

First-principles Study of Structural Properties of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ternary alloys

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Abstract. First-principles calculations have been carried out to investigate the structural and electronic properties of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ternary alloys. The calculations are performed using the full potential linearized augmented plane wave (FP-LAPW) method within the density functional theory(DFT). We conclude that the structural properties of these materials, in particular the composition dependence on the lattice constant and the band gap is found to be linear. The a -axis length in the lattice gradually increases, while the c -axis length decreases with the increase in Mg doping concentration, and be corresponded with the Vegard's law linear rule. The lattice parameters of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ternary alloys are consistent with experimental data and other theoretical results. We found in the conduction band portion, the Mg 2p 2s states are moved to high energy region as the Mg content increases, so the band gap increases.

1. Introduction

During the past few years, the II-VI compound semiconductors have received considerable interest from both experimental and theoretical points of view. This is due to their potential technological applications in light-emitting diodes (LEDs) and laser diodes (LDs)[1]. As a typical II-VI wide-gap semiconductor and oxide, ZnO have been of growing interest and have shown great potential in ultraviolet photoelectric devices application, especially in deep ultraviolet light emitters and detectors application, because of its wide band gap(3.37eV) and large exciton binding energy (60 meV) at room temperature[2-3]. It has wide range of technological applications such as transparent conducting[4] electrodes in solar cells and flat panel displays, surface acoustic wave devices and gas sensors[5-7]. All the time, there are two important requirements in fabricating ZnO laser diodes are p-type doping and band gap engineering in alloy semiconductors to create barrier layers and quantum wells which facilitate radiative recombination by carrier confinement. The addition of impurities among the wide band gap semiconductors often induces dramatic changes in their structural and optical properties. Ternary $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ compounds are ideal materials for the development of deep ultraviolet photoelectric devices because they have many particular advantages, such as availability of lattice-matched single-crystal substrates, wide tunable band gap(3.3 to 7.8eV), low growth temperature (100-750 °C), high radiation hardness[8-9]. In addition, because the ionic radius of Mg^{2+} (0.57Å) is similar to that of Zn^{2+} (0.60Å), Zn can be substituted by Mg without much lattice distortion[10]. Furthermore, the bonding strength of Mg-O is stronger than that of Zn-O, therefore MgZnO is expected to have higher lattice stability than ZnO. Moreover, the accomplishment of UV LEDs based on MgZnO has been demonstrated very recently[11].



In order to understand the nature of these materials better we present the results of first-principles calculations of ternary alloys $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ in wurtzite structure. In this work, we study the electronic and structural properties of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ternary alloys in wurtzite phase over a wide range of compositions $0 \leq x \leq 1$ using the full potential linearized augmented plane wave (FP-LAPW) method within the density functional theory.

2. Calculation Method

The calculations presented in this work were performed using first-principles, plane-wave pseudopotential approach within the framework of density-functional theory (DFT) implemented in the Cambridge Serial Total Energy Package (CASTEP) codes [12]. For the exchange-correlation potential, we used the generalized gradient approximation (GGA) of Perdew and Wang, known as PW91 [13]. The plane-wave cutoff energy is set to be 400 eV in the present calculations. The special points sampling integration over the Brillouin zone is employed by using the Monkhorst-Pack method [14] with a $4 \times 4 \times 5$ special k-point mesh. The Mg $2p^6 3s^2$, Zn $3d^{10} 4s^2$ and O $2s^2 2p^4$ electrons are treated as valence states. The Brodyden-Fletcher-Goldfar-Shanno (BFGS) minimization scheme [15] was used in geometry optimization. The tolerances for geometry optimization were set as the difference in total energy being within 2×10^{-5} eV/atom, the maximum ionic Hellmann-Feynman force within 0.05 eV/Å, the maximum ionic displacement within 0.002 Å and the maximum stress within 0.1 GPa. Figure 1 depicts the schematics of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys.

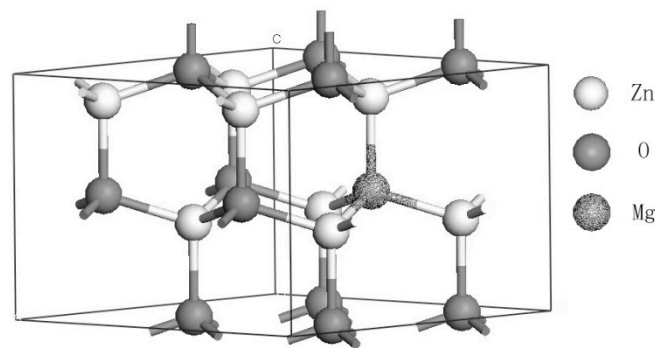


Figure 1. The crystal structure of wurtzite $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys.

3. Results and discussions

3.1 Structural properties

In the present work, we model the alloys at some selected compositions with the ordered structures described in terms of periodically repeated supercells with sixteen atoms per unit cell. For the considered structures, we perform the structural optimization by minimizing the total energy with respect to the cell parameters and also the atomic positions. Our calculated values for the equilibrium lattice constants for $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys are given in Table 1. Usually, in the treatment of alloy problems, it is assumed that the atoms are located at ideal lattice sites and the lattice constants of alloys should vary linearly with compositions x according to the so-called Vegard's law [16]. So the lattice constant of ternary $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys can be expressed by Vegard's law.

$$a(\text{Mg}_x\text{Zn}_{1-x}\text{O}) = xa_{\text{MgO}} + (1-x)a_{\text{ZnO}} \quad (1)$$

Figure 2 shows the variation of the calculated equilibrium lattice constants versus concentration for $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys. From the figure 2 we can conclude that the a -axis length in the lattice gradually increases, while the c -axis length decreases with increasing Mg content, consistent with experimental results and other theoretical results [17]. The linear equation of lattice parameter a and c are obtained

using the linear fitting method. We reach the conclusion that the results are very close to that of other papers' conclusion [18].

$$a = 3.28162 + 0.06653x \quad (2)$$

$$c = 5.31564 - 0.15373x$$

Table 1. Calculated lattice parameter a and c for ZnO(WZ) and MgO(RS) and their alloys at equilibrium volume. Compared with other theoretical calculations and experimental results.

x	Lattice constant a (Å)			Lattice constant c (Å)		
	This work	Exp.	Other calculations	This work	Exp.	Other calculations
0	3.280	3.249 ^c	3.280 ^a 3.275 ^b	5.280	5.206 ^c	5.296 ^a 5.270 ^b
0.125	3.291			5.291		
0.25	3.295		3.297 ^b	5.288		5.248 ^b
0.375	3.303			5.269		
0.5	3.308		3.313 ^b	5.275		5.22 ^b
0.625	3.324			5.218		
0.75	3.327		3.325 ^b	5.215		5.203 ^b
0.875	3.337			5.191		
1	3.359		3.333 ^b	5.119		5.175 ^b

^aRef [19], ^bRef [17], ^cRef [20]

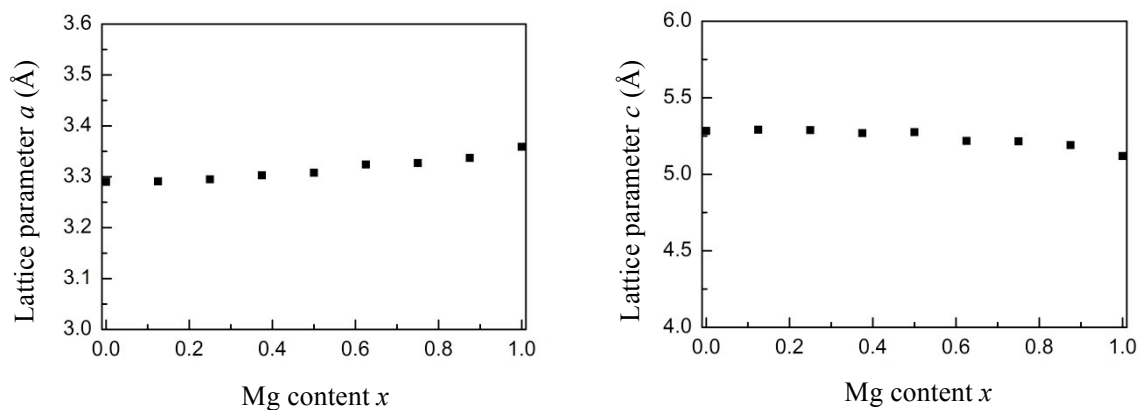


Figure 2. Calculated equilibrium lattice constants of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys for different Mg concentrations.

3.2. Electronic properties

3.2.1. Band structures

We have calculated the energy band for the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys along the high directions in the first Brillouin zone at the calculated equilibrium lattice constants. Figure 3 shows the variation of band gap with Mg content in hexagonal $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ crystals with $0 \leq x \leq 1$. In fact, it is well known that the GGA usually underestimates the experimental energy band gap and this is an intrinsic feature of the density functional theory (DFT), DFT being a ground-state theory is not suitable for describing

excited-state properties, such as the energy gap. However, it is widely accepted that GGA (LDA) electronic band structures are qualitatively in good agreement with the experiments as regards the ordering of the energy levels and the shape of the bands.

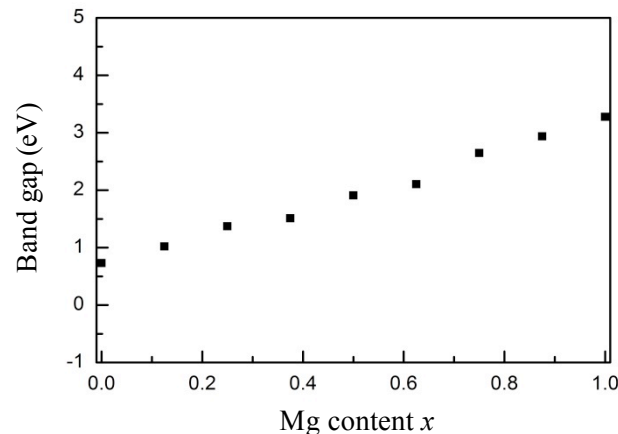


Figure 3. Composition dependence of the calculated band gap for $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys.

From the Figure 3 we found that with the increase of components the energy gap of the alloys is also increased, it is clearly seen that the calculated band gap exhibits strong composition dependence for $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys. This is different from conventional III-V alloys which show a weakly compositional dependent energy gap.

3.2.2. Density of states

We also calculated the partial and total density of states (DOS) of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ in the WZ structures. Due to the close similarity between the results obtained for these alloys, the DOS is given only for the $\text{Mg}_{0.75}\text{Zn}_{0.25}\text{O}$ compound as shown in Figure 4. From the partial DOS, we find that the anion (O) s states are strongly localized in the energy range from -17eV to -15eV and the upper valence band is derived mainly from the hybridization of Zn d and O p states. In the conduction band, the Mg, Zn and O states become partially occupied, while the conduction band is mainly dominated by cation states (Mg). In order to interpret the effect of Mg on the electronic structure, we have offered the changing curve of the density of states with different concentration.

It clearly indicates that in the conduction band portion the Mg 2p 3s states are moved to high energy region as the Mg content increases, and the Mg 2p state is more and more dominant in Figure 5. Therefore it leads to an increase in the band gap.

4. Conclusions

In this study, we have presented a complete theoretical analysis of the structural and electronic properties of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys by the first-principles density functional calculations. The structural parameters of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys are fully relaxed and have been optimized. The calculated results show the calculated lattice constants scale linearly with composition, showing the validity of Vegard's linear rule in the definition of lattice constants of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys. We have investigated the composition dependence of the lattice constant and band gap. It can be expected that some of our calculated results will be useful for the device applications of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys and can be verified in the future experiments.

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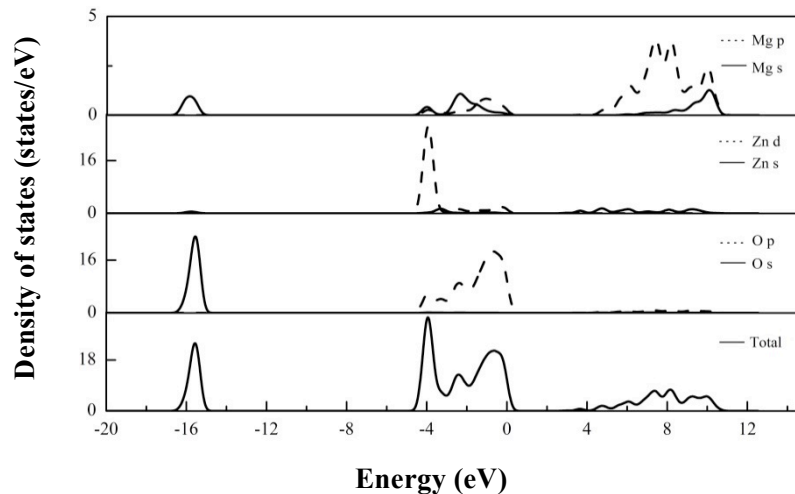


Figure 4. The partial density of states of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ with $x = 75\%$. The position of Fermi level is located at 0 eV.

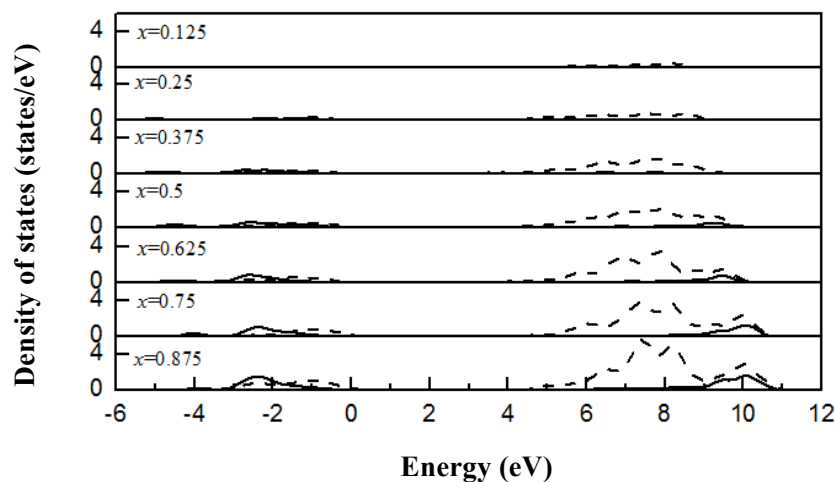


Figure 5. The partial density of states of Mg 2p(dashed line), 3s(solid line) bands in hexagonal $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ crystals($x = 0.125, 0.375, 0.5, 0.625, 0.75, 0.875$ respectively).

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