Ordering tendencies in octahedral MgO-ZnO alloys

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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 $E_{\alpha}(AC$

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 underdictions 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

well below conventional growth th ol 2s6 1 Tf 443 Tm (s) /F8 1 T0

e.g.,

sab6

O/ 5.D ( ) 2 Tj / 0 45 1 Tf a

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 $b_{\text{bowing}}=3.10$ 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±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 $x_{\text{Zn}}>0.67\%$, 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.

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