

RECENT ADVANCES IN NONLINEAR OPTICS OF KTiOPO_4

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ABSTRACT

Potassium titanyl phosphate (KTP) is an exceptional nonlinear optical material. First principles, energy band computation shows that its linear and nonlinear optical properties are essentially dominated by the Ti-O bonds. Optical channel waveguides and devices have been fabricated on KTP substrates by ion exchange. These waveguides and devices have outstanding performance characteristics. Recent advances in material understanding and device design are reviewed.

INTRODUCTION

KTiOPO_4 (KTP) is a relatively new material that is widely used for frequency doubling the 1 μm radiation of YAG:Nd lasers [1,2]. The combination of large nonlinear d coefficients (5 to 13.7 pm/V), large electrooptic r coefficients (8.8 to 35 pm/V), high optical damage threshold ($>10 \text{ GW/cm}^2$), large temperature bandwidth (25°C-cm) and low dielectric constant (11 to 15.4 at optical frequency) makes KTP a superior material for applications in frequency generation, switching and modulation. We have recently computed its electronic band structure and optical properties from first principles [3]. Our computational method and principal findings will be highlighted here.

Due to its crystal structure, the ionic conductivity of KTP is highly anisotropic: it is very large along the crystal z axis but very small in the x - y plane. Consequently, high-quality optical waveguides with very sharp rectangular cross-sections can be created in a KTP substrate by exchanging K^+ ions with suitable monovalent or divalent ions [4]. These waveguides have been used for electrooptic

modulation [5, 6] and second harmonic generation [7, 8]. In general, these waveguide devices have outstanding performance characteristics and are very stable against photorefractive and temperature fluctuations. Recent advances will be reviewed.

BAND STRUCTURE AND OPTICAL PROPERTIES

Crystal Structure

KTP has an orthorhombic unit cell and belongs to the space group $Pna2_1$ [9]. There are 64 atoms or 8 formula units in the unit cell. The lattice constants are $a = 12.814 \text{ \AA}$, $b = 6.404 \text{ \AA}$, and $c = 10.616 \text{ \AA}$. The structure is characterized by chains of TiO_6 octahedra that are linked at two corners. There are two chains per unit cell and the chain direction alternates between $[011]$ and $[0\bar{1}1]$. Alternating long and short Ti-O bonds occur along these chains, which result in a net polarization along the z direction.

The K ions are weakly bonded to both the TiO_6 octahedra and PO_4 tetrahedra. The K ions are located in two positions and surrounded by 8 and 9 oxygen ions, respectively. Channels exist along the z direction whereby K ions can diffuse through a vacancy mechanism [10]. The ionic conductivity along z direction is, therefore, several orders of magnitude greater than the conductivity in the x - y plane.

Band Structure

We have computed self-consistently the band structure of KTP from first principles by the pseudofunction (PSF) method [11]. This method has been successfully used to study the electronic and superconducting properties of high T_c superconductors [12] and the electronic and magnetic properties of ruthenate pyrochlores [13]. All these oxides, like KTP, have complex crystal structures with a large number of atoms in the unit cell. In the PSF method, we divide the crystal potential into two parts: the spherical muffin-tin potential around each atom and the non-spherical remainder. Exchange and correlation are treated by the local density approximation [14]. The Schrodinger equation is solved by iteration of the total potential and basis functions to self consistency. Our basis functions, the pseudofunctions, are composed of overlapping radial functions of the muffin-tin potential. The key features of these functions are: (1) they are orthogonalized to the core electronic states inside the core regions (and, therefore, the name pseudofunctions), (2) they are the full numerical solutions of the muffin-tin potentials and, therefore, faithful representations of the electrons in the interstitial bonding regions, and (3) they smoothly become a set of decaying Neuman functions (for the valence band states) or oscillatory Bessel functions (for the conduction band states) sufficiently far away. In other words, the pseudofunctions are optimally chosen and specifically designed for complex solids such as KTP. In our computation, we have used 272 basis functions which are consisted of four s and p functions each for the K, P and O atoms, and six d and s functions each for the Ti atoms in the unit cell.

The resultant band structure is very complex. The conduction bands near the optical gap are primarily Ti d states which are split by crystal field into two bands. The valence bands are composed of O $2p$ states and are split into 3 peaks

by virtue of the distorted TiO_6 octahedra. The splitting of the oxygen valence band was confirmed by photoelectron spectroscopy. From an analysis of the partial density of states, we concluded that the topmost O valence peak arises solely from the short Ti-O bonds along the z direction. These features suggest that the linear and nonlinear optical properties of KTP are dominated by the TiO_6 octahedra and, particularly, the short Ti-O bonds.

Optical Properties

The linear and nonlinear optical properties were computed by the standard momentum space formulation [15]. We found strong interband transitions between valence and conduction bands and pronounced polarization dependence of the transitions. We conclude that the optical gap is smallest along the z direction and largest along the x direction. This dependence is a direct result of the distortion of TiO_6 octahedra. The computed optical conductivity spectra were in excellent agreement with optical absorption data.

The computed second harmonic d coefficients have magnitudes in reasonable accord with data and the correct relative signs. Detailed analysis shows that the entire reciprocal space and electronic bands over a wide energy range contribute to the d coefficients. It is, therefore, difficult to distill a simple relationship between the electronic/crystal structure and nonlinear optical properties. Nevertheless, our computation suggests that the phosphate group does not contribute significantly to either the d coefficients or the linear optical properties in the UV range. Our results also suggest that cluster calculations [16] where complex crystal structures are approximated by a single distorted octahedron are over simplified in two important respects: (1) there appears to be no easily defined average k point that reproduces simultaneously the complex behavior of all the non-vanishing d coefficients, and (2) the TiO_6 octahedra have important interactions with the alkali atoms and phosphate groups. Additional details will be published elsewhere.

WAVEGUIDE DEVICES

Waveguide Fabrication

Optical channel waveguides have been fabricated in KTP substrates by an ion exchange process using standard chemicals [4,5]. The substrates are cut, polished, and covered by a suitable metal mask. Then they are immersed in molten nitrate salt of Rb, Cs, Tl, or mixtures of these salts at 300-400°C for 0.5-4 hr. Since the ionic conductivity is several orders of magnitude greater in the z direction than in the x-y plane, we will restrict our discussion in the following to channel waveguides on z-cut substrates. These guides have sharp boundaries and uniform cross sections. Typical increases in the surface refractive index are 0.02 for Rb- and Cs-exchanged guides and 0.2 for Tl-exchanged guides.

Since the ion exchange rate depends on substrate ionic conductivity, variations in conductivity will result in variations in waveguide properties. Such variations have been observed which in turn have caused some problems with device fabrication. To reduce the effects of variations in substrate conductivity and to further improve the waveguide uniformity, a divalent ion salt is added to the monovalent nitrate salt bath. For ions of the appropriate ionic radii, small amounts

of the divalent ion will substitute for K in the lattice resulting in the formation of K vacancies. These vacancies increase the ionic conductivity [10] which increases the monovalent ion exchange rate and, hence, reduces the effect of variations in substrate conductivity. Among the alkaline earth ions, Ba has an ionic radius best matched to K and thus appears to be the most effective.

Waveguide Devices

Several KTP electrooptic and nonlinear optic devices have been fabricated by the above process and fully characterized.

The measured halfwave voltage, V_{π} for several single-channel phase modulators indicates that the waveguide fabrication process does not alter the electrooptic coefficient. By coupling to the r_{c2} electrooptic coefficient, a V_{π} of 6 V-cm was obtained at 6328 Å from a 6 μm wide channel waveguide with a 200 nm of MgF₂ buffer layer, which is close to the theoretical value. These single-channel modulators are dc stable.

A Mach-Zehnder modulator has also been fabricated [6]. The modulator was constructed on a 1 mm thick, z-cut KTP substrate with a 400 nm SiO₂ buffer layer. The optical waveguides were 6 μm wide Rb exchanged guides; the traveling-wave electrodes had a 25 μm gap and a 1 cm interaction length with the optical waveguides. The bandwidth was 16 GHz and V_{π} was 10 V at 1.3 μm and 5 V at 0.633 μm, respectively. In addition to being dc and thermally stable, this modulator did not exhibit any instabilities due to optical damage or photorefraction, which are commonly observed in other materials.

Second harmonic generation (SHG) in KTP channel waveguides has also been established. Using a 6 μm wide Rb exchanged guide and a diode pumped YAG:Nd laser, a conversion efficiency of 4%/W-cm² was established for type II SHG at 1.064 μm. The conversion efficiency has since been improved considerably in a segmented waveguide configuration. In this new configuration, ion exchange took place in alternating segments of the channel only whereas, for the normal configuration, ion exchange took place uniformly throughout the entire channel. The length of each segment is a few μm and chosen such that the phase mismatch in one segment is exactly cancelled by the phase mismatch in the adjacent segment [7]. A conversion efficiency of 15%/W-cm² at 1.064 μm and about 5%/W-cm² at 1.3 μm was achieved in these waveguides. Very recently, we discovered that periodic reversal of ferroelectric domains occurred spontaneously in segmented waveguides. We were, therefore, able to phase-match primary wavelength < 1 μm and successfully generated blue to ultra-violet light by type I SHG with very high efficiency, >50%/W-cm² [8].

CONCLUSIONS

The nonlinear optical properties of KTP were shown to originate from the distorted TiO₆ octahedra by a first-principles energy-band calculation. The computed valence band density of states and optical conductivity were in good agreement with photoelectron and optical absorption data. In addition to the well-known bulk applications, KTP is an excellent candidate for guided-wave optic and integrated

optic applications due to its unique anisotropic ion diffusion and exchange processes. Prototypical electrooptic and nonlinear optic waveguide devices have been fabricated and outstanding performances have been demonstrated.

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