Oxygen vacancies in KTiOPO₄: Optical absorption from hybrid DFT

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Density functional theory is used to calculate the optical absorption of oxygen vacancies in potassium titanyl phosphate (KTiOPO₄, KTP) crystals. A modified hybrid functional is used for the description of the midgap defect states and the optical excitation energies. Oxygen vacancies in the +2 charge state lead to rather minor modification of the bulk KTP optical response, while the +1 and neutral charge states give rise to characteristic midgap optical absorption covering the whole near-infrared and visible spectrum. Its intensity is strongly polarization dependent and strongest for light polarized parallel to the z axis. The modification of the KTP optical absorption by oxygen vacancies predicted here corroborates the picture that the gray-track formation in KTP, i.e., its photochromic damage, is related to a successive charging of oxygen vacancies.

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I. INTRODUCTION

Ferroelectric potassium titanyl phosphate (KTiOPO₄, KTP) is an excellent material for nonlinear-optical devices. Its broad transparency band (350–4500 nm) [1] and large nonlinear-optical coefficients together with high damage thresholds [1–4] make it suitable, e.g., for frequency doubling in Nd:YAG lasers [5]. Its application, however, is limited by a strong optical nonlinearity of the material. The K atoms are only weakly bonded and show high mobilities along [001] directions. Thus the O sites can be classified according to their coordination: O(1)–O(8) are coordinated with P and Ti, while O(9) and O(10) are located between two Ti atoms [11,12,20–23]. In fact, several Ti³⁺ defect centers have been detected in gray-track-affected samples by electron paramagnetic resonance (EPR) [20,21] and electron nuclear double resonance (ENDOR) spectroscopy [20,21]. However, only one of them is stable at room temperature [21]. It has been unambiguously attributed to the positively charged O vacancy $V_{O(10)}^{+}$ [21,24]. In addition to the EPR-active +1 charge state, its +2 and neutral charge states are also thermodynamically stable [24] and may be thus relevant for gray tracking.

This motivates the present work, which extends earlier studies by some of the present authors on the KTP optical response [25] and point defects characteristic to KTP [19,24]. Here, we use hybrid density functional theory to calculate the optical absorption of KTP hosting $V_{O}$ vacancies. In the case of $V_{O(10)}$, the occurrence of characteristic midgap absorption is found. It is strongly dependent on the defect charge state as well as the polarization of the incident light and thus suitable to explain the experimental observations in the early stage of gray tracking. This suggests that $V_{O(10)}$ vacancies not only play an important role in charge compensation, but also are directly involved in the photochromic damage.

II. METHODOLOGY

The determination of the ground-state geometries in this paper is based on density functional theory (DFT) as...
implemented in the open-source package QUANTUM ESPRESSO (QE) [26,27]. The calculations are performed for 64-atom supercells using periodic boundary conditions. The electron-ion interactions are modeled via norm-conserving pseudopotentials that treat the Ti $3d^3\ 4s^1$, P $3s^2\ 3p^3$, K $4s^1$, and O $2s^2\ 2p^4$ states as valence states. The electron exchange and correlation (XC) effects are described within the generalized gradient approximation (GGA) using the revised Perdew-Burke-Ernzerhof functional PBEsol [28]. Additionally, a $5.1$-eV Hubbard [24,29] energy correction is applied to the Ti $3d$ states. In principle, changes in the local chemical environment within the oxide can be taken into account by using site-depending $U$ values [29–31]. However, in Ref. [24] we have determined the Hubbard-$U$ values for O vacancies in KTP self-consistently and found values that do not deviate by more than ±0.25 eV from $5.1$ eV. Hence, for the sake of simplicity, we use this average value throughout this paper. Thereby, we use the simplified version given by Cococcioni and de Gironcoli [29], using an effective Hubbard-$U$ value and atomic wave functions to build the required projectors on localized orbitals. This PBEsol + $U$ methodology allows for the highly accurate modeling of KTP bulk and defect structures as verified earlier by comparison of calculated and measured magnetic signatures of KTP defects [24]. Optical response calculations are performed within the independent-particle approximation (IPA) using the open-source code YA-MBO [32,33] based on the geometries structurally optimized within PBEsol + $U$. The Brillouin zone is sampled with a $3 \times 6 \times 3\ \Gamma$-centered mesh, which ensures well-converged optical spectra.

DFT with (semi)local exchange-correlation (XC) functionals typically suffers from an underestimation of the single-particle excitation energies. Therefore optical absorption spectra calculated within the IPA based on the DFT electron structure typically agree with experiment only qualitatively [34]. The calculated excitation energies are redshifted compared with the measured data. A more realistic description of the experiment is obtained using the independent-quasiparticle approximation (IQA), which accounts for electronic self-energy effects [34]. Realistic quasiparticle energies may be obtained by calculating self-energy corrections within the $GW$ approximation [35,36] (DFT + $GW$). The subsequent solution of the Bethe-Salpeter equation (BSE) allows one to account for excitonic effects and leads to a redistribution of oscillator strengths to lower excitation energies, often partially compensating the blueshift resulting from the self-energy corrections [36–39]. The combined $GW$ + BSE methodology typically results in calculated optical spectra in close agreement with experiment. This holds also for KTP [see Fig. 2(e)], where a self-energy blueshift of about $2$ eV is partially compensated by an excitonic redshift of about $1.5$ eV; see discussion in Ref. [25]. For comparison, the $GW$ + BSE approach has been applied in this paper to one defect structure, the $O(10)$ vacancy. These calculations are numerically on the same footing as used in Ref. [25]. The large unit cell in conjunction with the low symmetry forced us, however, to reduce the $k$-point sampling to the $\Gamma$-centered $1 \times 2 \times 1$ mesh.

The success of the $GW$ approximation, at least in the case of non-self-consistent $GW$, depends on the quality of the electronic structure on which it is based. This renders its application to $V_{O(10)}$ difficult: The use of (semi)local functionals such as PBEsol leads to delocalized defect states within the KTP conduction band [see Fig. 3(a)]. Consequently, DFT-PBEsol places the charge transition levels (+2/+1) and (+1/0) above the band gap and fails to describe the EPR-active $V_{O(10)}^{++}$ state. Its modeling requires a Hubbard energy correction $U = 5.1$ eV on the Ti $3d$ states [24]. Unfortunately, this PBEsol + $U$ approach, while providing an occupied midgap defect state [see Fig. 3(b)], still suffers from an
underestimated bulk gap ($E_g^{\text{expt}} = 3.2–3.8$ eV [44,40–42] vs $E_g^{\text{PBEsol+U}} = 2.8$ eV) and is not a suitable starting point for optical response calculations [see Fig. 2(a)]. The PBEsol + $U$ calculations could probably provide a valid starting point for self-consistent GW, which is, however, beyond our present computational possibilities, given the size and low symmetry of the defect supercell.

Hybrid DFT is often a viable alternative: An adjustable fraction $\alpha$ of exact exchange (EXX) [43] from Hartree-Fock theory via hybrid functionals is frequently used to correct single-particle excitation energies [44–49]. At the same time, hybrid DFT leads to a more accurate description of strongly localized electronic states and the related defect levels than can be achieved with (semi)local XC functionals [49–51].

The application of the PBE0 functional [52], which describes the electron correlation within the PBE [53] but replaces a fraction $\alpha = 25\%$ of the PBE exchange with Hartree-Fock exchange, leads to a band gap of 5.33 eV for bulk KTP, close to the value of 5.23 eV obtained within the GW approximation [25]. Moreover, we verified that the PBE0 functional leads to defect geometries and hyperfine tensors in close agreement with our previous PBEsol + $U$ results [24]. This provides additional credibility to this approach.

As expected from the large band gap, the dielectric function calculated in the independent-particle approximation (IPA) from the PBE0 electronic structure [Fig. 2(b)] is blueshifted by about 1.5 eV compared with experiment and GW + BSE theory [Fig. 2(c)]. As mentioned above, electronic self-energy effects and electron-hole interaction effects cancel each other to some extent [37–39,54,55]. We exploit this cancellation here by modifying the PBE0. Specifically, we use a reduced EXX fraction $\alpha = 10\%$. This method, called PBE0-10% in the following, leads to an IPA bulk optical response in close agreement with the GW + BSE data from Ref. [25]; see Figs. 2(c) and 2(d). The present PBE0-10% calculations are also in qualitative agreement with the BSE data of Ghoohestani et al. [56], with respect to both the onset of the optical absorption and the line shapes of the diagonal components of the dielectric function.

The PBE0-10% approach gives rise to an occupied $V_{O(1)}$ defect state within the KTP band gap [see Fig. 3(d)]. Similarly to the PBE0 scheme, it is positioned at about 2.4 eV above the valence band maximum. The unoccupied defect states, as well as the KTP conduction band, are lowered by 1.5 eV in PBE0-10% compared with PBE0. This explains the good agreement between the bulk KTP optical spectra based on the PBE0-10% electronic structure with GW + BSE theory. Below we address the question of which accuracy can be expected from PBE0-10% calculations in the case of defect optical signatures.

III. RESULTS AND DISCUSSION

A. Vacancy $V_{O(1)}$

The $V_{O(1)}$ vacancy is located between Ti and P. It is characterized by a strongly localized and twofold occupied defect level. This level is positioned within the KTP band gap but already on the DFT-PBEsol level of theory [19]. Therefore it is directly accessible to both GW + BSE and PBE0-10%. It can thus be used to establish errors bars relevant for the application of PBE0-10% to defect states.

Figure 4 compares the $V_{O(1)}$ optical absorption spectra calculated on the GW + BSE and PBE0-10% levels of theory. Since there are no additional absorption peaks in the low-energy region, we focus on the energy range 2–5 eV. The spectra agree qualitatively. There are, however, clear differences in the peak positions. On the one hand, the main optical absorption peak characteristic for the bulk is blueshifted within PBE0-10% by up to 0.5 eV. The shift is most pronounced for the $zz$ component. On the other hand, the calculated defect signature is redshifted within PBE0-10% by up to 0.2 eV. Thus we estimate the error bars of our PBE0-10%
method to be up to 0.5 eV, which correspond to the maximum difference in the peak positions with respect to the GW + BSE spectra. The limited resolution of the present GW + BSE calculations due to the restricted Brillouin zone sampling clearly hampers the comparison. For example, the defect signature in the spectroscopies. The limited resolution of the present method to be up to 0.5 eV, which correspond to the maximum difference in the peak positions with respect to the GW + BSE spectra. The limited resolution of the present method to characterize the optical absorption due to both bulk and defect states in KTP.

B. Vacancy Vo(10)

The vacancy Vo(10) can assume three different charge states (\(q = +2, +1, +0\)). The ground state of the neutral vacancy is a spin triplet (\(S = 1\)), where two singly occupied Ti 3d-related one-particle states occur in the gap, localized at Ti(1) and Ti(2) near the vacancy (see configuration A in Fig. 5). Two spin-singlet (\(S = 0\)) configurations, with both electrons localized in a single orbital, are calculated to be 1.03 and 1.24 eV higher in energy (see configurations B and C, respectively, in Fig. 5). Although these diamagnetic, i.e., EPR-silent, configurations are energetically less favorable, they may form upon charge transition or optical excitation and thus be visible in the optical response.

In Fig. 6 the diagonal components of the calculated dielectric function of KTP hosting an oxygen vacancy Vo(10) in its three possible charge states are shown together with the KTP bulk optical response. The calculations are performed within the IPA using the PBE0-10% electronic structure. Obviously, the vacancy formation leads to a redistribution of the oscillator strength for the first main absorption peak (around 4.5 eV) to energies within the optical gap, especially for \(E_{\text{zz}}\) and \(q = 0, +1\). The charge state \(q = +2\) does not feature any midgap defect level or related absorption. All Ti\(^{3+}\)-related defect levels remain empty and yield resonances in the conduction bands. Due to the defect-related relaxation of the selection rules, electronic transitions from the upper valence band into these states contribute to the absorption. They manifest themselves mainly in the shoulder, which arises on the low-energy side of the main absorption peak, in the energy range between 3 and 4 eV. Its intensity is highest in the charge state +2 but remains still visible (in decreasing order) in \(q = +1\) and \(q = 0\), where one and two levels are populated by the extra electrons, respectively.

The occupied gap levels in the charge states +1 and 0 give rise to a broad absorption band in the optical gap, which covers the whole near-infrared and visible spectrum. Thereby, the optical absorption is strongly polarization dependent: It is highest for the \(zz\) component and decreases successively for \(yy\) and \(xx\). In \(z\) polarization, three relative maxima (\(a_1, a_2, a_3\)) can be identified in the energy range 0.5–2.5 eV for the EPR-active \(V_{\text{O(10)}}^{+1}\) configuration, featuring one occupied defect level. They can be attributed to electronic transitions from the occupied gap level to the unoccupied Ti\(^{3+}\) levels located in the lower part of the conduction band (\(a_1, a_2\)) and into Ti 3d resonances (\(a_3\)) in the lower part of the conduction band, respectively. Notably, the neutral charge state within the \(S = +1\) spin configuration leads to an absorption similar to that of the charge state +1. Both \(S = 0\) defect geometries, however, give rise to a much enhanced optical absorption in the band gap, also regarding the \(xx\) and \(yy\) components. In fact, both
configuration B and configuration C show not only a broader and higher absorption band in the energy range 0.5–2.0 eV, but also an additional absorption band in the ranges 2.4–3.2 eV (configuration B) and 2.0–2.3 eV (configuration C), respectively. These can be attributed to transitions from the occupied defect level into the Ti(1) 3d states located at about 5.6 eV (configuration B) and 5.0 eV (configuration C).

The charge transfer in Ti$^{3+}$-Ti$^{4+}$ pairs has been discussed [10,57] as being responsible for an increase in optical absorption related to the gray-track formation. This finding is supported by the present results, as can be seen in Fig. 7, where the initial state as well as three final states corresponding to the $a_{1,2,3}$ absorption peaks are shown. It can be seen that the optical transitions correspond largely to a charge transfer from Ti(2) to Ti(1)-related states.

The computational finding that the O-vacancy absorption is highest for $z$-polarized light, irrespective of the charge state, agrees with the observation that the crystals’ resistance to gray tracking is weakest for laser beams polarized parallel to the $z$ axis [7,8]. The dependence of the mid-gap absorption on the vacancy’s charge state also suggests that the gray-track formation is related to O vacancies: It was found that the resistance against gray tracking is enhanced for Pb-doped material [58,59], while crystals with a higher K-vacancy concentration are particularly strongly affected by gray-track formation [13,18]. The replacement of K$^+$ with Pb$^{2+}$ will lower the Fermi energy and thus increase the probability for twofold positively charged O vacancies with little absorption in the band gap, while low K concentrations are expected to increase the Fermi energy and thus the concentration of the more strongly absorbent $V_{O(10)}^{+}$ and $V_{O(10)}^{0}$ [24] (cf. Fig. 6).

It was observed that the absorption of 1064-nm (1.17-eV) light increases in the initial state of gray tracking [60,61]. In addition, experiments showed that gray tracks give rise to a wide absorption band, covering the whole visible spectrum and the near-ultraviolet spectrum with maxima for the range between 380 and 440 nm and the range between 500 and 600 nm [9], respectively (2.82–3.26 and 2.07–2.48 eV, respectively). As discussed in Sec. III A, the accuracy of the PBE0-10% optical spectra is limited. In addition, the present calculations do not account for thermal broadening and the motional relaxation of selection rules. Still, they are in accord with the experimental findings. Notably, the strongest absorption of $V_{O(10)}^{+}$ is located in the range between 0.8 and 1.3 eV corresponding to the initial stage of gray tracking. The metastable spin-singlet ($S = 0$) configurations of the neutral charge state, on the other hand, match the high-energy absorption maxima (around 2.3 and 3.0 eV) discussed in Ref. [9].

Thus our calculations corroborate the picture that defect-stabilized electron-hole pairs formed upon optical excitation transform $V_{O(10)}^{+2}$ into $V_{O(10)}^{+1}$ and $V_{O(10)}^{0}$, and thus increase the optical absorption by promoting the formation of gray tracks. In addition, the excitation of defect states may explain the broad luminescence in the energy range of 1–1.8 eV that was observed subsequent to irradiation with a 514.5-nm (2.4-eV) argon laser [62].

**IV. CONCLUSION**

The signatures of O vacancies in the KTP optical absorption were explored using hybrid DFT. A modified PBE0 functional containing 10% exact exchange was found to allow for the modeling of localized defect states and to provide optical excitation energies in fair agreement with GW + BSE data.

The calculations suggest oxygen vacancies at the O(10) site to be responsible for gray tracking, i.e., photochromic damage of the material. More precisely, the computational findings suggest that O vacancies are related to gray tracking not only due to their charge-compensating properties, but also due to their optical absorption: The calculated spectra for the $q = +1$ and neutral charge state in the $S = 1$ spin configuration are dominated by defect-related peaks at 1.1 eV, in agreement with the experimental observation that in the initial stage of gray tracking the absorption of 1064-nm (1.17-eV) light increases. In addition, the neutral $S = 0$ spin configurations give rise to an optical absorption that matches the measured absorption maxima characteristic for gray tracks [9]. The calculated midgap optical absorption depends strongly on the light polarization. It is highest for $z$-polarized light, in agreement with the experimental observation that the crystals’ resistance to gray tracking is weakest for laser beams polarized parallel to the $z$ axis [7,8]. The present calculations find the O-vacancy absorption to depend on the charge state. It is weakest for the +2 charge state and successively increases for the +1 and the neutral charge. This suggests Fermi level lowering as a means to suppress the optical absorption leading to gray tracking.

While the present computational results clearly indicate that O-vacancy-related light absorption is instrumental for the initial stages of gray tracking, the subsequent steps that include structural modifications still need to be understood.

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