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A direct first principles study on the structure and electronic properties of $Be_xZn_{1-x}O$

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We present a systematic study on the structural and electronic properties of all alloy configurations of $Be_xZn_{1-x}O$ in a unit cell with 16 cations using density functional theory (DFT) methods. The 2^{16} complexity is reduced by considering the symmetry of the parent structures. The experimental structures and electronic properties of the bulk material are reasonably reproduced by the DFT methods. The lattice constants of the alloy are found to follow Vegard's law [Z. Phys. **5**, 17 (1921)] and are comparable with the experimental values. Examining the formation enthalpy of all alloy configurations suggests the possible existence of three metastable order states. The calculated band gap of the $Be_xZn_{1-x}O$ is also compared with the experimental measurements and the authors found that some alloy configurations with the same concentration can have band gaps differed by ~1.5 eV. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2789692]

ZnO is recognized as a next generation UV light emitting material due to its wide band gap (3.37 eV at RT) and large exciton binding energy (60 meV).[1] It is now possible to grow stable and reliable *p*-type ZnO semiconductor material by doping with either nitrogen[2] or arsenic.[3] Another critical step in producing high-efficiency ZnO-based light emitting devices is the fabrication of quantum wells and superlattices of ZnO-based semiconductor alloy by mixing with materials with even larger band gaps. $Mg_xZn_{1-x}O$, with MgO ($E_g=7.7$ eV), has been studied quiet extensively and this material can cover a range that varies from blue to deep UV.[4] However, due to the different crystal structures and large lattice mismatches between ZnO ($B4$) and MgO ($B1$), crystal phase segregation was theoretically predicted[5,6] and experimentally confirmed[7] for $x \geqslant 1/3$.

BeO ($E_g=10.6$ eV) is also a good candidate for achieving wider band gap modulation. An appealing property of BeO is that it has the same hexagonal wurtzite structure as ZnO. However, due to its high degree of toxicity, $Be_xZn_{1-x}O$ alloy remains underexplored. It was only until recently that Ryu *et al.* had synthesized $Be_xZn_{1-x}O$ films using the hybrid beam deposition method.[8,9] Inspired by this recent work, the present paper reports a theoretical investigation on the detailed structural and electronic properties of $Be_xZn_{1-x}O$. In particular, we aim to seek for the existence of ordered stoichiometric intersemiconductor compounds $Be_xZn_{1-x}O$ that can be thermodynamically more stable than the disorder states. If such ordered states exist, what are their electronic properties compared to the random configurations?

In recent years, density functional theory (DFT)-based first principles methods have gained increasing popularity and been routinely employed for material simulations due to their high accuracy and efficiency. Nevertheless, one of the major obstacles in studying the $Be_nZn_mO_{n+m}$ alloy is to deal with the 2^{n+m} possible configurations. One of the commonly used algorithms proposed for dealing with such complexity is the cluster-expansion theory[10] which can effectively map the relative stability of the alloy configurations to an effective Hamiltonian. This effective Hamiltonian can be then be used to explore the enormous (2^{n+m}) configuration space and study the thermal properties of the alloy. As a preliminary step towards a comprehensive study, our goal is to study the detailed structural and electronic properties of all alloy configurations in a given unit cell. In the present work, we consider a supercell of $Be_xZn_{1-x}O$ containing 32 atoms and if we simply consider the replacement of cations (Be and Zn) with one another, the total number of configurations becomes $2^{16}=65\,536$. Direct first principles calculation of such a large number of configurations is infeasible in practice. Moreover, it is well known that the physical properties of a system will not be changed under the symmetry operations of the system. We employ this old wisdom to reduce the number of configurations in the abovementioned unit cell. Thanks to the high symmetry of the hexagonal wurtzite structure (symmetry group=$P6_3mc$), the number of symmetrically distinct configurations is reduced to 652. In short, leveraging from the symmetry properties of the parent scaffold, we have reduced the amount of computation by more than 100 times.

The structural and electronic properties of the 652 alloy configurations are examined directly using the DFT in the

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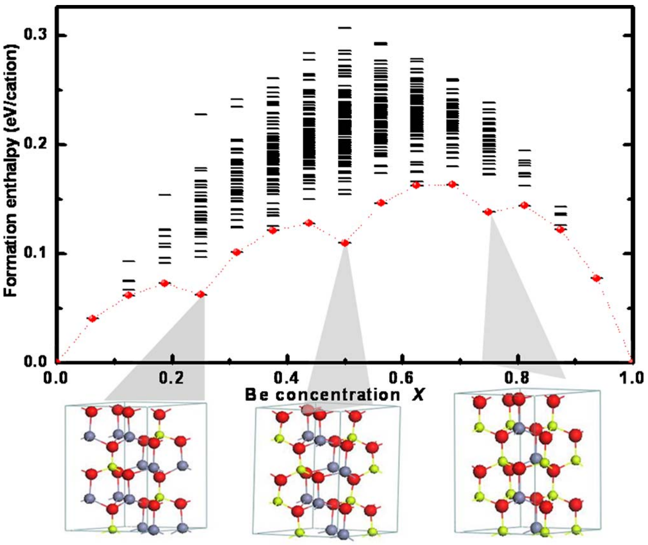

FIG. 1. (Color online) Formation enthalpy of all 652 symmetrical distinct $Be_xZn_{1-x}O$ alloy configurations in a unit cell of 16 cations. The ground-state line is highlighted by a red line. The lattice structures of three metastable ordered states with Be concentrations of 25%, 50%, and 75% are shown in the inset (red sphere for O atom, green sphere for Be atom, and blue sphere for Zn atom).

local density approximation[11] (LDA) as implemented in the VASP program package.[12] We have carried out tests on the *k*-space integral and plane-wave basis to ensure the total energy is converged at the 1 meV/cation level. We found that using an energy cutoff of $E_{\text{cut}}=1200$ eV and a $3\times3\times2$ Monkhorst-Pack-type mesh in the first Brillouin zone[13] is sufficient for the semiconductor alloy $Be_xZn_{1-x}O$. The total energies were obtained after the geometrical optimization finished. It is worth noting that one must carefully relax not just the atomic positions but also the lattice constants of any alloy configurations to allow convergence to their most stable conformation.

A standard method to access the relative stability of an alloy configuration (σ) is to calculate their excess energy (the formation enthalpy) which is defined as the difference in energy between the alloy and the weighted sum of the constituents,

$$\Delta E(\sigma,x) = E(\sigma,\mathrm{Be}_x\mathrm{Zn}_{1-x}\mathrm{O}) - xE(\mathrm{BeO}) - (1-x)E(\mathrm{ZnO}),$$

where $x(\sigma)$ is the concentration of configuration σ. The formation enthalpies of all 652 alloy configurations, as depicted in Fig. 1, have a concave feature which imply that random alloy configurations are not stable with respect to the pure species. However, if we focus at the ground-state line, there are three regions (at $x=0.25$, 0.50, and 0.75) with convexity. The convexity/concavity of a configuration (σ) can be accessed by calculating the local potential depth $\Delta(\sigma)$, defined by Ferreira *et al.*[14] as

$$\Delta(\sigma) = \Delta E(\sigma) - \frac{x(\sigma)-x(\alpha)}{x(\beta)-x(\alpha)}\Delta E(\beta) - \frac{x(\beta)-x(\sigma)}{x(\beta)-x(\alpha)}\Delta E(\alpha),$$

where α, β, and σ are three configurations with concentrations in the order of $x(\alpha)<x(\sigma)<x(\beta)$. A locally stable ground state is defined with $\Delta(\sigma)<0$. We found that when the concentrations of Be are 0.25, 0.5, and 0.75, the respective local potential depths are −24.8, −27.15, and −15.35 meV/cation. These convex regions suggest the existence of ordered metastable structures and the formation of such ordered structures is possible when the Be concentration is between two vertices, the alloy is likely to lower its energy by local decomposition. We should point out here that by comparing the overall feature of the formation enthalpy of $Be_xZn_{1-x}O$ (shown in Fig. 1) and that of $Mg_xZn_{1-x}O$ (Fig. 2 of Ref. 6), one would expect that the solubility $Mg_xZn_{1-x}O$ would be better than $Be_xZn_{1-x}O$.

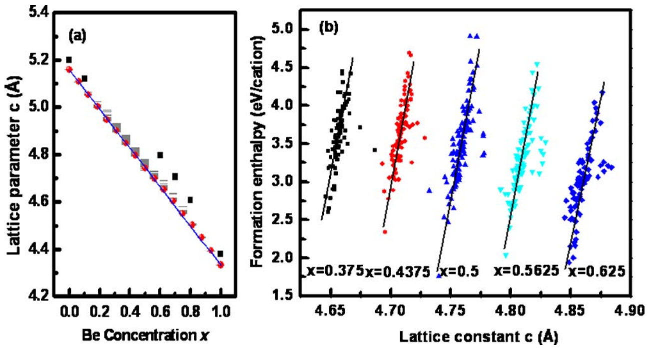

FIG. 2. (Color online) The *c*-axis lattice constant of $Be_xZn_{1-x}O$ as a function of Be concentration is shown on the left. The lattice constants of the ground states at each concentration are highlighted by red spheres. The experimental values of reported in Ref. 8 are shown as black squares. The lattice constants, especially those of the ground states follow Vegard's laws well. However, small deviation from the linear extrapolation is notable for some excited states. It is clear from the right hand figure that there is a strong correlation between the relative stabilities of an alloy configuration with its lattice constants.

The structures deriving from our LDA calculations agree well with experiments. For the bulk materials, we arrived at the following lattice constants: ZnO ($a=3.195$ Å and $c=5.158$ Å) and BeO ($a=2.667$ Å and $c=4.333$ Å). These values are found to be slightly below the experimental values [ZnO ($a=3.249$ Å) and BeO ($a=2.698$ Å)] in literature.[15] The underestimate of the lattice constants based on the LDA method is reasonable and can be well understood by the thermal effects in the experimental samples.

In order to compare with the experimental work of Ryu *et al.*[8] on the structures of the $Be_xZn_{1-x}O$ alloy, we derive the lattice constants of the alloy configurations from their optimized supercell size by setting the a/c ratio at linearly interpolated values. The lattice constants of all 652 configurations are shown in Fig. 2(a). It is found that at each concentration the lattice constants of the ground states are generally smaller than the excited states. This observation is in line with the expectation that ground state structures are configurations with stronger bonding characters thus resulting in smaller volume. This notion is also confirmed by examining the dependence of the formation enthalpy and lattice constants at different Be concentrations, as shown in Fig. 2(b)—which reminds us that lattice relax plays an important role in finding the relative stability of alloy configurations. The blue line in Fig. 2(a) is drawn to connect the lattice constants of the bulk material. It is obvious that the lattice constants of the ground states follow Vegard's law[16] closely, although notable deviation from the linear extrapolation is possible for some excited states.

Since both ZnO and BeO have direct band gaps, we estimated the band gaps of individual alloy configurations by calculating the band gaps at Γ point with a self-consistent calculation that can generate high quality charge density. The

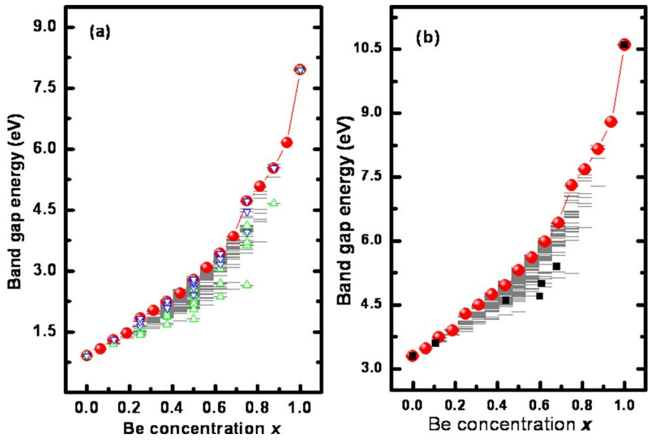

FIG. 3. (Color online) (a) The energy band gaps of $Be_xZn_{1-x}O$ alloy at the Γ point predicted by LDA method as a function of x are shown. The band gaps of the ground states are shown as red spheres. The band gaps of the [100] and [001] SCs are shown as Δ and ∇, respectively. (b) The corrected band gaps and the experimental band gaps from experiment from Ref. 8 are shown in (b).

calculated band gaps for ZnO and BeO are 0.905 and 7.946 eV, while the experimental values are 3.3 and 10.6 eV, respectively. This large error in the band gap is a well-known problem of the LDA method, which fails quantitatively in dealing with excited-state properties and tends to underestimate the band gap. However, the difference found between our calculated band gaps and the experimental ones will not affect our analyses which refer only to the relative value of band gaps.

The band gaps of all 652 alloy configurations calculated using the LDA method are depicted in Fig. 3(a). It is found that the band gaps of the ground states structures are generally larger than the excited states for a given concentration. In order to compare with the experimental report,[8] the LDA band gaps are "corrected" by linear interpolation to fit the bulk values. The corrected band gaps are shown in Fig. 3(b). Note that the experimental values are found to be smaller than the calculated ones for the ordered states. This may be attributed to errors in experimental measurements and/or the dominance of the disordered excited states in the sample.

The structures of the three metastable states, shown at the bottom of Fig. 1, all have periodicity along the *c* axis. Motivated by this observation, we further investigate whether the band gaps are sensitive to directional decompositions. Since our supercell is not large enough to allow too many general directions, we have focused only on the [100] and [001] supercell structures (SCs). It is clear from Fig. 3 that the [001] SCs (meaning structures with periodicity along the [001]) have higher band gaps than the rest, and there is no systematic trend among the [100] SCs. One of the implications is that the [001] SCs of $Be_xZn_{1-x}O$, if it can be grown, is expected to have larger and more consistent (due to the smaller deviations in the band gaps among all the [001] SCs) band gaps than random decompositions.

In summary, we have demonstrated that using the symmetry of the parent structures can provide significant reduction in the complexity of the alloy systems. Thanks to the high symmetry of the hexagonal wurtzite structure, a factor of more than 100 has been achieved by reducing the 2^{16} possible alloy configurations to 652 symmetrically distinct configurations. This reduction in complexity enables us to examine the detailed structural and electronic properties of $Be_xZn_{1-x}O$ by the first principles method.

We found that DFT methods can accurately reproduce the structure of bulk materials. In the alloy configurations we found that the relative stability of a given alloy configuration has a linear dependence with its lattice constants. Examine the formation enthalpy, we also identify three convex regions which suggest the existence of metastable order states at Be concentrations $x=0.25$, 0.50, and 0.75. These results would be useful for designing the growth process and application of the electronic properties of alloy $Be_xZn_{1-x}O$.

The electronic properties are found to be more sensitive to alloy configurations. In particular, we found that while the lattice constants of the alloy configurations follow Vegard's law with only a small deviation, their band gap at the Γ point can be differed by ~1.5 eV. Supercell structures along [001] are found to have larger band gaps than the random configurations. A more comprehensive study on $Be_xZn_{1-x}O$ is undergoing and we hope this systematic calculation and analyses of the structural and electronic properties of all alloy configurations reported here will prove to be useful to experimentalists and further stimulate more detailed and accurate investigations.

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