

First-principles investigation of $R_2O_3(ZnO)_3$ ($R = Al, Ga, \text{ and } In$) in homologous series of compounds

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Abstract

Atomic and electronic structures of $R_2O_3(ZnO)_3$ ($R = Al, Ga, \text{ and } In$), which are included in homologous series of compounds, are investigated using first-principles calculations based on density functional theory. Three models with different R atom arrangements in the five-fold and four-fold coordination sites are examined. Al and Ga prefer the five-fold coordination sites. The formation energies are much larger than those of the competing phases, ZnR_2O_4 , with a normal spinel structure. On the other hand, $In_2O_3(ZnO)_3$ shows no clear site preference and can be more stable than the spinel at high temperatures when configurational entropy contribution is taken into account. Electronic states near the conduction band bottom are mainly composed of Zn-4s orbital in $Al_2O_3(ZnO)_3$, while the contributions of Ga-4s and In-5s are comparable to Zn-4s in $Ga_2O_3(ZnO)_3$ and $In_2O_3(ZnO)_3$.

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1. Introduction

Zinc oxide-based materials are widely used in modern technology as catalysts for organic syntheses, varistors for electronic equipments, host materials for transparent semiconductors, diluted magnetic semiconductors, just to mention a few examples [1–8]. For such applications, pure and stoichiometric compounds are rarely used. Most of materials are doped with aliovalent impurities. Trivalent cations are most widely used among them. When doping level is below the solubility limit, they are thought to be present at the substitutional site of Zn, forming either carrier electrons or negatively charged Zn vacancies. Above the solubility limit of the primary solid solution, the formation of double oxides has been reported. Al and Ga are known to form ZnR_2O_4 with a normal spinel

structure, whereas $ZnIn_2O_4$ with a spinel structure is believed to be metastable. Instead of that, a series of homologous compounds are known to be present in the ZnO– In_2O_3 system with a general formula of $In_2O_3(ZnO)_m$ (m : integer ≥ 3) [9,10].

The homologous compounds with similar structures are known to be formed in many systems. According to systematic studies by Kimizuka et al., they have a general formula of $(AM_3O_3)_n(BO)_m$ where $A = In, Sc, Y, \text{ and } Ln$ (lanthanides); $M = Fe, Ga, \text{ and } Al$; $B = Zn, Fe, \text{ and } \text{other divalent elements}$ [11–15]. A and M are formally trivalent. Similar compounds are found in chalcogenides such as In_2ZnS_4 [16].

Fig. 1 shows a part of the atomic arrangement of the compound with $n = 1$ and $m = 3$. The real height of the unit cell along the c -axis is three times larger than that of the unit shown in Fig. 1. The three units are stacked with 120° rotation with respect to each other, which constitutes the crystal with the space group of $R\bar{3}m$ (No. 166) [17]. As shown in Fig. 2, there are three different kinds of cation sites with coordination numbers (CN) of 6, 4, and 5, respectively. The octahedrally coordinated cation site

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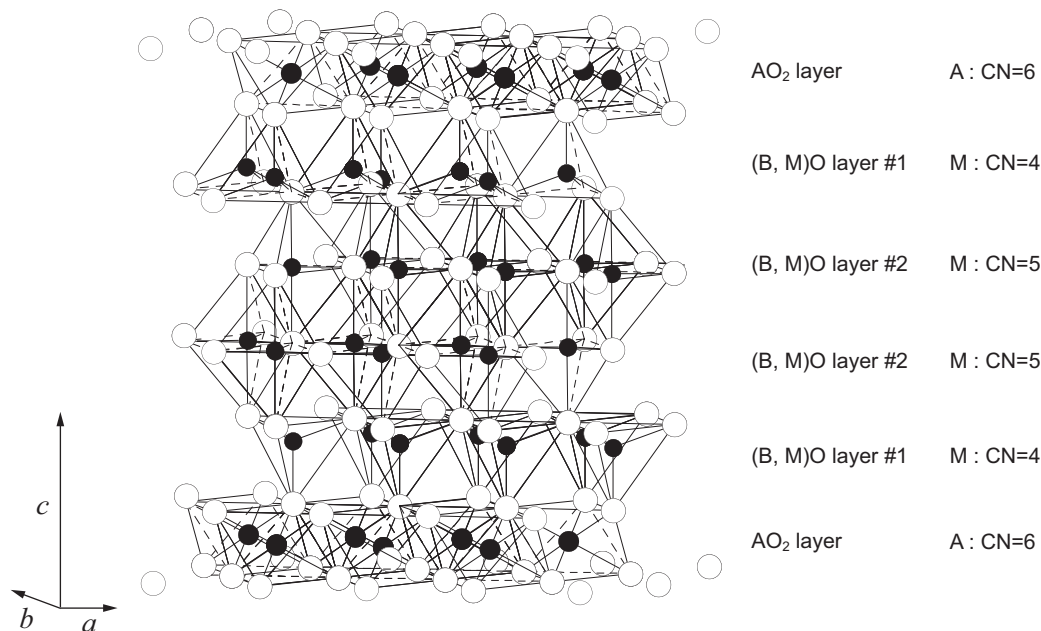


Fig. 1. Atomic arrangement in a $(AMO_3)(BO)_3$ homologous compound with a hexagonal lattice.

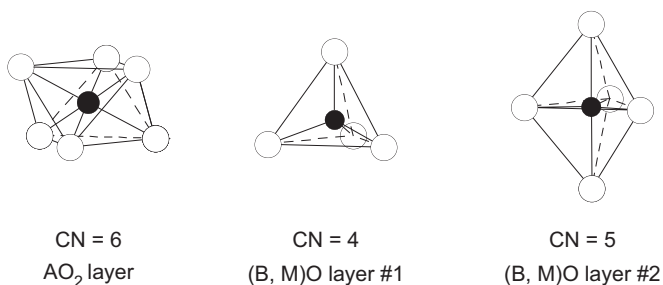


Fig. 2. Local coordination of cation sites in $(AMO_3)(BO)_3$.

($3a$ site, CN = 6) forms AO_2 sheets together with surrounding oxygen atoms. The first nearest sheets to the AO_2 layer form (B, M)O sheets (layer #1 in Fig. 1). The cations in these layers ($6c$ site) are tetrahedrally coordinated (CN = 4). The second nearest sheets (layer #2 in Fig. 1) also form (B, M)O sheets, where cations show trigonal-bipyramidal coordination ($6c$ site, CN = 5). Trivalent cations with large ionic radii seem to have a tendency to occupy the $3a$ site with CN = 6. For instance, Kimizuka et al. reported for $\text{LuFeO}_3(\text{ZnO})_m$ that Lu is located at the CN = 6 site, and Fe and Zn are distributed in the CN = 4 and CN = 5 sites [15]. For $\text{In}_2\text{O}_3(\text{ZnO})_3$, Schinzer et al. made a detailed X-ray diffraction study and concluded that half of In occupies the CN = 6 site, and the rest is located at both trigonal-bipyramidal (CN = 5) and tetrahedral (CN = 4) sites with an equal occupancy [17]. In other words, both CN = 5 and CN = 4 sites are occupied by 25% of In and 75% of Zn atoms.

Among $\text{ZnO-R}_2\text{O}_3$ ($R = \text{Al, Ga, and In}$) systems, homologous compounds with different crystal structures were reported for $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ by Li et al. [18]. They are

composed only of cations with CN = 4. The synthesis of homologous compounds in $\text{ZnO-Al}_2\text{O}_3$ has not been successful for a long time [19]. It is worth mentioning that we have recently reported that the local atomic arrangement of a supersaturated solid solution of wurtzite ZnO-19at\% Al is close to that of the hypothetical $\text{Al}_2\text{O}_3(\text{ZnO})_3$ with Al of CN = 6, 5, and 4 as characterized by X-ray absorption spectroscopy in conjunction with first-principles calculations [20]. The present study aims at a systematic investigation of the atomic arrangements of a series of compounds $R_2\text{O}_3(\text{ZnO})_3$ ($R = \text{Al, Ga, and In}$) using first-principles calculations. Their energetics and electronic structures are discussed as well.

2. Computational procedures

The structure of $\text{In}_2\text{O}_3(\text{ZnO})_3$ with a 33-atom unit cell ($R\bar{3}m$, No. 166, $Z = 3$) as refined by Schinzer et al. [17] was adopted as the prototype, which will be hereafter called Schinzer-Heyd-Mater (SHM) model. The unit cell was expanded by $2 \times 2 \times 1$ to make a 132-atom supercell. The supercell was used to examine the distribution of M ($M = \text{Al, Ga, and In}$) and Zn atoms in CN = 5 and CN = 4 sites. Three kinds of different cation arrangements as shown in Fig. 3 were compared. M and Zn atoms are equally distributed in two cation layers in model 2, as in the case of the SHM model. M atoms are located only at the CN = 4 and CN = 5 sites in models 1 and 3, respectively. The calculations were performed using the projector augmented wave (PAW) method [21] as implemented in the VASP code [22–24]. For the exchange correlation, we employed the generalized-gradient approximation (GGA) in the Perdew, Burke, and Ernzerhof (PBE) form [25]. The

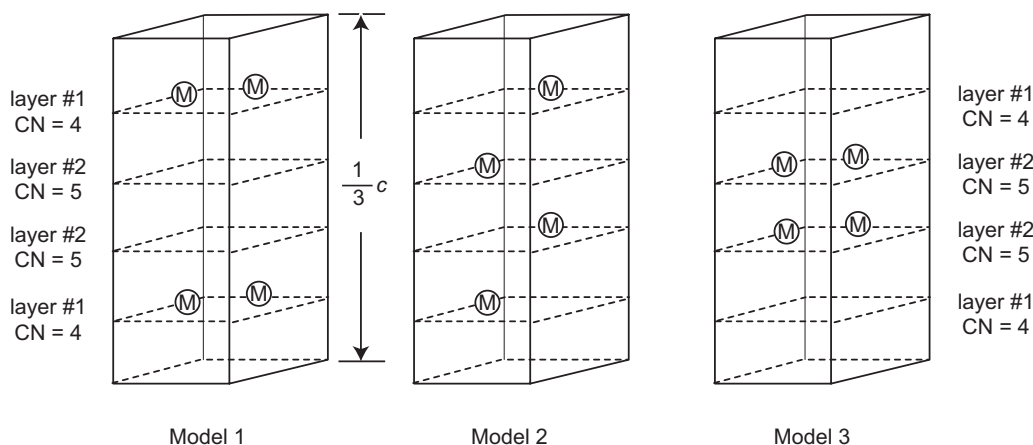


Fig. 3. Schematics of the models for three different cation arrangements used in the present calculations.

plane wave cut-off energy was set to be 500 eV. A Monkhorst–Pack k -point grid [26] of $3 \times 3 \times 1$ was used for the 132-atom cell. The atomic positions and cell parameters were fully optimized until the residual forces and stresses converged to be smaller than 0.005 eV/Å and 0.05 GPa, respectively. Density of states was calculated for the optimized geometries using a $8 \times 8 \times 2$ k -point grid. Additional calculations under similar conditions were made for seven reference crystals, i.e., ZnO, R_2O_3 , and ZnR_2O_3 ($R = Al, Ga, \text{ and } In$).

3. Results and discussion

Among $R_2O_3(ZnO)_3$, experimental crystal structure is available only for the ZnO– In_2O_3 system. The theoretical structural parameters for $In_2O_3(ZnO)_3$ are compared with the experimental values [17], i.e., those of the SHM model, in Table 1. All the three models show theoretical lattice parameters greater than the experimental values by 0.7–2.7%. However, they are still within typical GGA errors. In the SHM model, Zn and In atoms in $6c$ sites are randomly distributed with site occupancy factors of $N_{In} = 0.25$ and $N_{Zn} = 0.75$ both in layers #1 and #2. Therefore, the atomic positions are given as a statistical average. In Table 1, we show individual atomic coordinates in the z -direction. The differences in Zn and In positions in layers #1 and #2 are small for all of the three models. The coordinates are in reasonable agreement with the experimental SHM model.

The calculated formation energies of spinel ZnR_2O_4 and the three models for $R_2O_3(ZnO)_3$ are summarized in Table 2. They are referenced to ZnO (wurtzite), Al_2O_3 (corundum), Ga_2O_3 (β -gallia), and In_2O_3 (bixbyite). The normal spinel structure was taken for ZnR_2O_4 , according to the combined cluster-expansion method and first-principles study that predicted the ground-state structures of ZnR_2O_4 ($R = Al, Ga, \text{ and } In$) to be the normal spinel [27]. The formation energies are negative for $ZnAl_2O_4$ and $ZnGa_2O_4$, while positive for $ZnIn_2O_4$. This is consistent

Table 1
Theoretical structural parameters for $Zn_3In_2O_6$

Lattice parameter (Å)	This work			SHM model
	Model 1	Model 2	Model 3	
a	3.44	3.43	3.42	3.35
c	42.82	42.81	43.50	42.51
Fractional atomic coordinate, z				
Atom	Model 1	Model 2	Model 3	SHM model
In	0	0	0	0
O1	0.025	0.025	0.025	0.025
Layer #1				
Zn	0.070	0.071	0.070	0.073
In	0.078	0.078	–	–
O2	0.084	0.084	0.084	0.085
Layer #2				
Zn	0.137	0.133	0.129	0.135
In	–	0.137	0.135	–
O3	0.144	0.141	0.141	0.140

Table 2
Theoretical formation energies (eV/cation) with reference to ZnO and R_2O_3

	Spinel ZnR_2O_4	Homologous $R_2O_3(ZnO)_3$		
		Model 1	Model 2	Model 3
Al	–0.14	0.22	0.19	0.16
Ga	–0.17	0.09	0.06	0.04
In	0.06	0.10	0.10	0.10

with the fact that the formation of $ZnIn_2O_4$ has not been reported by experiments.

For all of $R = Al, Ga, \text{ and } In$, the formation energies of $R_2O_3(ZnO)_3$ are positive and higher than those of the

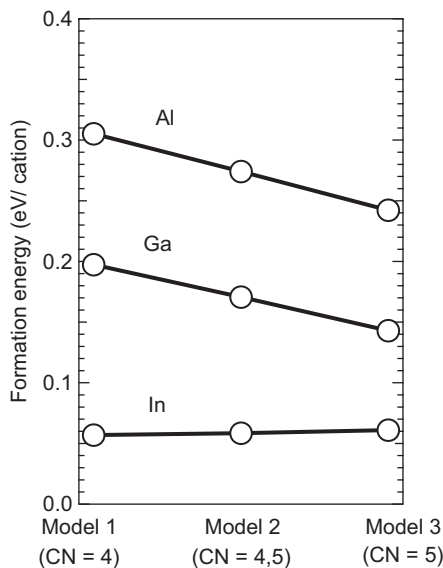


Fig. 4. Formation energies of $R_2O_3(ZnO)_3$ with reference to ZnO and spinel ZnR_2O_4 .

competing ZnR_2O_4 phases. $Ga_2O_3(ZnO)_3$ is slightly lower in formation energy than $In_2O_3(ZnO)_3$, while $Al_2O_3(ZnO)_3$ is higher. When the formation energies are computed with reference to ZnO and spinel ZnR_2O_3 as shown in Fig. 4, it is clear that these two homologous compounds are energetically much less favorable than $In_2O_3(ZnO)_3$. This is not surprising since the formation energies of the reference spinel crystals, $ZnAl_2O_4$ and $ZnGa_2O_4$, respectively, are 0.20 and 0.23 eV/cation lower than that of $ZnIn_2O_4$. These results suggest a strong preference of the formation of the spinel phases for $R = Al$ and Ga , although the homologous compounds may exist as metastable phases.

The three models for $In_2O_3(ZnO)_3$ also show positive formation energies with reference to ZnO and $ZnIn_2O_4$. This is seemingly contradictory to the experimental results in which homologous phases are formed instead of the spinel phase. The contradiction can be solved by taking account finite temperature effects. As can be seen in Fig. 4, while there is a strong preference of CN = 5 for M ($M = Al$ and Ga) atoms in $Al_2O_3(ZnO)_3$ and $Ga_2O_3(ZnO)_3$, the formation energies for $In_2O_3(ZnO)_3$ are almost independent of the choice of In/Zn sites. This means that there is no preferential site for In/Zn atoms. In other words, two kinds of cations can be easily disordered within the layers #1 and #2. The mixing entropy for the disordered solid solution can be approximately estimated as $\Delta S = -k_B(N_{In} \ln N_{In} + N_{Zn} \ln N_{Zn})$, where k_B is Boltzmann constant. Assuming the absence of the other temperature-dependent effects in the free energy such as the vibrational entropy, disordering in the layers #1 and #2 with $N_{In} = 0.25$ and $N_{Zn} = 0.75$ has a free energy benefit of 0.06 eV/cation at 1273 K. The formation energy of $In_2O_3(ZnO)_3$ with reference to ZnO and $ZnIn_2O_4$ is only

+ 0.06 eV/cation, which may be overcome by the mixing entropy contribution at high temperatures.

Electronic density of states (DOS) and the projected density of states (PDOS) on cation orbitals are shown in Fig. 5. For simplicity, only the results for model 3 with all M atoms at the layer #2 (CN = 5) are shown. The PDOSs of three $R_2O_3(ZnO)_3$ are compared with that of ZnO. The top of the valence band is composed of O-2p (not shown) that is mixed mainly with Zn-3d in all of four compounds. All of them show clear band gaps between the valence and conduction bands. The conduction bands are mainly composed of empty R -ns and R -np orbitals ($n = 3, 4, 5$) together with Zn-4s and Zn-4p orbitals. The relative energies of the R -ns and R -np states to the Zn-4s and Zn-4p states decrease in the order of Al, Ga, and In. This brings about the differences in the conduction band structures as well as the magnitude of band gaps. In particular, the electronic states near the conduction band bottom are characteristic to respective phases. They are mainly composed of Zn-4s orbital in $Al_2O_3(ZnO)_3$, while the contributions of Ga-4s and In-5s are comparable to, or even larger than Zn-4s in $Ga_2O_3(ZnO)_3$ and $In_2O_3(ZnO)_3$. The theoretical band gaps of the model 3 for $R_2O_3(ZnO)_3$ ($R = Al, Ga, \text{ and } In$) are 1.88, 1.10, and 0.75 eV, respectively. It is well known that the band gaps of IIB and IIIB oxides are significantly underestimated by the GGA or local density approximation (LDA). The band gap of ZnO, 3.44 eV [28], is underestimated to be 0.73 eV by the present calculation, which is close to previously reported values [29,30]. For $In_2O_3(ZnO)_3$, the band gap has been experimentally estimated to be 2.8–3.0 eV [10]. The magnitude of the underestimation is similar to the case of ZnO. It is implied that the band gap of $Al_2O_3(ZnO)_3$ is greater than ZnO, whereas that of $Ga_2O_3(ZnO)_3$ is close to or somewhat greater than ZnO.

The electronic structure of the $In_2O_3(ZnO)_3$ crystal was discussed in the paper by Schinzer et al., based on the results of first-principles calculations for a hypothetical ordered structure with a chemical formula of Zn_4InO_6 [17]. They used augmented spherical wave method with atomic sphere approximation and LDA. The band gap does not appear in their result. This could be ascribed to the use of the hypothetical structure, which brings about artificial distortion in the electronic structure to collapse the theoretical band gap.

4. Conclusion

The atomic and electronic structures and the energetics of homologous compounds $R_2O_3(ZnO)_3$ ($R = Al, Ga, \text{ and } In$) have been investigated using the first-principles PAW method. Major results can be summarized as follows:

- (1) We have constructed three models with different M atom arrangements in 132-atom supercells as shown in Fig. 3. For $In_2O_3(ZnO)_3$, all the three models provide structural parameters that agree well with the

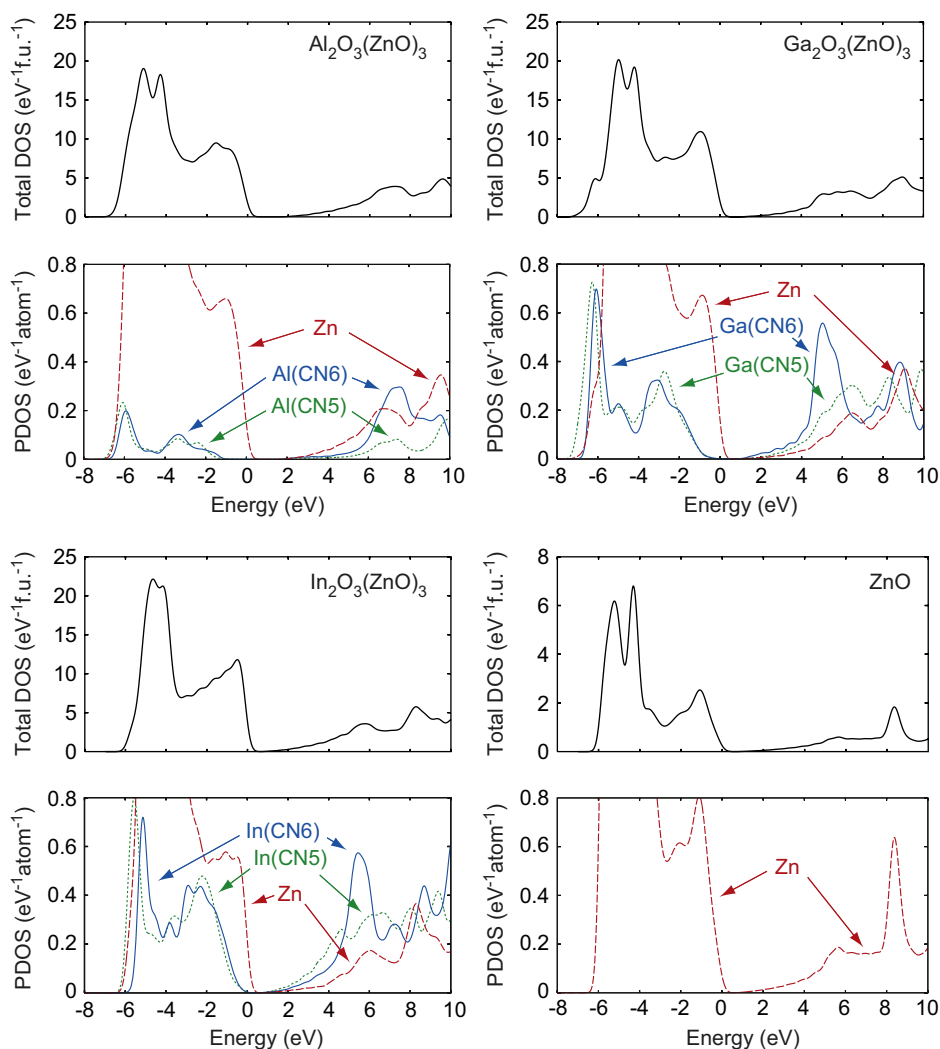


Fig. 5. Total density of states (DOS) and projected DOS (PDOS) for cation orbitals for $R_2O_3(ZnO)_3$ and ZnO.

experimental data. The formation energies of the three models are nearly the same, implying disordering of In atoms within #1 and #2 layers. Although $ZnIn_2O_4$ with a normal spinel structure shows a lower formation energy than $In_2O_3(ZnO)_3$, configurational entropy contribution may stabilize $In_2O_3(ZnO)_3$ at high temperatures.

- (2) The structures of hypothetical $Al_2O_3(ZnO)_3$ and $Ga_2O_3(ZnO)_3$ have been determined using the SHM model as the prototype. The formation energies of the three models for $Ga_2O_3(ZnO)_3$ with reference to ZnO and Ga_2O_3 are slightly smaller than that of $In_2O_3(ZnO)_3$ (Table 2). On the other hand, $Al_2O_3(ZnO)_3$ shows higher formation energies than the others. When the formation energies are computed with reference to ZnO and ZnR_2O_4 (normal spinel), the formation energies of $Al_2O_3(ZnO)_3$ and $Ga_2O_3(ZnO)_3$ are much larger than that of the $In_2O_3(ZnO)_3$. These results suggest a strong preference of the formation of the spinel phases for $R = Al$ and Ga , although the homologous compounds may be metastable.

- (3) For $Al_2O_3(ZnO)_3$ and $Ga_2O_3(ZnO)_3$, a strong preference of M ($M = Al$ and Ga) atoms in layer #2 with CN = 5 has been shown.
- (4) The conduction bands of $R_2O_3(ZnO)_3$ are composed of empty $R-ns$ and $R-np$ orbitals ($n = 3, 4, 5$) together with Zn-4s and Zn-4p orbitals. The relative energies of the $R-ns$ and $R-np$ states to the Zn-4s and Zn-4p states decrease in the order of Al, Ga, and In. This brings about the change in the conduction band structures as well as the magnitude of band gaps.

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