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$NaTiOPO_4$ and $KTiOPO_4$ at 110 K

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Abstract

The title compounds, sodium titanyl phosphate and potassium titanyl phosphate, are isostructural, belonging to a family of compounds with interesting non-linear optical properties. The effect of substitution of K by Na has been analysed by X-ray diffraction at 110 K. The substitution does not modify the geometry of the phosphate groups; however, the Ti—O coordination distances are changed, as well as the relative orientation of the Ti and P polyhedra.

Comment

This study is part of a series of determinations of crystal structures of non-linear optical materials belonging to the $KTiOPO_4$ (KTP) family (Marnier, 1986, 1988; Marnier, Boulanger & Menaert, 1989). The crystal structure of KTP at room temperature was first reported by Tordjmann, Masse & Guitel (1974). A large number of compounds isostructural with KTP, of general formula $(K,Rb,Tl,Na,Ag)TiO(P,As)O_4$, have been synthesized by hydrothermal or flux methods at high temperature, or by alkaline-ion diffusion (Stucky, Phillips & Gier, 1989). The great variety of accessible compounds offers an excellent opportunity to study the effects of each constituent from the fundamental (physical and structural properties) and the applied (*e.g.* non-linear optical properties) point of view. With this in mind, we have compared the crystal structure of $NaTiOPO_4$ (NaTP) at 110 K with that of KTP at the same temperature.

KTP has already been studied at this temperature (Belokoneva, Slovokhotova, Antipin, Tsirel'son & Struchkov, 1992) but our measurements were carried out to a higher spatial resolution [$(\sin\theta/\lambda)_{\max} = 1.14\ \text{Å}^{-1}$] which leads to more accurate anisotropic displacement parameters. An accurate structure of NaTP at 110 K in the space group $Pna2_1$ has not been published previously. The following compounds isostructural with KTP have been characterized: $Na_{0.5}K_{0.5}TiOPO_4$ (Crennell, Owen, Gray, Cheetham, Kaduk & Jarman, 1991), $Na_{0.95}K_{0.05}TiOPO_4$ (Phillips, Harrison, Stucky, McCarron, Calabrese & Gier, 1992), $Na_{0.58}K_{0.42}TiOPO_4$ and $Na_{0.57}K_{0.43}TiOPO_4$ (Crennell, Morris, Cheetham & Jarman, 1992). These compounds are derived from KTP by substitution of K^+ by Na^+. We have attempted a complete substitution of K^+ by Na^+ using the same technique as that used by Phillips, Harrison, Gier & Stucky (1989).

All atoms are on general positions in the unit cell, which contains eight formula units of $(Na,K)TiOPO_4$. There are two crystallographically independent Na, K, Ti and P positions coordinated by O atoms. A view of the KTP structure parallel to the *b* axis is shown in Fig. 1. Both structures can be described as a three-dimensional network formed from chains of alternating TiO_6 octahedra and PO_4 tetrahedra sharing corners. These chains result in the formation of wide helical channels along the *c* axis in which K or Na cations are located. The octahedra are connected by titanyl O atoms, OT1 and OT2, and form infinite zigzag TiO_6 chains along the [011] and $[0\bar{1}1]$ directions. The characteristic feature of these chains is the long–short alternation of the Ti—O bond lengths. X-ray diffraction analysis shows that NaTP presents an antiparallel slide of the —TiO_6—PO_4— chains along the *a* axis. Because of the rigidity of the TiO_6 and PO_4 groups, the substitution of K^+ by Na^+ in KTP results in distortion of the cavities formed by the O atoms around the Na cations. Unlike

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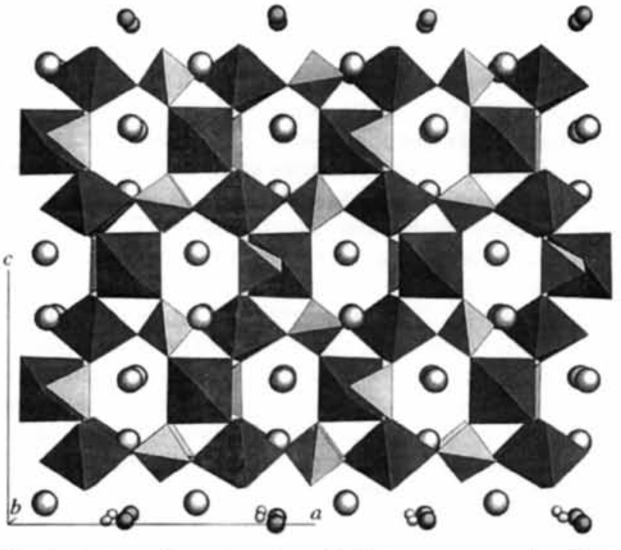

Fig. 1. A perspective view of the KTP structure along the [010] direction.

the K1 and K2 ions in KTP, which have coordination numbers of 8 and 9, respectively, Na1 and Na2 are only five and seven coordinate. Analysis of the cation–O atom distances shows that Na1—OT2 is shorter than K1—OT2 (by 0.21 Å) and that the titanyl O atom OT2 is only coordinated to Na1 in NaTP but is coordinated to K1 and K2 in KTP. The OT1 atom is coordinated in a bidentate manner to both cations in both structures.

The TiO_6 octahedra are characterized by a short bond (Ti1—OT2 and Ti2—OT1), a long bond and four intermediate bonds. Although they have a rigid nature, the short Ti—OT bonds are sensitive to the substitution of K^+ by Na^+ and the Ti1—OT2 bond contracts by 0.015 Å. Since this bond is 5.5° out of the (*ac*) plane, its contraction induces a decrease in the cell parameter *a*. On the other hand, the Ti2—OT1 bond shows a 0.01 Å increase, probably due to the Na2—OT1 distance [2.599 (1) *versus* 2.7632 (7) Å for K2—OT1 in KTP]. The result of this is a decrease in the Ti2—OT1—Ti1 angle [130.23 (4)° in NaTP *versus* 135.49 (4)° in KTP]. The O1 atom in the first neighbouring shell of the cation and belonging to the Ti1 octahedron is 2.365 (1) Å from Na2 in NaTP and 2.6799 (7) Å from K2 in KTP. Therefore, this O atom interacts more strongly with Na^+ than with K^+, explaining why the Ti1—O1 bond is longer in NaTP than in KTP [2.2287 (6) *versus* 2.1455 (6) Å, respectively]. The volume of the Ti2 octahedron is reduced by the substitution (10.07 Å^3 in KTP and 9.91 Å^3 in NaTP), whereas the Ti1 octahedron does not show any volume variation. The Ti1 and Ti2 distances to the octahedron centre-of-mass are 0.255 and 0.196 Å, respectively, in NaTP (0.218 and 0.169 Å in KTP). Because of the difference between the short and long bond lengths, the Ti1 octahedron is more distorted in NaTP than in KTP (0.52 and 0.42 Å, respectively); for the Ti2 octahedron, however, there is no difference in this respect between NaTP and KTP.

The PO_4 tetrahedra are less sensitive to the cation substitution, with a mean bond length of 1.54 (1) Å in both compounds.

Even though the X-ray data for KTP and NaTP were collected at the same temperature, the atomic displacement parameters are not identical. An average increase in the equivalent isotropic displacement parameters of 1.06 is observed, excluding the Na^+ ions, for which the increase is 1.56 compared to the K^+ ions in KTP. This result is not unexpected because the Na^+ ions are lighter; also, since the coordination numbers for Na1 and Na2 are 7 and 5, respectively, compared to 8 and 9, respectively, for K1 and K2, the Na^+ ions have more freedom to vibrate. The stronger vibration of the Na^+ ions affects the surrounding Ti and P atoms *via* the coordinating O atoms. This explains why the displacement parameters of the Ti and P atoms in NaTP are higher (by 21 and 15%, respectively) than their homologues in the KTP structure. The O atoms in general show a 4% mean increase in their displacement parameters, although there are some exceptions, notably for U^{33}(OT2), which is 15% lower in NaTP.

A comparative study of the structures of these compounds and their electron density determined at several temperatures will be presented in a subsequent publication.

Experimental

The KTP crystal was grown by a flux method at a temperature below the ferroelectric phase transition (Marnier, 1988). The sample used was ground into a sphere (diameter 0.26 mm). The NaTP crystal was obtained from $KTiOPO_4$ by sodium ion exchange: $NaNO_3$ and $KTiOPO_4$ in a molar ratio of 300:1 were placed in a crucible, heated to 623 K and kept for 3 d at this temperature. White and opaque crystals were obtained after dissolving the nitrate in boiling dilute nitric acid. Microprobe chemical analysis revealed that the K^+ ions were substituted to at least 99% by Na^+ ions.

NaTP

Crystal data

$NaTiOPO_4$
M_r = 181.86
Orthorhombic
$Pna2_1$
a = 12.555 (2) Å
b = 6.258 (2) Å
c = 10.554 (2) Å
V = 829.2 (3) Å^3
Z = 8
D_x = 2.915 Mg m^{-3}
D_m not measured

Ag $K\alpha$ radiation
λ = 0.56087 Å
Cell parameters from 25 reflections
θ = 9.5–25.1°
μ = 1.256 mm^{-1}
T = 110 (3) K
Prism
0.3 × 0.3 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

$R_{\rm int}$ = 0.0102
$\theta_{\max}$ = 38.1°

$\omega/2\theta$ scans
Absorption correction:
ABSORB (DeTitta, 1985)
$T_{\min} = 0.759$, $T_{\max} = 0.845$
10 684 measured reflections
4734 independent reflections
4330 reflections with
$I > 3\sigma(I)$

$h = -28 \rightarrow 28$
$k = -7 \rightarrow 14$
$l = -12 \rightarrow 21$
3 standard reflections
frequency: 120 min
intensity decay: 5%

Refinement

Refinement on F
$R = 0.013$
$wR = 0.012$
$S = 1.06$
3929 reflections
257 parameters
$w = 1/[\sigma^2(F^2) + (0.008F^2)^2]$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.200$ e Å^{-3}
$\Delta\rho_{\min} = -0.190$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for NaTP*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Ti1	0.37281 (1)	0.52051 (2)	0	0.00289 (2)
OT2	0.29095 (6)	0.5462 (1)	−0.12855 (7)	0.0052 (1)
Ti2	0.22859 (1)	0.28885 (2)	0.23696 (2)	0.00287 (2)
OT1	0.25563 (5)	0.4934 (1)	0.12769 (7)	0.0049 (1)
P1	0.48113 (1)	0.34054 (3)	0.26904 (2)	0.00312 (3)
O1	0.47256 (5)	0.5242 (1)	0.17468 (6)	0.00536 (9)
O2	0.49351 (5)	0.4322 (1)	0.40437 (6)	0.00532 (9)
O3	0.38023 (4)	0.20199 (9)	0.26988 (6)	0.00469 (8)
O4	0.57531 (4)	0.19186 (9)	0.23620 (7)	0.00499 (8)
P2	0.18359 (1)	0.52416 (3)	0.50642 (2)	0.00314 (3)
O5	0.11745 (5)	0.32975 (9)	0.54468 (6)	0.00525 (9)
O6	0.10849 (4)	0.71437 (9)	0.49746 (7)	0.00493 (8)
O7	0.27016 (5)	0.5546 (1)	0.60905 (6)	0.00536 (9)
O8	0.24163 (5)	0.4929 (1)	0.38020 (6)	0.00531 (9)
Na1	0.34398 (3)	0.79843 (6)	0.27765 (4)	0.01088 (7)
K1	0.382 (1)	0.806 (1)	0.324 (1)	0.01088 (7)
Na2	0.09995 (3)	0.75271 (7)	0.07597 (5)	0.01325 (8)

Table 2. *Selected bond lengths (Å) for NaTP*

P1—O1	1.5244 (6)	Ti2—O3	2.0101 (5)
P1—O2	1.5469 (6)	Ti2—O4$^{\rm v}$	1.9283 (6)
P1—O3	1.5352 (6)	Ti2—O7$^{\rm iii}$	1.9931 (6)
P1—O4	1.5440 (6)	Ti2—O8	1.9857 (6)
P2—O5	1.5274 (6)	Na1—OT2$^{\rm vi}$	2.501 (1)
P2—O6	1.5215 (6)	Na1—O5$^{\rm ii}$	2.514 (1)
P2—O7	1.5461 (6)	Na1—O8	2.545 (1)
P2—O8	1.5308 (6)	Na1—O3$^{\rm vii}$	2.568 (1)
Ti1—OT2	1.7096 (7)	Na1—O1	2.595 (1)
Ti1—OT1	2.0024 (7)	Na1—OT1	2.717 (1)
Ti1—O1	2.2287 (6)	Na1—O7$^{\rm ii}$	2.791 (1)
Ti1—O2$^{\rm i}$	1.9806 (6)	Na2—O1$^{\rm viii}$	2.365 (1)
Ti1—O5$^{\rm ii}$	1.9956 (6)	Na2—O2$^{\rm ii}$	2.433 (1)
Ti1—O6$^{\rm iii}$	1.9304 (5)	Na2—O7$^{\rm ii}$	2.520 (1)
Ti2—OT2$^{\rm iv}$	2.0930 (7)	Na2—OT1	2.599 (1)
Ti2—OT1	1.7559 (7)	Na2—O5$^{\rm ix}$	2.797 (1)

Symmetry codes: (i) $1 - x, 1 - y, z - \frac{1}{2}$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (vii) $x, 1 + y, z$; (viii) $x - \frac{1}{2}, \frac{3}{2} - y, z$; (ix) $-x, 1 - y, z - \frac{1}{2}$.

KTP

Crystal data

$KTiOPO_4$
$M_r = 197.97$
Orthorhombic
$Pna2_1$
$a = 12.7982$ (9) Å
$b = 6.3937$ (7) Å
$c = 10.5853$ (9) Å
$V = 866.2$ (1) Å^3
$Z = 8$
$D_x = 3.037$ Mg m^{-3}
D_m not measured

Ag $K\alpha$ radiation
$\lambda = 0.56087$ Å
Cell parameters from 23 reflections
$\theta = 19$–$33°$
$\mu = 1.65$ mm^{-1}
$T = 110$ (3) K
Sphere
0.13 mm (radius)
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: spherical
$T_{\min} = 0.732$, $T_{\max} = 0.732$
18 156 measured reflections
7056 independent reflections
6402 reflections with
$I > 3\sigma(I)$

$R_{\rm int} = 0.0123$
$\theta_{\max} = 40°$
$h = -29 \rightarrow 29$
$k = -7 \rightarrow 14$
$l = -12 \rightarrow 24$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F
$R = 0.012$
$wR = 0.012$
$S = 1.00$
4762 reflections
305 parameters
$w = 1/[\sigma^2(F^2) + (0.008F^2)^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.170$ e Å^{-3}
$\Delta\rho_{\min} = -0.150$ e Å^{-3}

Extinction correction: isotropic type I Lorentzian (Becker & Coppens, 1974)
Extinction coefficient: $9.93\,(11) \times 10^2$
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for KTP*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Ti1	0.37309 (1)	0.49989 (2)	0	0.00239 (1)
OT2	0.27624 (5)	0.5413 (1)	−0.11043 (7)	0.00514 (9)
Ti2	0.24641 (1)	0.26951 (2)	0.25125 (2)	0.00234 (1)
OT1	0.27523 (5)	0.4673 (1)	0.14306 (6)	0.00465 (9)
P1	0.49787 (2)	0.33640 (3)	0.25999 (3)	0.00266 (3)
O1	0.48577 (5)	0.4873 (1)	0.14987 (6)	0.00503 (9)
O2	0.50947 (5)	0.4654 (1)	0.38309 (6)	0.00494 (9)
O3	0.40007 (5)	0.1990 (1)	0.27899 (7)	0.00462 (8)
O4	0.59353 (5)	0.1931 (1)	0.24065 (7)	0.00494 (9)
P2	0.18102 (2)	0.50196 (4)	0.51245 (2)	0.00281 (3)
O5	0.11228 (5)	0.3107 (1)	0.54068 (6)	0.00462 (9)
O6	0.11166 (5)	0.6918 (1)	0.48717 (7)	0.00523 (9)
O7	0.25303 (5)	0.5385 (1)	0.62785 (6)	0.00503 (9)
O8	0.25325 (6)	0.4610 (1)	0.39909 (6)	0.00510 (9)
K1	0.37683 (2)	0.77983 (3)	0.30901 (3)	0.00743 (4)
K2	0.10553 (2)	0.69986 (3)	0.06362 (3)	0.00789 (4)

Table 4. *Selected bond lengths (Å) for KTP*

P1—O1	1.5212 (7)	Ti2—O8	1.9889 (6)
P1—O2	1.5492 (7)	K1—OT2$^{\rm vi}$	2.7129 (7)
P1—O3	1.5423 (6)	K1—O3$^{\rm vii}$	2.7154 (7)
P1—O4	1.5428 (6)	K1—O2	2.7456 (7)
P2—O5	1.5356 (7)	K1—O8	2.7507 (7)
P2—O6	1.5276 (7)	K1—O5$^{\rm ii}$	2.8506 (7)
P2—O7	1.5479 (7)	K1—O1	2.8773 (7)
P2—O8	1.5372 (7)	K1—OT1	2.9613 (7)

Ti1—OT2	1.7242 (7)	K1—O7^{ii}	3.0289 (8)
Ti1—OT1	1.9761 (6)	K2—O1^{viii}	2.6799 (7)
Ti1—O1	2.1455 (6)	K2—OT1	2.7632 (7)
Ti1—O2^{i}	1.9596 (6)	K2—O5^{ix}	2.7990 (7)
Ti1—O5^{ii}	2.0422 (6)	K2—O7^{ii}	2.9030 (7)
Ti1—O6^{iii}	1.9838 (6)	K2—O2^{ii}	2.9496 (7)
Ti2—OT2^{iv}	2.0872 (7)	K2—O8^{ii}	3.0146 (8)
Ti2—OT1	1.7455 (6)	K2—O3^{ii}	3.0137 (8)
Ti2—O3	2.0387 (6)	K2—OT2	3.0325 (8)
Ti2—O4^{v}	1.9744 (6)	K2—O4^{v}	3.1381 (7)
Ti2—O7^{iii}	1.9717 (7)		

Symmetry codes: (i) $1-x, 1-y, z-\frac{1}{2}$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$; (v) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (vii) $x, 1+y, z$; (viii) $x-\frac{1}{2}, \frac{3}{2}-y, z$; (ix) $-x, 1-y, z-\frac{1}{2}$.

The intensities were corrected for Lorentz and polarization effects using the program *DREAR* (Blessing, 1987). The structure refinement was carried out using the multipole model least-squares program *MOLLY* (Hansen & Coppens, 1978), which employs generalized atomic scattering factors that are the Fourier transforms of pseudoatom electron density parameterized to model chemical bonding. Following the structure refinement of NaTP, residual electron-density maps indicated that the Na substitution on site 1 was not quite complete. Refining the K content for this site led to the chemical formula $Na_{1-x}K_xTiOPO_4$ with $x = 0.008 (4)$.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *DREAR* (Blessing, 1987); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *MOLLY* (Hansen & Coppens, 1978); molecular graphics: *CRIC* (Boudias & Monceau, 1994).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DU1171). Services for accessing these data are described at the back of the journal.

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Caesium Pentafluoroterbate, $CsTbF_5$

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Abstract

The structure of caesium terbium(IV) pentafluoride has been determined by single-crystal X-ray methods. $CsTbF_5$ has a layered structure. The layers, which stack along the [100] direction, are built from edge- and corner-sharing $(TbF_8)^{4-}$ dodecahedra and are held together by 11-coordinate Cs^+ ions. $CsTbF_5$ is closely related to $TlZrF_5$.

Comment

Up to now many fluorinated compounds containing tetravalent terbium have been mentioned in the literature (Hoppe, 1985, and references therein), but because the thermal instability of TbF_4 (Gibson & Haire, 1988) generates some difficulties in growing crystals, all structural studies have been carried out on polycrystalline samples. Recently, we succeeded in growing single crystals of tetravalent terbium complex fluorides. The refinements of the structures of these compounds have been performed with the aim of forming a database of information on tetravalent terbium.

$CsTbF_5$ was first mentioned as an unknown structure by Hoppe & Rödder (1961). The determination of the crystal structure reported here shows that $CsTbF_5$ and $TlZrF_5$ (Avignant, Mansouri, Chevalier & Cousseins, 1981) are closely related. The Tb^{4+} ion is surrounded by eight fluorine ions in the form of a dodecahedron with an average Tb—F distance of 2.168 (4) Å. The dodecahedra share one F(3)—F(3) edge (the shortest F—F distance in the structure) with an adjacent dodecahedron and four corners [F(1) twice and F(2) twice] with four additional dodecahedra to form infinite $(TbF_5)^-$ layers parallel to the (100) plane. The remaining F(4) corners of each polyhedron, which have the shortest Tb—F distances, are unshared and point out on both sides of the layer. The layers are held together by caesium ions, each of which is surrounded by 11 fluorine ions. The Cs—F distances in the CsF_{11} polyhedra range from 2.924 (4) to 3.419 (3) Å. Successive $(TbF_5)^-$ layers are shifted relative to each other by **b**/2.

It is worth noting that a pseudo quaternary symmetry axis is apparent in the $(TbF_5)^-$ isolated layer (in agreement with the *b* and *c* parameters being equal to within less than one s.u.). This pseudo quaternary axis

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