

Nonlinear Optical Properties of New KTiOPO_4 Isostructures

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[†] Sandia National Laboratories, Albuquerque, NM 87185[†] Department of Chemistry, University of California
Santa Barbara, CA 93106ABSTRACT

The atomic structures of the nonlinear optical materials potassium titanyl phosphate (KTiOPO_4 , or KTP) and potassium titanyl arsenate (KTiOAsO_4) feature one-dimensional channels through which the potassium ions are relatively free to migrate. Ion exchange results when these materials are immersed in molten salts containing alkali metal ions. Sodium, lithium and silver all exchange readily for K^+ in single crystals of both KTP and KTA to yield the exchanged derivatives $\text{Na}_{.95}\text{K}_{.05}\text{TiOPO}_4$ (NaTP), $\text{Na}_{.83}\text{K}_{.17}\text{TiOAsO}_4$ (NaTA), $\text{Ag}_{.85}\text{K}_{.15}\text{TiOPO}_4$ (AgTP), $\text{Ag}_{.98}\text{K}_{.02}\text{TiOAsO}_4$ (AgTA), $\text{Li}_{.45}\text{K}_{.55}\text{TiOPO}_4$ (KLTP), and $\text{Li}_{.46}\text{K}_{.54}\text{TiOAsO}_4$ (KLTA), which are all KTP isostructures. The optical nonlinearities (measured as SHG intensities) of the limiting compositions in the NaTA, KLTP, and KLTA systems are similar to that of KTP, but are much smaller in NaTP, AgTP and AgTA. Single crystal X-ray data have revealed differences in coordination of the mobile cations to oxygen atoms linking the TiO_6 groups in these compounds, and these differences correlate with changes in optical nonlinearity. The observed nonlinearities can be rationalized if they are viewed as being dependent on the degree to which delocalized charge-transfer excited state character can be mixed into ground state bonding and nonbonding orbitals in the TiO_6 chains. The relative lack of association of Na^+ and Li^+ ions with these chains in NaTA, KLTP, and KLTA allows extensive excited state delocalization, and thus significant electronic hyperpolarizability.

1. INTRODUCTION

Potassium titanyl phosphate (KTP) has emerged as a highly promising material for frequency conversion and electrooptic modulation, with high power conversion efficiency for second harmonic generation (SHG) and sum-frequency generation (SFG), high threshold to laser damage, and large linear electrooptic coefficients coupled with low dielectric constants.¹ The NLO properties and crystal growth of KTP's structural analogue potassium titanyl arsenate (KTA) are under investigation, and early results show some improvement in KTA's SHG and electrooptic figures of merit over those of KTP.²

Like other metal oxide ferroelectrics such as BaTiO_3 and LiNbO_3 , the KTiOPO_4 structure belongs to a noncentrosymmetric crystallographic point group, and contains highly distorted octahedral metal-oxygen units. This distortion of the MO_6 groups has been associated with large second-order NLO and linear (Pockels) EO coefficients in such materials.³ In the KTP structure, distorted TiO_6 groups are linked through corners and thus form one-dimensional chains which are oriented diagonally with respect to the optic axis (the c axis, or [001]). These Ti-O chains are bridged by tetrahedral phosphate or arsenate groups, forming an open framework containing channels parallel to the c axis (Figure 1). The cations (K^+ in KTiOPO_4) are sited in these channels, in which they are relatively free to migrate. This contributes to the highly anisotropic ionic conductivities of KTP and KTA.⁴

The TiO_6 groups are linked such that the "titanyl" oxygen atoms which bridge the

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octahedra are alternately *cis* and *trans* with respect to the central Ti atoms, and that these Ti-O bonds which comprise the chain are alternately long (ca. 2.0 Å) and short (ca. 1.75 Å) (Figure 2). We can compare these long-short metal oxygen bonds in the KTP Ti-O chain (and in other metal oxide ferroelectrics) to the alternating single and double bonds of conjugated π systems in organic compounds. In fact, it has been postulated that this conjugation results in a delocalized excited state, in which unoccupied higher-energy orbitals of metallic character overlap to form a charge transfer band.^{5,6} Distortion of the TiO_6 groups allows the dipolar excited state character to mix with the ground (bonding) electronic states, imparting strong hyperpolarizability to the titanyl chain in a fashion analogous to the mechanism used to describe microscopic second order NLO susceptibility in organic molecules such as 2-methyl 4-nitroaniline (MNA).⁷

Over forty isostructures of KTP have been synthesized through isovalent substitution on the cation (K) sites, the octahedral (Ti) sites and the tetrahedral (P) sites. Substituting late first row and second row transition metals and main group elements for Ti yields structures very similar to KTP, but the characteristic distortion of the TiO_6 is all but eliminated by the substitution. This is due to the unavailability of empty low-lying d orbitals in such metals, which reduces the mixing coefficients that determine the both the magnitude of MO_6 distortion and the amount of charge-transfer character in the bonding orbitals. As a result, such compounds have very small, though measurable, optical nonlinearities. Replacing P with As to give KTA results in slightly improved frequency doubling and Pockels coefficients, though arsenic substitution has the opposite effect if NH_4^+ , rather than K^+ , occupies the cation sites: the powder SHG intensity of $\text{NH}_4\text{TiOAsO}_4$ (NTA) is only one-fifth that of $\text{NH}_4\text{TiOPO}_4$ (NTP) or of KTP.⁸

Substituting monovalent cations larger than K^+ (e.g. Rb^+ , NH_4^+ , Tl^+) onto the K sites appears to have little effect on optical nonlinearity. Smaller cations (e.g. Na^+ , Ag^+ , Li^+) are, however, very deleterious to NLO properties in certain cases. The focus of this investigation is to determine the crystal structures of these small-cation KTP isomorphs and relate structure to optical nonlinearity. This requires synthesizing these phases in powder form for use in powder SHG measurements, and growing single crystals of these materials for structural characterization. Unfortunately, small-cation KTP derivatives are inaccessible via the direct synthetic techniques (flux and hydrothermal methods) used to grow KTP and KTA single crystals. Instead, these conditions give centrosymmetric phases such as $\alpha\text{-NaTiOPO}_4$, which is isomorphous with the mineral titanite, CaTiOSiO_4 (monoclinic, $\text{P2}_1/\text{c}$).⁹

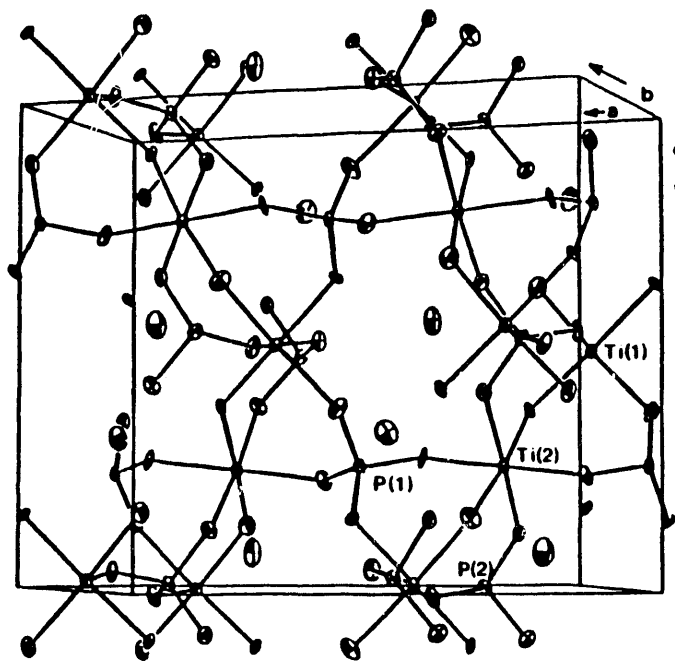
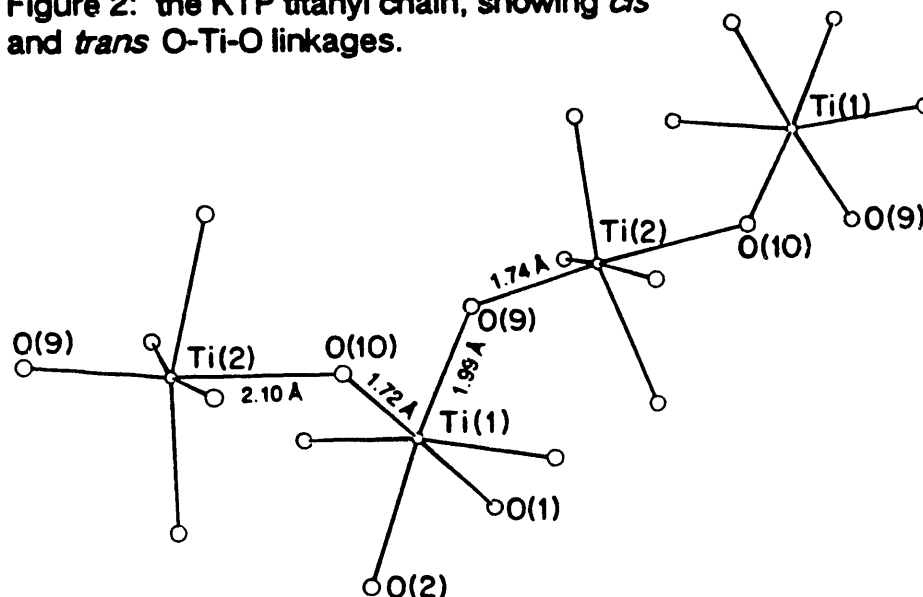


Figure 1: the KTiOPO_4 unit cell.

Figure 2: the KTP titanyl chain, showing *cis* and *trans* O-Ti-O linkages.



However, the mobility of the cations in KTP and KTA affords the possibility of obtaining KTP-type phases containing Na, Li and Ag through ion exchange, and we have developed a synthetic method which yields these metastable compounds by exchanging KTP and KTA crystals in low-temperature nonaqueous melts. Single crystal X-ray results have identified changes in the coordination of the cations with the framework, and of any changes in the geometry of the TiO_6 groups, and powder SHG data revealed changes in optical nonlinearity on cation substitution. We report here the syntheses, structures and SHG intensities of $\text{Na}_{.95}\text{K}_{.05}\text{TiOPO}_4$ (NaTP), $\text{Na}_{.83}\text{K}_{.17}\text{TiOAsO}_4$ (NaTA), $\text{Ag}_{.85}\text{K}_{.15}\text{TiOPO}_4$ (AgTP), $\text{Ag}_{.98}\text{K}_{.02}\text{TiOAsO}_4$ (AgTA), $\text{Li}_{.45}\text{K}_{.55}\text{TiOPO}_4$ (KLTP), and $\text{Li}_{.46}\text{K}_{.54}\text{TiOAsO}_4$ (KLTA).

2. EXPERIMENTAL

KTP crystals were precipitated from a melt prepared by heating 0.020 mol TiO_2 , 0.064 mol KH_2PO_4 and 0.0064 mol K_2HPO_4 at 950 °C in a platinum crucible. This was cooled to 910°C at the rate of 1°C/h. Excess flux was poured off, and the crucible was allowed to cool to room temperature in the furnace to help prevent thermal shock. The remaining flux was dissolved in hot water, and the crystals were recovered by filtration. Crystal sizes ranged from 10 μm to several mm in diameter.

KTA crystals were prepared hydrothermally by dissolving TiO_2 in a 10 M solution of KH_2AsO_4 and K_2HAsO_4 in water. The reagents were sealed in a gold tube, which was heated in a pressure vessel at 650°C under 3,000 bar. Crystals were precipitated by cooling to 450°C at a rate of 2°C/h. The vessel was then cooled rapidly to room temperature. Crystals ranging from 0.5 mm to 3 mm in diameter were recovered; these were washed with water and filtered.

All new compositions were synthesized by soaking several small (0.2-1.0 mm diameter) crystals of KTP or KTA in nonaqueous molten salts contained in 30 mL Pyrex beakers at 1 bar. NaTP and NaTA crystals were synthesized by immersing crystals of KTP and KTA in a melt prepared by fusing 5.0g each of NaNO_3 , NaNO_2 and $\text{NaOOCCH}_3 \cdot 3\text{H}_2\text{O}$ for 48 h at 215°C. KLTP and KLTA crystals were made by exchanging crystals of KTP and KTA in 5.0g molten LiNO_3 at 290°C for 48 h. Exchanging KTP and KTA crystals in a melt consisting of 2.5g each of AgNO_3 and AgClO_3 at 185°C over 40 h resulted in AgTP and AgTA, respectively.

Chemical compositions of the product phases were determined through elemental analysis. Lattice constants for KLTA and AgTA were refined using powder X-ray diffraction data obtained with a Scintag automated θ - θ powder diffractometer (Cu K_{α} radiation, $\lambda = 1.5418 \text{ \AA}$). Single crystal X-ray diffraction data were collected on NaTP, NaTA, AgTP and KLTP with a Huber four-circle automated diffractometer (Mo K_{α} radiation, $\lambda = 0.71069 \text{ \AA}$). Lattice constants for these crystals were obtained from centered reflections using an autoindexing routine. Powder SHG intensity data were collected from samples of similar crystallite size using the method described by Dougherty and Kurtz.¹⁰ The $1.064 \mu\text{m}$ pump beam was supplied by a Spectra-Physics Q-switched Nd:YAG laser, which generated 8 ns pulses at a rate of 2 Hz. Light emerging from the sample was directed into a grating monochromator selected to 532 nm. SHG intensity was measured using a Tektronix 400 MHz analog oscilloscope equipped with a digitizing camera system. Randomly oriented quartz microcrystals of approximately $60 \mu\text{m}$ diameter were used as the intensity standard.

3. RESULTS

All crystals were recovered intact from their respective melts. In general, smaller exchanged crystals are clear, larger ones are translucent or opaque white. When viewed in transmission between crossed polars in an optical microscope, all but the smallest crystals (0.1-0.2 mm diameter) appear striated.

Powder X-ray diffraction data showed that all crystals had retained the KTiOPO_4 space group ($\text{Pna}2_1$) after exchange, though the cell parameters of the exchanged derivatives are generally smaller (Table I). Single crystal X-ray data were modeled using the KTP atomic coordinates.¹¹ NaTP, NaTA, AgTP and KLTP are all structurally very similar to KTP, with each crystallographically independent Ti atom coordinating to four oxygen atoms shared with P or As (identified as O(1)-O(8)), and two oxygen atoms shared with titanium atoms adjacent in the chain (O(9) and O(10)). Relevant atomic distances are reported for each structure in Table II.

SHG intensities relative to quartz are reported for the new phases, along with KTP and KTA, in Table I. In general, SHG intensity is marginally altered by partial Li exchange, and sharply reduced by Ag exchange. The effect of Na substitution appears more subtle. While the difference in the SHG intensities of KTA and NaTA is slight, NaTP's SHG intensity is only one-tenth that of KTP. A comprehensive structure/property relationship for this class of materials must account for these observations.

Table I: Lattice Constants and SHG Intensities for MTiOXO_4 Compounds

Formula	$a, \text{ \AA}$	$b, \text{ \AA}$	$c, \text{ \AA}$	SHG intensity/ quartz
KTiOPO_4	12.823(4)	6.416(6)	10.589(3)	910
KTiOAsO_4	13.416(5)	6.584(2)	10.771(6)	990
$\text{Na}_{.95}\text{K}_{.05}\text{TiOPO}_4$	12.611(2)	6.281(1)	10.595(2)	100
$\text{Na}_{.87}\text{K}_{.13}\text{TiOAsO}_4$	12.888(1)	6.4095(3)	10.7393(6)	790
$\text{Ag}_{.85}\text{K}_{.15}\text{TiOPO}_4$	12.534(2)	6.294(1)	10.524(1)	7
$\text{Ag}_{.98}\text{K}_{.02}\text{TiOAsO}_4$	12.792(3)	6.422(2)	10.683(4)	10
$\text{K}_{.55}\text{Li}_{.45}\text{TiOPO}_4$	12.778(2)	6.370(1)	10.560(1)	620
$\text{K}_{.54}\text{Li}_{.46}\text{TiOAsO}_4$	13.059(9)	6.588(6)	10.734(8)	970

Table II: Bond distances in MTiOXO₄ compounds (Å)

	KTP	KTA ¹²	NaTP	AgTP	NaTA	KLTP
Ti(1)-O(1)	2.161(4)	2.138	2.226(6)	2.23(1)	2.257(8)	2.13(1)
Ti(1)-O(2)	1.957(4)	1.947	1.978(6)	2.00(1)	1.982(7)	2.03(1)
Ti(1)-O(5)	2.047(4)	2.002	2.000(6)	1.99(1)	1.967(8)	2.01(1)
Ti(1)-O(6)	1.900(4)	2.004	1.937(5)	1.94(1)	1.937(7)	1.98(1)
Ti(1)-O(9)	1.993(4)	1.957	2.005(6)	2.00(1)	2.001(8)	1.91(1)
Ti(1)-O(10)	1.718(4)	1.735	1.717(6)	1.71(1)	1.718(7)	1.77(1)
Δ Ti(1)	0.443	0.403	0.509	0.52	0.539	0.36
Ti(2)-O(3)	2.037(3)	2.025	2.019(5)	1.98(1)	2.024(7)	1.99(1)
Ti(2)-O(4)	1.979(3)	1.989	1.924(5)	1.90(1)	1.939(7)	1.98(1)
Ti(2)-O(7)	1.966(4)	1.941	1.991(6)	1.99(1)	1.992(8)	1.98(1)
Ti(2)-O(8)	1.994(4)	1.983	1.999(6)	2.00(1)	1.967(7)	1.99(1)
Ti(2)-O(9)	1.738(4)	1.770	1.758(6)	1.78(1)	1.777(8)	1.84(1)
Ti(2)-O(10)	2.101(4)	2.097	2.099(6)	2.07(1)	2.103(7)	2.01(1)
Δ Ti(2)	0.363	0.327	0.341	0.29	0.326	0.17
P(1)-O(1)	1.523(4)	1.63	1.516(6)	1.55(1)	1.673(8)	1.52(1)
P(1)-O(2)	1.550(4)	1.66	1.557(6)	1.54(1)	1.696(7)	1.57(1)
P(1)-O(3)	1.549(4)	1.72	1.539(5)	1.56(1)	1.677(7)	1.51(1)
P(1)-O(4)	1.547(4)	1.71	1.549(5)	1.57(1)	1.693(7)	1.57(1)
P(2)-O(5)	1.541(4)	1.63	1.527(6)	1.53(1)	1.667(7)	1.53(1)
P(2)-O(6)	1.533(4)	1.68	1.521(5)	1.54(1)	1.683(7)	1.52(1)
P(2)-O(7)	1.551(4)	1.69	1.559(6)	1.53(1)	1.693(8)	1.55(1)
P(2)-O(8)	1.543(4)	1.70	1.532(6)	1.53(1)	1.712(7)	1.55(1)
M(1)-O(1)	2.900(4)	2.69	2.634(7)	2.62(1)	2.65(1)	
M(1)-O(2)	2.743(4)	2.77			2.58(2)	
M(1)-O(3)	2.717(4)	2.65	2.595(7)	2.53(1)	2.46(1)	2.75(1)
M(1)-O(4)						
M(1)-O(5)	2.874(4)	2.98	2.569(7)	2.69(1)	2.46(1)	
M(1)-O(6)						2.89(2)
M(1)-O(7)	3.059(4)	3.15	2.809(8)		2.93(1)	
M(1)-O(8)	2.762(4)	2.72	2.568(7)	2.56(1)	2.45(1)	2.91(1)
M(1)-O(9)	2.987(4)	2.87	2.745(8)		2.84(1)	
M(1)-O(10)	2.717(4)	3.10	2.525(7)	2.54(1)	2.68(1)	2.65(2)
M(2)-O(1)	2.679(4)	2.69	2.398(8)	2.37(1)	2.36(1)	2.71(2)
M(2)-O(2)	2.979(4)	3.01	2.493(8)	2.70(1)	2.45(1)	3.11(1)
M(2)-O(3)	3.046(4)	3.13				3.13(1)
M(2)-O(4)	3.125(4)	3.07			2.92(1)	2.96(1)
M(2)-O(5)	2.799(4)	2.58	2.789(8)		2.80(1)	2.72(1)
M(2)-O(6)						
M(2)-O(7)	2.917(4)	2.91	2.571(9)	2.53(1)	2.69(1)	3.04(1)
M(2)-O(8)	3.044(4)	3.12				
M(2)-O(9)	2.765(4)	3.15	2.644(8)	2.33(1)	2.61(1)	2.69(1)
M(2)-O(10)	3.055(4)	2.86				3.15(1)

It is conceivable that inclusion of small cations might alter the Ti-O bonds in a fashion that reduces the difference between long and short bond distances in the chain, rendering the TiO_6 groups more regular. We can define a measure of distortion, Δ , as the difference of the short titanyl bond in a TiO_6 group and the long Ti-O *trans* to it. The value of Δ about Ti(2) is the more useful indicator of titanyl chain conjugation, as both the short bond Ti(2)-O(9) and the long bond *trans* to it (Ti(2)-O(10)) are in the chain. In fact, for most KTP isostructures, SHG intensity roughly follows Δ Ti(2) (or more generally, Δ M(2)) (Figure 3). However, AgTP and NaTP are glaring exceptions to this trend, since low SHG intensities persist in these compounds despite a healthy degree of TiO_6 group distortion. Therefore, arguments for the loss of optical nonlinearity in these phases cannot be based solely on changes in the Ti coordination sphere.

On the other hand, there are subtle differences in the bonding of the cations with the framework that could explain the variations of SHG intensity among these new phases. We have previously shown how coordination of the cations to the framework oxygen atoms can play a significant role in defining optical nonlinearity in this structure type.⁵ The degree to which charge-transfer character can be mixed into the valence orbitals depends not only on the distortion of the TiO_6 groups, but also on the nature of the cation-framework interaction. Shorter cation-oxygen bond lengths and increased cation electronegativity interfere with excited state mixing and thus reduce the hyperpolarizability of the electrons in the bonding orbitals.

We can invoke this argument to explain the differences in NLO response among the MTiOXO_4 compounds reported here. Though the cation-oxygen distances are generally shorter in the exchanged derivatives than in KTP and KTA, this alone does not explain, for example, the different SHG intensities of NaTA and NaTP, as the average Na-O distances are very similar in these structures (Table III). However, it should be noted from the preceding discussion that cation coordination to the titanyl oxygen atoms (O(9) and O(10)) should exert more influence on electronic polarizability in the Ti-O chain than should coordination to the framework oxygen atoms (O(1) through O(8)). In fact, we find that if only bond distances between *titanyl* oxygen atoms and cations are considered, SHG intensities roughly follow average cation-titanyl oxygen bond distance (Figure 4).

Table III: Comparison of cation-oxygen distances in KTP isostructures

Compound	average M-O distance	avg. framework M-O distance	avg. titanyl M-O distance
KTiOPO_4	2.89 Å	2.89 Å	2.88 Å
KTiOAsO_4	2.91	2.88	2.99
$\text{Na}_{.95}\text{K}_{.05}\text{TiOPO}_4$	2.61	2.60	2.64
$\text{Ag}_{.85}\text{K}_{.15}\text{TiOPO}_4$	2.54	2.57	2.43
$\text{Na}_{.87}\text{K}_{.13}\text{TiOAsO}_4$	2.64	2.62	2.71
$\text{K}_{.55}\text{Li}_{.45}\text{TiOPO}_4$	2.79	2.82	2.67

The principal influences that govern cation-oxygen distances in these structures are the ionic radii of the cations, and the relative basicities of the oxygen atoms. The larger potassium ions give rise to longer cation-oxygen distances overall, compared with the smaller Na, Ag and Li ions. While the average Na-O distances in NaTA and NaTP are nearly equal, bonding between Na and the titanyl chain is weaker in NaTA, due to the increase in framework oxygen basicity upon replacing P with As. This substitution effectively draws the sodium ions away from the titanyl oxygen atoms. The higher charge density of the small Ag ion causes it to be strongly attracted to the highly basic oxygen atoms in the chain, resulting in the shortest cation-oxygen interaction identified (2.33 Å) in this series of compounds. The average cation-oxygen distance in KLTP is closer to that in KTP than those of the other isostructures reported here, though coordination is influenced by the small Li ion, and the (K,Li)-O(9) distances are even shorter on average than the analogous interactions in NaTA.

In general, the exchanged cations coordinate more strongly to O(9) than to O(10) (Table II), possibly due to a higher degree of basicity for O(9). We have previously reported that changes in cation coordination upon ion exchange affect the Ti(1)-O(9)-Ti(2) bond angle in the compounds $(\text{NH}_4)_5\text{H}_5\text{TiOPO}_4$ (NHTP), AgTP and NaTP, and that a decrease in the value of this angle is associated with a drop in SHG intensity.¹³ The compounds NaTA and KLTP follow this trend as well. The

Figure 3: SHG intensity vs. $\text{Ti}(2)\text{O}_6$ distortion in the KTP structure field.¹³

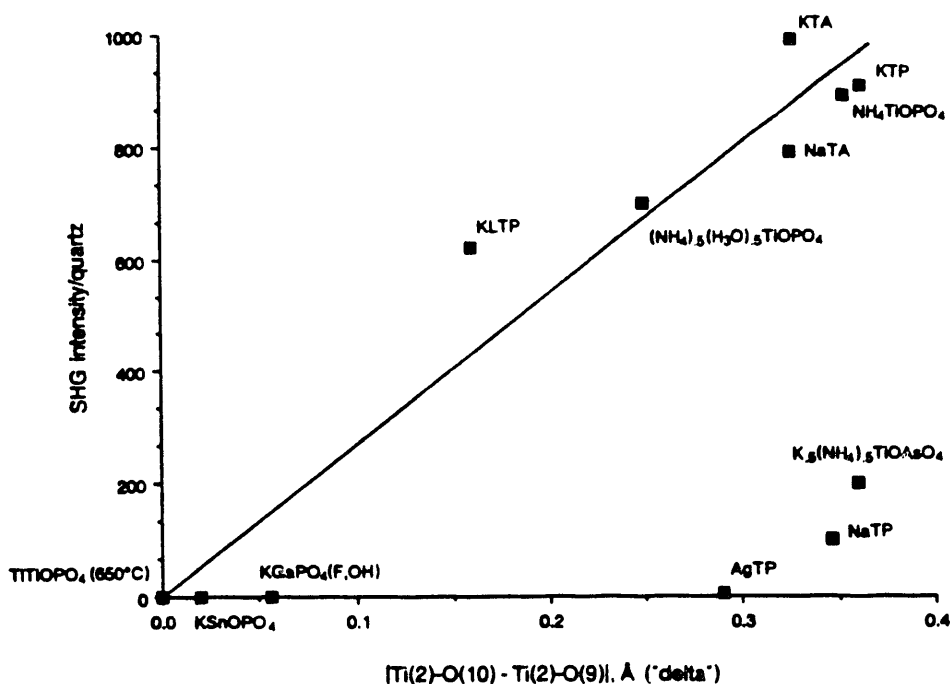
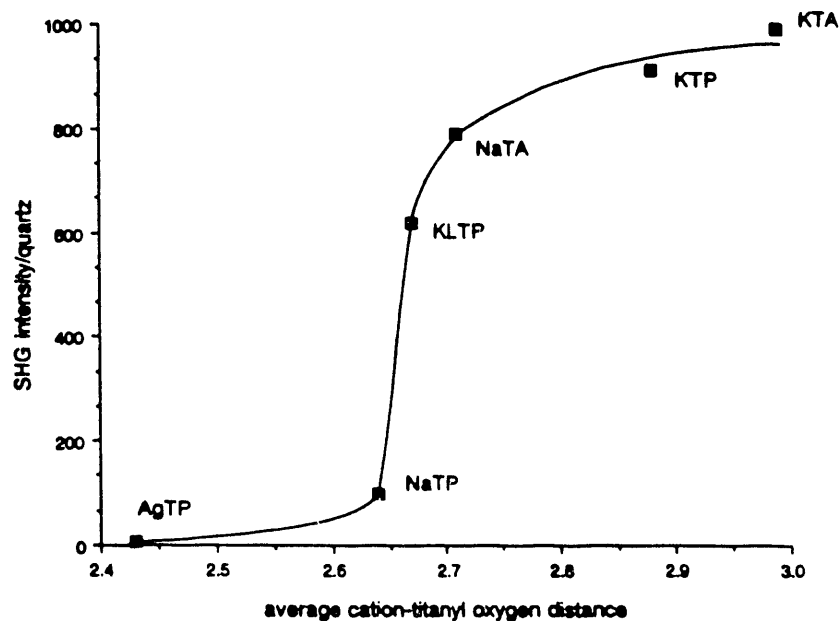


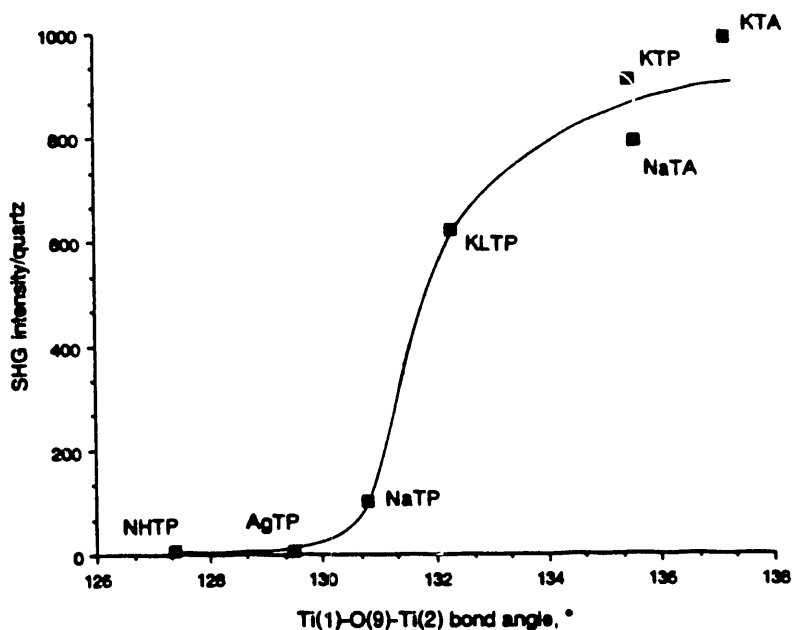
Figure 4: SHG intensity vs. average cation - titanyl oxygen bond distance in KTP isostructures.



effect of coordination to O(9) on the titanyl chain in ion-exchanged derivatives of KTP and KTA is seen in the Ti(1)-O(9)-Ti(2) bond angles of these structures, which range from 127.4° in NHTP to 137.2° in KTA. SHG intensity varies with this angle in much the same fashion as it does with cation-titanyl oxygen distance (Figure 5). The effect of cation coordination on the Ti(1)-O(10)-Ti(2) angle is much less significant, indicating that coordination to O(9) has a disproportionate influence on both titanyl chain geometry and NLO susceptibility.

It is worth noting that the SHG intensities of the arsenate derivatives are all higher than those of the analogous phosphates. It is possible that arsenic draws Ag and Li away from the Ti-O chain in AgTA and KLTA as it apparently does in NaTA, and single crystal X-ray diffraction studies now underway will determine if this is the case. If so, this may explain the larger optical nonlinearities of the arsenate phases (vs. AgTP, KLTP, and NaTP) as a result of either improved mixing of delocalized conduction band character into the valence electronic states, or improved delocalization of the conduction band states themselves.

Figure 5: Optical nonlinearity and titanyl chain angle in ion-exchanged KTP and KTA derivatives.



4. SUMMARY

Though their instability at high temperatures precludes their synthesis via conventional methods, six isostructures of KTiOPO_4 have been prepared as single crystals, using a low-temperature ion exchange technique. The optical nonlinearities (measured as powder SHG intensity) of the compounds $\text{Na}_{.95}\text{K}_{.05}\text{TiOPO}_4$ (NaTP), $\text{Na}_{.83}\text{K}_{.17}\text{TiOAsO}_4$ (NaTA), $\text{Ag}_{.85}\text{K}_{.15}\text{TiOPO}_4$ (AgTP), $\text{Ag}_{.98}\text{K}_{.02}\text{TiOAsO}_4$ (AgTA), $\text{Li}_{.45}\text{K}_{.55}\text{TiOPO}_4$ (KLTP), and $\text{Li}_{.46}\text{K}_{.54}\text{TiOAsO}_4$ (KLTA) vary over three orders of magnitude. Single crystal X-ray refinements show that ion exchange results in no changes in the immediate coordination environment of the titanium atoms in NaTP, NaTA, AgTP and KLTP which could account for the differences in optical nonlinearity among these materials. SHG intensity correlates with the average length of the interaction between cations and the titanyl oxygen atoms which link adjacent TiO_6 octahedra. It is postulated that stronger cation coordination to the titanyl chain decreases the extent to which charge-transfer excited state character may be mixed into the bonding and nonbonding orbitals of the TiO_6 groups, reducing the hyperpolarizability of these electronic states and thereby attenuating macroscopic nonlinear susceptibility.

5. ACKNOWLEDGMENTS

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6. REFERENCES

1. For a review of the material properties of KTP, see J. C. Jacco, "KTiOPO₄(KTP): Past, Present and Future", *Proc. SPIE* 968, pp. 93-9, 1988.
2. J. D. Bierlein, H. Vanherzeele, A. A. Ballman, "Linear and Nonlinear Optical Properties of Flux-Grown KTiOAsO₄", *Appl. Phys. Lett.* 54 (9), pp. 783-5, 1989.
3. B. F. Levine, "Bond-Charge Calculation of Nonlinear Optical Susceptibilities for Various Crystal Structures", *Phys. Rev. B* 7(6), pp. 2600-2626, 1973.
4. P. A. Morris, A. Ferretti, J. D. Bierlein, G. M. Loiacono, "Reduction of the Ionic Conductivity of Flux-Grown Potassium Titanyl Phosphate (KTiOPO₄) Crystals", *J. Cryst. Growth* 109, pp. 367-75, 1991.
5. M. L. F. Phillips, W. T. A. Harrison, T. E. Gier, G. D. Stucky, G. V. Kulkarni, J. K. Burdett, "Electronic Effects of Substitution Chemistry in the KTiOPO₄ Structure Field: Structure and Optical Properties of Potassium Vanadyl Phosphate", *Inorg. Chem.* 29(11), pp. 2158-63, 1990.
6. G. Blasse, L. H. Brixner, "The Luminescence of KTiOPO₄:Nb,Ga", *Mat. Res. Bull.* 24, pp. 1099-1102, 1989.
7. D. J. Williams, "Organic Polymeric and Non-Polymeric Materials with Large Optical Nonlinearities", *Angew. Chem. Int. Ed. Engl.* 23, pp. 690-703, 1984.
8. M. L. F. Phillips, W. T. A. Harrison, T. E. Gier, G. D. Stucky, "SHG Tuning in the KTP Structure Field", *Proc. SPIE* 1104, pp. 225-31, 1989.
9. M. L. F. Phillips, W. T. A. Harrison, G. D. Stucky, E. M. McCarron, J. C. Calabrese, T. E. Gier, "The Effects of Substitution Chemistry in the KTiOPO₄ Structure Field", submitted for publication, *Chem. Mater.*
10. J. P. Dougherty, S. K. Kurtz, "A Second Harmonic Analyzer for the Detection of Non-Centrosymmetry", *J. Appl. Cryst.* 9, pp. 145-57, 1976.
11. KTiOPO₄ structure data were obtained from I. Tordjman, R. Masse, J. C. Guitel, "Structure cristalline du monophosphate KTiPO₅", *Z. Kristallogr.* 139, pp. 103-15, 1974.
12. KTiOAsO₄ structure data were obtained from M. El Brahim, J. Durand, "Structure et Propriétés d'Optique Non Linéaire de KTiOAsO₄", *Rev. Chim. Minéral.* 23(2), 146-53, 1986. Potassium-oxygen distances listed here were calculated from published atomic positions.
13. G. D. Stucky, M. L. F. Phillips, T. E. Gier, "The Potassium Titanyl Phosphate Structure Field: A Model for New Nonlinear Optical Materials", *Chem. Mater.* 1(5), 492-509, 1989. Bond distances in Figure 3 that are not reported in this work were obtained from this reference.

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