Structure sensitive properties of KTP-type crystals

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Abstract **Adding various dopants during the growth of the parent KTiOPO4 (KTP) crystal has given rise to an extensive series of KTP-type crystals. The doped KTP or KTP-type crystals often have very subtle structural variations from pure KTP crystals. As a result of these structural changes the KTP-type crystals often exhibit different physical properties, which may be referred to as structure sensitive properties. It is possible to fine-tune the nonlinear optical properties of KTP crystals through doping. This results in a broad range of applications for KTP-type crystals.**

Keywords: KTP-type crystals, structure sensitive properties.

Potassium titanyl phosphate ($KTiOPO_4$ or KTP) is a superior nonlinear optical material[1, 2]. It has many attractive properties including large nonlinear optical and electrooptical coefficients, a high laser damage threshold, a wide range of transmission wavelengths, realization of type Ⅰ and type Ⅱ phase matching over a wide range of temperatures, and good chemical and thermal stabilities. Near the Nd-laser wavelength of around 1 μm, the frequency doubling effect of KTP is far superior to any other crystals. KTP crystals are widely used in many laser applications such as frequency doubling, frequency summing, frequency subtraction, parametric oscillation and amplification, electro-optical modulation and deflection, Q-switch and acousto-optical modulation, optical waveguide devices, and integrated optical devices. Though KTP has many useful nonlinear optical properties and is widely used, it has several shortcomings that limit its applications. For example, since the birefringence of KTP is rather small and its cutoff wavelength for type Ⅱ phase matching is 994 nm, it is inadequate for the bulk frequency doubling of lasers operating at wavelengths shorter than 994 nm. This limits its use in the technologically important blue spectral region. Since the 1980s, many people have successfully enhanced and improved the nonlinear optical properties of KTP-type crystals. The structural diversity of KTP has resulted in extensive study of the KTP crystal family including KTP, doped KTP and its isomorphs.

Recently, Satyanaryan et al.[3] provided a comprehensive overview of the KTP crystal family, which included many aspects of material synthesis, crystal growth, crystal defects, nonlinear optical properties, and applications. The authors particularly emphasized the importance of KTP-type crystals in optical waveguides and other photonic devices. Non-critical phase matching (NCPM), measurements of nonlinear and electro-optic properties, and laser damage thresholds of KTP-type crystals have been surveyed by Wang et al.[4]. Recent advances in the elimination of “gray tracking” in KTP and the importance of manufacturing $KTiOAsO_4$(KTA) and $RbTiOAsO_4$(RTA) crystals have been reviewed by Loiacono et al.[5]. Chani et al.[6] have recently developed a new series of doped KTP crystals based on the substitution of Zr^{4+} or V^{5+} for Ti^{4+} and Nb^{5+} or Si^{4+} for Ti^{4+}, P^{5+}, or As^{5+} in KTP or KTA. Scheidt et al.[7] have made tunable noncritically phase matched cw KTP-optical parameter oscillators (OPO) which are pumped by single-mode Ti:Al_2O_3 lasers. Using KTP crystals, Huo et al.[8] have realized intracavity frequency doubling and electrooptic Q-switched operation of a diode laser-pumped Nd:YVO_4 laser, thereby achieving low loss and high efficiency in comparison with the conventional frequency-doubling and Q-switched configuration.

Current studies of the growth, properties and applications of doped KTP and KTP isomorphous crystals lag behind the corresponding investigations of KTP crystal. However, the family of doped KTP crystals is growing rapidly. Further studies of these KTP-type crystals may lead to new applications that can have a significant impact on science and technology.

The reason that KTP-type crystals possess superior nonlinear optical and electro-optic properties, and hence promise a wider application capability stems mainly from the diversity and variation of the crystal structure of KTP.

For many years, we have been studying the fundamentals of the KTP family crystals[2], with the hope of enhancing and improving their nonlinear optical properties. By taking advantage of the diversity of the KTP crystal family, we have demonstrated that when one or two component atoms of the KTP are partially or totally replaced by other dopant atoms, the KTP crystal structure can undergo subtle, local microscopic changes. These microscopic structural changes induce those in the macroscopic physical properties of the crystals, which may be referred to as structure sensitive properties of the crystal. Of course, the extent and effect of these crystal structure sensitive properties may vary from system to system. Structure sensitive properties can be used to fine-tune particular properties of the crystals, thereby improving their potential application prospects.

In this review, the structure sensitive properties of KTP-type crystals are presented.

1 Crystal structure of KTP and KTP-type crystals

(ⅰ) Crystal structure of KTP. Though the crystal symmetry is the same, the constituent atoms of KTP-type crystals can vary. Hence, the structure sensitive properties of KTP-type crystals relate to the specific atoms that constitute the structure of each KTP-type crystal. In 1974, the crystal structure of KTP was first determined by Tordjman et al.[9]. KTP crystallizes in the noncentrosymmetric orthorhombic system, point group C_{2v}-mm2, space group

$Pna2_1$, with lattice parameters of a = 12.814 Å, b = 6.404 Å, and c = 10.616 Å. The structure is characterized by helical chains of distorted TiO_6 octahedra that are linked at two corners and are separated by PO_4 tetrahedra. The distorted TiO_6 octahedra in the c-axis (001) direction bridge the PO_4 tetrahedra to make a framework, forming an infinite $—PO_4—TiO_6—PO_4—TiO_6—$lattice array. The K^+ lattice sites are in the channels of the framework. These channels are along the c-axis (001) direction, along which K^+ easily diffuses via the vacancy mechanism. The Ti atom is six-coordinated, the P atom is four-coordinated, and the K atom is eight- or nine-coordinated by O atoms. Each of the TiO_6 distorted octahedra contains an anomalously short Ti = O double bond (1.74 Å) and an anomalously long Ti-O bond (2.10 Å). The maximum difference of either bond is 0.36Å, resulting in highly distorted TiO_6 octahedra. The KTP crystal structure is shown in fig. 1[3].

Each unit cell of the KTP crystal structure contains two groups of crystallographically non-equivalent $KTiOPO_4$ molecules (Z=8). These two non-equivalent $KTiOPO_4$ molecules form a motif. Each unit cell contains four nonsymmetrical motifs. Four different atoms (K, Ti, O, P) in each motif are all in the general positions of the space group $Pna2_1$[10]. Therefore, each unit cell contains two nonequivalent Ti (Ti(1) and Ti(2)), K (K(1) and K(2)), and P (P(1) and P(2)) lattice sites, and ten nonequivalent O (O(1), O(2), O(3), ⋯, O(10)) lattice sites, for a total of 16 nonequivalent lattice sites in one unit cell. The large number of variables of the KTP-type crystal structure provides a unique opportunity to study structure sensitive properties.

(ⅱ) Crystal structure of KTP-type system[1]. Since the KTP crystal structure possesses great diversity and versatility, it has inspired extensive studies of KTP-type crystals. In KTP-type crystals, the host-guest relationship and the presence of two formula units in one asymmetric unit cell make a large number of synthetic permutations of the crystal structure possible. This approach has been proven quite effective in the development of new nonlinear optical materials based on KTP or its isomorphs and has contributed to a better understanding of the structure sensitive properties of KTP-type crystals. All KTP-type crystals, doped KTP and isomorphous KTP crystals, originate from KTP. The structure diversity of the KTP crystal allows a series of KTP-type crystals to be formed using either the doped single crystal growth method or ion-exchange processing technique. KTP is the main member of the family of compounds with the general formula $MM'OXO_4$[11], where M = K, Na, Ag, Tl, Rb, or Cs; M' = Ti, Sn, Zr, Ge, Al, Cr, Fe, V, Nb, Ta, Sc, Ga, or Ce; and X = P, As, or Si. The choice of M, M', and X has a dramatic effect on the observed nonlinear optical properties of the crystal. In the KTP crystal structure, the K atom can be partially or totally replaced by another element. $K_{1-x}Rb_xTiOPO_4(x<1)$[12] is an example of a doped KTP crystal. When x = 1, the compound is known as an isomorphous KTP crystal, i.e. $RbTiOPO_4$, rubidium titanyl phosphate (RTP). In the KTP crystal structure, the Ti atom can also be partially or totally replaced by another element. An example is the $KTi_{1-x}Nb_xOPO_4$ ($x<1/2$) crystal[13]. When another element totally replaces Ti in the KTP crystal, fundamental structure changes can occur. For example, when Ti is totally replaced by Sn in KTP, the $KSnOPO_4$(KSP) crystal[14] is formed. Unfortunately, the structure of this crystal is fundamentally different from that of KTP. The KSP crystal is very close to the centrosymmetric structure. It deviates from the KTP-type crystal

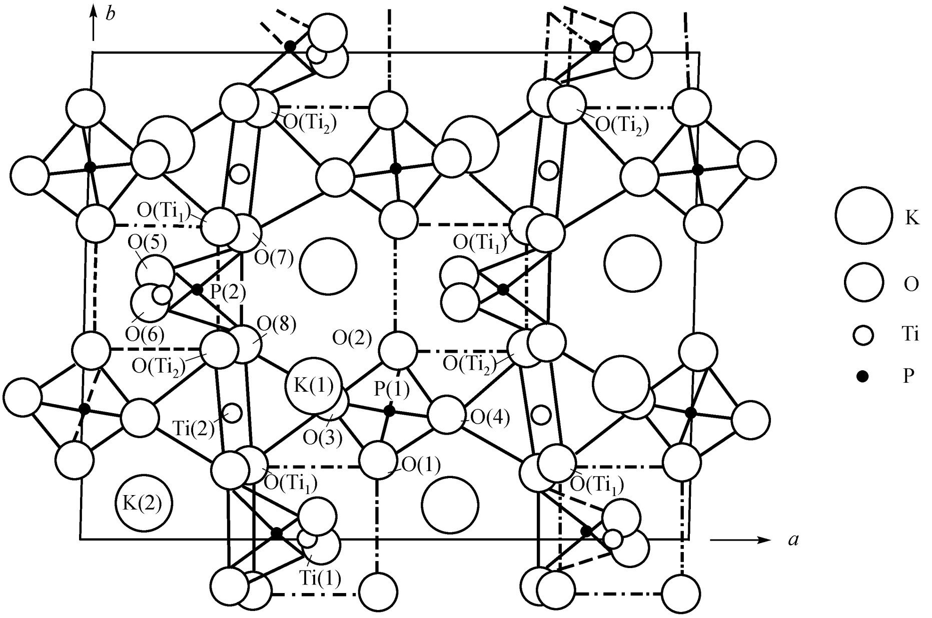

Fig. 1. Projection of KTP crystal structure in the (001) direction.

structure system and does not exhibit second order nonlinear optical properties. In the KTP crystal structure, the P atom can be partially or totally replaced by As. When P is partially replaced, it forms a $KTiOP_{1-x}As_xO_4$ solid solution crystal[5]. When P is totally replaced, it forms the KTP isomorphous $KTiOAsO_4$ (KTA) crystal[15]. There also exists many doubly doped KTP-type crystals, such as $K_{1-x}Rb_xOP_{1-y}As_yO_4$($x$,$y$<1) and $KTi_{1-x}Nb_x$- $OP_{1-y}As_yO_4$.

Since 1980 the family of KTP-type crystals has expanded to over 100 members[1]. This forms a large synthetic crystal system, far larger than other functional crystals. To date, the number of KTP-type crystals continues to increase, as exemplified by the study of mixed valence, doubly doped KTP-type crystals[16].

2 Origin of the nonlinear optical properties of KTP crystals

KTP-type crystals are derivatives of the KTP crystal. When studying the structure sensitive properties of KTP-type crystals, it is of interest to relate the nonlinear optical properties of the crystals to their microscopic structures.

Zumsteg et al.[12,17] calculated the bond parameters and Miller coefficients (Δ) of the $RbTiOPO_4$ crystal using Levine's bond charge model[18] in 1976 based on their extensive studies of crystal growth, crystal structure, and nonlinear optical properties of Rb-doped KTP, $K_{1-x}Rb_x$-$TiOPO_4$. The results show that the anomalously large nonlinear optical properties of $RbTiOPO_4$ crystals arise from the exceptionally short Ti=O bond length in the deformed TiO_6 octahedra. The other Ti-O bonds, the PO_4 tetrahedra and the $(K_xRb_{1-x})O$ groups also contribute, but to a lesser extent. Since Zumsteg et al. and other scientists have made significant contributions to the understanding of the origin of the nonlinear optical properties of KTP. For example, using bond theory, Jarman et al.[14] have calculated the electronic structure of deformed TiO_6 octahedra. Their calculations show that among the lowest energy structures, the higher occupancy orbits in the deformed TiO_6 octahedra contribute the most to the nonlinear optical coefficient of the KTP crystal. At the same time, optic-electron spectra of KTP crystals have been determined, showing that the nonlinear optical properties are critically dependent upon the electronic structure of the covalent bond. A detailed account of X-ray diffraction measurements on KTP single crystals is given by Hanseng et al.[19]. Their experiments were carried out at room temperature and the data were used for the analysis of the electron-deformation density. They found a much more pronounced excess electron density in the short Ti=O bond than in the other bonds. The PO_4 group to Ti interaction seemes to be of an electrostatic nature. The short Ti = O bond possesses a strong polar covalent bond character. The nonlinearity of KTP crystals can be explained by the high hyperpolarizability of the extraordinarily short Ti = O bond. This is the origin of the nonlinear optical effect of KTP crystals. Thomas[20] calculated the refractive index of KTP using point-dipole theory and interpreted it within the existing model of the structural origin of its high nonlinear response. It is shown that both the magnitude and the sign of the optical anisotropy result from the increased polarizability of the oxygen atom in the anomalously short Ti = O bond. Munowitz et al.[21] have studied second harmonic generation (SHG) of the model polymeric structure $[TiO_5\text{-}TiO_6\text{-}TiO_5]$ using the standard quantum mechanics sum-over-states approach. The center TiO_6 group is a distorted octahedron with the 4-fold axis defined by O_1-Ti-O_2. An idealized model of the TiO_6 chain in KTP is shown in fig. 2.

Results of the study show that nonlinear optical effects of the center TiO_6 group will be enhanced as the Ti-O-Ti bond angle increases and chain-oxygen electronegativity decreases. This can be understood that as the Ti-O-Ti bond angle increases, charge moves to the farther O_1 site, thereby causing the increases in the electronic third dipole moment as well as the local polarizability. The results of this theoretical study are in accord with the relationship between the SHG effect and the Ti-O-Ti bond angle of KTP-type crystals determined by experiments. Burdett et al.[22] utilized molecular orbital theory to draw comparisons between the long and short metal-oxygen bonds in the KTP Ti-O chain and the alternating single and double bonds of conjugated π systems in organic compounds. They postulated that this conjugation results in a delocalized excited state in which unoccupied high energy orbitals of a metallic character overlap to form a charge-transfer bond. A major source to the nonlinear optical coefficients of the KTP crystal is attributed to the distortion of TiO_6 octahedra which allows the dipolar excited states to mix with the bonding electronic states producing a strong hyperpolarizability on the Ti = O bond.

The origin of the superior nonlinear optical properties of the KTP crystal has attracted a great deal of interest for many years. The problem has now been solved and a consistent conclusion has been reached from both theory and experiment. The superior nonlinear optical properties of the KTP crystal originate mainly from the distorted TiO_6 octahedra. The extraordinarily short Ti = O bond of the distorted TiO_6 octahedra possesses a very strong covalent bond character. Since Ti(Ⅳ) has a d^0 configuration of relatively low energy, charge can easily transfer between the Ti and O atoms, and is very susceptible to the applied optical field of lasers.

3 KTP-type crystal structure sensitive properties

The theory explaining the origin of the superior nonlinear optical properties of KTP crystals is quite mature. Based on the theory, we shall discuss the structure sensitive properties of doped KTP and isomorphous KTP

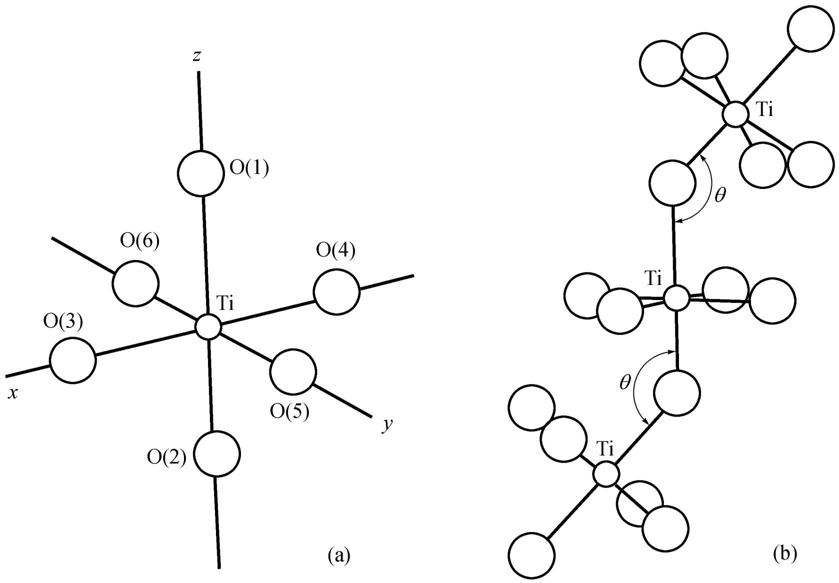

Fig. 2. Ideal model of TiO_6 chain in KTP. (a) Coordinate system defined by TiO_6 subunit; (b) polymeric structure [TiO_5-TiO_6-TiO_5].

crystals.

(i) Substitution of the P lattice site of the KTP crystal. The PO_4 tetrahedra in KTP crystals can be partially or completely substituted by AsO_4 tetrahedra, producing $KTiOP_{1-x}As_xO_4$ (KTPA) or $KTiOAsO_4$ (KTA) crystals. The substitution of the P lattice site alters the overall structural framework of the KTP crystal and hence influences its nonlinear optical properties. For example, a birefringency change results from such a crystal structure change.

(1) $KTiOP_{1-x}As_xO_4$(KTPA) series of crystals ($0<x<1$)[6, 23]. Single domain solid solution KTPA crystals have been grown by using the high temperature solution method. Addition of a minute amount of In_2O_3 aids in the single domain crystal growth. The distribution coefficient (K_P) of P atoms in the KTPA crystals of various different x contents is a constant (0.88). It has been shown that the distribution coefficient of As atoms in KTPA crystals is also a constant. The occupancies for P and As atoms at both $P_{(1)}$ and $P_{(2)}$ lattice sites are random, therefore, KTPA crystal forms a disordered solid solution. The refractive indices along the X, Y, and Z axial directions are linearly proportional to the percentage of As and P in the crystals, revealing a structure sensitive property of the KTPA crystals.

The atomic concentration of As (or P) in the KTPA crystals is controlled by the P/As ratio of the crystal growth solution. The optical properties of KTPA can be adjusted between that of KTP and KTA and is determined by the atomic concentration of As (or P) in the crystal. Critical phase matching (CPM) for 1.064 μm laser light occurs in KTP crystals but not in KTA. Thus by controlling the atomic concentration of As (or P) one can achieve critical phase matching for 1.064 μm laser light in KTPA crystals. Conversely, by measuring the critical or non-critical phase matching for 1.064 μm laser light, one can also predict the preferred composition of KTPA. In addition, angle non-critical phase matching can be accomplished by adjusting the temperature of the KTPA crystal. Achieving critical phase matching or non-critical phase matching can enhance the nonlinear optical effects of the crystal.

(2) $KTiOAsO_4$(KTA) crystal[24]. In comparison with KTP, KTA crystals possess a higher figure of merit for second harmonic generation (SHG), larger electrooptic coefficients, lower ionic conductivities, a lower dielectric constant, and significantly improved nonlinear optical properties.

KTA crystals have been grown by using the high temperature solution method. High quality KTA crystals have been obtained using K_2CO_3-H_3AsO_4-WO_3 as the solvent system.

Mayo et al.[25] have precisely determined the crystal structure of KTA. They found that the difference between the long Ti(1)-O(5) bond and the extremely short Ti(1)-O(6) bond is 0.222 Å while the difference between the long Ti(2)-O(6) bond and the extremely short Ti(2)-O(5) bond is 0.288 Å. The distortion of the TiO_6 octahedra in KTA crystals is less severe than that in KTP crystals, which have corresponding long and short Ti-O bond values of 0.265 and 0.395 Å, respectively. For that reason it can be predicted that the nonlinear optical coefficient of KTA should be smaller than that of KTP. This, however, contradicts to the experimental results obtained so far. The range of bond angles in the $As(1)O_4$ and $As(2)O_4$ groups are the same as that in the corresponding PO_4 groups, but the As-O bond lengths show a much smaller spread, particularly in the $As_{(1)}O_4$ group. Even through the individual

TiO_6 groups that make up the framework of KTA are less distorted than their counterparts in KTP, the MISSYM program calculates that the whole framework of KTA is more distorted than that of KTP. The size of the AsO_4 tetrahedron is larger than that of the PO_4 tetrahedron because the ionic radius of As^{5+}(0.047 nm) is greater than that of P^{5+}(0.035 nm). The AsO_4 tetrahedron in KTA is slightly bent. This bend compresses the KTA framework causing the Ti(2)-O(9)-$As_{(2)}$ angle (126.35°) to be much smaller than the Ti(1)-O(8)-As(2) angle (132.69°), as shown in fig. 3. As a result of this structure distortion, the nonlinear optical coefficient of the KTA crystal is larger than that of the KTP crystal. This is a typical case of a structure sensitive property of a crystal.

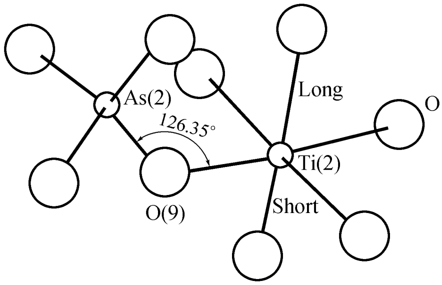

Fig. 3. Ti(2)-O(9)-As(2) bond angle of KTA crystal.

(ii) Substitution of the K lattice site in the KTP crystal. The K^+ ions are located in the channels formed by the crystal framework of KTP. They are not in direct contact with the Ti atoms of the distorted TiO_6 octahedra. Hence, the K^+ ions play a less important role in influencing the SHG effect of the KTP crystal. The K^+ ions in the KTP crystal structure can be substituted partially or completely by monovalent cations.

(1) $K_{1-x}Na_xTiOPO_4$(KNTP) series of crystals (x = 0~1)[26—28]. KNTP crystals have been grown without macro-defects using the high temperature solution method. Since the ionic radius of Na^+ (0.95 Å) is less than that of K^+(1.33 Å), the volume of the unit cell of the KNTP crystal is less than that of KTP crystal. The unit cell volume of the KNTP crystal decreases with increasing Na^+ concentration. By adjusting the volume of the unit cell, one can vary the refractive index ellipsoid of the crystal and achieve type Ⅱ phase matching in KNTP crystals. The efficiency of laser frequency doubling is larger for type Ⅱ phase matching than for type Ⅰ. In addition, non-critical phase matching (θ=90, ϕ=0) can also be achieved by adjusting the Na^+ content of the KNTP crystal. The $K_{0.5}Na_{0.5}TiOPO_4$ crystal can be obtained by the ion exchange processing of the KTP crystal. Both neutron diffraction and NMR spectroscopy show completely ordered Na^+ substituted on the $K_{(1)}$ lattice site in $K_{0.5}Na_{0.5}$- $TiOPO_4$. This kind of doped KTP crystal has many important applications in waveguide technology.

In order to utilize Na^+ to tune the properties of KTP, it is necessary to precisely control the concentration of dopant Na^+ in the KNTP crystal. The X-ray analysis of the crystal structure shows that the Ti(1)-O(9)-Ti(2) bond angle decreases with Na^+ content increasing. This results in a decrease in the unit cell volume. The completely substituted $NaTiOPO_4$(NaTP) crystal (shown in fig. 4) has a Ti(1)-O(9)-Ti(2) bond angle of 130.78°, slightly less than the corresponding bond angle of 135.52° in KTP. The smaller bond angle of the NaTP results in a lower polarization intensity of the short Ti = O bond and thus the SHG intensity of the NaTP crystal is only about 1/10 of that of KTP.

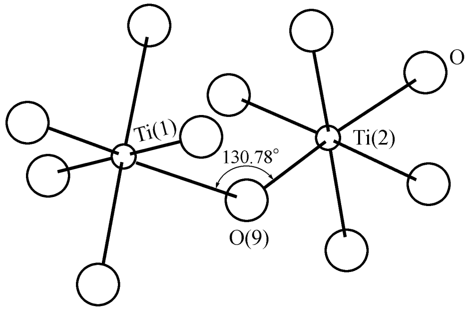

Fig. 4. Ti(1)-O(9)-Ti(2) bond angle of NaTP crystal.

(2) The $K_{1-x}Rb_xTiOPO_4$(KRTP) series of crystals (x = 0~1)[12, 29, 30]. The radii of K^+ and Rb^+ are 1.33 and 1.48 Å respectively. The difference between the two ionic radii is less than 10%, while the charge and electronegativity of the two ions are essentially the same. In general, K^+ and Rb^+ can form the $K_{1-x}Rb_xTiOPO_4$ solid solution crystal in any molar ratio. When Rb^+ is completely substituted for K^+ in KTP, the $RbTiOPO_4$(RTP) crystal is obtained. The refractive indices, nonlinear optical coefficient and electrooptical coefficient of RTP are larger than those of KTP. Since Rb^+ is larger than K^+, the channels along which K^+ would transfer freely are impeded. This results in a lower conductivity and thus a higher laser damage threshold for the RTP crystal. For these reasons, RTP forms electrooptical devices superior to those made of KTP. This is a rather outstanding example of structure sensitive properties.

KRTP series crystals can be obtained using the ion-exchange process. The $K_{0.5}Rb_{0.5}TiOPO_4$ crystal is one of the more important optical waveguide materials. KRTP crystals have been grown using the high temperature solution method. However, the growth of high quality KRTP and RTP crystals is rather difficult. This is most likely because the large Rb^+ ion introduced into the KTP crystal structure induces lattice distortion and stress which decreases crystal structure stability.

(3) $RbTiOAsO_4$(RTA) and $CsTiOAsO_4$(CTA) crystals. RTA and CTA crystals can be regarded as derivatives of the KTP crystal. Both crystals have been grown using the high temperature solution method.

The RTA crystal[3,31,32]. RTA crystals tend to form ferroelectric multidomains. The addition of certain trivalent oxides of Sc and In (such as Sc_2O_3 and In_2O_3) results in the formation of single domain crystals. The conductivity of RTA is quite low for this isomorphic series, resulting from the restricted mobility of the large Rb^+ cation. As a result, the RTA crystal exhibits a hystereses loop at room temperature. Its refractive indices are higher than those of KTP. The nonlinear optical coefficients d_{32} and d_{33} are larger than those of KTP while d_{31} is smaller. Phase matching measurements indicate that RTA is capable of type Ⅰ phase matching for second harmonic generation (SHG) of 1.064 μm laser light with the best matching at angles of $\theta = 52.7^\circ$ and $\phi = 39.8^\circ$. RTA is also capable of type Ⅱ phase matching. The transmission range of RTA extends from 0.35 to 5.3 μm. Bulk RTA crystals are good candidate materials for the construction of broadly tunable infrared femtosecond and picosecond optical parametric oscillators.

The large unit cell volume of the RTA crystal can easily accommodate doping by the relatively large lanthanum series ions. The nonlinear optical properties of doped RTA crystals are very sensitive to the dopant concentration. The second harmonic intensity is found to decrease exponentially with lanthanum series ion concentration increasing. Doping with lanthanum series ions reduces anomalous dispersion in phase matched SHG and blue-shifts the type Ⅱ non-critical phase matched wavelength of the crystal.

The CTA crystal[3, 31—34]. The CTA crystal exhibits larger second order nonlinear susceptibility than the parent KTP crystal. This is because the larger Cs^+ and As^{5+} cations are more easily polarized than the smaller K^+ and P^{5+} cations. CTA has the largest unit cell of any member of the two KTP type crystal families: $MTiOPO_4$ and $MTiOAsO_4$. High quality CTA crystals are difficult to grow. The growth rate along the (110) direction is nearly an order of magnitude faster than that along the (100) direction, revealing the strongly anisotropic growth habit of the CTA crystal. The addition of certain trivalent oxides such as Sc_2O_3 and In_2O_3 into the solution promotes the growth of single domain CTA. The conductivity and dielectric properties of CTA are superior to those of KTP and KTA. In the CTA, the large Cs^+ ions pack closely in the channels leaving no voids, resulting in a nearly negligible conductivity along the polar axis. In comparison with KTP, CTA crystals have a smaller birefringence and are suitable for frequency doubling applications in the spectral region from 1.3 to 1.5 μm. The smaller birefringence enables the phase matching angles for frequency doubling of the 1.32 μm Nd∶YAG laser to be blue-shifted. Higher refractive indices and lower dielectric constants (ε_{33}) give this crystal a bulk modulator figure of merit 2.5 times higher than that of KTP. The nonlinear optical properties of CTA are superior to those of KTA and RTA, especially for type Ⅱ SHG of 1.32 μm fundamental laser light. The CTA crystal with an improved infrared transmission range from 0.37 to 5.3 μm, a larger angular tolerance, and a higher conversion efficiency has added advantages for optical parameter oscillation (OPO) device applications. However, there exists a structure stability problem in CTA crystals. It decomposes into a cubic cesium deficient compound ($Cs_{0.75}TiOAsO_4$) at the relatively low temperature of 920℃. This thermal decomposition can be understood by using a “threatened structure” model based on the interaction between the Cs^+ sublattice and the covalent $TiOAsO_4$ framework. The covalent framework ($TiOAsO_4$) in KTA is more or less rigid. The volume of the helical channels containing the K^+ ions is fixed. As the K^+ ions are replaced with the much larger Cs^+ ions, the covalent framework is strained. At a sufficiently high temperature, the framework falls apart in preference to a cubic crystal structure containing fewer Cs^+ ions. This decomposition not only changes the physical and chemical properties of the crystal, but also changes the chemical composition.

In the $MTiOAsO_4$ ($M=K^+$, Rb^+, Tl^+, or Cs^+) crystal series, the structural stability of the crystal gradually increases with ion radius decreasing. In order of structural stability, the crystals are ranked as follows:

$$\begin{array}{ccccccccc}
\mathrm{CsTiOAsO_4} & \rightarrow & \mathrm{RbTiOAsO_4} & \leftrightarrow & \mathrm{TlTiOAsO_4} & \rightarrow & \mathrm{KTiOAsO_4} & \rightarrow & \mathrm{KTiOPO_4} \\
\mathrm{C_{2v}\text{-}mm2} & & \mathrm{mm2} & & \mathrm{mm2} & & \mathrm{mm2} & & \mathrm{mm2} \\
 & & \text{stable} & & \text{stable} & & \text{stable} & & \text{most stable}
\end{array}$$

Hence, when $K_{1-x}Cs_xTiOAsO_4$ crystals are grown with the high temperature solution method, tuning the x value in crystal can increase the structural stability of the crystal. Various properties of KTP and its important isomorphs (KTA, RTP, RTA, and CTA) are listed in table 1.

(iii) Substitution of the Ti lattice site in the KTP crystal. The Ti atom sits in the center of the TiO_6 distorted octahedron in the crystal structure, where it plays a key role in generating the superior nonlinear optical properties of the KTP crystal. Substitution of the Ti lattice site by other metallic ions including 3, 4, and 5 valence metallic ions of main group elements, sub-group elements, and partial rare earth elements has been extensively studied resulting in a wide variety of new KTP type crystals.

(1) $KTi_{1-x}Zr_xOPO_4$ (KTZP) ($x < 0.01$ mol) series of crystals[35, 36]. Zr and Ti are both group IVB elements, with very similar physical and chemical properties. The outermost electronic configuration of Zr^{4+} is $4d^0$ and thus the ion does not absorb visible light. The empty d_π orbital of Zr^{4+} can bond with the p_π orbital of O^{2-} to form a ZrO_6 octahedron. The ionic radius of Zr^{4+}(0.78 Å) is larger than that of Ti^{4+}(0.68 Å). The substitution of a minute amount of Zr^{4+} for Ti^{4+} in KTP increases the degree of distortion of the TiO_6 octahedron enhancing SHG in the resulting crystal. KTZP crystals have been grown with the high

Table 1 Various properties of KTP and its important isomorphs (KTA, RTP, RTA, and CTA)[3]

Parameter properties		KTP	KTA	RTP	RTA	CTA
Lattice Parameters/Å	a	12.804	13.130	12.974	13.264	13.486
	b	6.404	6.581	6.494	6.682	6.8616
	c	10.616	10.781	10.564	10.7697	10.688
	$\alpha=\beta=\gamma=90^\circ$					
Density/g • cm^{-3}		2.99	3.48	3.60	4.05	4.51
Dielectric constant ε_{33} (22℃)		55 (100 KHz)	26 (200 KHz)	18 (100 KHz)	19 (200 KHz)	36 (100 KHz)
Conductivity σ_{33}/S • cm^{-1}		9.9×10^{-6}	10^{-6}	2.5×10^{-6}	3.2×10^{-8}	2.7×10^{-9}
Curir temperature/℃		892—960	803—880	785—829	765—810	644—680
Refractive Indices (1064 nm)	n_x	1.740	1.782	1.779*	1.803	1.850
	n_y	1.748	1.790	1.788*	1.809	1.865
	n_z	1.830	1.868	1.875*	1.881	1.920
Transparency/nm		350—4500	350—5300	350—4500	350—5300	370—5300
Laser damage threshold (GW/cm^2, 1064 nm)		31 1 pulse, 8.5 ns	1.2 10^3 pulse, 8 ns	0.9	–	–
NLO Coefficients (1064 nm, Pm • v^{-1})	d_{31}	2.54	2.8	3.3	2.24	2.1
	d_{32}	4.35	4.2	4.1	7.73	3.4
	d_{33}	16.9	16.2	17.1	19.62	18.1
Electrooptic coefficients (632.8 nm, Pm • v^{-1})	γ_{13}	9.5	15	9.7	13.5	14.2
	γ_{23}	15.7	21	10.8	17.5	18.5
	γ_{33}	36.3	40	22.5	40.5	38
	γ_{24}	9.3	–	14.9	–	–
	γ_{15}	7.3	–	7.6	–	–

*, 706.5 nm.

temperature solution method. However, the addition of Zr^{4+} to the growth solution has several effects on the properties of the system including decreasing the solubility, increasing the saturation temperature, and increasing the viscosity. High quality KTZP crystals are extremely difficult to grow because multinucleation occurs frequently during crystal growth. The distribution coefficient of Zr^{4+} ions in KTZP crystals has been calculated to be 0.19 to 0.39, which shows that Zr^{4+} ions can be easily substituted into the KTP crystal structure. The larger radius of the Zr^{4+} ion results in a larger unit cell volume in KTZP crystals. The transparency range of KTZP is nearly identical to that of KTP. Measurement of KTZP crystal powder shows a larger SHG than KTP, because the presence of ZrO$_6$ octahedron in the KTZP crystal increases the disparity between the long Ti-O bond and the extremely short Ti=O double bond of the distorted TiO$_6$ octahedron. The disparity increases the electron density around the O atom at the end of the extremely short Ti=O double bond resulting in an increase in the polarizability. Substitution of Zr into the O—Ti—O—Ti— long bond increases the structural asymmetry enhancing the SHG effect of the KTZP crystal.

(2) KTi$_{1-x}$Nb$_x$OPO$_4$(KTNP)(x<0.01) series of crystals[37—40]. KTNP single crystals have been grown with the high temperature solution method. Substituting Nb into KTP causes significant changes in the growth habit. It causes a substantial decrease in the growth rate in the (100) direction, resulting in a platelet morphology for the KTNP crystals. The electron configuration of Nb^{5+} is 4d^0 which is similar to the 3d^0 configuration of Ti^{4+} in which both ions possess an empty, low energy d^0 orbital. Therefore, substitution of Nb^{5+} does not affect the excited state charge transfer mixing coefficient of the Ti-O bond, which leaves the TiO$_6$ distorted octahedra unchanged. The frequency doubling effect of KTNP crystal powder samples is essentially the same as KTP, except that the effect is enhanced when Nb/Ti < 0.1. Substitution of Nb^{5+} for the Ti^{4+}—K$^+$ pair in KTP substantially increases the optical birefringence ($n_z - n_x$, n_y) of KTP and blue-shifts the SHG cutoff wavelength for propagation along the *X* and *Y* axes. The phase matching SHG cutoff wavelength is shifted from 994.3 nm to as short as 892 nm. The Nb dopant concentration can be used to control the birefringence of the KTNP crystal. Since the birefringences of n_Z-n_X and n_Z-n_Y are both increased, it is possible to achieve type Ⅱ phase matching along both the *X* and *Y* axes. The Nb concentration can also be adjusted to achieve non-critical phase matching in the KTNP crystal enhancing the nonlinear optical effect.

(3) KTi$_{1-x-y}$Zr$_x$Ga$_y$OPO$_4$ (KTZGP) (x, y<<1) series of crystals[35, 41]. Crystals of the KTZGP series have been grown with the high temperature solution method, however, it is difficult to obtain single crystals. The concentration of Ga^{3+} in these crystals has been measured by ICP-AES. The distribution coefficient of Ga in these crystals is k_{Ga} = 0.039, which is roughly an order of magnitude lower than that of Zr (k_{Zr}=0.305). The unit cell volume of KTZGP crystals has been determined by using X-ray diffraction and been found to be almost identical to KTP, because the radius of Zr^{4+} (0.79 Å) is larger than that

of Ti^{4+}(0.68 Å) while the radius of Ga^{3+} (0.62 Å) is less than that of Ti^{4+}. When a Zr^{4+} ion and a Ga^{3+} ion are substituted for a pair of Ti^{4+} ions, the resulting unit cell volume is left unchanged. The charge imbalance is overcome by the addition of a surplus of K^{+}. The frequency doubling effect of doubly doped KTZGP measured with the powder method is larger than that measured for either of the singly doped compounds KTGP or KTZP. The *c*-axis conductivity of KTZGP is $10^{-9}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$. This is larger than KTGP ($10^{-10}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$) but less than KTZP ($10^{-7}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$). This anomalously large nonlinear optical effect and conductivity change are synergic effects of two dopants with different oxidation states, not the collective behavior of the two dopants.

4 Conclusions

(1) The complex nature of the KTP crystal structure allows a diverse family of KTP type crystals to be grown. This large isomorphic crystal family has attracted extensive ongoing research for many years. The structure sensitive properties of the KTP family of crystals allows the fine tuning of the nonlinear optical properties expanding the range of applications of these crystals.

(2) Additional research into the stucture sensitive properties of the KTP family of crystals including doped KTP and its isomorphs can further our understanding of the nonlinear optical properties of these crystals.

(3) Studies of the substitution of monvalent ions for K^{+} ions in KTP reveal that the substitution of large cations such as Rb^{+} or Tl^{+} enhances the nonlinear optical properties while substitution of smaller cations such as Na^{+} or Ag^{+} has an extremely deleterious effect. When As^{5+} is substituted for P^{5+} in KTP, a single crystal of the solid solution $KTiOP_{1-x}As_xO_4$ is formed. The $KTiOAsO_4$ crystal has significantly improved nonlinear optical properties. Substitution of d^{0} cations, such as Nb^{5+}and Ta^{5+} for Ti^{4+} preserve the distorted TiO_6 octahedra and hence sustain the SHG effect. However, substitution of other transition metal ions such as V^{5+}, Cr^{3+}, or Fe^{3+} for Ti^{4+} diminishes the SHG effect because of the absorption of visible light.

(4) The presence of dopants in the KTP crystal results in microscopic defects that alter the observed nonlinear optical and electrooptic properties of the crystal. Further investigation is needed to optimize the growth techniques[1] and obtain high quality crystals.

(5) The understanding of structure sensitive properties is in general of great importance to the understanding of all functional crystals.

(6) The investigation of structure sensitive properties of KTP type crystals, in particular, has a profound and lasting theoretical meaning and practical application value. It gives us a deeper understanding of the relationship among the structure, composition, and properties of crystals. It establishes new ideas, foresight, and theoretical models for further research on the discovery of novel inorganic nonlinear optical crystals.

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