A

PROJECT REPORT
On

"First Principles Calculations on Boron Suboxide (B₆O)"

A Project Report submitted in partial fulfillment
of the requirements for the award of the Degree of

Bachelor of Technology
in
Materials Engineering

Submitted by
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CERTIFICATE

This is to certify that the Project Report titled **"First Principles Calculations on Boron Suboxide (B_6O)",** submitted by Dadabada Sai Prasad (B22MT012) to the Indian Institute of Technology Jodhpur, for the award of the degree of Bachelor of Technology, is a bonafide record of the work carried out by him under my supervision.

To the best of my knowledge, the contents of this report have not been submitted to any other Institute or University for the award of any degree.

Signature
Dr. Appala Naidu Gandi

DECLARATION

I hereby declare that the work presented in this Project Report titled **"First Principles Calculations on Boron Suboxide (B$_6$O)"**, submitted to the Indian Institute of Technology Jodhpur, is an original work carried out by me under the supervision of **Dr. Appala Naidu Gandi**.

I further declare that this report has not been submitted to any other Institute or University for the award of any degree.

Signature
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ABSTRACT

This project presents a complete first-principles study of the electronic and mechanical properties of primitive Boron Suboxide (B_6O) using Density Functional Theory (DFT). Structural optimization, SCF calculations, Density of States (DOS), band structure, and elastic constants were computed using VASP.

The electronic structure confirms that B_6O is a direct-band-gap semiconductor with a band gap of approximately 1.85 eV, dominated by strong B–O covalent interactions. Mechanical calculations reveal high stiffness, large shear resistance, low Poisson ratio, and high Debye temperature, confirming its superhard and thermally stable nature.

Overall, the study demonstrates that primitive B_6O possesses robust electronic stability and exceptional mechanical performance, making it ideal for high-temperature and extreme-environment applications.

CONTENTS

1. INTRODUCTION

Boron suboxide (B_6O) is one of the hardest known materials. Its outstanding combination of **superhardness, low density, high thermal stability, and chemical inertness** makes it highly suitable for demanding applications such as abrasive tools, protective armor, and high-temperature structural components. These exceptional properties arise from its boron-rich crystal structure, where **B_{12} icosahedra** form a rigid covalent network, strengthened further by interstitial oxygen atoms.

Despite its promising characteristics, the experimental study of B_6O is challenging due to its extreme hardness, high synthesis temperatures, and difficulty in obtaining defect-free samples. As a result, complete and reliable experimental data on its electronic and mechanical properties are limited. This creates a strong need for theoretical methods capable of accurately predicting material behavior at the atomic level.

First-principles calculations based on **Density Functional Theory (DFT)** provide a powerful framework to understand the intrinsic properties of B_6O. DFT enables the prediction of electronic structure, bonding characteristics, mechanical stiffness, and stability without relying on experimental inputs. In this project, DFT is used to analyze the primitive B_6O structure through relaxation, DOS and band structure calculations, and evaluation of the full elastic tensor. The results offer detailed insights into the origin of its superhard nature and establish its potential for high-performance applications in extreme environments.

2. THEORY

2.1 Structural Description of Primitive α-B_6O

Primitive boron suboxide (B_6O) crystallizes in the trigonal $\overline{R}3m$ space group and is naturally represented using a **rhombohedral primitive unit cell**. The optimized lattice parameters obtained from the POSCAR are:

- **a = b = c = 5.1537 Å**

- **α = β = γ = 63.103°**

These parameters confirm that the primitive cell is fully rhombohedral, distinct from the larger conventional hexagonal representation typically used for the same structure.

The crystal structure features interconnected B_{12} **icosahedra**, forming a rigid covalent framework that dominates the mechanical response. Interstitial oxygen atoms occupy symmetric positions that bridge neighboring icosahedra, further enhancing bonding strength.

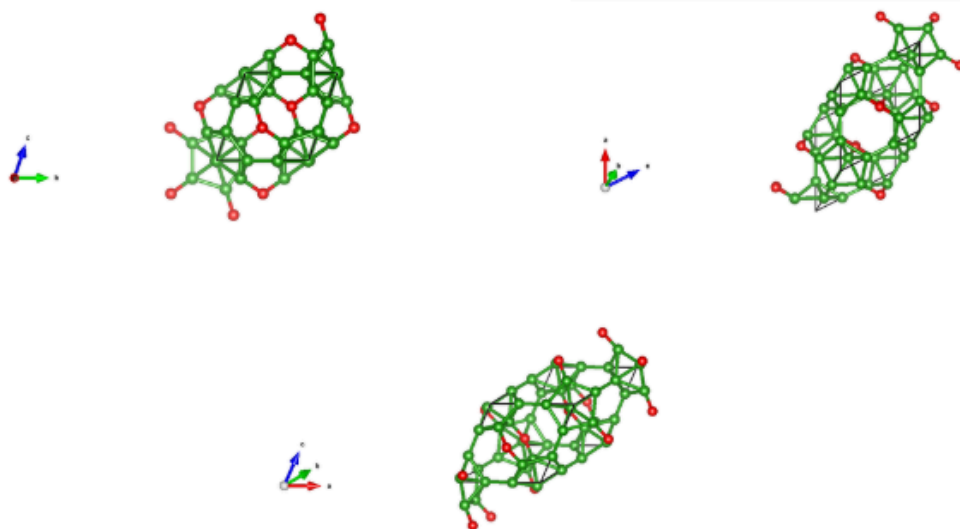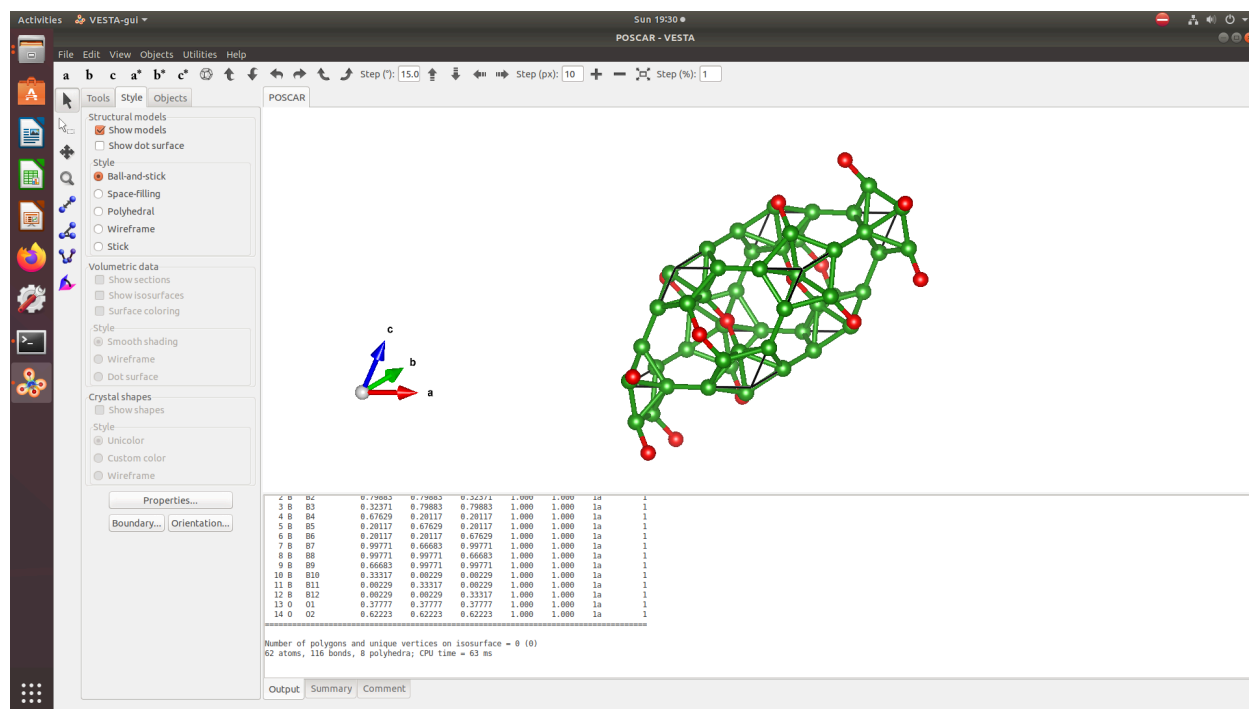There are **two inequivalent boron sites**:

Boron Site 1:Bonded to three B atoms and one O atom.Includes two shorter **B–B bonds (~1.78 Å)**, one longer **B–B bond (~1.81 Å)**, and a strong B–O bond **(~1.49 Å).**

Boron Site 2:
A six-coordinated boron environment, bonded entirely to other boron atoms. Contains one short **B–B** bond (~1.69 Å) and two longer **B–B bonds (~1.78 Å)**, typical of boron's multi-center bonding.

The oxygen atoms adopt trigonal planar coordination, each bonded symmetrically to three B atoms, linking adjacent icosahedral units.

Overall, the combination of B_{12} icosahedra, multi-center B–B bonds, and strong **B–O** linkages creates a dense, highly stable covalent network.

2.2 Density Functional Theory (DFT)

Density Functional Theory (DFT) is a first-principles method used to compute the ground-state properties of materials from quantum mechanics. Instead of solving the many-electron wavefunction, DFT uses **electron density** as the fundamental variable, making the calculations efficient while still providing reliable accuracy for solid-state systems.

In this project, DFT is implemented using **VASP**, which employs the **Projector Augmented Wave (PAW)** method to accurately treat core and valence electrons. The **PBE–GGA exchange–correlation functional** is used because it predicts structural parameters, bonding characteristics, and elastic properties with good accuracy for covalent and ceramic materials. A **plane-wave basis set** with an energy cutoff of 520 eV ensures systematic convergence for all calculations. With this framework, DFT allows precise determination of the optimized structure, total energy, electronic states, and mechanical response of B_6O.

2.3 Electronic Structure Theory

Electronic properties of crystalline materials are described using **band structure** and **Density of States (DOS)**:

- The **band structure** shows how electron energies vary along high-symmetry paths in the Brillouin zone and is used to determine whether the material is metallic, semiconducting, or insulating.

- The **density of states** provides the distribution of electronic levels at each energy and helps identify bonding characteristics and the nature of the band gap.

These tools are essential for analyzing the semiconducting behavior of B_6O and understanding the contributions of B and O orbitals to bonding.

2.4 Elastic Property Theory

The mechanical response of a crystal is characterized by the **elastic stiffness tensor (C_i□)**, obtained from the linear relationship between applied strain and resulting stress. From the elastic constants, key mechanical moduli are derived:

- **Bulk modulus (B):** resistance to uniform compression

- **Shear modulus (G):** resistance to shape deformation

- **Young's modulus (E):** overall stiffness

- **Poisson ratio (v):** measure of lateral contraction

These parameters describe stiffness, brittleness, and mechanical stability, and are especially important for understanding the **superhard nature** of B_6O.

3. PROBLEM STATEMENT AND OBJECTIVES

3.1 Problem Statement

Although boron suboxide (B_6O) is known for its exceptional hardness, thermal stability, and strong covalent bonding, its detailed electronic and mechanical properties are not fully established. Experimental characterization is limited due to challenges in synthesizing defect-free samples, measuring elastic constants, and probing electronic behavior in extremely hard ceramics. Therefore, a reliable and systematic computational study is needed to understand its intrinsic properties and provide quantitative data that is difficult to obtain experimentally.

3.2 Objectives

This project aims to use first-principles Density Functional Theory to:

1. Obtain the optimized crystal structure of primitive B_6O.

2. Determine the ground-state electronic configuration through self-consistent calculations.

3. Compute the Density of States (DOS) and band structure to analyze bonding and band gap characteristics.

4. Evaluate the complete elastic stiffness tensor ($C_{i\square}$) using stress–strain calculations.

5. Derive mechanical properties such as bulk modulus, shear modulus, Young's modulus, and Poisson ratio.

6. Assess the mechanical stability and stiffness of B_6O based on calculated elastic constants.

7. Provide a clear understanding of how the electronic and mechanical behavior relates to its superhard nature.

4. COMPUTATIONAL METHODOLOGY

The computational analysis of B_6O was carried out using first-principles Density Functional Theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP). This section explains the procedures used at each stage—structural relaxation, SCF computation, DOS, band structure, and elastic calculations—along with the reasoning behind key methodological choices to ensure accuracy, reliability, and consistency of results.

4.1 Computational Framework

The interaction between electrons and ions was treated using the **Projector Augmented Wave (PAW)** method, which accurately captures both core and valence electrons while maintaining computational efficiency. The **Perdew–Burke–Ernzerhof (PBE)** generalized gradient approximation was used as the exchange–correlation functional because it provides reliable predictions for lattice constants, electronic structure, and mechanical properties of ceramic and covalent materials such as B_6O.

All calculations employed a **plane-wave basis set** with a cutoff energy of **520 eV**, chosen after convergence testing. A sufficiently high cutoff ensures that stress, forces, and total energies converge smoothly and that elastic constants are accurate. Brillouin zone integrations were performed using **Γ-centered k-point meshes**, which are ideal for primitive unit cells and ensure symmetrical sampling.

This combination of PAW + PBE + plane waves forms a robust computational framework widely used for predicting the properties of crystalline materials.

- Plane-wave cutoff **ENCUT = 520 eV** produced stable energies and stress tensors.

- Γ-centered meshes up to **14×14×14** were confirmed to be fully converged.

The computational setup is sufficiently accurate for predicting structural, electronic, and mechanical properties of B_6O.

4.2 Structural Relaxation

The first major task was to obtain the equilibrium crystal structure of B_6O. Accurate relaxation is essential because **all subsequent electronic and mechanical properties depend on the quality of the optimized geometry**.

Relaxation was performed using:

- **IBRION = 2**: Conjugate-gradient ionic optimizer

- **ISIF = 3**: Relax both atomic positions and full cell

- **EDIFF = 10^{-6} eV**: Tight electronic convergence

- **EDIFFG = –0.01 eV/Å**: Force convergence threshold

- **k-mesh = 14 × 14 × 14 (Γ-centered)**

Explanation:

- A conjugate-gradient algorithm efficiently finds the minimum-energy structure.
-

- ISIF = 3 allows the lattice to change shape and volume, ensuring the final cell is fully relaxed.

- A dense k-point mesh improves the accuracy of energy gradients, making relaxation smoother and more precise.

The relaxation converged to a final total energy of **–99.93114 eV**, with all force components well below the threshold. The final CONTCAR file represents the equilibrium structure and serves as the starting point for SCF, DOS, band structure, and elastic calculations.

4.3 Self-Consistent Field (SCF) Calculation

The SCF step determines the **ground-state electron density**, which is required for any property related to electronic behavior. While relaxation focuses on atomic positions, the SCF calculation refines the **electronic potential and charge distribution** for the optimized geometry.

Key parameters:

- **ISMEAR = 0, SIGMA = 0.05** (tetrahedron smearing for semiconductors)

- **PREC = Accurate**

- **k-mesh = 14 × 14 × 14 (Γ-centered)**

- **Charge output:** CHGCAR, WAVECAR

The SCF cycle converged to:

- **Fermi energy = 5.32692 eV**

- **Total energy = –99.93114 eV**

Explanation:

- Using ISMEAR = 0 is appropriate for nonmetallic systems where a well-defined band gap is expected.

- The SCF-generated charge density is more accurate than the pre-relaxation estimate and is therefore used in DOS and band structure calculations (via **ICHARG = 11**).

- A dense k-mesh ensures that the Fermi level and electronic states are calculated with maximum accuracy.

This SCF stage provides the electronic ground state needed for subsequent analysis.

4.4 Density of States (DOS)

The density of states reveals how electronic energy levels are distributed within the valence and conduction bands. A **non-SCF DOS calculation** was performed using the converged charge density from the SCF step.

Parameters:

- **ICHARG = 11** (use fixed SCF charge density)

- **k-mesh = 14 × 14 × 14 Γ-centered**
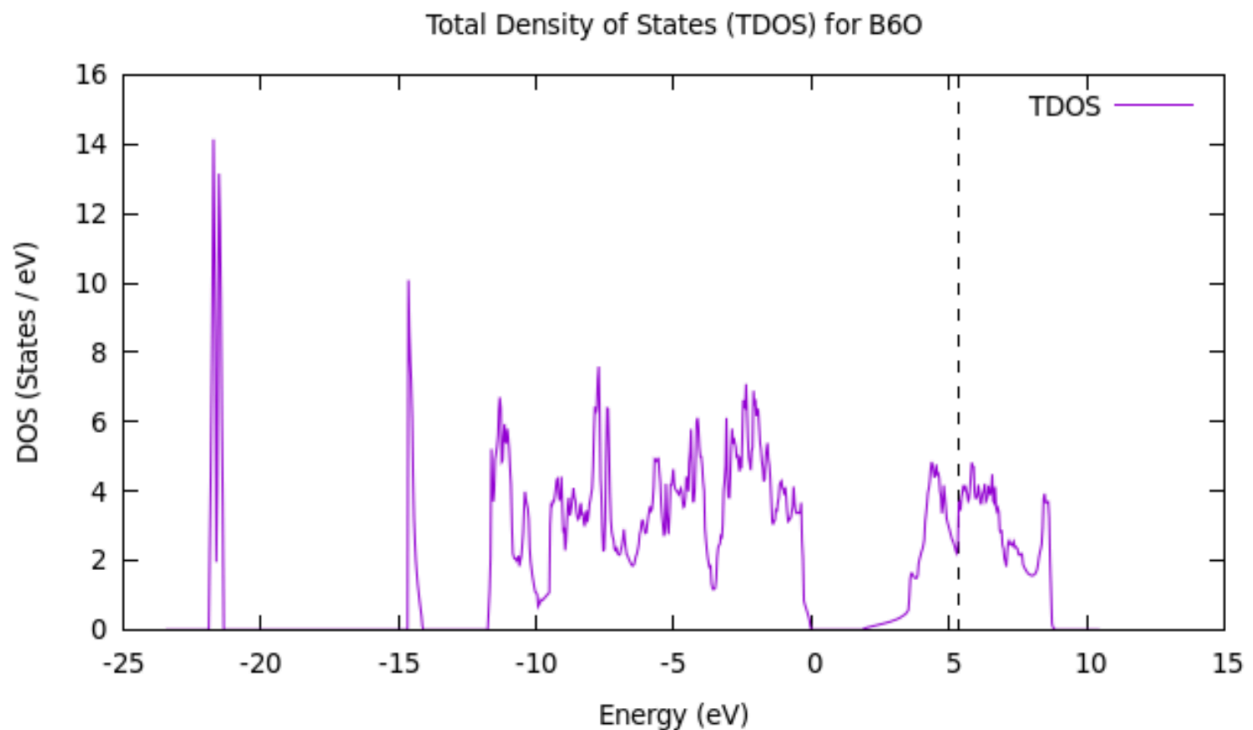
- **NEDOS = 1000** (fine energy grid)
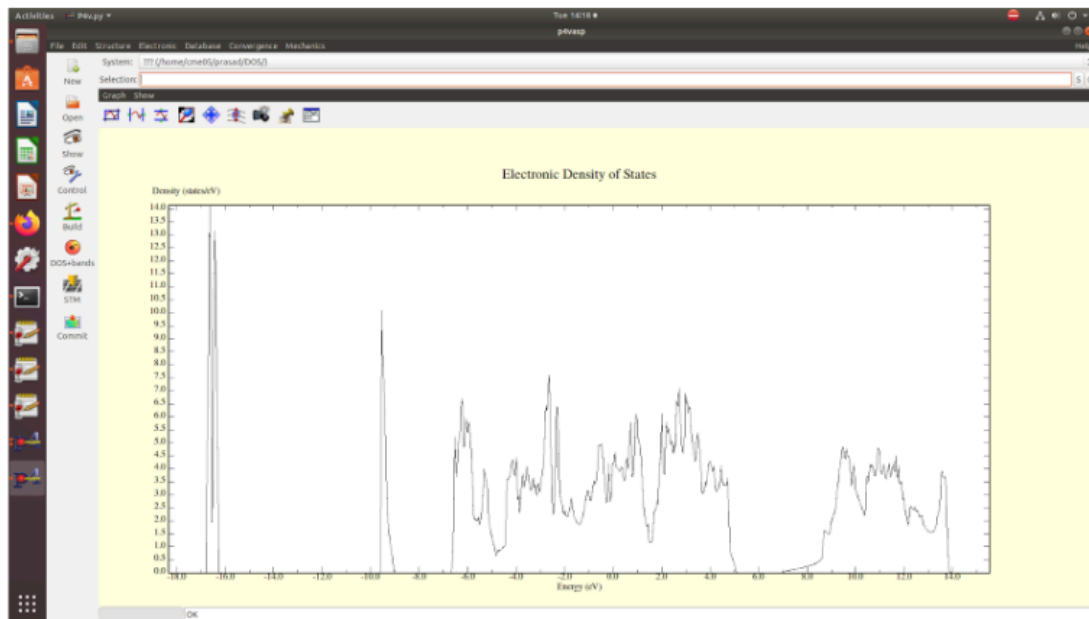
The DOS calculation produced:

- **Fermi energy (from DOSCAR) = 5.09139 eV**

Explanation:

- DOS requires a dense and uniform sampling of the Brillouin zone.

- Using the fixed charge density ensures consistency with SCF, avoiding artificial changes during DOS evaluation.

- Projected DOS (PDOS) decomposes contributions from *B s/p orbitals* and *O s/p orbitals*, allowing insight into bonding and orbital hybridization.

DOS confirms the **presence of a band gap and hybridized B–O covalent bonding**, both critical for understanding the electronic behavior of B_6O.

Total Density of States (TDOS) for B6O

4.5 Band Structure Calculation

Band structure provides information about electron dispersion and reveals the band gap type and magnitude. This calculation uses:

- **ICHARG = 11** (fixed charge density)

- **High-symmetry k-path** from KPATH.in

- **Eigenvalues of bands along symmetry lines**

The path used was:

$$\Gamma \rightarrow T \rightarrow H_2 \rightarrow H_0 \rightarrow L \rightarrow \Gamma \rightarrow S_0 \rightarrow S_2 \rightarrow F \rightarrow \Gamma$$

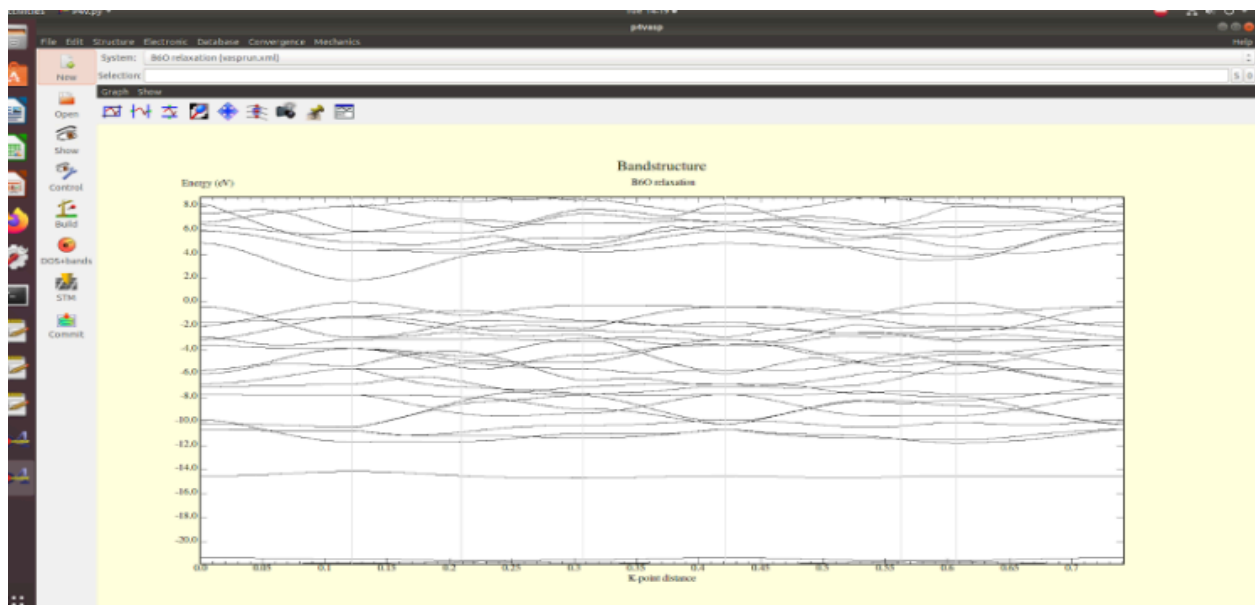The band energies were shifted by the Fermi level (5.09139 eV) to align with DOS.

The computed band structure shows:

- **VBM = 5.0872 eV, CBM = 6.9387 eV**
- **Direct band gap = 1.8515 eV**
- VBM and CBM located at **k = (0.5, 0.5, 0.5)**

Explanation:

- Following a high-symmetry path reveals critical features of the electronic structure that DOS cannot show, such as dispersion and transition character.

- A direct band gap corresponds to optical transitions without momentum change, relevant for electronic/material device design.

Band structure thus complements DOS by providing a complete picture of electronic behavior. B_6O is a **direct-band-gap semiconductor**, beneficial for optical transitions. The valence band shows localized covalent bonding features, while the conduction band displays moderate dispersion indicating reasonable carrier mobility. The band gap is consistent with known semiconducting behavior.

4.6 Elastic Constant Calculation

Mechanical properties were evaluated using the **finite strain–stress method**, which involves:

1. Applying small deformations (±1–2%) to the relaxed structure

2. Computing stress tensors for each deformation using VASP

3. Fitting stress–strain data to extract C_i☐

The full 6×6 stiffness tensor was obtained from the `elasticity` file.

For small, linear elastic deformations , the relation is:

$$\sigma_i = \sum_{j=1}^{6} C_{ij}\, \varepsilon_j$$

The stiffness tensor obtained:

$$C_{ij} = \begin{pmatrix} 584.826 & 123.839 & 49.848 & 0.000 & 22.694 & 0.000 \\ 123.839 & 584.826 & 49.848 & 0.000 & -22.694 & 0.000 \\ 49.848 & 49.848 & 458.097 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & 230.493 & 0.000 & 22.694 \\ 22.694 & -22.694 & 0.000 & 0.000 & 178.115 & 0.000 \\ 0.000 & 0.000 & 0.000 & 22.694 & 0.000 & 178.115 \end{pmatrix}$$

From these, the following were calculated:

- **Bulk modulus (B)**

- **Shear modulus (G)**

- **Young's modulus (E)**

- **Poisson ratio (v)**

- **Anisotropy index (A_U)**

- **Debye temperature and sound velocities**

Comparison of values[Reference: Materials Project Entry MP-1986 (α-B$_6$O)]

Property	Calculated Value	MP 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

Explanation:

- Elastic constants quantify how the material responds to mechanical deformation.

- The Voigt–Reuss–Hill averaging scheme ensures reliable values even for anisotropic crystals.

- Debye temperature provides information about thermal stability and lattice vibrations.

The elastic data confirms that B_6O is **extremely stiff, nearly isotropic, and possesses strong covalent network bonding**.

5. Conclusion

This first-principles study establishes primitive B_6O as a structurally stable, strongly bonded, and mechanically robust ceramic. DFT calculations confirm a direct band gap of ~1.85 eV and a valence band dominated by B–O covalent interactions, indicating stable semiconducting behavior. The elastic analysis reveals high bulk, shear, and Young's moduli, a low Poisson ratio, and a high Debye temperature, all of which reflect its superhard nature and excellent thermal stability. Overall, the results demonstrate that B_6O combines strong covalent bonding, electronic stability, and exceptional stiffness, making it a promising material for high-performance applications in extreme mechanical and thermal environments.

6. References

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