Single-Crystal Structures and Optical Properties of the Nonlinear Optical KTiOPO$_4$-Type Materials K$_{0.55}$Li$_{0.45}$TiOPO$_4$ and K$_{0.54}$Li$_{0.46}$TiOAsO$_4$ Prepared by Molten Salt Ion-Exchange

William T. A. Harrison

Department of Chemistry, University of Western Australia, Nedlands, WA 6907, Australia

Mark L. F. Phillips

Department 1815, Sandia National Laboratories, Albuquerque, New Mexico 87185

Galen D. Stucky

Department of Chemistry, University of California, Santa Barbara, California 93106-9510

Received October 9, 1996. Revised Manuscript Received February 24, 1997[⊗]

Single crystals of the KTiOPO$_4$ (KTP) type phases K$_{0.55}$Li$_{0.45}$TiOPO$_4$ and K$_{0.54}$Li$_{0.46}$TiOAsO$_4$ have been prepared by molten salt ion-exchange reactions from their potassium-containing precursors. After ion-exchange, both phases maintain the distinctive distorted TiO$_6$ octahedra seen in KTiOPO$_4$ and KTiOAsO$_4$. The pattern of lithium-ion substitution differs for these two phases: In K$_{0.55}$Li$_{0.45}$TiOPO$_4$, Li substitutes for both of the two crystallographically distinct potassium cations to roughly equal extent, whereas in K$_{0.54}$Li$_{0.46}$TiOAsO$_4$, the 9-coordinate K(2) atom is preferentially replaced by Li. The lithium cations occupy six-rings of TiO$_6$ and PO$_4$ polyhedra and adopt approximate square-planar coordination in both these materials. Second harmonic generation at 1064 nm is not significantly affected by lithium substitution in either of these phases. Crystal data: K$_{0.55}$Li$_{0.45}$TiOPO$_4$: $M_r = 183.55$, orthorhombic, space group *Pna*2$_1$ (No. 33), $a = 12.741(2)$ Å, $b = 6.357(1)$ Å, $c = 10.535(2)$ Å, $V = 853(2)$ Å^3, $Z = 8$, $R(F) = 3.31\%$ for 1393 reflections with $I > 3\sigma(I)$. K$_{0.54}$Li$_{0.46}$TiOAsO$_4$: $M_r = 227.11$, orthorhombic, space group *Pna*2$_1$ (No. 33), $a = 13.018(2)$ Å, $b = 6.589(1)$ Å, $c = 10.766(2)$ Å, $V = 923(2)$ Å^3, $Z = 8$, $R(F) = 3.76\%$ for 1637 reflections [$I > 3\sigma(I)$].

Introduction

Potassium titanyl phosphate, KTiOPO$_4$ (KTP), and its substantial family of isostructures are of great current interest to solid-state scientists due to their exceptional nonlinear optical and electrooptical properties.[1−3] These materials are employed in frequency-doubling crystals, particularly for the second harmonic generation (SHG) of 1064 nm Nd:YAG laser radiation, as well as optical parametric oscillators and bulk and waveguide electrooptic modulators.[3] The infinite vertex-sharing chains of distinctive, distorted TiO$_6$ octahedra found in titanium-containing KTP-type materials[4] are considered to be of the greatest importance in defining their exceptional optical properties,[5−7] although a comprehensive structure−property correlation for KTP-type materials must also consider interactions between univalent cations (K,

Rb, Cs, Na, NH$_4$, Tl, ...) and the Ti/(P,As)/O "framework".[8] As well as providing insight into the mechanism of SHG in these phases,[9] the study of cation substitutions into the KTP structure is important in the practical applications of these materials. The ionic conductivity and laser damage threshold may be affected by cation substitutions,[10−12] and the operation of devices such as waveguides relies upon controlled ion-exchange to set up a differential in refractive indices inside a crystal.[3,13]

In this paper, we report the syntheses, single-crystal structures, and optical properties of the KTP-type materials K$_{0.55}$Li$_{0.45}$TiOPO$_4$ and K$_{0.54}$Li$_{0.46}$TiOAsO$_4$, in which lithium partially replaces potassium as the extraframework cation. Some preliminary data on K$_{0.55}$Li$_{0.45}$TiOPO$_4$ were reported earlier.[14] Both these materials must be prepared by ion-exchange reactions from

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

(1) Zumsteg, F. C.; Bierlein, J. D.; Gier, T. E. *J. Appl. Phys.* **1976**, *47*, 4980.

(2) Stucky, G. D.; Phillips, M. L. F.; Gier, T. E. *Chem. Mater.* **1989**, *1*, 492 and included references.

(3) Hagerman, M. E.; Poeppelmeier, K. R. *Chem. Mater.* **1995**, *7*, 602 and included references.

(4) Tordjman, I.; Masse, R.; Guitel, J. C. *Z. Kristallogr.* **1974**, *139*, 103.

(5) Munowitz, M.; Jarman, R. H.; Harrison, J. F. *Chem. Mater.* **1992**, *4*, 1296.

(6) Phillips, M. L. F.; Harrison, W. T. A.; Gier, T. E.; Stucky, G. D.; Kulkarni, G. V.; Burdett, J. K. *Inorg. Chem.* **1990**, *29*, 2158.

(7) Burdett, J. K.; Hughbanks, T. *Inorg. Chem.* **1985**, *24*, 1741.

(8) Phillips, M. L. F.; Harrison, W. T. A.; Stucky, G. D.; McCarron III, E. M.; Calabrese, J. C.; Gier, T. E. *Chem. Mater.* **1992**, *4*, 222.

(9) Thomas, P. A.; Mayo, S. C.; Watts, B. E. *Acta Crystallogr.* **1992**, *B48*, 401.

(10) Roelofs, M. G.; Morris, P. A.; Bierlein, J. D. *J. Appl. Phys.* **1991**, *70*, 720.

(11) Morris, P. A.; Ferretti, A.; Bierlein, J. D.; Loiacono, G. M. *J. Cryst. Growth* **1991**, *109*, 367.

(12) Morris, P. A.; Crawford, M. K.; Roelofs, M. G.; Bierlein, J. D.; Baer, T. M. *Proc. SPIE* **1991**, *1104*, 104.

(13) Bierlein, J. D.; Vanherzeele, H. J. *J. Opt. Soc. Am.* **1989**, *B6*, 622.

(14) Phillips, M. L. F.; Harrison, W. T. A.; Stucky, G. D. *Proc. SPIE* **1991**, *1561*, 84.

their potassium-containing precursors. Directly prepared LiTiOPO₄[15] has a centrosymmetric crystal structure distinct from that of KTP-type materials.

Experimental Section

Synthesis of K₀.₅₅Li₀.₄₅TiOPO₄. A 30 mL capacity platinum crucible was charged with 1.60 g of TiO₂, 8.64 g of KH₂PO₄, and 1.44 g of K₂HPO₄·3H₂O (starting K:Ti:P ratio ≈ 3.7:1:3.5) and slowly heated to 950 °C. After 4 h at this temperature, the flux was decanted into a 15 mL Pt crucible, which was reheated to 950 °C and then cooled to 910 °C at 1 °C/h. The flux was again decanted, and the crucible containing the crystals was allowed to cool slowly in the furnace. The cooled crucible was immersed in hot water to dissolve the flux, and the crystals were recovered by filtration. The yield was 1.45 g of KTiOPO₄ crystals with maximum linear dimensions of up to 1 mm.

A mass of 0.214 g of KTiOPO₄ crystals was placed in a porcelain crucible with 5.2 g of LiNO₃. The mixture was heated to 290 °C for 48 h and then cooled to room temperature. The crucible was immersed in hot water, and the solids were recovered by filtration. The yield was 0.184 g of clear rhomboidal and irregular crystals with the composition K₀.₅₅Li₀.₄₅TiOPO₄ (elemental analysis by Galbraith Laboratories, Knoxville, TN).

Synthesis of K₀.₅₄Li₀.₄₆TiOAsO₄. Single crystals of up to ~2 mm maximum linear dimension of KTiAsO₄ were prepared as described earlier.[16] A mass of 0.297 g of KTiOAsO₄ crystals was placed in a porcelain crucible with 5.2 g of LiNO₃. The mixture was heated to 290 °C for 48 h and then cooled to room temperature. The crucible was immersed in hot water, and the solids were collected by filtration. A yield of 0.277 g of translucent rhomboidal and irregular crystals with the composition K₀.₅₄Li₀.₄₆TiOAsO₄ (by elemental analysis) was recovered.

Optical Measurements. Powder second harmonic generation (PSHG) responses on carefully ground and sieved samples of K₀.₅₅Li₀.₄₅TiOPO₄ and K₀.₅₄Li₀.₄₆TiOAsO₄ were made as described earlier[6] and normalized to signals from similarly prepared crystals of their all-potassium precursors. Substantial PSHG values of 0.68 × KTiOPO₄ for K₀.₅₅Li₀.₄₅TiOPO₄ and 0.98 × KTiOAsO₄ for K₀.₅₄Li₀.₄₆TiOAsO₄ were obtained, definitively indicating that both title compounds crystallize in noncentrosymmetric space groups.

Crystal Structure Determinations. Room-temperature [25 (1) °C] single-crystal data were collected for K₀.₅₅Li₀.₄₅TiOPO₄ (transparent rhomb, dimensions ca. 0.3 × 0.3 × 0.4 mm) and K₀.₅₄Li₀.₄₆TiOAsO₄ (translucent rhomb, 0.3 × 0.4 × 0.4 mm) on a CAD4 automated diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å) as summarized in Table 1. The systematic absences (00l, $l \neq 2n$; h0l, $h \neq 2$; 0kl, $k + l \neq 2n$) in the reduced data for both K₀.₅₅Li₀.₄₅TiOPO₄ and K₀.₅₄Li₀.₄₆TiOAsO₄ were consistent with space groups *Pna*2₁ (No. 33) and *Pnam* (nonstandard setting of *Pnma*, No. 62).

The structure of K₀.₅₅Li₀.₄₅TiOPO₄ was refined in space group *Pna*2₁ (No. 33), using the atomic coordinates of KTiOPO₄[2,4] as a starting model. The refinement converged, with the Ti, P, and O atoms behaving normally. Refinement of the isotropic thermal factors for the potassium cations led to very large values ($U_{iso} \approx 0.5$ Å²), indicating that these sites were not fully occupied in this plane. The potassium fractional site occupancies were varied and refined to values of about 0.5, leading to an improvement in fit, and more reasonable U_{iso} values for these atoms. A difference Fourier synthesis revealed two significant extraatom features with reasonable geometry for lithium cations. These were added to the model, and the fit improved. On anisotropic refinement of the potassium atoms, K(1) refined to a very anisotropic thermal envelope, with the major axis aligned along the polar *c* direction. This species

(15) Nagornyi, P. G.; Kapshuk, A. A.; Stus', N. V.; Slobodyanik, N. S.; Chernega, A. N. *Zh. Neorg. Khim.* **1991**, *36*, 2766.
(16) Phillips, M. L. F.; Stucky, G. D. *Inorg. Synth.* **1995**, *30*, 143.

Table 1. Crystallographic Parameters

	K₀.₅₅Li₀.₄₅TiOPO₄	K₀.₅₄Li₀.₄₆TiOAsO₄
emp formula	TiK₀.₅₅PO₅Li₀.₄₅	AsTiK₀.₅₄O₅Li₀.₄₆
formula wt	183.55	227.11
crystal system	orthorhombic	orthorhombic
a (Å)	12.741(2)	13.018(2)
b (Å)	6.357(1)	6.589(1)
c (Å)	10.535(2)	10.766(2)
V (Å³)	853(2)	923(2)
Z	8	8
space group	*Pna*2₁ (No. 33)	*Pna*2₁ (No. 33)
T (°C)	25(2)	25(2)
λ (Mo Kα) (Å)	0.710 73	0.710 73
ρ_{calc} (g/cm³)	2.84	3.26
μ (cm⁻¹)	27.8	93.5
total data	1767	3035
obsd data[a]	1393	1637
parameters	158	154
$R(F)$[b]	3.31	3.76
$R_w(F)$[c]	3.28	2.75

[a] $I > 3\sigma(I)$ after data merging. [b] $R = 100\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = 100[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Atomic Positional Parameters for K₀.₅₅Li₀.₄₅TiOPO₄

atom	x	y	z	U_{eq}[a]	occ[b]
K(11)	0.0980(5)	0.327(1)	0.9470(5)	0.018(2)[c]	0.275(8)
K(12)	0.1018(6)	0.300(1)	0.8237(7)	0.048(3)[c]	0.265(7)
K(2)	0.0965(3)	0.6723(7)	0.0877(6)	0.0388	0.59(1)
Li(1)	0.238(4)	0.759(7)	0.267(5)	0.03(1)[c]	0.28(4)
Li(2)	0.605(1)	0.469(4)	−0.002(3)	0.013(7)[c]	0.40(4)
Ti(1)	0.37058(5)	0.5010(3)	0.0064(2)	0.0096	
Ti(2)	0.2503(2)	0.2625(2)	0.2573(2)	0.0108	
P(1)	0.4995(2)	0.3393(1)	0.2617(3)	0.0089	
P(2)	0.18333(7)	0.5017(4)	0.5134(3)	0.0081	
O(1)	0.4912(5)	0.481(1)	0.1453(5)	0.0099	
O(2)	0.5096(5)	0.473(1)	0.3828(4)	0.0108	
O(3)	0.4017(4)	0.1987(9)	0.2802(5)	0.0082	
O(4)	0.5962(4)	0.198(1)	0.2486(6)	0.0105	
O(5)	0.1150(4)	0.3117(9)	0.5375(5)	0.0130	
O(6)	0.1148(4)	0.6937(9)	0.4863(5)	0.0094	
O(7)	0.2584(6)	0.543(1)	0.6278(4)	0.0085	
O(8)	0.2573(6)	0.469(1)	0.4011(4)	0.0090	
O(9)	0.2746(6)	0.463(1)	0.1432(4)	0.0082	
O(10)	0.2243(6)	0.032(1)	0.3864(4)	0.0145	

[a] U_{eq} (Å²) = $[U_1U_2U_3]^{1/3}$. [b] Fractional site occupancy, if not unity. [c] U_{iso} (Å²).

was modeled as being split over two adjacent sites [atoms K(11) and K(12)]. The final refinement cycles optimized U_{iso} and *occ* for K(11), K(12), Li(1), and Li(2), U_{ij} and *occ* for K(2), U_{ij} for Ti, As, and O, and all atomic positional parameters and led to satisfactory convergence (Table 2). Pseudosymmetry was apparent during the K₀.₅₅Li₀.₄₅TiOPO₄ refinement, especially among the oxygen atoms in the structure.[17] For K₀.₅₅Li₀.₄₅TiOPO₄, a significant nonzero PSHG response (vide supra) definitely indicates a noncentrosymmetric space group[2] and thus rules out the possibility of this phase crystallizing in the centrosymmetric modification (space group *Pnan*) of the KTP structure type,[18] as observed above the strongly second-order[19] ferroelectric to paraelectric phase transition for a number of KTP isostructures.[20] We note that in most titanium-containing KTP-type phases, this phase transition occurs well above room temperature.[21] The high-temperature space group *Pnan* also has an additional systematic absence condition (*hk*0, $h + k \neq 2n$) which is not consistent with the observed data for K₀.₅₅-

(17) Thomas, P. A.; Glazer, A. M.; Watts, B. E. *Acta Crystallogr.* **1990**, *B46*, 333.
(18) Harrison, W. T. A.; Gier, T. E.; Stucky, G. D.; Schultz, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 540.
(19) Serhane, M.; Moch, P. *J. Phys. C* **1994**, *6*, 3821.
(20) Favard, J.-F.; Verbaere, A.; Piffard, Y.; Tournoux, M. *Eur. J. Solid State Inorg. Chem.* **1994**, *31*, 995.
(21) Yanovskii, V. K.; Voronkova, V. I. *Phys. Status Solidi* **1980**, *93*, 665.

Table 3. Bond Distances (Å) for K$_{0.55}$Li$_{0.45}$TiOPO$_4$

K(11)−O(1)	3.17(1)	K(11)−O(2)	2.72(1)
K(11)−O(3)	2.945(9)	K(11)−O(4)	3.181(8)
K(11)−O(6)	2.745(9)	K(11)−O(7)	3.20(1)
K(11)−O(8)	2.97(1)	K(11)−O(9)	3.175(9)
K(11)−O(10)	2.69(1)		
K(12)−O(1)	3.01(1)	K(12)−O(2)	2.60(1)
K(12)−O(3)	2.57(1)	K(12)−O(5)	3.02(1)
K(12)−O(6)	3.247(9)	K(12)−O(7)	3.26(1)
K(12)−O(8)	2.88(1)	K(12)−O(9)	3.27(1)
K(12)−O(10)	2.74(1)		
K(2)−O(1)	2.651(8)	K(2)−O(2)	3.184(9)
K(2)−O(3)	3.244(9)	K(2)−O(4)	2.902(8)
K(2)−O(5)	2.748(8)	K(2)−O(7)	3.022(8)
K(2)−O(9)	2.696(7)	K(2)−O(10)	3.241(8)
Li(1)−O(7)	2.33(5)	Li(1)−O(8)	2.33(5)
Li(1)−O(9)	2.34(5)	Li(1)−O(10)	2.15(5)
Li(2)−O(1)	2.13(2)	Li(2)−O(2)	1.93(2)
Li(2)−O(7)	2.22(2)	Li(2)−O(8)	2.07(2)
Ti(1)−O(1)	2.127(5)	Ti(1)−O(2)	2.013(6)
Ti(1)−O(5)	2.011(6)	Ti(1)−O(6)	1.974(6)
Ti(1)−O(9)	1.906(6)	Ti(1)−O(10)	1.760(6)
Ti(2)−O(3)	1.985(5)	Ti(2)−O(4)	1.982(5)
Ti(2)−O(7)	1.956(5)	Ti(2)−O(8)	2.008(5)
Ti(2)−O(9)	1.777(6)	Ti(2)−O(10)	2.027(6)
P(1)−O(1)	1.525(6)	P(1)−O(2)	1.538(6)
P(1)−O(3)	1.546(6)	P(1)−O(4)	1.531(6)
P(2)−O(5)	1.511(6)	P(2)−O(6)	1.528(6)
P(2)−O(7)	1.560(6)	P(2)−O(8)	1.527(6)

Table 4. Selected Bond Angles (deg) for K$_{0.55}$Li$_{0.45}$TiOPO$_4$

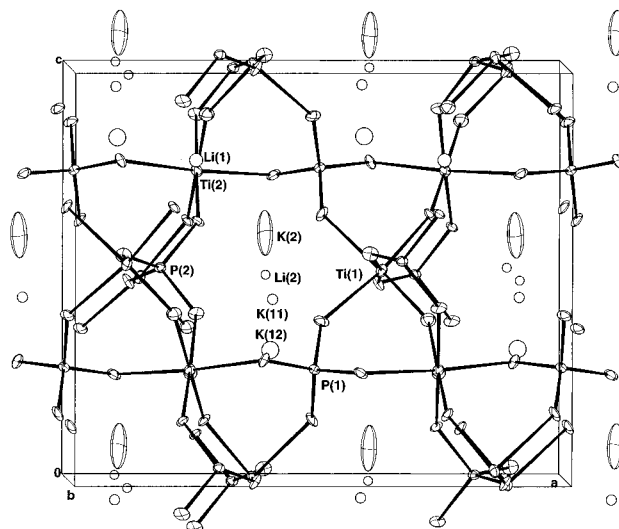|			
O(7)−Li(1)−O(8)	172.8(25)	O(7)−Li(1)−O(9)	105.7(23)
O(8)−Li(1)−O(9)	71.5(12)	O(7)−Li(1)−O(10)	75.2(13)
O(8)−Li(1)−O(10)	106.9(24)	O(9)−Li(1)−O(10)	173.2(26)
O(1)−Li(2)−O(2)	86.4(7)	O(1)−Li(2)−O(7)	94.7(11)
O(2)−Li(2)−O(7)	170.7(13)	O(1)−Li(2)−O(8)	158.7(12)
O(2)−Li(2)−O(8)	107.3(13)	O(7)−Li(2)−O(8)	69.1(5)
Ti(1)−O(1)−P(1)	129.7(4)	Ti(1)−O(2)−P(1)	130.2(4)
Ti(2)−O(3)−P(1)	130.5(4)	Ti(2)−O(4)−P(1)	136.0(4)
Ti(1)−O(5)−P(2)	134.9(4)	Ti(1)−O(6)−P(2)	135.8(3)
Ti(2)−O(7)−P(2)	128.5(4)	Ti(2)−O(8)−P(2)	130.3(4)
Ti(1)−O(9)−Ti(2)	135.6(4)	Ti(1)−O(10)−Ti(2)	132.5(4)

Figure 1. CAMERON[31] view of the structure of K$_{0.55}$Li$_{0.45}$TiOPO$_4$ viewed just oblique to [0$\bar{1}$0], with selected atoms labeled.
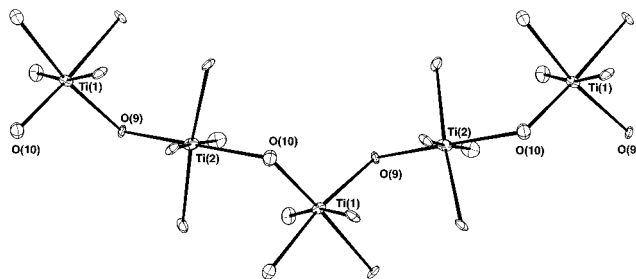

Figure 2. Detail of the K$_{0.55}$Li$_{0.45}$TiOPO$_4$ structure showing the TiO$_6$ chain connectivity. Note that the titanyl oxygen atoms [as parts of short Ti(1)=O(10) and Ti(2)=O(9) bonds] are in cis configuration with respect to Ti(1) and trans configuration with respect to Ti(2).

Li$_{0.45}$TiOPO$_4$. No reasonable starting atomic model could be established in the centrosymmetric space group *Pnam* (the other space group consistent with the systematic absence conditions), nor have any other KTP-type structures been observed to crystallize in this space group.

The structure of K$_{0.54}$Li$_{0.46}$TiOAsO$_4$ was refined in space group *Pna*2$_1$ (No. 33), using the atomic coordinates of KTiO-AsO$_4$[22] as a starting model. The refinement led to a chemically reasonable solution for the Ti, As, and O atoms. The isotropic thermal factor for one of the K atoms in K$_{0.54}$Li$_{0.46}$TiOAsO$_4$ refined to a large value, indicating partial fractional occupancy. Both K atom site occupancy factors were refined: one of these converged to ∼0.2, and one remained close to unity. A difference Fourier map indicated a single chemically reasonable lithium atom position, which was added to the atomic model. Further refinement cycles varying U_{ij} and *occ* for K, U_{iso} and *occ* for Li, U_{ij} for Ti, As, and O, and all atomic positions, led to convergence (Table 5). No further chemical species could be located from Fourier maps. All the crystallographic calculations were performed using the Oxford CRYSTALS[23] system.

Results

Structure of K$_{0.55}$Li$_{0.45}$TiOPO$_4$. Final atomic positional and thermal parameters for K$_{0.55}$Li$_{0.45}$TiOPO$_4$ are listed in Table 2, with selected bond distance and angle data given in Tables 3 and 4, respectively. K$_{0.55}$Li$_{0.45}$TiOPO$_4$ crystallizes as a typical KTP-type phase in space group *Pna*2$_1$. The KTP structure type (Figures 1 and 2) is described in detail elsewhere.[2,3,6,9]

The TiO$_6$ groups in K$_{0.55}$Li$_{0.45}$TiOPO$_4$ show their typical KTP-type distortion mode, in which the titanium atom makes a nominal displacement from the center of its octahedron along a Ti−O bond axis, which results in short (*d* < 1.8 Å) bonds formed between Ti(1) and

O(10) and Ti(2) and O(9). Each Ti center makes two Ti−O−Ti′ bonds [via O(9) and O(10)] and four Ti−O−P bonds. Bond valence sum (BVS) values[24] for the titanium atoms are consistent with the expected value of 4.00 for Ti^{IV}: BVS[Ti(1)] = 4.10, BVS[Ti(2)] = 4.10. The individual bond valences of the short "titanyl" Ti(1)=O-(10) and Ti(2)=O(9) bonds of ∼1.1 are approximately double the magnitudes of the other Ti−O bond valences. A simple measure of the degree of distortion, Δ_{Ti}, of the two distinct TiO$_6$ entities in K$_{0.55}$Li$_{0.45}$TiOPO$_4$ may be gained by taking the difference in length between the short Ti=O bond, and the longer Ti−O bond trans to this link. Values of Δ_{Ti} = 0.37 Å for Ti(1) and Δ_{Ti} = 0.25 Å for Ti(2) result for this bond-length differential [comparable values for KTiOPO$_4$: Δ_{Ti} = 0.44 Å for

(22) El Brahimi, M.; Durand, J. *Rev. Chim. Miner.* **1986**, *23*, 146.
(23) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. CRYSTALS User Guide; Chemical Crystallography Laboratory, Oxford University, UK, 1996.
(24) Brown, I. D.; Wu, K. K. *Acta Crystallogr.* **1975**, *B32*, 1957.
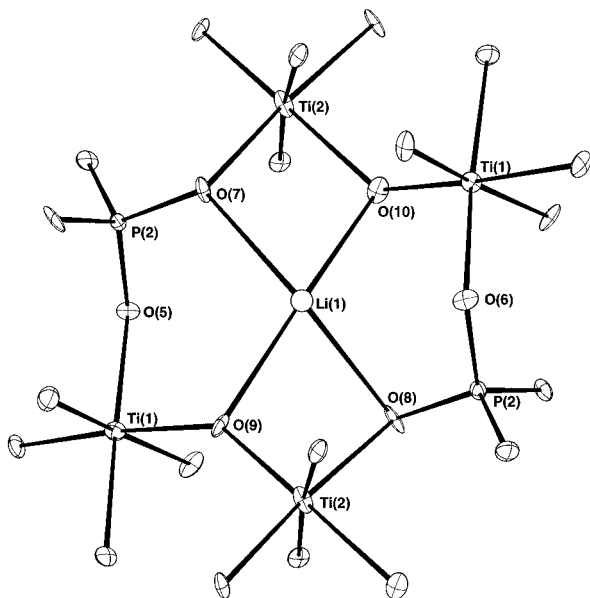
Figure 3. View of a fragment of the $K_{0.55}Li_{0.45}TiOPO_4$ structure showing the six-ring surrounding the approximately square-planar coordinated Li(1) species. View direction approximately down [100].

Ti(1), Δ_{Ti} = 0.36 Å for Ti(2)]. Both phosphate groups in $K_{0.55}Li_{0.45}TiOPO_4$ are typically regular (BVS[P(1)] = 5.07, d_{av}[P(1)−O] = 1.535 (3) Å; BVS[P(2)] = 5.12, d_{av}-[P(2)−O] = 1.532 (3) Å), and all eight P−O vertexes link to Ti atoms [θ_{av}(Ti−O−P) = 132.0°].

The main point of structural interest in $K_{0.55}Li_{0.45}$-$TiOPO_4$ concerns the guest potassium and lithium species. There are three K sites and two Li sites in $K_{0.55}$-$Li_{0.45}TiOPO_4$. All of these species are partially occupied (Table 2), compared to the situation of just two distinct, fully occupied cation sites in most other KTP-type materials.[2,6,9] The "split" K(11) and K(12) species have a nominal separation of 1.31 (1) Å and are roughly equidistant from the nominal K(1) position in other KTP-type structures. K(11) is 9-fold coordinated by O atoms in irregular geometry (d_{av}[K(11)−O] = 2.977 (4) Å, BVS[K(11)] = 0.97) and makes a bond to O(6), which is the only oxygen atom *not* involved in bonding to guest cations in most other KTP-type materials. K(12) is also nine-coordinate, with d_{av}[K(12)−O] = 2.955 (3) Å and BVS[K(12)] = 1.20. K(2) occupies approximately the same site as its equivalent atom in $KTiOPO_4$ and the Rb(2) species in $RbTiOPO_4$[9] and is irregular eight-coordinate with d_{av}[K(2)−O] = 2.961 (3) Å and BVS[K(2)] = 0.96.

The two lithium ions in $K_{0.55}Li_{0.45}TiOPO_4$, Li(1) and Li(2), occupy "six-ring" windows in the Ti/P/O framework (rings built up from six vertex-linked TiO_6 and PO_4 polyhedra, for a total of 12 atoms in each ring) and are both approximately square planar with respect to their four nearest-neighbor oxygen atoms. The other two Li−O contacts to the O atoms forming their six-ring enclosures are very long [d > 2.8 Å] and cannot be considered as significant chemical bonds. Both these lithium cation sites are quite distinct from the typical 8- and 9-fold coordinated [001] channel sites occupied by larger cations. Li(1) [fractional site occupation factor = 0.28 (4)] occupies a site in a pseudo-[100] channel (Figure 3) and bonds to the Ti−O−P-bridging oxygen atoms O(7) and O(8) and the titanyl-chain (Ti=O−Ti′)
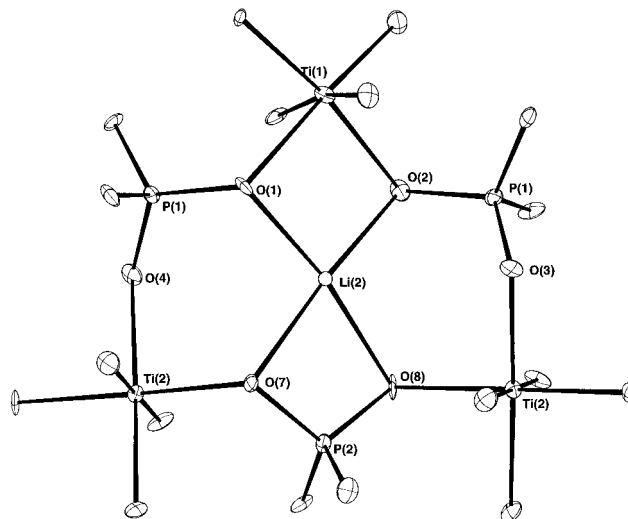

Figure 4. Detail of the $K_{0.55}Li_{0.45}TiOPO_4$ structure showing the six-ring surrounding the Li(2) species. View direction approximately down [010].

Table 5. Atomic Positional Parameters for $K_{0.54}Li_{0.46}TiOAsO_4$

atom	x	y	z	$U_{eq}{}^a$	occ^b
K(1)	0.3920(3)	0.8027(5)	0.3211(4)	0.0420	0.891(7)
K(2)	0.102(1)	0.673(3)	0.079(2)	0.0362	0.178(7)
LI(2)	0.602(2)	0.567(3)	0.037(2)	$0.015(8)^c$	0.68(4)
Ti(1)	0.3709(1)	0.5155(4)	0.0052(3)	0.0091	
Ti(2)	0.2432(2)	0.2816(3)	0.2518(3)	0.0102	
As(1)	0.4951(1)	0.3289(1)	0.2670(2)	0.0096	
As(2)	0.18287(6)	0.5144(2)	0.5145(2)	0.0103	
O(1)	0.4910(6)	0.499(1)	0.1537(7)	0.0132	
O(2)	0.5012(6)	0.457(1)	0.4024(6)	0.0098	
O(3)	0.3888(5)	0.182(1)	0.2785(8)	0.0048	
O(4)	0.5953(6)	0.172(1)	0.2562(8)	0.0152	
O(5)	0.1132(6)	0.312(1)	0.5554(8)	0.0118	
O(6)	0.1078(6)	0.714(1)	0.4868(8)	0.0114	
O(7)	0.2718(7)	0.557(2)	0.6301(7)	0.0095	
O(8)	0.2617(8)	0.470(2)	0.3954(7)	0.0146	
O(9)	0.2768(7)	0.465(2)	0.1443(7)	0.0094	
O(10)	0.2124(7)	0.058(2)	0.3888(7)	0.0119	

^{a} U_{eq} (Å²) = $[U_1 U_2 U_3]^{1/3}$. ^{b} Fractional site occupancy, if not unity. ^{c} U_{iso} (Å²).

oxygen atoms O(9) and O(10). The octahedral and tetrahedral nodal atoms (four Ti and two P) of the six-ring surrounding Li(1) are, in order, Ti(1), Ti(2), P(2), Ti(1), Ti(2), and P(2). The second lithium cation site in $K_{0.55}Li_{0.45}TiOPO_4$, Li(2), which is 0.40 (4) occupied on average, is found in a six-ring window site roughly perpendicular to the [010] direction (Figure 4). This lithium species bonds to four distinct Ti−O−P bridging oxygen atoms, and the nodal Ti and P atoms (three Ti and three P) *alternate*, as Ti(1), P(1), Ti(2), P(2), Ti(2), and P(1), in contrast to the situation noted above for Li(1).

Structure of $K_{0.54}Li_{0.46}TiOAsO_4$. Final atomic positional and thermal parameters for $K_{0.54}Li_{0.46}TiOAsO_4$ are listed in Table 5, with selected bond distance and angle data given in Tables 6 and 7, respectively. $K_{0.54}$-$Li_{0.46}TiOAsO_4$ crystallizes as a KTP-type structure, in the characteristic room-temperature $Pna2_1$ space group observed for this class of materials.

The TiO_6 groups in $K_{0.54}Li_{0.46}TiOAsO_4$ show their typical KTP-type distortion mode, with short titanyl bonds formed between Ti(1)=O(10) and Ti(2)=O(9). BVS values for the titanium(IV) atoms in $K_{0.54}Li_{0.46}TiOAsO_4$ are consistent with the expected value of 4.00: BVS-

Table 6. Bond Distances (Å) for $K_{0.54}Li_{0.46}TiOAsO_4$

K(1)−O(1)	2.986(9)	K(1)−O(2)	2.826(9)
K(1)−O(3)	2.543(9)	K(1)−O(5)	2.86(1)
K(1)−O(6)	3.330(9)	K(1)−O(8)	2.88(1)
K(1)−O(9)	3.29(1)	K(1)−O(10)	2.97(1)
K(2)−O(1)	2.72(2)	K(2)−O(2)	2.98(2)
K(2)−O(3)	3.24(2)	K(2)−O(4)	2.97(2)
K(2)−O(5)	2.81(2)	K(2)−O(7)	3.06(2)
K(2)−O(8)	3.30(2)	K(2)−O(9)	2.75(2)
K(2)−O(10)	3.26(2)		
Li(2)−O(1)	1.96(2)	Li(2)−O(2)	1.98(2)
Li(2)−O(7)	2.09(2)	Li(2)−O(8)	2.36(2)
Ti(1)−O(1)	2.239(8)	Ti(1)−O(2)	2.008(8)
Ti(1)−O(5)	2.040(9)	Ti(1)−O(6)	2.014(9)
Ti(1)−O(9)	1.962(8)	Ti(1)−O(10)	1.681(9)
Ti(2)−O(3)	2.026(8)	Ti(2)−O(4)	1.949(8)
Ti(2)−O(7)	1.988(9)	Ti(2)−O(8)	1.997(9)
Ti(2)−O(9)	1.732(9)	Ti(2)−O(10)	2.12(1)
As(1)−O(1)	1.657(9)	As(1)−O(2)	1.685(7)
As(1)−O(3)	1.692(7)	As(1)−O(4)	1.668(9)
As(2)−O(5)	1.670(8)	As(2)−O(6)	1.667(8)
As(2)−O(7)	1.722(8)	As(2)−O(8)	1.669(9)

Table 7. Selected Bond Angles (deg) for $K_{0.54}Li_{0.46}TiOAsO_4$

O(1)−Li(2)−O(2)	87.4(10)	O(1)−Li(2)−O(7)	100.5(10)
O(2)−Li(2)−O(7)	148.4(12)	O(1)−Li(2)−O(8)	160.8(12)
O(2)−Li(2)−O(8)	91.6(9)	O(7)−Li(2)−O(8)	71.0(7)
Ti(1)−O(1)−As(1)	125.5(4)	Ti(1)−O(2)−As(1)	124.2(5)
Ti(2)−O(3)−As(1)	124.8(5)	Ti(2)−O(4)−As(1)	132.7(6)
Ti(1)−O(5)−As(2)	129.7(5)	Ti(1)−O(6)−As(2)	132.9(5)
Ti(2)−O(7)−As(2)	122.1(6)	Ti(2)−O(8)−As(2)	129.0(6)
Ti(1)−O(9)−Ti(2)	141.8(6)	Ti(1)−O(10)−Ti(2)	139.1(6)

[Ti(1)] = 4.10, BVS[Ti(2)] = 4.10. Octahedral distortion values of $\Delta_{Ti} = 0.56$ Å for Ti(1) and $\Delta_{Ti} = 0.39$ Å for Ti(2) result for $K_{0.54}Li_{0.46}TiOAsO_4$ [comparable values for $KTiOAsO_4$: $\Delta_{Ti} = 0.44$ Å for Ti(1), $\Delta_{Ti} = 0.36$ Å for Ti(2)]. Both arsenate groups in $K_{0.54}Li_{0.46}TiOAsO_4$ are typically regular (BVS[As(1)] = 5.14, d_{av}[As(1)−O] = 1.676(4) Å; BVS[As(2)] = 5.03, d_{av}[As(2)−O] = 1.682(4) Å). The average Ti−O−As bond angle is 127.6°, some 4.4° less than the corresponding value for the Ti−O−P bonds in $K_{0.55}Li_{0.45}TiOPO_4$.

Despite their essentially identical atomic compositions in terms of degree of lithium substitution for potassium, the cation distribution in $K_{0.54}Li_{0.46}TiOAsO_4$ is distinctly different from the situation in $K_{0.55}Li_{0.45}TiOPO_4$. In $K_{0.54}Li_{0.46}TiOAsO_4$, one potassium site, K(1), is eight-coordinate to oxygen [$d_{av} = 2.961(4)$ Å, BVS = 0.99) with a site occupation factor of 0.891(7). This location corresponds to the split [K(11)/K(12)] potassium ion sites in $K_{0.55}Li_{0.45}TiOPO_4$ (combined K(11) + K(12) occupancy in $K_{0.55}Li_{0.45}TiOPO_4$ = 0.54). K(2) is nine-coordinate with $d_{av} = 3.010(7)$ Å, BVS[K(2)] = 0.88, and a greatly reduced site occupation factor of 0.18(1). A single lithium site, Li(2), was located in $K_{0.54}Li_{0.46}TiOAsO_4$ and has a site occupation factor of 0.68(4). This corresponds closely to the equivalent Li(2) site [site occupation 0.40-(4)] in $K_{0.55}Li_{0.45}TiOPO_4$ and forms bonds to the same four oxygen atoms (Table 6; compare Figure 4) in a six-ring window perpendicular to [010]. The Li(2) site in $K_{0.54}Li_{0.46}TiOAsO_4$ is roughly square planar with d_{av}-(Li−O) = 2.10(1) Å and BVS[Li(2)] = 0.76.

Discussion

The KTP-type phases $K_{0.55}Li_{0.45}TiOPO_4$ and $K_{0.54}Li_{0.46}$-TiOAsO_4 have been prepared by molten salt ion-

exchange reactions from their all-potassium precursors. Strong support for the partial replacement of potassium by lithium in both materials is provided by the elemental analysis data and the crystal structure results. The crystallographic data show that a simple two-site cation distribution as observed in most other KTP-type phases is inadequate to describe the situation in these phases. Rather, the K^+ and Li^+ species occupy distinct, partially occupied sites, which may be correlated with the ionic radii of the species involved: The lithium cations are far too small to directly substitute onto the [001]-channel potassium cation sites, and they occupy sites more suited to their small size, although an unusual square-planar coordination arises for both Li(1) and Li-(2) as a result of this process. A similar situation occurs in $K_{0.42}Na_{0.58}TiOPO_4$,[25] in which potassium and sodium cations occupy different, partially occupied sites in the [001] channels, which may be correlated with their different ionic radii. The different site preferences for lithium in $K_{0.55}Li_{0.45}TiOPO_4$ versus $K_{0.54}Li_{0.46}TiOAsO_4$ may reflect both "size-matching" effects for the Li^+ species (the ability of the Li^+ cation to attain reasonable Li−O bonds in the two distinct six-ring windows) and possibly differences in basicity of the oxygen species in these two compounds arising from the substitution of arsenic for phosphorus, making the Li(2) site more favorable in $K_{0.54}Li_{0.46}TiOAsO_4$.

The elemental analysis data and crystal structure results are in excellent agreement with respect to the fractional potassium contents of $K_{0.55}Li_{0.45}TiOPO_4$ (55% K from elemental analysis, with an estimated error of 2%; 57% K from crystal structure) and $K_{0.54}Li_{0.46}$-TiOAsO_4 (54% K from elemental analysis; 54% K from crystal structure). The lithium content, as determined from the diffraction data (34% for $K_{0.55}Li_{0.45}TiOPO_4$; 34% for $K_{0.54}Li_{0.46}TiOAsO_4$), is somewhat low for both phases. This may be due to uncertainties resulting from refining both site occupancies and thermal factors for the Li species. The resulting X-ray scattering power is low; it would be desirable to obtain neutron diffraction data to determine the lithium atom positions to a higher accuracy to overcome this ambiguity. Alternately, there may be additional lithium atom positions with low site occupancies that are not detectable in the X-ray diffraction experiments.

The crystal structure results show that the distorted TiO_6 groups characteristic of $KTiOPO_4$ and $KTiOAsO_4$ are maintained in the lithium-doped phases—indeed, on the basis of Δ_{Ti} values, the TiO_6 groups in $K_{0.54}Li_{0.46}$-TiOAsO_4 appear to be somewhat more distorted than the corresponding species in $KTiOAsO_4$. At first glance, this correlates well with the large PSHG responses for these phases. However, it is known that the presence of highly distorted TiO_6 moieties is not a *sufficient* criterion for a large PSHG response to be observed in all KTP-type materials, as illustrated in Figure 5.[8] Rather, we must consider the KTP structure as a whole and identify the effects of the various components of the structure on the observed physical properties in order to arrive at a complete structure−property model for this family of phases.

A chain of distorted TiO_6 groups in a KTP-type structure possesses a significantly delocalized conduc-

(25) Crennell, S. J.; Morris, R. E.; Cheetham, A. K.; Jarman, R. H. *Chem. Mater.* **1992**, *4*, 82.
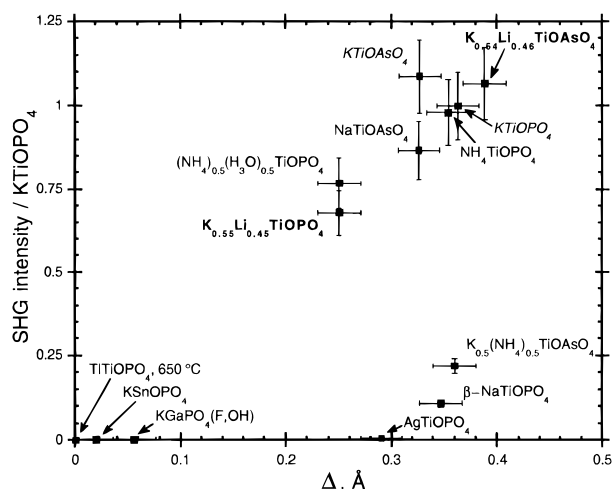
Figure 5. Plot of PSHG response versus the distortion of the $Ti(2)O_6$ species as quantified by the Δ_{Ti} parameter (see text) in various KTP-type materials.

Figure 6. Plot of PSHG response versus the $Ti(1)-O(9)-Ti(2)$ bond angle in $KTiOPO_4$, $KTiOAsO_4$, and various KTP-type materials prepared by ion-exchange.

tion band,[5,26,27] which leads to a high degree of microscopic polarizability of the Ti=O bonds and consequent substantial bulk optical response.[3] This extended band structure is disrupted by most atomic substitutions onto the octahedral titanium sites in the KTP-type structure,[2,26,28] which reduce the degree of distortion of the TiO_6 groups and usually result in a very substantial reduction in the observed SHG response.[2]

The degree to which charge-transfer character can be mixed into the valence orbitals depends not only on the degree of distortion of the TiO_6 groups but also on the nature of the *cation–framework interactions*, which must be determined experimentally by diffraction measurements. 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.[8] We further suggest 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 bonds to the other framework oxygen atoms [O(1) through O(8)] involved in Ti–O–P linkages. This line of reasoning may account for the fact that substitution of arsenic for phosphorus at the tetrahedral site in KTP materials tends to be *favorable* for a larger optical response because the more basic oxygen atoms associated with the AsO_4 moieties (as parts of Ti–O–As bonds; oxyen atoms O(1) to O(8) in our notation) tend to "draw away" cations from the titanyl oxygen atoms [O(9) and O(10)], forming the interoctahedral Ti–O–Ti bonds.[8]

Structurally, the effects of differences in affinities between cations and the titanyl chain are most visible in the $Ti(1)-O(9)-Ti(2)$ bond angle (Figure 6),[2] as was also observed by Crennell et al.[25] It is apparent from Figure 6 that both $K_{0.55}Li_{0.45}TiOPO_4$ and $K_{0.54}Li_{0.46}$-$TiOAsO_4$ follow this (nonlinear) trend. Interestingly, $K_{0.54}Li_{0.46}TiOAsO_4$ has the largest $Ti(1)-O(9)-Ti(2)$ bond angle of any KTP isostructure yet studied, consistent with its large SHG response.

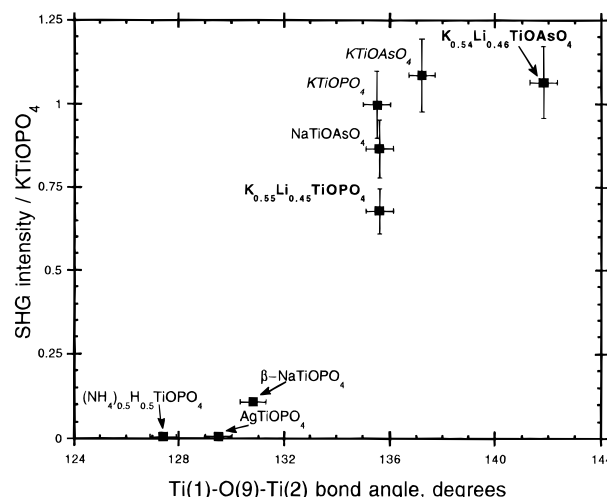However, the structural behavior[29] of $KTiOPO_4$ above the high-pressure first-order isosymmetric (no change of space group) phase transition at 5.8 GPa indicates that the relationship between the $Ti(1)-O(9)-Ti(2)$ bond angle and nonlinear optical response is not necessarily a straightforward one. Above the high-pressure phase transition, the $Ti(1)-O(10)-Ti(2)$ bond angle and SHG response show abrupt decreases (of ca. 6° and ~80%, respectively). Conversely, the $Ti(1)-O(9)-Ti(2)$ bond angle does not appear to show any significant discontinuity at the phase transition.

The relationship between cation distributions and optical response in the phases under study here are consistent with the above arguments: In $K_{0.55}Li_{0.45}$-$TiOPO_4$ there is only a weak interaction of one of the partially occupied lithium ions with O(9) and O(10), and in $K_{0.54}Li_{0.46}TiOAsO_4$, the single lithium species does not interact at all with either O(9) or O(10). Thus, the PSHG response of $K_{0.55}Li_{0.45}TiOPO_4$ is somewhat attenuated, compared to that of $KTiOPO_4$, whereas that of $K_{0.54}Li_{0.46}TiOAsO_4$ is essentially unaffected by lithium substitution, relative to that of $KTiOAsO_4$. These results suggest that partial Li exchange might be used to modify the refractive indices of $KTiOPO_4$ and $KTiOAsO_4$ without a serious loss in SHG efficiency in such practical applications as waveguiding.[3] Further work is required to study this effect.

Conclusions

The KTP-type phases $K_{0.55}Li_{0.45}TiOPO_4$ and $K_{0.54}Li_{0.46}$-$TiOAsO_4$ have been prepared by molten salt ion-exchange reactions from their all-potassium precursors. Contrary to initial expectations,[30] it is possible for lithium to substitute for potassium to a significant extent in these structures, despite the small ionic radius of the Li^+ species. However, *direct* reaction of Li/Ti/P/O precursors leads to different phases. Although the fractional K/Li compositions of $K_{0.55}Li_{0.45}TiOPO_4$ and

(26) Blasse, G.; Brixner, L. H. *Mater. Res. Bull.* **1989**, *24*, 1099.
(27) Jarman, R. H.; Munowitz, M.; Harrison, J. F. *J. Cryst. Growth* **1991**, *9*, 353.
(28) Harrison, W. T. A.; Phillips, M. L. F.; Stucky, G. D. *Chem. Mater.* **1995**, *7*, 1849.

(29) Allan, D. R.; Nelmes, R. J. *J. Phys.: Condens. Matter* **1996**, *8*, 2337.
(30) Loiacono, G. M.; Stoltzenberger, R. A.; Loiacono, C. N. *Appl. Phys. Lett.* **1994**, *64*, 16.
(31) Pearce, L. J.; Watkin, D. J.; Prout, C. K. CAMERON User Guide; Chemical Crystallography Laboratory, University of Oxford, UK, 1996.

$K_{0.54}Li_{0.46}TiOAsO_4$ are similar, they adopt different partial substitution schemes in terms of occupations of the distinct K/Li sites in the crystal structures. For both materials, lithium occupies roughly square-planar site(s) in a framework "6-ring" quite distinct from the typical 8- or 9-coordinate [001] channel cation sites found in most other KTP-type phases. PSHG data for $K_{0.55}Li_{0.45}TiOPO_4$ and $K_{0.54}Li_{0.46}TiOAsO_4$ show that lithium substitution for potassium in $KTiOPO_4$ and particularly in $KTiOAsO_4$ has only a small effect on nonlinear optical properties. This is consistent with the limited interactions that the lithium cations make with the titanyl−chain framework oxygen atoms O(9) and O(10) in these phases.

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