Origin of the structural diversity of M_2O_3 (M=Al, Ga, In)

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Oxide materials have many unique physical properties, including structural diversity. For example, isovalent Al_2O_3 , Ga_2O_3 , and In_2O_3 are all important materials for technological applications. Although they have the same chemical composition, their crystal structures are all different. Using first-principles calculations, we investigate the structural stability of these oxides. We show that the structural diversity in oxides is due to a subtle balance between the Coulomb energy and the covalent binding energy in these materials. We find that the observed structural stability trends can be explained by the size of the cation atom and the energies of the cation valence electrons.

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I. INTRODUCTION

Isovalent Al_2O_3 , Ga_2O_3 , and In_2O_3 are all important materials with many novel technical applications [1–3]. Al_2O_3 is an important dielectric material [4] with a band gap of ~ 9.25 eV [5], and it is widely used as an insulating substrate for thin-film growth. Ga_2O_3 has a band gap of ~ 5 eV [6], and it is widely used in lasers, as well as a dielectric coating in electrical devices [7]. In_2O_3 has a fundamental band gap of ~ 2.9 eV, but due to the dipole-forbidden optical transitions at the band edges [8], it has an optical band gap of ~ 3.7 eV. When doped with Sn, it is one of the best transparent conducting oxides (TCOs) [9, 10].

Due to the technical importance of these oxides, extensive studies have been carried out to understand their structural, electronic, and optical properties [11]. However, some questions about these materials still exist. One puzzling phenomena observed in these systems, and more generally in oxides, is that although the three oxide compounds are isovalent and have the same chemical composition, their structures are very different. The most common form of crystalline Al_2O_3 adopts the corundum mineral structure (HEX) with O forming a hexagonal close-packed arrangement and Al occupying octahedral sites [12]. The most stable phase of Ga_2O_3 adopts the base-centered monoclinic structure (MON) with O forming a distorted cubic close-packed arrangement and Ga occupying a combination of tetrahedral and octahedral sites [13]. In_2O_3 adopts the body-centered cubic bixbyite structure (BIX), which is a defective $2 \times 2 \times 2$ superstructure of the fluorite mineral structure with In forming a roughly octahedral structure [14]. The three structures are illustrated in Fig. 1.

The structural diversity here is quite surprising, because conventional semiconductors, such as the arsenides MAs ($\text{M}=\text{Al}, \text{Ga}, \text{In}$) all adopt the same zincblende structure, and the nitrides MN ($\text{M}=\text{Al}, \text{Ga}, \text{In}$) all adopt the same wurtzite structure. The stability of these two tetrahedral structures has been well discussed in literatures and is attributed to the Coulomb interaction in the compounds [15]. However, such a simple explanation does not hold for oxides, because the structures of oxides are more complex and the local environments of cations are different between any two structures. Therefore, it is imperative to develop theories to understand the cohesive properties in these oxide materials and the chemical trends of their structural stability.

Here, using first-principles methods, we have studied the stabilities of M_2O_3 ($\text{M}=\text{Al}, \text{Ga}, \text{In}$) focusing on the three structures described above, as they are the most stable structures

observed for these compounds. To understand the trends of the structural stability, we consider the formation of these oxides as a three-step process, and calculate the Coulomb interaction and the orbital interaction energies of the three oxides in each of the three ground state structures, respectively. We find that the energy trends of the Coulomb interaction can be explained by the size of the cation atom, and the energy trends of the orbital interaction can be explained by the energies of the cation valence electrons. Specifically, if the size of the cation atom is small and the energies of the cation valence electrons are low, the MON structure should be stable, which is the case for Ga_2O_3 ; if the size of the cation atom is large and the energies of the cation valence electrons are high, the BIX structure should be stable, which is the case for In_2O_3 ; if the size of the cation atom is small and the energies of the cation valence electrons are high, the HEX becomes more stable, which is the case for Al_2O_3 .

II. COMPUTATIONAL METHOD

Our calculations are based on density functional theory (DFT) [16] within the generalized gradient approximation (GGA) formulated by Perdew, Burke, and Ernzerhof (PBE) [17] as implemented in VASP code [18]. The projector augmented wave (PAW) pseudopotentials [19] are employed, and the valence wavefunctions are expanded in a plane-wave basis with an energy cutoff as high as 600 eV. The Brillouin zone integration is sampled with $6 \times 6 \times 6$ k-point mesh. The primitive cells of the three structures are employed, respectively. Larger energy cutoffs and finer k-point meshes have been tested, and the change of the energy difference is negligible. In the following calculations, all the structural parameters, including both lattice parameters and atomic positions, have been fully optimized.

III. RESULTS AND DISCUSSIONS

The cohesive energies of these three oxides in each of the three structures are summarized in Table I. We find that the most stable structures of the Al, Ga, and In oxides are the HEX, MON, and BIX structures, respectively, which is in agreement with the experimental results discussed above. Our calculations also indicate that, for Al_2O_3 the BIX structure is the least stable among the three structures, for Ga_2O_3 the HEX and BIX structures are

almost degenerate with a small preference for the HEX structure, and for In_2O_3 the MON structure is the least stable.

The formation of M_2O_3 ($\text{M}=\text{Al}, \text{Ga}, \text{In}$) can be regarded as a three-step process. First, charges are transferred from cation atoms to oxygen atoms. In this step, the neutral cation (M) and O atoms become charged M^{q_1+} and O^{q_2-} ions. Because the atomic levels of cation s and p electrons are all higher in energy than that of oxygen 2p electrons, the system gains energy from the charge transfer. The Bader charge analysis shows that the charge transfers for a certain compound in the three structures are similar. Therefore, the charge transfer only gives the same constant shift in energy for all the structures of a certain oxide, so it does not affect the structural stability and is thus not discussed in details here.

Second, the charged ions move to the equilibrium positions from isolated positions. The system gains energy from the Coulomb attraction between the ions. The Coulomb energy E_{coul} per M_2O_3 ($\text{M}=\text{Al}, \text{Ga}, \text{In}$) is defined as

$$E_{\text{coul}} = \frac{5}{N} \sum_{i>j} \frac{q_i q_j}{r_{i,j}}, \quad (1)$$

where $r_{i,j}$ is the equilibrium distance between ions i and j in the compound, q_i is the charge of the i th ion, and N is the total number of atoms in the cell. Because we are studying the oxides that are strongly ionic, the nominal charge $q = +3$ for cation atoms and $q = -2$ for anion atoms are appropriate. For more covalent compounds, one may get the q values from the Bader charge analysis. In the equation above, the screening effect is not considered and the ions are treated as point charges. The Coulomb energy is calculated exactly using the Ewald method [20, 21]. This term contains the bond length information of the structures and becomes more negative as the size of the cation atom decreases.

Third, the atomic orbitals of the ions interact with their neighbors and broaden into bands. The system gains energy from the orbital interaction. We define the orbital interaction energy E_b per M_2O_3 ($\text{M}=\text{Al}, \text{Ga}, \text{In}$) as

$$E_b = E_{\text{band}}(\text{M}_2\text{O}_3) - 2E_{\text{orb}}(\text{M}^{q_1+}) - 3E_{\text{orb}}(\text{O}^{q_2-}), \quad (2)$$

where E_{band} is the summation of all the occupied eigenvalues weighted by k-point sampling of the oxide compound, and E_{orb} is the summation of all the occupied atomic energy levels of the isolated ion. To exclude the potential shift in different cells, the 1s core levels of the ions are aligned in the calculations. Because the oxides are strongly ionic, we take $q_1 = 3$

and $q_2 = 2$ in the calculations. After these three steps, the oxide is formed from isolated atoms. The energy trends of E_{coul} and E_b determine the trends of the cohesive energies of the oxides.

To investigate how the size of the cation atom and the energies of the cation valence electrons can affect the trends of the Coulomb interaction, the orbital interaction, and therefore the structural stability, we apply an empirical external potential onto the cation valence states, following the method in Ref.[22]. When adding a positive external potential, both the s and p electrons of cation atom move up in energy, and vice versa. The external potential has two effects: (i) as the electron levels move up/down, the electrons become more delocalized/localized at the nucleus, the size of the cation atom increases/decreases, and therefore the equilibrium size of the oxide expands/shrinks; (ii) because the oxygen 2p electrons are below the cation s and p valence electrons in energy, as the energy of the cation electrons move up/down, the energy separations between the cation valence electrons and the oxygen 2p electrons increase/decrease, and therefore the orbital interaction between the cation and anion atoms becomes weak/strong. These two effects have strong impacts on the structural stability, as will be shown below.

We first look at the Coulomb interaction energy E_{coul} . The Coulomb energy differences between the three structures as a function of the external potential are displayed in Fig. 2. The general trend is that, as the external potential becomes more negative, the Coulomb attraction of the MON structure increases the fastest (i.e., the Coulomb energy becomes more negative compared to the other two structures), and that of the BIX structure increases the slowest. These energy trends can be explained by the size effect. As discussed above, when the external potential becomes more negative, the size of the cation atom decreases. Therefore, the cation-anion bond lengths decrease. The Coulomb energy is proportional to the inverse of the bond length, so the Coulomb energies of all three structures become more negative. As the bond length changes by a similar amount, the Coulomb energy changes more significantly if the bond length is shorter. In the MON structure, tetrahedral sites exist at which the cation-anion bond length is the shortest among all the sites in the three structures. Therefore, the Coulomb attraction of the MON structure increases the fastest as the cation atom size decreases. The HEX and BIX structures only have octahedral sites. In the HEX structure, all the octahedral sites have three short cation-anion bonds. In the BIX structure, some of the octahedral sites have six equal bond length, and the other octahedral

sites have two short cation-anion bonds. On average, the HEX structure has more short cation-anion bonds than the BIX structure. Therefore, the Coulomb attraction of the BIX structure increases the slowest as the cation atom size decreases. In general, if the size of the cation atom is small, the MON structure is preferred by the Coulomb energy; if the size of the cation atom is large, such as in the In case, the Coulomb energy differences $E_{coul}(\text{MON}) - E_{coul}(\text{BIX})$ and $E_{coul}(\text{HEX}) - E_{coul}(\text{BIX})$ are positive, so the BIX structure is preferred instead.

Next, we look at the orbital interaction energy E_b . The orbital interaction energy differences between the three structures as a function of the external potential are displayed in Fig. 3. The general trend can be described as follows. When the external potential becomes more negative, the magnitude of the orbital interaction energy of the MON structure increases the fastest (i.e., the orbital interaction energy becomes more negative compared to the other two structures). The energy trends can be explained by the energies of the cation valence electrons. As discussed above, when the energies of the cation valence electrons move down, the energy separations between the cation and oxygen valence electrons decrease and the system becomes more covalent according to the tight-binding model [23]. Generally, covalent materials can gain more energy from the orbital interaction at the tetrahedral sites than at the octahedral sites. Because the MON structure has tetrahedral sites, as the energy separations between the cation and oxygen valence electrons decrease, the magnitude of the orbital interaction energy of the MON structure increases the fastest. For the Al and Ga oxides, the orbital interaction energy difference between the HEX and BIX structures increases with the external potential, whereas for In_2O_3 it decreases. However, the magnitude of the change of the orbital energy difference between these two structures is relatively small, because they only have octahedral sites. In general, as the energy separations between the cation valence electrons and oxygen 2p electrons decrease, the MON structure becomes more preferred by the orbital interaction energy; as the energy separations increase, either the HEX structure or the BIX structure is preferred, but the orbital interaction energy difference between the two structures is relatively small.

Having established the energy trends of the Coulomb energy and the orbital interaction energy, we can now discuss the trends of the cohesive energy, which are determined by the trends of the two terms discussed above. The cohesive energy differences between the three structures as a function of the external potential are displayed in Fig. 4. When

the external potential becomes more negative, the size of the cation atom and the energy separations between the cation and oxygen valence electrons both decrease. According to the discussions above, the MON structure is preferred by both the Coulomb interaction and the orbital interaction, so its cohesive energy becomes more negative compared to the other two structures. Between the HEX and BIX structures, because the Coulomb attraction of the HEX structure increases faster, the cohesive energy of the HEX structure becomes more negative, as the external potential becomes more negative, but the change of the cohesive energy difference is not significant.

Among the three elements (Al, Ga, and In), Ga has the lowest valence electron energies, and therefore Ga_2O_3 is the most covalent among the three oxides. Furthermore, Ga is small in size. As the trends discussed above, the MON structure is preferred by both the Coulomb energy (because the size is small) and the orbital interaction energy (because the energy separations between the Ga and oxygen valence electrons are small), so the most stable structure of Ga_2O_3 is the MON structure. The HEX and BIX structures of Ga_2O_3 have similar Coulomb energies and similar orbital interaction energies with small preferences for the HEX structure, so the cohesive energy of the HEX structure is ~ 13 meV smaller than that of the BIX structure.

In has higher valence electron energies than Ga. As discussed above, the orbital interaction prefers either the BIX or the HEX structure, because the energy separations between the In and oxygen valence electrons are large. Furthermore, In is the largest in size of the three elements, so the Coulomb interaction prefers the BIX structure. Therefore, the BIX structure is the most stable for In_2O_3 . The MON structure has both the smallest Coulomb attraction (due to the large size) and orbital interaction (due to the large energy separations between valence electrons), so it is the least stable.

Al has the smallest size among the three elements. As discussed above, the MON structure is the most preferred and the HEX structure is the second preferred by the Coulomb energy. On the other hand, Al has the highest valence electron energies of the three elements, so Al_2O_3 is the least covalent. Therefore, the MON structure is least preferred by the orbital interaction energy. The competition between the two terms determines the structural stability. The HEX structure is the most preferred by the orbital interaction and the second preferred by the Coulomb interaction, so it turns out to be the most stable structure for Al_2O_3 . The MON structure, although has the largest Coulomb energy gain, is not preferred

by the orbital interaction energy, so it is less stable than the HEX structure. The BIX structure has a similar (slightly smaller) orbital interaction energy gain compared to the HEX structure, but its Coulomb energy gain is the least among the three, so it is the least stable structure.

IV. SUMMARY

In conclusion, the structural stability of the Al, Ga, and In oxides have been studied. We find that the structural diversity in these systems is due to a subtle balance between the Coulomb interaction and orbital interaction. The observed trends can be explained by the size of the cation atom and the energies of the cation valence electrons. Generally speaking, if the size of the cation atom is small and the energies of the cation valence electrons are low, the MON structure should be stable, which is the case for Ga_2O_3 ; if the size of the cation atom is large and the energies of the cation valence electrons are high, the BIX structure should be stable, which is the case for In_2O_3 ; if the size of the cation atom is small and the energies of the cation valence electrons are high, the HEX becomes more stable, which is the case for Al_2O_3 . We would like to address here that the purpose of this study is to understand the structure stability of the group-III oxides, rather than to predict new stable structures. The method can also be generalized to other systems. We believe the structural stabilities for other systems may also be understood by the trends of the Coulomb energy and the orbital interaction energy.

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TABLE I: The calculated cohesive energies (eV) per M_2O_3 (M=Al, Ga, In) in HEX, MON, and BIX structures. The cohesive energy of the most stable structure is set to 0 for every compound.

	Al_2O_3	Ga_2O_3	In_2O_3
HEX	0.000	0.146	0.148
MON	0.047	0.000	0.456
BIX	0.148	0.159	0.000

FIG. 1: The HEX (left panel), MON (middle panel), and BIX (right panel) structures of the group-III oxides. The green balls represent cation atoms and the red ones represent oxygen atoms.

FIG. 2: The Coulomb interaction energy differences between the three structures as a function of the external potential for M_2O_3 ($\text{M}=\text{Al}, \text{Ga}, \text{In}$).

FIG. 3: The orbital interaction energy differences between the three structures as a function of the external potential for M_2O_3 ($\text{M}=\text{Al}, \text{Ga}, \text{In}$).

FIG. 4: The cohesive energy differences between the three structures as a function of the external potential for M_2O_3 ($M=Al, Ga, In$).

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