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The electronic structures and optical properties of yttrium-doped zinc oxide with zinc interstitial defects calculated by first-principles

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ABSTRACT

The geometric structures of ZnO, yttrium doped ZnO (YZO), ZnO with Zn interstitial (ZIO) and yttrium doped ZnO with Zn interstitial (YZIO) systems are investigated using the first-principle method based on density functional theory. The results show that doping yttrium ions can decrease the formation energy of Zn_i defects adjacent to yttrium ions. The electronic structures and absorption spectra of these systems are further obtained after revising the value of bandgap. Compared with ZnO, YZO and ZIO systems, there is an impurity level (E_r) near the center of the forbidden band in YZIO, which will enhance the luminescence peak in yellow region. Besides, the bandgap of YZIO will increase with the increase of yttrium doping concentration, which suggests that the UV emission of YZIO would have a blue shift. In addition, the absorption property of YZIO system is also improved in both the visible and UV regions, which can be used in converting solar energy into electricity.

1. Introduction

ZnO is a kind of II–VI semiconductor which has been extensively studied in the fields of light-emitting diodes [1,2], UV detectors [3], solar cell [4–6] and so on, due to its wide bandgap (3.37 eV) and large exciton binding energy (60 meV) [7]. By selective doping, the electric and optical properties of ZnO can be controlled for better applications [8–13].

Among various extra foreign element-doped ZnO systems, recently, yttrium (Y) doped ZnO (YZO) has been paid more attentions especially for its luminescent property [14–20]. In fact, Y ions can enhance the UV emission and decrease the deep level emission (DLE) band in the green range of ZnO [15,19]. The green emission band is believed to be contributed by at least two different defect origins (oxygen vacancy (V_O) and zinc vacancy (V_{Zn})). Thus, it is generally recognized that doping Y into ZnO lattice will reduce the quantity of nonradiative recombination centers (V_O and V_{Zn}), and increase the possibility of the near band-edge transition of ZnO, hence improving the corresponding UV emission [15–17]. Besides, Y doping can be used for tuning the DLE in ZnO. Yang et al. [19] found that the peak position with maximum intensity in DLE band of ZnO was gradually tuned from 539 nm to 598 nm as the concentration of Y doping increased from 0% to 5%. After that, Gao et al. [15] observed the yellow–orange emission band of YZO broaden compared with that of ZnO. These two groups regarded that Y ions attracted more native defects

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Table 1
The calculated lattice parameters c of ZnO and $Zn_{1-x}Y_xO$, and δ of $Zn_{1-x}Y_xO$.

Supercell size		3 × 3 × 2	2 × 2 × 2	2 × 2 × 1
x		0.0278	0.0625	0.125
c (Å)	ZnO	10.6071	10.6133	5.3051
	$Zn_{1-x}Y_xO$	10.6690	10.7420	5.4079
δ (%)		0.583	1.213	1.938

related to the yellow emission, such as oxygen interstitial (O_i) and zinc interstitial (Zn_i). Moreover, Li et al. [21] studied the YZO as a detector of acetic acid. And it was found that Y induced the electron donor defects (Zn_i and V_O), causing the increase of the conductivity and active sites on the surface of ZnO, which could enhance the gas sensing of YZO. Gao et al. [15] also measured the Raman spectra of YZO and found that doping Y introduced more lattice mismatch and distortion in the ZnO lattice, which was likely to increase the native defects (V_O and Zn_i).

In conclusion, Y ions can adjust the performance of ZnO by interacting with the native defects (especially Zn_i) in most cases. For Zn_i, one of the native defects in ZnO, is a kind of shallow donor but has higher formation energy [22]. Its effect on the properties of ZnO has been studied experimentally and theoretically (like n-type conductivity [23], luminescence properties [24] and gas sensing [25]). However, no detail studies have been reported on the Y doped ZnO with Zn_i (YZIO) systems in theory up to now, to the best of our knowledge.

In this paper, the first-principle calculation of YZIO has been performed compared with that of ZnO, Y doped ZnO (YZO) and ZnO with Zn_i (ZIO) systems. The crystal structures of the ZnO, YZO and ZIO systems are firstly calculated to ensure the rationality of the models and the influence of yttrium on Zn_i defects in terms of formation energy is investigated in detail. Then, the corresponding absorption spectrum of YZIO is obtained and compared with that of ZnO, YZO and ZIO systems. Under the band structures and density of states, the electron transition processes corresponding to the emission and absorption peaks are further analyzed.

2. Details of calculation

All calculations in this paper were carried out by the CASTEP tool based on the first-principals. In order to minimize the plane wave vector, ultrasoft pseudopotential was used for describing the interaction between the ion core and its valence electrons. The cutoff energy was 340 eV. The valence atomic configurations were $3d^{10}4\,s^2$ for Zn, $2\,s^2 2p^3$ for O and $4d^1 5\,s^2$ for Y. Exchange correlation potential of electrons was approximated by PBE solution under the generalized gradient approximation (GGA). All systems were calculated in reciprocal space, but different k-point samplings were selected for different size of supercells. Specific settings: 4 × 4 × 5 Monkhorst–Pack grid for 2 × 2 × 1 supercell, 4 × 4 × 2 grid for 2 × 2 × 2 supercell, and 3 × 3 × 2 for 3 × 3 × 2 supercell. In the optimization process, using the BPGS method, the energy change and the maximum tolerances of the force, stress, and displacement were set to 1×10^{-5} eV /atom, 0.03 eV/Å, 0.05 Gpa and 0.01 Å, respectively [26]. The GGA+U method was used to optimize the energy of systems, so as to correct the value of bandgap of ZnO. And the $U_{p,O}$ value of 7 eV, $U_{d,Zn}$ value of 10 eV [27], and $U_{d,Y}$ value of 2 eV were adopted in the GGA+U method.

3. Results and discussions

3.1. Crystal structure

The calculated lattice parameters *c* of different size of ZnO and YZO ($Zn_{1-x}Y_xO$) (x=0.0278, 0.0625, and 0.125) supercells are listed in Table 1. The experimental c of pure ZnO is about 5.2 Å [15,28], which is slightly smaller than the calculated one. This is because the GGA method always overvalues the lattice constant. *δ* showed in Table 1 is used to measure the variance between c_{YZO} and c_{ZnO} (i.e., $\delta = (c_{YZO} - c_{ZnO})/c_{ZnO}$). It can be seen that the value of *δ* increases with the increase of Y doping concentration (x), indicating that the higher the Y doping concentration, the more serious the lattice distortion. Fig. 1 displays the calculated X-ray powder diffraction diagrams (XRD) of $Zn_{1-x}Y_xO$ with different concentration. The radiation source is Cu-K_α (λ=1.540562 Å). It is observed that the diffraction peaks of Y-doped ZnO gradually move to small angel direction with increasing Y content. The calculated XRD patterns are fit with the experimental results [17,18], which confirms that the YZO structure models in this paper are reasonable and practical. In Y-doped ZnO, Y ions will substitute in Zn sites and because the ionic radius and covalent radius of Y (0.90 Å, 1.62 Å) are bigger than those of Zn (0.74 Å, 1.25 Å), the values of *δ* are positive and increase with the increase of Y content.

In fact, there are four kinds of initial positions to place a Zn atom interstitially in ZnO structures. They are the centers of 1. the octahedron surrounded by oxygen atoms (oct_O), 2. the octahedron surrounded by zinc atoms (oct_{Zn}), 3. the tetrahedron surrounded by oxygen atoms (tet_O), and 4. the tetrahedron surrounded by zinc atoms (tet_{Zn}). These four kinds of Zn_i models in 2 × 2 × 1 ZnO supercell are shown in Fig. 2. It is seen that the coordinates of $Zn_i(oct_{Zn})$

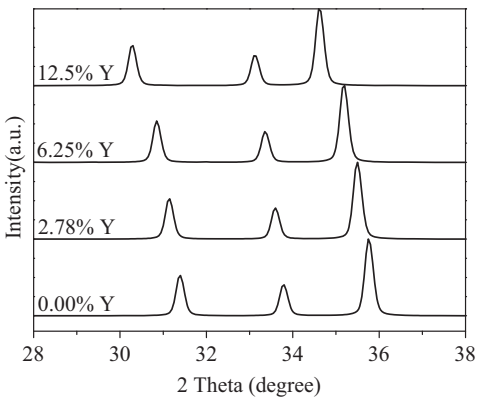

Fig. 1. XRD patterns of $Zn_{1-x}Y_xO$ with different concentrations (x=0.00, 0.0278, 0.0625, and 0.125).