Effect of Ba in KDP crystal on the wavelength dependence of laser-induced damage

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Received November 22, 2010; accepted April 11, 2011; posted online June 16, 2011

Ba impurity in potassium dihydrogen phosphate (KDP) is studied with the first-principle simulation method. The relaxed configurations and density of the states of KDP crystal with Ba impurity are calculated. We find that Ba can generate a K vacancy and an interstitial O-H unit for charge compensation. The band gap of KDP crystal narrowed down to about 3.9 eV, which is consistent with the experimental data from previously reported studies and indicates that Ba may be a source of low-damage threshold.

OCIS codes: 140.3330, 140.3440.

doi: 10.3788/COL201109.091402.

Potassium dihydrogen phosphate (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]. KDP has been incorporated into various laser systems for harmonic generation and electro-optic switching[2,3]. Understanding the susceptibility of KDP crystals to laser-induced damage at high laser fluence is a long-standing issue[4]. Fluence refers to an order of magnitude below the expected intrinsic breakdown limits. The damage is initiated by small absorbers that are present in the crystal before irradiation or are formed at the beginning of irradiation. Carr *et al.*[5] employed a novel experimental approach to reveal the mechanisms of laser-induced damage of KDP crystals. A damage threshold versus the wavelength graph was generated. Two notable sharp steps centered at 2.55 eV (487 nm) and 3.90 eV (318 nm) were clearly demonstrated in their experimental results. The steps located at 2.55 and 3.90 eV are close to the integer fractions of 7.8 eV (band gap of pure KDP crystals). In order to explain this result, a defect-assisted multi-step photon mechanism assuming the existence of intraband states was proposed. Hydrogen vacancies, interstitial hydrogen atoms, and interstitial oxygen atoms can produce the states in the gap[6,7] required by the proposed defect-assisted multi-photon model. Our aim was to try to find the different sources of the low-damage threshold in KDP crystal.

Ba is a kind of common impurities in KDP raw materials and is difficult to be completely removed[8]. Thus, it will enter the KDP crystal lattice during the growth process. Experiments[8] revealed that this kind of impurity can largely decrease the transmittance in the ultraviolet band even at very low impurity concentrations. This means that the band width may be changed in the adulteration. The simulation method is an effective way to study the change in the crystal's optical bandwidth[9]. In this letter, we study the KDP crystal with Ba defect in detail by using CASTEP, which is one of the most popular codes used in simulation[6,7,10].

In our work, a study of Ba in KDP was presented firstly. We studied the Ba substituting for K point defect, Ba in 0.25, 0.35, and 0.125[11] cavity, and Ba in 0.75, 0.22, and 0.125[11] cavity point defects, and we found that the formation energies were 8.90, 8.30, and 10.77 eV, respectively. Hence, we considered that the reasonable sites were in the 0.25, 0.35, and 0.125 positions for Ba impurity. The calculations were performed based on the density-functional theory (DFT) using the CASTEP code[12], and the total energy ultrasoft pseudopotential[13] method was used. The cut-off energy of the plane-wave basis function was set to be 680 eV, yielding a convergence for the total energy that was better than 1 meV per atom. The Perdew-Burke-Ernzerh of gradient-corrected function[14] was used to calculate the exchange-correlation energy. We performed convergence tests for (2×2×2), (4×4×4), and (5×5×5) divisions along the reciprocal lattice directions in the primitive unit cell of pure KDP according to the Monkhorst-Pack scheme[15] and found that the total energy converged better than 0.1 meV per atom if a (4×4×4) K point was used. An appropriately scaled grid was used for the KDP supercell that contained the defect, a technique which yielded well-converged results for the total energy. In our calculations, a tetragonal supercell consisting of eight KDP formula units was used. The supercell is fully relaxed, including all atoms and lattice constants, with the use of conjugate gradient techniques.

Figure 1 shows the change in the relaxed atomic structure induced by a Ba atom with its neighbor P-O-H bonds. In order to clarify the discussion, we have labeled the atoms that are closely associated with the interstitial Ba atom as P_1, O_1, O_2, and H_1. The interstitial Ba breaks the P_1-O_1 and O_2-H_1 bands synchronously, as shown in Fig. 1(b). This results in the formation of an interstitial O-H unit. The O-H band length is 0.98 Å, which is close to the value of H_2O (0.96 Å) molecule. The existence of Ba impurity also generates a K vacancy (marked in the figure). The fractional coordinates of K changes from 0.50, 1, and 0.12 to 0.56, –0.13, and 0.13, respectively. The Ba atom has two outermost electrons

and has a strong metallicity; it is easy to lose electrons. The K vacancy and interstitial O-H unit are the results of charge compensation.

In Fig. 2, the density of the states of pure KDP and Ba-doped KDP crystals is shown. Despite the well-known intrinsic deficiencies of DFT in yielding too low band gaps compared to the experiments, we note that the unoccupied defect states in the Ba-doped crystal narrowed down the energy gap to about 3.9 eV.

Figure 3 illustrates the orbital-resolved and atom-resolved partial density of states (PDOS) for the Ba-doped KDP crystal. The unoccupied defect states are mainly made up of the p state of P_1 and the d states of the Ba atom. This means that the interaction of interstitial Ba and P_1 leads to the narrowing down of the KDP band gap.

In conclusion, the KDP crystal generates an O-H unit and a K vacancy for charge compensation when a Ba impurity turns into crystal. The interaction of the interstitial Ba and P_1 narrows the band gap to about 3.9 eV, which is consistent with the second sharp step at 3.9 eV[6]. We, therefore, conclude that Ba may play an important role in the wavelength dependence of laser-induced damage in KH_2PO_4 crystal.

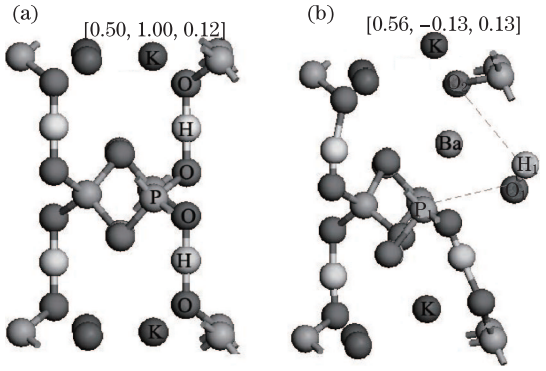

Fig. 1. Configurations of Ba impurity in KDP crystal.

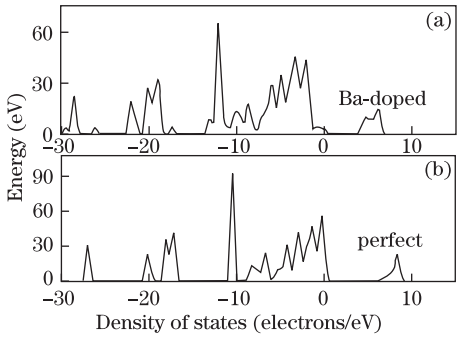

Fig. 2. Density of the states of (a) Ba-doped KDP and (b) pure KDP crystal.

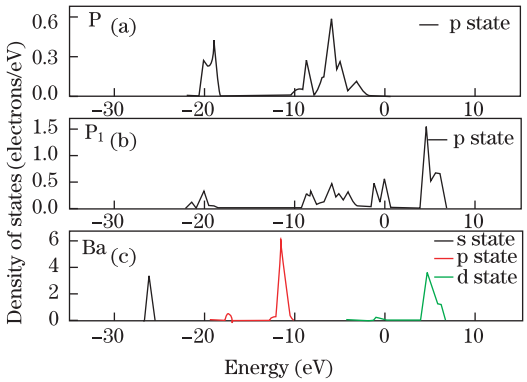

Fig. 3. Orbital-resolved and atom-resolved PDOS for Ba-doped KDP crystal. (a) p state of P atom; (b) p state of P_1 atom; (c) s, p, and d states of Ba atom.

The work was supported by the National Natural Science Foundation of China under Grant Nos. 10676019 and 50721002.

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