Communication

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Nanotwinned Boron Suboxide (B₆O): New Ground State of B₆O

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Abstract: Nanotwinned structures in superhard ceramics rhombohedral boron suboxide (R-B₆O) have been examined using a combination of transmission electron microscopy (TEM) and quantum mechanics (QM). QM predicts negative relative energies to R-B₆O for various twinned R-B₆O (denoted as τ-B₆O, 2τ-B₆O, and 4τ-B₆O), consistent with the recently predicted B₆O structure with Cmcm space group (τ-B₆O) which has an energy 1.1 meV / B₆O lower than R-B₆O. We report here TEM observations of this τ-B₆O structure, confirming the QM predictions. QM studies under pure shear deformation and indentation conditions are used to determine the deformation mechanisms of the new τ-B₆O phase which are compared to R-B₆O and 2τ-B₆O. The lowest stress slip system of τ-B₆O is (010)/<001> which transforms τ-B₆O to R-B₆O under pure shear deformation. However, under indentation conditions, the lowest stress slip system changes to (001)/<110>, leading to icosahedra disintegration and hence amorphous band formation.

Keywords: Superhard ceramics, Stacking faults energy, DFT, Deformation mechanism.
Crystal twins are ubiquitous in crystalline metals and ceramics, where they form during growth and deformation processes. They have been studied extensively in metals, where they modify significantly the mechanical, thermal and electrical properties.\textsuperscript{1–5} In particular they significantly improve the materials strength by blocking dislocation movements.\textsuperscript{6–8} In some twinned structures the electrical conductivity of the pure metal is retained with the increased strength,\textsuperscript{9} making these planar defects potentially useful for electronic engineering.

However, for ceramics, the twinned structures are more complex than for simple metals. For example, we recently used QM and high resolution TEM (HRTEM) to identify a special asymmetric twin structure in boron carbide (B\textsubscript{4}C) that arises from the interplay of stoichiometry, atomic positioning, twinning, and structural hierarchy.\textsuperscript{10} Dislocations in ceramics are often sessile at normal temperatures because of the rigid structures arising from the covalent or ionic bonding. Thus, the strengthening mechanism through twinning in metals does not generally apply to ceramics. However, recent experiments found that nanoscale twins in c-BN and diamond dramatically increase the hardness of these strong covalent solids,\textsuperscript{11,12} leading to examining the roles of twins in deformation processes of other strong covalent solids.\textsuperscript{13,14}

Twin boundaries (TBs) are normally coherent grain boundaries with low interfacial energy compared with normal grain boundaries having random orientations. In general such TBs are planar defects with positive stacking faults energy (SFE). Even the well-known 4H-SiC and 6H-SiC stacking structures has positive SFEs of 14.7 and 2.9 mJ/m\textsuperscript{2},\textsuperscript{15} but they are more favorable at high temperature above 1700 °C because of the entropic effects.
Boron suboxide (B$_6$O) belongs to the family of icosahedral compounds that combine such promising properties as high hardness, low density and chemical inertness.$^{16-18}$ Abundant twinned structures with TB along $\{100\}_r$ plane have been observed in rhombohedral B$_6$O (R-B$_6$O),$^{16}$ indicating a unique microstructure for the twinned structure in B$_6$O. We used subscript “r” to represent the planes and directions in R-B$_6$O and the others without “r” represent the ones in the new predicted twinned B$_6$O. Thus, understating how the twinned structure in B$_6$O affects the mechanical properties may offer the possibility of designing materials with improved mechanical properties.

The present studies combined quantum mechanics (QM) calculations with spherical-aberration-corrected scanning transmission electron microscopy (STEM) to demonstrate the formation of the nanotwinned B$_6$O that have negative SFE, which is consistent with recent predictions of a new B$_6$O phase$^{19}$ more stable than R-B$_6$O. The newly predicted B$_6$O phase exhibits $1 \times 1$ zig-zag twinned B$_6$O, which we denote as τ-B$_6$O. We also identify other twinned phases, denoted as 2τ-B$_6$O, and 4τ-B$_6$O, and used QM to examine their mechanical properties, which are compared to R-B$_6$O.

Normal synthesis of B$_6$O leads to a rhombohedral unit cell with eight B$_{12}$ icosahedral clusters at the apexes and two O atom chains along the [111]$_r$ direction.$^{16,20}$ Recent studies,$^{19}$ using evolutionary crystal structure prediction methods,$^{21}$ found a new B$_6$O crystal structure with Cmcm space group as shown in Fig. 1(a). This structure was predicted to be 1.1 meV/B$_6$O lower in energy than R-B$_6$O.$^{19}$ To validate the existence of this new structure in experiments, we
performed STEM measurements on as-synthesized B₆O²² (experimental details are in the supplementary information, SI). Besides the R-B₆O shown in Fig. S1 of SI, we observed the new τ-B₆O structure within some grains, as shown with STEM and HRTEM images in Fig. 1(b), Fig S2 and Fig. S3 of SI, providing experimental evidence supporting the theoretical prediction. The new τ-B₆O structure belongs to the Cmcm space group. Fig. 1a shows the projection along the <100> direction, which shows the B₁₂ icosahedra and the Oxygen atom (O-O) chains. The BF-STEM image (Fig. 1b) displays this zig-zag pattern with the icosahedra alignment alternating every other plane. This zig-zag structure has a mirror symmetry across the {010} planes and appears to be a uniformly twinned version of R-B₆O (Fig. S1). The STEM images (Fig. 1b and Fig S2) are analogous to the direct projection of structure model (Fig. 1a) along the same crystallographic direction.

To further validate that this experimentally observed phase is the predicted one, we extracted the electron diffraction pattern from STEM measurements and compared it to the simulated STEM image computed from the QM structure [Fig. 1(c) and (d)]. The basic electron diffraction vectors from experiments and QM predictions agree very well, confirming that the observed phase is the τ-B₆O phase. However, our experimental pattern shows low intensity spots half-way between two very strong spots that would not be present in the perfect sample. To explore the origin of these weak spots, we considered models of τ-B₆O containing ordered patterns of either B-vacancies or O-vacancies, as shown in Fig. S4 of SI. Our calculated diffraction patterns (Fig. S4 of SI) for both cases lead to low intensity spots half-way between
the very strong spots exactly where we observe them experimentally.

The new predicted $\tau$-B$_6$O phase is similar to our previously predicted twinned R-B$_6$O structure$^{14}$ with the $\tau$-B$_6$O having $1 \times 1$ zig-zag structure along the direction perpendicular to the twin plane while the n$\tau$-B$_6$O twinned structure has an $n \times n$ ($n > 1$) zig-zag structure. The most stable structure in Table 1 is $\tau$-B$_6$O. Comparing the energy to R-B$_6$O, we can say that the stacking fault energy (SFE) to form R-B$_6$O is 1.51 mJ/m$^2$. The other n$\tau$-B$_6$O cases all have energies between $\tau$-B$_6$O to R-B$_6$O (Table 1), indicating that it is favorable to put twins into R-B$_6$O.

To gain insight into why the $\tau$-B$_6$O phase is more stable than R-B$_6$O, we calculated the natural bond orbital (NBO) charge distributions$^{22}$ of the B$_{12}$ unit and O atoms in both structures. The electron counting rules suggest that two electrons must be added to the B$_{12}$ unit in R-B$_6$O to satisfy Wade’s rule. In R-B$_6$O, the QM calculations find that the O atoms transfer only 0.65 electrons to nearby B$_{12}$ unit, leading to $(B_{12})^{1.3^-}$, which is short from the value expected from Wade’s rule. In contrast, for $\tau$-B$_6$O each O atom transfers 1.05 electrons to a nearby B$_{12}$ unit, leading to $(B_{12})^{2.1^-}$. Thus, the charge transfer in the $\tau$-B$_6$O structure nearly exactly matches Wade’s rule, suggesting that $\tau$-B$_6$O is more stable structure.

To determine the stability of the two phases at finite temperature, we calculated the free energy as a function of temperature, including the vibrational entropy. We first computed the phonon frequencies of these two phases using a finite difference method.$^{24}$ These calculations used the $2 \times 2 \times 2$ supercell for R-B$_6$O and the $2 \times 2 \times 1$ supercell for $\tau$-B$_6$O. The entropy and the
Helmholtz free energy were computed from the phonons frequencies for temperature up to 2300 K, which is near the melting temperature of B$_6$O.$^{25}$ The entropy difference ($S_{R-B_6O} - S_{\tau-B_6O}$) and the Helmholtz free energy (A) difference ($A_{R-B_6O} - A_{\tau-B_6O}$) between these two phases are small, as displayed in Fig. S5 of the SI. The $\tau$-B$_6$O phase has a lower Helmholtz free energy than R-B$_6$O for all temperature up to melting, but the difference decreases gradually to zero at melting. The entropy of $\tau$-B$_6$O is slightly higher than that of R-B$_6$O for $T < 72$ K but lower for higher temperatures.

To examine how the negative SFEs affect the mechanical properties, we used QM to predict the elastic moduli of $\tau$-B$_6$O and compare with R-B$_6$O and 2,4$\tau$-B$_6$O. The predicted elastic moduli are listed in Table S1-S3 of SI. For $\tau$-B$_6$O this leads to a calculated bulk modulus $B = 225.9$ GPa and a shear modulus $G = 209.2$ GPa using Voigt–Reuss–Hill averaging.$^{26}$ These values are slightly smaller than the $B = 232.0$ and $G = 210.9$ GPa for R-B$_6$O.$^{20}$ For 2$\tau$-B$_6$O and 4$\tau$-B$_6$O structures, the $B = 226.2$ GPa, $G = 208.5$ GPa; and $B = 221.8$ GPa, $G = 206.6$ GPa, respectively, which are similar to those of $\tau$-B$_6$O. Thus, all four structures have similar elastic properties, indicating that the slightly negative SFEs have insignificant influence on the elastic properties of B$_6$O.

To examine if the twinned structures influence the mechanical properties of R-B$_6$O, we calculated the hardness of $\tau$-B$_6$O, R-B$_6$O, and twinned R-B$_6$O based on the G/B values.$^{27}$ The computed hardness values are summarized in Table 1. Although the calculated hardness values for these structures are similar, the twinned structures appear slightly harder than the R-B$_6$O,
indicating that twins make B$_6$O stronger.

Amorphous shear band formation is the major failure mechanism for failure of superhard ceramics B$_6$O$^{28}$ and B$_4$C$^{29-32}$. To determine the deformation mechanism leading to brittle failure of the new τ-B$_6$O phase, we applied pure shear deformation to τ-B$_6$O (simulation details in the SI). We first determined the most plausible slip system by shearing along four possible slip systems of (100)/<010>, (100)/<001>, (010)/<001>, and (001)/<110>. The (001)/<110> slip system corresponds to the slip along the twin boundaries (TBs) in the twinned R-B$_6$O. The stress-strain relationships of these slip systems are displayed in Fig. 2. Among these four slip systems, the (010)/<001> slip system has the lowest shear stress of 39.4 GPa while the other slip systems (100)/<010>, (100)/<001>, and (001)/<110> are 43.5, 47.5 and 45.1 GPa, respectively. Thus, the (010)/<001> is the least stress slip system for τ-B$_6$O. For 2τ-B$_6$O, QM leads to an ideal shear stress along (010)/<001> of 37.5 GPa. Thus, the τ-B$_6$O is slightly stronger than 2τ-B$_6$O, consistent with its higher predicted hardness.$^{19}$

To compare with R-B$_6$O, we shear the R-B$_6$O along the (011)/<2111> slip system, which is the reverse slip system of (010)/<001> for τ-B$_6$O. The ideal shear stress of R-B$_6$O shearing along (011)/<2111> is 37.9 GPa, which is lower than the shear along (001)/<100> of 43.5 GPa we examined earlier.$^{20}$ Thus, the lowest stress slip system for R-B$_6$O is actually (011)/<2111>, not (001)/<100> that we examined previously. Comparing the ideal shear stress for lowest stress slip systems for these three structures, the sequence from high to low strength is τ-B$_6$O > R-B$_6$O ~ 2τ-B$_6$O.
In addition, we note that the slip along the TBs [(001)/<110> slip system] has an ideal shear stress of 45.1 GPa, which is larger than 2τ-B₆O of 43.3. However, the ideal shear stress along this slip system for the perfect (non-twinned) R-B₆O is 43.5 GPa, which is similar to 2τ-B₆O.

Figure 3 displays the deformation mechanism of τ-B₆O for shear along the slip system (010)/<001>. The intact structure is displayed in Fig. 3(a). As the system is sheared to 0.276 strain (corresponding to a maximum stress of 39.4 GPa) the B27-B28 bond between icosahedra is stretched from 1.697 to 2.491 Å as shown in Fig. 3(b). But it is not broken as shown from the electron localization function (ELF)\(^{33}\) (inserted image of Fig. 3(b)). As the system is sheared continuously to 0.369 strain, the B27-B28 bond breaks, but this releases the shear stress only slightly to 35.6 GPa because the icosahedra do not disintegrate. As the critical strain of 0.369 is exceeded, a new B23-B24 bond forms and the structure transforms to R-B₆O with no broken bonds in the icosahedral clusters. However, the “a” and “c” axes are now along [211] and [011] directions of R-B₆O, respectively. This deformation is similar to the pure shear deformation of R-B₆O\(^{20}\) and twinned R-B₆O\(^{14}\) where the icosahedral clusters do not deconstruct.

To examine the possible reverse transition from R-B₆O to τ-B₆O, we performed pure shear deformation on the R-B₆O along the slip system of (011)/<211>, which is the reverse slip from τ-B₆O to R-B₆O. The stress-strain relationship and structural changes are displayed in Fig. 4(a). We found that the R-B₆O cannot transform back to τ-B₆O, instead the icosahedra disintegrate, leading to the amorphous band formation, as shown in Fig. 4(b)-(d). Indeed previous experimental studies show amorphous band formation in R-B₆O\(^{28}\) However, our
previous QM simulations show structure recovery for R-B\textsubscript{6}O shearing along (001)/<100>.\textsuperscript{20} Here we show that shearing along (011)/<2\overline{1}\overline{1}> has a lower ideal shear stress, resulting in icosahedra disintegration that leads to amorphous band formation. Thus, our simulations predict that the amorphous band in R-B\textsubscript{6}O is along the (011) plane. This is not consistent with previous experiments\textsuperscript{28} which might arise from the complex stress conditions in experiments.

Normally indentation experiments are used to evaluate the strength of brittle materials. To mimic the stress conditions under indentation,\textsuperscript{13} we applied biaxial shear stress on τ-B\textsubscript{6}O along slip system (010)/<001> which is the lowest stress slip system and the TBs, which is the (001)/<110> slip system. We also sheared the 2τ-B\textsubscript{6}O and R-B\textsubscript{6}O along the similar slip systems for comparison. The shear-stress–shear-strain relationships for these three structures are displayed in Fig. 5(a). We see that the ideal shear stress of τ-B\textsubscript{6}O shearing along (001)/<110> is 36.2 GPa, while it is 41.0 GPa shearing along (010)/<001> slip system. Thus, the easiest slip system for τ-B\textsubscript{6}O changes from (010)/<001> to (001)/<110> under the simulated indentation conditions. A similar change for the lowest stress slip system appears for 2τ-B\textsubscript{6}O where the ideal shear stresses are 36.9 and 40.8 GPa for shearing along (001)/<110> and (010)/<001>, respectively. However, for the perfect R-B\textsubscript{6}O, the ideal shear stresses are 39.9 and 37.2 GPa for shearing along (001)/<100> and (011)/<2\overline{1}\overline{1}>, respectively. This indicates that (011)/<2\overline{1}\overline{1}> is still the most plausible slip system in R-B\textsubscript{6}O. Under the biaxial shear stress conditions, the sequence from high to low strength is R-B\textsubscript{6}O ~ 2τ-B\textsubscript{6}O > τ-B\textsubscript{6}O, which is reverse compared to the pure shear deformation.
The deformation mechanism for $\tau$-B$_6$O along (001)/<110> under the biaxial shear stress conditions is displayed in Fig. 5(b),(c). The icosahedra disintegrate directly under the biaxial stress conditions at 0.254 strain as the shear stress goes above 36.2 GPa. To examine why the most plausible slip system changes from (010)/<001> to (001)/<110> in $\tau$-B$_6$O under biaxial shear conditions, we plotted the structural changes by shearing along (010)/<001> in Fig. 5(d)-(f). We see that the $\tau$-B$_6$O also transforms to R-B$_6$O at biaxial stress conditions, which is the same as for pure shear deformations. The 2$\tau$-B$_6$O exhibits a similar deformation mechanism under indentation conditions: the icosahedra disintegrate when shearing along (001)/<110> with a lower shear stress of 36.9 GPa, while the structure changes to R-B$_6$O when shearing along (010)/<001> with a higher minimum shear stress of 40.8 GPa (Fig. S6 of SI). For R-B$_6$O, the icosahedra disintegrate for both shear along (001)/<100>$^{14}$ and along (011)/<2-1-1> (Fig. S7 of SI).

Structural transformations between solids have been widely examined in metals,$^{34,35}$ semiconductors,$^{36,37}$ and superhard ceramics.$^{20,29}$ Recent studies shows that a possible path for transforming the zinc-blende (ZB) structure to the wurzite phase is a collective glide of Shockley partial dislocations on the (111) plane.$^{36,37}$ We calculate that the shear deformation from R-B$_6$O to $\tau$-B$_6$O requires a shear stress over 35 GPa at 0 K. Thus, it is unlikely that $\tau$-B$_6$O is formed from mechanical twinning of R-B$_6$O. Instead we expect that $\tau$-B$_6$O may be formed during nucleation and growth from the melt, as favored by the lower free energy of $\tau$-B$_6$O compared to R-B$_6$O.
Summarizing, we confirm with QM and STEM experiments the existence of the new \( \tau\)-B\(_6\)O phase predicted by Dong \textit{et al.}\(^{19}\). The stacking fault energies for nanotwinned R-B\(_6\)O are negative and the free energy of the \( \tau\)-B\(_6\)O phase is lower than that of the R-B\(_6\)O, demonstrating that the twinned structures are more stable than the R-B\(_6\)O phase. However, the negative SFEs have trivial influence on the elastic properties of the twinned R-B\(_6\)O. Applying a pure shear deformation on the new \( \tau\)-B\(_6\)O structure transforms it to R-B\(_6\)O along the lowest stress slip system (010)/<001> but this transformation is irreversible. Imposing biaxial shear stress in a way similar to the loading conditions for indentation, we find that the new \( \tau\)-B\(_6\)O phase transforms to an amorphous phase in which the lowest stress slip system changes from (010)/<001> to (001)/<110>. We found that the \( \tau\)-B\(_6\)O phase is stronger than R-B\(_6\)O under pure shear deformation, while it is weaker than R-B\(_6\)O for indentation conditions.

ASSOCIATED CONTENT

Supporting Information

The supporting Information includes details of the experimental and simulation method, the predicted elastic moduli for \( \tau\)-B\(_6\)O, 2\( \tau\)-B\(_6\)O, 4\( \tau\)-B\(_6\)O, the STEM image for R-B\(_6\)O, the STEM and HRTEM images for R-B\(_6\)O and \( \tau\)-B\(_6\)O, the computed electron diffraction patterns for perfect \( \tau\)-B\(_6\)O and vacancy models, the entropy (S) and Helmholtz free energy (A) difference between R-B\(_6\)O and \( \tau\)-B\(_6\)O at finite temperature, the transformed structure at 0.345 strain for 2\( \tau\)-B\(_6\)O phase shearing along (010)/<001> slip system, and the structural change for R-B\(_6\)O shear along (011)/<2\( \bar{1}\>\bar{1}> under indentation conditions. This material is available free of charge via the
Internet at http://pubs.acs.org.

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**Additional information**

Notes

The authors declare no competing financial interests.
References


Table 1. The predicted absolute energies (eV/B\textsubscript{6}O), relative energy, elastic modulus, and hardness of \(\tau\)-B\textsubscript{6}O, R-B\textsubscript{6}O, and twinned R-B\textsubscript{6}O from VASP. Comparing the total energy of \(\tau\)-B\textsubscript{6}O with R-B\textsubscript{6}O we can say that the energy to insert stacking faults into \(\tau\)-B\textsubscript{6}O to form R-B\textsubscript{6}O, is 1.51 mJ/m\textsuperscript{2}.

<table>
<thead>
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<th>Structure</th>
<th>(\tau)-B\textsubscript{6}O</th>
<th>R-B\textsubscript{6}O</th>
<th>2(\tau)-B\textsubscript{6}O</th>
<th>3(\tau)-B\textsubscript{6}O</th>
<th>4(\tau)-B\textsubscript{6}O</th>
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<td>-50.1361</td>
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<td>Relative energy (meV/B\textsubscript{6}O)</td>
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<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
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<td>226.2</td>
<td>–</td>
<td>221.8</td>
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<tr>
<td>Shear modulus (GPa)</td>
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<td>210.9</td>
<td>208.5</td>
<td>–</td>
<td>206.6</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>38.6</td>
<td>37.9</td>
<td>38.3</td>
<td>–</td>
<td>38.6</td>
</tr>
</tbody>
</table>
Fig. 1. The Structure of the τ-B₆O phase from QM prediction and STEM experiments: (a) QM predicted τ-B₆O phase projected along (100) direction. (b) STEM image showing the τ-B₆O phase. (c) An experimental SAED pattern recorded for the region imaged in (b) and indexed to be the τ-B₆O structure. (d) Simulated SAED pattern from the QM predicted structure projection along the (100) direction. In the experimental and simulated SAED (000) represents the transmitted beam. The identified g vector spots near the transmitted beam are given. The QM structure is predicted at 0 K without thermal fluctuations.
Fig. 2. The shear-stress shear-strain relationship of $\tau$-B$_6$O along various slip systems. The (010)/<001> is the least stress shear condition, with a maximum shear stress of 39.4 GPa.
Fig. 3. The deformation mechanism for shear along the least shear slip system, (010)/<001>
(note that each O bonds to three icosahedra, so that is formally $O^\dagger$): (a) The intact structure. (b)
The structure at 0.276 strain which corresponds to the maximum shear stress of 39.4 GPa. (c)
The structure at 0.369 strain before phase transition. (d) The structure at 0.392 strain after the phase transition where all bonds are reconnected for the sheared phase.
Fig. 4. The stress-strain relationship and the structural changes as the R-B$_6$O shear along (011)/<211> (reverse deformation of τ-B$_6$O along (010)/<001>): (a) Stress-strain relationship. (b) Structure at 0.280 strain corresponding to the maximum shear stress of 37.9 GPa. The B-B bond between icosahedra is stretched to 2.40 Å (dashed line). (c) Structure at 0.397 before failure. (d) Failed structure at 0.413 strain.
Figure 5

![Graph showing stress-strain relationship](image)

(b) Strain = 0.231

(c) Strain = 0.254

(d) Strain = 0.276

(e) Strain = 0.322

(f) Strain = 0.345

Fig. 5. The stress-strain relationships of $\tau$-B$_6$O, R-B$_6$O, and twinned R-B$_6$O shearing along various slip systems and the structural changes for $\tau$-B$_6$O under indentation conditions. (a) Stress-strain relationship. (b) $\tau$-B$_6$O structure at 0.231 strain shearing along (001)/<110> before failure. (c) $\tau$-B$_6$O structure at 0.254 strain shearing along (001)/<110> before failure. (d)-(f) Structural changes of $\tau$-B$_6$O shear along (010)/<001> slip system which results in phase transition from $\tau$-B$_6$O to R-B$_6$O.