

## The complex phosphate $K_{0.92}In_{0.46}Nb_{0.54}OPO_4$ : a new representative of the $KTiOPO_4$ family

Artem A. Babaryk,<sup>a\*</sup> Igor V. Zatovsky,<sup>a</sup> Vyacheslav N. Baumer,<sup>b</sup> Nikolay S. Slobodyanik<sup>a</sup> and Konstantin V. Domasevitch<sup>a</sup>

<sup>a</sup>Department of Inorganic Chemistry, Taras Shevchenko National University, 64 Volodymyrska Street, 01033 Kyiv, Ukraine, and <sup>b</sup>STC Institute for Single Crystals, NAS of Ukraine, 60 Lenin Avenue, 61001 Kharkiv, Ukraine  
Correspondence e-mail: babaryk@bigmir.net

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Aliovalent  $K_{0.92}In_{0.46}Nb_{0.54}OPO_4$  (KINP, potassium indium niobium oxide phosphate) features a chain structure involving corner-sharing  $[MO_6]$  octahedra ( $M = In/Nb$ ), which allows this compound to be recognized as a member of the  $KTiOPO_4$  (KTP) family. However, its crystallization in the polar space group  $P4_1$  belonging to the  $4/m$  Laue group generates its own subclass of KTP-related compounds. The unit cell contains 18 symmetry-independent atoms occupying general positions. The *cis-cis* principle of octahedral arrangement is observed for each of the separate  $[MO_6]_{\infty}$  chains. The observed variations in the *cis-cis* linkage are critically important for nonlinear optical properties and distinguish the present compound from other KTP-related structures. The anionic framework adopts one-dimensional tunnels running orthogonal to the *ab* plane. The  $K^+$  ions are arranged in the  $[001]$  direction at a distance of  $\frac{1}{4}c$ . Merohedral twinning was detected during the structure refinement.

### Comment

Compounds related to the  $KTiOPO_4$  (KTP) structure have received steady attention since its outstanding nonlinear optical properties were reported (Zumsteg *et al.*, 1976). Its metal–oxygen chain structure is constructed on a special *cis-trans* principle which, in combination with a strong distortion of the  $[TiO_6]$  octahedra, provokes a significant nonlinear effect (Bierlein, 1989). Previously, it was shown that  $KTiOPO_4$  can serve as a model for the exploration of structure–property relationships by means of aliovalent substitution of K, Ti or P atoms (Stucky *et al.*, 1989). Among the range of KTP family compounds, the nonlinear polarizabilities of  $Nb^V$ - and  $Ta^V$ -doped  $KTiOPO_4$  crystals are characterized by a high  $\beta(\text{parallel})/\beta(\text{perpendicular})$  ratio, by means of which the

nonlinear response of Nb(Ta)–O bonds has been described in terms of a bond-additivity model (Bergman & Crane, 1975). These compounds may serve as ferroelastic-based multipurpose laser sources for scientific instruments, optical communications, optical signal processing, data storage, *etc.* (Canalias, 2005).

Replacement of  $Ti^{IV}$  atoms by  $Nb^V$  is limited to 15 mol%, due to the structure transformations (Alekseeva *et al.*, 2001) that accompany the decrease in the framework anionic charge and consequent lesser quantity of  $K^+$  cations relative to the parent  $KTiOPO_4$ . Therefore, two necessary conditions need to be addressed for the design of NLO materials, namely the retention of the KTP structure and the prevalence of  $Nb^V$  in the composition of the target compound. This work continues the systematic study of the aliovalent combination approach  $[M^{III} + M^V]$  towards KTP-related structures and we report here the structure of a mixed  $In^{III}/Nb^V$ -substituted phase of formula  $K_{0.92}In_{0.46}Nb_{0.54}OPO_4$  (hereinafter denoted KINP). A brief discussion of its merohedral twinning is also included.

Despite our expectations, the structure of KINP is essentially different from earlier reported structures of  $KM_{0.5}^{III}Nb_{0.5}^VOPO_4$  phases with  $M = V, Cr$  or  $Fe$  (Rangan *et al.*, 1998; Babaryk *et al.*, 2006). The overwhelming majority of previously reported KTP family compounds containing three- and five-valent cations belong to the orthorhombic crystal system (*mmm* Laue group) and crystallize in either  $Pna2_1$  (noncentrosymmetric) or  $Pnan$  (centrosymmetric) space groups, which are related by a ferroelectric–paraelectric phase transition (Belokoneva *et al.*, 1990, 1993; Stefanovich *et al.*, 1996). The precedent for increasing lattice symmetry has been observed for  $KMg_{0.333}Nb_{0.667}OPO_4$  (KMNP; MacCarron & Calabrese, 1993) and  $KNi_{0.5}W_{0.5}OPO_4$  (KNiWP; Peuchert *et al.*, 1995). These compounds belong to the tetragonal crystal system ( $4/mmm$  Laue group). By contrast, the KINP crystal structure displays  $4/m$  Laue symmetry, unlike all previously

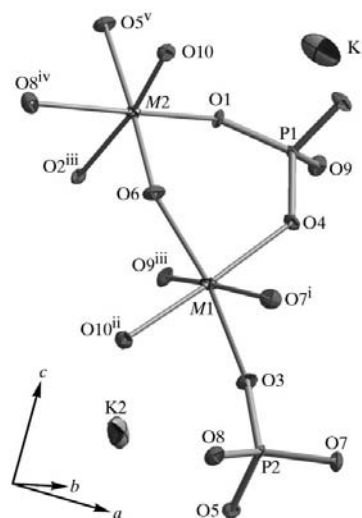


Figure 1

A connected set of numbered atoms, showing displacement ellipsoids at the 70% probability level.  $M$  is In or Nb. [Symmetry codes: (i)  $1 - y, x, \frac{1}{4} + z$ ; (ii)  $-x, 1 - y, \frac{1}{2} - z$ ; (iii)  $-1 + y, 1 - x, -\frac{1}{4} + z$ ; (iv)  $-x, 1 - y, \frac{1}{2} + z$ ; (v)  $-1 + y, 1 - x, \frac{3}{4} - z$ .]

published structures of the KTP family. This change in crystal symmetry may be associated with a gradual increase of octahedrally coordinated metal ion radii from 0.76–0.79 (Cr–Fe) to 0.83–0.94 Å (Mg–In).

The unit cell of KINP (Fig. 1) contains the atomic set (all atoms are in general positions) corresponding to  $\text{KTiOPO}_4$ . The In(Nb)2 atoms are located in a significantly distorted octahedral environment, with four In(Nb)2–O bonds of typical length (Table 1) close to the sum of the corresponding ionic radii and two bonds that are much shorter. For comparison of the local geometry of the octahedra, the bond-valence sum (BVS) method was used (Brown, 2002). The BV parameter was additionally weighted to correct its value for competitive occupation of the octahedral position by the following equation:

$$BV = BV_{M1}q_{M1} + BV_{M2}q_{M2},$$

where BV is the bond valence,  $q$  is the site occupancy, and  $M1$  and  $M2$  are In or Nb, respectively.

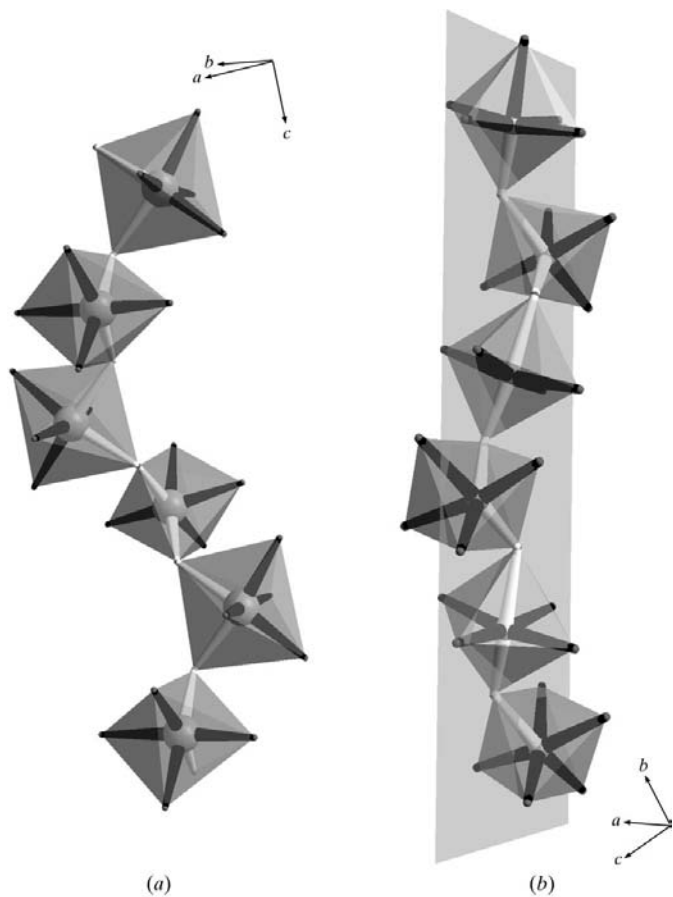
BV parameter values for the shortened bonds are 1.254 and 1.214, while the shortest bonds of the  $[\text{TiO}_6]$  octahedra in the KTP structure correspond to BV values of 1.300 and 1.231

(Brown & Altermatt, 1985; Brese & O’Keeffe, 1991; Tytko *et al.*, 1999). The  $[\text{In}(\text{Nb})\text{O}_6]$  octahedron adopts a comparatively undistorted configuration (Table 1). The In atoms selectively occupy the In(Nb)1 position [ $q_{\text{In}} = 0.8307$  (12) and  $q_{\text{Nb}} = 0.1693$  (12)], while In(Nb)2 are preferentially occupied by Nb [ $q_{\text{In}} = 0.086$  (3) and  $q_{\text{Nb}} = 0.914$  (3)]. Based on the distribution of the metal atoms over the two positions, it is clear that the degree of distortion of the octahedron depends on the nature of the metal which is in preference at the site.

Sequential alternation of two regular In(Nb)1–O6 and In(Nb)1–O10 bonds and two shorter In(Nb)2–O6 and In(Nb)2–O10 bonds forms an infinite helical chain stretching along the  $[001]$  direction, in contrast with the reference KTP structure where the Ti atoms are coplanar. Owing to this circumstance, the only possible means of chain linkage is a *cis–cis* type (Fig. 2a). This type of chain was reported earlier for orthorhombic  $\gamma\text{-NaTiOPO}_4$  (Nagorny *et al.*, 1990), and tetragonal  $\text{KMg}_{0.333}\text{Nb}_{0.667}\text{OPO}_4$  (MacCarron & Calabrese, 1993) and  $\text{KNi}_{0.5}\text{W}_{0.5}\text{OPO}_4$  (Peuchert *et al.*, 1995). Each KINP octahedron is bonded to two neighbours *via* oxygen vertices along the O6–O10 edge, whereas in  $\text{KTiOPO}_4$ , the octahedra are additionally linked *via* apical vertices, giving rise to *trans* fragments (Fig. 2b). In KINP, the formation of the *cis–cis* chain is essentially associated with the connectivity of  $\text{Nb}^{\text{V}}$  atoms. However, differences in the local geometry of the octahedra distinguish the *cis–cis* linkages of the tetragonal aliovalent analogues. For KMNP, only shortened bonds [ $\text{Nb–O} = 1.980$  (1) Å] participate in the construction of the chain and hence no alternation is observed. In KNiWP, both Ni and W atoms possess twofold axis symmetry requiring the equal approach of the W atom to two Ni atoms.

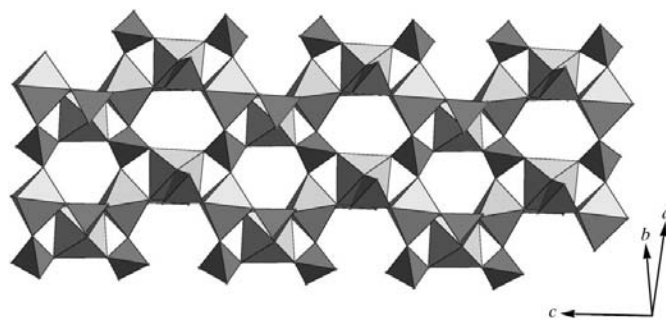
The symmetry relations within the  $[\text{In}(\text{Nb})\text{O}_6]_{\infty}$  chains determine the polarity along the chains, which is critically important for an NLO medium (Shaldin *et al.*, 2006). The In(Nb)–O bonds that are not involved in the formation of the chains complete the coordination of the In(Nb) atoms through the two independent  $\text{PO}_4$  groups. In turn, each  $\text{PO}_4$  tetrahedron bonds to the two closest  $[\text{In}(\text{Nb})\text{O}_6]$  octahedra in adjacent chains, giving a framework structure (Fig. 3).

An anionic sublattice contains one-dimensional hollow channels running orthogonal to the  $ab$  plane (Fig. 4). These



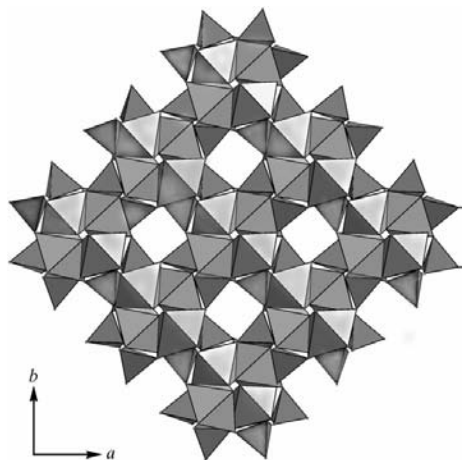
**Figure 2**

(a) The *cis* linkage of  $[\text{In}(\text{Nb})\text{O}_6]$  octahedra in KINP arranged into a helical chain. (b) The alternating *cis* and *trans* fragments within the single  $[\text{TiO}_6]_{\infty}$  chain in KTP (Tordjman *et al.*, 1974). All Ti atoms lie in the same plane.



**Figure 3**

The architecture of the anionic sublattice  $\{[\text{In}_{0.46}\text{Nb}_{0.54}\text{OPO}_4]_{\infty}\}^{-}$  in the best-view projection.  $[\text{PO}_4]$  tetrahedra and  $[\text{In}(\text{Nb})\text{O}_6]$  octahedra are shaded dark grey and light grey, respectively.



**Figure 4**

A view, along the  $c$  axis, of the square tunnels that are occupied by  $K^+$  cations (not shown).

channels are populated by the K atoms, which are separated by a  $\frac{1}{4}$  translation along  $c$ . Both K1 and K2 are coordinated by eight O atoms, with K1–O distances of 2.674 (5)–3.306 (5) Å and K2–O distances of 2.655 (5)–3.194 (4) Å.

## Experimental

Crystal growth experiments for  $K_{0.92}In_{0.46}Nb_{0.54}OPO_4$  were carried out by a self-flux method in the melted system  $K_2O$ – $In_2O_3$ – $Nb_2O_5$ – $P_2O_5$ . The initial mixture of  $KPO_3$  (analytically pure),  $K_4P_2O_7$  (analytically pure),  $In_2O_3$  (extra pure) and  $Nb_2O_5$  (extra pure) was melted at 1373 (20) K and exposed at this temperature for 1–2 h. The melt was stirred once or twice every 30 s using a platinum stirring rod during the exposure period. The melt was cooled at a rate of 20 K  $h^{-1}$  to the temperature range 1033–1093 K. Biaxial prismatic crystals were separated from the flux by decantation at the final crystallization temperature and were washed with dilute  $H_3PO_4$  solution. The quantities of  $In_2O_3$  and  $Nb_2O_5$  were equimolar and they constituted 10–15% weight of the initial mixture. Suitable values of the  $K_2O:P_2O_5$  ratio for the synthesis vary in the range 1.4–1.5. However, the pure compound could only be obtained when the ratio was equal to 1.5. Decreasing this ratio provokes langbeinite-type tetrahedral and octahedral crystalline impurities (Zatovskii *et al.*, 2006). Precise unit-cell parameters were determined using an automated Siemens D500 powder diffractometer operating in a Bragg–Brentano ( $\theta/2\theta$ ) geometry (Cu  $K\alpha$  radiation,  $\lambda = 1.54184$  Å; curved graphite monochromator on the counter arm; step size 0.021; scanning rate 10 s per point). The In and Nb contents were determined using X-ray fluorescence analysis (Philips PW1400 spectrometer). Additional analysis of the elements K, In, Nb and P was performed by energy dispersive spectroscopy using a Link Isis analyser mounted on a Philips XL 30 FEG scanning electron microscope.

### Crystal data

$K_{0.92}In_{0.46}Nb_{0.54}OPO_4$	$Z = 8$
$M_r = 249.76$	Mo $K\alpha$ radiation
Tetragonal, $P4_1$	$\mu = 4.71$ mm $^{-1}$
$a = 9.3091$ (3) Å	$T = 293$ (2) K
$c = 10.9744$ (4) Å	$0.15 \times 0.1 \times 0.1$ mm
$V = 951.03$ (6) Å $^3$	

### Data collection

Oxford Diffraction Xcalibur-3 diffractometer	2769 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	2769 independent reflections
$T_{\min} = 0.596$ , $T_{\max} = 0.615$	2713 reflections with $I > 2\sigma(I)$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$	$\Delta\rho_{\max} = 1.5$ e Å $^{-3}$
$wR(F^2) = 0.053$	$\Delta\rho_{\min} = -0.94$ e Å $^{-3}$
$S = 1.06$	Absolute structure: Flack (1983), with 1317 Friedel pairs
2769 reflections	Flack parameter: $-0.03$ (3)
153 parameters	
4 restraints	

**Table 1**

Selected bond lengths (Å).

In1–O10 <sup>i</sup>	2.087 (4)	In2–O6	1.831 (4)
In1–O6	2.093 (4)	In2–O10	1.843 (4)
In1–O4	2.100 (4)	In2–O1	2.026 (3)
In1–O7 <sup>ii</sup>	2.123 (3)	In2–O8 <sup>iv</sup>	2.073 (3)
In1–O3	2.145 (4)	In2–O5 <sup>v</sup>	2.153 (4)
In1–O9 <sup>iii</sup>	2.185 (3)	In2–O2 <sup>iii</sup>	2.158 (4)

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

The structure twinning was initially indicated by a low value of  $E^2 - 1$ . The space group was chosen from among those in the  $4/m$  Laue class, despite the small difference in  $R_{\text{int}}$  values compared with space groups belonging to the  $4/mmm$  Laue class, which served as an additional reason to consider twinning by merohedry. All attempts to solve the structure in space groups of higher symmetry failed. The TWINLAW (Schlessman & Litvin, 1995) analysis of the data is in good agreement with that of the TWINROT/MAT subroutine implemented in the PLATON software package (Spek, 2003). The twinning corresponds to a twofold axis rotation along the [110] direction, which is a recognized phenomenon for tetragonal structures (Parsons, 2003). The cause of the twinning might be a phase transition, as mentioned for aliovalent KTP analogues (Peuchert *et al.*, 1997), accompanied with loss of symmetry elements (Parsons, 2003).

Competitive occupancies of In and Nb atoms were refined according to chemical analysis results using free variables with linear restraints (SHELXL97; Sheldrick, 1997).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3098). Services for accessing these data are described at the back of the journal.

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