Formation energies and electronic structures of native point defects in potassium dihydrogen phosphate*

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The formation energies and the equilibrium concentration of vacancies, interstitial H, K, P, O and antisite structural defects with P and K in KH_2PO_4 (KDP) crystals are investigated by *ab initio* total-energy calculations. The formation energy of interstitial H is calculated to be about 2.06 eV and we suggest that it may be the dominant defect in KDP crystal. The formation energy of an O vacancy (5.25 eV) is much higher than that of interstitial O (0.60 eV). Optical absorption centres can be induced by defects of O vacancies, interstitial O and interstitial H. We suggest that these defects may be responsible for the lowering of the damage threshold of the KDP. A K vacancy defect may increase the ionic conductivity and therefore the laser-induced damage threshold decreases.

Keywords: KH_2PO_4 crystal, laser-induced damage, point defects, *ab initio*

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1. Introduction

Potassium dihydrogen phosphate (KDP) and its isotopic compound DKDP are remarkable materials that have been incorporated into various laser systems for harmonic generation and electro-optic switching, such as the high-power large-aperture laser systems located at the National Ignition Facility.[1] More and more attention has been paid to the improvement of the optical performance of (D)KDP crystals, including the ability to preserve the phase and the polarization of the propagating laser beam and the resistance to the laser-induced damage in high-power laser applications.[2] With the development of rapid growth methods for the large-aperture KDP crystals used in mega laser systems,[3] the improvement of both growth rate and nonlinear optical (NLO) qualities as well as the laser-induced damage threshold becomes more and more interesting.

Understanding the damage mechanism of KDP crystals induced by high laser fluencies is a long-standing issue.[4] A considerable number of experimental studies have been dedicated to the optical absorption and the laser-induced damage in KDP crystals. Recently, in order to explain the low intrinsic damage threshold of as-grown KDP crystals, Carr *et al.*[5] proposed a defect-assisted multi-step photon absorption mechanism, and suggested that the defect states in the gap change the cross section for multi-photon absorption. For the transient optical absorption mechanism, point defects induced by laser irradiation may play an important role. Furthermore, study on the point defects has been a subject of great interest and importance for improving device performance and material quality. Recently, theoretical efforts have predominantly focused on understanding the role of H defects in KDP with various charge states.[6]

In this paper, we report the calculation results of the formation energy and electronic structure of various native point defects in KDP crystals based on first-principles theory.

2. Computational method

The first-principles calculations we performed are based on density-functional theory (DFT) with the CASTEP code.[7] The total energy ultrasoft pseudopotential method is used.[8] The cutoff energy of the plane-wave basis function is set to be 680 eV, yielding a convergence for the total energy better than 1 meV per atom. The Perdew–Burke–Ernzerhof gradient-corrected functional[9] is used for the exchange-correlation energy. The Monkhorst–Pack (MP) special K-point method is used for the reciprocal space integration. Convergence tests are performed for $2 \times 2 \times 2$, $4 \times 4 \times 4$, and $5 \times 5 \times 5$ divisions along the reciprocal-lattice directions and the total energy converges to less than 0.1 meV per atom.

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Table 1. Formation energies of various point defects in KDP crystal (eV).

V_K	K_i	V_O	O_i	V_H	H_i	V_P	P_i	K_P	P_K
6.5	13.07	5.25	0.60	3.15	2.03	24.68	14.66	24.47	4.1
K Frenkel		O Frenkel		H Frenkel		P Frenkel		Schottky	
19.57 (9.78)		5.85 (2.95)		5.21 (2.60)		39.34 (19.67)		87.38 (10.92)	

An isolated defect is simulated in periodic boundary conditions via a repeated supercell which consists of 64 ± 1 atoms.[6]

From the calculated total energies one can deduce the formation energies E_f of the various point defects, which in turn determines their equilibrium concentration. The formation energy for a single vacancy or a single interstitial is defined as[10]

$$E_f = E^{N\pm1} - E^N \pm \mu, \tag{1}$$

where E_f is the formation energy of defects, $E^{N\pm1}$ is the total energy of the defective supercell, E^N is the energy for the defect-free supercell, and μ is the chemical potential of atoms such as P, O, H and K. These quantities are calculated using a simple cubic cell of lattice constant 10.8 Å. Then the formation energy for the P, O, H and K Frenkel pair can also be calculated. The results are summarized in Table 1. We also calculate the equilibrium concentration of point defects in KDP crystals at room temperature to be

$$\frac{n}{N} = \exp\left(\frac{-E}{2kT}\right), \tag{2}$$

where E is the formation energy of a point defect, k is the Boltzmann constant and T is the temperature. We can see that the concentration (n/N) of thermal defects in KDP is dependent on the temperature and the formation energy of defects.

In order to deduce the favourable positions for interstitial atoms, we first study the unfilled cavities in KDP. We find that two empty cavities exist in KDP crystal. For each interstitial point defect, we insert an atom into the centre for each of the two cavities and then perform geometrical optimization for the two configurations. As a result, the favourable position for the interstitial atom can be deduced.

3. Results and discussion

From Table 1 we can see that the formation energy of interstitial H (H_i) with neutral state is 2.03 eV and therefore the equilibrium concentration at 298 K is about 1.21×10^{-17} mol%. Considering the energetics of the system, we suggeste that H_i may be the dominant native point defect in KDP crystal. In recent years, electron paramagnetic resonance[11] and resonance Raman scattering[12] experiments have provided direct spectroscopic evidence of the existence of H_i in KDP crystal. This possibility was studied in detail by Liu *et al.*[13] in 2003 by *ab initio* calculations. They found that the interstitial neutral H atom has no bonding with neighbouring host atoms and thus induces occupied H derived states in the gap of perfect KDP. The band gap for H_i is reduced to 2.6 eV compared with the corresponding calculated value of DFT in pure KDP, 5.9 eV. At the same time, positively charged H_i^+ will be trapped by neighbouring O^{2-} ions and therefore O–H bonds (with bond length of 0.98 Å) are formed. The reaction and the activation energy are calculated to be about 1.2 eV. The negatively charged H_i attracts the H in the neighbouring O–H–O bond chain and forms the $H_2 + V_H$ configuration (V_H is the H vacancy). The ejection of H from the O–H–O chain induces the bond length to increase from 2.48 to 3.36 Å. As a result, H_i in both charged states severs the H-bonded network.

We know that H is tightly bound between O–O (the calculated overlap population,[14] a measurement of the shared electronic density between two atoms, is 0.54) in KDP, so it needs to overcome a much higher energy for H to be ejected from within the KDP. The calculated formation energy of an H vacancy is 3.15 eV, therefore the equilibrium concentration at 298 K is calculated to be about 2.18×10^{-23} mol%. The H vacancy concentration is low at room temperature but the concentration can be rapidly increased high-energy laser beam irradiation. So the effect of the H vacancies on laser-induced damage of KDP crystals may not be neglected. The ejection of H between the O–O bond increases the O–O bond length from 2.48 to 2.73 Å. A negatively charged H vacancy increases the O–O bond length considerably from 2.48 to 3.19 Å and a positively charged H vacancy reduces the O–O bond length considerably from 2.48 to 1.48 Å corresponding to that of hydrogen peroxide. A positively charged H vacancy reduces the DFT band gap to 2.5 eV and may play an important role in the optical absorption at a wavelength of 355 nm observed

in the experiments.[13,15] In order to reduce the concentration of H defects we perform thermal annealing for KDP crystals under different H gas concentrations, and we find that the laser-induced damage threshold can be increased.[16]

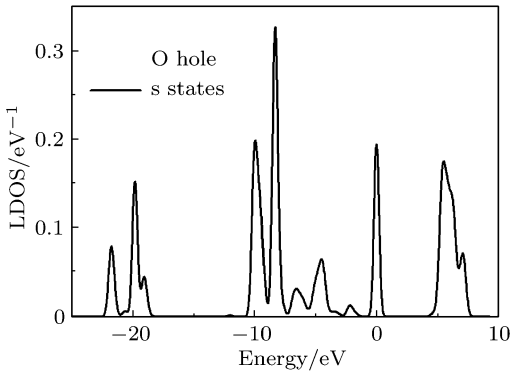


Fig. 1. LDOS for O vacancies in KDP crystal.

The formation energy of an O vacancy V_O (5.25 eV) is much higher than that of an O interstitial V_i (0.60 eV). It is likely that O is covalently bonded to P and therefore a PO_4 tetrahedron is formed. It is not easy for O atoms to escape from KDP crystals. The overlap population for P–O is about 0.85. From the local density of states (LDOS) for O vacancies (Fig. 1), we note that the defect level of the vacancies is induced in the upper region of the valence band. We suggest that an optical absorption centre may be formed due to the O vacancies and it may be responsible for the lowering of the damage threshold in KDP crystals. In addition, an interstitial O atom also induces defect states in the band gap. Figures 2(a)–2(c) show the wave function distributions of the levels located at 0 eV, –7.134 eV, and –17.31 eV in the DOS for interstitial O defects. It can be seen that the occupied states at the Fermi level are composed primarily of the nonbonding O p_y-derived states. The states at the level of –7.134 eV are composed of the bonding σ molecular orbital formed by the p_x-derived states of the O atoms. At the level of –17.31 eV below the Fermi level, the states are mainly the s-derived states of O atoms.[17] We suggest that the thermal annealings of KDP crystal in an O atmosphere at different temperatures might improve the O defect structure and therefore increase the damage threshold of KDP crystal.

The formation energy of antisite defect P_K (a P atom substitutes at the lattice position of K) is also relatively low (4.1 eV) among various native point defects in KDP. On the one hand, the radius of P is only half that of K. On the other hand, P can contribute more electrons to the O atoms than K. It appears from this argument that P_K antisite defects can be highly concentrated in KDP crystal. From the wave function distribution of the level in the gap for P_K as shown in Fig. 3, we can see that the impurity states in the gap are mainly derived by the p states of the antisite P atom. P_K antisite defect can play an important role in laser-induced damage if it exists in KDP. Fortunately, in KDP growth solution P is covalently bonded to four neighbouring O atoms and the PO_4 tetrahedron is absorbed into the lattice as one unit. As a result, no isolated P atoms in the solution could be absorbed into the lattice and therefore an antisite P_K defect has almost no chance to form in KDP.

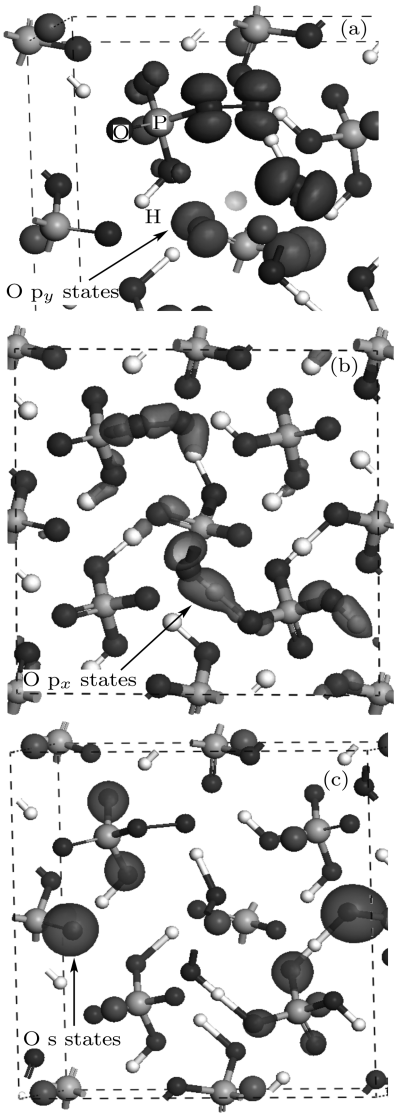


Fig. 2. Wave function distributions of the levels located at (a) 0 eV, (b) –7.134 eV, and (c) –17.31 eV in DOS for neutral interstitial O defects. The states at the level of 0, –7.134 and –17.31 eV are composed primarily of the nonbonding p_y-, bonding p_x- and s- derived states of O atoms, respectively.

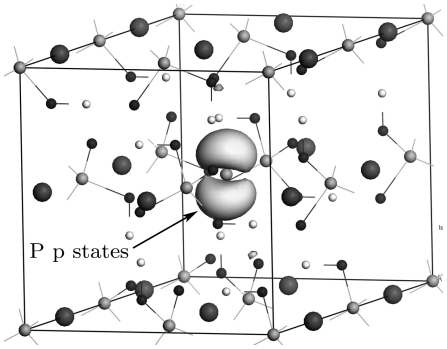


Fig. 3. Wave function distribution of the impurity level in the gap of the P_K point defect.

The formation energy of a K vacancy V_K (6.5 eV) is much lower than that for a K interstitial K_i defect (13.07 eV). Although the radius of K is the largest in KDP, the calculated overlap population for K–O is only 0.05, resulting in weak bonding to the neighbouring O atoms. Furthermore, channels in KDP crystals open the door for the K atoms to escape. As a result, K vacancy defects maybe exist in KDP with a relatively high concentration. Our calculations show that the lattice parameters of KDP can be increased by K vacancy to be $a = +0.8\%$, $b = +0.8\%$, and $c = +1.2\%$.

The distances from the K vacancy to the eight coordinated O atoms are elongated by about 0.150 Å by the vacancy. That is, a K vacancy enlarges the volume of the void surrounded by the eight O atoms by about 3.2%. This result is favourable to the transference of K atoms and promotes the impurity atoms to fill in the void in KDP. The increase of the K mobility ratio leads to an increase of the ionic conductivity of the KDP. Therefore, the laser-induced damage threshold will be decreased. Figure 4 shows the band structure of the K vacancies in KDP crystal. From this figure we can see that no defect states are induced in the gap by K vacancies.

The formation energy of neutral interstitial K is calculated to be 13.1 eV and so is difficult to form at room temperature. According to our calculation, K_i point defects have no important effect on the DOS distributions in KDP crystal. From the viewpoint of multi-photon absorption, K_i defects play no important role in reducing the laser damage threshold. From Table 1 we also see that the formation energies of V_P, P_i and K_P are much higher, and therefore they have no chance to form isolated defects in KDP crystal.

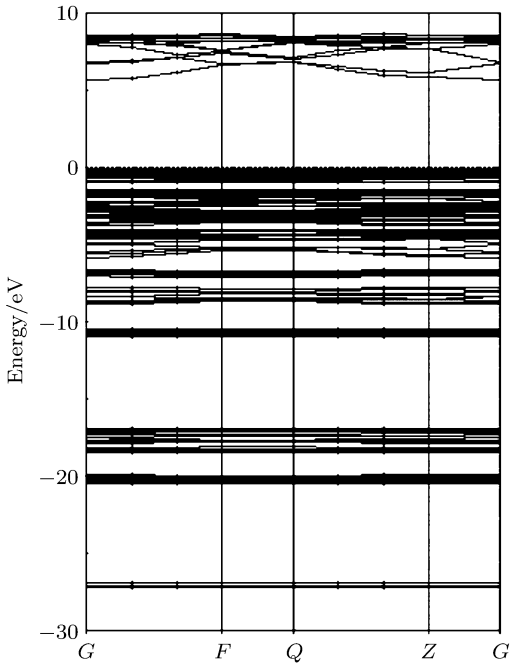


Fig. 4. The band structure of the K vacancies in KDP crystal.

The induced defect states and the final configurations of various point defects in KDP are summarized in Table 2. It can be seen that defect states can be induced by O vacancies, O interstitial and H interstitial. No defect states are induced in the gap by H vacancy and K defects, indicating that they have no contribution to the unwanted optical absorption in the 300–650 nm spectral region when they are irradiated by intense ultraviolet or X-ray.[15,18−20]

Table 2. Induced defect states and final configurations of various point defects in KDP crystal (eV).

Point defect	V_K	K_i	O_i	V_O	H_i	V_H
Defect states/eV	no	no	4.2	4.0	2.6	no
productions	V_K	K_i	O_i–O_h[a)]	V_O+e^{-1}	H_i	V_H

[a)] O_h is the host O atom.

4. Conclusion

The *ab initio* calculation is performed and we find that interstitial H may be the dominant point defect in KDP crystal. In order to improve the H defect structure we anneal the KDP crystal under different H atmospheres and the laser-induced damage threshold of KDP is increased. Interstitial O and K vacancies can also be formed, each with a high concentration, in KDP crystal. In order to further improve the optical quality of KDP crystal, the electronic structure,

binding energy as well as the final configurations of these defects should be investigated in more detail in the future.

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