FIRST PRINCIPLES CALCULATIONS ON BORON SUBOXIDE(B_6O)

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INTRODUCTION

- Boron Suboxide (B_6O) is a boron-rich covalent ceramic known for its extreme hardness, low density, and excellent thermal stability.
- It is considered one of the hardest materials after diamond and cubic boron nitride.
- Theoretical (first-principles) calculations help us understand its crystal structure, bonding nature, electronic properties, and mechanical strength.

WHY STUDY B_6O?

- B_6O exhibits a superhard nature (~45 GPa hardness) with a high melting point (>2000 °C).
- Its icosahedral boron framework imparts excellent strength and stiffness.
- Useful for abrasives, armor, and high-temperature structural components.

ALPHA-B_6O STRUCTURE

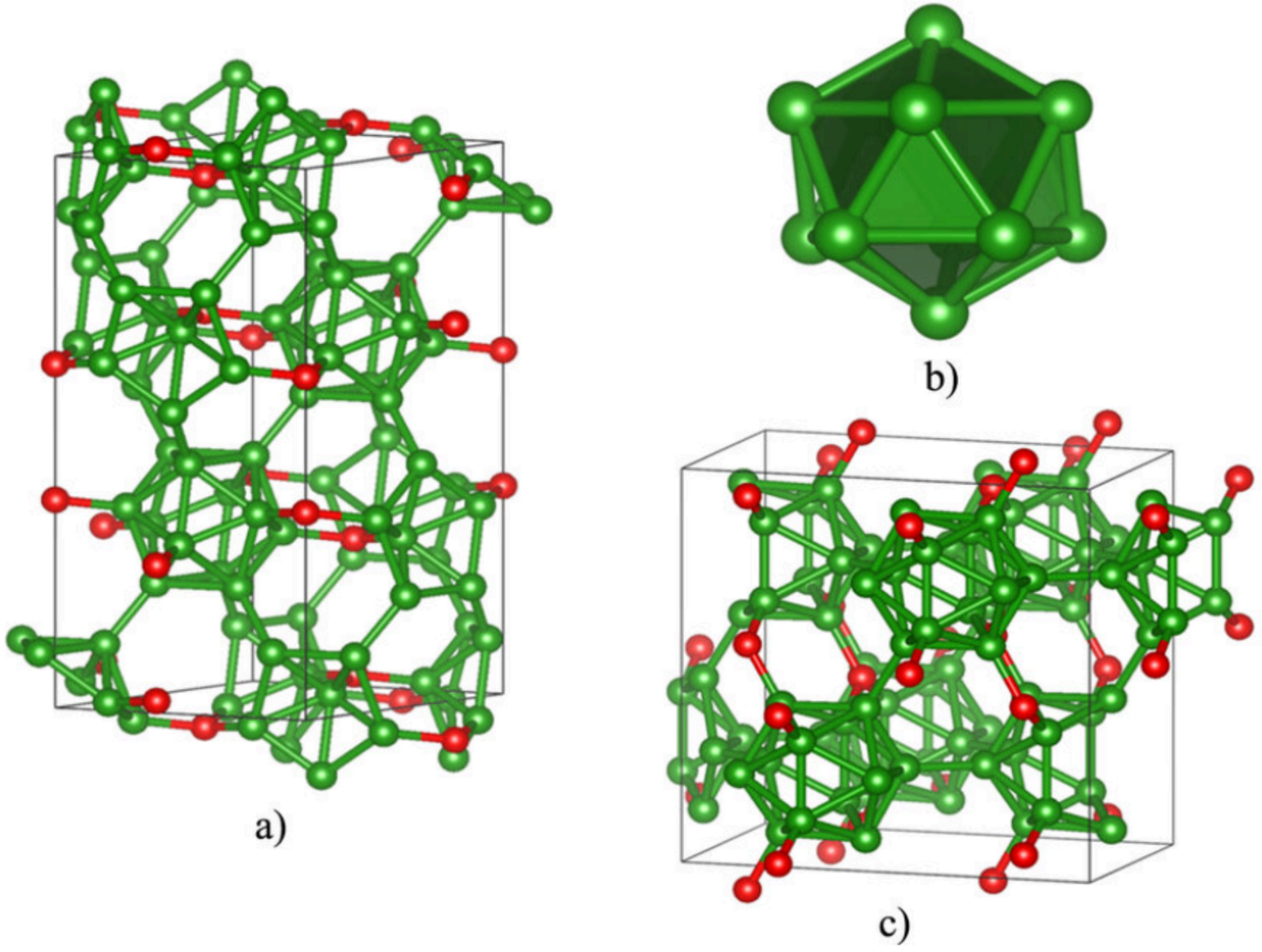
- Space group: R-3m (No. 166) (rhombohedral)
- Stoichiometry: B_6O (36 B + 6 O in conventional hex cell; primitive rhombohedral cell descriptions exist).
- Typical bond lengths : **B–O ≈ 1.49 Å**, **O–O ≈ 3.08 Å**; internal **B–B** bonds inside icosahedra are **~1.69–1.78Å** (varies locally)
- Structure is often described as “**oxygen-stuffed α-boron**”: a cubic-close-packing of B_{12} icosahedra with oxygen atoms filling octahedral voids.

BETA-B_6O STRUCTURE

- β-B_6O was predicted in 2016 by Dong, Oganov as a new ground-state candidate.
- Space group: Cmcm (No. 63) (orthorhombic)
- In β, there is no simple close-packing sequence – icosahedra form a 3-D interconnected orthorhombic network contrasting α's ABC stacking.
- lattice parameters:**a ≈ 5.39 Å, b ≈ 8.78 Å, c ≈ 8.74 Å**
- β-B_6O is slightly more stable than α under ambient conditions .

Alpha-B_6O Structure

Feature	Rhombohedral Setting (Primitive Cell)	Hexagonal Setting (Conventional Cell)
Crystal system	Trigonal (Rhombohedral primitive)	Trigonal expressed in hexagonal axes
Space group	$R\bar{3}m$ (No. 166)	P1 (No. 1) – symmetry removed
Cell type	Primitive (rhombohedral)	Conventional (hexagonal)
Lattice Parameters	a=b=c=5.137 Å, **α = β = γ = 63.04°**	**a = b = 5.376 Å ; c = 12.276 Å ; α = β = 90° ; γ = 120°**
Atoms / cell	14 (12 B + 2 O) → 2 formula units	42 (36 B + 6 O) → 6 formula units
Cell Volume	102.43 $Å^3$ (Exactly 1/3 of the hexagonal volume)	307.30 $Å^3$

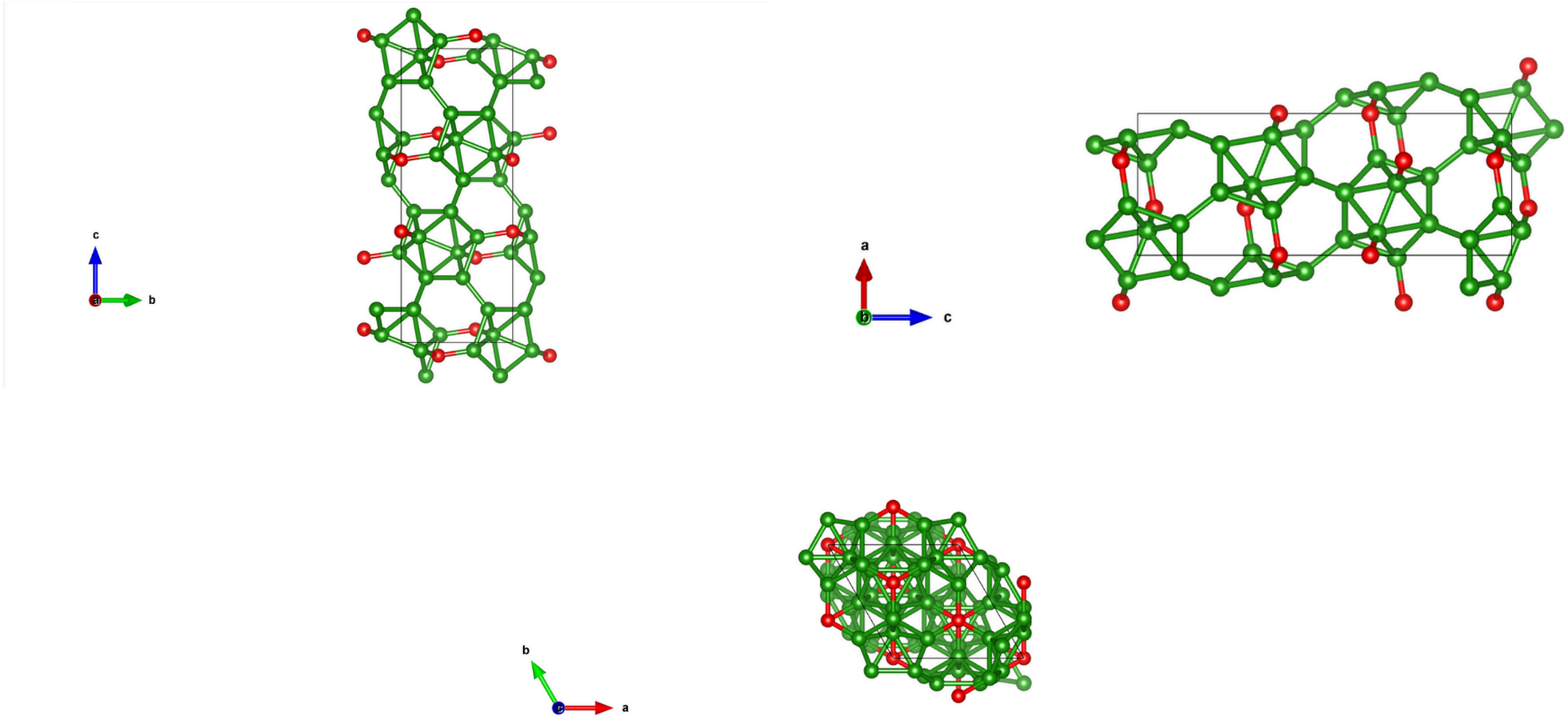


Crystal structures of (a) α-B6O; (b) B12 icosahedra; (c) β-B6O. Green and red spheres denote boron and oxygen atoms, respectively.

COMPARISON OF ALPHA VS BETA (STRUCTURE & PROPERTIES)

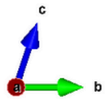
Feature	**α-B_6O**	**β-B_6O**
Space group	R-3m	Cmcm
Stacking of icosahedra	ABC (ccp)	Not a simple close-packing sequence – icosahedra form a 3-D interconnected orthorhombic network
Volume	51.71 $Å^3$	51.69 $Å^3$
Hardness (DFT)	~38 GPa	~39 GPa
Band gap type	Direct (~1.85 eV)	Indirect (~1.81 eV)

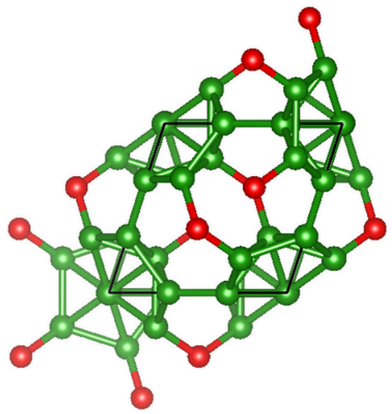
α-B_6O: Hexagonal (Expanded P1) Representation

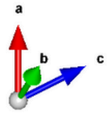


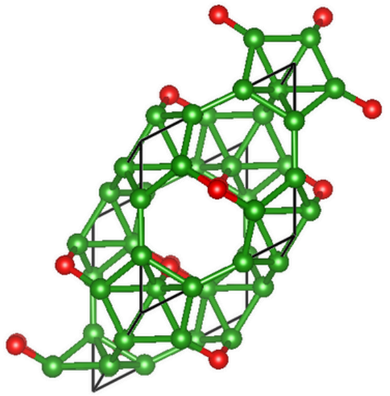
HEXAGONAL (CONVENTIONAL) SETTING

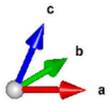
Primitive α-B_6O

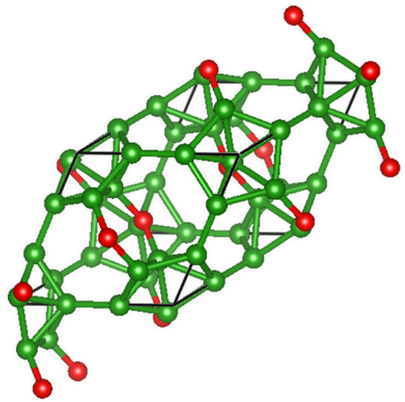












Setting	Total Atoms	Wycoff Positions
Hexaginal Setting(Conventional)	42 ($B_{36}O_6$)	• O: 6c --- (1/3, 2/3, 0.044564) • B_1: 18h --- (0.491569, 0.508431, 0.307049) • B_2: 18h --- (0.443729, 0.556271, 0.554067)
Rhombohedral Setting (Primitive Cell)	14 ($B_{12}O_2$)	• O: 2c • B_1: 6h • B_2: 6h

Part 1: Structural Relaxation

- **Objective:** To find the lowest-energy, stable ground-state structure of B6O.

- **Why?** This optimized structure is the required starting point for all other property calculations (DOS, Band Structure, and Elastic Properties).

- **Method:**
  - We start with an initial structure (POSCAR), in this case, the α-B_6O example primitive cell from the Materials Project (mp-1346).
  - We use VASP to calculate the forces on all atoms and the stress on the lattice.
  - The calculation then moves the atoms and changes the cell shape/volume to minimize these forces and stresses, until a stable (converged) structure is found (CONTCAR).

Part 2: Static SCF

- **What is this step?**
  - A high-precision, static calculation is performed on the previously relaxed structure.
  - "Static" means the atoms are held in their final, stable positions.
  - A Self-Consistent Field (SCF) loop is run to find the precise, stable electronic ground state.
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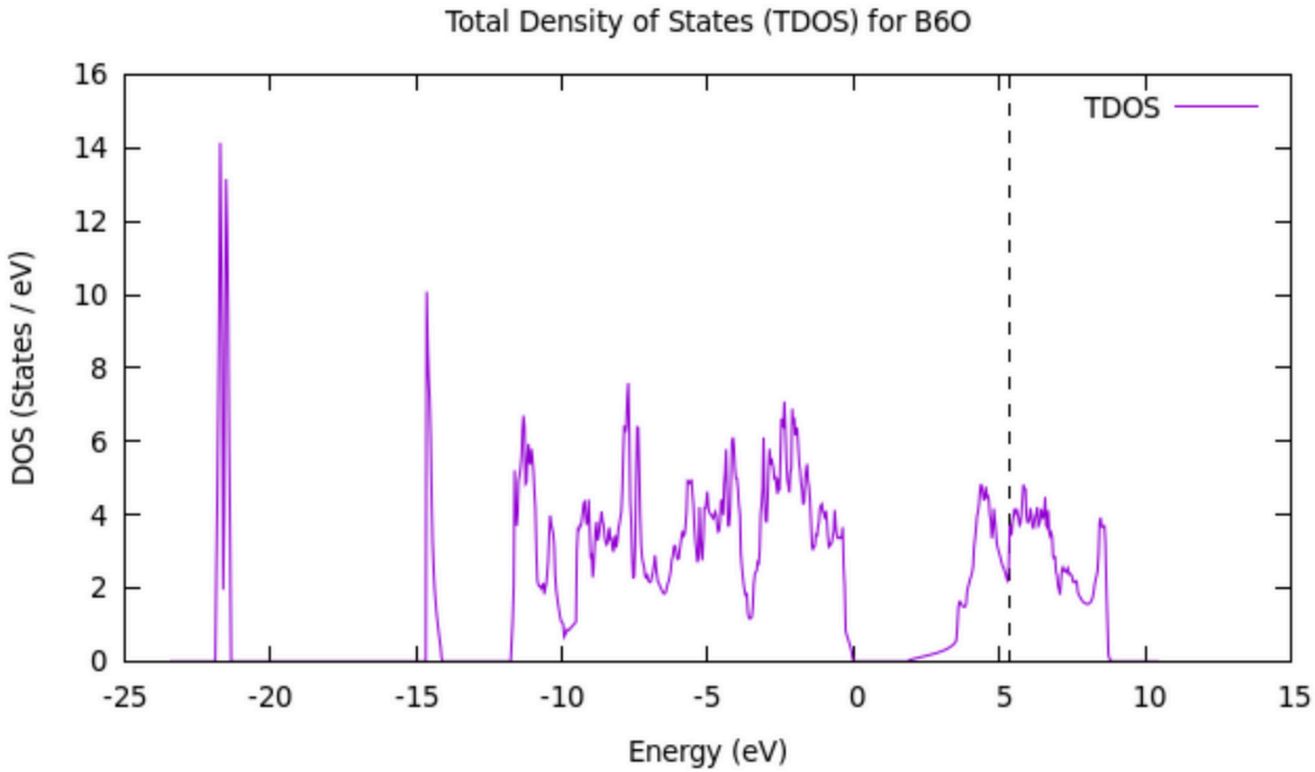
- **Why is this done?**
  - This is the primary "data collection" step for electronic properties.
  - Its main purpose is to generate the high-resolution data needed for the Density of States (DOS).
  - This static calculation provides a much more accurate and detailed electronic snapshot than is possible during the structural relaxation.

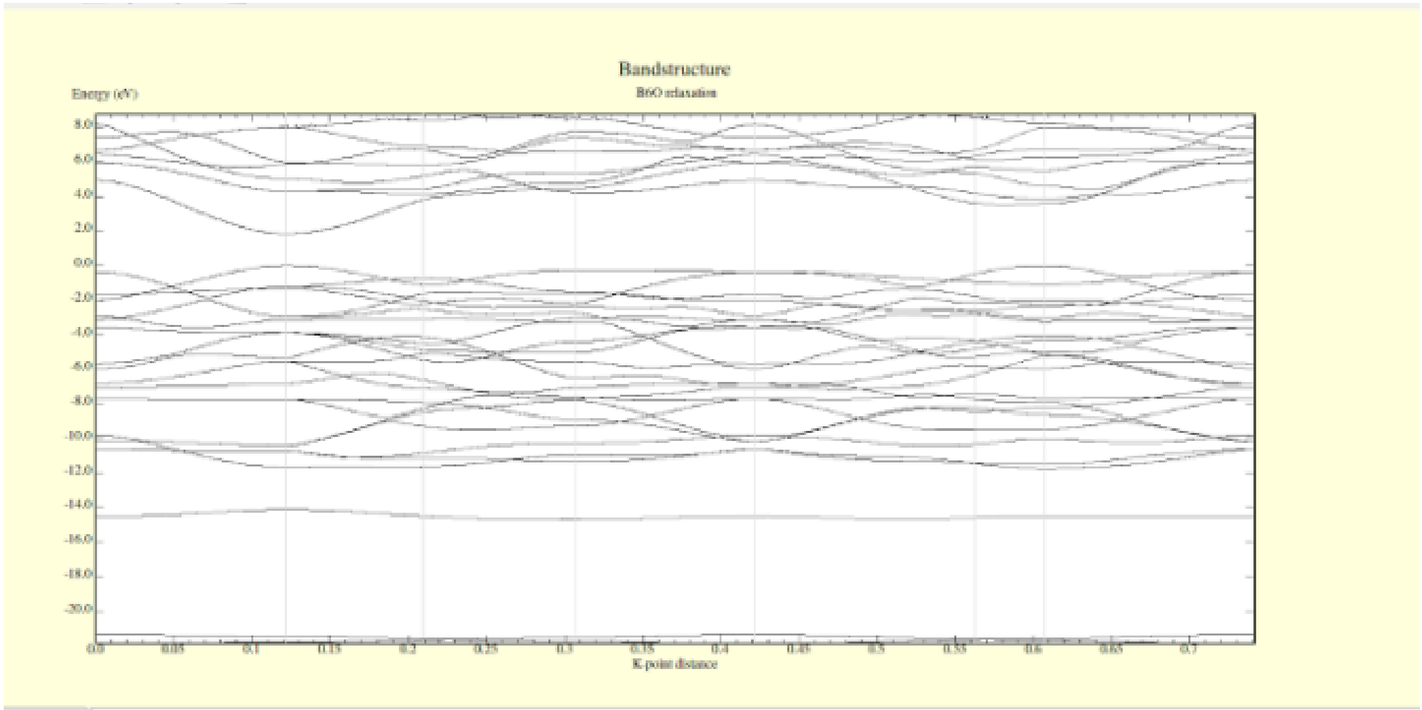
Part 3: Density of States

- The DOS spectrum reveals the distribution of electronic states across energy levels for primitive B_6O.
- A clear semiconducting nature is observed, with a distinct region of zero states near the Fermi level
- A strong, localized bonding peak appears near –22 eV, characteristic of deep B–O bonding states
- The Fermi level lies at 5.091 eV (shifted to 0 eV in the DOS plot for clarity).
- The DOS profile confirms strong covalent bonding and a stable electronic structure influenced by B_{12} icosahedra.



Part 4: Band Structure

- The calculated band structure of primitive B_6O shows a direct band gap.
- Band Gap: 1.8515 eV
- VBM (Valence Band Maximum):
  - Energy: 5.0872 eV
  - k-point: (0.5, 0.5, 0.5)
- CBM (Conduction Band Minimum):
  - Energy: 6.9387 eV
  - k-point: (0.5, 0.5, 0.5)



- The valence bands are relatively flat, showing localized bonding states due to strong B–O covalent interactions.
- The conduction bands are more dispersive, implying better electron mobility once excited.
- Overall, the band structure confirms that B_6O is a stable wide-gap semiconductor with strong covalent bonding.

Elastic Properties

What Are Elastic Constants (Cij)?

- (Cij) are components of the stiffness tensor, describing how a material responds to stress.

- They relate stress and strain via Hooke's Law in tensor form: $\sigma_i = \sum_j C_{ij}\,\epsilon_j$

- Determine stiffness, hardness, brittleness, sound velocity, and mechanical stability.

Cij	1	2	3	4	5	6
1	584.826	123.839	49.848	0.000	22.694	0.000
2	123.839	584.826	49.848	0.000	–22.694	0.000
3	49.848	49.848	458.097	0.000	0.000	0.000
4	0.000	0.000	0.000	230.493	0.000	22.694
5	22.694	–22.694	0.000	0.000	178.115	0.000
6	0.000	0.000	0.000	22.694	0.000	178.115

Comparison

Property	Calculated Value	Actual Value
Bulk Modulus (GPa)	227.4	237
Shear Modulus (GPa)	207.6	210
Young’s Modulus (GPa)	477.5	480
Poisson Ratio	0.165	0.16
Anisotropy (AU)	0.193	0.20
Debye Temp. (K)	1633	~1600

Reference: Materials Project Entry MP-1986 (α-B_6O)

Interpretation of Elastic Properties

- **High Bulk Modulus (227 GPa)**
  - Material is highly incompressible, showing very strong overall bonding strength

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- **Large Shear Modulus (208 GPa)**
  - Indicates excellent resistance to shape deformation, a signature of superhard materials.

- **Very High Young's Modulus (477 GPa)**
  - Reflects extremely high stiffness; small strain is produced even under high stress.
  - Confirms strong directional covalent bonding.

- **Low Poisson Ratio (0.165)**
  - Characteristic of brittle materials.

- **High Debye Temperature (1633 K)**
  - Suggests strong atomic bonding and excellent thermal stability.
  - Also correlates with high hardness and low lattice vibrations.

Conclusion

- Primitive B_6O shows a direct band gap (1.85 eV) and strong B–O covalent bonding, confirming stable semiconducting behavior.
- Mechanical results indicate very high stiffness, incompressibility, and shear resistance, characteristic of superhard materials.
- Overall, B_6O is a strong, stable, and high-performance material suitable for extreme mechanical and thermal applications.

References

1) **ResearchGate:** https://www.researchgate.net/publication/252700902_Crystal_Structure_of_B6O

2) **ARXIV:** https://arxiv.org/abs/1604.00586

3) **Materials Project :** https://materialsproject.org/materials/mp-1346