Computational Materials Science 102 (2015) 196–201

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

GGA+U study of the electronic and optical properties of hexagonal BN phase ZnO under pressure

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ARTICLE INFO

Article history:
Received 7 October 2014
Received in revised form 3 February 2015
Accepted 19 February 2015
Available online 10 March 2015

Keywords:
BN phase
ZnO
First principle
Optical property
GGA+U

ABSTRACT

We used the CASTEP program with a GGA+U method to study the electronic and optical properties of BN (B_k) phase ZnO under pressure. At transition pressure, the properties of B_k phase have been compared with those of wurtzite (B4) phase ZnO. The BN phase has been predicted recently. The GGA+U method can provide an accurate band gap, which is more suit for strongly correlated ZnO. The calculated band gap shows BN phase is an insulator. The band gap increases with increasing pressure. The increasing band gap induces a blue-shift optical properties. A linear equation was used to fit the relation between band gap and pressure. The dielectric function ($\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2(\omega)$) has been calculated. The relations between $\varepsilon_2(\omega)$ and density of states have been discussed. The other optical constants have also been calculated. The relation between absorption coefficient ($\alpha(\omega)$) and pressure was also fitted by another linear equation. The linear equation about $\alpha(\omega)$ can be used to measure pressure. The optical constants show B_k phase ZnO is transparent. Our study can be used to identify the BN phase and some geological processes. Our calculations also provide theoretical data for potential applications of BN phase ZnO in the future.

1. Introduction

ZnO has attracted widely attention because it can be used in many optical devices, such as semiconductor lasers [1], photoelectrochemical water splitting [2], optically transparent electrodes [3], ultraviolet photodetectors [4], transparent thin-film transistors and metal–insulator–semiconductor diodes [5]. ZnO is also an important mineral in the deep earth [6,7]. The deep earth has a higher pressure than the surface. Pressure can shorten the chemical bond of ZnO and improve the overlap and repulsion of the electron cloud, which can induce some novel optical properties. ZnO has a wurtzite (B4) structure at normal atmosphere. With the developments of modern computer [8] and high-pressure technology and equipment [9], more and more experts devote to finding new phase and studying their novel properties of ZnO under pressure. Some experts found and studied the high-pressure phase NaCl phase (B1) by experiment and theory [5,10,11]. With theory, other experts also predicted and studied the possible high-pressure phase (such as CsCl (B2), PbO (B10) and NiAs phase) [12–14]. Among them, Molepo and Joubert have found a possible phase ($BN(B_k)$) of ZnO under pressure, recently [15].

As an important optical material, the studies about the optical properties of B_k phase ZnO under pressure are important. The optical properties can be used to measure pressure, identify B_k phase ZnO and indicate some geological processes [16]. The optical properties are also important in designing optical devices of B_k phase ZnO under pressure. The studies of the optical properties of B_k phase ZnO under pressure have significance in optics, physics, material, chemistry and geoscience. However, based on our knowledge, there are few studies about B_k phase ZnO. The studies about the optical properties of B_k phase ZnO are urgently needed.

However, high-pressure devices (such as Diamond Anvil Cell (DAC)) cannot be immediately used in practice. The properties under pressure are interesting for future applications. The B4 phase ZnO is stable in normal atmosphere. We can get B4 phase ZnO in our nature. The B4 phase has been studied for many years [5]. Accordingly, applications of B4 mainly focus on the normal atmosphere. Properties of B4 phase ZnO under pressure are new properties, which are interesting for future applications. On the other hand, B_k phase is a new phase. Recently, some experiments found the B_k phase film can be stable in normal atmosphere [17]. The film is a promising material and has been studied less. The bulk B_k phase has been predicted stable above 24.5 GPa. In normal atmosphere,

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http://dx.doi.org/10.1016/j.commatsci.2015.02.035
0927-0256/

the applications mainly concentrate on the B_k phase film. The bulk of B_k phase ZnO is interesting for future applications.

First-principles method is useful to study optical properties [18–22]. But standard first-principles method has a flaw, which underestimates the band gap of strongly correlated materials [23]. The materials include ZnO, high temperature superconductor and colossal magnetoresistance materials. Because optical properties relate closely to a band gap, an inaccurate band gap cannot get accurate optical properties. Fortunately, first principles with Hubbard U can provide an accurate band gap [24–26], which can generate accurate optical properties. Based on the above discussions, we use the GGA+U method to study the optical properties of B_k phase ZnO under pressure. Our calculations mainly focus on the changes of optical properties at the transition pressure and the dependence of the optical properties of B_k phase on pressure.

2. Method of calculation

Our calculations were performed by the CASTEP code [27], which implemented in the Materials Studio software. The software is based on the density functional theory (DFT). We used GGA+U method to perform our calculations. The values of U ($U_{Zn,d}$ = 10.5 eV and $U_{O,p}$ = 7.5 eV) are referred to the report [24]. In Ref. [24], the authors have performed extensive tests to determine the values of U. The essay has been widely cited and checked by different experts. We can get an accurate band gap (3.4 eV) by the values of U, which is close to the experimental band gap of ZnO. So we used $U_{Zn,d}$ = 10.5 eV and $U_{O,p}$ = 7.5 eV in our calculations.

We first optimized the crystals of the wurtzite (B4) and BN (B_k) phase ZnO. Then the electronic and optical properties were calculated. The used valence electrons of Zn and O are $3d^{10}4s^2$ and $2s^22p^4$. The first Brillouin zone was sampled by $8 \times 8 \times 6$ and $9 \times 9 \times 6$ k points [28]. After tests, the used cutoff energy (E_f) is 1200 eV. Ultrasoft pseudopotential [29] and BFGS algorithm [30] were used in our calculations. The convergence tolerances are $5.0e^{-6}$ eV/atom, 0.02 GPa, 0.01 eV/Å and $5.0e^{-4}$ Å for energy, maximum stress, maximum force and maximum displacement, respectively. The independent-particle model approximation has been used for the dielectric matrix calculations. All calculations were performed in a reciprocal space.

3. Results and discussions

3.1. Structure and enthalpies

The optimized crystals of B4 and B_k phase ZnO are shown in Fig. 1. The calculated lattice constants of B4 phase ZnO are $a = b$ = 3.249 Å and c = 5.204 Å, which close to the experiment [5]. On the other hand, the calculated lattice constants of B_k phase ZnO are $a = b$ = 3.397 Å and c = 5.132 Å, which also close to the other theoretical report [15].

We also calculated the enthalpies of B4 and B_k phase under pressure, which can be used to determine the transition pressure. The phase with lower enthalpy is more stable. The pressure of equal enthalpy is the transition pressure. We calculated the enthalpies of the B4 and B_k phase between 0 and 45 GPa (Fig. 2). As shown in Fig. 2, the enthalpy increases with increasing pressure. Below 24.5 GPa, the enthalpy of B4 phase lower than B_k phase, which means B4 phase is more stable. On the other hand, the enthalpy of B_k phase lower than B4 phase above 24.5 GPa, which means B_k phase is more stable. The enthalpy equal to each other at 24.5 GPa, which is the transition pressure (P_{Tr}). The calculated P_{Tr} agrees well with the other report [15].

3.2. Band structure and band gap

Because bands and the density of states (DOS) relate closely to the optical properties, we first calculated the bands (Fig. 3) and DOS under different pressure (Fig. 4). Fig. 3 shows the band gaps of B4 and B_k phase ZnO are direct. The phase transition and pressure cannot change the type (direct or indirect) of band. The calculated bands of B4 phase under 0 and 24.5 GPa (transition pressure (P_{Tr})). The Fermi level was set at the valence band maximum. The band gap of B4 phase (0 GPa) is 3.42 eV, which agree well with experiment (3.4 eV) [5]. To compare with B_k phase ZnO well, we calculated the band of B4 phase at P_{Tr}. Fig. 3a shows the band gap increases when pressure increases from 0 to 24.5 GPa. The conduction band shifts to higher energy while the valence band shifts to lower energy. The shift of the valence band comes from the enhanced hybridization of Zn and O states. The shift of the conduction band is because of the increased repulsion between Zn and O states, which come from the pressure-decreased bond and the improved repulsion of the electron cloud.

The bands of B_k phase were also calculated. The calculations were at and above the transition pressure (P_{Tr}) (24.5, 35 and 45 GPa). We first discuss band gaps at P_{Tr}. At P_{Tr}, the band gap abruptly increases from 3.69 eV (B4 phase) to 3.82 eV (B_k phase). The increased band gap will induce changes in according electronic and optical properties, which can be used to identify the phase transition. The band gaps of B_k phase under 24.5 (P_{Tr}), 35 and 45 GPa are 3.83, 3.95 and 4.04 eV, respectively. The wide band gap means B_k phase ZnO is an insulator. The band gap increases with increasing pressure. The increased band gap will induce a blue shift in optical properties. The conduction band also shifts to higher energy while the valence band shifts to lower energy. The reasons for the shifts are similar to those of B4 phase.

To describe the evolution law of the band gap of B_k phase, we calculated the band gaps of B_k phase at 24.5, 30, 35, 40 and 45 GPa (Fig. 4). Fig. 4 shows the band gap of B_k phase ZnO increases

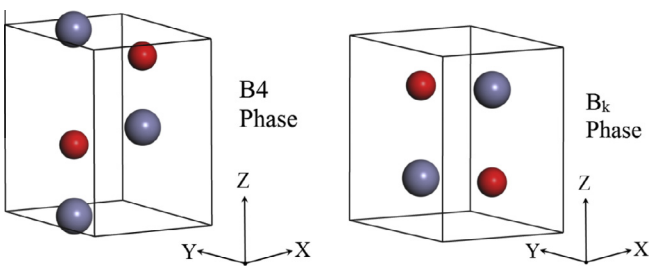

Fig. 1. The optimized equilibrium crystal structures of B4 and B_k. The small (red) balls represent oxygen atoms, while the large (gray) balls represent zinc atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

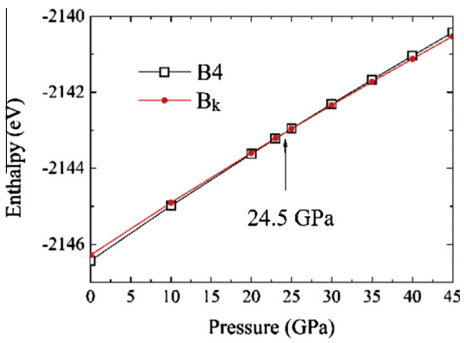

Fig. 2. The enthalpies of B4 and B_k phase ZnO versus pressure.