

Theoretical investigation of the electronic and optical properties of pseudocubic Si_3P_4 , Ge_3P_4 and Sn_3P_4

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Abstract: Group-IV phosphides are relatively unknown materials as compared to the Group-IV carbide. In this work, we detailed the first principles calculations of the electronic and optical properties of the pseudocubic M_3P_4 ($\text{M}=\text{Si}, \text{Ge}, \text{Sn}$) using the density function theory (DFT). Results are in good agreement with those previous works. Furthermore, the optical constants, such as the dielectric function, energy loss function and effective number of valence electrons are calculated and presented in the study.

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References and links

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1. Introduction

IV-V compounds have attracted great attentions in the last decade due to their important applications. C₃N₄, Si₃N₄ and Ge₃N₄ are well known for their high bulk moduli and wide band gaps to be used as the high-performance engineering materials [1-3]. Recently, Feng *et al* investigated the structural properties and bulk moduli of C₃P₄, Si₃P₄, Ge₃P₄ and Sn₃P₄ by using the first principles calculations successfully to predict that the most stable phase of those compounds is the pseudocubic structure [4-9]. Their results show that the bulk modulus decreases as the group-IV atom changed from C to Sn and it is much smaller than that of the corresponding Nitrides. For Bulk M₃P₄, however, there is still lack of the experimental data for the crystalline M₃P₄. In this work, we made continuous efforts to study the structural and optical properties of bulk M₃P₄ in consideration of their stable phase.

The electronic structures and optical properties of pseudocubic M₃P₄ are studied based on the first-principles density function theory [10, 11] with the generalized gradient approximation (GGA) [12]. We first carefully calculated the electronic structures, because the optical properties depend on both the inter- and intra-band transitions. Afterwards, we present the optical properties of pseudocubic M₃P₄ in our work, including the dielectric function, electron energy loss function and effective number of the valence electrons. The paper is organized as follows: A brief description of the calculation method is given in Sec. II; the results for optimized structural parameters, band structures, dielectric properties and some discussions are shown in Sec. III; and a summary is finally drawn in Sec. IV.

2. Computational method

First-principles total-energy calculations were performed using the CASTEP code [13]. The generalized gradient approximation for exchange-correlation effects and the Vanderbilt ultrasoft pseudopotentials were used in the calculations. The maximum plane-wave cutoff energy was taken as 300eV and the numerical integration of the Brillouin zone was performed using a 5×5×5 Monkhorst-Pack k-point sampling procedure.

3. Results and discussion

The structural properties, including the crystal structure, lattice constant and bulk modulus, are very important to understand other properties of the material fundamentally. Previous works showed that the pseudocubic Si₃P₄, Ge₃P₄ and Sn₃P₄ all have the lower energy than

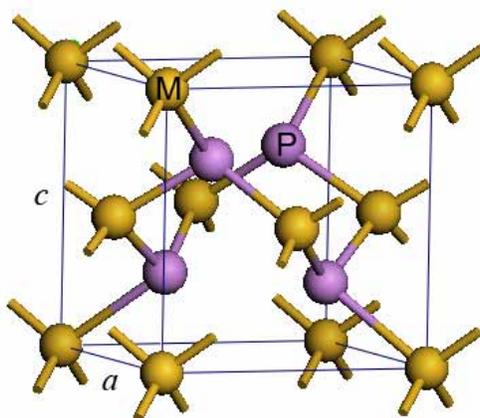


Fig. 1. Ball-stick model of pseudocubic-M₃P₄

other structures in the study [6-9]. The pseudocubic phase (Fig. 1), which is a type of the defective zinc-blend structure, belongs to the $P\bar{4}2m$ space group and is both energetically and mechanically stable when M_3P_4 compounds are formed.

In this work, we first optimized the geometrical structure of M_3P_4 compounds in the ground states. In table 1, we present the calculated lattice constants (a and c), the bulk modulus (B_0) and bond length as compared to the theoretical results in previous works. Our results of the lattice constant agree well with other theoretical results within the difference of about 1% and there is no big difference between a and c , especially for Si_3P_4 and Ge_3P_4 . Therefore, this pseudocubic phase shows little anisotropic properties though atoms are missed on the planes of the ideal zinc-blend structure along the c -axis.

Table 1 Calculated equilibrium structure parameters and properties of the pseudocubic M_3P_4

		Si_3P_4	Ge_3P_4	Sn_3P_4
Lattice constant (Å)				
This work	a	5.038	5.142	5.531
	c	5.038	5.142	5.504
Previous work (Ref.6)	a	5.027		
	c	4.998		
Bulk modulus (GPa)				
This work		74.28	61.83	47.51
Previous work B_0		77(Ref. 6)	62(Ref. 8)	36(Ref.8)
Bond length(Å)		2.26	2.32	2.51

By applying the small strains onto the equilibrium lattice, the bulk moduli of M_3P_4 are obtained by fitting the calculated total energy vs volume data to Murnaghan equation of states. The calculated bulk moduli given in table 1 are close to that of previous works. The small differences maybe come from the parameters selected in our calculations. For example, we used the exchange correlation potential of the PBE form of GGA, while the work of Ref. 6 selected the PW91 form.

The calculated band structures of the pseudocubic M_3P_4 are plotted in Fig. 2. The results show that they all have the small and indirect band gaps. The indirect band gap of Si_3P_4 occurs

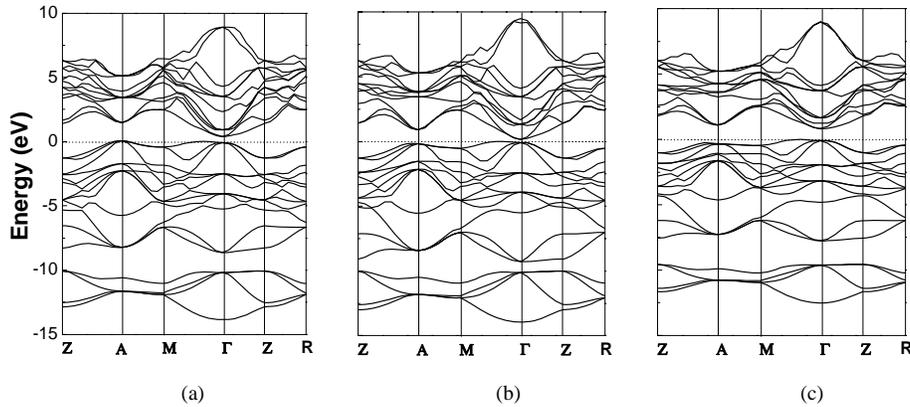


Fig. 2. Calculated band structure for pseudocubic- M_3P_4 . (a) Si_3P_4 , (b) Ge_3P_4 and (c) Sn_3P_4

between the A and Γ points corresponding to the valence and conduction bands, respectively. The tops of the valence bands of the Ge_3P_4 or Sn_3P_4 structures, however, are located at the points that are near the Γ point along the Γ -M direction.

The values of calculated band gaps of Si_3P_4 , Ge_3P_4 and Sn_3P_4 are 0.33eV, 0.17eV and 0.83eV, respectively. Since the GGA method may underestimate the band gap and there is no experiment carried out for these compounds, the band gap calculated by GW quasiparticle theory may give more accurate value [14, 15]. Anyway, the results show that all three compounds are indirect band gap semiconductors and the band gap of Sn_3P_4 is wider than the others.

The gross features of the density of states (DOS) from M_3P_4 compounds are quite similar, so we only show the result for Si_3P_4 as an example in Fig. 3. It can be seen that there are three regions in the energy range of the valence band. In the first region, the band with the energy ranging from -14 eV to -9 eV is mainly from the 3s states of P and Si sites. In the second region, the band with the energy ranging from -9 eV to -6 eV is hybridized by the 3s and 3p states. The third region of the valence band ranging from -6eV to 0 eV, combined with the conduction band above the energy level of 0 eV, is mostly originated from the 3p states of the P and Si sites.

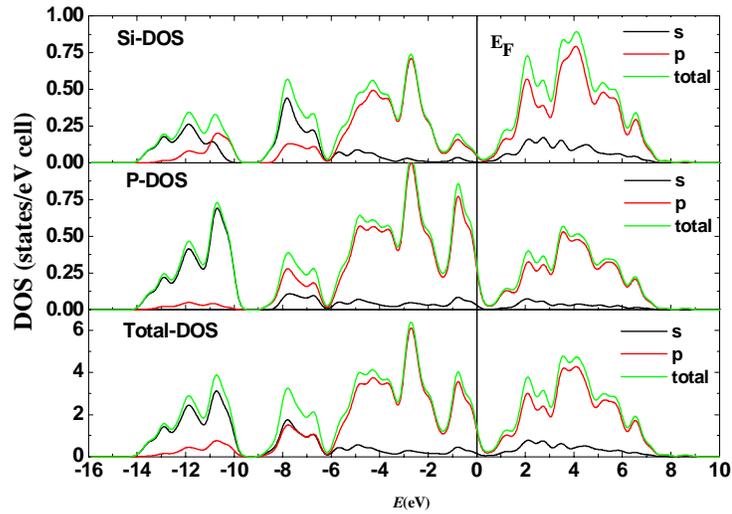


Fig. 3. Calculated total and partial density of states for pseudocubic- Si_3P_4

It is well known that the linear electronic response of a system to an external electromagnetic field can be measured by the complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The imaginary part of the dielectric function $\epsilon_2(\omega)$ can be obtained from the electronic structure calculations by using the matrix elements between the occupied and unoccupied wave functions.

In terms of the electric-dipole approximation, the imaginary part of the dielectric functions can be calculated by the following formula:

$$\epsilon_2(\omega) = \frac{8\pi^2 e^2}{\omega^2 m^2 V} \sum_{c,v} \sum_{\mathbf{k}} |\langle c, \mathbf{k} | \hat{\mathbf{e}} \cdot \mathbf{p} | v, \mathbf{k} \rangle|^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) \quad (1)$$

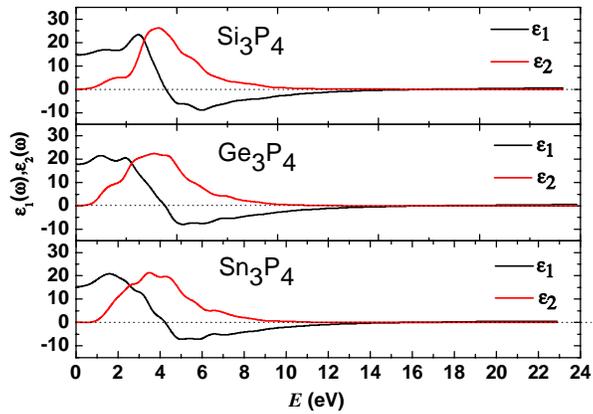
where c and v represent the conduction and valence bands, respectively; $|n, \mathbf{k}\rangle$ is the eigenstate obtained from band structure calculations; \mathbf{p} is the momentum operator; $\hat{\mathbf{e}}$ is the external field vector; and ω is the frequency of incident photons.

The real part $\epsilon_1(\omega)$ can be derived from the $\epsilon_2(\omega)$ by the Kramer-Kronig transformation. Furthermore, other optical properties like the energy loss function $L(\omega)$ can be derived from $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ as

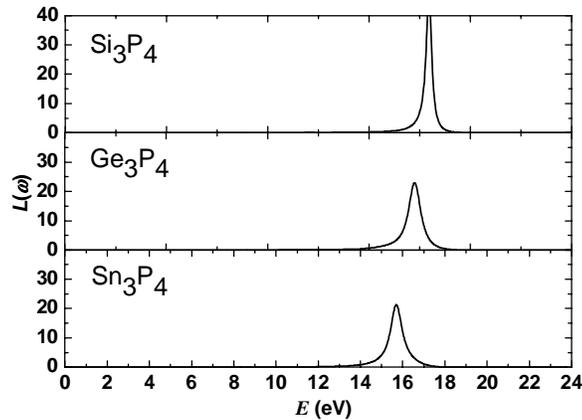
$$L(\omega) = \epsilon_2(\omega) / (\epsilon_1^2(\omega) + \epsilon_2^2(\omega)) \quad (2)$$

We calculated both of the longitudinal and transverse dielectric functions to see that these two functions are almost identical within the difference of about 1%. It indicates that the IV-V compounds with the pseudocubic phase are not strongly anisotropic though they are structurally asymmetric. Therefore, only the longitudinal optical properties of M_3P_4 are taken into consideration in the study.

The comparison of the calculated optical properties for the three pseudocubic compounds is given in Fig. 4. The imaginary dielectric function $\epsilon_2(\omega)$ represents the optical absorption of the material. Each spectrum has a prominent absorption peak. They are located at about 4.0, 3.9 and 3.5 eV photon energy, respectively. The imaginary part $\epsilon_2(\omega)$ of Si_3P_4 around 4.0 eV is mainly attributed to the transitions at the Γ point from 0.41 eV to 4.05 eV and 4.28 eV to -0.09 eV. The $\epsilon_2(\omega)$ peak of Ge_3P_4 is located at about 3.9 eV, corresponding to the transitions from 0.17 eV to -3.9 eV and 4.1 eV to -0.1 eV at the Γ point. For the Sn_3P_4 structure, the peak occurs at about 3.5 eV and is due to the main part of transitions from 1.6 eV to -1.9 eV at the Γ point. It is noted that the peak shown in the $\epsilon_2(\omega)$ spectra is not just due to the single interband transition since the multiple direct and indirect transitions will happen around the same energy peak positions.



(a)



(b)

Fig. 4. Dielectric functions (a) and energy-loss function (b) of M_3P_4

The real dielectric function $\epsilon_1(\omega)$ is obtained from $\epsilon_2(\omega)$ by the Kramers-Kronig transformation. In the zero frequency limit, $\epsilon_1(\omega)$ is the static dielectric constant, excluding any contribution from the lattice vibrations. The static dielectric constants for the three compounds are 14.66, 18.03 and 15.32, respectively. These values seem larger than that of c -(Si, Ge) $_3$ N $_4$ in the cubic spinal structure [16].

The energy loss function is an important optical parameter to show the peak often associated with the plasma frequency and described as the plasma resonance [17]. Above and below the plasma frequency the material will have the dielectric and metallic properties, respectively. The calculated peak of $L(\omega)$ of Si $_3$ P $_4$ is located at about 18 eV, while those of Ge $_3$ P $_4$ and Sn $_3$ P $_4$ are shifted to lower energies at about 17.5 eV and 15 eV, respectively.

Since the plasma resonance is intrinsically arisen from the collected oscillations of free electrons, the effective number $n_{eff}(\omega_m)$ of valence electrons per atom that contributes to the interband transitions can be calculated in terms of the expression as

$$n_{eff}(\omega_m) = \frac{2m\epsilon_0}{\pi e^2} \int_0^{\omega_m} \omega \epsilon_2(\omega) d\omega \quad (3)$$

where ω_m denotes the upper limit of integration, and the quantities m and e are the electron mass and charge, respectively. The results are shown in Fig. 5. The effective number of valence electrons of M $_3$ P $_4$ decreases with increasing atomic number. The saturated $n_{eff}(\omega_m)$

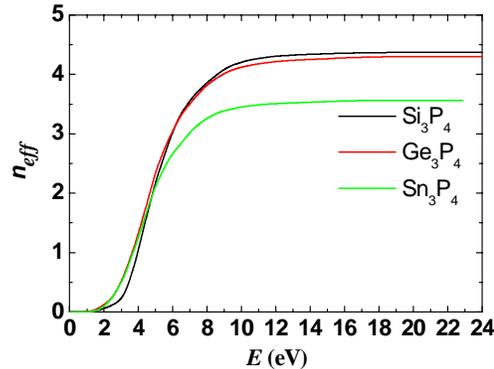


Fig.5. The calculated effective number of valence electrons (n_{eff}) participating in the interband optical transitions of M $_3$ P $_4$

above 10 eV is close to the average number of the valence electrons per atom in M $_3$ P $_4$. The discrepancies of peak positions in the energy loss function [see Fig. 4(b)] partly attribute to the different saturated values of n_{eff} for the Si $_3$ P $_4$, Ge $_3$ P $_4$ and Sn $_3$ P $_4$ structures.

4. Conclusion

The electronic structures and optical properties of the pseudocubic Si $_3$ P $_4$, Ge $_3$ P $_4$ and Sn $_3$ P $_4$ have been studied by using the first principles density functional method. The energy band and density of states are calculated as compared to that of previous works. Results are in good agreement with early ones to show that the pseudocubic Si $_3$ P $_4$, Ge $_3$ P $_4$ and Sn $_3$ P $_4$ all have indirect band gaps. The bulk modulus of M $_3$ P $_4$ is lower than that of M $_3$ N $_4$. The complex dielectric and energy loss functions are also calculated based on the band structure. The effective number of the valence electrons of M $_3$ P $_4$, which contributes to the interband optical transitions, decreases with increasing atomic number. The results show that the electronic and optical properties of the M $_3$ P $_4$ compounds having the pseudocubic phase are nearly isotropic.

Acknowledgments

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