2008

Optical property and electronic band structure of a piezoelectric compound Ga3PO7 studied by the first-principles calculation

Zhenxiang Cheng
University of Wollongong, cheng@uow.edu.au

Xiaolin Wang
University of Wollongong, xiaolin@uow.edu.au

Publication Details

Cheng, Z & Wang, X (2008), Optical property and electronic band structure of a piezoelectric compound Ga3PO7 studied by the first-principles calculation, Applied Physics Letters, 92(26), pp. 261915-1-261915-3.

Optical property and electronic band structure of a piezoelectric compound Ga3PO7 studied by the first-principles calculation

Abstract

The structure, electronic and optical properties of a piezoelectric material, Ga_3PO_7 were studied by first-principles calculations in the framework of density functional theory. The calculated structure is in agreement with the experimental data. Band structure reveals that Ga_3PO_7 has a band gap of 3.69 eV. Analysis of partial density of states and Mulliken charge population indicates existence of GaO_5 and PO_4 anion groups in Ga_3PO_7. Furthermore, its optical properties, including dielectric constant, absorption, reflectivity, refractive index, and electron loss were calculated and analysed, which show that Ga_3PO_7 has potential applications based on combination of its piezoelectric and optical properties.

Keywords

Optical, property, electronic, band, structure, piezoelectric, compound, Ga3PO7, studied, first, principles, calculation

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Cheng, Z & Wang, X (2008), Optical property and electronic band structure of a piezoelectric compound Ga3PO7 studied by the first-principles calculation, Applied Physics Letters, 92(26), pp. 261915-1-261915-3.

Optical property and electronic band structure of a piezoelectric compound Ga_3PO_7 studied by the first-principles calculation

Z. X. Cheng and X. L. Wang[a)]
Spintronic and Electronic Materials Group, Institute for Superconducting and Electronic Materials, University of Wollongong, New South Wales 2522, Australia

(Received 15 May 2008; accepted 17 June 2008; published online 3 July 2008)

The structure, electronic, and optical properties of a piezoelectric material, Ga_3PO_7, were studied by first-principles calculations in the framework of density functional theory. The calculated structure is in agreement with the experimental data. Band structure reveals that Ga_3PO_7 has a band gap of 3.69 eV. Analysis of partial density of states and Mulliken charge population indicates existence of GaO_5 and PO_4 anion groups in Ga_3PO_7. Furthermore, its optical properties, including dielectric constant, absorption, reflectivity, refractive index, and electron loss were calculated and analyzed, which show that Ga_3PO_7 has potential applications based on combination of its piezoelectric and optical properties. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2955827]

Ga_3PO_7, having a noncentrosymmetric trigonal structure with the space group of $R3m$, provides great potential in applications based on its optical, piezoelectric, and pyroelectric properties.[1] However, for a quite long time after Ga_3PO_7 was initially discovered, there were no further reports on its physical properties. This is mainly due to the difficulty in growing single crystals with sufficient size for measurement and application, especially optical measurement and application. Very recently, Ga_3PO_7 single crystals with sizes up to several centimeters have been grown by the high temperature flux method, which paves the way for further exploration of its optical and electro-optical properties, and eventually for practical applications.[2] Therefore, it is practically meaningful to study its optical and electronic structures. In this work, we present a series of first-principles density function calculations on the structural, electronic, and optical properties of Ga_3PO_7 material.

The calculations were performed using the plane-wave pseudopotential method based on density functional theory (DFT) with the generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof.[3] The ion-electron interaction was modeled by ultrasoft Vanderbilt-type pseudopotentials.[4] Mulliken charges were calculated according to the formalism described by Segall *et al.*[5] A plane-wave cutoff energy of 400 eV was employed throughout the calculation. For the sampling of the Brillouin zone, the electronic structures and optical properties use $5\times5\times5$ and $8\times8\times8$ k-point grids, respectively, generated according to the Monkhorst–Pack scheme.[6]

The optical properties of Ga_3PO_7 are determined by the frequency-dependent dielectric function $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$, which is mainly connected to the electronic structures. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function $\varepsilon(\omega)$ is calculated from the momentum matrix elements between the occupied and unoccupied electronic states and given by

$$\varepsilon_2=\frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{k,v,c}|\langle\psi_k^c|\hat{u}\cdot r|\psi_k^v\rangle|^2\delta(E_k^c-E_k^v-E), \quad (1)$$

where ω is the light frequency, e is the electronic charge, and ψ_k^c and ψ_k^v are the conduction band (B) and valence band (VB) wave functions at k, respectively. The real part $\varepsilon_1(\omega)$ is derived from the imaginary part $\varepsilon_2(\omega)$ by the Kramers–Kronig transformation. All the other optical constants, such as the absorption spectrum, refractive index, and reflectivity are derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$.[7]

The structure of Ga_3PO_7 comprises PO_4 tetrahedral and GaO_5 trigonal bipyramids connected by edges to form Ga_3O_{10} clusters. The structure is isotopic with Fe_3PO_7 and Ga_3PO_7 is the third known compound in the Ga–P–O system.[1,8] Figure 1 shows the perspective views of the Ga_3PO_7 structure. We used experimentally measured x-ray diffraction data as the initial input for geometry optimization. The lattice parameters was calculated and fitted to third order Birch–Murnaghan equations of states.[9,10] Table I compares the experimental and calculated data. The results show that the optimized structure expands slightly in comparison to the experimental data, which is natural due to the experimental data is derived from the single crystal grown in a high pressure environment. However, the volume difference is quite small with a value of 2.7%.

The energy band structure is calculated along the high-symmetry directions in the Brillouin zone, as shown in Fig. 2. The total density of states (DOS) and the partial DOS (PDOS) are plotted in Fig. 3.

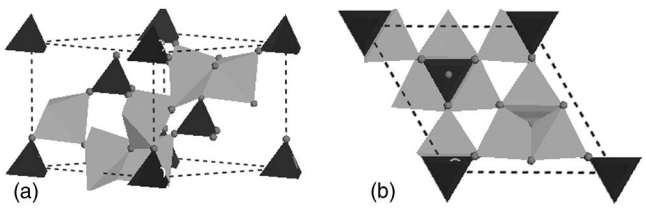

FIG. 1. Crystalline structure of the Ga_3PO_7 crystal. (a) Perspective view from original position. (b) Perspective view projected along the c axis with the a axis horizontal and the b axis close to vertical. The GaO_5 and PO_4 polyhedra are represented in black and light gray.

[a)]Electronic mail: xiaolin@uow.edu.au.

TABLE I. Calculated and experimental lattice parameters of Ga_3PO_7.

		a (Å)	c (Å)	V (Å^3)
Ga_3PO_7	Calc.[a]	7.971	6.764	372.15
Ga_3PO_7	Expt.[b]	7.885	6.727	362.20

[a]This work.
[b]Reference.

The top of the VB is mainly composed of O 2*p* states, some P 3*p* states, and a slight contribution from Ga 4*p* and 4*s* states. The bottom of the CB is dominated by Ga 4*p*, in addition to a tiny amount of O 3*p* states and P 3*p* states. Ga_3PO_7 presents a direct band gap of 3.69 eV at the Γ point, which corresponds to an absorption edge of 336 nm. The band gaps predicted by the DFT are usually smaller than the experimental data, which means that the calculated results underestimate the real band gaps implying that the absorption edge should be shorter than 336 nm. In our calculation, the scissor operators on both the electronic structure and the optical properties were not considered. The energy bands below −20 eV are contributed by P 3*s* states. The energy bands between −16 and −20 eV are mainly comprised of O 2*s* states and P 3*p* states. Ga 3*d* states form the energy bands around −12 eV, which are highly localized, as evidenced by a very sharp peak in the DOS. The states of O 2*p*, Ga 4*p* and 4*s*, and P 3*p* form the energy bands from −10 eV to the Fermi surface. In the CB, the states are formed by unoccupied Ga 4*p*, Ga 4*s*, P 3*s*, P 3*p*, and O 2*p*. By analyzing the PDOS, it was found that the O 2*p* states had a strong admixture with P 3*s* states, as well as Ga 4*p* and 4*s* states, which is evidenced by the large number of peaks and the big width of the PDOS of Ga and P in the VB region. The small value of the PDOS of the Ga 4*p* and 4*s*, and P 3*s* states in this region, in contrast to the large value of O 2*p*, indicates the electron transfer to O 2*p* from P 3*p*, and Ga 4*p* and 4*s*. Therefore, Ga_3PO_7 has a strong covalent character, involving both Ga–O and P–O bonds. However, the P–O bond is more covalent than the Ga–O bond. The bond analysis is in accordance with the character of the structure of Ga_3PO_7, with two anion groups of PO_4 tetrahedra and GaO_5 trigonal bipyramids.

To better understand the bonding behavior of Ga_3PO_7, A calculation of the Mulliken charge population was performed, which is shown in Table II. The charge transfers from Ga and P to O are about 1.52*e* and 2.27*e*, respectively. The bond order analysis shows that the P–O bond has values of 0.59 and 0.71, depending on the coordination environment, while the Ga–O bond has more variable bond order values of 0.55, 0.5, 0.43, and 0.14, depending on the coordination environment in the Ga_3PO_7 structure. The closer to 1 of the bond order is the more covalent character the bond has. Therefore, the P–O bond shows more covalent character than the Ga–O bond.

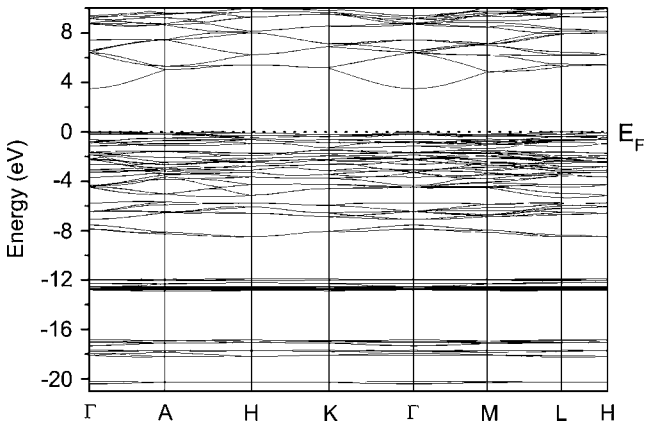

FIG. 2. Energy band structure of the trigonal Ga_3PO_7. The high-symmetry k point Γ, A, H, K, M, and L in the figure represent the points (0, 0, 1/2), (−1/3,2/3,1/2), (−1/3,2/3,0), (0, 0, 0), (0,1/2,1/2), and (−1/3,2/3,1/2), respectively.

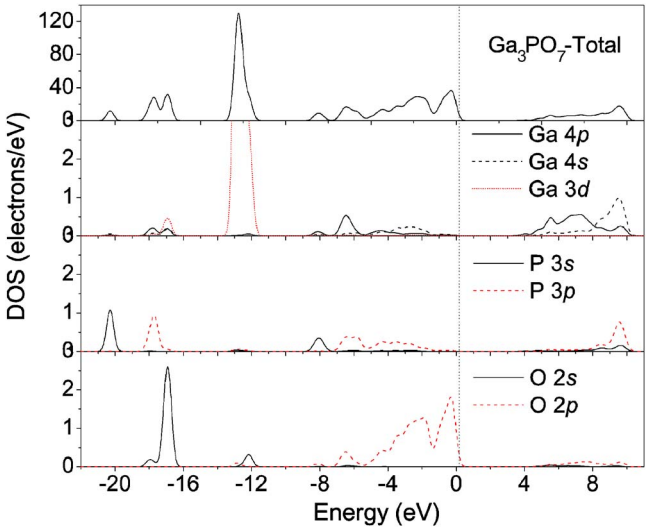

FIG. 3. (Color online) Total DOS and PDOS of trigonal Ga_3PO_7.

The calculated dielectric functions of Ga_3PO_7 when the incident radiation has linear polarization along the [001] and [100] directions are shown in Fig. 4. Due to the symmetry of the crystal structure, the dielectric function when the incident radiation is polarized along the [100] direction has the same form as the one where the incident polarization is along the [010] direction. The peaks of the imaginary part of the dielectric function are related to the electron excitation. These peaks with relatively strong intensity are located at 6.12 eV (A), 8.2 eV (B), 10.13 eV (C), 15.7 eV (D), 22.1 eV (E), and 26.6 eV (F) for the curve with incident radiation along the [100]/[010] directions. Peaks A, B, and C correspond to the electron transition from the O 2*p* VB to the Ga 4*p* and 4*s* CB. Peak D corresponds to the transition from the O 2*p* VB to the P 3*p* CB. Peaks E and F are ascribed to the transition of inner electron excitation from O 2*s* and P 3*s* to the CB. The peaks corresponding to electron excitation when the incident light is polarized along the [001] direction are located at similar positions, however, the peak intensities are somewhat different, due to the structure anisotropy of the compound. The calculated static dielectric constants, $\varepsilon_1(0)$, are 2.36 and 2.30, when incident radiation is polarized along the [001] and the [010/100] directions, respectively.

TABLE II. Mulliken charge population of Ga_3PO_7.

Species	s	p	d	Total (e)	Charge (e)
O_1	1.84	5.08	0	6.92	−0.92
O_2	1.82	5.22	0	7.03	−1.03
O_3	1.84	5.13	0	6.97	−0.97
P	0.89	1.84	0	2.73	2.27
Ga	0.54	0.95	9.99	11.48	1.52

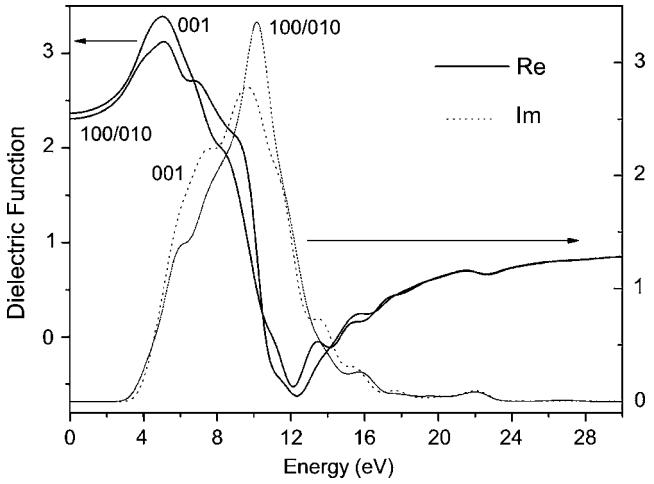

FIG. 4. Anisotropic dielectric function of trigonal Ga_3PO_7.

The calculated results on the anisotropic optical absorption spectrum, refractive index, reflectivity, and energy-loss spectrum are shown in Figs. 5(a)–5(d). In our calculation, we use Gaussian smearing of 0.5 eV. The optical absorption starts at 3.7 eV for the incident radiation polarized along both the [100/010] and the [001] directions, which corresponds to light with a wavelength of 334 nm, which is close to the 350 nm of the $KTiPO_4$ crystal, a famous nonlinear optical phosphate.[11] Above 3.7 eV, the absorption increases continuously before reaching a maximum. However, the absorption is just 10% of the peak absorption intensity at 5.10 eV (242 nm). Simultaneously, this material has a very low reflectivity over a large range of energy for both types of polarized incident radiation (<0.1 below 5.17 eV, 239 nm). These results indicate that Ga_3PO_7 is transparent to the light with wavelengths longer than 334 nm. The calculated refractive index is found to be 1.64 at 400 nm along the two directions, [100/010] and [001], which is very close to the ~1.62 of $GaPO_4$, a famous piezoelectric phosphate having the same PO_4 tetrahedra in its structure as Ga_3PO_7.[12] From the similarity of the values of the absorption edges and the refractive indices of these phosphates, it is obvious that these two properties are decided by PO_4 anions group. The energy-loss spectrum describes the energy loss of a fast electron traversing the material and is usually large at the plasma energy. Three prominent peaks were found at 13.02, 14.84, and 16.01 eV along the [001] direction, which are consistent with the roots of $\varepsilon_1(\omega)$ and correspond to a rapid reduction in the reflectance.

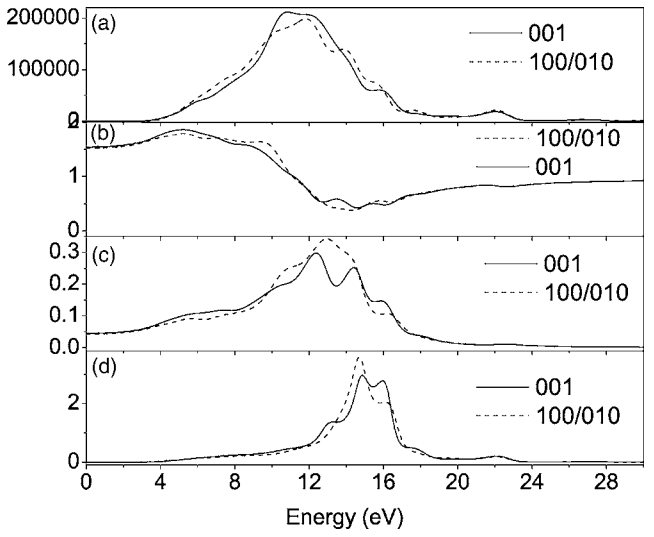

FIG. 5. Anisotropic optical properties of the Ga_3PO_7 (a) absorption spectrum, (b) refractive index, (c) reflectivity, and (d) energy-loss spectrum.

In summary, we calculated the structural parameters, electronic structures, and optical properties of Ga_3PO_7 by means of the DFT within GGA. Our structural parameters are in agreement with the experimental data. The electronic structures of Ga_3PO_7 show that the top of the VB and the bottom of the CB are determined by O $2p$ and Ga $4p$ states, respectively. Although the P–O bond shows stronger covalent bonding than the Ga–O bond, both bonds are regarded as covalent, which proves that the existence of the two functional anion groups in Ga_3PO_7. Anisotropic dielectric and optical properties, including dielectric function, absorption, reflectivity, and energy loss, were calculated and discussed in detail. The results show that Ga_3PO_7 has potential applications in optoelectric devices.

This work was supported by the Australian Research Council through Discovery Projects (DP0558753 and DP0665873).

[1]S. Boudin and K.-H. Lu, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **C54**, 5 (1998).
[2]G. Xu, J. Li, J. Wang, H. Zhao, X. Cheng, and W. Gao, Appl. Phys. Lett. **92**, 101906 (2008).
[3]J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[4]D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[5]M. D. Segall, C. J. Pickard, R. Shah, and M. C. Payne, Mol. Phys. **89**, 571 (1996).
[6]H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[7]S. Saha, T. P. Sinha, and A. Mookerjee, Phys. Rev. B **62**, 8828 (2000).
[8]A. Modaressi, A. Courtois, R. Gerardin, B. Malaman, and C. Gleitzer, J. Solid State Chem. **47**, 245 (1983).
[9]F. Birch, J. Geophys. Res. **83**, 1257 (1978).
[10]F. Birch, Phys. Rev. **71**, 809 (1947).
[11]W. Y. Ching and Y. N. Xu, Phys. Rev. B **44**, 5332 (1991).
[12]S. Defregger, G. F. Engel, and P. W. Krempl, Phys. Rev. B **43**, 6733 (1991).