CHIN. PHYS. LETT. Vol. 36, No. 3 (2019) 037801

Electronic Structure and Optical Property Calculation of an Oxygen Vacancy in $NH_4H_2PO_4$ Crystals *

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(Received 17 October 2018)

The electronic structure of perfect ammonium dihydrogen phosphate (ADP) and defective ADP with an oxygen (O) vacancy are calculated by screened-exchange hybrid density functional HSE06. The optimized structural parameters of the defective ADP crystal are analyzed. The PO_4 tetrahedron with an O vacancy is distorted and its symmetry is broken. The band gap of the defective ADP with an O vacancy is about 1.5 eV lower than the perfect ADP, which is due to the new O vacancy defect states near the valence band maximum. Moreover, more peaks appear in the low-energy region (lower than 6 eV) in the curves of the linear optical properties for the defective ADP. The results indicate that the O vacancy will significantly influence the laser damage performance of ADP crystals.

PACS: 78.20.-e, 61.72.-y, 71.15.Mb, 71.20.-b DOI: 10.1088/0256-307X/36/3/037801

Large-size potassium dihydrogen phosphate (KDP) crystals and deuterated KDP crystals (DKDP) are key materials of nonlinear optics in high-power laser systems such as the Laser MégaJoule (LMJ) or National Ignition Facility (NIF) for developing inertial confinement fusion.[1,2] Recently, their analogs, i.e. ammonium dihydrogen phosphate (ADP) crystals and deuterated ADP crystals, are reported for fourth harmonic generation applications with high-frequency conversion efficiencies up to 70%.[3,4] However, these crystal optics will suffer laser-induced damage (LID) when used in high-power laser systems. One critical challenge for operating the LMJ or NIF was developing damage mechanism avoidance strategies for these optics, especially the tripler optics.[5,6] Advanced crystal growth technologies like the point seed rapid growth method or defined crystallographic direction technique have been developed.[7–9] The possible relationships between boule growth conditions and the resistance of the crystal material to LID also prompted intensive research.[10,11] The origin of LID in these crystals is still not well understood. However, it is believed that damage initiation from nanosecond pulses arises from defects formed during the growth.

Experiments were carried out on specific samples to reveal the nature of these defects, which are important to fully understand the laser damage process. Surmin *et al.* reported the identification of lattice imperfections in KDP/DKDP frequency triplers with a non-destructive x-ray topographic setup. Combined with the ICP-AES technique it is shown that absorbing inclusions (less than fractions of ppb) within the optics are most likely the critical defects that are responsible for the 5 J/cm^2 damage threshold observed on triplers.[12] In addition, atomically dispersed impurity ions do not change the damage characteristics of the material and the clusters of impurities may play the key role in damage initiation.[13] The native defects which affect the optical characteristics and performance of KDP/DKDP/ADP crystals have been identified using electron paramagnetic resonance (EPR) spectroscopy and fluorescence spectroscopy. Garces *et al.*[14] found that after x-ray irradiation, some broad optical absorption bands were observed to peak at nearly 230, 390, 450, and 550 nm, which are associated with point defects such as oxygen (O) vacancy centers or silicon-associated hole centers by EPR spectra. These defects may be responsible for the damage of KH_2PO_4 crystals irradiated with a high-power ultraviolet laser. Impurity or defects (emissions in the 300–500 nm range by laser pumping at 248 nm) were exhibited in several kinds of KDP samples by fluorescence measurements, as reported by Pommiès *et al.*, and their incorporation rate strongly depends on the growth polysectorality.[15] However, these fluorescent impurities or defects have not been identified.

On the other hand, many theoretical efforts have been made to understand the roles of point defects on laser damage resistance of these crystals. Liu *et al.* have calculated the electronic structure of KDP with H defects and O vacancies.[16,17] The neutral H interstitial and the positively charged H vacancies may play an important role in the experimentally observed optical absorption. Chen *et al.* investigated the linear optical properties of KDP with O vacancies using first-principles density functional theory calculation.[18] A new optical absorption within the energy range from 4.8 eV to 7.0 eV has been confirmed in defective KDP

*Supported by the National Natural Science Foundation of China under Grant No 51402173, the Fundamental Research Funds for the Central Universities under Grant No FRF-TP-15-099A1, and the Funding Project of China Scholarship Council under Grant No 201806465071.

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with O vacancies. Other extrinsic point defects such as Fe and Ba that commonly appear in raw materials for KDP crystal growth have also been investigated with theoretical methods.[19,20]

So far, most works have focused on point defects in KDP crystals. The O vacancy defects may be the critical precursors for laser-induced damage in KDP family crystals. There has been no first-principles study that focuses on the linear optical properties of ADP with O vacancies. Thus, in this Letter, we focus on the electronic structure and optical property calculation of the O vacancy in ADP crystals.

The calculations are based on the Vienna *ab initio* simulation package (VASP).[21,22] The core electron states are represented by the projector augmented-wave (PAW) method, and the Heyd–Scuseria–Ernzerhof (HSE06) functional[23] is used for the exchange-correlation functional among electrons. Tests on the cutoff kinetic energy for plane waves show that the cutoff energy of 500 eV yields a convergence of the total energy less than 1 meV/atom. The force convergence criterion is 0.01 eV/Å. Convergence tests for K points along the reciprocal lattice directions in a pure ADP system according to the Monkhorst–Pack scheme[24] have shown that the total energy will converge better than 0.1 meV/atom if K point spacing is set to 0.3 $Å^{-1}$. A tetragonal supercell consisting of four $NH_4H_2PO_4$ units (48 atoms) is used to calculate O defects in the crystal with a defect concentration of 2.08 mol%.

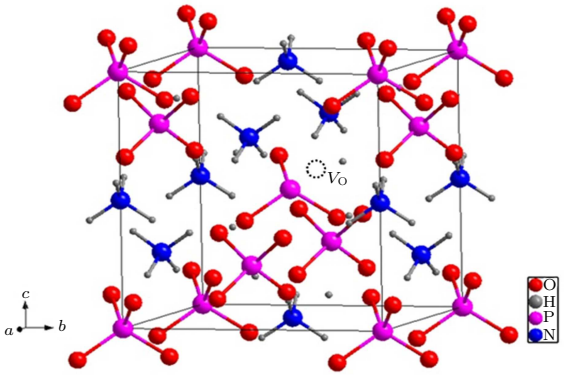

Fig. 1. The primitive cell of defective ADP crystal with an O vacancy (dotted circle, V_O).

The ADP crystal structure is tetragonal with $I\bar{4}2d$ space group as shown in Fig. 1. The contiguous PO_4 groups are interlinked through one O–H···O hydrogen bond. Each body-centered PO_4 group connects to six adjacent NH_4^+ cation groups by eight O–H–N hydrogen bonds.[25] Here the relaxed atomic structure induced by an O vacancy within the PO_4 tetrahedral units is compared with that in a perfect ADP cell. The optimized cell parameters of perfect ADP are $a = b = 7.415$ Å and $c = 7.458$ Å with a deviation of less than 2% (1.51%, 1.84%) with respect to the experimental values of $a = b = 7.502$ Å and $c = 7.546$ Å.[26] For defective ADP, the constants ($a = b = 7.514$ Å, $c = 7.461$ Å) are slightly larger in comparison to perfect ADP. The lengths of the three adjacent P–O bonds with an O vacancy are 1.629 Å, 1.618 Å and 1.617 Å, which are larger than the P–O bond with a length of 1.555 Å in perfect ADP. This is due to the fact that the lone pair electrons of the P atom repulse the three O atoms. This means that the binding strength of the P–O bond is weakened. The PO_4 tetrahedron with an O vacancy is distorted and its symmetry is broken. The length of the O–H···O hydrogen bond increases slightly from 2.412 Å to 2.495 Å, whereas the H atom obviously moves to the PO_4 group with the O vacancy. However, the H atom adjacent to the vacancy site slightly moves and approaches another O atom. The changes are also reflected in the optical properties of defective ADP, which will be discussed in the following. On the other hand, the effective charges of P, O and H atoms near the O vacancy in the defective ADP are 2.22$|e|$, −1.42$|e|$ and 0.63$|e|$, while for perfect ADP the values are 3.67$|e|$, −1.45$|e|$ and 0.64$|e|$, respectively. The removal of O at the origin makes the other O atoms attract fewer electrons from the P atom, and they can capture more electrons from the adjacent H atoms or N atoms for electron deficient character. Moreover, the defect formation energy of an O vacancy in ADP crystal is 5.63 eV using Eq. (1) of Ref. [19], which is larger than the H vacancy formation energy of 4.70 eV.[27]

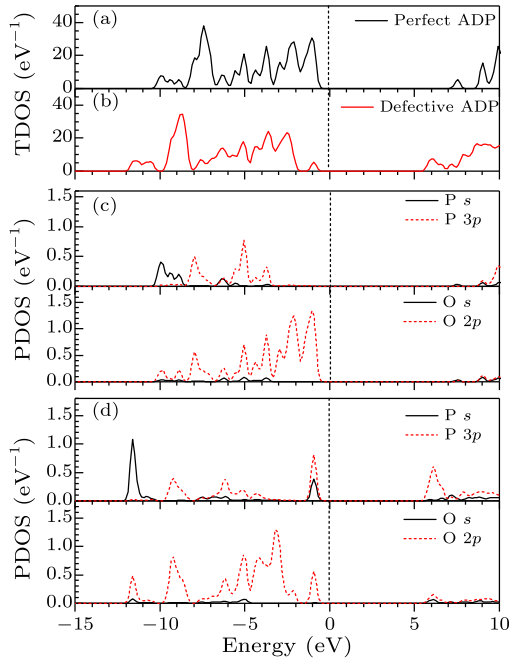

Fig. 2. The total and partial density of states of perfect ADP (a,c) and defective ADP (b,d).

The total density of states (TDOS), orbital-resolved and atom-resolved density of states for the perfect and defective ADP are shown in Fig. 2. From Figs. 2(a) and 2(b), the band gap of perfect ADP is 6.75 eV, which is in good agreement with the previ-

ous experimental data of 6.96 eV.[28] The band gap of defective ADP with an O vacancy is 5.20 eV. It is much lower than the perfect ADP, which is due to the fact that the new O vacancy defect states are mainly located at the band gap, marked by the arrow in Fig. 2(b). For defective ADP, the unoccupied defect states are located around 6.10 eV above the Fermi energy. Comparing the partial density of states (PDOS) with the TDOS, the valence band maximum is contributed mostly from the O $2p$ states for perfect ADP while it comes from the O $2p$, P $3s$ and P $3p$ states for defective ADP. Moreover, for perfect ADP all the O atoms have the same environment and their PDOSs are identical. In contrast, the O atoms in the defective ADP, especially those in the PO_3 group with an O vacancy, have different PDOSs. One of them is shown in Fig. 2(d).

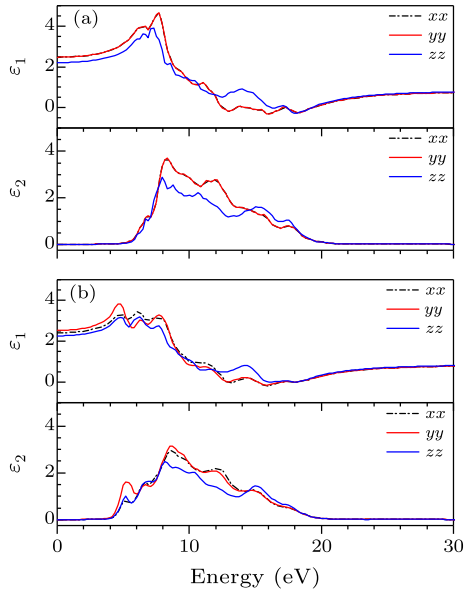

Fig. 3. The real part and imaginary part of the complex dielectric functions of perfect ADP (a) and defective ADP with O vacancy (b).

The frequency-dependent dielectric function $\varepsilon(\omega)$ has been calculated to describe the linear properties of perfect ADP and defective ADP from the electronic structures of these two systems. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function can be calculated by the momentum matrix elements from the occupied and unoccupied states within the selection rules. The real part $\varepsilon_1(\omega)$ can be derived using the Kramers–Kroning relations

$$\varepsilon_1(\omega) = 1 + 2p/\pi \int_0^{\infty} \varepsilon_2(\omega')\omega' d\omega' / (\omega'^2 - \omega^2). \quad (1)$$

Then the linear optical properties including the energy loss function $L(\omega)$, extinction coefficient $k(\omega)$, refractive index $n(\omega)$, and reflectivity $R(\omega)$ can be calculated from the dielectric function as the equations given in Refs. [17,19]. As we know, the imaginary part of the dielectric function is related to the energy loss of light propagating in the medium. The peaks on the dispersion curve of $\varepsilon_2(\omega)$ represent the resonance absorption of light in the material. Meanwhile, these peaks are connected with particular interband transitions. Due to the tetragonal structure of ADP, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ have two separate components, xx (yy) direction along the a (b) axis, and zz direction along the c axis. From Fig. 3 it can be seen that because of the structural distortion induced by the O vacancy the dielectric function components along the xx and yy directions of the defective ADP have different trends. As compared with perfect ADP, more adsorption peaks in the low-energy range in the $\varepsilon_2(\omega)$ for defective ADP mean greater probability of optical absorption. The O vacancy defect results in a redshift of the absorption peaks as shown in Fig. 4. An additional peak located at about 240 nm (5.17 eV) appears, which may be related to the electron transition between O $2p$ and P $3p$ states.

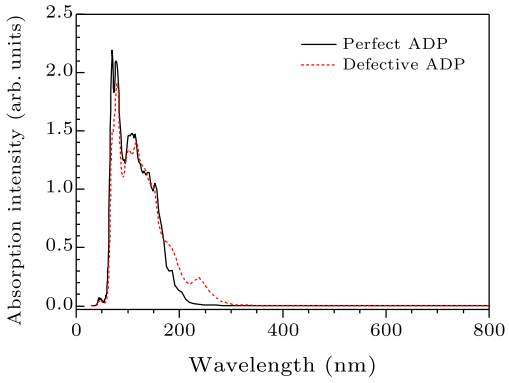

Fig. 4. Absorption spectra of perfect ADP and defective ADP.

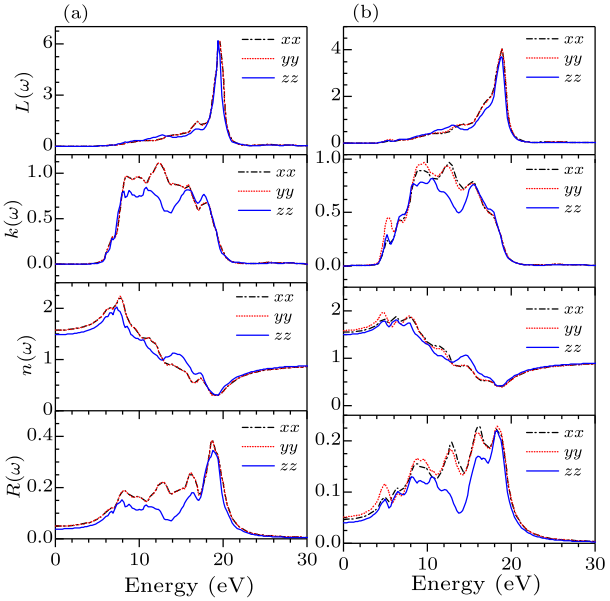

Fig. 5. The energy loss function $L(\omega)$, extinction coefficient $k(\omega)$, refractive index $n(\omega)$ and reflectivity $R(\omega)$ of perfect (a) and defective (b) ADP crystal.

The linear optical properties of perfect ADP and

detective ADP with an O vacancy are shown in Fig. 5. It is shown that all the optical constants of defective ADP move to the low-frequency region and become wider than those in perfect ADP. For instance, the curve of the absorption coefficient for defective ADP is in the energy region from 4.0 eV to 20 eV, which is wider than that from 6.0 eV to 20 eV for perfect ADP. It indicates that the O vacancy deeply affects the optical properties of ADP optics. The ADP crystal with the O vacancy will absorb the energy of the laser irradiation from 4 eV, which is far less than the perfect ADP. Thus the defective ADP with narrow band gap and high absorptivity in the ultraviolet region will intensively absorb the laser fluence, which is harmful, especially for use as fourth-harmonic-generation or third-harmonic-generation optical elements. The absorption will cause energy deposition near the defect site and will make the electrons transition from the ground state to an excited state of high energy. Finally, it may become able to perform impact ionization, a process in which, in an electron–electron collision, another electron is excited to the conduction band, increasing the free-electron density even more. The material becomes strongly absorbent and the laser energy is deposited in the electronic system. Now energy can be transferred to the lattice and can cause damage.

In conclusion, the electronic structures of perfect ADP and defective ADP with an O vacancy have been calculated by screened-exchange hybrid density functional HSE06. The PO_4 tetrahedron with O vacancy is distorted and its symmetry is broken. The band gap of the defective ADP with the O vacancy is much lower than the perfect ADP, which is due to the new O vacancy defect states near the valence band maximum. Moreover, the linear optical properties are calculated and analyzed. The O vacancy defect results in a redshift of the absorption edge. The ADP crystal with the O vacancy will absorb the energy of a new energy region which is lower than 6.0 eV. As reported previously, for KDP the clusters of holes trapped near oxygen sites are the key constituent defects of the laser damage precursors. Here, the above results indicate that the O vacancy also significantly influences the laser damage resistance of ADP crystal.

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