Ordering tendencies in octahedral MgO-ZnO alloys

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ordering tendencies in octahedral MgO-ZnO alloys

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(Received 18 August 2003; published 24 October 2003)

Isostructural II-VI alloys whose components are either rocksalt stable (e.g., CaO-MgO) or zincblende stable (e.g., ZnS-ZnSe) are known to be thermodynamically unstable at low temperatures, showing a miscibility gap and no bulk ordering. In contrast, we show that heterostructural MgO-ZnO is stable, under certain conditions, in the sixfold-coordinated structure for Zn concentrations below 67%, giving rise to spontaneously ordered alloys. Using first-principles calculations, we explain the origin of this stability, the structures of their low-temperature ordered phases, short-range-order patterns, and their optical band-gap properties.

DOI: 10.1103/PhysRevB.68.155210

PACS numbers: 71.55.Gs, 71.20.Nr

I. INTRODUCTION

Binary II-VI compounds appear 1 largely as fourfold-coordinated (CN4) zincblende/wurtzite structures (ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, and CdTe) or as sixfold-coordinated (CN6) rocksalt structures (MgO, CaO, and CdO). Isovalent and isostructural alloys of II-VI constituents are generally thermodynamically unstable, in that their mixing enthalpy, in either the CN6 rocksalt (B1) structure or in the CN4 (B3) or wurtzite (B4) structures,

\[ \Delta H_\alpha(A_xB_{1-x}C) = E_\alpha(A_xB_{1-x}C) - [x E_\alpha(AC) + (1-x)E_\alpha(BC)], \]

(1)
is positive. 2–4 Here, \( \alpha \) denotes fourfold or sixfold coordinated crystal structure, and \( E_\alpha(AC) \) is the total energy of compound \( AC \) in crystal structure \( \alpha \). For example, \( \Delta H_{B1} \) of isovalent alloys whose constituents are B1 stable (CaO, MgO, and CdO) are generally positive, 2 as are \( \Delta H_{B3} \) of isovalent alloys 5 whose constituents are B3 stable (ZnS, ZnSe, and ZnTe). This can be seen both experimentally 5 and from local-density approximation (LDA) total-energy calculations on 50–50% alloys, modeled via (quasirandom) supercells. 3 Because \( \Delta H > 0 \), the isovalent and isostructural alloys can be thermodynamically miscible only at high temperatures where the entropy term \( -TS \) is sufficiently negative. However, as the temperature is lowered, the alloys phase separate, showing no ordered intermediate structures. 3

An interesting case is an isoalvalent II-VI alloy made from nonisostructural components, e.g., wurtzite+rocksalt (B4-B1). Such alloys, e.g., ZnO-MgO became of great interest recently, 5 since in principle a B4-B1 combination spans a wider range of optical band gaps than either a B1-B1 or a B4-B4 alloy. For example, alloys of ZnO (\( E_g = 3.4 \) eV) with MgO (\( E_g = 7.7 \) eV) could span a range from blue to deep UV, which is of interest for optical laser and light-emitting diode applications. 5 However, it is not known if nonisostructural II-VI alloys are, in principle, thermodynamically stable or not.

II. SUMMARY OF FINDINGS

We report here on first-principles total-energy calculations which show the following.

(1) Sixfold-coordinated \( \text{Mg}_{1-x}\text{Zn}_x\text{O} \) alloys have \( \Delta H_{B1} < 0 \) for Mg-rich compositions, in contrast with the opposite sign for isostructural B1 oxides (e.g., \( \text{Mg}_{1-x}\text{Ca}_x\text{O} \) in Table I). We thus predict that high Mg concentration \( \text{Mg}_{1-x}\text{Zn}_x\text{O} \) alloys will be stable and order in the NaCl (B1) structure.

(2) Fourfold-coordinated \( \text{Mg}_{1-x}\text{Zn}_x\text{O} \) alloys have \( \Delta H_{B4} < 0 \) for Zn-rich compositions, in contrast with the opposite sign for isostructural B4 or B3 alloys, 5 e.g., \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \). We thus predict that high Zn concentration \( \text{Mg}_{1-x}\text{Zn}_x\text{O} \) alloys will be stable and order in a fourfold-coordinated structure.

(3) The results (1) and (2) suggest that if coherency with the alloy medium (or epitaxial substrate) can be maintained, such alloys will exhibit ordering tendencies at low temperatures, not phase separation like Mg 0.5 Zn 0.5 O 0.163-1829/2003/68(15)/155210(5)/$20.00 68 155210-1 ©2003 The American Physical Society
FIG. 1. Calculated total energies of some sixfold-coordinated (CN6) structures (+ symbols) and some of their fourfold-coordinated (CN4) analogs (open circles) [Ref. 11]. For x=±2/3 the sixfold structures are lower in energy than their fourfold analogs consistent with the experimental observation (Ref. 9) that a CN6 to CN4 transition occurs at x=67%. Three lines connect the end points MgO(CN6)-ZnO(CN6) (solid line), MgO(CN6)-ZnO(CN4) (dashed line), and MgO(CN4)-ZnO(CN4) (long dashed line). The crossover of the CN4-CN4 and CN6-CN6 lines determined by the end-point energies near x=67% is also consistent with the observed CN6-CN4 transition.

functional for ∼3×10^6 possible configurations, we identify Mg2ZnO4 (D023) and Mg2ZnO8 as ordered B1-like ground-state structures.

(5) The formation energy E_a (Mg_{1-x}Zn_xO) changes from being lowest in the sixfold-coordinated structure (B1), to being lowest in the fourfold-coordinated (B4) structure for Zn concentrations near 67%. This CN6 to CN4 transition has been observed experimentally^9 at x_{Zn}=67%. We see evidence of such a rocksalt-wurtzite transition in Fig. 1, where we compare sixfold-coordinated alloys and their fourfold-coordinated analogs^10 and find that near x_{Zn}=67% the fourfold analogs become more stable than the sixfold structures.

(6) Despite ∆H_{B1}<0 and ∆H_{B4}<0, we find that the enthalpy ∆H_{B1,B4} taken relative to the stablest form of each end-point constituent (fourfold-coordinated ZnO and sixfold-coordinated MgO),

$$\Delta H_{B1,B4}(Mg_{1-x}Zn_xO) = E_a(Mg_{1-x}Zn_xO) - xE_{B1}(MgO) - (1-x)E_{B4}(ZnO),$$

(2)
is positive for the alloy being in either α being fourfold- or sixfold-coordinated structures. This means that if coherency with the medium cannot be maintained (so each constituent can adopt its stablest coordination), the alloy will phase separate.

(7) Random alloys of Mg_{1-x}Zn_xO have a calculated band-gap bowing parameter of b=3.1 eV, in close agreement to recent experimental observations of b=3.6 ±0.6 eV. The physical mechanisms responsible for these observations are described in the following section.

Observations (1) and (2) above are shown in Fig. 1, which shows the (first-principles) calculated formation energy^12 E_a (Mg_{xZn_{1-x}O}) for α=CN4 ordered structures and for α = CN6 ordered structures. For the end-point compounds, we find that MgO is stablest in the CN6 (B1) form. The CN4 (B4) form of ZnO is 206 meV/cation higher than CN6 (B1). The energies of the CN6-Mg_{1-x}Zn_xO alloys are below the (MgO, CN6)-(ZnO, CN6) tie line for x_{Zn}=67%, and the energy of the CN4-Mg_{1-x}Zn_xO alloys are below the (MgO, CN4)-(ZnO, CN4) tie line for x_{Zn}≥67%. Thus, CN6 (B1) alloys are stable for x_{Zn}<67% whereas CN4 alloys are stable for x_{Zn}=67%, consistent with the extended solid solubility observed in this system.^5

III. PHYSICAL ORIGINS OF HETEROSTRUCTURAL STABILITY

To clarify the origin of this unexpected stability, we decomposed ∆H_{B1} into three physically recognizable components:^16

(i) the “volume deformation” component ∆E_{VD} due to the dilution B1-MgO and compression of B1-ZnO from their equilibrium lattice parameters (4.16 Å and 4.22 Å, respectively) to the common (Vegard-like) lattice constant of the alloy.

(ii) The “charge exchange” energy ∆E_{CE} released when MgO and ZnO, already prepared at common lattice constant, combine to give Mg_{0.5}Zn_{0.5}O in a random arrangement, modeled via the “quasirandom structures” concept. At this constant-volume reaction all cell-internal degrees of freedom of the alloy are held fixed at their ideal positions.

(iii) The “structural relaxation” energy ∆E_{SR} released when the cell-internal degrees of freedom of the random alloy are relaxed. Thus, ∆H=∆E_{VD}+∆E_{CE}+∆E_{SR}.

Table I shows that in B1-Ca_{0.5}Zn_{0.5}O and B1-Ca_{0.5}Mg_{0.5}O, the large size mismatch (∆a/a) between the constituents leads to a very large and positive ∆E_{VD} that overwhelms ∆E_{CE}+∆E_{SR}. On the other hand, in B1-Mg_{0.5}Zn_{0.5}O the volume deformation energy is very small (owing to the small lattice mismatch), and the negative charge-exchange and the structural-relaxation energies prevail, leading to ∆H_{B1}<0. We have carefully tested that this basic result is not changed when we use a linearized augmented plane wave method (WIEN97) instead of pseudopotentials, or when we replace the local-density approximation (LDA) by a generalized gradient approximation. Results of these tests are shown in Table II.

Stolbov and Cohen^18 have recently calculated the mixing enthalpy of CaO-MgO assuming the spherical muffin-tin approximation (rather than full potential), and neglecting cell internal atomic relaxation, finding for the 50–50% alloy ∆H=300 meV. This is much higher than our result for the same alloy (163.7 meV, Table I). The difference can be mostly attributed to the neglect of cell internal relaxation (∆E_{SR}∼−110 meV term in Table I).

IV. MODELING THE MgO-ZnO ALLOY

A. The cluster expansion

Having established that the CN6, Mg-rich Mg_{1-x}Zn_xO alloy will order, the next question is what ordered structures
are the most stable. To answer this we have parametrized 32
B1 total-energy calculations of Mg2nZnO2n structures
(show open squares in Fig. 2) into a cluster expansion.
Within the cluster-expansion method one selects an
underlying parent lattice (e.g., fcc) and defines a configuration Σ
by specifying the occupations of each of the lattice sites by
an A or a B atom (spin index s = −1 and +1, respectively).

The excess energy (with respect to equivalent amounts of
solid A and B) of any spin configuration at its locally
atomically-relaxed minimum-energy state is then expanded
as

\[ \Delta H_{CE}(\sigma) = \sum J_{pair}(\mathbf{k}) |S(\mathbf{k}, \sigma)|^2 + \sum D_j J_j \bar{\Pi}_j(\sigma) \]

\[ + \sum \frac{\Delta E_{CS}(x, \hat{k})}{4x(1-x)} |S(\mathbf{k}, \sigma)|^2 F(\mathbf{k}). \]  

The first summation includes all pair figures corresponding
to pair interactions with arbitrary separation. J_{pair}(\mathbf{k}) is the
Fourier transform of the pair interaction energies and S(\mathbf{k}, \sigma)

![FIG. 2. LDA-formation energies and CE predicted energies.](image)

LDA calculated formation energies [Eq. (1)] are shown as open
squares. The ground states predicted by the cluster expansion are
indicated as solid squares. The energy of the random alloy is given
by the solid line. The numbers 1, 2, 3, 4, and 5, refer to the struc-
tures Mg5Zn1O14, Mg3Zn2O7, Mg2Zn3O10, Mg4Zn2O6, and
Mg3Zn3O7, respectively.

The terms \( \Delta E_{CS}(x, \hat{k}) \) and \( \Delta H(\sigma) \) in Eq. (3) are
derived from first-principles total-energy calculations.
\( \Delta E_{CS}(x, \hat{k}) \) is obtained from a set of calculations on biaxially
strained A and B solids. We determine \( \{J_{pair}(\mathbf{k})\} \) and \( \{J_j\} \)
by fitting \( \Delta H_{CE}(\sigma_{ord}) \) to a set \( \{\sigma_{ord}\} \) of LDA calculated formation
energies \( \Delta H_{LDA}(\sigma_{ord}) \) of ordered (not necessarily
ground states) \( A_x B_{1-x} \) compounds. For each structure, we relax
both the cell-external lattice vectors and the atomic cell-
internal degrees of freedom to obtain minimum energies. The
interactions in Eq. (3) \( (J_f \text{ and } J_{pair}) \) were chosen to minimize
both the fitting errors and the prediction errors. This is done
by eliminating from the fit several of the ordered structures
\( \{\sigma_{ord}\} \) and choosing the interactions that result in an accurate
fit to the structures retained as well as accurate predictions
for the eliminated structures. The process is repeated using
different sets of eliminated structures to ensure a set of inter-
actions that work well generally. We find that only 20 pair
interactions and three many-body interactions, along with the
(infinitely ranged) strain pair interactions, are needed to obtain
a fit error of 0.26 meV/cation and a prediction error of
1.67 meV/cation.

**B. Finding the ground states**

Using the function \( \Delta H_{CE}(\sigma) \), we have searched the en-
ergy of all supercells with a total of \( n + m = 20 \) cations (more
than \( 3 \times 10^5 \) structures in total). Figure 3 shows the results of
this ground-state search. The “breaking points” correspond
with the cluster-expansion pre-

**TABLE II. Cubic \( (a) \) and tetragonal ratio \( (c/a) \) of lattice constants and formation energies of selected B1
structures using pseudopotential (PP) method within LDA and GGA approximation and LDA-LAPW method.
The units for the lattice constants and formation energies are in angstroms and meV/cation, respectively.**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>PP LDA</th>
<th>PP GGA</th>
<th>LAPW LDA</th>
<th>PP LDA</th>
<th>PP GGA</th>
<th>LAPW LDA</th>
<th>ΔH</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>4.16, 1</td>
<td>4.24, 1</td>
<td>4.17, 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>4.22, 1</td>
<td>4.33, 1</td>
<td>4.20, 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li2</td>
<td>4.18, 1</td>
<td>4.27, 1</td>
<td>4.18, 1</td>
<td>11.0</td>
<td>10.4</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td>DO22</td>
<td>4.17, 1001</td>
<td>4.27, 1002</td>
<td>4.17, 1001</td>
<td>12.7</td>
<td>12.0</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>Li0</td>
<td>4.19, 0998</td>
<td>4.29, 0998</td>
<td>4.19, 0998</td>
<td>15.1</td>
<td>13.2</td>
<td>17.3</td>
<td></td>
</tr>
</tbody>
</table>
dictions within 0.3 meV/atom. Although several “breaking points” exist, the energetically “deepest” structures occur at \(x = 0.25\) and \(x = 0.5\). For \(x = 0.25\), the ground state is a \(D0_{22}\)-type structure with lattice constants \(a = 4.174\) Å and \(c = 4.179\) Å. For \(x = 0.50\), the ground state is an orthorhombic structure with lattice constants \(a = 4.189\) Å, \(b = 4.187\) Å, and \(c = 8.900\) Å. The atomic positions and lattice vectors of predicted ground states are shown in Table III. The common structural motif for these ground-state structures is that they are \(-201\) superstructures. It is known that \(-201\) superstructures have low Madelung energies\(^7\) and our calculations show that the constituent strain energy along the \(-201\) direction is softer with respect to the other principal directions.

C. Thermodynamic modeling

Figure 2 shows the energy of the random \(B1\) solid solutions (solid line), obtained by performing high-temperature (40000 K) Monte Carlo simulations with Hamiltonian, \(E_{CE}(\sigma)\). The open symbols denote the energies of ordered structures, used as input to the cluster expansion, whereas the energies of the ground-state structures are denoted by solid squares. We see that the energy difference between the stable ordered ground-state structures and the random alloy of the same composition (e.g., \(x = 0.5\)) is rather small (−6.5 meV/ cation), so the order-disorder transition temperature will be well below conventional growth temperatures (Monte Carlo simulations give \(T_c = 79\) K). Nevertheless, ordering tendencies could be monitored even in the disordered alloy by observing its short-range-order (SRO) patterns. Figure 4 shows our calculated SRO obtained from Monte Carlo simulation of the cluster-expanded energy at finite temperatures. Clear ordering signatures (peaks away from the Brillouin-zone centers) are predicted.

Figure 1 shows that the \(Mg_1 - xZn_xO\) alloy has a lower absolute total energy in the sixfold-coordinated structure than in fourfold-coordinated structure up to \(x_{Zn} \approx 0.67\)%, but that beyond this region the fourfold-coordinated structure is more stable. This CN6 to CN4 transition has also been calculated by Kim et al.\(^{19}\) and observed\(^9\) by Ohtomo et al. Figure 1 also demonstrates that both CN4 and CN6 ordered alloys have higher energies than the stablest forms of the constituents. This indicates that once coherency is lost, and a coexistence of \(B1\)-MgO with \(B4\)-ZnO precipitates is possible, the alloy will phase separate. Indeed, such tendencies were seen experimentally.\(^{20}\)

V. CONCLUSIONS

We conclude that the \(B1-Mg_1 - xZn_xO\) alloys have \(\Delta H_{B1} < 0\) due to small elastic strains and favorable chemical energy, forming low-temperature ordered \(Mg_3ZnO_4\) and \(Mg_5Zn_4O_8\) structures and distinct short-range-order patterns

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**TABLE III. Predicted ground states by the CE for \(Mg_1 - xZn_xO\) system.** Atomic positions of oxygen atoms can be found by shifting the atomic positions of Mg and Zn by \((0.5, 0.5, 0.5)\).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Lattice vectors</th>
<th>Atomic positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Mg_3ZnO_4)</td>
<td>0 1 0</td>
<td>Mg (0, 0, 0), Mg (−0.5, 0, 0.5)</td>
</tr>
<tr>
<td>((D0_{22}))</td>
<td>−(\frac{1}{2}) −(\frac{1}{2}) 1</td>
<td>Mg (−0.5, 0.5, 0), Zn (0.5, 0, −0.5)</td>
</tr>
<tr>
<td></td>
<td>1 0 0</td>
<td></td>
</tr>
<tr>
<td>(Mg_5Zn_4O_8)</td>
<td>1 0 0</td>
<td>Mg (0.5, 0.5, 0), Mg (1, 0.5, 0.5)</td>
</tr>
<tr>
<td></td>
<td>0 1 0</td>
<td>Mg (0.5, 0.5, 1), Mg (1, 0.5, 1.5)</td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2}) (\frac{1}{2}) 2</td>
<td>Zn (0, 0, 0), Zn (0.5, 0.5, 0.5)</td>
</tr>
<tr>
<td></td>
<td>1 1 1</td>
<td>Zn (1, 1, 1), Zn (0.5, 1, 1.5)</td>
</tr>
</tbody>
</table>

---
at high temperatures. The random alloy has an LDA band gap of 2.49 eV at $x = 0.5$ (using a special quasirandom structure\cite{17}), and hence a bowing coefficient $b_{\text{bowing}} = 3.10$ eV, where $E_g(x) = (1 - x)E_{\text{MgO}} + xE_{\text{ZnO}} - x(1 - x)b_{\text{bowing}}$. This value of the bowing coefficient is in good agreement with the value of $3.6 \pm 0.6$ eV measured recently by Schmidt et al.\cite{10} The ordered structure at $x = 0.5$ has a lower band gap than the random alloy by 0.39 eV. There is a CN6 to CN4 transition for $x_{\text{Zn}} > 0.67\%$, whereas the coherent alloy is B1 stable below this composition. If MgO and ZnO can (incoherently) adopt their own crystal structures (B1 and B4, respectively), the alloy is predicted to phase separate.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, SC-BES-OER Grant No. DE-AC36-98-GO10337.

10. The positions of the magnesium and zinc atoms in the sixfold structures and their fourfold analogs are the same, that is, the occupations of the metal fcc sublattice (centered at $[0,0,0]$) are identical. In the fourfold analogs, the oxygen site is shifted to $(1/4,1/4,1/4)_{\text{o}}$ from $(1/2,1/2,1/2)_{\text{o}}$. Because a structure and its analog are identical except for oxygen coordination, their energy difference reveals the effect of oxygen coordination only and is not affected by differences in alloy configuration.
12. We use the local-density approximation (LDA) within a plane-wave total-energy formalism (Ref. 13), using ultrasoft pseudopotentials (Ref. 14) as implemented in the vasp package (Ref. 15). We use a highly converged basis set and an equivalent $k$-point mesh to assure precision of 0.1 meV/cation for the calculated formation energies. For $AB$ and $A_2B$ ($AB_2$) stoichiometries we choose $8 \times 8 \times 8$ and $9 \times 9 \times 9$ $k$ meshes, respectively.