Rules of Structure Formation for the Homologous InMO$_3$(ZnO)$_n$ Compounds

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The formation mechanisms that lead to the layered M-modulated InMO$_3$(ZnO)$_n$ structures (M = In, Ga, and Al; n = integer) are revealed and confirmed by first-principles calculations based on density functional theory. We show that all ground state structures of InMO$_3$(ZnO)$_n$ satisfy the octahedron rule for the InO$_2$ layers; they contain an inversion domain boundary located at the M and Zn fivefold trigonal bipyramid sites and maximize the hexagonality in the (MZn$_n$)O$_{n+1}$ layers. They also obey the electronic octet rule. This understanding provides a solid basis for studying and understanding the physical properties of this group of homologous materials.

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The homologous compounds RMO$_3$(AO)$_n$ (R = Sc, Fe, Ga, Y, In, Er, Tm, Yb, Lu; M = In, Ga, Al, Fe, A = Mg, Mn, Co, Zn; n = integer) form a group of unique materials with interesting physical properties [1–5]. Among them, In$_2$O$_3$(ZnO)$_n$ and InGaO$_3$(ZnO)$_n$ are currently under intensive study [2–14], because indium sesquioxide (In$_2$O$_3$) is one of the best transparent conducting materials [15,16] and zinc oxide (ZnO) has been widely considered for optoelectronic applications [17]. Thus, combining these two materials to form layered structures is expected to introduce new physical and chemical properties that can be tuned, e.g., by controlling the compositions [3]. Several groups have succeeded in synthesizing layered RMO$_3$(AO)$_n$ compounds by solid state reactions [1,3,8,18], reactive solid-phase epitaxy [12], and epitaxial growth by magnetron sputtering [11]. However, due to the complexity of the crystal structures of the nonisovalent binary constituents, it is still a great challenge to characterize the stable crystal structures at the atomic level for these materials, which is a prerequisite to design and tune the physical properties of these materials.

In$_2$O$_3$(ZnO)$_n$ ($n = 2$–$5, 7$) was first synthesized by Kasper [6], who showed that it has a layered structure and crystallizes in the rhombohedral or hexagonal crystal lattices. Cannard and Tilley confirmed Kasper's results using x-ray diffraction (XRD) and high-resolution electron microscopy (HREM) experiments [7]. They proposed that In$_2$O$_3$(ZnO)$_n$ is composed of a sequence of ZnO and In$_2$O$_3$ layers stacked along the [0001] direction (c axis) [7]. However, because the binary constituents have different crystal structures [In$_2$O$_3$ crystallizes in the bixbyite [19] structure, whereas ZnO is most stable in the wurtzite (WZ) structure], it is not clear how these two layers are connected to each other. Recently, the atomic structure of RMO$_3$(AO)$_n$ was refined using XRD by several groups [1,3,8,20]. Kimizuka *et al.* [1,8] proposed that InMO$_3$(ZnO)$_n$ (M = In, Ga, Al, and Fe) are isostructural with LuFeO$_3$(ZnO)$_n$ [20]. The crystal has space group $R\bar{3}m$ (rhombohedral lattice) when n is odd and $P6_3/mmc$ (hexagonal lattice) when n is even. The In atoms form an octahedron InO$_2$ layer, which are interconnected by the (MZn$_n$)O$_{n+1}$ layers. The M atoms in the (MZn$_n$)O$_{n+1}$ layers are randomly distributed in the metal sites, forming fivefold trigonal bipyramid structures [20], while the Zn atoms are located in tetrahedral sites surrounded by four O atoms. The formation of an octahedron InO$_2$ layer was also confirmed by atomic-resolution Z-contrast experiments for In$_2$O$_3$(ZnO)$_n$ [10]. Among all the proposed structure models, the hexagonal or rhombohedral structures are closely related with the WZ structure and characterized by an in-plane a axis and a long c axis that increases with the number of ZnO units. In contrast to the XRD studies [1,3,8,20], recent HREM experiments [4,9,18,21] have indicated that In, Fe, and Ga atoms can form ordered modulated structures with a zigzag shape in the (MZn$_n$)O$_{n+1}$ layers, which was recently confirmed by Yan *et al.* [14] using first-principles calculations for In$_2$O$_3$(ZnO)$_6$.

Despite the various structure models proposed for RMO$_3$(ZnO)$_n$, the key questions [i.e., what is the ground state structure of this type of material and the underlying mechanisms that lead to the stability of the ground state structure of the RMO$_3$(ZnO)$_n$ compounds] are still under debate. To address these questions, in this Letter, we have performed first-principles calculations for the prototype InMO$_3$(ZnO)$_n$ (M = In, Ga, Al, $n = 1$–6) systems and identified the rules that should be followed to lower the crystal total energy. These include the octahedron rule for the InO$_2$ layers and the existence of an inversion domain boundary (IDB), maximized hexagonality in the (MZn$_n$)O$_{n+1}$ layers [22], minimum strain in the interface between the InO$_2$ and (MZn$_n$)O$_{n+1}$ layers, and the electron octet counting rule. Based on these rules, we have identified the ground state structures for this group of materials, which are consistent with recent experimental observations.

Our total-energy calculations are based on the all-electron projected augmented wave method [23,24] and the generalized gradient approximation (GGA-PBE) [25], to the density functional theory as implemented in the

Vienna *ab initio* simulation package (VASP) [26,27]. A plane-wave cutoff energy of 400 eV (800 eV) was used for the total-energy (stress tensor) calculations. The Brillouin-zone integrations were performed with a **k**-point grid of $(6 \times 6 \times 1)$ for the $InMO_3(ZnO)_1$ structures and similar quality **k**-point grids for the other structures employing up to 408 atoms per unit cell. The total energies and equilibrium volumes at zero temperature were obtained by full relaxation of the cell volume and atomic positions to minimize the quantum mechanical stresses and forces. In the following, we discuss the general rules that need to be satisfied to lower the crystal energy of the $InMO_3(ZnO)_n$ compounds.

a. The octahedron rule for the InO_2 *layer.*—The In and O atoms in the bixbyite In_2O_3 structure are six-, four-, and fourfold coordinated [19], respectively, whereas both Zn and O atoms are fourfold coordinated in the WZ structure. In the highly symmetric spinel In_2ZnO_4 structure (space group $Fd\bar{3}m$), the In, Zn, and O atoms are also six-, four-, and fourfold coordinated, respectively. This is related to the fact that In and Zn have three and two valence electrons, respectively, whereas oxygen always has a valence of -2 (i.e., the octet rule is fully satisfied). The In atoms in the InO_2 layers also should prefer to form sixfold coordinated octahedrons like in the spinel In_2ZnO_4 and bixbyite In_2O_3 structures. To test this, we have performed calculations for two types of sixfold coordinated InO_2 layers, namely, a nonoctahedron structure and an octahedron structure. In both configurations, the In atom is located at the origin (A site in the hexagonal lattice; see Fig. 1). In the nonoctahedron structure, O atoms occupy only the B (or C) sites in the hexagonal lattice, whereas in the octahedron structure, the O atoms below and above the In plane occupy the B and C sites, respectively (see Fig. 1). We found that the octahedron structure is about $1\ \text{eV}/InO_2$ lower in energy than the nonoctahedron structure. This is consistent with the fact that the octahedron structure maximizes the atomic separation between the ionized O atoms. Similar results are also obtained when an InO_2 layer is passivated by pseudo-H atoms, which indicates that the energy gain due to the formation of the octahedron structure does not depend on the atomic configuration of the M atoms in the $(MZn_n)_{n+1}$ layer. The observation that the In and O atoms in the InO_2 layer form an octahedron structure is consistent with experimental observations [1,8,10,20,28].

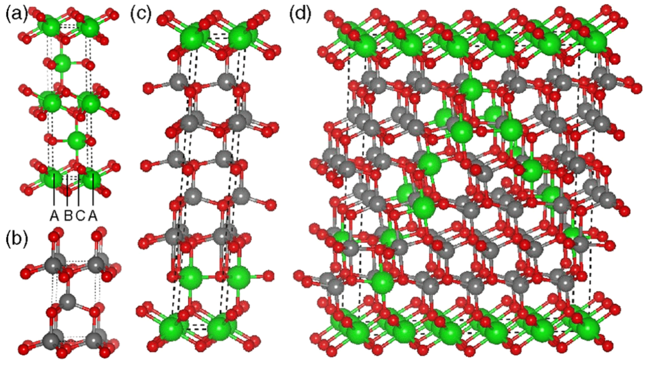

FIG. 1 (color online). Schematic crystal structures. (a) In_2O_3 in the $InFeO_3$ structure. (b) ZnO in the wurtzite structure. (c) $In_2O_3(ZnO)_5$ using the single In-layer model. (d) $In_2O_3(ZnO)_5$ using the In-modulated structure model. The large green, medium gray, and small red balls denote the In, Zn, and O atoms, respectively. The high symmetry sites in the hexagonal cell are indicated by A, B, and C in (a).

The In–O distances in the octahedron InO_2 layers are in the range of 2.20–2.30 Å, while the angle O–In–O deviates by 1°–5° from the ideal value of 180°. The smallest deviations (1°) occur when O atoms in the corner of the octahedrons bind with Zn atoms. Thus, the binding of Zn atoms to the O atoms at the corner of the octahedron InO_2 layers stabilizes the formation of an almost perfect octahedron InO_2 structure, whereas binding to the In atoms induces a larger distortion. These findings are consistent with the formation of distorted and perfect octahedron structures in the bixbyite In_2O_3 and the spinel In_2ZnO_4 structures.

b. Inversion domain boundary in the $(MZn_n)O_{n+1}$ *layer.*—In $InMO_3(ZnO)_n$, the octahedron InO_2 layers are connected by the WZ-like $(MZn_n)O_{n+1}$ layers [see Fig. 1(c)]. In this case, the O atom at the corner of the octahedron connects to three In atoms in the InO_2 layers and one atom in the $(MZn_n)O_{n+1}$ layer. This indicates that the polarity at the bottom and top of the $(MZn_n)O_{n+1}$ layers is reversed. Therefore, an IDB in the $(MZn_n)O_{n+1}$ layer must exist to reverse the polarity. In the simplest case, in which the M atoms form a single layer of fivefold trigonal bipyramids as shown in Fig. 1(c), the IDB is located on the M atom sites. However, as we will discuss below, other distributions of the M atoms in the $(MZn_n)O_{n+1}$ layer can reduce the strain energy and satisfy the electron counting rule, thus further lowering the total energy. In general, the polarity inversion is located on the M and Zn atoms, which form fivefold trigonal bipyramid structures with the surrounding O atoms in the $(MZn_n)O_{n+1}$ layers [see Figs. 1(d) and 2].

c. Stacking fault in the $(MZn_n)O_{n+1}$ *layer.*—As discussed above, in the octahedron InO_2 layer, the O atoms below and above the In plane occupy the B and C sites, respectively, in a hexagonal lattice. Therefore, in order to have a smooth connection between two InO_2 layers, two scenarios can exist. In the first scenario, the In atoms in two neighboring InO_2 layers are at the A sites, and, hence, $InMO_3(ZnO)_n$ can be represented by a simple hexagonal lattice. In this case, to match the B and C sites of the O atoms at the top and bottom of the InO_2 layer, one or more stacking faults (SFs) must exist in the $(MZn_n)O_{n+1}$ layer that disrupt the stacking sequence of the WZ-like lattice. By assuming a single M layer for the atomic distribution of the M atoms in the $(MZn_n)O_{n+1}$ layer, as in Fig. 1(c), we find that the minimum energy structure has a single SF layer just below the InO_2 layer (i.e., the Zn atom is located at the C site). This is consistent with the fact that ZnO has the lowest energy in the WZ structure; therefore, to lower

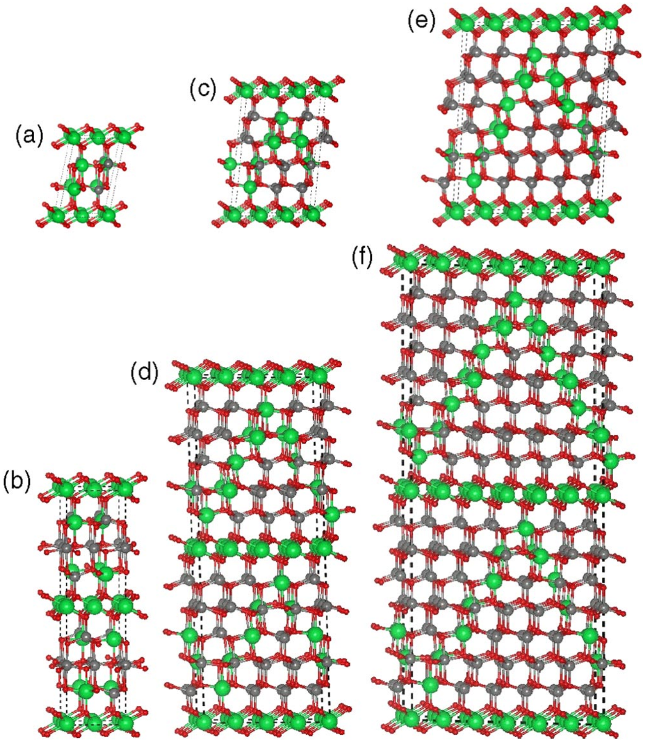

FIG. 2 (color online). Most stable density functional theory structure models for $In_2O_3(ZnO)_n$. (a) $n = 1$, (b) $n = 2$, (c) $n = 3$, (d) $n = 4$, (e) $n = 5$, (f) $n = 6$. The large green, medium gray, and small red balls indicate the In, Zn, and O atoms, respectively. The dashed lines indicate the hexagonal unit cells for $n = 2$, 4, and 6, and monoclinic unit cells for $x = 1$, 3, and 5. There are 28 atoms in (a) [4 formula units (f.u.)], 72 atoms in (b) [8 f.u.], 66 atoms in (c) [6 f.u.], 208 atoms in (d) [16 f.u.], 150 atoms in (e) [10 f.u.], and 408 atoms in (f) [24 f.u.].

the energy, it will try to preserve the hexagonality as much as it can [22], without destroying the octahedron rule in the InO_2 layer. In the second scenario, the hexagonality of the $(MZn_n)O_{n+1}$ layer is kept, and the matching to the O atoms in the InO_2 layer is realized by displacing the InO_2 layer in the c plane (i.e., move the In atom in the InO_2 layer to the B or C sites). Consequently, the conventional hexagonal unit cells are now composed of two or three InO_2 layers separated by an equal number of $(MZn_n)O_{n+1}$ layers in which n equals even or odd. This leads to a hexagonal primitive unit cell for n even and rhombohedral (monoclinic) for n odd. We find that the second scenario gives a lower total energy (≈70 meV per f.u. for $n = 1$–6) than the first one because the maximum hexagonality is preserved in the $(MZn_n)O_{n+1}$ layer. Our result is consistent with experimental observations derived from analysis of XRD data [1,8].

d. M modulation in the $(MZn_n)O_{n+1}$ layer.—Early experimental studies based on XRD assumed that the M trigonal bipyramid structures form a single layer in the $(MZn_n)O_{n+1}$ layers [see Fig. 1(c)]. However, if the ideal in-plane lattice constants of this plane differ significantly from that of ZnO, an elastic strain can build up in the ZnO layer with the strain energy increasing as the ZnO layer number n increases. Our calculations show that the in-plane lattice constant of $InMO_3$ in the hexagonal $InFeO_3$ structure [28] (see Fig. 1) is larger by 8.4%, 2.4%, and 0.0% for $M =$ In, Ga, and Al, respectively, compared with the lattice constant of ZnO in the WZ structure ($a_0 = 3.29$ Å). Therefore, for $M =$ In, a large strain exists in the ZnO and InO layers if the In atoms form a planar layer. The in-plane strain decreases for $M =$ Ga and is almost zero for $M =$ Al. The ideal way to release the strain would be to distribute the M atoms uniformly along the c axis of the hexagonal cell while in the meantime preserving the fivefold M trigonal bipyramid acting as an IDB site and satisfing the electronic octet rule. To realize this, the M atoms in the $(MZn_n)O_{n+1}$ layers are distributed in zigzag modulated structures, in which the modulation period is proportional to the number of ZnO units. The modulation is formed by M and Zn atoms fivefold trigonal bipyramid structures, as shown in Figs. 1(d) and 2.

Our calculations show that the M-modulated structures have significantly lower energies than those based on the single M-layer model. For example, for $n = 5$, the energy gain is ≈653, 74, and 3 meV/f.u. for $M =$ In, Ga, and Al, respectively. The energy difference between the two models increases with the number of ZnO units, which is due to the increased built-in strain energy in the ZnO layer as n increases. Therefore, the formation of the M-modulated structures with a zigzig shape is more favorable for large ZnO compositions. Furthermore, the energy gain decreases from In to Al atoms, which is explained as a consequence of a reduced strain energy moving from In to Al. These results are consistent with experimental HREM studies [4,9,18,21], which observed clearly the formation of In- and Ga-modulated structures in the $(MZn_n)O_{n+1}$ layers for n larger than 5 ZnO units [9], while there is no indication of Al modulation [4].

It is worthwhile to point out that, to reduce strain between the RO_2 and the $(MZn_n)O_{n+1}$ layers, the R atoms (e.g., In) should always be larger than or equal to the M atom (e.g., Ga or Al), because the O–O distance in a sixfold octahedral environment (e.g., in the rocksalt structure) is smaller than in the fivefold or fourfold (e.g., in the WZ structure). Our calculations indeed show that the total energy of the $InO_2(GaZn)O_2$ structure is 1.64 eV/f.u. lower than that of $GaO_2(InZn)O_2$.

e. Electronic octet rule for the O atoms in the $(MZn_n)O_{n+1}$ layers.—All of the M and O atoms in the $(MZn_n)O_{n+1}$ layers are five- and fourfold coordinated, respectively (i.e., the M and O atoms form trigonal bipyramid structures). On the other hand, to accommodate the zigzig modulation, the Zn atoms located in the row with the M atoms in the M-modulated structure also form fivefold trigonal bipyramid structures with the surrounding O atoms, whereas the remaining Zn atoms are fourfold coordinated as in the WZ structure. We found that the minimum energy structure obeys the electronic octet rule; i.e., the O

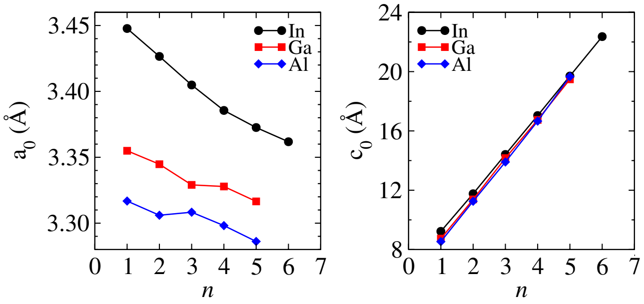

FIG. 3 (color online). Calculated equilibrium lattice constants (a_0, c_0) of the InMO$_3$(ZnO)$_n$ compounds (M = In, Ga, and Al) as a function of the number of ZnO units n.

atoms are surrounded by $4 \times \text{Zn}(4)$ atoms, or $2 \times \text{Zn}(4) + 1 \times \text{In}(5) + 1 \times \text{Zn}(5)$, or $2 \times \text{In}(5) + 2 \times \text{Zn}(5)$, where the numbers in parentheses indicate the coordination of the In and Zn atoms, so that each O atom always obtains two electrons from neighboring cation atoms. Furthermore, the octet rule is also satisfied for oxygen pairs along the in-plane In and Zn rows, e.g., $2 \times \text{Zn}(4) + 3 \times \text{Zn}(5) + 3 \times \text{In}(5)$, and for O atoms in the InO$_2$ layers.

Based on the above analysis and our first-principles calculations, we show in Fig. 2 the most stable crystal structures for the particular case of M = In, which satisfy the above rules. Similar structures are obtained for M = Ga and Al. The interlayer distance between the InO$_2$ layers, defined as c_0, increase linearly with the number of ZnO units (see Figs. 2 and 3), while $c_0^{M=\text{In}} > c_0^{M=\text{Ga}} > c_0^{M=\text{Al}}$ for all n. We found that a_0 decreases with the number of ZnO units and approaches the lattice constant of ZnO for large n, as expected. Furthermore, $a_0^{M=\text{In}} > a_0^{M=\text{Ga}} > a_0^{M=\text{Al}}$, which is consistent with decreasing strain from In to Ga to Al. All calculated lattice constants a_0 and c_0 deviate by less than 2% compared with the experimental results [3,8,29,30], which is typical for GGA-PBE calculations [31].

In summary, we found that the ground state InMO$_3$(ZnO)$_n$ structures follow the following rules: the octahedron rule for the InO$_2$ layer; the existence of the inversion domain boundary located at the M and Zn atoms, which form fivefold trigonal bipyramid structures; and the strong tendency to preserve the hexagonality [22] in the (MZn$_n$)O$_{n+1}$ layers. They also obey the electronic octet rule, and the M atoms form modulated zigzag structures in the (MZn$_n$)O$_{n+1}$ layers to reduce strain energy. We believe that the identified ground state structures and revealed formation mechanisms can be applied for most of the homologous RMO$_3$(AO)$_n$ compounds (R = Sc, Fe, Ga, Y, In, Er, Tm, Yb, Lu; M = In, Ga, Al, Fe, A = Mg, Mn, Co, Zn). Therefore, these findings provide a solid basis for studying and understanding the physical properties of this group of materials.

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