

Electronic Properties of Orthorhombic, Tetragonal and Monoclinic KDP by First-Principles Calculations

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Abstract

The electronic properties of KDP (KH_2PO_4), in orthorhombic, tetragonal and monoclinic phases, have been investigated by using the generalized gradient approximation (GGA) within density functional theory. The comparison of the calculated band gap of the tetragonal crystal and the experimental results shows that the band gap of this paper is very close to the experimental results. In addition, this work calculates the effective mass of KDP for the first time. The effective mass of electrons in the conduction bands of the orthorhombic phase is greater than that of the tetragonal phase, so the mobility of electrons in the tetragonal phase is higher than that of the orthorhombic phase. The calculated DOS shows that the lower conduction band is composed of the K-3p states, P-3p states and O-2p states. There is a strong hybridization between P and O orbitals.

1. Introduction

Potassium dihydrogen phosphate (KH_2PO_4 , KDP) crystal is a large-sized single crystal. KDP crystal is the perfectly artificial crystal due to its excellent nonlinear optical properties [1–2]. KH_2PO_4 is a typical member of the large family of ferroelectric compounds. Since Busch and Scherrer (1935) first discovered that KDP itself has a ferroelectric transition [3–6], KDP are widely used in high-power laser systems due to its high laser damage threshold, large nonlinear optical coefficient, easy phase matching, large transmission frequency bandwidth and others excellent properties [2, 7]. At room temperature, KDP is paraelectric and has a tetragonal crystal structure (space group $I2d$) [8]. At present, it is mainly used in electro-optical shutters, electro-optical modulation and solid-state light modulation, and it is also an indispensable optical element for manufacturing large laser systems [7, 9]. However, the existence of shortcomings in KDP crystals has greatly affected its application. Because KDP is soft and brittle, easy to deliquesce, sensitive to temperature changes, anisotropy and other unfavorable processing characteristics, it is currently recognized as one of the difficult to process optical materials. In addition, KDP crystals are also susceptible to external factors, such as high temperature and high pressure [10–11].

KDP ferroelectric materials are widely studied, such as the effect of pressure on the soft acoustic mode of KDP [12], attenuation of low-frequency elastic oscillation of KH_2PO_4 -type ferroelectric crystals [13], anomalous dielectric behavior of KH_2PO_4 -type crystal in the ferroelectric phase [14], frequency angle spectrum of polarized light passing through porous structure KH_2PO_4 [15]. Zhang et al. [16] the electronic structure of the paraelectric and ferroelectric phases of KH_2PO_4 was calculated using the pseudopotential method. Wang et al. [17] reported that potassium dihydrogen phosphate is an important material that has been incorporated into the harmonic generation and electro-optical switching of various laser systems. Recently, Menchón et al. [18] studied the lattice dynamics of potassium dihydrogen phosphate (KDP) and its deuterated simulated DKDP through first-principles DFT calculations. The smallest model describing the isotope effect in KDP should involve at least three fully coupled vibration modes. From the above literatures, the nature and application of KDP crystals have attracted widespread attention. However,

most of the studies on KDP crystals focus on optical properties and anomalous dielectric behaviors, and few studies on the electronic properties of KDP. Therefore, the main purpose of this study is to study the electronic structure of KDP.

First of all, we established orthorhombic, tetragonal and monoclinic structure models of KDP crystals. Secondly, these structures are calculated using first-principles methods to obtain a stable KDP crystal structure. Finally, we selected five structures with different space group to analyze the electronic properties of KDP crystals.

2. Computational Methods

The first-principles methods were enforced using the norm conserving pseudopotentials based on density functional theory [19] as applied in CASTEP [20]. The Perdew-Burke-Ernzerhof + Grimme (PBE + G) form of the generalized gradient approximation (GGA) [21, 22] was used as the energy function of exchange correlation [23]. The H $1s^1$ orbitals, O $2s^2 2p^4$ orbitals, P $3s^2 3p^3$ orbitals, and K $3s^2 3p^6 4s^1$ orbitals were regarded as valence states. The cutoff energy was 830 eV. A k -point mesh according to the Monkhorst-Pack scheme [24] was used for integration over the first Brillouin zone. The maximum force was less than $0.01 \text{ eV}/\text{\AA}$, maximum displacement and maximum stress were less than $5.0 \times 10^{-4} \text{ \AA}$ and 0.02 GPa, respectively.

3. Results And Discussion

3.1 Band structures and band gaps

In this paper, the KDP structures of five different space groups are analyzed. The orthorhombic space groups belong to $Fdd2$ and $P2_1 2_1 2_1$, the tetragonal space group belongs to $I2d$, and the monoclinic space groups belong to $C12/c1$ and $P12/c1$.

The band structures of the orthorhombic, monoclinic and tetragonal crystals of KDP are calculated along the direction of high symmetry in the Brillouin zone, as shown in Fig.1. The calculated band gaps of orthorhombic KDP crystals are 5.201 eV (space group belongs to $Fdd2$) and 4.965 eV (space group belongs to $P2_1 2_1 2_1$), respectively. The band gap of the tetragonal (space group belongs to $I2d$) crystal is 5.438 eV, while the band gap of the monoclinic crystal is 5.401 eV (space group belongs to $C12/c1$) and 4.785 eV (space group belongs to $P12/c1$), respectively. In Fig.1, the energy scale in all graphs is in eV, and the top of the valence band is set to zero (Fermi level) on the energy scale. It can be clearly seen from the figure that the band gap of KDP is obvious. The calculated band gap of the tetragonal crystal (5.438 eV) is compared with the theoretical values 4.35 eV [25] and 4.178 eV [26], as well as the experimental value 7.12 eV [27]. The calculated value of the tetragonal KDP bandgap is greater than the other theoretical values, and the calculated result is closer to the experimental value, indicating that the calculation method in this paper is more accurate and reliable. Figure 1 shows that the band gap of

paper is smaller than the experimental result, but larger than the other theoretical results. This difference in density functional theory (DFT) calculations is mainly due to the approximation used to exchange correlations. The comparison between the calculated band gap of the tetragonal crystal and the experimental results shows that the band gap of this paper is very close to the experimental results.

On the other hand, we use the following well-known relationship for calculating effective mass [28]:

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2}$$

According to the above formula, the effective mass of electrons and holes is calculated. The effective mass of electrons (holes) is determined by fitting the band structure of electrons (holes) to a parabolic function. The GGA-PBE + G method is adopted in the first Brillouin zone. The effective mass of electron for the orthorhombic, monoclinic and tetragonal KDP are obtained from the curvature of the conduction band at G point.

The effective mass of the obtained KDP electrons (holes) is shown in Fig. 2. The calculated electron effective mass for orthorhombic (space group belongs to $Fdd2$) KDP in the X→Y direction is $1.802 m_0$, and the effective mass of the hole in the Z→G direction is $5.086 m_0$. In a similar way, the calculated electron effective mass for orthorhombic (space group belongs to $P2_12_12_1$) KDP in G→Z direction is $2.741 m_0$, and hole effective mass in the S→U direction is $6.050 m_0$, respectively. On the other hand, the electron effective mass of tetragonal KDP is $1.254 m_0$. The effective mass of electrons in the conduction band of the orthorhombic phase is greater than that of the tetragonal phase, so the mobility of electrons in the tetragonal phase is higher than that of the orthorhombic phase. In Fig. 2, the electrons effective mass of monoclinic (space group belongs to $C12/c1$) KDP in the G→V direction is $0.573 m_0$, and the effective mass of hole in the L→M direction $0.077 m_0$, respectively. Corresponding, the electrons effective mass of monoclinic (space group belongs to $P12/c1$) KDP in the Z→Y direction is $2.3 m_0$, and the effective mass of hole in the G→Y direction are $0.069 m_0$, respectively. At present, there is no theoretical study on the effective mass of KDP. We hope that some conclusions of this work can provide reference for future research.

3.2 Density of states

The electron distribution in energy is described by the density of states (DOS). The calculated total density of states (TDOS) and partial density of states (PDOS) for KDP are shown in Fig.3. For orthorhombic (space groups belong to $Fdd2$ and $P2_12_12_1$) and tetragonal (space group belongs to $I4d$) crystals of KDP, the trend of DOS is similar. Obviously, the valence band structure of the orthorhombic and tetragonal KDP contains many peaks, and the density of states is relatively large. In Fig.3, the DOS of KDP mainly divided into two parts. The first part of the energy between -12 eV to 0 eV mainly come from the contribution of the K-3p, H-1s, P-3p and O-2p states, and part of the P-3s state. The

second part of the energy between 0 eV to 12 eV mainly come from the contribution of the P-3s state, P-3p state and portion of K-3s, K-3p, P-

3s, O-2p states. The DOS configuration of monoclinic KDP (space group belongs to $C12/c1$) crystal is mainly separated into two parts. The first part from -12 eV to 0 eV is mainly composed of K-3p, H-1s, P-3s and O-2p states, and part P-3p and O-2s states. The second section between 0 eV to 15 eV is mainly composed of H-1s, P-3s, P-3p states and part of K-3s, K-3p, O-2p states. Similarly, the DOS of monoclinic(space group belongs to $P12/c1$) KDP crystals mainly divided into two parts. The first portion from -12 eV to 0 eV mainly come from the contribution of K-3p, H-1s, P-3p and O-2p states and portion of P-3s, O-2s states. Secondly, from 0 eV to 15 eV is determined by the main H-1s, P-3p and O-2p states and part of K-3s, K-3p, P-3s states. To sum up, for orthorhombic and tetragonal crystals of KDP, Fig.3 shows that there are many relatively local states at the top of the valence band, mainly from P-3p and O-2p, and there is a covalent mixture between them. The lower conduction band is composed of K-3p state, P-3p state and O-2p state. The localized K-p state is located at about -12.5 eV for orthorhombic, and the tetragonal and monoclinic phases are between -12.5 eV and -10 eV. There is a strong hybridization between P and O orbitals.

4. Conclusions

The electronic properties of KDP in orthorhombic, monoclinic and tetragonal phases were studied using DFT with GGA-PBE+G. The calculated fundamental band gaps of orthorhombic KDP crystals are 5.201 eV (space group belongs to $Fdd2$) and 4.965 eV (space group belongs to $P2_12_12_1$), respectively. The band gap of the tetragonal (space group belongs to $I2d$) crystal is 5.438 eV, while the band gap of the monoclinic crystal is 5.401 eV (space group belongs to $C12/c1$) and 4.785 eV (space group belongs to $P12/c1$), respectively. The comparison between the calculated band gap of the tetragonal crystal and the experimental results shows that the band gap of this paper is very close to the experimental results. In addition, the effective mass of electrons in the conduction band of the orthorhombic phase is greater than that of the tetragonal phase, so the mobility of electrons in the tetragonal phase is higher than that of the orthorhombic phase. The calculated DOS shows that the lower conduction band is composed of the K-3p state, P-3p state and O-2p state. There is a strong hybridization between P and O orbitals.

Declarations

Author contribution Xia Xu: conceptualization, data curation, formal analysis, investigation, methodology, writing—original draft

Ning Yang: investigation, methodology, writing—review and editing

Bin Tang: methodology, software, writing—review and editing

Qi-Jun Liu: conceptualization, investigation, methodology, project administration, supervision, resources, writing—review and editing

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Data availability The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Code availability N/A

Conflict of interest The authors declare no competing interests.

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Figures

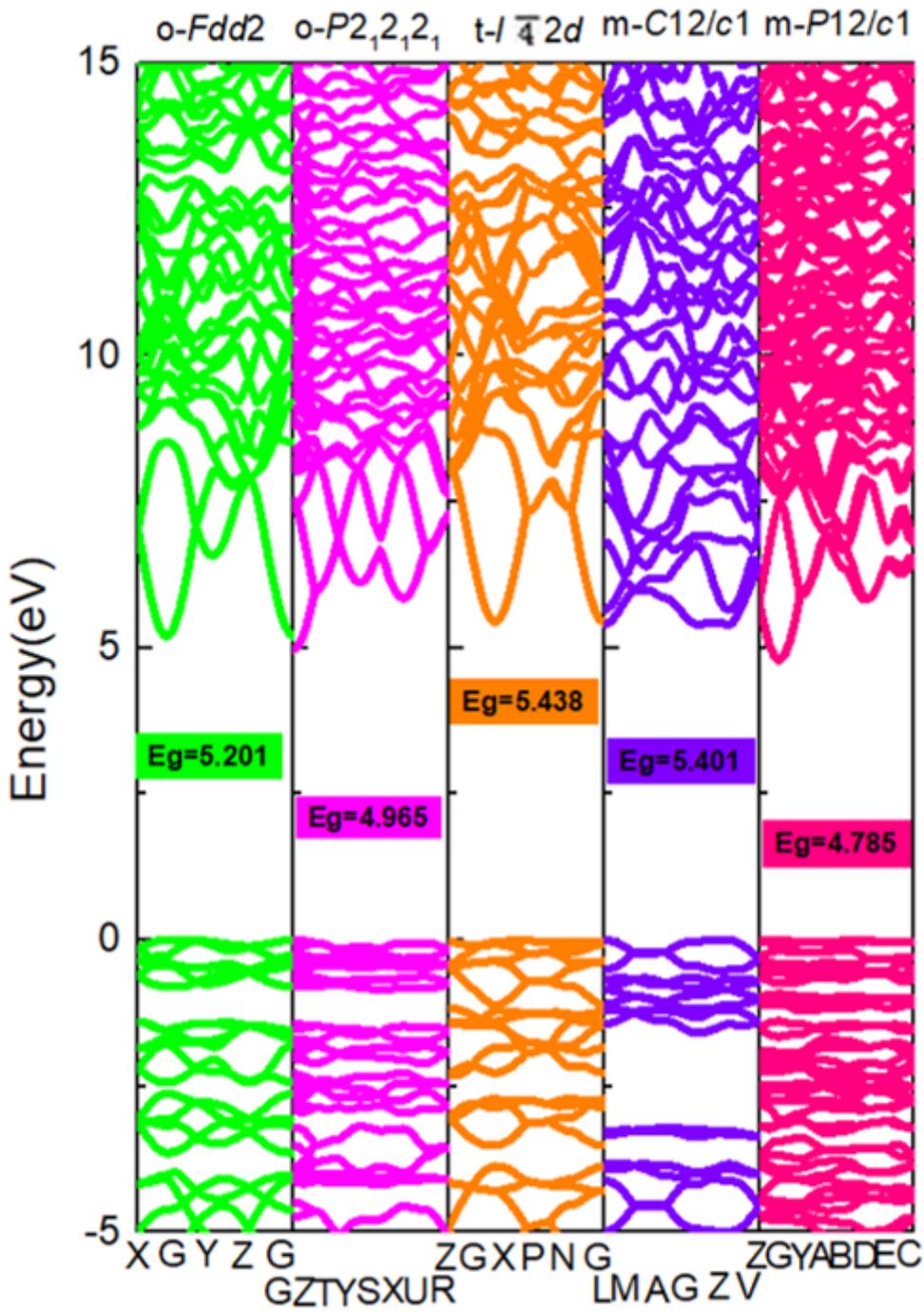


Figure 1

The electronic band structure for KH₂PO₄ crystal.

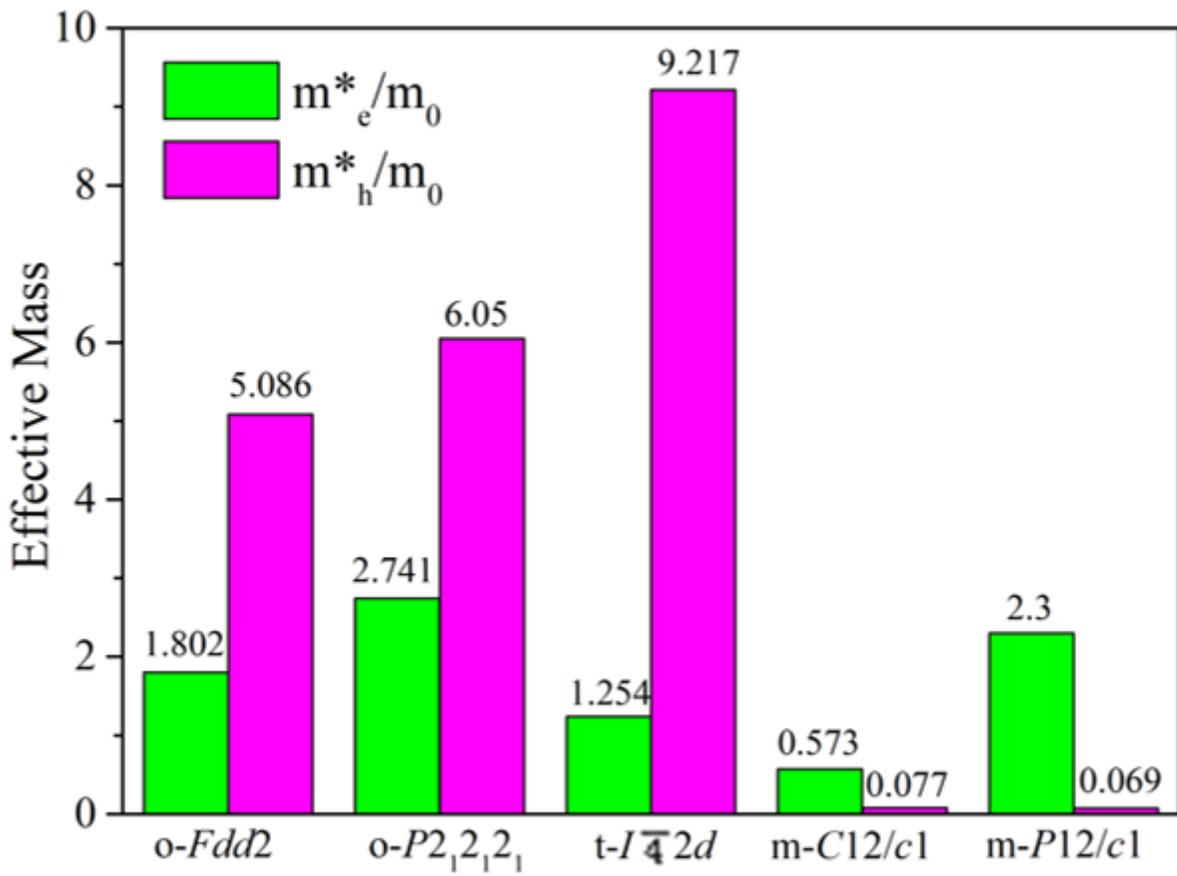
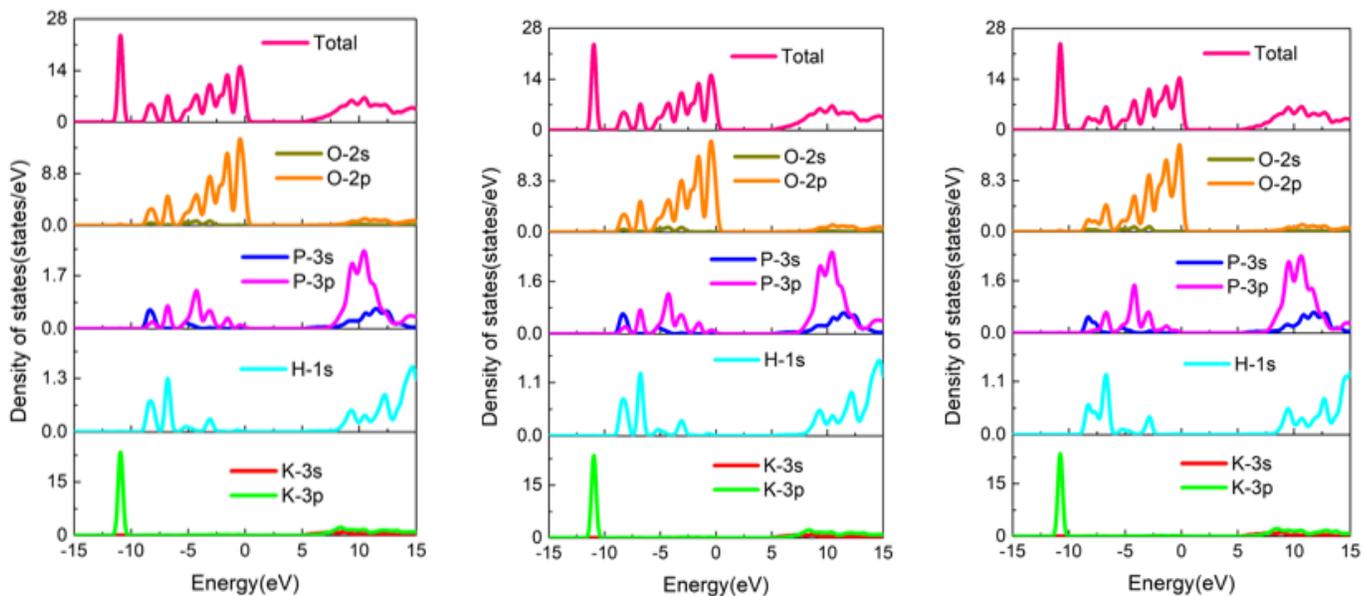


Figure 2

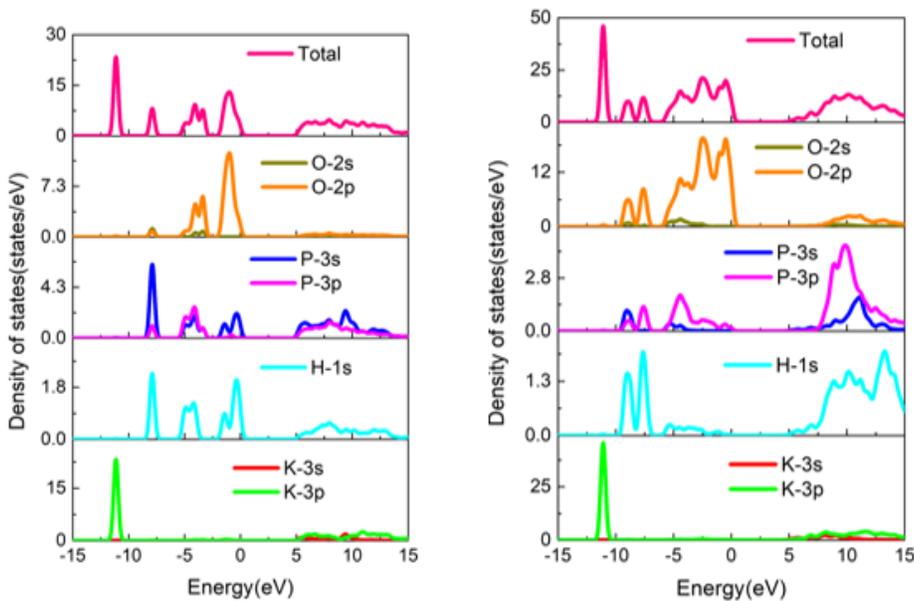
The effective mass for KH₂PO₄ crystal.



o-Fdd2

o-P212121

142d



m-C12/c1

m-P12/c1

Figure 3

The TDOS and PDOS for KH₂PO₄ crystal.