

Electronic structures and optical properties of ZnO doped with Ba atoms: the first-principles calculations

H. M. CHEN^{a,*}, Z. P. CHEN^a, R. ZHANG^a, X. L. LIN^a, F. C. PAN^a, Z. MA^a, J. N. XU^a, H. S. ZHAO^b

^a*School of Physics and Electronic-Electrical Engineering, Ningxia University, Yinchuan 750021, PR China*

^b*Department of Physics, Xingtai University, Xingtai 054001, PR China*

The electronic structures and the optical properties of wurtzite ZnO doped with Ba atoms ($Zn_{1-x}Ba_xO$) are studied using first-principles based on the framework of plane wave ultra-soft pseudo-potential approximation. The calculated results show that the energy band gap of $Zn_{1-x}Ba_xO$ is amplified and the main peaks of the imaginary part of dielectric function, the reflection spectrum and the absorption spectrum shift to the side of lower energy with the concentration of doped Ba increase. It is also found that the onset of absorption spectrum shifts to the side of higher energy with the dopant increase and the $Zn_{1-x}Ba_xO$ compound has a new absorption peak compared with pure ZnO. The blue-shift phenomenon and the presence of the new absorption peak imply that $Zn_{1-x}Ba_xO$ can be as a potentially candidate for optoelectronic materials.

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1. Introduction

Wurtzite ZnO is one of the important semiconducting compounds with a direct wide band gap. It has been widely used as optoelectronic devices, spintronic devices and detectors due to its wider band gap (~3.37 eV) and higher exciton-binding energy (~60 meV), including being used in ultraviolet semiconductor laser, solar cells, and liquid crystal display [1-7]. Doped ZnO is attracting a great deal of attention in research field and technological application. For instance, Chang et al. [8] has grown the Li-doped ZnO nanowire on silicon substrates with seed layer by the hydrothermal method and investigated their piezoelectric properties. Rajeshwari and Chandra prepared Al doped ZnO nanostructures and investigated their absorption-emission properties [9]. Srine et al. [10] prepared Ni doped ZnO samples by the solid state route and studied their structural, optical and dielectric properties.

Except of many experimental works being done, first-principles calculation is a powerful research technique in the aspect of theoretical calculation [11-13]. It has been chosen to predict the physical properties of ZnO and doped ZnO in the past decades [14-18], such as references [19] predicted that ZnO doped with Ag can improve the semiconducting character. Luo et al [20] analyzed the electronic structure and optical properties of (Zr-Al) doped ZnO using first-principles calculation. Several first-principles calculations indicated that Cd-doped ZnO achieves red-shifts at the onset of optical absorption spectra, which is in line with the very recent experimentally results [21-23].

Generally, perovskites are used for functional devices which are structurally complicated and difficult to synthesize [24]. More interestingly and very recently, the

Ba-doped ZnO is noted as a potential alternative for application in opt-electronic devices, electronic devices, solar cells and photocatalytic process. For instance, Gunjan Srinet et al. [25] prepared Ba-doped wurtzite ZnO by a low cost thermal decomposition method successfully, which is highly controversial due to the atomic radius of Ba (217 pm) is far greater than that of Zn atom (133 pm). L. H. S. Lacerda et al. [26, 27] investigated the doping effect on the ferroelectricity and optical properties of Ba-doped ZnO material theoretically. The work of references [25-27] motivates us to investigate the electronic structures and the optical properties of Ba-doped ZnO using first-principles calculation. In this paper, the dependences of the dielectric function spectra, the absorption spectra and the reflection spectra of $Zn_{1-x}Ba_xO$ with different doping concentration are analyzed systematically based on the calculated band gap values and the density of states (DOS). To the authors' knowledge, the theoretical investigation of electronic structures and optical properties by using first-principles calculation on the Ba-doped ZnO is less reported in literatures.

2. Model and calculating configuration

As illustrated in Fig. 1, a $2 \times 2 \times 1$ supercell containing 16 atoms is constructed for calculations. The dopant concentration is set as 0, 0.125, 0.375 and 0.625 respectively. All calculations have been implemented by the CASTEP package code [28]. The exchange-correlation potential and electron-ion interaction are described by the GGA-PBE functional and ultra soft pseudo-potentials respectively [16, 29]. The valence-electron configurations are chosen as O- $2s^2 2p^4$, Zn- $3d^{10} 4s^2$, and Ba- $5s^2 5p^6 6s^2$

respectively. The cutoff energy is set as 380eV and $6 \times 6 \times 7$ Monkhorst-Pack grid points are adopted. The electronic iterations convergence is 1×10^{-6} eV. The energy imposed on each atom is less than 0.01 eV and the stress is set as 0.1 GPa. All calculations are performed in the reciprocal space.

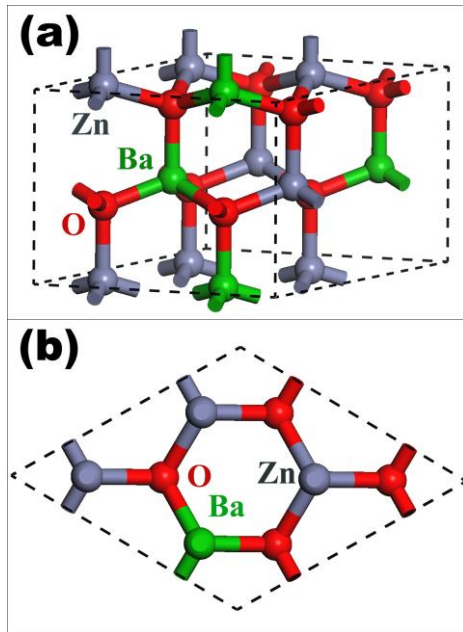


Fig. 1. Schematic view of $Zn_{0.625}Ba_{0.375}O$ supercell structure (a) side view, (b) top view

3. Results and discussion

3.1. Energy band structures and DOS

In order to analyze the optical properties of ZnO doped with different Ba concentration, the energy band structures and the density of states (DOS) of $Zn_{1-x}Ba_xO$ are calculated. The calculated band gap of pure ZnO is 0.71eV, which is close to the results of Wu et al (0.727eV) [30] (Fig. 2a). In spite of the calculated value of band gap is lower than that of experimental results (3.37eV), it can be improved by scissor approximation approach during optical properties calculation. Therefore, it does not affect the qualitative analysis for the optical properties of doped ZnO. Fig. 2b, Fig. 2c, and Fig. 2d show the calculated energy band structures and DOS of $Zn_{1-x}Ba_xO$ ($x=0, 0.125, 0.375, 0.625$) respectively. It can be seen that the Ba-doped ZnO is still a direct band gap compound. Some new energy bands have been arisen in the bottom of valence band and the intensity of the DOS which is corresponded to the new bands is intensified with the doping concentration increasing from 0.125 to 0.625. It also shows that the band gap of Ba-doped ZnO is amplified with the concentration of doped Ba increase (Fig. 2a ~ Fig. 2b), implying that the electronic cloud overlap between O and Zn atoms is weakened due to the positions of Zn atoms occupied by Ba atoms. It leads to the bond energy decrease and the bottom of the conduction band shifting toward the high - energy state.

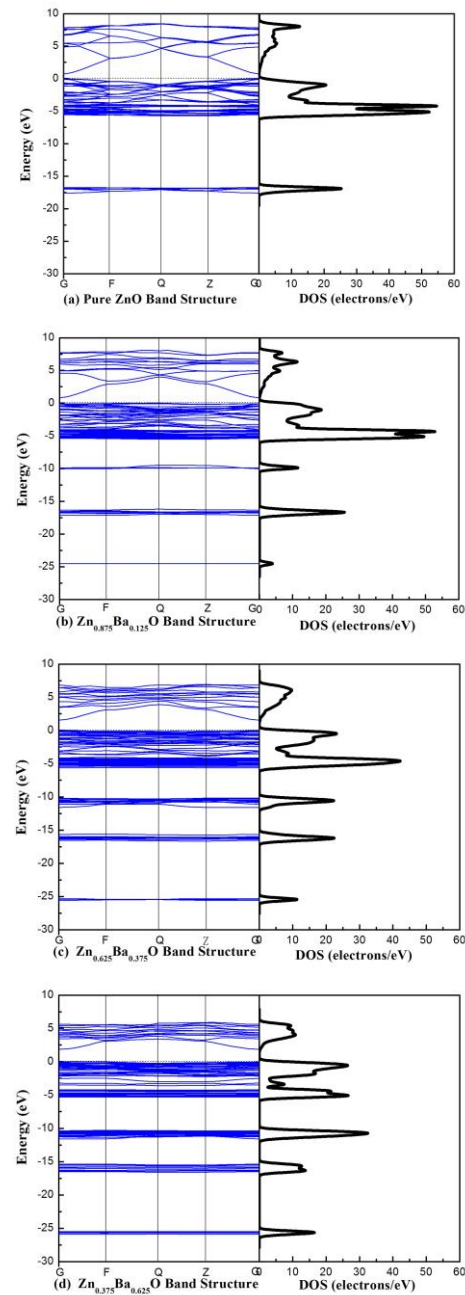


Fig. 2. Energy band structures of $Zn_{1-x}Ba_xO$ ($x=0, 0.125, 0.375, 0.625$)

The partial density of states (PDOS) of $Zn_{1-x}Ba_xO$ ($x=0, 0.125, 0.375, 0.625$) are shown in Fig. 3. It can be seen that the valence band of pure ZnO is primarily composed of three parts (Fig. 3a). The total DOS (TDOS) in the energy range of $-16.5\text{eV} \sim -17.8\text{eV}$ is dominantly contributed by the O-2s state, which appears the characteristic of high localization and less interaction with other valence band. The TDOS in the energy range of $-4.0\text{eV} \sim -6.3\text{eV}$ is contributed by Zn-3d state and the O-2p state. The TDOS of the top of valence band is mainly contributed by O-2p state. The TDOS of conduction band is determined by the contributions of Zn-4s state and O-2p state. When the pure ZnO has been doped with Ba (Fig. 3b, Fig. 3c, Fig. 3d), some new PDOS peaks have arisen in the range of -10eV

and -25eV. The reason is attributed to the contributions of Ba-p state and Ba-s state.

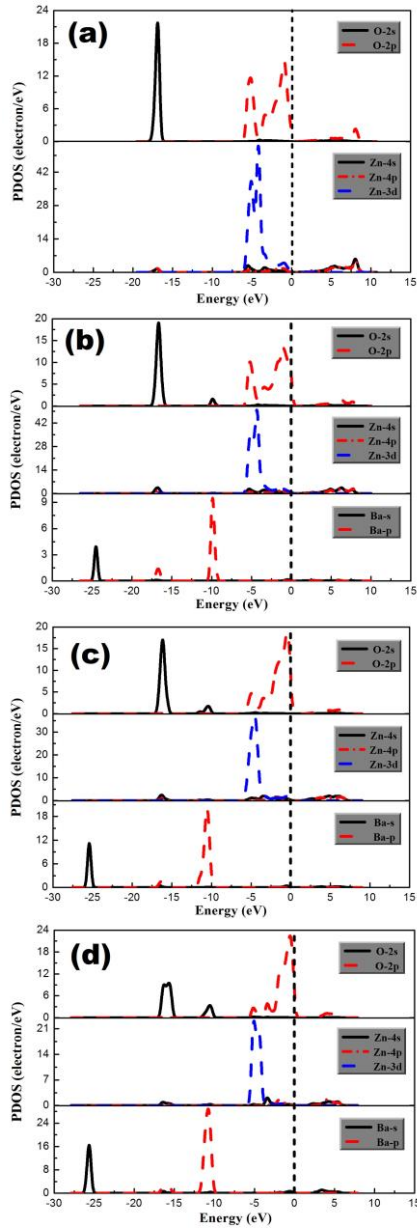


Fig. 3. PDOS of electrons (a)ZnO, (b) $Zn_{0.875}Ba_{0.125}O$, (c) $Zn_{0.625}Ba_{0.375}O$, (d) $Zn_{0.375}Ba_{0.625}O$

In order to understand the effect of dopant concentration on the DOS detailedly, the dependences of PDOS of Zn-3d, Zn-4s, O-2s, O-2p, Ba-s and Ba-p state versus dopant concentration ($x=0, 0.125, 0.375, 0.625$) are shown in Fig. 4. It can be seen that the intensity of PDOS peaks of Zn-3d, Zn-4s, O-2s and O-2p is decreased with the dopant concentration increase. With the Zn atoms reducing, which is replaced by Ba atoms, the contribution of Ba-s and Ba-p state into the TDOS is intensified gradually. In addition, the intersectional position of the peak Zn-4s is shifted to the right side gradually with the doping atoms increase, implying that the band gap is increased with dopant increase, which is in line with the results depicted in Fig. 2.

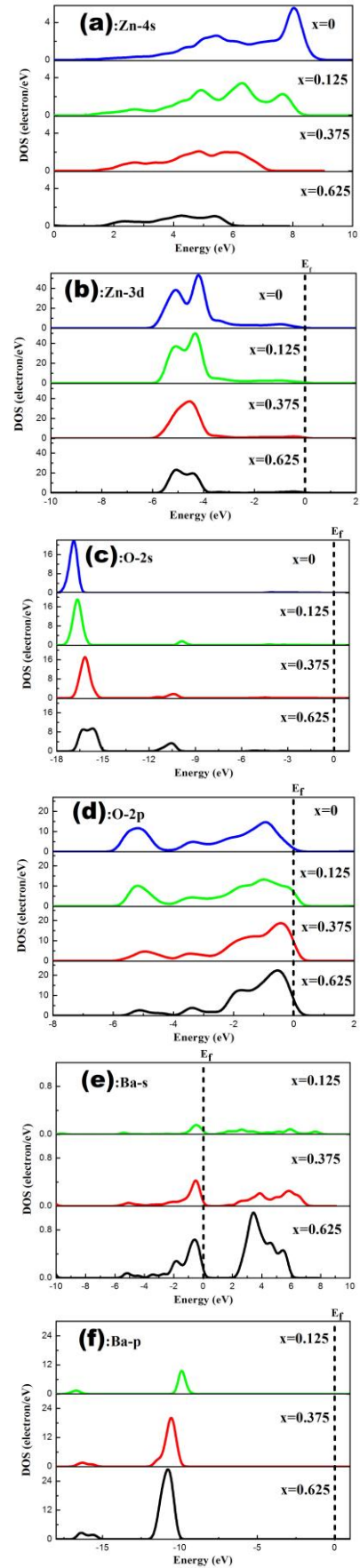


Fig. 4. PDOS comparison of $Zn_{1-x}Ba_xO$ with different dopant concentration ($x=0, 0.125, 0.375, 0.625$)

3.2. Optical properties

Concerning the assessed value of band gap being lower than that of experimental value, the scissor approximation approach, which can rectify the conduction band structure to agreement with the experimental results, is adopted to calculate the optical properties of $Zn_{1-x}Ba_xO$ ($x=0, 0.125, 0.375, 0.625$) in this work. The calculated dependences between the imaginary part of the dielectric function and the energy are shown in Fig. 5. It can be seen that the main peak of dielectric function of the pure ZnO is located at 12.2eV. With the dopant increasing, the main peak is shifted to the side of lower energy and the peak relative intensity is intensified, implying that the bridge effect of impurity energy levels, which can reduce the required activation energy for the electron transition, takes an important effect during the process of electron transition. Compared with pure ZnO, the sub-peaks of Ba-doped ZnO shift to the side of higher energy (in the vicinity of 18eV). It can be ascribed to the electron transition between s state and p states of Ba atoms.

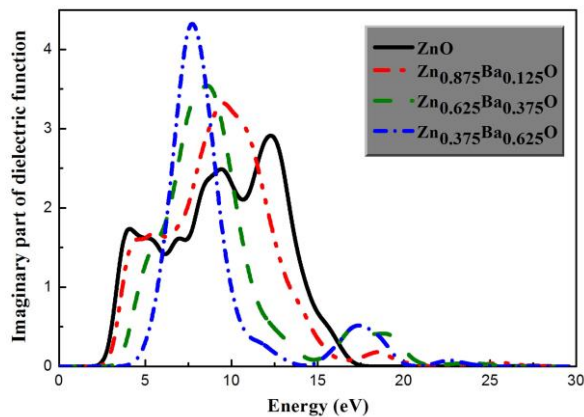


Fig. 5. Dependences of dielectric function versus energy

The absorption spectra of $Zn_{1-x}Ba_xO$ are shown in Fig. 6. It can be seen that the main peak is also shifted to the side of lower energy with the dopant increase. However, the onset of the absorption spectra have been shifted to the side of higher energy with the dopant increase, namely, Blue Shift Phenomenon occurred. The reason is that the forbidden band gap has been broadened with the dopant increasing, therefore, the higher energy photons are needed to make the electrons being transitioned from forbidden band to conduction band, resulting in the Blue Shift Phenomenon occurring. In addition, the peak width becomes narrow with the dopant increase, and a new absorption peak, which arises in the side of high energy, appears in the absorption spectrum of $Zn_{1-x}Ba_xO$. It is related to the change of band gap. With the dopant concentration increase, the DOS intensity of Zn-4s state is weakened meanwhile the DOS intensity of Ba-s state is enhanced, resulting in the band gap broadened.

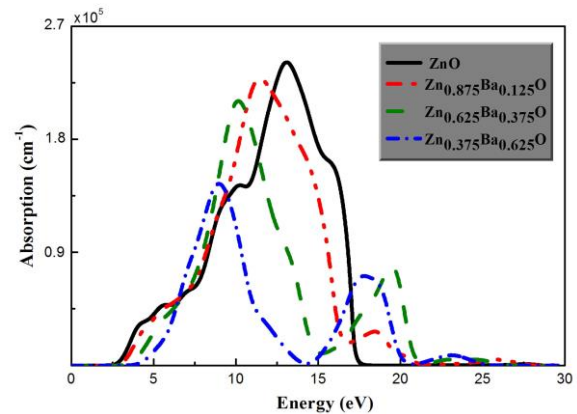


Fig. 6. Absorption spectra of $Zn_{1-x}Ba_xO$ ($x=0, 0.125, 0.375, 0.625$)

Fig. 7 shows the calculated reflection spectra of $Zn_{1-x}Ba_xO$ ($x=0, 0.125, 0.375, 0.625$). It can be seen that there are three obvious reflection peaks for pure ZnO, which are located in 3.7eV, 14.2eV and 16.8eV respectively. The interband transition is mainly occurred in the energy range of 12eV ~ 17eV. With the dopant concentration increase, the interband transition shifts to the range of 6eV ~ 11eV. The reason induced such changing is attributed to the change of energy band structure caused by dopant, namely, the impurity energy level arises near the Fermi level.

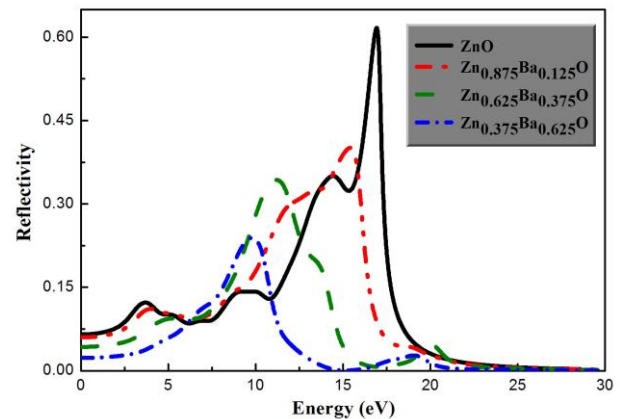


Fig. 7. Reflection spectra versus energy

4. Summary

The energy band structure, the DOS, the imaginary part of dielectric function and the reflection spectrum as well as the absorption spectrum of wurtzite $Zn_{1-x}Ba_xO$ are analyzed systematically using first-principles approach. Compared with pure ZnO, the electronic structures and the optical properties of wurtzite $Zn_{1-x}Ba_xO$ are changed obviously. With the dopant concentration increasing, the electronic cloud overlap between O atoms and Zn atoms is weakened gradually, leading to the bottom of the conduction band being shifted to the higher energy state and the band gap of wurtzite $Zn_{1-x}Ba_xO$ being broadened. Correspondingly, the main peaks of the dielectric function,

the reflection spectrum and the absorption spectrum shift to the side of lower energy with the concentration of doped Ba increasing. The calculated blue-shift phenomenon and the presence of new absorption peak which arises in the side of high energy imply that $Zn_{1-x}Ba_xO$ can be as a potentially candidate for optoelectronic materials.

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*Corresponding author: bschm@163.com