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Ab initio study of structural and electronic properties of $BiAlO_3$ and $BiGaO_3$

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Abstract

The first principles within the full potential linearized augmented plane wave (FP-LAPW) method was applied to study the structural and electronic properties of cubic perovskite-type compounds $BiAlO_3$ and $BiGaO_3$. The lattice constant, bulk modulus, its pressure derivative, band structure and density of states were obtained. The results show that $BiGaO_3$ should exhibit higher hardness and stiffness than $BiAlO_3$. The Al–O or Ga–O bonds are typically covalent with a strong hybridizations as well as Bi–O ones that have a significant ionic character. Both materials are weakly ionic and exhibit wide and indirect band gaps, which are typical of insulators.

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Keywords: Ab initio; Electronic structure; Perovskite structure; Ferroelectrics

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1. Introduction

Piezoelectric materials, most often lead zirconate titanate (PZT)-based compositions, are of importance and find their extensive applications as sensor (or transducers, actuators) materials in smart structures, medical imaging devices, and micro electro-mechanical systems (MEMS). As environmental problems resulting from the toxicity of lead is well-known, one expects a lead-free piezoelectric material whose properties match those of PZT so as to identify nontoxic alternatives for it. With this motive, many efforts have already been made toward their search in the recent years. The solid solutions based on $BaTiO_3$ are being explored [1]. A very recent report of large piezoelectric constants in solid solutions of $(K_{0.5}Na_{0.5})NbO_3$ with $LiTiO_3$ is particularly promising [2]. Bi-based compounds are of particular interest as individual lead-free piezoelectrics because they are nontoxic and also have 6s2 lone pairs [3,4], which is the origin of large ferroelectric polarizations in Pb-based compounds.

Recently, Baettig et al. [5] theoretically predicted the large ferroelectric polarization and piezoelectricity in the hypothetical perovskite-structure oxides bismuth aluminate ($BiAlO_3$) and bismuth gallate ($BiGaO_3$). They show that $BiGaO_3$ have a *tetragonal* structure similar to $PbTiO_3$, but with much stronger tetragonal distortion and improved ferroelectric properties. $BiAlO_3$ shares structural characteristics with antiferrodistortive $PbZrO_3$ with space group R3c, and also with a large polarization. Therefore, they proposed the $Bi(Al,Ga)O_3$ system as a replacement for the widely used piezoelectric material, $Pb(Zr,Ti)O_3$ (PZT), that will avoid the environmental toxicity problems of lead-based compounds. On the other band, $BiAlO_3$ and $BiGaO_3$ were experimentally synthesized using a high-pressure high-temperature technique [6]. It is reported that $BiAlO_3$ is isotypic with multiferroic perovskite-like $BiFeO_3$ with space group R3c (consistent with theoretical predictions); while $BiGaO_3$ has the *orthorhombic* structure closely related to pyroxene-like KVO_3 with space group Pcca

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(inconsistent with theoretical views). In addition, it is exciting to find a monoclinic phase of $BiAl_{1-x}Ga_xO_3$ solid solutions structurally related to $PbTiO_3$. First-principles study of cubic phase, a high-temperature phase or hypothetical phase, is of importance for the understanding the origin of ferroelectricity in perovskite. Although ferroelectricity was theoretically predicted both in $BiAlO_3$ and $BiGaO_3$, the absence in latter were experimentally demonstrated. So, first-principles study of cubic $BiAlO_3$ and $BiGaO_3$ is useful for understanding the difference between both structural and electronic properties and gave our insight into the origin of ferroelectricity in $BiMO_3$ materials.

In this study, we present the structural and electronic properties of cubic perovskite compounds $BiAlO_3$ and $BiGaO_3$ based on the calculations using the full potential linearized augmented plane wave (FP-LAPW) method. The paper is organized in the following way. Section 2 gives the details in our calculations. The calculated ground state and electronic properties are presented, and discussed in Section 3. Finally, the conclusion is given in Section 4.

2. Computational methods

The first-principles calculations are performed with the FP-LAPW method [7] as implemented in WIEN2k code. The Kohn–Sham equations are solved self-consistently using FP-LAPW method. In the calculations reported here, we use a parameter $R_{MT}K_{max} = 8$, which determines matrix size (convergence), where K_{max} is the plane wave cut-off and R_{MT} is the smallest of all atomic sphere radii. We have chosen the muffin-tin radii (MT) for Bi, Al, Ga and O to be 2.5, 1.8, 1.8 and 1.6 a.u., respectively. The exchange-correlation potential are treated by local density approximation (LDA) [8]. The semirelativistic approximation without spin–orbit effects was employed in the calculation of the valence states, whereas the core levels were treated fully relativistically [9]. The dependence of the total energy on the number of k-points in the irreducible Brillouin zone (IBZ) has been explored within the linearized tetrahedron scheme [10] by performing the calculation for 64 k-points (grid of $7 \times 7 \times 7$ meshes, equivalent to 500 k-points in the entire Brillouin zone) and extrapolating to an infinite number of k-points.

The $BiAlO_3$ and $BiGaO_3$ compounds considered here have a cubic perovskite-type crystal structure. The space group (Pm3m 221) contains 48 symmetry operations including inversion. The Wyckoff positions of the atoms are Bi 1a (0.0, 0.0, 0.0), Al or Ga 1b (0.5,0.5, 0.5) and O 3c (0.0, 0.5, 0.5).

3. Results and discussion

3.1. Structural properties

The total energy is obtained as a function of volume and fitted to a Murnaghan equation of state [11] to obtain the equilibrium lattice constant (a_0), bulk modulus (B), and the pressure derivative of the bulk modulus (B'). In Table 1 we summarize our data at the equilibrium and compare them with the previous calculations. It seems that the structural parameters are in good agreement with the results of previous studies.

Table 1
Calculated lattice constant a (Å), bulk modulus B (GPa) and its pressure derivative B' compared to the previous work of $BiAlO_3$ and $BiGaO_3$ perovskites

Material	Lattice constant	Bulk modulus	Pressure derivative B′
$BiAlO_3$	3.724	208	4.61
	3.750[a]	–	–
$BiGaO_3$	3.816	218	4.41
	3.83[a]	–	–

[a] Ref. [5].

It is observed that $BiGaO_3$ has a larger lattice constant and bulk modulus than of $BiAlO_3$. The large lattice constant can be explained by considering the radius of B cations (Al and Ga). The lattice constant increases when replacing Al with the larger Ga ion. The large bulk modulus indicates that Ga–O octahedra have higher hardness and stiffness than Al–O ones. Vanderbilt's paper [12] also showed this simple trend in different ABO_3 perovskite compounds. A strong correlation between hardness and a bulk modulus value has been confirmed in a number of recent papers [13,14]. For cubic compounds, the bulk modulus should be quite a good indicator of hardness, since it is related to an isotropic deformation [15].

3.2. Electronic structure calculations

3.2.1. The density of states (DOS)

The density of states (DOS) is computed by the tetrahedron method [16]. From the eigenvalues and eigenvectors solved at a sufficient number of *k-points* in the Brillouin zone, the total DOS can be projected into its partial components or partial DOS (PDOS) with respect to the different atoms. The densities of states of two perovskite compounds were computed at their equilibrium lattice constants and the results were displayed in Figs. 1–3. The Fermi energy is located at 0 eV.

There is an overall topological resemblance of the present DOS for $BiAlO_3$ and $BiGaO_3$ (see Fig. 1). There are no less than 18 peaks, indicating the strong hybridization in the whole region $[-11, 7]$ including covalence and conduction band. In the conduction band region, two compounds have the same number of peaks with slightly different amplitudes, which only have a shift as smaller as 0.5 eV contributed to the different B-site atoms. In the vicinity of Fermi level, the DOS is substantially similar. In the case of covalence band, $BiAlO_3$ showed an additional peak at -2.5 eV, while $BiGaO_3$ have two peaks with large anomaly amplitude located at −10 and −1.3 eV, respectively. Indeed, such an anomaly may result from the strong hybridization between Ga-p,d and O-2p states as shown in Fig. 3. At the region [−5, −2.5], the shift of three peaks are visible. For both the compounds, it is found that the upper valence bands (between −6 and 0 eV), are essentially dominated by O-2p states, with a minor admixture from Al-s, p and d states (or Ga-s, p and d states in $BiGaO_3$). Moreover, the presence of this latter in the bonding region suggests a covalent bonding contribution in these materials. The s, p, d states of Bi atoms also contribute to the valence bands, but the values of the corresponding densities of states are quite small compared to O-2p states as shown in Fig. 2. The Bi atoms have partial density of states fairly similar to Pb atoms in $PbTiO_3$ [17].

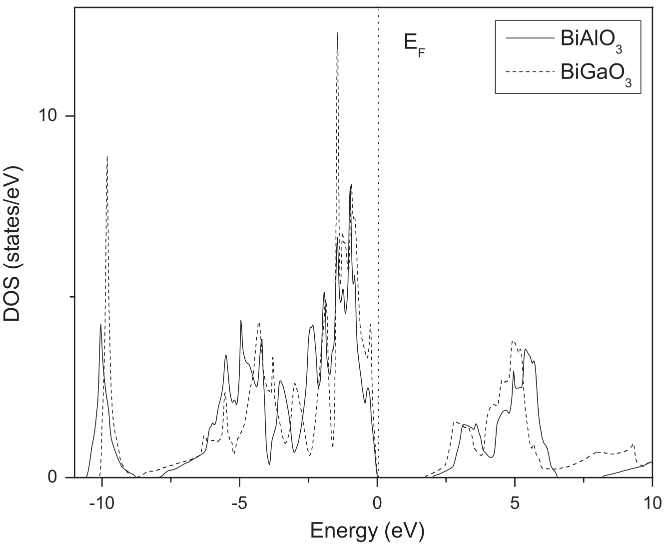


Fig. 1. Calculated total density of states (DOS) of $BiAlO_3$ and $BiGaO_3$, at the predicted equilibrium lattice constant.

The bottom of the conduction bands is dominated by Bi-6p states which hybridize with O-2p states in both $BiAlO_3$ and $BiGaO_3$ compounds. All of these states are distributed in a wide energy range of 2.0–6.5 eV. On the other hand, there is an energy gap between the occupied O-2p states and the unoccupied Bi-6p states, as seen from the analysis of the partial densities of states. In addition, the Ga-s, p states have contribution to the conduction bands of $BiGaO_3$, while the Al-s, p states do not have in $BiAlO_3$. In a word, M–O (M = Al, Ga) have strong hybridization like Bi–O, and influence the latter. As a consequence, the conduction band have a slight shift.

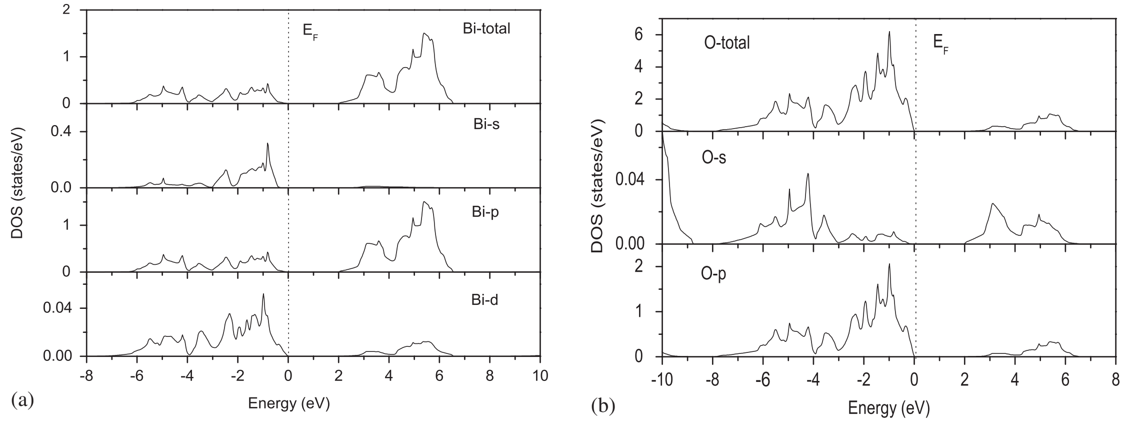


Fig. 2. Total and partial density of states (PDOS) of Bi and O atoms in $BiAlO_3$.

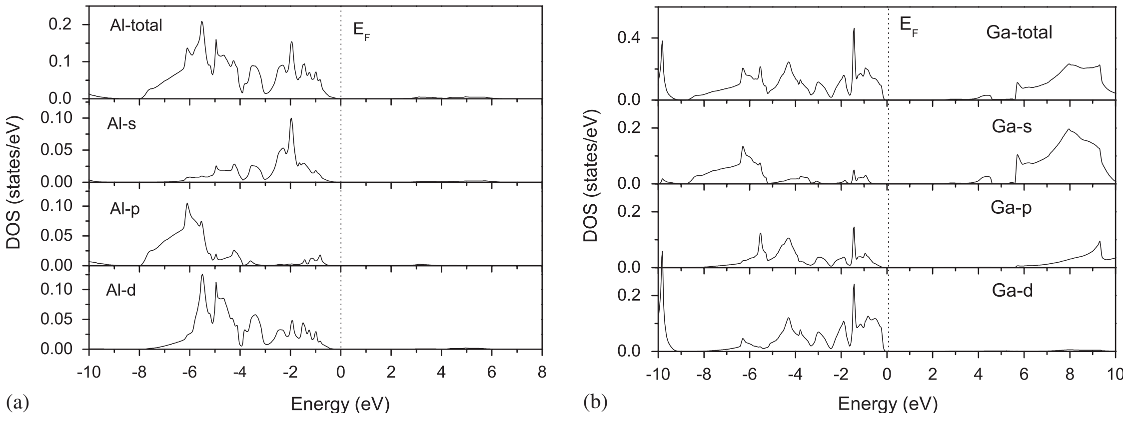


Fig. 3. Total and partial density of states (PDOS) of Al atom in $BiAlO_3$ and Ga atom in $BiGaO_3$.

3.2.2. The electronic band structure

Fig. 4 shows the calculated electronic band structures of the cubic phases of both $BiAlO_3$ and $BiGaO_3$. The band structure can be interpreted in a way roughly similar to that of the ABO_3 perovskite structure. There are strong hybridizations between Al and O in $BiAlO_3$ (Ga and O in $BiGaO_3$) as well as Bi–O ions. Compared to $PbTiO_3$, a direct insulator with a band gap of 1.65 eV at the X point [17], the two compounds are found to have indirect band gaps; the valence band maximum occurs at M ($k = 2\pi/a(1\,1\,0)$) in the Brillouin zone, whereas the conduction band minimum is at the X ($k = 2\pi/a(1\,0\,0)$) point. The band gaps are large with the values of 1.70 and 1.41 eV for $BiAlO_3$ and $BiGaO_3$, respectively. The width of gap indicates the presence of an insulating feature. It is well known that the LDA calculations usually underestimate the fundamental gap of semiconductors. So, $BiAlO_3$ and $BiGaO_3$ may have a larger gap than predicted one.

3.2.3. Charge density

Contour maps of charge densities along the [1 1 0] direction in $BiAlO_3$ and $BiGaO_3$ are shown in Fig. 5. This latter shows that our choice for the muffin-radii is about right, since we capture most of the spherical regions inside the muffin-tin spheres. Both $BiAlO_3$ and $BiGaO_3$ compounds are found to have similar charge densities, which

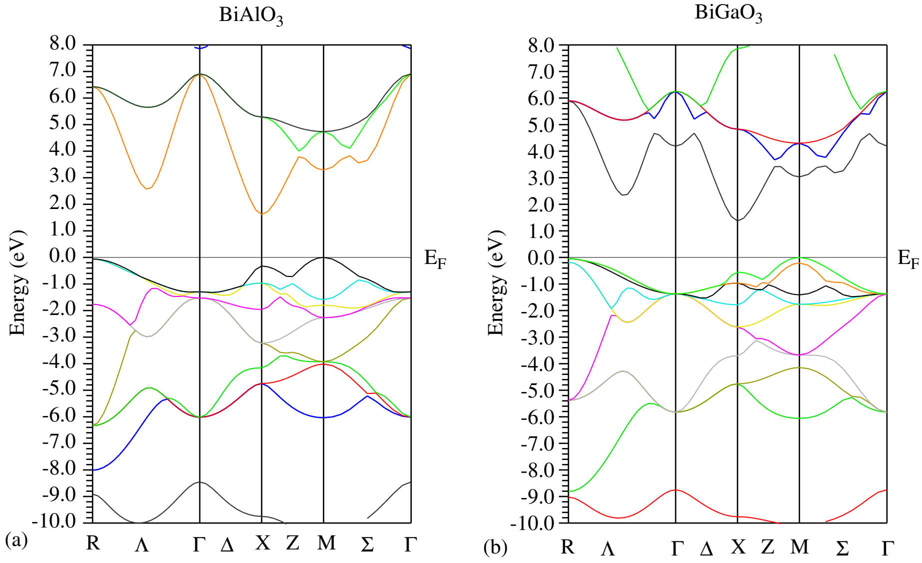
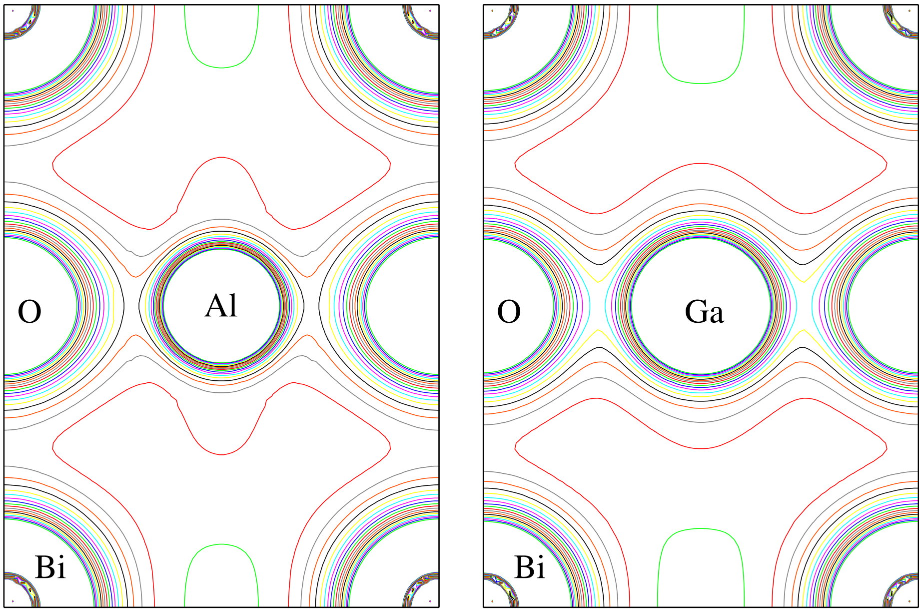


Fig. 4. Calculated electronic band structure of cubic $BiAlO_3$ and $BiGaO_3$.



(a) (b)

Fig. 5. Calculated charge density along the [1 1 0] direction in $BiAlO_3$ (a) and $BiGaO_3$ (b) at the predicted equilibrium lattice constant.

have the same characters as those of $KNbO_3$ [18]. Therefore, the bonding has a significant covalent character due to the hybridization effect between Al-3s (also including 3p and 3d states) and O-2p orbitals as was analyzed above. This result should explain the high bulk moduli of these ceramics. The bonds between bismuth and oxygen atoms seem to have an ionic character as seen in perovskite $PbZrO_3$ [19]. Moreover, the charge transfer occurs mainly from the other atomic species towards the oxygen atoms. Furthermore, the Ga–O bond is more ionic than the Al–O bond, i.e. Al–O bands have stronger hybridization than Ga–O ones. Indeed, as you move down a column for a group, the sizes of atoms increase. The electrons in larger atoms are not held as strongly as those in smaller atoms. Therefore, the larger the atom, the less likely it will attract electrons from other atoms. Hence, electronegativity decreases. Additionally, when a chemical bond is formed with another element and the difference of electronegativity is large, the bond tends to be more ionic [20]. Our results show that both $BiAlO_3$ and $BiGaO_3$ are weakly ionic as the previously reported titanate by King-Smith et al. [12]. It is observed that the charge density (chemical bonding environment) of $BiAlO_3$ is more similar to $KNbO_3$ than $BiGaO_3$. Both are rhombohedral phases. On the contrary, $BiGaO_3$ is closer to $CaTiO_3$, which have orthorhombic phase at room temperature.

4. Conclusion

The structural and electronic properties have been studied by using the FP-LAPW in the framework of density functional theory (DFT) for cubic $BiAlO_3$ and $BiGaO_3$. The ground-state properties including lattice constants and bulk modulus were calculated. The results show that both $BiAlO_3$ and $BiGaO_3$ have relatively high bulk modules, which is a result of strong covalent bonding between III-group metal and oxygen-2p states. Furthermore, $BiGaO_3$ should exhibit higher hardness and stiffness than $BiAlO_3$, which can be explained using the simple chemical idea based on the size of ions. On the other hand, the electronic structure calculations showed that both $BiAlO_3$ and $BiGaO_3$ exhibit wide and indirect band gaps. The analysis of the DOS also revealed that the conduction band is mainly composed of O-2p with some mixture of Bi-6p and Ga-3s states for $BiGaO_3$ and only with Bi-6p for $BiAlO_3$, while the valence band is essentially dominated by O-2p states. The Bi-O bond has a significant ionic character while the Al–O and Ga–O bonds are typically covalent. There is a good understanding of the difference of structural phase at room temperature for $BiAlO_3$ and $BiGaO_3$. We can draw a conclusion that both compounds have interesting ferroelectric properties like titanate.

Acknowledgments

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