Ordering tendencies in octahedral MgO-ZnO alloys

Mahdi Sanati,[1] Gus L. W. Hart,[2] and Alex Zunger[1]
[1]*National Renewable Energy Laboratory, Golden, Colorado 80401, USA*
[2]*Department of Physics & Astronomy, Northern Arizona University, Flagstaff, Arizona 86011-6010, USA*
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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.

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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,

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

is *positive*.[2–4] Here, α denotes fourfold or sixfold coordinated crystal structure, and $E_\alpha(AC)$ is the total energy of compound AC in crystal structure α. For example, ΔH_{B1} of isovalent alloys whose constituents are $B1$ stable (CaO, MgO, and CdO) are generally positive,[2] as are ΔH_{B3} of isovalent alloys[4] whose constituents are $B3$ stable (ZnS, ZnSe, and ZnTe). This can be seen both experimentally[2,3] and from local-density approximation (LDA) total-energy calculations on 50–50 % alloys, modeled via (quasirandom) supercells.[4] 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 *isovalent* 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 $Mg_{1-x}Zn_xO$ alloys have $\Delta H_{B1}<0$ for Mg-rich compositions, in contrast with the opposite sign for isostructural $B1$ oxides (e.g., $Mg_{1-x}Ca_xO$ in Table I). We thus predict that high Mg concentration $Mg_{1-x}Zn_xO$ alloys will be stable and order in the NaCl ($B1$) structure.

(2) Fourfold-coordinated $Mg_{1-x}Zn_xO$ alloys have $\Delta H_{B4}<0$ for Zn-rich compositions, in contrast with the opposite sign for isostructural $B4$ or $B3$ alloys,[4] e.g., $Cd_{1-x}Zn_xS$.[6] We thus predict that high Zn concentration $Mg_{1-x}Zn_xO$ 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 $Mg_{1-x}Ca_x$

functional for $\sim 3\times 10^6$ possible configurations, we identify Mg_3ZnO_4 ($D0_{22}$) and $Mg_4Zn_4O_8$ as ordered $B1$-like ground-state structures.

(5)

are the most stable. To answer this we have parametrized 32 $B1$ total-energy calculations of $Mg_mZn_nO_{m+n}$ structures (shown as open squares in Fig. 2) into a cluster expansion. Within the cluster-expansion method[7] one selects an under-

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 (40 000 K) Monte Carlo simulations with Hamiltonian, $E_{\mathrm{CE}}(\ )$. 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 b
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at high temperatures. The random alloy has an LDA band gap of 2.49 eV at $x=0.5$ (using a special quasirandom structure[17]), and hence a bowing coefficient $b_{\mathrm{bowing}}=3.10$ eV, where $E_g(x)=(1-x)E_{\mathrm{MgO}}+xE_{\mathrm{ZnO}}-x(1-x)b_{\mathrm{bowing}}$. This value of the bowing coefficient is in good agreement with the value of 3.6 ± 0.6 eV measured recently by Schmidt *et al.*[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 $x_{\mathrm{Zn}}>0.67\%$, 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.

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