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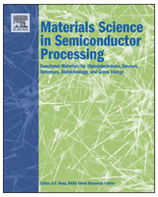

# A first principle study of pressure-induced effects on phase transitions, band structures and elasticity of zinc oxide

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## ABSTRACT

Using the first-principles projector-augmented wave (PAW) method, the pressure induced effects on solid–solid phase transition, electronic band structures and elasticity of zinc oxide are investigated. The four possible structures are considered here, including rocksalt (B1), CsCl (B2), zinc blende (B3), and wurtzite (B4). It is found that structural properties and phase transition points by the PBEsol method are better than those computed using the standard local density approximation and Perdew, Burke and Ernzerhof functionals. Moreover, using the hybrid HSE06 functional, the band structures around phase transition points are displayed. The predicted fundamental gaps of the four considered structures provide improvements over directly density functional theory calculations. Meanwhile, the effective masses for the electrons in the conduction band and the holes in the valence band are derived. Furthermore, the elastic abnormal behavior is achieved around the phase transition points. For B4, B1 and B2 structures, the longitudinal and transverse sound velocities are evaluated along significant symmetry directions with pressure, and it still awaits experimental confirmation.

## 1. Introduction

Zinc oxide (ZnO) is a popular semiconductor, exhibiting attractive properties such as nontoxicity and good electrical, optical, and piezoelectric behaviors. Its structural and electronic properties are, in particular, important for applications such as chemical sensors in gas detecting systems and catalysts for hydrogenation and dehydrogenation reactions. Especially, the wide band gap of ZnO (3.44 eV) makes it appealing for the development of light-emitting diodes, photocatalysists, gas sensors, solar cells. There is also a continuing interest in the high-pressure behavior of ZnO in the areas of geophysics and fundamental materials physics. Contrary to other IIB–VIA binary compounds which adopt different metastable structures, bulk ZnO is known to crystallize only in the hexagonal wurtzite (B4) structure under normal conditions. The zinc blende (B3) ZnO structure can be stabilized only by growth on cubic substrates and it could improve the possibilities for optoelectronic device. The main difference between these two structures lies in the stacking sequence of closed-packed diatomic planes. A number of experimental measurements [1–3] and theoretical calculations [4–7] have shown that B4 structure will transform into a cubic rocksalt (B1) structure at the pressure of ~9 GPa. The X-ray diffraction experiment by Liu et al. [8] has shown that the B1 phase remains stable under high pressure up to 209 GPa at room temperature, being the maximum pressure achieved in any experiment on ZnO so far. With recent progress in computational strategy and performance, computer simulations are increasingly used by theorists to understand properties of matter and make

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specific predictions for real materials and experimentally observable phenomena. These years, a vast amount of theoretical investigations [4–7,9–10] have reported that a phase transition from the B1 to the eightfold-coordinated B2 (cubic CsCl) structure occurs at pressure around 260 GPa. Once a crystal undergoes a phase transition, the most concerned problem is the change of mechanical properties. The most common assessment of mechanical properties can be made by the determination of elastic constants of the crystalline solids. Experimentally, it is difficult to measure elastic properties under high pressure. Nowadays, the first-principles calculation is enough mature to evaluate the elastic constants of materials with a great accuracy [11]. Particularly, it is difficult to experimentally measure elastic properties under high pressure conditions. So it is realistically meaningful to study the elasticity at high pressure based on the first-principles calculations. The systematic study of the elastic properties of materials also provides powerful guidelines for future experimental measurements.

Based on DFT, the local density approximation (LDA) or generalized gradient approximations (GGA) have been directly used to investigate ZnO [4–7,9–10]. However, the contrasting result raises several disadvantages: Firstly, LDA often underestimates lattice parameters of semiconductor, while the GGA overestimates them. This is the general feature of the local density versus generalized gradient approximations. Secondly, the electron–electron interactions of the electron gas, causing the well-know underestimation of the band gap is difficult to obtain accurate results from density-functional depiction. This is a large error for ZnO, with LDA giving a gap of ~0.9 eV [12] compared to experimental result 3.44 eV. The main reason is that the LDA and GGA lead to a spurious self-interaction which places occupied states too high (too low) energy. In comparison, the Hartree–Fock (HF) method uses a nonlocal exchange, so it can be self-interaction free. But on the other hand, HF lacks inter-electronic correlation, and its exchange is unrealistically long ranged due to an absence of screening. Therefore, the aim of the present work is threefold. Firstly, to obtain accurate equilibrium properties of ZnO, we employ so-called PBEsol [13] functional which is a revised Perdew–Burke–Ernzerhof GGA. Secondly, The Heyd, Scuseria, Ernzerhof (HSE) functional [14] uses the error function to separate the exchange into long-range and short-range parts, and replaces a fraction of the short-exchange GGA exchange by the respective fraction of a nonlocal Fock exchange potential. So the screened HF functional becomes possible to calculate the accuracy band structure of ZnO. Last but not least, it is necessary to investigate the behavior of elasticity in the vicinity of the phase transition points.

In this work, we perform first principles calculations of ZnO on the four most studied structures, namely, B4, B3 (cubic zinc-blende), B2 and B1. After this introduction presents in this section, the rest of the paper is organized as follows: in Section 2, we outline the main functionals used for our first-principle calculations, along with practical details of the calculations. The calculated pressure-induced phase transition, band structures and high pressure elastic behaviors of ZnO are reported and discussed in Section 3. Finally, we present our summary and conclusions in Section 4.

## 2. Details of calculations

Our first-principles calculations were performed using the Vienna *ab initio simulation* package (VASP) [15,16] based on density functional theory. The interaction between ions and valence electrons was described by the projector-augmented wave (PAW) potential method [17]. The Zn $(3d)^{10}(4s)^2$ and O $(2s)^2(2p)^4$ electrons were treated as valence electrons. Three different electronic exchange–correlation interactions were treated in the calculations of mechanical properties such as lattice parameters, phase transition pressures through LDA as parameterized by Perdew and Zunger [18], the GGA of Perdew, Burke and Ernzerhof (PBE) [19], and the so-called PBEsol [13] class. Meanwhile, using a particular hybrid functional of Heyd–Scuserial–Ernzerhof (HSE06), the electronic band structure was calculated. More details about the implementation of hybrid functionals in the VASP program can be found in Refs. 20–21. For most materials, the screening parameter $u=0.2$ Å$^{-1}$ used in HSE06 performs better than the old HSE functionals to calculate the band gap. The one-electron pseudo-orbitals were expanded over a plane-wave basis set that included all plane waves whose kinetic energy $\hbar^2k^2/2m<E_{cut}$. In the expression above, $k$ is the wave vector, $m$ is the electron mass, and $E_{cut}$ is the chosen cutoff energy. For all the calculated results in this paper, the basis set contained plane-waves up to energy cutoff of $\geq 400$ eV. In the calculational process, the Brillouin zone integrations were performed using $15\times15\times15$ K-points mesh sampling for cubic crystals and $13\times13\times9$ for hexagonal polymorphs. The chosen planewave cutoff and the number of K-points allowed a convergence of the total energy to within $10^{-3}$ meV/atom. We also used the Tetrahedron method with Blöchl corrections to improve convergence with respect to the number of K-points. This method converges rapidly with the number of K-points and does not require any empirical parameters, and is known to yield highly accurate results for bulk materials [22].

## 3. Results and discussion

### 3.1. Structural properties and phase transition pressures

The structural properties are very important for understanding the solid properties from the microscopic viewpoint. Using the first-principles calculations, we calculated the structural properties for the four considered polymorphs with three functionals of LDA, PBE and PBEsol. After geometry optimization, the total energy as a function of volume is calculated through above three functionals. The obtained energy-volume dependences $E=E(V)$ are fitted to the three-order Brich–Murnaghan equation of state (BM3-EOS) [23]. The equilibrium volumes for the volume $V_0$ and the lowest total energy $E_0$ per cation–anion pair, as well as the isothermal bulk modulus $B_0$ are obtained. Meanwhile, the obtained structural parameters for the considered four phases of ZnO are summarized in