Nanotwinned Boron Suboxide (B$_6$O): New Ground State of B$_6$O

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ABSTRACT: Nanotwinned structures in superhard ceramics rhombohedral boron suboxide (R-B$_6$O) have been examined using a combination of transmission electron microscopy (TEM) and quantum mechanics (QM). QM predicts negative relative energies to R-B$_6$O for various twinned R-B$_6$O (denoted as r-R$_{6}$B$_{6}$O, 2r-R$_{6}$B$_{6}$O, and 4r-R$_{6}$B$_{6}$O), consistent with the recently predicted B$_6$O structure with Cmcm space group (r-1) which has an energy 1.1 meV/B$_{6}$O lower than R-B$_{6}$O. We report here TEM observations of this r-B$_{6}$O structure, confirming the QM predictions. QM studies under pure shear deformation and indentation conditions are used to determine the deformation mechanisms of the new r-B$_{6}$O phase which are compared to R-B$_{6}$O and 2r-B$_{6}$O. The lowest stress slip system of r-B$_{6}$O is (010)/⟨001⟩ which transforms r-B$_{6}$O to R-B$_{6}$O 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.$^{1-6}$ In particular they significantly improve the materials strength by blocking dislocation movements.$^{5-8}$ In some twinned structures the electrical conductivity of the pure metal is retained with the increased strength,$^9$ 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$_{6}$C) that arises from the interplay of stoichiometry, atomic positioning, twinning, and structural hierarchy.$^{10}$ 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.$^{11,12}$ Therefore, investigating the roles of twins in deformation processes of other strong covalent solids.$^{13,14}$

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 have positive SFEs of 14.7 and 2.9 mJ/m$^2$, respectively, 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⟩ 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

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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 $1 \times 1$ zigzag twinned B$_6$O, which we denote as $\tau$-B$_6$O. We also identify other twinned phases, denoted as $2\tau$-B$_6$O and $4\tau$-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 one B$_{12}$ icosahedral cluster 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 Figure 1a. 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 B$_6$O$^{22}$ (experimental details are in the Supporting Information, SI). Besides the R-B$_6$O shown in Figure S1 of SI, we observed the new $\tau$-B$_6$O structure within some grains, as shown with STEM and HRTEM images in Figure 1b, Figures S2 and S3 of SI, providing experimental evidence supporting the theoretical prediction. The new $\tau$-B$_6$O structure belongs to the Cmcm space group. Figure 1a shows the projection along the $\langle 100 \rangle$ direction, which shows the B$_{12}$ icosahedra and the oxygen atom (O−O) chains. The BF-STEM image (Figure 1b) displays this zigzag pattern with the icosahedra alignment alternating every other plane. This zigzag structure has a mirror symmetry across the {010} planes and appears to be a uniformly twinned version of R-B$_6$O (Figure S1). The STEM images (Figure 1b and Figure S2) are analogous to the direct projection of structure model (Figure 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 (Figure 1c and d). The basic electron diffraction vectors from experiments and QM predictions agree very well, confirming that the observed phase is the $\tau$-B$_6$O phase. However, our experimental pattern shows low intensity spots halfway 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
indicating that it is favorable to put twins into R-B6O. and compare with R-B6O and 2,4 B6O is more stable structure. from the value expected from Wade plane, while the 1 zigzag structure along the direction perpendicular to the twin moduli are listed in Tables S1 ff. To determine the stability of the two phases at temperature, including the vibrational entropy. We added to the B12 unit in R-B6O to satisfy Wade s rule. In contrast, for R-B6O, the stress corresponding to the slip along the twin boundaries (TBs) in the twinned R-B6O. To gain insight into why the τ-B6O phase is more stable than R-B6O, we calculated the phonon frequencies of these two phases using QM to predict the elastic moduli of B6O.28 and B4C.29 To determine the deformation mechanism leading to brittle failure of the new τ-B6O phase, we applied pure shear deformation to τ-B6O (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-B6O. The stress—strain relationships of these slip systems are displayed in Figure 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 charge transfer in the τ-B6O structure nearly exactly matches Wade’s rule, suggesting that τ-B6O 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.33 These calculations used the 2 × 2 × 2 supercell for R-B6O and the 2 × 2 × 1 supercell for τ-B6O. The entropy and the Helmholtz free energy were computed from the phonon frequencies for temperature up to 2300 K, which is near the melting temperature of B6O.25 The entropy difference (Sr−B6O − Sr−B6O) and the Helmholtz free energy (A) difference (Ar−B6O − Ar−B6O) between these two phases are small, as displayed in Figure S5 of the SI. The τ-B6O phase has a lower Helmholtz free energy than R-B6O for all temperature up to melting, but the difference decreases gradually to zero at melting. The entropy of τ-B6O is slightly higher than that of R-B6O for T < 72 K but lower for higher temperatures. To examine if the twinned structures influence the mechanical properties of R-B6O, we calculated the hardness of τ-B6O, R-B6O, and twinned R-B6O 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-B6O, indicating that twins make B6O stronger. Amorphous shear band formation is the major failure mechanism for failure of superhard ceramics B6O28 and B4C.29 To determine the deformation mechanism leading to brittle failure of the new τ-B6O phase, we applied pure shear deformation to τ-B6O (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-B6O. The stress—strain relationships of these slip systems are displayed in Figure 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-B6O. For 2τ-B6O, QM leads to an ideal shear stress along (010)/(001) of 37.5 GPa. Thus, the τ-B6O is slightly stronger than 2τ-B6O, consistent with its higher predicted hardness. To compare with R-B6O, we shear the R-B6O along the (011)/(2T1) slip system, which is the reverse slip system of (010)/(001) for τ-B6O. The ideal shear stress of R-B6O 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-B6O. For 2τ-B6O, QM leads to an ideal shear stress along (010)/(001) of 37.5 GPa. Thus, the τ-B6O is slightly stronger than 2τ-B6O, consistent with its higher predicted hardness. To compare with R-B6O, we shear the R-B6O along the (011)/(2T1) slip system, which is the reverse slip system of (010)/(001) for τ-B6O. The ideal shear stress of R-B6O

Table 1. Predicted Absolute Energies (eV/B6O), Relative Energy, Elastic Modulus, And Hardness of τ-B6O, R-B6O, and Twinned R-B6O from VASP

<table>
<thead>
<tr>
<th>structure</th>
<th>τ-B6O</th>
<th>R-B6O</th>
<th>2τ-B6O</th>
<th>3τ-B6O</th>
<th>4τ-B6O</th>
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<tr>
<td>energy (eV/B6O unit)</td>
<td>−50.1366</td>
<td>−50.1355</td>
<td>−50.1362</td>
<td>−50.1361</td>
<td>−50.1360</td>
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<td>0.5</td>
<td>0.6</td>
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<td>bulk modulus (GPa)</td>
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<td>232.0</td>
<td>226.2</td>
<td>221.8</td>
<td>221.8</td>
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<tr>
<td>shear modulus (GPa)</td>
<td>209.2</td>
<td>210.9</td>
<td>208.5</td>
<td>206.6</td>
<td>206.6</td>
</tr>
<tr>
<td>hardness (GPa)</td>
<td>38.6</td>
<td>37.9</td>
<td>38.3</td>
<td>38.3</td>
<td>38.6</td>
</tr>
</tbody>
</table>

“Comparing the total energy of τ-B6O with R-B6O, we can say that the energy to insert stacking faults into τ-B6O to form R-B6O is 1.51 mJ/m².
shearing along (011)r/⟨21̅1̅⟩r is 37.9 GPa, which is lower than the shear along (001)r/⟨100⟩r of 43.5 GPa we examined earlier. Thus, the lowest stress slip system for R-B6O is actually (011)r/⟨21̅1̅⟩r, not (001)r/⟨100⟩r, 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-B6O > R-B6O ~ 2τ-B6O.

Figure 3. 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⁺): (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.

Figure 4. Stress–strain relationship and the structural changes as the R-B6O shear along (011)/⟨21̅1̅⟩ (reverse deformation of τ-B6O 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. Stress–strain relationships of τ-B$_6$O, R-B$_6$O, and twinned R-B$_6$O shearing along various slip systems and the structural changes for τ-B$_6$O under indentation conditions. (a) Stress–strain relationship. (b) τ-B$_6$O structure at 0.231 strain shearing along ⟨001⟩/⟨110⟩ before failure. (c) τ-B$_6$O structure at 0.254 strain shearing along ⟨001⟩/⟨110⟩ before failure. (d–f) Structural changes of τ-B$_6$O shear along ⟨010⟩/⟨001⟩ slip system which results in phase transition from τ-B$_6$O to R-B$_6$O.

In addition, we note that the slip along the TBs [(001)/⟨110⟩ slip system] has an ideal shear stress of 43.1 GPa, which is larger than 2τ-B$_6$O of 43.3 GPa. However, the ideal shear stress along this slip system for the perfect (nontwinned) R-B$_6$O is 43.5 GPa, which is similar to 2τ-B$_6$O.

Figure 3 displays the deformation mechanism of τ-B$_6$O for shear along the slip system ⟨010⟩/⟨001⟩. The intact structure is displayed in Figure 3a. 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 Figure 3b. But it is not broken as shown from the electron localization function (ELF)13 (inserted image of Figure 3b). 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-B$_6$O with no broken bonds in the icosahedral clusters. However, the “a” and “c” axes are now along [211], and [011], directions of R-B$_6$O, respectively. This deformation is similar to the pure shear deformation of R-B$_6$O13 and twinned R-B$_6$O14 where the icosahedral clusters do not deconstruct.

To examine the possible reverse transition from R-B$_6$O to τ-B$_6$O we performed pure shear deformation on the R-B$_6$O along the slip system of ⟨011⟩/⟨21T⟩, which is the reverse slip from τ-B$_6$O to R-B$_6$O. The stress–strain relationship and structural changes are displayed in Figure 4a. We found that the R-B$_6$O cannot transform back to τ-B$_6$O, instead the icosahedra disintegrate, leading to the amorphous band formation, as shown in Figure 4b–d. Indeed previous experimental studies show amorphous band formation in R-B$_6$O.28 However, our previous QM simulations show structure recovery for R-B$_6$O shearing along ⟨001⟩/⟨100⟩.28 Here we show that shearing along ⟨011⟩/⟨21T⟩, 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$_6$O is along the ⟨011⟩ plane. This is not consistent with previous experiments28 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,13 we applied biaxial shear stress on τ-B$_6$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$_6$O and R-B$_6$O along the similar slip systems for comparison. The shear-stress–shear-strain relationships for these three structures are displayed in Figure 5a. We see that the ideal shear stress of τ-B$_6$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$_6$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$_6$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$_6$O, the ideal shear stresses are 39.9 and 37.2 GPa for shearing along ⟨001⟩/⟨100⟩, and ⟨011⟩/⟨21T⟩ respectively. This indicates that ⟨011⟩/⟨21T⟩, is still the most plausible slip system in R-B$_6$O. Under the biaxial shear stress conditions, the sequence from high to low strength is R-B$_6$O ~ 2τ-B$_6$O > τ-B$_6$O, which is reverse compared to the pure shear deformation.

The deformation mechanism for τ-B$_6$O along ⟨001⟩/⟨110⟩ under the biaxial shear stress conditions is displayed in Figure 5b,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 τ-B$_6$O under biaxial shear conditions, we plotted the structural changes by shearing along ⟨010⟩/⟨001⟩ in Figure 5d–f. We see that the τ-B$_6$O also transforms to R-B$_6$O at biaxial stress conditions, which
is the same as for pure shear deformations. The 2r-B6O exhibits a similar deformation mechanism under biaxial stress conditions: the icosahedra disintegrate when shearing along (001)/(110) with a lower shear stress of 36.9 GPa, while the structure changes to R-B6O when shearing along (010)/(001) with a higher minimum shear stress of 40.8 GPa (Figure S6 of SI). For R-B6O, the icosahedra disintegrate for both shear along (001)/(110), and along (011)/(211), (Figure S7 of SI).

Structural transformations between solids have been widely examined in metals, semiconductors, and superhard ceramics. Recent studies show that a possible path for transforming the zinc-blende (ZB) structure to the wurtzite structure is a collective glide of Shockley partial dislocations on the (111) plane. We calculate that the shear deformation from R-B6O to r-B6O requires a shear stress over 35 GPa at 0 K. Thus, it is unlikely that r-B6O is formed from mechanical twinning of R-B6O. Instead we expect that r-B6O may be formed during nucleation and growth from the melt, as favored by the lower free energy of r-B6O compared to R-B6O.

In summary, we confirm with QM and STEM experiments the existence of the new r-B6O phase predicted by Dong et al. The stacking fault energies for nanotwinned R-B6O are negative and the free energy of the r-B6O phase is lower than that of the R-B6O, demonstrating that the twinned structures are more stable than the R-B6O phase. However, the negative SFEs have trivial influence on the elastic properties of the twinned R-B6O. Applying a pure shear deformation on the new r-B6O structure transforms it to R-B6O 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 r-B6O phase transforms to an amorphous phase in which the lowest stress slip system changes from (010)/(001) to (001)/(110). We found that the r-B6O phase is stronger than R-B6O under pure shear deformation, while it is weaker than R-B6O for indentation conditions.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.6b01204.

Details of the experimental and simulation method, the predicted elastic moduli for r-B6O, 2r-B6O, and 4r-B6O, the STEM image for R-B6O, the STEM and HRTEM images for r-B6O, the computed electron diffraction patterns for perfect r-B6O and vacancy models, the entropy (S) and Helmholtz free energy (A) difference between R-B6O and r-B6O at finite temperature, the transformed structure at 0.345 strain for 2r-B6O phase shearing along (010)/(001) slip system, and the structural change for R-B6O shear along (011)/(211), under indentation conditions (PDF)

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Notes
The authors declare no competing financial interest.

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