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Band structure and linear optical properties of $KTiOPO_4$

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The electronic structure and optical properties of $KTiOPO_4$ have been calculated using a first-principles self-consistent method. It is shown that the electronic structure is characterized by localized molecular units of TiO_6 and PO_4. Effective-charge calculation shows K and Ti to be highly ionized while P is also positively ionized because of the charge transfer to O atoms. The presence of the short Ti-O bonds in $KTiOPO_4$ has a profound effect on its electronic structure. The calculated optical properties and their anisotropy are in good agreement with recent experimental measurement.

$KTiOPO_4$ (KTP) is a nonlinear optical material with the large second-harmonic generation of the Nd-doped lasers.[1,2] This excellent nonlinear optical property coupled with high optical damage threshold and other desirable material properties rendered KTP a very promising material for many electron-optical applications.[1-3] The large nonlinear optical susceptibilities in this crystal also lead to the possibility of ferroelectric phase transitions at higher temperatures.[4] The fundamental electronic structure and bonding of this interesting crystal have not been studied theoretically in detail. KTP belongs to a family of inorganic crystals with a formula unit of $MTiOXO_4$ where M can be K, Rb, or Tl, and X can be P or As. A detailed understanding of its fundamental physical properties in relation to its structure and constituent elements may lead to discoveries of even better nonlinear optical materials. In this paper, we present the electronic structures of KTP calculated by the first-principles orthogonalized linear combinations of atomic orbitals method (OLCAO). In addition, the linear optical properties of this crystal are also studied and compared with the very recent experimental measurement using vacuum ultraviolet (VUV) spectroscopy.[5] A similar study on another very important nonlinear optical crystal, LiB_3O_5, has been presented before.[6]

There are two types of KTP crystal samples, one made by the low-temperature hydrothermal technique and another using the high-temperature flux growth. The slightly different properties of these two types of samples are probably related to the presence of different defects such as K or O vacancies, or OH^- ions.[7] For theoretical calculation of the electronic structures, we use the crystal structure as measured by Tordjman, Masse, and Guitel.[8] The orthorhombic cell (space group $Pna2_1$) contains eight formula units with a total of 64 atoms. The reported lattice constants are $a=12.814$ Å, $b=6.404$ Å, and $c=10.616$ Å. There are two inequivalent types of K, Ti, and P atoms per cell [labeled as K(1), K(2); Ti(1), Ti(2); P(1), and P(2)] and ten different O sites [labeled as O(1)-O(8), O(Ti1), and O(Ti2)]. The structure can be viewed as consisting of chains of distorted TiO_6 octahedra and chains of distorted PO_4 tetrahedra with K ions residing in the open channels.[1] Such open structure facilitates the ionic conduction of the K ions along the z direction. A particular feature of the KTP crystal is the presence of two short Ti-O bonds of 1.718 Å [Ti(1)]-O(Ti2)] and 1.738 Å [Ti(2)-O(Ti1)]. The other Ti-O bond lengths in the TiO_6 octahedra range from 1.90 to 2.16 Å. The normal Ti-O bond length in rutile (TiO_2) is 1.96 Å. The presence of these two short Ti-O bonds in the chain results in a net z-direction polarization and is responsible for the large optical nonlinearity in KTP.[1]

The electronic structure of KTP crystal is calculated using the first-principles self-consistent OLCAO method within the local-density approximation.[9] The basis function consists of the atomic orbitals of K (argon core plus $4s$, $4p$, and $3d$), Ti (argon core plus $4s$, $4p$, and $3d$), P (neon core plus $3s$, $3p$), and O ($1s$, $2s$, $2p$). Because of the large unit cell, additional excited-state orbitals are not included in the basis set. The crystal potential and the charge density of the crystal are linearly fitted to a sum of atom-centered Gaussian functions with a fixed set of exponentials.[9] We have achieved a fitting accuracy of 0.169 electrons out of a total of 320 valence electrons in the cell.

The band structure of KTP is shown in Fig. 1. Both the valence bands (VB) and the conduction bands (CB) are very flat, typical of inorganic crystals with localized molecular units as building blocks. A direct band gap of about 4.9 eV at the zone center is obtained. This is about 1 eV larger than reported from optical measurement.[5] This is quite unusual since local-density calculations generally underestimate the gap value. Had an extended basis set including the excited atomic orbitals been used in the calculation, the band gap would be expected to decrease because of the increased variational freedom in better agreement with the experiment. However, such a

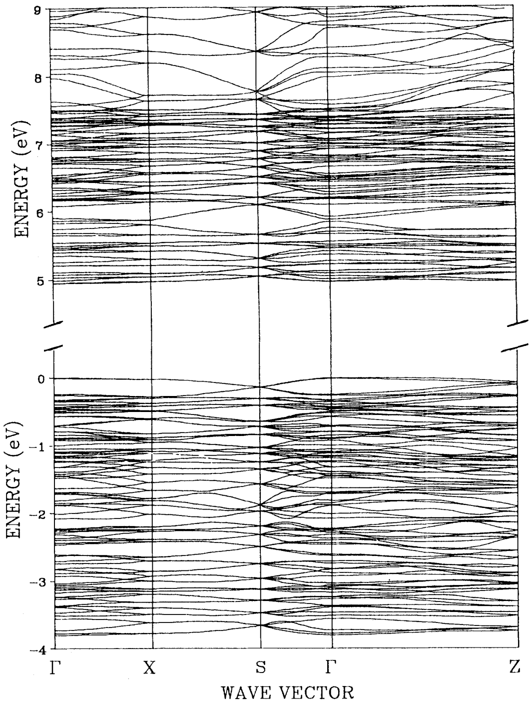

FIG. 1. Calculated band structure of KTP.

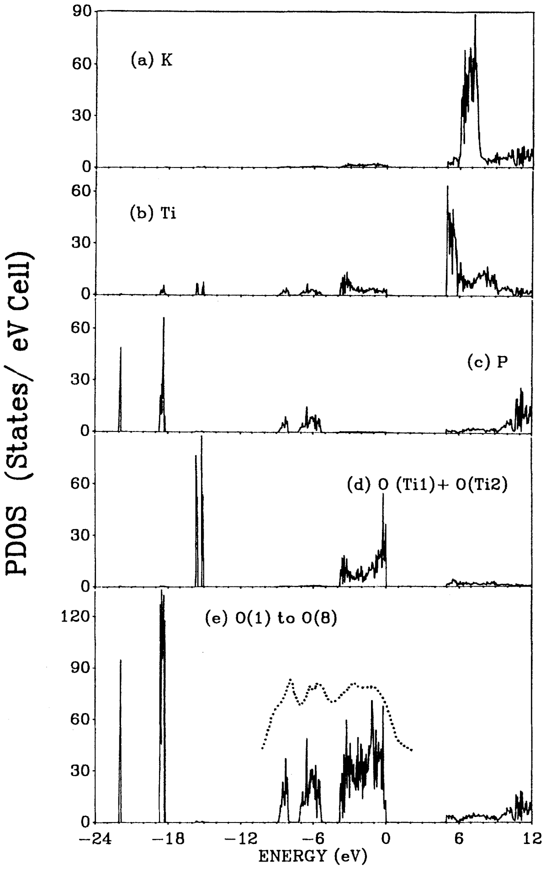

FIG. 2. Calculated PDOS of KTP: (a) K; (b) Ti; (c) P; (d) O(Ti1) and O(Ti2); (e) O(1)–O(8). The dotted line is the experimental data from Ref. 5.

large basis set for a crystal as complicated as KTP may still be prohibitively cumbersome. It is also possible that the sample used in the measurement contains some trace of impurities and defects which generally affect the measured band gap.

The electronic structure and bonding in KTP are best described by the atom-resolved partial density of states (PDOS) shown in Fig. 2. The basic features in the DOS can be summarized as follows: (1) The K atoms are highly ionized with an empty-state band 1.8 eV wide at 6–7.8 eV in the CB. (The zero of energy is set at the top of VB.) (2) The Ti atoms are also significantly ionized. The bottom of the CB is composed mainly of Ti $3d$ orbitals. This Ti CB is about 1 eV wide, from 4.9–5.9 eV. The presence of some PDOS of Ti in the VB region shows that the Ti-O bond is at least partially covalent. We may divide the PDOS of the Ti VB into three energy regions labeled as *A* (0 to −3.8 eV), *B* (−5.3 to −7.2 eV), and *C* (−8.0 to −8.9 eV). Ti atoms interact with O in all three regions. (3) The PDOS of P ion is the most interesting. The sharp peak at −21.9 and −18.3 eV shows strong interaction with the O $2s$ orbitals in forming tetrahedral bonding in PO_4. Its interaction with the O $2p$ orbitals is limited to the regions *B* and *C*. There is also significant presence of P states in the CB region from 10.7 to 13 eV, indicating that P atoms may be positively ionized. (4) The O atoms in KTP can be divided into two distinctive groups with vastly different electronic structures. The first group consists of O(1)–O(8); the second group consists of O(Ti1) and O(Ti2) which contains the short Ti-O bonds as discussed earlier. The $2s$ levels of the first group are at −21.9 and −18.5 eV as the result of interaction with the P atoms. The O $2p$ PDOS of the first group cover all three regions *A*, *B*, and *C*. For the second group, the $2s$ levels are at −15.7 and −15.1 eV while the O $2p$ PDOS is present only in the region *C*. Inspection of wave functions at the zone center shows the states at the top of the VB are derived predominantly from the $2p_x$ and $2p_z$ orbitals of the O(Ti1) and O(Ti2) atoms. (5) The three energy regions of O $2p$ PDOS are in good agreement with the data from the VB x-ray photon-emission measurement,[5] which shows three overlapping peak structures in the same region. This is sketched in Fig. 2(e) as a dotted line.

The calculated effective charges on each type of atom using a Mulliken scheme[10] are listed in Table I. The Mulliken scheme, when used with a minimal basis set, gives a

TABLE I. Calculated effective charges on each ion in KTP crystal.

Ion	Q^* (elec.)	Ion	Q^* (elec.)
K(1)	0.59	O(1)	6.72
K(2)	0.53	O(2)	6.70
Ti(1)	2.67	O(3)	6.69
Ti(2)	2.62	O(4)	6.75
P(1)	3.36	O(5)	6.69
P(2)	3.35	O(6)	6.78
O(Ti1)	6.57	O(7)	6.71
O(Ti2)	6.55	O(8)	6.70

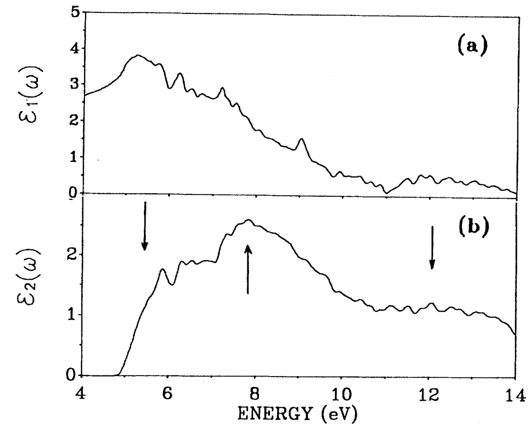

FIG. 3. Calculated (a) real and (b) imaginary parts of a portion of the dielectric function of KTP. The arrows show the approximate peak positions in the experimental data.

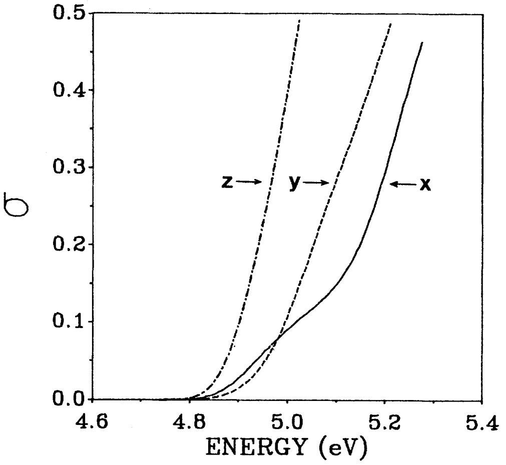

FIG. 4. Calculated optical conductivity of KTP near the threshold in x, y, and z directions.

pretty good qualitative description of the effective ionic charges. While a high degree of ionicity for K and Ti are expected, it is quite surprising to see that P in KTP is actually electropositive, losing an average of about 1.6 electrons to the O atoms per P ion. We also note that O(Ti1) and O(Ti2) which contain short O-Ti bonds are less electronegative than other O atoms.

The interband optical conductivity of KTP is calculated using the energy eigenvalues and wave functions at 36 **k** points in $\frac{1}{8}$ of the Brillouin zone. For each component, the diagonal conductivity tensor elements are evaluated according to

$$\sigma_{xx}(E)=\frac{2\pi e^2}{mE\Omega}\frac{\Omega}{(2\pi)^3}\int d\mathbf{k}\sum_{nl}|\langle\psi_n(\mathbf{k},\mathbf{r})|\mathbf{P}_x|\psi_l(\mathbf{k},\mathbf{r})\rangle|^2 f_l(\mathbf{k})[1-f_n(\mathbf{k})]\delta(E_n(\mathbf{k})-E_l(\mathbf{k})-E)\,, \tag{1}$$

where $E=\hbar\omega$ is the photon energy, $f_l(\mathbf{k})$ the Fermi distribution function. The momentum matrix elements between an occupied VB state l and an unoccupied CB state n are fully taken into account in Eq. (1). From the conductivity curve, the real $[\varepsilon_1(\omega)]$ and the imaginary $[\varepsilon_2(\omega)]$ parts of the dielectric function (averaged over three Cartesian directions) can be obtained and are shown in Figs. 3(a) and 3(b), respectively.[9] Recent VUV measurements show three very prominent peaks at 5.3, 7.8, and 12 eV in $\varepsilon_2(\omega)$ in this frequency from 0 to 14 eV region. Our calculation does show structures in $\varepsilon_2(\omega)$ at 5.9, 7.9, and 12 eV with some additional smaller structures. The slightly larger discrepancy in the position of the first peak reflects the difference in the band gap. From the PDOS diagrams of Fig. 2, the three experimentally observed structures can be roughly assigned as due to transitions from the top of the VB to Ti-, K-, and P-dominated CB, respectively. However, our calculated peaks in $\varepsilon_2(\omega)$ are less sharp than the measured ones. The origin of this discrepancy is unknown at this moment. At 4 eV, the calculated $\varepsilon_1(\omega)$ is 2.70, which is close to the measured value of about 3.4 at the same energy.[5]

One of the important features of the linear optical properties in KTP is its optical anisotropy.[1,5,11] Figure 4 shows the calculated optical conductivity which is directly related to absorption in the three crystallographic directions near the absorption edge. It shows the threshold is smallest in the z direction and largest in the x direction. This is in full agreement with the near-edge absorption measurement.[5] This same anisotropy accounts for the different refractive indices [also $\varepsilon_1(\omega)$] along the three principal directions and could play a crucial role in the optical nonlinearity in this crystal. The origin of this anisotropy near the threshold resides on the nature of the Bloch functions at the top of the VB and the bottom of the CB. As has been stated above, the top of the VB consists of O $2p_x$ and O $2p_z$ orbitals of the O(Ti1) and O(Ti2) atoms and the bottom of the CB consists of a mixture of the Ti $3d$ orbitals, it is clear that the nonlinear optical properties in KTP is basically controlled by the distorted bonding structure in the Ti-O_6 octahedra.

In conclusion, we have calculated a band structure of the KTP crystal using a first-principles method. The electronic structure shows the characteristic of localized molecular units of TiO_6 octahedra and PO_4 tetrahedra. The O(Ti1) and O(Ti2) atoms which share very short bonds with the Ti atoms have electronic structures distinctively different from other O atoms. The calculated optical properties are in good agreement with the experimental data, especially with the optical anisotropy near the threshold region. We are currently extending our calculations to a higher photon energy range by enlarging our basis set and by studying the electronic and the electro-optical properties of the analog crystal $KTiOAsO_4$, which shows quite different optical properties from KTP.[12,5]

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