

Calculation of Second-Order Nonlinear Optical Coefficients of KTiOPO_4 and KTiOAsO_4

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The second-order nonlinear optical tensor coefficients of both KTiOPO_4 (KTP) and KTiOAsO_4 (KTA) are calculated from the chemical bond viewpoint. All constituent chemical bonds of both crystals are considered, and contributions of each type of bond to the total linearity and nonlinearity are determined. Calculated results agree satisfactorily with experimental data in both signs and numerical values. The calculation shows that though TiO_6 groups and P(1)O_4 or As(1)O_4 groups have relatively larger linear contributions, they can only produce an advantageous environment for KO_x ($x = 8, 9$) groups and P(2)O_4 or As(2)O_4 groups in nonlinear optical contributions. The origin of nonlinearity of KTP family crystals comes from the KO_x ($x = 8, 9$) and P(2)O_4 groups in their crystal structures. Furthermore, the difference in optical nonlinearities of KTP type crystals is analyzed, based on the detailed calculation of nonlinearities of both KTP and KTA. © 1999 Academic Press

INTRODUCTION

Potassium titanyl phosphate, KTiOPO_4 (KTP), and its substantial family of isostructures have been of interest in recent years because of their exceptional nonlinear optical (NLO) and electrooptical properties (1–3), especially for the second harmonic generation (SHG) of 1.064- μm Nd lasers (4). Many isostructural analogues have been synthesized by partial or full isomorphous substitution of K, Ti, P, and/or O, which constitute a structural field with more than 100 compounds (2, 3, 5–7), and, therefore, this family of compounds now forms a particularly advantageous series for the investigation of the relationship between the crystal structure and its optical properties.

KTP is a member of the family of compounds with the general formula $MM'OXO_4$, where $M = \text{K, Rb, Na, Cs, Tl}$, or NH_4 , $M' = \text{Ti, Sn, Sb, Zr, Ge, Al, Cr, Fe, V, Nb, or Ta}$, and $X = \text{P, As, or Si}$. All members are orthorhombic, biaxial crystals and belong to the acentric point group $mm2$ (space group $Pna2_1$); there are two different types of

“molecules,” designated (1) and (2), in each unit cell (8, 9). For such a complicated crystal structure with 37 kinds of constituent chemical bonds, authors have believed Ti–O bonds are the major contributor to KTP’s large nonlinear optical coefficients, because of the highly distorted TiO_6 octahedra (2, 10–12). However, an important problem is that it was assumed that contributions of MO_x ($x = 8, 9$) groups and XO_4 groups could be neglected when NLO properties of these KTP type crystals were discussed. Currently, this viewpoint faces much trouble, especially since some NLO coefficients of potassium titanyl arsenate (KTA) are indeed enhanced over those of KTP (13) and KTA has a figure of merit (d_{eff}^2/n^2) about a factor 1.4 larger than that of KTP at 0.66 μm (14). Therefore, many researchers have been trying to explain this obvious difference.

After realizing this weak point that the TiO_6 octahedra were the only considered structural unit, Bierlein *et al.* (15) began to search for the origin of the increased NLO coefficients using KTA, focusing on the AsO_4 tetrahedra instead of the TiO_6 octahedra, because of the highly distorted AsO_4 tetrahedra compared with the PO_4 tetrahedra in KTP. However, recent structural data show that distortions of TiO_6 octahedra and AsO_4 tetrahedra are comparable with the corresponding values of KTP (8). Other authors believed that the observed increase of certain NLO coefficients of KTA should be derived principally from the increase in the linear refractive indices brought about by the substitution of phosphorous by arsenic in the structure (8). Moreover, experiments show that the SHG intensity in KTP isomorphs is very sensitive to a substitution of K^+ ions by other monovalent ions such as Na^+ or Ag^+ (2, 3). An obvious decrease in SHG intensity at 1.064 μm of the $\text{K}_{0.55}\text{Li}_{0.45}\text{TiOPO}_4$ phase was observed, and SHG is hardly affected by lithium substitution in the $\text{K}_{0.54}\text{Li}_{0.46}\text{TiOAsO}_4$ phase (5). Experiments also show that Ti^{4+} cations in KTA crystals can be completely substituted with $\text{Nb}^{5+}-\text{M}^{3+}$ cation pairs ($M = \text{Al, Cr, Ga, Fe, or In}$) without reducing SHG response (6); furthermore, the SHG property of the parent KTP and KTA is not adversely affected by the

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coupled substitution of Nb and Si for Ti and P/As (7). These findings and also the previous theoretical investigation (9) lead to the conclusion that for a thorough treatment of NLO properties in the structure field of KTP, a consideration of the chemical bonding situation of all constituent elements is crucial.

In our opinion, the macroscopic physical properties of a given crystal must have a direct relationship with the chemical bonding structure of constituent atoms; therefore, it is reasonable to investigate the optical nonlinearity by studying the properties of all constituent chemical bonds in this crystal (i.e., starting from the chemical bond viewpoint). In a previous paper (9), we reported the nonlinear origin of KTP; in the present paper we present a detailed comparison of NLO properties of these KTP type isostructural analogues.

By using the chemical bond theory of complex crystals (16), the PV (Phillips and Van Vechten) dielectric theory (17, 18), and the modified bond charge model (9, 19, 20), we have constructed a theoretical method allowing us to quantitatively calculate the optical nonlinearities of complex crystals with various structures (9, 19, 20).

THEORY

According to the PV dielectric theory (17, 18), the susceptibility of any bond μ is

$$\chi^\mu = (4\pi)^{-1} (\hbar\Omega_p^\mu/E_g^\mu)^2, \quad [1]$$

where Ω_p^μ is the plasma frequency, E_g^μ is the average energy gap between the bonding and antibonding states, which can be separated into the homopolar E_h^μ and heteropolar C^μ parts (16–18, 21), $(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2$, and

$$E_h^\mu = 39.74/(d^\mu)^{2.48} \quad [2]$$

$$C^\mu = 14.4b^\mu \exp(-k_s^\mu r_0^\mu) [(Z_A^\mu)^* - n(Z_B^\mu)^*]/r_0^\mu, \quad [3]$$

where d^μ is the nearest-neighbor distance (i.e., bond length). $r_0^\mu = d^\mu/2$ is the average radius of A and B . $(Z_A^\mu)^*$ and $(Z_B^\mu)^*$ are the effective valence electrons of A and B ions. n is the ratio of the element B to A in the subformula (16). $\exp(-k_s^\mu r_0^\mu)$ is the Thomas–Fermi screening factor. b^μ is a correction factor related to structural changes, i.e., to the average coordination number N_C^μ . Levine found that one possible relation between b and N_C is the simple power law behavior $b \propto (N_C)^p$ (21); the actual value for p depends on the given crystal structure. Levine also found $p = 2$ gives a satisfactory empirical account of the interrelationship between these fundamental crystal parameters in AB crystals, A_mB_n crystals, and some ABC_N crystals (21). In the process of our calculation of NLO crystals with complex

structures, we find that the value of p decreases with increasing value of N_C^μ (9, 19, 20, 22). In crystals with H–O bonds, the coordination number of the H atom is always less than 3, so the average coordination number N_C^μ will be less than 3, and the value for p is 3 (19, 22). In KTP and KTA, there are so many higher coordination number cations in one crystal molecule that the common expression for b^μ is $b^\mu = \beta(N_C^\mu)^{1.48}$ when $N_C^\mu > 5$ and $b^\mu = \beta(N_C^\mu)^2$ when $N_C^\mu \leq 5$ (9). Moreover, β can be deduced from the above equations when the index of refraction for the crystal is known; here for KTP, $n_r = 1.86$ (23) and for KTA, $n_r = 1.868$ (15), at 1.064 μm . In the calculation of KTP family crystals, the value of β can be deduced by the equation

$$\beta = \sqrt{\frac{(n_0^2 - 1)^{-1} \sum_\mu F^\mu (\hbar\Omega_p^\mu) - \sum_\mu 39.74/(d^\mu)^{2.48}}{\sum_\mu 14.4(N_C^\mu)^p \exp(-k_s^\mu r_0^\mu) [(Z_A^\mu)^* - n(Z_B^\mu)^*]/r_0^\mu}}, \quad [4]$$

where the sum over μ runs over all different kinds of bonds in the unit cell.

According to the chemical bond theory of complex crystals (16), the relationship between the crystal formula and its constituent chemical bonds can be expressed as the subformula equation (the bond-valence equation), which shows the crystal formula is a linear combination of all types of its constituent bond subformulae. The subformula of any kind of chemical bond $A-B$ in the multibond crystal $A_aB_bD_dG_g \dots$ can be obtained by the formula

$$[N(B-A) \times a/N_{CA}] A [N(A-B) \times b/N_{CB}] B \quad [5]$$

where A, B, D, G, \dots represent different elements or different sites of the same element in the crystal formula and a, b, d, g, \dots represent the numbers of the corresponding element. $N(B-A)$ represents the number of B ions in the coordination group of A ion, and N_{CA} represents the nearest coordination number of atom A .

After listing the subformula equation of a complex crystal, we can calculate chemical bond parameters of each type of bond in this crystal by using the above equations.

If the crystal is composed of different types of bonds (labeled μ), then the total χ (which is related to its principal refractive index n_r at the long wavelength, $4\pi\chi = n_r^2 - 1$) can be resolved into contributions χ^μ from the various types of bonds (21, 24),

$$\chi = \sum_\mu F^\mu \chi^\mu = \sum_\mu N_b^\mu \chi_b^\mu, \quad [6]$$

where χ^μ is the total macroscopic susceptibility which a crystal composed entirely of bonds of type μ would have. F^μ is the fraction of bonds of type μ composing the actual crystal, χ_b^μ is the susceptibility of a single bond of type μ , and N_b^μ is the number of bonds of type μ per cm^3 .

The fractional ionicity f_i^μ and covalency f_c^μ of the individual bonds can be determined as (17, 21)

$$\begin{aligned} f_i^\mu &= (C^\mu)^2/(E_g^\mu)^2 \\ f_c^\mu &= (E_h^\mu)^2/(E_g^\mu)^2. \end{aligned} \quad [7]$$

The bond nonlinearities had been evaluated on the basis of linear results by the bond charge model of Levine (24), and the complete expression for the total nonlinear optical tensor coefficient d_{ij} can be written as

$$d_{ij} = \sum_{\mu} d_{ij}^{\mu} = \sum_{\mu} F^{\mu} [d_{ij}^{\mu}(C) + d_{ij}^{\mu}(E_h)], \quad [8]$$

where d_{ij}^{μ} is the total macroscopic nonlinear contribution of constituent chemical bonds of type μ . $d_{ij}^{\mu}(C)$ is the ionic fraction of the nonlinear optical coefficient, and $d_{ij}^{\mu}(E_h)$ the covalent fraction,

$$F^{\mu} d_{ij}^{\mu}(C) = \frac{G_{ij}^{\mu} N_b^{\mu} (28.8) b^{\mu} \exp(-k_s^{\mu} r_0^{\mu}) [(Z_A^{\mu})^* + n(Z_B^{\mu})^*] (\chi_b^{\mu})^2 C^{\mu}}{(E_g^{\mu})^2 (d^{\mu})^2 q^{\mu}} \quad [9]$$

$$F^{\mu} d_{ij}^{\mu}(E_h) = \frac{G_{ij}^{\mu} N_b^{\mu} s(2s-1) [r_0^{\mu}/(r_0^{\mu} - r_c^{\mu})]^2 f_c^{\mu} (\chi_b^{\mu})^2 \rho^{\mu}}{d^{\mu} q^{\mu}}. \quad [10]$$

G_{ij}^{μ} is the geometrical contribution of constituent chemical bonds of type μ , which can be calculated from

$$G_{ij}^{\mu} = 1/n_b^{\mu} \sum_{\lambda} \alpha_i^{\mu}(\lambda) \alpha_j^{\mu}(\lambda), \quad [11]$$

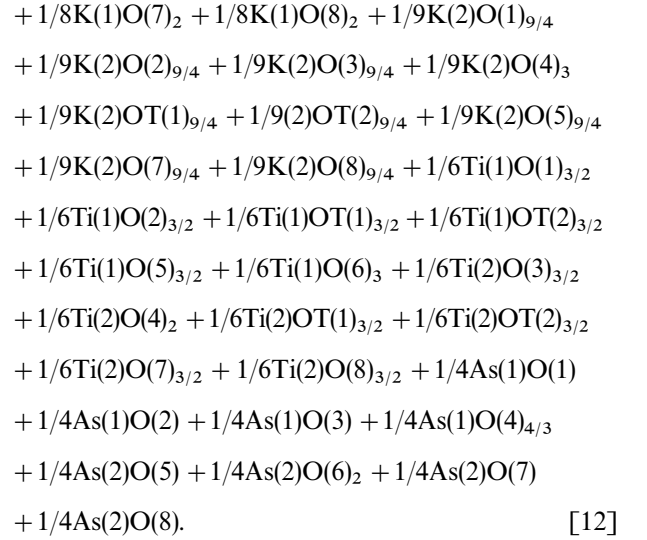
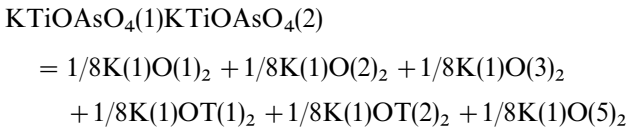
where the sum on λ is over all n_b^{μ} bonds of type μ in the unit cell and $\alpha_i^{\mu}(\lambda)$ is the direction cosine with respect to the i th coordinate axis of the λ th bond of type μ in the unit cell.

The difference in the atomic sizes $\rho^{\mu} = (r_A^{\mu} - r_B^{\mu})/(r_A^{\mu} + r_B^{\mu})$; r_A^{μ} and r_B^{μ} are the covalent radii of atoms A and B taken from Ref. (25), and $r_c^{\mu} = 0.35r_0^{\mu}$ is the core radius. q^{μ} is the bond charge of the μ th bond; its detailed expression has been given in Ref. (9).

RESULTS AND DISCUSSION

For KTP, the lattice constants are $a = 12.819 \text{ \AA}$, $b = 6.399 \text{ \AA}$, and $c = 10.584 \text{ \AA}$ (26); its subformula equation has been presented in the previous work (9).

For KTA, the lattice constants are $a = 13.130 \text{ \AA}$, $b = 6.581 \text{ \AA}$, and $c = 10.781 \text{ \AA}$ (8). According to the established theoretical method (9, 16), the crystal formula of KTA can be converted into the subformula equation (i.e., the bond-valence equation) as follows:



Restrictions imposed by the crystal symmetry and Kleinman symmetry conditions (27) on NLO tensor coefficients result in three independent nonlinear optical tensor coefficients d_{31} , d_{32} , and d_{33} allowed in these KTP type crystals. Then, the linear and nonlinear optical properties of all constituent chemical bonds of both KTP and KTA can be calculated by using the above theories, and the calculated values are listed in Tables 1 and 2, respectively.

From the results shown in Tables 1 and 2, we find that each type of constituent chemical bond contributes in part to the total linearity and nonlinearity of these KTP type crystals. In fact, TiO_6 groups and PO_4 or AsO_4 groups play a dominant role in contributions to the total linearity χ , and from the value of the bond length d^{μ} we can see TiO_6 groups have a more distorted configuration than any other group in both crystal structures. Therefore, from an approximate viewpoint, it is easy to find these TiO_6 groups and regard them as the major contributor to the total nonlinearity. However, in our calculation the main contributions to the total nonlinearity of these crystals are not all from those groups consisting of chemical bonds with dominant linear contributions, but mainly from $\text{K}(1)\text{O}_8$ groups and $\text{P}(2)\text{O}_4$ or $\text{As}(2)\text{O}_4$ groups. Our calculated results show that nonlinear contributions of each kind of constituent chemical bond do have a connection with their linear contributions, but those parameters listed in Eqs. [9] and [10] are also the important factors that should be considered necessarily in a quantitative calculation; therefore, one kind of chemical bond with larger linear contributions cannot simply lead to the dominant contribution to the total nonlinearity. From Table 3, we find that our calculated results are in good numerical agreement with the experimental data, and all of these three independent NLO tensor coefficients have the same sign, which agree with the observed ones (28). Therefore, the following discussion based on the calculation of both KTP and KTA crystals is meaningful.

TABLE 1
Chemical Bond Parameters, Linear and Nonlinear Optical Properties of Each Type of Bond, and Their Contributions to the Total Linearity and Nonlinearity of KTP

$A-B$	d^μ	E_h^μ	C^μ	f_c^μ	χ^μ	χ_b^μ	q^μ/e	G_{31}^μ	d_{31}^μ	G_{32}^μ	d_{32}^μ	G_{33}^μ	d_{33}^μ
K(1)O(1)	2.8942	2.8486	3.4818	0.4010	3.0778	1.4368	0.1580	0.1349	-2.1822	0.2497	-4.0395	0.2068	-3.3449
K(1)O(2)	2.7383	3.2679	3.9297	0.4088	2.8039	1.3089	0.1677	-0.1052	1.4498	-0.1486	2.0490	-0.0207	0.2850
K(1)O(3)	2.7124	3.3459	4.0115	0.4103	2.7600	1.2884	0.1692	0.0014	-0.0191	0.1233	-1.6558	0.0021	-0.0281
K(1)OT(1)	2.9959	2.6148	3.2257	0.3965	3.2656	1.5244	0.1523	0.1151	-2.0657	0.2693	-4.8354	0.2095	-3.7602
K(1)OT(2)	2.7223	3.3158	3.9799	0.4097	2.7767	1.2962	0.1686	-0.1619	2.1957	-0.1143	1.5503	-0.0282	0.3826
K(1)O(5)	2.8719	2.9038	3.5416	0.4020	3.0376	1.4180	0.1594	0.0017	-0.0273	0.0045	-0.0704	0.9907	-15.6659
K(1)O(7)	3.0570	2.4871	3.0838	0.3941	3.3820	1.5787	0.1489	0.1908	-3.6455	0.1879	-3.5904	0.2577	-4.9240
K(1)O(8)	2.7549	3.2193	3.8785	0.4079	2.8323	1.3222	0.1665	-0.1138	1.5964	-0.1836	2.5747	-0.0376	0.5273
K(2)O(1)	2.6771	3.4564	4.5641	0.3645	2.0450	0.9546	0.1746	-0.1078	0.6484	-0.1863	1.1203	-0.0360	0.2163
K(2)O(2)	2.9818	2.6456	3.6143	0.3489	2.4384	1.1383	0.1567	0.1610	-1.2815	0.2137	-1.7010	0.2777	-2.2101
K(2)O(3)	3.0448	2.5119	3.4516	0.3462	2.5257	1.1790	0.1532	0.0006	-0.0048	0.0000	0.0000	0.9991	-8.4331
K(2)O(4)	3.1174	2.3693	5.2670	0.1683	1.1439	0.5340	0.2205	-0.0014	0.0002	-0.3831	0.0621	-0.2072	0.0336
K(2)OT(1)	2.7655	3.1888	4.2572	0.3594	2.1545	1.0057	0.1691	-0.1831	1.1936	-0.0863	0.5624	-0.0257	0.1675
K(2)OT(2)	3.0567	2.4877	3.4220	0.3458	2.5424	1.1868	0.1526	0.3163	-2.6995	0.0666	-0.5685	0.2283	-1.9482
K(2)O(5)	2.8062	3.0753	4.1251	0.3572	2.2061	1.0299	0.1667	0.0945	-0.6396	0.0005	-0.0003	0.0009	-0.0059
K(2)O(7)	2.9176	2.7916	3.7898	0.3517	2.3521	1.0980	0.1602	-0.0870	0.6525	-0.1247	0.9354	-0.0110	0.0829
K(2)O(8)	3.0475	2.5064	3.4449	0.3461	2.5294	1.1808	0.1531	0.2075	-1.7560	0.1774	-1.5010	0.1972	-1.6689
Ti(1)O(1)	2.1501	5.9529	17.0529	0.1086	1.1290	0.5271	0.6247	-0.3350	-0.0561	-0.0012	-0.0002	-0.4018	-0.0673
Ti(1)O(2)	1.9580	7.5081	20.9191	0.1141	0.9815	0.4582	0.6706	0.3711	0.0447	0.0079	0.0010	0.2555	0.0308
Ti(1)OT(1)	1.9811	7.2929	38.4957	0.0346	0.8947	0.4176	2.0615	-0.3064	-0.0205	-0.0097	-0.0006	-0.4506	-0.0301
Ti(1)OT(2)	1.7161	10.4127	53.9391	0.0359	0.6910	0.3226	2.3079	0.3499	0.0143	0.0160	0.0007	0.3131	0.0128
Ti(1)O(5)	2.0424	6.7621	22.8107	0.0808	1.0240	0.4780	0.8755	-0.0018	-0.0002	-0.2016	-0.0282	-0.0097	-0.0014
Ti(1)O(6)	1.9873	7.2366	15.2082	0.1846	6.1960	2.8924	0.6864	0.0007	0.0001	0.0635	0.0126	0.0003	0.0001
Ti(2)O(3)	2.0443	6.7465	19.0507	0.1114	1.0457	0.4882	0.6498	-0.1327	-0.0186	-0.0070	-0.0010	-0.0029	-0.0004
Ti(2)O(4)	1.9814	7.2902	21.8170	0.1004	2.0426	0.9535	0.9238	0.0553	0.0245	0.0008	0.0004	0.0002	0.0001
Ti(2)OT(1)	1.7334	10.1569	47.3003	0.0441	0.7297	0.3407	1.8716	0.0295	0.0015	0.3438	0.0181	0.2848	0.0150
Ti(2)OT(2)	2.0919	6.3722	30.5325	0.0417	1.0156	0.4741	1.6085	-0.0144	-0.0014	-0.3418	-0.0341	-0.3452	-0.0344
Ti(2)O(7)	1.9647	7.4448	25.9282	0.0762	1.3376	0.6244	1.0848	~0	~0	0.3709	0.0991	0.2941	0.0786
Ti(2)O(8)	1.9903	7.2096	25.1690	0.0758	1.3672	0.6382	1.0715	-0.0013	-0.0004	-0.3003	-0.0839	-0.4831	-0.1351
P(1)O(1)	1.5186	14.1010	41.5664	0.1032	2.5855	1.2070	1.7168	0.0081	0.0055	0.3079	0.2086	0.4506	0.3052
P(1)O(2)	1.5481	13.4439	39.7554	0.1026	2.6717	1.2472	1.6784	-0.0086	-0.0062	-0.2400	-0.1748	-0.5904	-0.4299
P(1)O(3)	1.5441	13.5305	39.9948	0.1027	2.6599	1.2417	1.6835	-0.0852	-0.0615	-0.0422	-0.0304	-0.0022	-0.0016
P(1)O(4)	1.5412	13.5937	18.7365	0.3449	4.1502	1.9374	0.6803	0.0829	-0.1317	0.0467	-0.0742	0.0023	-0.0036
P(2)O(5)	1.5351	13.7281	38.7507	0.1115	2.6308	1.2281	1.5740	-0.0641	-0.0463	-0.1259	-0.0908	-0.0077	-0.0056
P(2)O(6)	1.5283	13.8800	14.7326	0.4723	8.6731	4.0487	0.7459	0.0576	-1.0800	0.1072	-2.0079	0.0049	-0.0914
P(2)O(7)	1.5481	13.4439	38.0059	0.1112	2.6683	1.2456	1.5587	-0.2782	-0.2071	-0.0197	-0.0146	-0.4911	-0.3655
P(2)O(8)	1.5374	13.6772	38.6176	0.1115	2.6374	1.2312	1.5713	0.2820	0.2045	0.0218	0.0158	0.4784	0.3469

Note. ~0 indicates the value approaches 0.

As a new member of the KTP family, KTA displays a quite large NLO response compared to that of KTP (13, 14). The failed explanation of the conventional viewpoint (the origin of nonlinearity in KTP type crystals is from TiO₆ groups) to account radically for the observed phenomena in KTA made researchers search for their differences in AsO₄ and PO₄ groups (15) and all effects on KTA introduced by the substitution of As for P (8). All of these attempts to explain the difference cannot finally produce a quantitative interpretation, and it is difficult for them to do so, because this approximation neglects some kinds of constituent groups (K(1)O₈, K(2)O₉, and PO₄ groups) and takes only one kind of group (TiO₆ group) as the research

object. Therefore, this case would finally lead to the failure of the explanation. For KTP and KTA, the obvious difference of their NLO responses cannot be explained reasonably by only considering Ti-O bonds, which have similar bond length and bond angle in KTP and KTA (8). Just realizing this weak point, we in the current work start from all constituent chemical bonds of their crystal structures (KTP and KTA) to investigate the connection between the crystal structure and its optical properties. Our calculation can clearly and quantitatively show us the nonlinear origin in these KTP type crystals, especially the effects on bond parameters and the geometrical factor G_{ij}^μ of each type of constituent chemical bond by the substitution of As for P in

TABLE 2
Chemical Bond Parameters, Linear and Nonlinear Optical Properties of Each Type of Bond, and Their Contributions to the Total Linearity and Nonlinearity of KTA

$A-B$	d^μ	E_h^μ	C^μ	f_c^μ	χ^μ	χ_b^μ	q^μ/e	G_{31}^μ	d_{31}^μ	G_{32}^μ	d_{32}^μ	G_{33}^μ	d_{33}^μ
K(1)O(1)	2.9985	2.6092	3.2758	0.3882	3.1611	1.5834	0.1533	0.1419	-2.4594	0.2407	-4.1711	0.2308	-3.9992
K(1)O(2)	2.8066	3.0743	3.7893	0.3969	2.8254	1.4152	0.1646	-0.1103	1.5731	-0.1636	2.3331	-0.0273	0.3897
K(1)O(3)	2.6825	3.4391	4.1798	0.4037	2.6211	1.3129	0.1725	0.0010	-0.0120	0.1399	-1.7593	0.0030	-0.0374
K(1)OT(1)	3.1172	2.3697	3.0038	0.3836	3.3815	1.6938	0.1468	0.1025	-2.0041	0.2811	-5.4956	0.2198	-4.2964
K(1)OT(2)	2.8868	2.8668	3.5625	0.3930	2.9627	1.4840	0.1597	-0.1485	2.2975	-0.1111	1.7183	-0.0224	0.3469
K(1)O(5)	2.8802	2.8831	3.5805	0.3933	2.9512	1.4782	0.1601	0.0044	-0.0682	0.0034	-0.0520	0.9882	-15.1875
K(1)O(7)	3.1776	2.2595	2.8767	0.3815	3.4976	1.7519	0.1437	0.2031	-4.2209	0.1795	-3.7309	0.2308	-4.7970
K(1)O(8)	2.7166	3.3331	4.0673	0.4018	2.6762	1.3405	0.1703	-0.0986	1.2829	-0.1779	2.3162	-0.0283	0.3686
K(2)O(1)	2.6844	3.4331	4.6158	0.3562	1.9819	0.9927	0.1761	-0.1011	0.5833	-0.1657	0.9562	-0.0248	0.1430
K(2)O(2)	3.0097	2.5852	3.6027	0.3399	2.3881	1.1962	0.1569	0.1583	-1.2270	0.2198	-1.7036	0.2610	-2.0229
K(2)O(3)	3.1562	2.2977	3.2428	0.3342	2.5882	1.2964	0.1492	0.0003	-0.0003	0.0010	-0.0093	0.9984	-8.8615
K(2)O(4)	3.0506	2.5001	5.6226	0.1651	1.0545	0.5282	0.2288	-0.0008	0.0001	-0.3834	0.0495	-0.2127	0.0274
K(2)OT(1)	2.8557	2.9448	4.0407	0.3469	2.1895	1.0967	0.1656	-0.1621	1.0914	-0.0799	0.5379	-0.0175	0.1175
K(2)OT(2)	3.1567	2.2968	3.2417	0.3342	2.5889	1.2967	0.1492	0.3274	-2.9073	0.0544	-0.4833	0.2374	-2.1081
K(2)O(5)	2.8414	2.9817	4.0849	0.3476	2.1716	1.0877	0.1665	0.0862	-0.5733	~0	~0	0.0007	-0.0044
K(2)O(7)	2.9164	2.7952	3.8600	0.3440	2.2663	1.1352	0.1621	-0.0796	0.5668	-0.1387	0.9875	-0.0123	0.0873
K(2)O(8)	3.1467	2.3150	3.2647	0.3346	2.5748	1.2897	0.1497	0.1897	-1.6691	0.1924	-1.6929	0.2346	-2.0636
Ti(1)O(1)	2.1258	6.1231	17.7907	0.1059	1.0595	0.5307	0.6435	-0.3473	-0.0558	-0.0008	-0.0001	-0.3693	-0.0593
Ti(1)O(2)	1.9668	7.4251	21.0756	0.1104	0.9438	0.4727	0.6814	0.3786	0.0465	0.0054	0.0007	0.2164	0.0266
Ti(1)OT(1)	1.9649	7.4429	39.9674	0.0335	0.8384	0.4199	2.1224	-0.3045	-0.0189	-0.0203	-0.0013	-0.4301	-0.0267
Ti(1)OT(2)	1.7435	10.0116	52.9282	0.0345	0.6759	0.3386	2.3266	0.3348	0.0138	0.0244	0.0010	0.3360	0.0139
Ti(1)O(5)	2.0475	6.7204	23.0818	0.0781	0.9806	0.4912	0.8925	-0.0030	-0.0004	-0.2248	-0.0310	-0.0142	-0.0020
Ti(1)O(6)	1.9969	7.1506	15.3043	0.1792	6.0051	3.0079	0.6933	0.0017	0.0009	0.0963	0.0516	0.0010	0.0005
Ti(2)O(3)	2.0273	6.8877	19.7372	0.1086	0.9865	0.4941	0.6669	-0.1266	-0.0173	-0.0108	-0.0015	-0.0028	-0.0004
Ti(2)O(4)	1.9899	7.2132	21.9860	0.0972	1.9675	0.9855	0.9428	0.0630	0.0282	0.0025	0.0011	0.0003	0.0001
Ti(2)OT(1)	1.7872	9.4154	44.9013	0.0421	0.7310	0.3661	1.8684	0.0380	0.0021	0.3285	0.0183	0.3112	0.0173
Ti(2)OT(2)	2.0748	6.5032	31.6975	0.0404	0.9520	0.4769	1.6585	-0.0249	-0.0023	-0.3245	-0.0301	-0.3660	-0.0340
Ti(2)O(7)	1.9675	7.4186	26.3014	0.0737	1.2797	0.6410	1.1093	0.0024	0.0006	0.3719	0.0970	0.2748	0.0717
Ti(2)O(8)	1.9878	7.2321	25.6894	0.0734	1.3021	0.6522	1.0987	-0.0051	-0.0014	-0.3205	-0.0866	-0.4281	-0.1157
As(1)O(1)	1.6612	11.2871	34.3006	0.0977	2.2766	1.1403	1.8596	0.0057	0.0025	0.3199	0.1436	0.4281	0.1922
As(1)O(2)	1.6912	10.7970	32.8741	0.0974	2.3517	1.1780	1.8198	-0.0037	-0.0018	-0.2357	-0.1136	-0.6077	-0.2929
As(1)O(3)	1.6917	10.7891	32.8510	0.0974	2.3530	1.1786	1.8191	-0.0778	-0.0375	-0.0395	-0.0191	-0.0017	-0.0008
As(1)O(4)	1.6901	10.8145	15.5825	0.3251	5.0789	2.5440	0.5866	0.0775	-0.3111	0.0470	-0.1888	0.0020	-0.0081
As(2)O(5)	1.6807	10.9651	31.9413	0.1054	2.4628	1.2336	1.6361	-0.0764	-0.0427	-0.1440	-0.0804	-0.0127	-0.0071
As(2)O(6)	1.6769	11.0268	12.1523	0.4516	11.0043	5.5120	0.6414	0.0632	-2.7667	0.1108	-4.8549	0.0058	-0.2546
As(2)O(7)	1.7008	10.6465	31.0573	0.1052	2.5158	1.2602	1.6126	-0.2986	-0.1748	-0.0141	-0.0083	-0.4583	-0.2684
As(2)O(8)	1.6807	10.9651	31.9413	0.1054	2.4628	1.2336	1.6361	0.2891	0.1615	0.0206	0.0115	0.4649	0.2597

Note. ~0 indicates the value approaches 0.

KTA. In the calculation, each type of constituent chemical bond is regarded as an inseparable constituent part of this KTP type complex crystals.

TiO₆ and P(1)O₄ or As(1)O₄ groups, in a sense, are only the fundamental groups in KTP family crystals, which construct a useful coordination environment for other constituent groups, KO_x ($x = 8, 9$) groups and P(2)O₄ or As(2)O₄ groups, because of their dominant linear properties and good coordination environments. From Tables 1 and 2, we find the difference among KTP type crystals cannot be properly found by only considering any one constituent group, since K(1)O₈ groups and P(2)O₄ or As(2)O₄ groups are the major contributors. For K(1)O₈ groups and P(2)O₄ or As(2)O₄ groups in KTP family crystals, they have rela-

tively better linear optical properties, in addition to the larger geometrical contributions benefiting from this good coordination environment constructed by TiO₆ and P(1)O₄ or As(1)O₄ groups; therefore, they can produce much larger NLO contributions to the total nonlinearity than other constituent groups. By the constitution of As for P in KTA, the crystal structure finally leads to changes of coordination environments of all constituent elements, and the situation of each kind of constituent chemical bond becomes more advantageous to display their nonlinearities. This case can be found from their different bond length d^μ and geometrical factor G_{ij}^μ as shown in Tables 1 and 2. These structural changes make each group have different linear properties, especially the obvious effects on KO_x ($x = 8, 9$) groups.

TABLE 3
Comparison between Calculated Results and Experimental Data
of NLO Tensor Coefficients of KTP and KTA

	d_{31} (10^{-9} esu)		d_{32} (10^{-9} esu)		d_{33} (10^{-9} esu)	
	KTP	KTA	KTP	KTA	KTP	KTA
Expt	6.06 ^a	6.68 ^b	10.38 ^a	10.03 ^b	40.35 ^a	38.67 ^b
Theo ^c	-7.92	-10.92	-11.29	-15.29	-40.67	-42.39

Note. This table is taken from Ref. 9.

^aReference (29). Measured by Maker-fringe method at 1.064 μm .

^bReference (13). Measured by Maker-fringe method at 1.32 μm .

^cThis work, at 1.064 μm .

Therefore, the different NLO properties between KTP and KTA come from the changes of coordination environments of each constituent element. Although the substitution of As for P cannot produce the huge changes of their crystal structures, it surely changes the coordination environments of all constituent elements in KTP, and just these changes of coordination environments finally lead to better NLO properties in KTA.

Let us analyse other members of this KTP family. Since the origin of nonlinearity of the KTP family of crystals comes from KO_x ($x = 8, 9$) and $\text{P}(2)\text{O}_4$ groups, it is easy to understand the experimental observations that the SHG intensity in KTP isomorphs is very sensitive to a substitution of K^+ ions by Na^+ or Ag^+ ions (2, 3). In $\text{K}_{0.55}\text{Li}_{0.45}\text{TiOPO}_4$, Li substitutes for both of the two crystallographically distinct potassium cations to roughly equal extent, whereas in $\text{K}_{0.54}\text{Li}_{0.46}\text{TiOAsO}_4$, the 9-coordinate K(2) atom is preferentially replaced by Li (5). Our calculation shows the origin of nonlinearity of the KTP family of crystals comes from KO_x ($x = 8, 9$) and $\text{P}(2)\text{O}_4$ groups, and $\text{K}(1)\text{O}_8$ groups and $\text{P}(2)\text{O}_4$ or $\text{As}(2)\text{O}_4$ groups are the most important major contributors. Therefore, it is reasonable to find an obvious decrease in SHG intensity at 1.064 μm of the $\text{K}_{0.55}\text{Li}_{0.45}\text{TiOPO}_4$ phase (Li on sites of both K(1) and K(2)), and the SHG response is hardly affected by lithium substitution in the $\text{K}_{0.54}\text{Li}_{0.46}\text{TiOAsO}_4$ phase (Li on K(2) site (5)). Since TiO_6 groups have a relatively smaller contribution to the total nonlinearity, it is acceptable that new aliovalent analogues of KTA, $\text{K}[\text{Nb}, \text{M}]\text{OAsO}_4$ containing $\text{Nb}^{5+}-\text{M}^{3+}$ cation pairs ($M = \text{Al}, \text{Cr}, \text{Ga}, \text{Fe}, \text{or In}$) in octahedral positions of the KTP structure, were synthesized without reducing the SHG response (6). Therefore, the SHG property of the parent KTP and KTA is not adversely affected by the coupled substitution of Nb and Si for Ti and P/As in $\text{KTi}_{1-x}\text{Nb}_x\text{OX}_{1-x}\text{Si}_x\text{O}_4$ members (7).

However, it should be pointed out that the titanium sites in KTP family crystals have a very important effect on coordination environments of other ions on the potassium sites through their bonded oxygen ions. This can be seen from the K(1)-OT(1), K(1)-OT(2), K(2)-OT(1), and

K(2)-OT(2) bonds that possess the large NLO contributions to the total nonlinearities, as shown in Tables 1 and 2, where OT represents those O^{2-} ions on the oxygen sites that are bonded to the Ti^{4+} ions. Therefore, it is understandable that the complete or partial substitution of Ti by isolvent or aliovalent main-group ions or ion pairs or by transition-metal ions or ion pairs may result in the decrease of second harmonic intensity (compared with that of KTP), as summarized by Refs. (2), (3), and (30). It is self-evident that these effects of substitution chemistry in the KTP structure field on the microscopic coordination environments of all constituent ions are very strong. Unfortunately, to date there have been no reports concerning the detailed crystal structures of these isomorphous derivatives of KTP; therefore, we only can give the above qualitative analyses. It is necessary to carry out further studies on these isomorphous derivatives of KTP.

Finally, we want to say that our theoretical method belongs to the approximate methods which deal with the physical properties of complex crystals on the basis of the properties of their constituent chemical bonds. It is well known that to date the *ab initio* methods cannot deal with such a complicated system as KTP. In this paper, our method presents us a quantitative analysis of the optical nonlinearities of both KTP and KTA from the chemical bond viewpoint, from which we can find some useful information in modifying the optical nonlinearities of complex crystals such as KTP. Also, our method in a sense may give us a useful guide in searching for new NLO materials of this KTP type.

CONCLUSION

In this work, we start from the chemical bond viewpoint, investigate all kinds of constituent chemical bonds of both KTP and KTA, and find the origin of nonlinearity comes from KO_x ($x = 8, 9$) groups and $\text{P}(2)\text{O}_4$ or $\text{As}(2)\text{O}_4$ groups. The difference in optical nonlinearities between both crystals can be found from the effect on each chemical bond by the substitution of As for P in KTA. Furthermore, we conclude that the origin of nonlinearity of KTP type crystals comes from the KO_x ($x = 8, 9$) groups and $\text{P}(2)\text{O}_4$ groups. The difference in NLO properties of other KTP type members derived from KTP and KTA is explained reasonably on the basis of the calculated results of both crystals. This paper at the same time gives us a powerful tool to study all members in this KTP family of crystals; therefore, it also gives us a guide to search for new NLO materials of this type.

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