stable at ambient pressure. Therefore, it is possible to synthesize them at high pressure and quench to ambient pressure: Synthesis of $\text{Cmc}_{\text{2}1}\text{-B}_2\text{O}_3$ and $P_{\text{2}1\text{2}1\text{2}1}\text{-B}_2\text{O}_3$ requires pressures in the ranges 0.5–46 and 46–133 GPa, respectively (at zero Kelvin). A 6 × 8 double stage multianvil press with sintered diamond cubes as the second stage can generate pressure up to ∼50 GPa, with sample volumes ∼1 mm$^3$, suitable for synthesis of these phases, with hardness reaching 34 GPa; these phases are harder than stishovite (32 GPa) and represent the hardest known proper oxides ($\text{B}_6\text{O}$ suboxide is basically a boron-based insertion compound). Finally, we find that the sequence of coordination number changes of boron atoms in $\text{B}_2\text{O}_3$ under pressure is $[3]B \rightarrow [4]B \rightarrow [6]B$.

ACKNOWLEDGMENTS

H.D. and Q.W. gratefully acknowledge financial support from the National Natural Science Foundation of China.
(Grants No. 11604056 and No. 11504004) and the National Science Foundation of Guangdong, China Funds for Distinguished Young Scholar (Grants No. 2017B030306003 and No. 2016A030310352). X.Z. thanks the National Science Foundation of China (Grants No. 11674176 and No. 11874224) and the Tianjin Science Foundation for Distinguished Young Scholars (Grant No. 17JCIQJC44400). V.V.B. is grateful to the Russian Science Foundation for the financial support (Project No. 14-22-00093). A.R.O. acknowledges funding from the Russian Science Foundation (Grant No. 16-13-10459). H.D. expresses thanks for funding from the China Scholarship Council (ID No. 201708440119).