CHIN. PHYS. LETT. Vol. 27, No. 7 (2010) 073101

Effect of S Substitution for P Point Defects in KDP Crystals: First-Principles Study *

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(Received 28 February 2010)

The electronic structure and geometric distribution of phosphor replaced by sulfur in potassium dihydrogen phosphate (KDP) are investigated by first-principles calculations. The point defect narrows down the energy gap to about 4.9 eV, corresponding to a two-photon absorption of 355 nm after correction. This can explain the decrease of the laser damage resistance in KDP crystals. Moreover, the defects twist the crystal structure and weaken bonds, especially the O–H bonds, so these bonds may be the first sites to crack under laser irradiation.

PACS: 31. 15. Ae, 71. 20. −b, 71. 15. Mb DOI: 10.1088/0256-307X/27/7/073101

Potassium dihydrogen phosphate KH_2PO_4 (KDP) belongs to the family of ferroelectric crystals in which covalently bonded molecular PO_4 units are linked by a network of hydrogen bonds.[1] It is a kind of excellent material that has been incorporated into various laser systems for harmonic generation and electro-optic switching, such as the high-power large-aperture laser system located at the National Ignition Facility.[2,3] Point defects can be created during crystal growth or generated by irradiation and they are the major mechanism responsible for transient optical absorption.[4,5] Understanding the role played by point defects in KDP crystals is important for improving device performance and material quality, so studies in this area attract great interest from scientists. Sulfate is a common impurity ion in KDP raw materials and it cannot be easily removed. The structure of sulfate is similar to that of phosphate so it can join KDP crystal lattices through H bonding and electron attraction.[6] Therefore, in the process of crystal growth, it is not so difficult for a sulfur impurity to substitute for a phosphorus ion and hence to enter the KDP crystal lattice. Experiments have revealed that this kind of defect might largely decrease the transmittance in the ultraviolet band and cause cracks.[6] This shows that the defect seriously affects the quality of KDP crystals. Thus studying the mechanism of this defect is worthwhile.

In our work, an ab initio study of S substituting for P in KDP is presented. The ab initio calculations used in this study are based on the density-functional theory (DFT) with CASTEP implementation. The calculations are performed based on the density-functional theory (DFT) using the CASTEP code,[7] and the total energy ultrasoft pseudopotential method[8] is used. The cut-off energy of the plane-wave basis function is set to be 680 eV, yielding a convergence for the total energy of better than 1 meV/atom. The Perdew–Burke–Ernzerhof (PBE) gradient-corrected function[9] is used to calculate the exchange-correlation energy. Typical configurations for P and S are $2s^2 3p^3$ and $2s^2 3p^4$, respectively. We perform the convergence tests for $(2\times2\times2)$, $(4\times4\times4)$ and $(5\times5\times5)$ divisions along the reciprocal-lattice directions in the primitive unit cell of pure KDP according to the Monkhorst–Pack scheme[10] and find that the total energy converges better than 0.1 meV/atom if a $(4\times4\times4)$ K-point is used. An appropriately scaled grid is used for the KDP supercell that contains the defect, i.e. a technique which yields well-converged results for the total energy. We use a tetragonal supercell consisting of eight KH_2PO_4 formula units (64 atoms) with lattice vectors $A = a(i+j)$, $A = a(i-j)$, $C = ck$.[11–13] The lattice constant is $a = 7.430$ Å, $c = 6.970$ Å in experiments and it is very close to the theoretic lattice constant after relaxation (the relaxed lattice constants are $a = 7.485$ Å and $c = 7.020$ Å). The error is less than 0.717%.

The supercell is fully relaxed including all atoms and lattice constants with the use of conjugate gradient techniques. We substitute a sulfur atom for a phosphorus atom in the perfect crystal to simulate the defect and the supercell model of the KDP structure shown in Fig. 1. The total density of states (DOS) of perfect and S doped crystals is shown in Fig. 2. The energy gap is about 5.9 eV in the perfect crystals. Considering the underestimation of the band gap using DFT, a correction of 1.3 eV is proposed.[12] We

*Supported by the National Natural Science Foundation of China under Grant Nos 10676019 and 50721002, the Program for New Century Excellent Talents in University (NCET-10-0526), and the Natural Science Foundation of Shandong Province (ZR2009FM015).

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note that in the S doped crystal the unoccupied defect states, as indicated by the solid arrow, narrow down the energy gap to about 4.9 eV, corresponding to two-photon absorption of 355 nm (the third harmonic wave of KDP crystal) after correction. It is in agreement with the experimentally observed optical absorption in the ultraviolet band. Because of the impurity's strong laser absorption, the sharp temperature rise at the impurity possibly causes local melting around the point defect. Moreover, as a temperature gradient exists around the impurity, thermal stress will be generated to cause bond rupture and hence degrade the laser damage resistance. In order to further verify our view, a corresponding experiment was carried out. The sample was grown by the traditional temperature-lowering methods, the dopant concentration of sulfate was 50 ppm and it was cut to a $10 \times 5 \times 1\,\mathrm{cm}^3$ size plate, hand-polished on both sides. The damage test experiments were performed using a tripled Nd:YAG laser operating at 355 nm. The laser has a Gaussian temporal profile with a pulse duration of about 6 ns. The experimental bench used for the KDP damage test is the same as that of Hu *et al.*[14,15] The wet etch process was applied to expose the bulk damage site to surface, which gave us direct access to the modified material for scanning electron microscopy (SEM). The damage topography is shown in Fig. 3: the center cell has probably been melted; there are also some slight cracks on a larger outer region.

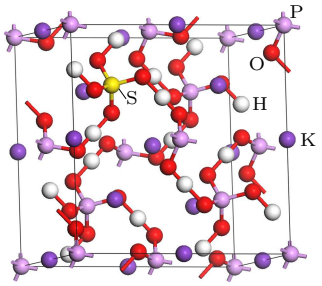


Fig. 1. Supercell structure of KDP crystals.

Table 1. Calculated structural parameters for perfect and S doped bond chains in the tetragonal phase.

Effective charge ($\|e\|$)					
Perfect			S doped		
P	O	H	S	O	H
2.20	−1.01	0.34	2.18	−0.92	0.37
Overlap populations ($\|e\|$)/bond lengths (Å)					
P–O	O–H		S–O	O–H	
0.64/1.53	0.40/1.20		0.53/1.54	0.18/1.49	

Table 1 lists the changes of surrounding atoms after sulfur–phosphor substitution. Only one of the four bond chains in the tetragonal phase is shown, and the other three bond chains are the same as this one. The effective charges change from $2.20|e|$ to $2.18|e|$ after sulfur–phosphor substitution. As we know, the S atom has stronger electro-negativity than the phosphor atom, so it does not share its extra electron with adjacent oxygen atoms but robs electrons from oxygen atoms around it (the effective charges of the oxygen atom change from $-1.01|e|$ to $-0.92|e|$). Hence the S–O band becomes slightly stretched and weakened (the band length changes from 1.53 Å to 1.54 Å and the overlap changes from $0.64|e|$ to $0.53|e|$). Moreover, the O–H band, which is the other band linking with the oxygen atom, is badly weakened (the band length changes from 1.20 Å to 1.49 Å and the overlap changes from $0.40|e|$ to $0.18|e|$) too. This means that the adulteration of S makes the O–H band much more brittle, so any perturbation may cause the O–H band to break.

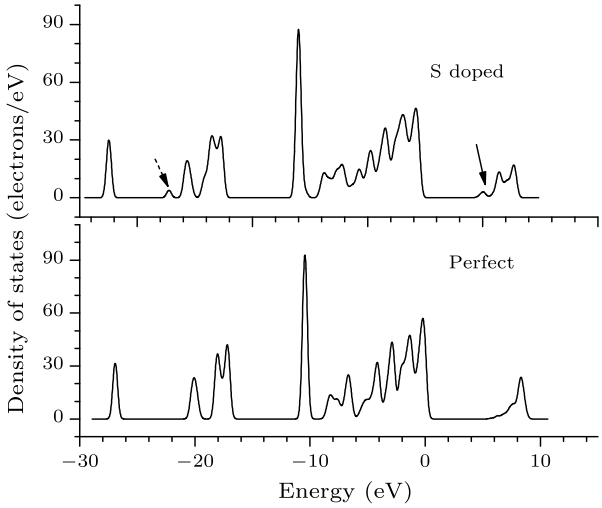


Fig. 2. Total density of states for perfect and S-doped KDP crystals.

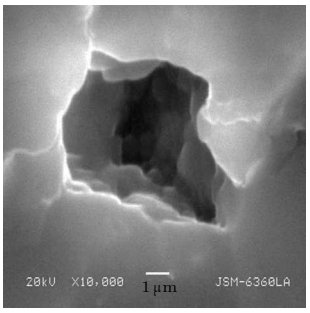


Fig. 3. Images of KDP bulk damage sites initiated with 355 nm light.

The angles of tetragonal phase are also changed (these data are not listed here). The angles of O_1–P–O_2 and O_3–P–O_4 are changed from 110.5° to 112.5° and the others are changed from 108.9° to 107.9°. The changes of angles mean that the tetragonal phase is contorted after sulfur–phosphor substitution.

From the above discussion we find that the point defects twist the crystal structure and weaken the bonds around the defect sites, especially the O–H bonds. Thus this may be the first site to crack under laser irradiation.

In conclusion, first-principles total energy calculations are performed to find that the energy gap narrowed from 5.9 eV to about 4.9 eV in sulfur doped KDP, corresponding to two-photon absorption of 355 nm after correction. Laser absorption may cause local melting and bond rupture. This will reduce the laser damage threshold. Moreover, the existence of sulfur twists the tetragonal phase and weakens the bonds around defect sites, especially the O–H bonds, so this bond may be the first site to crack under laser irradiation.

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