Piezoelectric properties of $\text{Ga}_2\text{O}_3$: a first-principle study

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The compounds exhibit piezoelectricity, which demands to break inversion symmetry, and then to be a semiconductor. For $\text{Ga}_2\text{O}_3$, the orthorhombic case ($\epsilon$-$\text{Ga}_2\text{O}_3$) of common five phases breaks inversion symmetry. Here, the piezoelectric tensor of $\epsilon$-$\text{Ga}_2\text{O}_3$ is reported by using density functional perturbation theory (DFPT). To confirm semiconducting properties of $\epsilon$-$\text{Ga}_2\text{O}_3$, its electronic structures are studied by using generalized gradient approximation (GGA) and Tran and Blaha’s modified Becke and Johnson (mBJ) exchange potential. The gap value of 4.66 eV is predicted with mBJ method, along with the the effective mass tensor for electrons at the conduction band minimum (CBM) [about 0.24 $m_0$]. The mBJ gap is very close to the available experimental value. The elastic tensor $C_{ij}$ and piezoelectric stress tensor $e_{ij}$ are attained by DFPT, and then piezoelectric strain tensor $d_{ij}$ are calculated from $C_{ij}$ and $e_{ij}$. In this process, average mechanical properties of $\epsilon$-$\text{Ga}_2\text{O}_3$ are estimated, such as bulk modulus, Shear modulus, Young’s modulus and so on. The calculated $d_{ij}$ are comparable and even higher than commonly used piezoelectric materials such as $\alpha$-quartz, ZnO, AIN and GaN.

I. INTRODUCTION

Wide-band gap semiconductors have potential application in high-power electronics, which requires high frequency, temperature and power. Gallium oxide ($\text{Ga}_2\text{O}_3$) has received a lot of attention as a wide band gap transparent semiconducting oxide$^{1-6}$. The $\text{Ga}_2\text{O}_3$ has five different phases, commonly referred to as $\alpha$, $\beta$, $\gamma$, $\delta$ and $\epsilon$, the monoclinic $\beta$ phase of which is the most thermodynamically stable with the energy gap 4.6-4.9 eV, transparency up to the UV-C range, and very high breakdown voltage$^{1,3}$. Piezoelectric materials can convert mechanical energy to electrical energy, which have potential application in sensors and energy harvesting$^7$. The ZnO, GaN and InN semiconductors with non-centrosymmetric wurtzite-structure are wildly used in the piezotronic and piezo-phototronic devices, and their nanostructures have potential applications in electromechanical coupled sensors and nanoscale energy conversion$^8-11$.

For piezoelectric materials, inversion symmetry need be eliminated. The bravais lattice, space group, point group and inversion center of five different polymorphs of $\text{Ga}_2\text{O}_3$ are shown in Table I. It is clearly seen that $\epsilon$-$\text{Ga}_2\text{O}_3$ breaks inversion symmetry and hence can exhibit piezoelectricity. The $\epsilon$-phase of $\text{Ga}_2\text{O}_3$ is confirmed as the second most stable structure after $\beta$-$\text{Ga}_2\text{O}_3$. When $\epsilon$-$\text{Ga}_2\text{O}_3$ is epitaxially stabilized, the symmetry will prevent the transform back into $\beta$-phase. The electronic structures of $\epsilon$-$\text{Ga}_2\text{O}_3$ have been reported, and the predicted gap is 2.465 eV with GGA$^{13}$, 2.32 eV with PBEsol, 4.62 eV with B3LYP$^{14}$ and 4.26 eV with HSE$^{15}$. The experimental gap is 4.41 eV by angle-resolved photoemission spectroscopy (ARPES) experiments$^{15}$, and is 4.6 eV from photoconductivity and optical absorption$^{16}$. The $\epsilon$-$\text{Ga}_2\text{O}_3$ is predicted to have a large spontaneous polarization (0.23-0.26 C/m$^2$)$^{12,14}$, along with piezoelectric coefficient $e_{33}$=0.77 C/m$^{212}$. Recently, piezoelectric strain constants ($d_{ij}$) of $\epsilon$-$\text{Ga}_2\text{O}_3$ are calculated from piezoelectric stress constants ($e_{ij}$) and elastic constants ($C_{ij}$)$^{17}$. The $e_{ij}$ are attained by polarization-strain relation, and the $C_{ij}$ are calculated by energy-stain relation$^{17}$. Here, we use DFPT to attain the $C_{ij}$ and $e_{ij}$, and then calculate the $d_{ij}$ by $e$ matrix multiplying $C$ matrix inversion.

To ensure the reliability of our results, the piezoelectric properties of commonly used piezoelectric materials such as ZnO, AIN and GaN are also studied by DFPT, and make a comparison with the related experiments$^{18-22}$. The mBJ is used to study the electronic structures of $\epsilon$-$\text{Ga}_2\text{O}_3$, and the calculated mBJ gap 4.66 eV is very close to experimental values$^{15,16}$. The mBJ is as cheap as local density approximation (LDA) or GGA, thus can be used to study very large systems such as doping $\epsilon$-$\text{Ga}_2\text{O}_3$ in an efficient way.

II. SYMMETRY ANALYSIS

The piezoelectric effect is an electromechanical coupling described by piezoelectric tensors $e_{ijk}$ and $d_{ijk}$, which are obtained as the sum of ionic and electronic contributions. In the following, the frequently used Voigt notation is employed, and the mapping of indices is 11→1, 22→2, 33→3, 23→4, 31→5 and 12→6. The Voigt notation allows to represent the tensor of elastic constants

| Name            | $\alpha$ | $\beta$ | $\gamma$ | $\delta$ | $\epsilon$ |
|-----------------|----------|---------|----------|----------|------------|
| Bravais lattice | Trigonal | Monocl. | Cubic    | Cubic    | Orthorh.   |
| Space group     | $R3c$    | $C2/m$  | $Fddd$   | $Ia3$    | $Pna2_1$   |
| Point group     | $\overline{3}m$ | $2/m$   | $m\overline{3}m$ | $m\overline{3}$ | mnn2      |
| Inversion center | $\sqrt{\times}$ | $\sqrt{\times}$ | $\sqrt{\times}$ | $\sqrt{\times}$ | $\times$   |
$C_{ijkl}$, piezoelectric tensors $e_{ijk}$ and $d_{ijk}$ as 6×6, 3×6 and 3×3 matrix $C_{ij}$, $e_{ij}$ and $d_{ij}$, with a maximum of 21, 18 and 18 independent elements. The number of independent components can be reduced due to the crystal symmetry in $C_{ij}$, $e_{ij}$ and $d_{ij}$ tensors. The $\epsilon$-Ga$_2$O$_3$ has the $\text{mm}2$ point group symmetry, giving:

$$e = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{24} & 0 & 0 \\ e_{31} & e_{32} & e_{33} & 0 & 0 & 0 \end{pmatrix}$$  \hspace{1cm} (1)$$

and

$$C = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{pmatrix}$$  \hspace{1cm} (2)$$

The elastic tensor $C_{ij}$ and piezoelectric stress tensor $e_{ij}$ can be attained by density functional theory (DFT) calculations, and the piezoelectric strain tensor $d_{ij}$ can be calculated by the relation:

$$e = dC$$  \hspace{1cm} (3)$$

and

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix}$$  \hspace{1cm} (4)$$

$\text{III. ELECTRONIC STRUCTURES}$

The crystal structure of $\epsilon$-Ga$_2$O$_3$ has 16 (24) Ga (O) atoms at four (six) different Wyckoff positions 4a, 4b, 4c and 6, with a maximum of 21, 18 and 18 independent elements. The number of independent components can be reduced due to the crystal symmetry in $C_{ij}$, $e_{ij}$ and $d_{ij}$ tensors. The $\epsilon$-Ga$_2$O$_3$ has the $\text{mm}2$ point group symmetry, giving:

$$e = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{24} & 0 & 0 \\ e_{31} & e_{32} & e_{33} & 0 & 0 & 0 \end{pmatrix}$$  \hspace{1cm} (1)$$

and

$$C = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{pmatrix}$$  \hspace{1cm} (2)$$

The optimized structure-related data are summarized in Table II by using GGA, which agrees well with previous calculated values$^{13}$. Firstly, the popular GGA is used to perform the self-consistent calculation, and the improved exchange-correlation functional including the mBJ exchange potential is adopted, which can improve the semiconductor gaps and d state positions for many kinds of materials. The energy bands calculated with GGA and mBJ are presented in Figure 2. The GGA gap value is 2.45 eV, and 4.66 eV for mBJ functional. Our GGA gap accords with other GGA value 2.465 eV$^{13}$. The mBJ gap is very close to HSE one (4.26 eV)$^{15}$ and B3LYP one (4.62 eV)$^{14}$, and is also close to experimental value 4.41 eV by ARPES experiments$^{15}$and 4.6 eV indicated by photoconductivity and optical absorption$^{16}$. Both GGA and mBJ results show a CBM at the G point. A quasi-2D gap is observed with the valence band maximum (VBM) is a bit off G in the G-X direction. The energy difference between G point and VBM only is 1.2 meV with GGA and 0.2 meV with mBJ. The experimental data suggest that the VBM is at or near the zone centre$^{15}$. The experimental gap for $\beta$-Ga$_2$O$_3$ has been reported in the range of 4.6-4.9 eV$^{13}$. The mBJ is used to study the electronic structures of $\beta$-Ga$_2$O$_3$ ($a=12.29$ Å, $b=3.05$ Å, $c=5.81$ Å and $\beta=103.77$). The mBJ gap value of $\beta$-Ga$_2$O$_3$ is 4.61 eV, which shows that mBJ can reproduce the gap of Ga$_2$O$_3$ very well. We also determine the effective mass tensor for electrons at the CBM, and the resulting results in units of the free electron mass $m_0$ are: $m_{zz}=0.237$, and $m_{xy}=m_{xz}=0.235$, which shows that

| atom | x     | y     | z     |
|------|-------|-------|-------|
| Ga1  | 0.18017 | 0.15153 | 0.99762 |
| Ga2  | 0.81334 | 0.16181 | 0.30879 |
| Ga3  | 0.19165 | 0.15083 | 0.58692 |
| Ga4  | 0.67799 | 0.03128 | 0.79570 |
| O1   | 0.97429 | 0.32590 | 0.42764 |
| O2   | 0.52161 | 0.48778 | 0.43308 |
| O3   | 0.65030 | 0.00345 | 0.20151 |
| O4   | 0.15460 | 0.15917 | 0.19757 |
| O5   | 0.84997 | 0.17145 | 0.67252 |
| O6   | 0.52301 | 0.16682 | 0.93836 |

FIG. 1. (Color online) The crystal structure of $\epsilon$-Ga$_2$O$_3$. The large green balls represent Ga atoms, and the small red balls for O atoms.
FIG. 2. The energy band structures of ϵ-Ga₂O₃ using GGA (Left) and mBJ (Right).

TABLE III. For ϵ-Ga₂O₃, bulk modulus (B), Shear modulus (G), Young’s modulus (E), Poisson’s ratio (ν), longitudinal wave velocity (υₐ), transverse wave velocity (υₜ), average wave velocity (υₐ), and Debye temperature (Θ_D).

|                | B (GPa) | G (GPa) | E (GPa) | ν   |
|----------------|---------|---------|---------|-----|
| ϵ-Ga₂O₃        | 209.22  | 82.50   | 218.75  | 0.33|

υₐ (km/s)    υₜ (km/s)    υₐ (km/s)    Θ_D (K)
7.24          3.68          4.12        565.81

the anisotropy is rather small. These effective masses are very close to ones of monoclinic and rhombohedral cases.¹³

TABLE IV. The elastic constants C_ij of ZnO, AlN and GaN, and the unit is GPa.

| Name    | C₁₁     | C₁₂     | C₁₃     | C₃₃     | C₄₄     |
|---------|---------|---------|---------|---------|---------|
| ZnO     | 204.3   | 133.2   | 115.8   | 209.3   | 34.3    |
| AlN     | 392.0   | 141.6   | 105.5   | 372.2   | 112.5   |
| GaN     | 344.8   | 133.4   | 93.9    | 379.6   | 89.6    |

IV. PIEZOELECTRIC PROPERTIES

The elastic tensor C_ij and piezoelectric stress tensor ε_ij are obtained by using DFPT²⁷ as implemented in VASP code²⁸-³⁰. The relaxed-ion elastic tensor and piezoelectric stress tensor are obtained from the sum of ionic and electronic contributions. Within DFPT, the electronic and ionic contributions to the piezoelectric tensor can be calculated directly in the VASP code. A 12×7×6 k-point mesh is used, and the exchange-correlation interactions are treated using the GGA-PBE with a kinetic-energy cutoff of 450 eV. It is noted that the order of indices in VASP code is 1(XX), 2(YY), 3(ZZ), 6(XY), 4(YZ), 5(ZX), and we have changed into the normal order in the following results for elastic and piezoelectric tensors. The elastic tensor C_ij are given (in GPa):

\[
\begin{pmatrix}
354.77 & 165.45 & 142.20 & 0 & 0 & 0 \\
165.45 & 316.08 & 150.21 & 0 & 0 & 0 \\
142.20 & 150.21 & 302.61 & 0 & 0 & 0 \\
0 & 0 & 0 & 82.75 & 0 & 0 \\
0 & 0 & 0 & 0 & 61.75 & 0 \\
0 & 0 & 0 & 0 & 0 & 102.61
\end{pmatrix}
\] (5)

Based on C_ij, average mechanical properties of ϵ-Ga₂O₃ can be attained, including bulk modulus, Shear modulus, Young’s modulus, Poisson’s ratio, longitudinal wave velocity, transverse wave velocity, average wave velocity and Debye temperature. The Born criteria of mechanical stability for an orthorhombic crystal is³¹:

\[ C_{11} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0 \] (6)

\[ C_{11}C_{22} > C_{12}^2 \] (7)

\[ C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 > 0 \] (8)

The calculated C_ij satisfy these conditions, proving that ϵ-Ga₂O₃ is mechanically stable. The related data are summarized in Table III. The bulk (shear) modulus B (G) manifests the resistance to fracture (plastic deformation). A high (low) B/G ratio may indicates its
ductility (britleness), and the critical value is around 1.75, which can be used to separate ductile and brittle materials. The value of ε-Ga₂O₃ is 2.54, and it can be classified as a ductility material.

The piezoelectric stress tensor $e_{ij}$ are shown (in C/m²):

$$
\begin{pmatrix}
0 & 0 & 0 & 0 & 0.595 & 0 \\
0 & 0 & 0 & 0.194 & 0 & 0 \\
0.011 & -0.319 & 0.941 & 0 & 0 & 0
\end{pmatrix}
$$

(9)

The piezoelectric strain tensor $d_{ij}$ are derived by Equation 3, giving (in pm/V):

$$
\begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 9.622 & 0 \\
0 & 0 & 0 & 2.345 & 0 & 0 & 0 \\
-0.489 & -3.060 & 4.858 & 0 & 0 & 0 & 0
\end{pmatrix}
$$

(10)

The ε-Ga₂O₃ possesses five independent components of the piezoelectric tensor, namely $d_{31}$, $d_{32}$, $d_{33}$, $d_{15}$ and $d_{24}$. The magnitudes of $d_{ij}$ range from 0.489 pm/V to 9.622 pm/V, the $d_{33}$ and $d_{15}$ of which are comparable and even higher than commonly used piezoelectric materials such as α-quartz, ZnO, AlN and GaN. We note that $d_{31}$ is smaller by 1 order of magnitude compared to other $d_{ij}$, which is due to very small $e_{31}$. The $d_{15}$ is the largest among the $d_{ij}$, which is due to the large $e_{15}$ and the smallest $e_{35}$ ($d_{15}=e_{15}/C_{35}$). Our calculated $d_{ij}$ are close to previous theoretical values ($d_{32}=\pm 3.43$ pm/V, $d_{33}=\pm 4.06$ pm/V, $d_{24}=\pm 2.69$ pm/V, $d_{15}=\pm 14.60$ pm/V) except $d_{31}$ (1.37 pm/V)17. In previous calculations, the elastic tensor $C_{ij}$ are attained by fitting the DFT-calculated unit-cell energy to a series of strain states, and the piezoelectric stress tensor $e_{ij}$ are calculated by evaluating the change of unit-cell polarization after imposing small strain17. Here, these tensors are calculated by DFPT. To ensure the reliability of our results or method, the piezoelectric properties of ZnO, AlN and GaN with P6₃mc space group are also studied by DFPT. Due to 6mm point group of P6₃mc, they have five independent elastic constants ($C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$ and $C_{44}$), and three piezoelectric constants ($\varepsilon/d_{31}$, $\varepsilon/d_{33}$ and $\varepsilon/d_{15}$). The elastic constants of ZnO, AlN and GaN are in Table IV, which agree well with previous calculated values15. The piezoelectric tensors of ZnO, AlN and GaN are summarized in Table V, along with the related experimental values of ZnO18, AlN19 and GaN19-22.

V. DISCUSSIONS AND CONCLUSION

It is clear that mBJ gives much better energy gap of ε-Ga₂O₃ than GGA toward the experimental values. Although HSE or B3LYP also can give reasonable energy gap, they need more CPU time and memory than mBJ. Thus, mBJ may be more suitable for dopant studies of ε-Ga₂O₃. It is noted that the energy gap and the effective masses (at CBM) of ε-Ga₂O₃ are very close to ones of β case, but ε phase shows good piezoelectric properties, which can add more freedom for electronic devices.

In summary, the electronic structures have been studied by GGA and mBJ, and the elastic and piezoelectric tensors are attained by DFPT. The mBJ gap is consistent with previously calculated HSE or B3LYP one, and has very better agreement with experiment than GGA one. The values of $d_{ij}$ are found to be comparable to or even superior than conventional piezoelectric materials such as α-quartz, ZnO, AlN and GaN. These results show the possibility of employing piezoelectric effects in ε-Ga₂O₃ for electronics and energy applications. Our works can stimulate further experimental works to study piezoelectric properties of ε-Ga₂O₃.

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