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Electronic structure and optical properties of boron suboxide B_6O system: First-principles investigations

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ABSTRACT

The structural, mechanical, electronic, and optical properties of B_6O were explored by means of first-principles calculations. Such a system is mechanically stable and also a relatively hard material which are derived from obtained elastic constants and bulk moduli. Bulk B_6O is a direct-gap semiconductor with a bandgap of about 2.93 eV within G_0W_0 approximation. Furthermore, the optical properties, such as real and imaginary parts of dielectric functions, refractive index and extinction coefficient, and the comparison of optical properties between the density-functional theory (DFT) and G_0W_0 Bethe–Salpeter equation (G_0W_0-BSE) results, were computed and discussed. The results obtained from our calculations open a possibility for expanding its use in device applications.

1. Introduction

Boron rich compounds, such as boron carbide and boron suboxide, exhibit a range of interesting physical and chemical properties and have attracted significant attention in recent years [1]. Most of those boron rich phases show many extraordinary features, including high hardness, high thermal stability, high chemical inertness and high melting temperature, due to their unique structures, which are based on a rigid boron network [2–4]. Boron suboxide, a prototypical example of boron rich materials, possesses two types of morphologies, rhombohedral and hexagonal structures, while the rhombohedral phase can always be described in terms of hexagonal axes and thus be often considered as a subdivision of a hexagonal system. The rhombohedral structure (space group $R-3m$, labeled as α-B_6O) containing two oxygen atoms whose location are at the interstitial sites in the structure along the [111] direction [5], is shown in Fig. 1a. The corresponding conformations can be viewed as eight rhombohedral unit cells located at the vertices of the icosahedron B_{12} unit, where oxygen atoms are located between the three-center bond linking the boron icosahedron [6–8], as illustrated in Fig. 1b.

B_6O is one of the most researched boron rich compounds and continues to be the subject of intensive study. For instance, some reports [9–14] showed that single crystal B_6O has a high hardness of 45 GPa, and thus has potential as a superhard material, surpassed only by diamond, cubic boron nitride and BC_2N solid solution. The results in literature also showed that B_6O materials have a series of useful features associated with the field of thermoelectric energy conversion, and may be applied to thermoelectric applications [15,16]. In order to take full advantage of the properties of B_6O for eventual technological applications, a better understanding of its electronic structure, mechanical and optical properties are required. However, to the best of our knowledge, an understanding of a number of basic characteristics of this compound is still far from complete.

In this work, we present a systematic study of B_6O through first-principles calculations. The paper is organized as follows:

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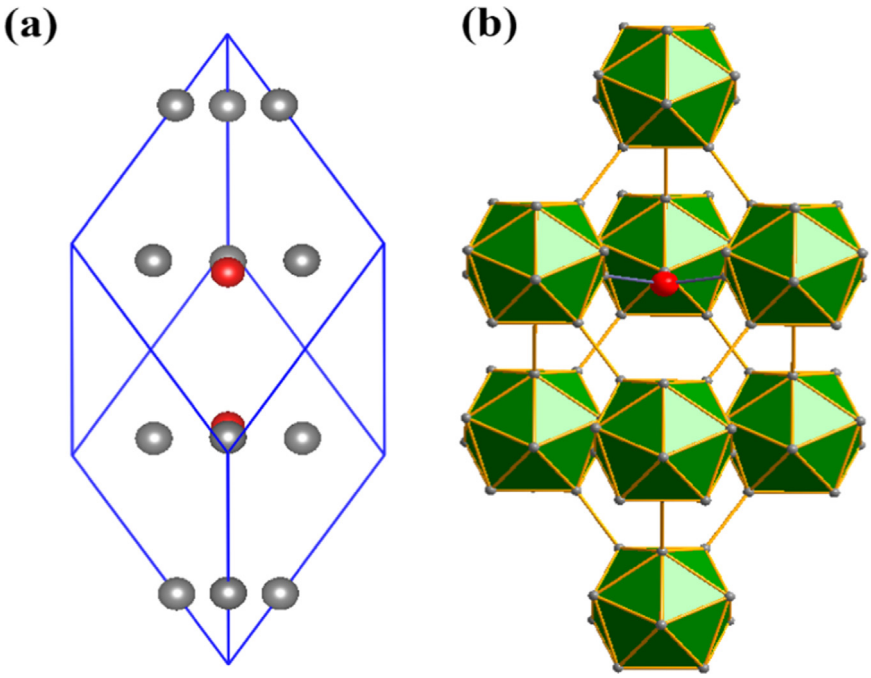

Fig. 1. (Color Online) Crystal structure for B_6O: (a) unit cell of rhombohedral phase, (b) structure of B_6O shown with eight icosahedra at the apexes of the unit cell (B: gray, O: red).

in Section 2, the computational techniques adopted in this study are described in detail. Results and discussion of the structural, electronic, mechanical and optical properties are presented in Section 3. Finally, conclusions are given in Section 4.

2. Computational details

The static lattice energy and the Hellmann–Feynman force calculations were performed using the Vienna a*b initio* simulation package (VASP) [17–19] with the projector-augmented wave (PAW) method. The generalized gradient approximation (GGA) in the form of the PW91 functional for exchange and correlation interactions was used [20,21]. The plane-wave energy cutoff was 520 eV. The k-point meshes were $5\times5\times5$ and $5\times5\times3$ for rhombohedral and hexagonal structures, respectively. The total energy was calculated with high precision, and converged to 10^{-6} eV/atom. The lattice constants and the atom coordinates were optimized until the interatomic forces were less than 10^{-2} eV/Å. The Voigt-Reuss-Hill approximation [22] was applied to calculate the elastic modulus, implemented in the VASP. For the sake of comparison, the BSE (Bethe–Salpeter Equation) calculations [23,24] were also performed on the top of G_0W_0 band structure. The dielectric function was obtained within the BSE calculations. During the calculations, the number of valence bands and conduction bands is 4 and 4 of each phase, respectively. All calculations were done in reciprocal space.

According to the theory of electromagnetic fields, the dielectric constant is a complex number which can be expressed as follows: $\varepsilon=\varepsilon_1+i\varepsilon_2$, of which ε_1 and ε_2 are, respectively, the real and imaginary parts of the dielectric constant. The dielectric function describes the optical response of the material to an electromagnetic field [25]. The imaginary part of the dielectric function is calculated from the momentum matrix elements between the occupied and unoccupied wave functions within the selection rules and given by [26,27]

$$\varepsilon_2=\frac{4\pi^2}{m^2\omega^2}\sum_{V,C}\int_{BZ}d^3k\frac{2}{2\pi}\left|e\cdot M_{CV}(k)\right|^2\times\delta\left[E_C(k)-E_V(k)-\hbar\omega\right], \quad (1)$$

Here, $|e\cdot M_{CV}(k)|^2$ is the momentum transition matrix element, BZ is the Brillouin zone, $E_C(k)$ and $E_V(k)$ are the intrinsic levels of conduction and valence bands, respectively. The real part of dielectric function follows from the Kramer–Kronig relationship [28]. Refractive index and extinction coefficient on the energy dependence can be derived from the dielectric function.

3. Results and discussion

3.1. Structural and mechanical properties

As is known, the hexagonal structure can be considered as a supercell of the rhombohedral structure. In this paper, the rhombohedral structure is chosen as a simple structural composition for computation of the physical properties, such as electrical properties, optical properties, bulk modulus, and elasticity coefficient. The elastic properties can be characterized through elastic constants, bulk moduli, shear moduli, and Young's moduli, where bulk moduli and shear moduli are two important factors in describing the incompressibility of materials. Young's modulus Y can be used to represent the hardness of solid materials, i.e., the larger the Y, the stiffer the material. In particular, the elastic constant of solids provides a link between the mechanical and dynamic behaviors of systems, and as such provides important information about the nature of the forces operating in solids, such as mechanical stability, stiffness and other related mechanical properties [29]. The stability of rhombohedral materials can be examined by mechanical stability criteria as follows [30]:

$$(C_{11}+C_{12})C_{33}-2C_{13}^2>0,$$
$$C_{11}-C_{12}>0,\ (C_{11}-C_{12})C_{44}-2C_{14}^2>0. \quad (2)$$

As the elastic constants of the material can satisfy the above