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# Structure, elastic and piezoelectric properties of $A_3BO_7$ (A = Ga, Al; B = P, As) compounds: A DFT study

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ABSTRACT

A first-principles study of the structure, elastic and piezoelectric properties of $A_3BO_7$ (A = Ga, Al; B = P, As) using the density functional perturbation theory (DFPT) has been performed. The structure-properties relation was established. We found that the piezoelectric constant is highly sensitive to the distortion of crystal structures. The larger A–O–B bridging angle $\theta$ is, the smaller piezoelectric stress coefficient $e_{15}$ will be. The obtained piezoelectric tensor $d_{15}$ of $Ga_3AsO_7$ is −23.9 pC/N, which is more than ten times larger than the $d_{11}$ of $SiO_2$. The new finding will be useful in the applications of $Ga_3AsO_7$ in the piezoelectric devices with high Curie temperature.



## 1. Introduction

Research in the area of piezoelectric has led to the development of a variety of important electronic and electromechanical devices. In the past decades, the investigations of piezoelectric have shown various kinds of crystals and ceramics. For example, $SiO_2$ has been widely used in all communication systems; $LiNbO_3$ and $LiTaO_3$ have been extensively prepared for multi-functional devices; PZT and $BaTiO_3$ ceramics have been applied in piezoelectric devices. However, they still cannot meet the pressing demands for stable and reliable piezoelectric devices with high Curie temperature. In this work, we aim to seek candidates with high Curie temperature and large piezoelectric constants.

In 2008, Xu et al. [1] had discovered that trigallium phosphorus heptaoxide ($Ga_3PO_7$) possessed excellent electromechanical properties. They found that the Curie point of $Ga_3PO_7$ is as high as 1364.8 °C, which is far above that of α-$SiO_2$, α-$AlPO_4$, $GaPO_4$ [2] and even larger than that of $LiNbO_3$ (1210 °C) [3]. Its thermal behavior, optical properties, Mohs hardness and Raman spectra have been investigated [1,2,4,5]. The obtained piezoelectric constant $d$ in the direction perpendicular to the (100) face is 4.5 pC/N, which is as large as that of $GaPO_4$, even greater than that of α-$SiO_2$ [2]. Due to the difficulty in determining piezoelectric tensors experimentally, its elastic properties and other piezoelectric tensors have not been reported so far, which has hindered its possibility for applications. This stimulates our interest on a comprehensive study of the elastic and piezoelectric properties of $A_3BO_7$(A = Ga, Al; B = P, As) isomorphic compounds, due to the experience that the isomorph should have similar properties [6,7].

The $Ga_3PO_7$ crystal was first synthesized by Boudin et al. in 1998 [8]. It has a non-centralized symmetric structure with space group R3mH. To the best of our knowledge, $Ga_3AsO_7$, $Al_3PO_7$ and $Al_3AsO_7$ have not been synthesized so far, those structures are simulated by substituting the corresponding elements, based on the structure of $Ga_3PO_7$ in this work. The framework structure of $A_3BO_7$ contains $A_3O_{10}$ clusters of three $AO_5$ trigonal bipyramids and $BO_4$ tetrahedrons (Fig. 1), with the O atoms at the summits and A, B atoms at the centers. Within a cluster, each $AO_5$ bipyramid shares two adjacent edges with two the others. As the piezoelectric constants are highly sensitive to the distortion of crystal structures [7,9,10], we describe the distortion by the A–O–B bridging angle $\theta$, as indicated in Fig. 1(a).

We calculate the structure, elastic and piezoelectric properties of $A_3BO_7$ based on density functional theory (DFT) within the local density approximation (LDA). Furthermore, the elastic and piezoelectric constants of $SiO_2$ have also been calculated in order to confirm the reliability of this calculation method. The aim of this work is to provide a prediction of elastic and piezoelectric properties for $A_3BO_7$ (A = Ga, Al; B = P, As). The results turn out that the $Ga_3AsO_7$ performs better than $Ga_3PO_7$ on piezoelectric. It possesses the largest piezoelectric constant $d_{15}$ (−23.9 pC/N) and the smallest bridging angle $\theta$ in $A_3BO_7$ (A = Ga, Al; B = P, As). This work supplies

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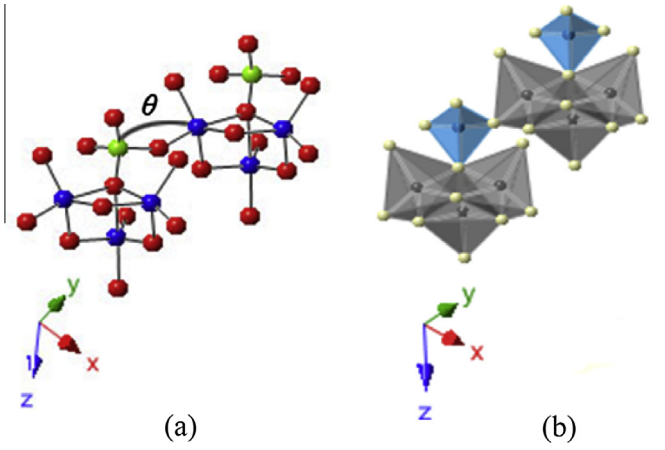


**Fig. 1.** The structure of $A_3BO_7$ compounds. Atoms showed in (a) with A, B and O colored blue, green and red respectively as well as the bridging angle $\theta$. Polyhedral structures were represent in (b) with $BO_4$ tetrahedrons in blue and three $AO_5$ trigonal bipyramids in dark gray. Besides, the direction of lattice was (a) $x$, (b) $y$ and (c) $z$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

useful information for further research on enhancing piezoelectric property by substituting elements.

## 2. Method and computation details

All the calculations were implemented in the Vienna Ab initio Simulation Package (VASP) [11]. The elastic properties were calculated by using the projector augmented-wave method (PAW) [12] with DFT. The exchange–correlation effects were treated within LDA [13]. As the elastic tensor was derived from the strain–stress relationship, an accurately predicted structure was needed [14]. We optimized structures with a plane wave cutoff energy of 1000 eV and a $9 \times 9 \times 9$ Monkhorst Pack grid for Brillouin-zone integration. The force and energy convergence criteria was set to be $10^{-2}$ eV/Å and $10^{-5}$ eV, respectively. Ga 3$d$ states were treated as valence electrons. As the guidelines of VASP show, the plane wave cutoff needs to be sufficiently large to converge the stress tensor [15], we used an energy cutoff of 900 eV and the same $k$-point grid to calculate elastic properties.

The piezoelectric properties were calculated within the framework of density functional perturbation theory (DFPT). To include microscopic changes of the exchange correlation potential, we calculated the piezoelectric properties without considering the random phase approximation, it follows closely the original work of Baroni and Resta [16]. The reason was explained in detail in Ref. [17].

## 3. Results and discussion

### 3.1. Optimized structure and the bridging angle $\theta$

The optimization ended with structural energy minimization when it reached the required accuracy. We have showed the unit-cell parameters, volume and the estimated density of $A_3BO_7$(A = Ga, Al; B = P, As) in Table 1. The corresponding experimental data of $Ga_3PO_7$ are also listed for comparison. Besides, the interatomic distances and angles are presented in Tables 2 and 3, respectively.

The LDA usually underestimates the lattice parameters, which can also be seen in our work. The maximum of underestimation occurs in volume with only −1.5% and it does not exceed −0.6% on the main distances, except one bond length of Ga–O (−1.2%).

**Table 1**
Optimized unit-cell parameters (Å), volume (Å$^3$) and the estimated density (g/cm$^3$) of each $A_3BO_7$ compounds. The percentage error compared with the experimental data are given in parenthesis.

| | $Ga_3PO_7$ | $Ga_3AsO_7$ | $Al_3PO_7$ | $Al_3AsO_7$ |
|---|---|---|---|---|
| $a$ | 7.8415 (−0.5%) | 8.1473 | 7.7769 | 7.9258 |
| $c$ | 6.6972 (−0.4%) | 6.9334 | 6.5711 | 6.6731 |
| $V$ | 356.6 (−1.5%) | 398.6 | 344.2 | 363.1 |
| $\rho$ | 4.919 (1.5%) | 4.951 | 3.241 | 3.676 |

**Table 2**
Bond length (Å) of each $A_3BO_7$ compounds.

| | $Ga_3PO_7$ | $Ga_3AsO_7$ | $Al_3PO_7$ | $Al_3AsO_7$ |
|---|---|---|---|---|
| $d_{A-O}$ | 1.851 (−0.6%) | 1.890 | 1.799 | 1.793 |
| | 1.858 (−0.4%) | 1.913 | 1.838 | 1.864 |
| | 1.880 (−0.3%) | 1.949 | 1.847 | 1.880 |
| | 2.113 (−1.2%) | 2.119 | 2.064 | 2.011 |
| $d_{B-O}$ | 1.515 (0.5%) | 1.689 | 1.517 | 1.673 |
| | 1.579 (0.3%) | 1.761 | 1.599 | 1.761 |

**Table 3**
Bond angle (°) of each $A_3BO_7$ compounds.

| | $Ga_3PO_7$ | $Ga_3PO_7$[a] | $Ga_3AsO_7$ | $Al_3PO_7$ | $Al_3AsO_7$ |
|---|---|---|---|---|---|
| O–A–O | 78.7 | 78.8 | 78.4 | 79.6 | 79.4 |
| | 90.8 | 90.5 | 90.9 | 91.7 | 91.2 |
| | 94.0 | 94.7 | 94.1 | 94.8 | 95.3 |
| | 101. | 100.3 | 103.7 | 97.7 | 100.8 |
| | 105.0 | 104.6 | 105.1 | 106.3 | 107.2 |
| | 125.4 | 125.5 | 125.9 | 125.2 | 125.3 |
| | 167.8 | 169.2 | 162.3 | 170.5 | 163.9 |
| O–B–O | 105.2 | 105.6 | 101.3 | 105.4 | 101.3 |
| | 113.4 | 113.0 | 116.3 | 113.2 | 116.3 |
| A–O–B | 123.4 | | 121.3 | 123.7 | 121.2 |
| $\theta$ | 149.5 | | 142.2 | 152.2 | 143.8 |

[a] Ref. [8].

**Table 4**
Theoretical values of the elastic constants (in GPa) of $SiO_2$ and the four $A_3BO_7$ compounds. Experimental data from Ref. [19] are given in parentheses.

| | $SiO_2$ | $Ga_3PO_7$ | $Ga_3AsO_7$ | $Al_3PO_7$ | $Al_3AsO_7$ |
|---|---|---|---|---|---|
| $C_{11}$ | 96.5 (86.7) | 237.0 | 199.6 | 303.3 | 276.5 |
| $C_{12}$ | 15.7 (6.9) | 109.0 | 81.9 | 125.6 | 119.7 |
| $C_{13}$ | 12.9 (11.9) | 141.0 | 119.2 | 133.2 | 123.2 |
| $C_{14}$ | 24.2 (17.9) | −11.5 | −4.8 | −11.1 | −2.5 |
| $C_{33}$ | 118.5 (107.1) | 310.0 | 262.8 | 346.0 | 286.7 |
| $C_{44}$ | 57.8 (57.9) | 70.5 | 72.5 | 97.0 | 97.6 |
| $C_{66}$ | 40.4 (39.9) | 64 | 59.3 | 88.9 | 78.4 |

In general, our results agree well with the experimental data reported in Ref. [8].

From Tables 1 and 2, it is clear that the $Ga_3AsO_7$ has the largest value of lattice parameters. Except two of Al–O bond lengths, $Al_3PO_7$ is the smallest one, slightly over that of $Al_3AsO_7$. It is maybe related to the outmost cutoff radius chosen in the pseudo-potential of every atom, that is, 2.3, 2.1, 1.9 and 1.9 Å for Ga, As, Al and P, respectively. Obviously, the combination of Ga and As atoms results in the largest volume. The trend of volume is showed as follows: $Ga_3AsO_7 > Al_3AsO_7 > Ga_3PO_7 > Al_3PO_7$.

However, there is no, as mentioned above, clear tendency between different bond angles, as showed in Table 3. The predicted O–A(B)–O angles of $Ga_3PO_7$ are very close to the available experimental data. Here we focus on the bridging angle $\theta$, which reflects the distortion degree of the lattice. The largest $\theta$ value is 152.2°, belonging to $Al_3PO_7$. $Ga_3AsO_7$ possesses the smallest $\theta$ value with 142.2°. The value of $\theta$ shows the order of $Ga_3AsO_7 < Al_3AsO_7$