The optical properties of NiAs phase ZnO under pressure calculated by GGA+U method

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ABSTRACT

To comprehend the optical properties of the recent-predicted NiAs phase ZnO under pressure, we used the generalized gradient approximation plus U (GGA+U) method to calculate the properties. The GGA+U method is more suited for the strong correlated NiAs phase. The direct band gap increases with increasing pressure. The calculated band gap shows that NiAs phase is an insulator, while the real part $\varepsilon_1(\omega)$ shows the NiAs phase expresses metallic behavior around 18.6 (22.5 GPa) and 26.0 eV (215 GPa). The relation between the imaginary part $\varepsilon_2(\omega)$ and PDOS was also discussed. The calculated optical constants show the NiAs phase is transparent and can be used in the vacuum ultraviolet region. We also compared the optical constants of NiAs with wurtzite and CsCl phases ZnO at according transition pressure. And the new-appeared peaks of optical constants can be used to identify the phase transition. The blue-shift optical constants of NiAs phase ZnO can be used to measure pressure after carefully calibrated. Our research provides a reference for identifying and using the NiAs phase ZnO under pressure.

1. Introduction

ZnO is an important optical material and widely used as optical devices, such as lasers, electro-optic devices, light-emitting diodes and photo detectors [1–3]. ZnO is also an important component of the lower mantle [4]. At normal temperature and pressure, ZnO crystallizes in a wurtzite (B4) phase. Under pressure, the wurtzite phase ZnO will transform to another phase, which has new properties. And the new phase is a potential candidate for optical applications. In the past, scientists reported that wurtzite phase ZnO will first transform to a NaCl (B1) phase around 9 GPa. And then the NaCl phase transformed to a CsCl (B2) phase around 210 GPa [5–9]. Recently, Molepo et al. have found another path of the transformation of wurtzite phase ZnO under pressure [10]. The path is wurtzite phase ZnO first transform to a NiAs (B81) phase and then transform to a CsCl phase.

As an important optical material, the optical properties are important for the NiAs phase. The study of the optical properties of NiAs phase under pressure is also important for geology, fundamental material physics and potential applications [11]. However, there are few reports about the optical properties of the NiAs

phase ZnO. The studies on the optical properties of NiAs phase under pressure will provide methods to identify the NiAs phase ZnO under pressure. As ZnO is an important optical material, the studies of the optical properties will also provide a reference in designing optical devices based on the NiAs phase ZnO.

First principles method is a powerful method to study the optical properties of materials [12–17]. In the studies of the optical properties of ZnO, we will seriously underestimate the band gap only using the standard generalized gradient approximation (GGA) with Perdew, Burke, and Ernzerhof (PBE) method. The reason is that ZnO is a strong correlated material. The underestimated band gap cannot provide accurate optical properties. Fortunately, the GGA+U method can provide accurate band gaps and optical properties [18,19]. Using the GGA+U method, we first optimized the structure of NiAs phase ZnO and then calculated the electronic and optical properties under pressure.

2. Computational details

Our calculations were performed by the Cambridge Serial Total Energy Package (CASTEP) program [20], which is implemented in the Materials Studio software. The software is based on the density functional theory.

The GGA+U method was used in our calculations. In the method, U are the important parameters in our calculations. ZnO is a strong

correlated material. The 3d orbital electrons are strongly localized. The 3d electrons have strong on-site Coulombic interactions among them. The band-gap calculation by standard GGA-PBE method did not consider the strong and on-site Coulombic interaction of these localized electrons. So, standard GGA-PBE cannot provide accurate band gap and optical properties.

U is a Hubbard-type parameter and it can describe the strong on-site Coulomb interactions in the calculations. The GGA method includes U is called GGA+U method. GGA+U method considers the strong Coulombic interaction in the strong correlated system. In the strong correlated ZnO, the calculations based on GGA+U method are closer to the actual electronic conditions than GGA-PBE method. And GGA+U method can provide an accurate band gap and optical properties. U should include p states except for the d states [21]. The used U in our calculations were $U_{d,Zn}=10.5$ eV and $U_{p,O}=7.0$ eV [22].

The Vanderbilt ultrasoft pseudopotentials [23] and Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [24] were used in our calculations. The used valence electrons of Zn and O were $3d^{10}4s^2$ and $2s^22p^4$. We first calculated the band gap of the wurtzite phase ZnO. The calculated band gap is 3.47 eV, which is close to the experiment (3.44 eV) [25]. We used $9\times9\times6$ (B4 phase), $12\times12\times6$ (B81 phase) and $12\times12\times12$ (B2 phase) Monkhorst mesh [26] to sample the first Brillouin zone. To gain both accuracy and speed, we used 1200 eV as the cutoff energy. Our calculations were performed in a reciprocal space. The self-consistent-field (SCF) tolerance is 5×10^{-7} eV/atom. The used electronic minimizer is density mixing. The charge and spin in the density mixing were 0.5 and 2.0. The used potentials in our calculations are O_00PBE and Zn_00PBE.

For the convergence tolerance aspect, the energy was less than 5×10^{-6} eV/atom. The max force was less than 0.01 eV/Å. The stress was less than 0.02 GPa. And the displacement was less than $5-10^{-4}$ Å. The basis set for variable cell is fixed basis quality. The used compressibility is hard. We first build the crystal of wurtzite (B4), NiAs (B81) and CsCl (B2) phase ZnO (Fig. 1a, c and e). Then, we set the initial lattice constant of B4, B81 and B2 phase. The initial lattice constants of B4 phase were used the experimental constants: $a=b=3.2498$ Å and $c=3.2496$ Å [8]. The initial lattice constant of B81 phase was used the other calculated constants: $a=b=2.975$ Å and $c=3.2496$ Å [9]. The initial lattice constants of B2 phased was used the other calculated constants: $a=b=c=2.6194$ Å [27].

We used the GGA+U method and convergence criteria to optimize these initial structures at 0 GPa. The optimized structures at 0 GPa were used as the initial structure in the following calculations. The different pressures were set in the CASTEP program. We calculated the enthalpies of B4 and B81 phases at 0, 10, 15, 20, 25, 30, 40 GPa. We also calculated the enthalpies of B81 and B2 phases at 180, 200, 210, 220 and 240 GPa. Through analyzing the enthalpies, we can get transition pressure. The electronic and optical properties were calculated at the according transition pressure.

3. Results and discussion

3.1. Phase transitions and lattice parameters

Because the structure relates closely to the electronic and optical properties, we first optimized the structure and then calculated the other properties. The optimized crystals of B4, B81 and B2 phase ZnO are shown in Fig. 1b, d and e, respectively. Fig. 1 shows the crystals before and after optimization are similar. And the changed calculated lattice constants, volume and bond length are listed in Table 1. We also compared our calculated lattice

parameters with previous experimental and other theoretical parameters. Table 1 shows the parameters are close to other experimental or theoretical reports. For example, the optimized equilibrium lattice (0 GPa) parameters of B81 phase are $a=b=2.9153$ Å, $c=5.1091$ Å, $\alpha=\beta=90°$ and $\gamma=120°$, which are in line with the other calculation [10]. With increasing pressure, the cell angles are not changed and the lattice constants are compressed. For instance, the cell angles of B81 phase are not changed. And the lattice constants of B81 phase are compressed to $a=b=2.5214$ Å and $c=4.5961$ Å at 215 GPa. With pressure increased from 0 to 22.5 GPa, the bond length of B4 and B81 phases decrease from 1.95 and 2.11 Å to 1.88 and 2.05 Å, respectively. The decreased bond length can enhance the hybridization in the Zn–O bond.

In the following, we will calculate the transition pressure of ZnO. As we known, the Gibbs free energy (G) can be calculated by $G=E+PV-TS$. The enthalpy (H) can be got by $H=E+PV$. At 0 K temperature, the enthalpy equal to the Gibbs free energy. The calculated enthalpy of the wurtzite, NiAs and CsCl phase ZnO varying with increasing pressure are shown in Fig. 2. The phase with lower enthalpy will be more stable. The transition pressure is determined by the equal enthalpy. From Fig. 2, we can see that wurtzite (B4) phase ZnO transform to NiAs (B81) phase at 22.5 GPa. The B81 phase transforms to CsCl (B2) phase at 215 GPa. Our calculated transition pressure is close to the other report [10]. For a covalent material, ZnO will transform to a higher coordination phase under pressure. We find that B4 phase (four-fold coordinate) first transforms to B81 phase (six-fold coordinate). Second, B81 phase transforms to CsCl phase (eightfold coordinate). Based on our calculation, B4, B81 and B2 phases can be stable in 0–22.5, 22.5–215 and above 215 GPa, respectively. The following calculations will be performed under according pressure.

3.2. Band structures and density of states

Because the bands and density of states (DOS) are related closely to the optical properties of ZnO, we calculated the bands and DOS before the optical properties. The calculated bands of B81, B4 and B2 phases at transition pressure (22.5 and 215 GPa) are shown in Fig. 3. We set the valence band maximum as zero. From Fig. 3, we can see the band is flat at the valence band maximum, which means they have heavy holes. Fig. 3a shows the calculated band of B4 and B81 phases ZnO at 22.5 GPa. We can see that the band of B4 and B81 phases have similar profile except for a different band gap (3.71 eV of B4 phase and 4.01 eV of B81 phase). The band gap of B4 phase at 22.5 GPa is direct (Γ–Γ), which agrees with another report. The band gap of B81 phase at 22.5 (4.01 eV) and 215 GPa (6.26 eV) are direct (Γ–Γ), too. The band gap of the B2 phase at 215 GPa (5.43 eV) is indirect (G–X). The direct and indirect band gap of B4 and B2 phases are in line with another report [5]. The phase transition (B4→B81) is not with the change of the type of band gap (direct or indirect), while the phase transition (B81→B2) is with the change of the type of band gap.

Fig. 3a shows the band of the NiAs phase ZnO becomes delocalized with increasing pressure. The delocalization is originated from the strong repulsion between Zn 3d and O 2p states. And the strong repulsion is caused by the reduced Zn–O bond length. The band gap of B81 phase ZnO increases with increasing pressure. And the band gap as the functions of the pressure is plotted in Fig. 3c (22.5–215 GPa). The relationship between the band gap (E_g) and pressure (P) is nearly linear and can be described by a quadratic equation: $E_g=3.67+0.017P-2.35\times10^{-5}P^2$. The units of E_g and P are eV and GPa. The pressure coefficient is 0.017 eV/GPa. The fit line is shown in Fig. 3c.

The density of states (DOS) and partial density of states (PDOS) have close relations with the band and optical properties. We first calculated DOS (PDOS) and then discussed the relations between