

Such a distortion of the anion would be induced by a slight shift of the Eu1 (and Eu1¹) position, which is associated with the displacement of several aqua ligands, especially atoms O52 and O54, which have large U_{iso} values of 0.21 (2) and 0.24 (2) Å², respectively. The coordination of a large number (eight) of aqua ligands and one O atom from the half-anion to an Eu atom explains the shift of the Eu atom due to the disordered structure of aqua ligands, which leads to the displacement of W, Ti and Ge atoms in the half-anion. The rather large residual maximum and minimum Fourier peaks (4.12 and -4.89 e Å⁻³, respectively) are located around the W9 atom at short distances of 0.48 and 1.05 Å, respectively. This is due to the large displacement of the W9 atom compared with the other atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992b). Program(s) used to solve structure: *SIR88* (Burla *et al.*, 1989). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*.

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas, 'New Development of Rare Earth Complexes', No. 06241104, from the Ministry of Education, Science, Sport and Culture.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1005). Services for accessing these data are described at the back of the journal.

References

- Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.
- Gerkin, R. E. & Reppart, W. J. (1984). *Acta Cryst.* **C40**, 781–786.
- Horrocks, W. D. & Sudnick, D. R. Jr (1981). *Acc. Chem. Res.* **14**, 384–392.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1992a). *MSC/AFC Diffractometer Control Software*. Version 4.3.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1992b). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Naruke, H., Ozeki, T. & Yamase, T. (1991). *Acta Cryst.* **C47**, 489–492.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Ozeki, T., Yamase, T., Naruke, H. & Sasaki, Y. (1994). *Inorg. Chem.* **33**, 409–410.
- Sugeta, M. & Yamase, T. (1993). *Bull. Chem. Soc. Jpn.* **66**, 444–449.
- Yamase, T. (1994). *Polyoxometalates: From Platonic Solids to Antiviral Activity*, edited by M. T. Pope & A. Müller, pp. 337–358. Dordrecht: Kluwer Academic Publishers.
- Yamase, T. & Naruke, H. (1991). *J. Chem. Soc. Dalton Trans.* pp. 285–292.
- Yamase, T., Naruke, H. & Sasaki, Y. (1990). *J. Chem. Soc. Dalton Trans.* pp. 1687–1696.
- Yamase, T., Ozeki, T., Sakamoto, H., Nishiyama, S. & Yamamoto, A. (1993). *Bull. Chem. Soc. Jpn.* **66**, 103–108.
- Acta Cryst.* (1997). **C53**, 1170–1173

A Caesium Zinc Phosphate Constructed from Ladder-Like Four-Ring Chains

PINGYUN FENG, XIANHUI BU AND GALEN D. STUCKY

Chemistry Department, University of California, Santa Barbara, CA 93106, USA. E-mail: pingyun@sbxray.ucsb.edu

(Received 2 January 1997; accepted 20 March 1997)

Abstract

The synthesis, thermal properties and crystal structure of caesium trizinc bis[hydrogenphosphate(2-)] phosphate, Cs[Zn₃(HPO₄)₂(PO₄)], are described. This new caesium zinc phosphate has a three-dimensional framework structure containing one-dimensional channels.

Comment

Divalent metal phosphates are of interest for a number of reasons, one of which is that they can form framework structures which are zeolite-like (Gier & Stucky, 1991). Zeolites are aluminosilicates containing cages and channels, and can be used for a variety of commercial applications such as heterogeneous catalysis, ion exchange and adsorption (Breck, 1974). In our search for novel framework structures based on divalent metal phosphates and arsenates (Feng, Bu & Stucky, 1995, 1997a,b; Bu, Feng & Stucky, 1996; Bu, Gier & Stucky, 1996; Feng, Bu, Tolbert & Stucky, 1997), we discovered a new caesium zinc phosphate. The synthesis, crystal structure and thermal properties of this material are reported here.

The asymmetric unit is Cs[Zn₃(HPO₄)₂(PO₄)]. All three unique Zn sites have tetrahedral coordination geometry. Of the 12 O atoms, two (O11 and O12) are terminating hydroxyl groups on P2 and P3, and two (O2 and O3) are trigonally coordinated (excluding the possible coordination to the extra framework Cs atoms) between two Zn cations and one P cation. The other eight O atoms are bicoordinated between one Zn cation and one P cation. The presence of trigonally coordinated O atoms and the associated three-membered rings (six-membered rings if O atoms are included) involving two Zn atoms and one P atom usually leads to a dense framework and is a feature that distinguishes this salt from zeolite-like open-framework zincophosphates.

The framework contains channels along the crystallographic *a* axis (Fig. 1). The rectangularly shaped window of each channel is elongated along the unit-cell *c* axis and the frame of the window opening contains as many as 16 tetrahedral atoms. The three-dimensional framework of this compound comprises structural units which are commonly used to build zeolite structures:

ladder-like four-ring chains and zigzag single chains of alternating Zn and P tetrahedra. There are two crystallographically unique ladder-like four-ring chains and only one unique single chain, all of which propagate along the crystallographic *a* axis. One four-ring chain is built from Zn2 and P3 tetrahedra and the O atoms involved are all bicoordinated (Fig. 2). Thus, this part of the structure is relatively open (Fig. 1). The other four-ring chain is built from Zn3 and P1 tetrahedra and trigonally coordinated O atoms are involved (Fig. 2). This part of the structure is of somewhat higher density (Fig. 1).

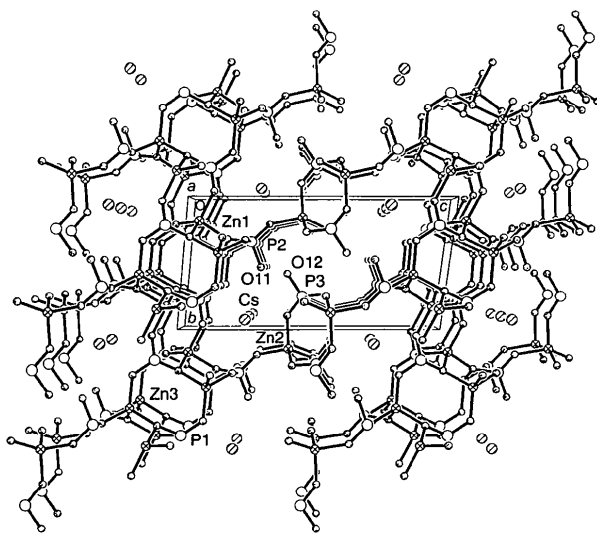


Fig. 1. The framework structure viewed along the channel direction (the crystallographic *a* axis). The three different chains are indicated through the labeling of the tetrahedral atoms. The hydroxyl groups on P2 and P3 protrude towards the center of the channels. The unconnected circles in the channels are Cs cations. Large open circles represent P cations and cross-hatched circles represent Zn cations.

The three-dimensional framework can thus be considered as a parallel arrangement of ladder-like four-ring chains crosslinked by the single zigzag chain (Fig. 2) of Zn1 and P2 tetrahedra propagating along the same direction. Each single chain bridges a total of three four-ring chains. This includes one Zn2–P3 chain connected through the bicoordinated O8 atom between P2 and Zn2 and one Zn3–P1 chain connected through the bicoordinated O1 atom between Zn1 and P1. The third four-ring chain (another Zn3–P1 chain) connects to the single chain through both O2 and O3, which are trigonally coordinated.

The four-ring chain of various configurations is one of the most important structural features of many zeolite frameworks. A ladder-like four-ring chain similar to the one seen here has been found in a number of zeolite structures. For example, in the zeolite ABW and

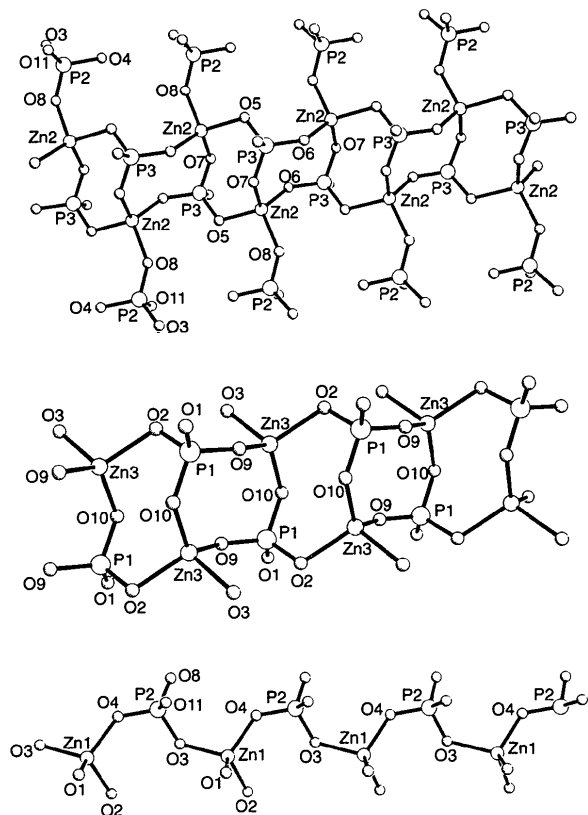


Fig. 2. Two unique ladder-like four-ring chains and one zigzag chain. Both four-ring chains have inversion symmetry.

cancrinite frameworks, the ladder-like four-ring chains are the only structural building blocks. A difference in the orientations of the ladder-like four-ring chains leads to different framework topologies for ABW and cancrinite, even though in both cases all four-ring chains propagate along the channel directions with the largest pore opening (Meier, Olson & Baerlocher, 1996).

In a tetrahedral framework with two different tetrahedral centers, the simplest way to achieve an equal number of the two different tetrahedral centers is to form a three-dimensional network with strictly alternating tetrahedra. Such is not the case in the title compound because it contains not only Zn–O–Zn linkages, but also terminating OH[−] groups. The presence of Zn–O–Zn linkages tends to increase the Zn/P ratio whereas the terminating OH groups on the P sites tend to decrease the Zn/P ratio. These two opposing effects are balanced and result in a framework containing the same number of Zn and P tetrahedral sites. The Zn/P ratio of 1:1 can be easily visualized if we consider the structural building units: both four-ring chains and single chains consist of strictly alternating Zn and P tetrahedra with a Zn/P ratio of 1:1.

Even though there are at least seven different sodium zinc phosphates (Harrison *et al.*, 1996),

there are relatively few caesium-containing zinc phosphates. Two other caesium zinc phosphates are known. Cs[H(ZnPO₄)₂] has a layered structure (Nenoff, Harrison, Gier, Calabrese & Stucky, 1993) while the other, Cs(ZnPO₄), has a zeolite ABW-type three-dimensional framework (Blum, Durif & Averbuch-Pouchot, 1986). There are also some other compounds which have the same stoichiometry as the title compound, but are structurally unrelated. A typical example is Na[Co₃(PO₄)(HPO₄)₂] which contains edge-sharing Co octahedra (Lii & Shih, 1994).

Experimental

Zn(NO₃)₂·6H₂O (1.24 g) was mixed with 11.18 g of distilled water. With stirring, 1.22 g of 85% H₃PO₄ was slowly added. The pH of the solution was adjusted using 50% CsOH solution to 2.47 as measured using a Ag/AgCl electrode pH meter. A total of 2.74 g of 50% CsOH solution was added. The mixture was heated at 453 K for 6 d in a Teflon-coated steel autoclave. The product was recovered by filtration and washed with deionized water. Translucent clear needle-like crystals, as large as several millimeters in one dimension, were obtained.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of 49.9 mg Cs[Zn₃(HPO₄)₂(PO₄)] were performed using a Netzsch Simultaneous Thermal Analysis (STA) 409 system in static air with a heating rate of 5 K min⁻¹ from 303 to 1273 K. The TGA diagram was simple and showed only one sharp peak for a weight loss of 2.6% (calculated 2.9% for the loss of one water molecule) between 643 and 703 K accompanied by an endothermic peak. There are two additional significant events, both endothermic, occurring at 1023 and 1093 K, the nature of which needs further investigation.

Crystal data

Cs[Zn ₃ (HPO ₄) ₂ (PO ₄)]	Mo K α radiation
$M_r = 615.95$	$\lambda = 0.71073 \text{ \AA}$
Triclinic	Cell parameters from 4352 reflections
$P\bar{1}$	$\theta = 1.38\text{--}28.28^\circ$
$a = 5.1636(1) \text{ \AA}$	$\mu = 9.715 \text{ mm}^{-1}$
$b = 8.0324(1) \text{ \AA}$	$T = 293(2) \text{ K}$
$c = 14.8009(2) \text{ \AA}$	Thin needle
$\alpha = 95.796(1)^\circ$	$0.470 \times 0.050 \times 0.017 \text{ mm}$
$\beta = 90.315(1)^\circ$	Colorless
$\gamma = 108.078(1)^\circ$	
$V = 580.16(2) \text{ \AA}^3$	
$Z = 2$	
$D_x = 3.526 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Siemens SMART CCD diffractometer	6023 measured reflections
ω scan	2774 independent reflections
Absorption correction: empirical, fitted by spherical harmonic functions (Blessing, 1995; Sheldrick, 1996)	$R_{\text{int}} = 0.0514$
$T_{\text{min}} = 0.34, T_{\text{max}} = 0.88$	$\theta_{\text{max}} = 28.28^\circ$
	$h = -6 \rightarrow 6$
	$k = -10 \rightarrow 10$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.110$
 $S = 0.988$
 2774 reflections
 173 parameters
 H atoms not located
 $w = 1/[\sigma^2(F_o^2) + (0.0549P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 1.61 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -2.14 \text{ e \AA}^{-3}$
 Extinction correction:
SHELXTL (Siemens, 1995a)
 Extinction coefficient:
 0.0330 (17)
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected bond lengths (\AA)

Cs1—O11	3.105 (5)	Zn2—O7	1.962 (5)
Cs1—O8 ⁱ	3.130 (5)	Zn2—O5	1.962 (5)
Cs1—O10 ⁱⁱ	3.192 (5)	Zn3—O9	1.897 (5)
Cs1—O7 ⁱⁱⁱ	3.200 (5)	Zn3—O10	1.924 (5)
Cs1—O9 ⁱⁱⁱⁱ	3.260 (5)	Zn3—O2	2.006 (4)
Cs1—O4 ^v	3.327 (5)	Zn3—O3 ^{vi}	2.027 (4)
Cs1—O1 ^{vii}	3.402 (5)	P1—O9 ^{viii}	1.516 (5)
Cs1—O6 ^{viii}	3.623 (5)	P1—O1	1.528 (5)
Cs1—O1	3.652 (5)	P1—O10 ^{ix}	1.540 (5)
Cs1—O8 ^x	3.708 (5)	P1—O2 ^x	1.572 (4)
Cs1—O7 ^{xi}	3.742 (5)	P2—O8	1.512 (5)
Cs1—O5 ^{xii}	3.764 (5)	P2—O4	1.512 (4)
Zn1—O1	1.896 (4)	P2—O3 ^{xiii}	1.561 (5)
Zn1—O4	1.931 (5)	P2—O11	1.579 (5)
Zn1—O3	1.977 (4)	P3—O6 ^{xiiii}	1.507 (5)
Zn1—O2	1.986 (4)	P3—O7	1.512 (5)
Zn2—O6	1.918 (5)	P3—O5 ^{xv}	1.534 (5)
Zn2—O8	1.943 (5)	P3—O12	1.600 (5)

Symmetry codes: (i) $1+x, 1+y, z$; (ii) $x, 1+y, z$; (iii) $-x, 1-y, -z$; (iv) $x-1, y, z$; (v) $-x, 1-y, 1-z$; (vi) $1-x, 1-y, -z$; (vii) $1-x, -y, 1-z$; (viii) $-x, -y, 1-z$.

The largest positive residual peak in the difference electron density is 0.99 \AA from Cs1 and the largest negative residual peak is 0.81 \AA from Cs1. The data collection nominally covered over a full sphere of reciprocal space by a combination of four sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω . The crystal-to-detector distance was 4.95 cm . Coverage of the data set is over 89% complete to at least 25° in θ .

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINTE* (Siemens, 1995b). Data reduction: *SAINTE*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1995a). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

This research was supported in part by the National Science Foundation under grant DMR 95-20971.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1177). Services for accessing these data are described at the back of the journal.

References

- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Blum, D., Durif, A. & Averbuch-Pouchot, M. T. (1986). *Ferroelectrics*, **69**, 283–292.
 Breck, D. W. (1974). In *Zeolite Molecular Sieves*. New York: John Wiley & Sons.
 Bu, X. H., Feng, P. Y. & Stucky, G. D. (1996). *J. Solid State Chem.* **125**, 243–248.

- Bu, X. H., Gier, T. E. & Stucky, G. D. (1996). *Acta Cryst.* **C52**, 1601–1603.
- Feng, P. Y., Bu, X. H. & Stucky, G. D. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1745–1747.
- Feng, P. Y., Bu, X. H. & Stucky, G. D. (1997a). *J. Solid State Chem.* **129**, 328–333.
- Feng, P. Y., Bu, X. H. & Stucky, G. D. (1997b). *J. Solid State Chem.* In the press.
- Feng, P. Y., Bu, X. H., Tolbert, S. H. & Stucky, G. D. (1997). *J. Am. Chem. Soc.* **119**, 2497–2504.
- Gier, T. E. & Stucky, G. D. (1991). *Nature*, **349**, 508–510.
- Harrison, W. T. A., Broach, R. W., Bedard, R. A., Gier, T. E., Bu, X. H. & Stucky, G. D. (1996). *Chem. Mater.* **8**, 691–700.
- Lii, K. H. & Shih, P. F. (1994). *Inorg. Chem.* **33**, 3028–3031.
- Meier, W. M., Olson, D. H. & Baerlocher, Ch. (1996). In *Atlas of Zeolite Structure Types*. New York: Elsevier.
- Nenoff, T. M., Harrison, W. T. A., Gier, T. E., Calabrese, J. C. & Stucky, G. D. (1993). *J. Solid State Chem.* **107**, 285–295.
- Sheldrick, G. M. (1996). *SADABS User Guide*. University of Göttingen, Germany.
- Siemens (1995a). *SHELXTL*. Silicon Graphics Version. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995b). *ASTRO and SAINT. Data Collection and Processing Software for the SMART System*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART Reference Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1997). **C53**, 1173–1176

NaTiOPO₄ and KTiOPO₄ at 110 K

SLIMANE DAHAOUI,^a NIELS K. HANSEN^a AND BERTRAND MENAERT^b

^aLaboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques (LCM3B), URA CNRS no 809, Université Henri Poincaré, Nancy 1, Faculté des Sciences, BP 239, 54506 Vandoeuvre lès Nancy CEDEX, France, and ^bLaboratoire de Physique du Solide, Faculté des Sciences Gabriel, Université de Bourgogne, 6 Boulevard Gabriel, 21000 Dijon, France. E-mail: hansen@lcm3b.u-nancy.fr

(Received 11 October 1996; accepted 17 March 1997)

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 KTiOPO₄ (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)O₄, 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 NaTiOPO₄ (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 [$(\sin\theta/\lambda)_{\max} = 1.14 \text{ \AA}^{-1}$] which leads to more accurate anisotropic displacement parameters. An accurate structure of NaTP at 110 K in the space group *Pna*2₁ has not been published previously. The following compounds isostructural with KTP have been characterized: Na_{0.5}K_{0.5}TiOPO₄ (Crennell, Owen, Gray, Cheetham, Kaduk & Jarman, 1991), Na_{0.95}K_{0.05}TiOPO₄ (Phillips, Harrison, Stucky, McCarron, Calabrese & Gier, 1992), Na_{0.58}K_{0.42}TiOPO₄ and Na_{0.57}K_{0.43}TiOPO₄ (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)TiOPO₄. 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 TiO₆ octahedra and PO₄ 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 TiO₆ 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 —TiO₆—PO₄— chains along the *a* axis. Because of the rigidity of the TiO₆ and PO₄ 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