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Centrosymmetric aliovalent KTP isomorphs $KM^{III}_{0.5}Nb_{0.5}OPO_4$ (*M* = Cr and Fe)

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Aliovalent KTP isomorphic compounds potassium chromium niobium oxide phosphate, $KCr_{0.5}Nb_{0.5}OPO_4$, and potassium iron niobium oxide phosphate, $KFe_{0.5}Nb_{0.5}OPO_4$, exhibit structures that differ from that of the non-centrosymmetric $KTiOPO_4$. There are two crystallographically independent octahedral sites, *M*1 and *M*2, statistically occupied by Nb and Cr (or Fe) atoms. The $M1O_6$ and $M2O_6$ octahedra are connected alternately to form a chain with a *cis–trans* arrangement. The Nb atoms prefer the *M*2 sites arranged in a *cis*-like configuration. Each PO_4 tetrahedon has the P atom on a twofold axis. Site-splitting at the K-atom position is observed in both compounds. In the isomorphous structures, one Nb atom lies on an inversion centre and the other on a twofold axis. Similarly with the pairs of Fe/Cr sites, one is on an inversion centre and the other on a twofold axis.

Comment

Compounds with the $KTiOPO_4$ (KTP) structure exhibit nonlinear optical properties (Zumsteg *et al.*, 1976). The Nb^{5+}-doped KTP crystal shows considerably improved second harmonic generation (SHG) (Thomas & Watts, 1990; Zhang *et al.*, 2004). Aliovalent isomorphs are constructed on the principle $xM^{5+} + yM^{2+} = zM^{4+}$, where *M* denotes a cation at an octahedral site. Such modelling for the replacement of Ti^{4+} ions is observed in $KMg_{0.33}Nb_{0.67}OPO_4$ (McCarron & Calabrese, 1993). The Nb(Mg)—O bond lengths peculiar to the undistorted octahedron explain the small value of the SHG intensity. Rietveld analysis of $KV_{0.5}Nb_{0.5}OPO_4$ (Rangan *et al.*, 1998) indicated a selective occupation of Nb at Ti1 and of V at Ti2 sites. The $Nb1(V1)O_6$ octahedron is more distorted than $Nb2(V2)O_6$. Compounds with general formula $KM_{0.5}M'_{0.5}OPO_4$ (*M* = Nb^V and Ta^V; *M'* = Ti^{III}, V^{III}, Cr^{III} and Fe^{III}) and their derivatives, such as $K_{0.5}M_{0.5}M'_{0.5}OPO_4$ (*M* = Nb^V and Ta^V; *M'* = Ti^{IV} and V^{IV}) have also been investigated by powder diffraction (Gopalakrishnan *et al.*, 1994).

The present research is devoted to studying new isomorphic KTP compounds, *viz.* $KCr_{0.5}Nb_{0.5}OPO_4$, (I), and $KFe_{0.5}Nb_{0.5}OPO_4$, (II) (Fig. 1). In these compounds, $M1O_6$ and $M2O_6$ octahedra are linked to each other *via* a common O2 atom and form an infinite chain along the [011] direction. The polyhedral linkage is based on the *cis–trans* arrangement observed in KTP (Tordjman *et al.*, 1974). In both structures, disorder of Nb and Cr (or Fe) atoms is observed at octahedral sites. Nb atoms preferentially occupy *M*2 sites, while Cr or Fe atoms

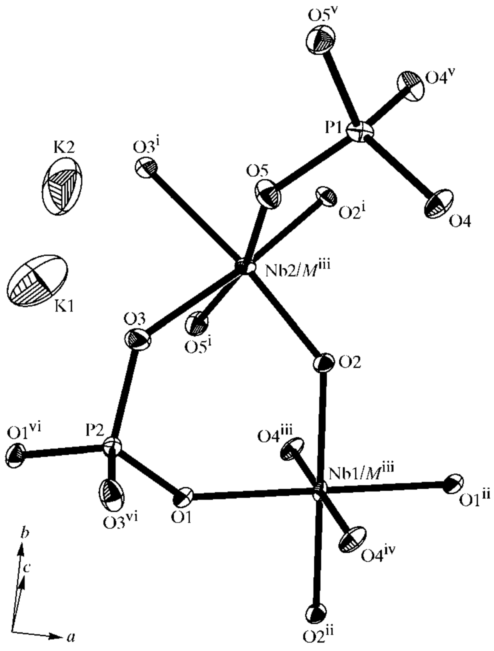

Figure 1
The common structure for $KCr_{0.5}Nb_{0.5}OPO_4$ and $KFe_{0.5}Nb_{0.5}OPO_4$ shown in the best view projection (50% probability displacement ellipsoids). [Symmetry codes: (i) $x, \frac{1}{2}-y, \frac{1}{2}-z$; (ii) $1-x, -y, -z$; (iii) $x, y, -1+z$; (iv) $1-x, -y, 1-z$; (v) $x, \frac{1}{2}-y, \frac{3}{2}-z$; (vi) $\frac{1}{2}-x, -y, z$.]

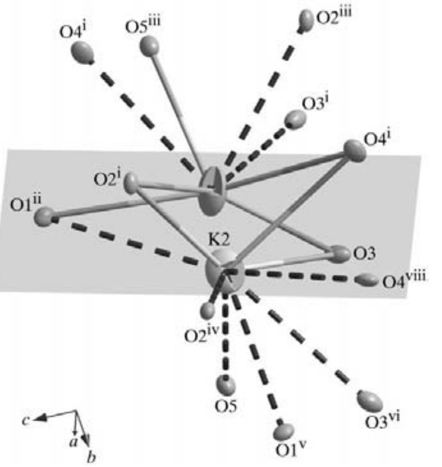

Figure 2
The planar arrangement of atoms O1, O2, O3 and O4, common for the K1 and K2 environments in $KCr_{0.5}Nb_{0.5}OPO_4$ and $KFe_{0.5}Nb_{0.5}OPO_4$. The symmetry codes are as given in Tables 1 and 2 (50% probability displacement ellipsoids).

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occupy *M*1 sites. The $M2O_6$ octahedra arranged in the *cis*-like principle along the chain are considerably distorted; the *M*2—O bond lengths are in the range 1.825 (9)–2.106 (7) Å for (I) and 1.832 (6)–2.113 (5) Å for (II) (Tables 1 and 2). The *M*2—O2 bond length along the chain is much shorter than the others. The $M1O_6$ octahedron is more regular than $M2O_6$, with *M*1—O bond lengths of 1.930 (1)–2.044 (1) Å.

The three-dimensional structure arises from the $[MO_6]_\infty$ chains interlinked by PO_4 tetrahedra. Each PO_4 tetrahedron has a symmetry of *mm*2. The anionic framework contains cavities in which K^+ ions are placed. K-site splitting into K1 and K2 is observed for both (I) and (II). The split K1 and K2 sites have occupancies of 0.5 and are distant from one another by 1.426 (4) Å for (I) and 1.481 (3) Å for (II). The K atoms are coordinated by eight O atoms, with K—O distances less than 3.2 Å. Four O atoms, namely, O1, O2, O3 and O4, lie practically on a plane parallel to (010) (Fig. 2), and are common for both the K1 and K2 environments, with short K—O distances [2.667 (6)–2.794 (6) Å for (I) and 2.693 (7)–2.994 (7) Å for (II)]. The other O atoms around K are at distances of up to 3.189 (6) Å in (I) and 3.163 (7) Å in (II). A similar splitting has been reported for the K atom in KTP structures (Thomas & Watts, 1990; Thomas *et al.*, 1990; Norberg & Ishizawa, 2005).

Experimental

Crystals of (I) were obtained by the self-flux method from KPO_3 (5.17 g), $K_4P_2O_7$ (7.14 g), $CrPO_4$ (1.16 g) and Nb_2O_5 (1.85 g). The mixture was powdered in an agate mortar, placed in a 25 ml platinum crucible, and then heated at 1323 K for 2 h under stirring every 0.5 h with a platinum mixer. The solution was cooled at a rate of 40 K h^{-1} to 1093 K. The rest of the glass was washed away with plenty of hot deionized water, adding 5% solutions of the disodium salt of ethylenediaminetetraacetic acid. Among a significant number of druses (crystal aggregates in which different crystal domains are joined in a chaotic way, *e.g.* a multiple twin), there were well formed green crystals with a typical KTP morphology (Bolt & Bennema, 1990). Similarly, red crystals of (II) were grown from KPO_3 (5.17 g), $K_4P_2O_7$ (7.14 g), Fe_2O_3 (1.16 g) and Nb_2O_5 (1.85 g) under the same conditions as described for (I) above. The amount of iron, chromium, and niobium was determined using X-ray fluorescence analysis. The composition of the single crystals was verified using scanning electron microscopy.

Compound (I)

Crystal data

$KCr_{0.5}Nb_{0.5}OPO_4$
M_r = 222.53
Orthorhombic, *Pnna*
a = 12.849 (3) Å
b = 10.672 (2) Å
c = 6.4635 (13) Å
V = 886.3 (3) Å^3

Z = 8
D_x = 3.335 Mg m^{-3}
Mo *Kα* radiation
μ = 3.86 mm^{-1}
T = 293 (2) K
Prism, dark green
0.4 × 0.15 × 0.06 mm

Data collection

Oxford Diffraction XCalibur-3 diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.510, T_{max} = 0.770

13131 measured reflections
1075 independent reflections
1066 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 28°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.114
S = 1.24
1075 reflections
88 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 16.1755P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 3.20 e Å^{-3}
$\Delta\rho_{min}$ = −1.50 e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

K1—K2	1.426 (4)	K2—O2^{iv}	3.133 (6)
K1—O3	2.667 (6)	K2—O1^{v}	3.162 (7)
K1—O2^{i}	2.696 (6)	K2—O3^{vi}	3.177 (6)
K1—O1^{ii}	2.734 (6)	K2—O4^{vii}	3.189 (6)
K1—O4^{i}	2.792 (6)	Cr1—O1	2.018 (1)
K1—O5^{iii}	2.994 (6)	Cr1—O2	1.930 (1)
K1—O3^{iii}	3.025 (6)	Cr1—O4^{viii}	1.992 (9)
K1—O4^{iii}	3.138 (6)	Cr2—O5	2.050 (3)
K1—O2^{iii}	3.152 (6)	Cr2—O2	1.825 (9)
K2—O3	2.717 (6)	Cr2—O3	2.106 (7)
K2—O2^{i}	2.726 (6)	P1—O4	1.529 (10)
K2—O5	2.797 (6)	P1—O5	1.540 (8)
K2—O4^{i}	2.981 (6)	P2—O1	1.530 (6)
K2—O1^{ii}	3.085 (7)	P2—O3	1.5437 (14)

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

Compound (II)

Crystal data

$KFe_{0.5}Nb_{0.5}OPO_4$
M_r = 224.45
Orthorhombic, *Pnna*
a = 12.9675 (13) Å
b = 10.705 (3) Å
c = 6.4638 (7) Å
V = 897.3 (3) Å^3

Z = 8
D_x = 3.323 Mg m^{-3}
Mo *Kα* radiation
μ = 4.22 mm^{-1}
T = 293 (2) K
Prism, dark red
0.2 × 0.15 × 0.1 mm

Data collection

Oxford Diffraction XCalibur-3 diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.387, T_{max} = 0.496 (expected range = 0.512–0.656)

18570 measured reflections
1087 independent reflections
1021 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 28.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.113
S = 1.33
1087 reflections
88 parameters

$w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 22.555P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.47 e Å^{-3}
$\Delta\rho_{min}$ = −1.32 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0048 (5)

The centrosymmetric space group *Pnna* was chosen, with R_{int} = 0.053 for (I) and R_{int} = 0.039 for (II). No indication of twinning was revealed during data processing. Linear combination restraints were applied in the process of the Cr/Nb and Fe/Nb ratio refinement (Sheldrick, 1997).

For both compounds, 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* (Bradenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Table 2
Selected bond lengths (Å) for (II).

K1—K2	1.481 (3)	K2—O2^{vii}	3.134 (7)
K1—O2^{i}	2.693 (7)	K2—O4^{i}	3.162 (7)
K1—O3	2.700 (7)	K2—O3^{viii}	3.163 (7)
K1—O1^{ii}	2.748 (7)	Fe1—O1	2.044 (0)
K1—O4^{iii}	2.774 (7)	Fe1—O2	1.950 (6)
K1—O5^{iv}	3.013 (7)	Fe1—O4^{viii}	2.011 (2)
K1—O3^{iv}	3.016 (7)	Fe2—O5	2.050 (7)
K1—O2^{iv}	3.113 (7)	Fe2—O2	1.832 (6)
K1—O4^{v}	3.117 (7)	Fe2—O3	2.113 (5)
K2—O3	2.734 (7)	P1—O4	1.527 (7)
K2—O2^{i}	2.743 (7)	P1—O5	1.537 (6)
K2—O5	2.844 (7)	P2—O1	1.524 (7)
K2—O4^{iii}	2.944 (7)	P2—O3	1.548 (3)
K2—O1^{vi}	3.132 (8)		

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3009). Services for accessing these data are described at the back of the journal.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Bolt, R. J. & Bennema, P. (1990). *J. Cryst. Growth*, **102**, 329–340.

Bradenburg, K. (2006). *DIAMOND*. Version 3.1b. Crystal Impact GbR, Bonn, Germany.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Gopalakrishnan, J., Rangan, K. K., Prasad, B. R. & Subramanian, C. K. (1994). *J. Solid State Chem.* **111**, 41–47.

McCarron, E. M. III & Calabrese, J. C. (1993). *J. Solid State Chem.* **102**, 354–361.

Norberg, S. T. & Ishizawa, N. (2005). *Acta Cryst.* C**61**, i99–i102.

Oxford Diffraction (2005). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.28p4beta (release 11-11-2005 CrysAlis171.NET). Oxford Diffraction Ltd, Abington, Oxfordshire, England.

Rangan, K. K., Verbaere, A. & Gopalakrishnan, J. (1998). *Mater. Res. Bull.* **33**, 395–399.

Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.

Thomas, P. A., Glazer, A. M. & Watts, B. E. (1990). *Acta Cryst.* B**46**, 333–343.

Thomas, P. A. & Watts, B. E. (1990). *Solid State Commun.* **73**, 97–100.

Tordjman, I., Masse, R. & Guitel, J. C. (1974). *Z. Kristallogr.* **139**, 103–115.

Zhang, G., Zhang, D., Shen, H., Liu, W., Huang, C., Huang, L. & Wei, Y. (2004). *Opt. Commun.* **241**, 503–506.

Zumsteg, F. C., Bierlein, J. D. & Gier, T. E. (1976). *J. Appl. Phys.* **47**, 4980–4985.