DFT characterization of cadmium doped zinc oxide for photovoltaic and solar cell applications

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ABSTRACT

Tailoring the energy gap of ZnO through Cd doping renders Cd:ZnO an intriguing material for photovoltaic and solar cell applications. Unfortunately, the Cd:ZnO blend is unstable, a feature attributed to the structural differences between the parent hexagonal ZnO and cubic CdO. We here report a comparative density functional theory (DFT) study of zinc-blend (ZB) and wurtzite (WZ) ZnO doped with Cd – upto 37.5% of the Zn atoms were substituted by an isovalent Cd. Interestingly, the nearly equivalent total energy of the ZB and WZ Cd:ZnO blends reflects the relative stability of the cubic phase. The formation enthalpies increase linearly with increasing Cd concentration. Cd insertion into ZnO is found to have an insignificant effect on the ZnO structure, with only a slight increase of the lattice constants that follow Vegard's formulation. Cd dopants efficiently reduce the electronic band gap of ZnO and in turn the absorption edge and optical energy gap are red-shifted. The Cd:ZnO blends exhibit a lower energy gap in the cubic phase as compared to the hexagonal phase, suggesting that a specific energy gap can be achieved at relatively lower Cd contents in the ZB. The lighter effective free-carrier masses in WZ-Cd:ZnO suggest a higher conductivity and mobility as compared to ZB and the parent ZnO. The narrow energy gaps indicate that both hexagonal and cubic Cd:ZnO systems have potential as material for solar energy applications.

1. Introduction

ZnO is an interesting and multifunctional semiconductor that plays a leading role in II–VI semiconductor family. The wide and direct band gap of 3.44 eV, intrinsically transparent nature over the whole visible range, abundant availability, low cost, high chemical and thermal stability make ZnO particularly attractive for photovoltaic (PV) and solar cell applications. ZnO is often highly doped with atomic impurities, and their now exists considerable academic research efforts to control ZnO doping to both improve existing physical properties and add new material dimensionalities, including varying the optoelectronic, magnetic, magneto-optic, electromagnetic, thermoelectric and piezoelectric properties [1–5]. The current ZnO application range includes many transparent electronic and photonic devices, such as solar cells, blue and ultraviolet light-emitting diodes, flat panel displays, among many others [1–5]. ZnO based transparent conducting oxides (TCOs) meet the stringent requirements for thin-film solar cells as it has both appropriate optoelectronic properties and high resistance to hydrogen rich plasmas [6–8]. Hence, doped ZnOs are considered as interesting alternatives to Sn-doped indium oxide (ITO).

The ability to engineer the energy gap of ZnO for photovoltaic/optoelectronic applications strongly depends on the nature of the dopant. The most studied dopant in this regard is Al [9–14]. Although Al-doped ZnO have shown some intriguing features, there remains an unresolved problem concerning the environmental stability. Therefore, considerable recent research has focused on alternative doping schemes. In this regard Cd:ZnO has been shown to be an interesting option [15–20]. Cd and Zn are isoelectronic transition metals, and hence CdO alloying with ZnO could manifest interesting features in fused CdO–ZnO structures [21]. Importantly, Cd doping reduces the energy band gap and results in a red-shift of absorption edge [15–17,22]; hence, one can envision varying the Cd-doping concentration to tailor the electronic gaps to produce materials of interest for photovoltaic applications. In addition, incorporation of Cd into ZnO produces a material with increased conductivity [22,23] and increased carrier concentration (upto 2.69×10^{20} cm^{-3}) versus the parent ZnO [24].

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Although, Cd:ZnO exhibits interesting features for PV applications, the difference in the stable structural geometries of the parent compounds (i.e. ZnO and CdO) might impede its usefulness. At ambient conditions, CdO is cubic, whereas ZnO is stable in the wurtzite (WZ) phase. This difference in structural phases is a major issue for practical applications as the resulting material has low thermal stability – the Cd ions in hexagonal ZnO matrix induce tension in the lattice of Cd:ZnO, producing tensile strain that makes it difficult to conserve the hexagonal phase [20]. These internal strains cause distortion in crystal lattice, and reduce the crystallinity of Cd:ZnO [25]. These problems might be overcome, however, through incorporation of Cd dopants into the zinc-blende (ZB) phase of ZnO. Synthesis of the ZnO in ZB phase has been reported on the cubic GaAs substrate [26,27]. To the best of our knowledge, the doping of Cd into ZB-ZnO has yet to be explored.

In this work, we employ density functional theory (DFT) methods to investigate the effect of Cd substitution in both the cubic and hexagonal phases of ZnO; the latter is expected to be a more favorable situation to accommodate a high concentration of Cd atoms with comparatively lower internal strains. Our DFT investigations employ the full potential linearized augmented plane wave (FP-LAPW) method, and make use of the mBJ functional to evaluate the electronic gap. Of particular emphasis in this study is the electronic properties of these blend materials as a function of structure so as to evaluate the potential of Cd:ZnO materials for photovoltaic (PV) and solar cell applications.

2. Computational details

FP-LAPW approach as implemented in the WIEN2k code [28] was employed. Though GGA-based DFT calculations provide pertinent results for many physical properties of conducting oxides, the methods tend to underestimate the energy gap. To overcome this difficulty a proper choice of the exchange and correlation (XC) potential functional is crucial. Tran-Blaha modified Becke Johnson (mBJ) functional [29,30], in particular, has been reported in several studies of semiconductors and insulators to calculate energy gap with high accuracy approaching the experimental value [31,32], and will be used here. In order to calculate the structural properties GGA proposed by Perdew et al. (PBE-GGA) is employed [33]. Whereas to predict electronic and optical properties, in addition to PBE-GGA, mBJ exchange potential is incorporated [29,30].

To expand the wave functions inside the Muffin-Tin (MT) spheres $l_{max}=10$ and in the interstitial region, an energy cutoff $K_{max}=8.0/R_{MT}$ (Ryd)$^{1/2}$ was used. Radius of MT spheres, R_{MT} were chosen for Zn and Cd as 1. 81 a.u, and for O as 1.55 a.u. Fourier expanded charge density was truncated at $G_{max}=16$ au^{-1}. Brillouin zone (BZ) integration has been performed using Monkhorst–Pack special k-points approach [34]. To ensure convergence of the energy, the integrals over the special BZ are preformed up to 203 $(9 \times 9 \times 5)$ k-points for WZ and $216(6 \times 6 \times 12)$ k-points for ZB phases. Total energy convergence was ensured to 10^{-5} Ryd/unit cell.

To investigate how the substitution of Cd impacts the structural and electronic properties of ZnO, supercells of 32 atoms were constructed; supercells for WZ-ZnO and ZB-ZnO were $2 \times 2 \times 2$ and $2 \times 2 \times 1$, respectively. Substitution of Cd atoms has a strong influence on the structural symmetry, with the symmetry impacted by the sites of substitution; see Fig. 1 and Tables 1 and 2 for the WZ and ZB geometries, respectively. Such symmetry breaking for WZ-Cd:ZnO is consistent with previous literature reports [17]. It is of interest that the total energies of the Cd:ZnO structures in the WZ and ZB phases are only marginally different, with the minor differences reflecting the equivalent stability of ZB Cd:ZnO to that of WZ. The two structures present similar local tetrahedral bonding, with the main difference being their stacking direction (111). Both the structures carry the same atomic coordination through the second nearest neighbor.

3. Results and discussions

3.1. Structure and energy: ZB versus WZ phase

Fig. 2(a) depicts the influence of Cd concentration on the E_{tot} and $\Delta E_{(WZ/ZB)}$. The linear increase in E_{tot} with increasing Cd concentration reflects the stability of Cd:ZnO for high Cd content. The material stability can be estimated by Helmholtz free energy, which is simply the sum of formation enthalpy (mixing energy, $\Delta H(x, T)$) and product of temperature and entropy ($\Delta S(x, T)$). The formation enthalpy, which is difference between the energy of the alloy and the weighted sum of its constituents, solely determines the relative stability of Cd:ZnO system and is calculated as $\Delta H(x) = E(Zn_{1-x}Cd_xO) - xE(CdO) - (1-x)E(ZnO)$, see Table 3. Fig. 2(b) shows that ΔH increases as a function of the Cd content, obeying Vegard's law. The linear fit for ΔH is $\Delta H = 2.56x - 0.062$.
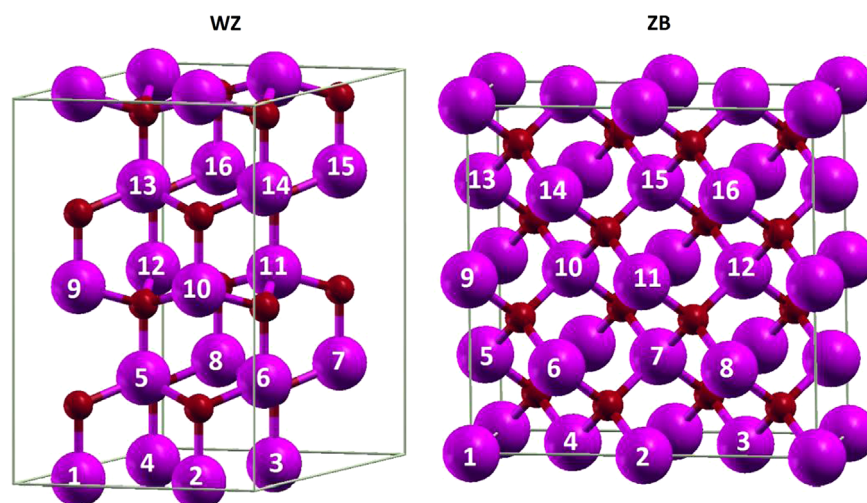
Fig. 1. The schematic structures of Cd:ZnO in WZ and ZB geometries. The numbers labeled spheres show the Cd/Zn substitutional sites. The purple colored big spheres and the red colored small spheres represent Zinc and oxygen atoms respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).