A Structural Comparison of Aliovalent Analogues: $K(Mg_{1/3}Nb_{2/3})PO_5$ and $KTiOPO_4$*

E. M. McCARRON III, J. C. CALABRESE, T. E. GIER, L. K. CHENG, C. M. FORIS, AND J. D. BIERLEIN

Du Pont Central Research, Experimental Station, Wilmington, Delaware 19880

$K(Mg_{1/3}Nb_{2/3})PO_5$ (KMNP) is an aliovalent analogue of potassium titanyl phosphate, $KTiOPO_4$ (KTP). Single crystals of KMNP were grown from a $3K_2O/2P_2O_5$ flux and their structure was determined. KMNP is not isostructural with KTP (noncentrosymmetric orthorhombic space group $Pna2_1$). Instead, it crystallizes in the noncentrosymmetric, enantiomorphic space groups $P4_122$ and $P4_322$ (tetragonal; $a = 6.5366(3)$, $c = 10.847(1)$ Å). Unlike KTP, KMNP exhibits vanishingly small (~0) second harmonic generation (SHG). The main structural differences between KMNP and KTP are the lack of a (Mg, Nb)—O bond equivalent to the very short titanyl Ti=O bond found in KTP and a change in the connectivity of the $MO_{6/2}$ octahedra—instead of the *cis-trans* arrangement of the $TiO_{6/2}$ chains in KTP, the $(Mg_{1/3}Nb_{2/3})O_{6/2}$ chains of KMNP are linked in an all-*cis* configuration. Phase evolution in and SHG data for the system $K[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]PO_5$ ($K[T_{1-x}(MN)_x]P$) are also reported. The results of this study suggest that the aliovalent substitution of $(Mg_{1/3}Nb_{2/3})$ for Ti is primarily responsible for the dramatic loss of SHG and that the change in space group is only of minimal importance. © 1993 Academic Press, Inc.

Introduction

Potassium titanyl phosphate, $KTiOPO_4$ (KTP), is a nonlinear optical material of technological importance for frequency-doubling light waves via second harmonic generation (SHG). In a recent review, Stucky *et al.* (*1*) cataloged structure/property relationships for both iso- and aliovalent analogues of KTP. Strong correlations between substitution chemistry and SHG signal were noted—the magnitude of the powder SHG values reported in that study varied between ~6000[1] for pure KTP and

~0 for certain substitutions. However, no completely satisfactory explanation for these large variations in nonlinear optical properties with chemistry has been developed.

For epitaxial waveguide applications (*2*), low dielectric constant, SHG-inactive substrate materials which could lattice-match either KTP or the isostructural potassium titanyl arsenate $KTiOAsO_4$ (KTA) were desired. $K(Mg_{1/3}Nb_{2/3})PO_5$ (KMNP) was chosen for this purpose as it was reported to be both isostructural with and well latticed-matched to KTA, and also to have vanishing SHG (*1*). In order to fully characterize this material, single crystals were grown and the structure determined. Unlike KTP (acentric space group $Pna2_1$: or-

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thorhombic; $a = 12.814$, $b = 6.402$, $c = 10.585$ Å) (3), KMNP crystallizes in the noncentrosymmetric, enantiomorphic space groups $P4_122$ and $P4_322$: tetragonal; $a = 6.5361(2)$, $c = 10.8452(7)$ Å. Phase formation is also reported for the system $K[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]PO_5$ ($K[T_{1-x}(MN)_x]P$) and x correlated with SHG.

Experimental

Crystals of KMNP were grown by slow cooling a solution of ~3 $KMNP/(3K_2O/2P_2O_5)$ flux from 1000°C to 800°C at 5°C/hr. Agitations were sometimes necessary as the KMNP solution tends to supercool and

TABLE II

UNIT CELL PARAMETERS FOR
$K[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]PO_5$

x	a	b	c	V
	Orthorhombic			
0.0	12.8213(8)	6.4051(4)	10.588 (1)	869.52
0.1	12.832 (2)	6.4169(6)	10.592 (2)	872.19
0.2	12.860 (3)	6.429 (1)	10.616 (1)	877.68
0.3	12.921 (2)	6.4451(7)	10.672 (2)	888.75
0.4	12.924 (2)	6.457 (1)	10.703 (2)	893.23
0.5	12.945 (1)	6.4627(9)	10.714 (3)	896.40
0.6	12.949 (3)	6.464 (1)	10.711 (2)	896.63
	Tetragonal			
0.6	6.521 (1)		10.789 (4)	458.83
0.7	6.5219(5)		10.788 (2)	458.87
0.8	6.5254(5)		10.803 (2)	459.98
0.9	6.5284(4)		10.811 (1)	460.75
1.0	6.5361(2)		10.8452(7)	463.32

TABLE I

POWDER PATTERN OF $K(Mg_{1/3}Nb_{2/3})PO_5$

h	k	l	$2\theta_{obs}$	d_{obs} (Å)[a]	d_{calc} (Å)[b]	I_{obs}[c]	I_{calc}[d]
1	0	0	13.537	6.535	6.535	21	39.1
1	0	1	15.813	5.599	5.596	100	100.0
1	1	0	19.189	4.621	4.620	8	7.6
1	1	1	20.870	4.253	4.250	28	38.7
1	0	2			4.172		2.3
1	1	2	25.303	3.517	3.516	3	2.6
1	0	3	28.190	3.163	3.162	48	47.7
2	0	1			3.128		6.0
1	1	3	31.400	2.8466	2.8466	1	4.2
2	1	1	31.670	2.8230	2.8218	57	64.4
2	0	2	31.941	2.7996	2.7984	71	70.3
0	0	4	33.012	2.7112	2.7103	12	15.6
2	1	2	34.833	2.5736	2.5725	20	26.2
1	0	4			2.5035		1.1
2	1	3	39.623	2.2728	2.2723	3	6.9
2	2	1	39.854	2.2601	2.2597	2	2.2
3	0	0	41.415	2.1785	2.1783	4	4.4
3	0	1			2.1356		0.9
2	0	4	43.323	2.0869	2.0860	8	7.7
3	1	0	43.760	2.0670	2.0665	2	1.4
1	0	5	43.947	2.0587	2.0579	3	3.7
3	1	1	44.595	2.0302	2.0300	7	12.6
3	0	2	44.800	2.0214	2.0212	3	5.1
2	1	4	45.603	1.9877	1.9873	4	4.3
1	1	5	46.192	1.9637	1.9629	2	3.7
2	2	3	46.607	1.9472	1.9466	3	2.2
3	1	2	47.026	1.9308	1.9310	1	0.6
3	0	3	48.757	1.8662	1.8656	8	8.5
3	2	0	50.294	1.8127	1.8125	9	10.2
2	0	5			1.8066		0.5
3	1	3	50.853	1.7941	1.7939	13	14.5
3	2	1	51.032	1.7882	1.7877	1	3.5
2	2	4	51.947	1.7588	1.7583	14	16.3
1	0	6			1.7415		1.0
2	1	5	52.491	1.7419	1.7413	9	10.3
3	2	2			1.7189		1.2
4	0	0	56.247	1.6342	1.6337	10	11.0
3	2	3	56.775	1.6202	1.6201	4	3.7
4	1	0	58.154	1.5850	1.5850	3	3.7
2	0	6	58.292	1.5816	1.5812	11	11.2
4	1	1	58.835	1.5683	1.5683	4	4.0

[a] Copper $K\alpha_1$ radiation; $\lambda = 1.5406$ Å (4, 5).
[b] Copper $K\alpha$ radiation; $\lambda = 1.5418$ Å.
[c] Intensity—transmission geometry.
[d] Intensity—reflection geometry.

quench into a glass. Small crystals of up to ~$2 \times 2 \times 2$ mm³ were recovered by pouring off the flux and etching in hot water. KMNP crystals grow as square bipyramids with the forms {100} and {110} missing. Inductively coupled plasma (ICP) atomic emission spectroscopy was used to analyze the (Mg/Nb) ratio which was approximately 1:2 (31.3 and 68.7%, respectively). When the ICP results were combined with chemical analysis for K and P, essentially a 1:1:1 ratio for $K:(Mg_{1/3}Nb_{2/3}):P$ was obtained. Powder synthesis of the $K[T_{1-x}(MN)_x]P$ system was accomplished by standard solid-state techniques from stoichiometric quantities of KH_2PO_4, TiO_2, MgO, and Nb_2O_5 at 750°C.

X-ray powder diffraction data for the $K[T_{1-x}(MN)_x]P$ samples were obtained with a Guinier–Hägg camera (diameter = 80 mm). The radiation used was Cu $K\alpha_1$ ($\lambda = 1.5406$ Å (4)) and the internal standard was Si (NIST SRM 640A) (5). Films (CEA Reflex 15, Ceaverken, AB) were measured with an LS-18 microdensitometer (Instrumentfirma) (6). The program Scanpi (7, 8), as modified by A. Brown (9), was used to

obtain 2θ positions, intensities, and d values. Lattice constants were obtained by a least-squares refinement of the data; the program used was Loopy, a modified version of PIDATA and PIRUM/PURUM (7, 8). The powder pattern of $K(Mg_{1/3}Nb_{2/3})PO_5$ is given in Table I (tetragonal: $a = 6.5361(2)$ and $c = 10.8452(7)$ Å; $F(20)$ (10) = 269 (0.00438, 17) and $M(20) = 147$ (11)) and lattice constants for the $K[T_{1-x}(MN)_x]P$
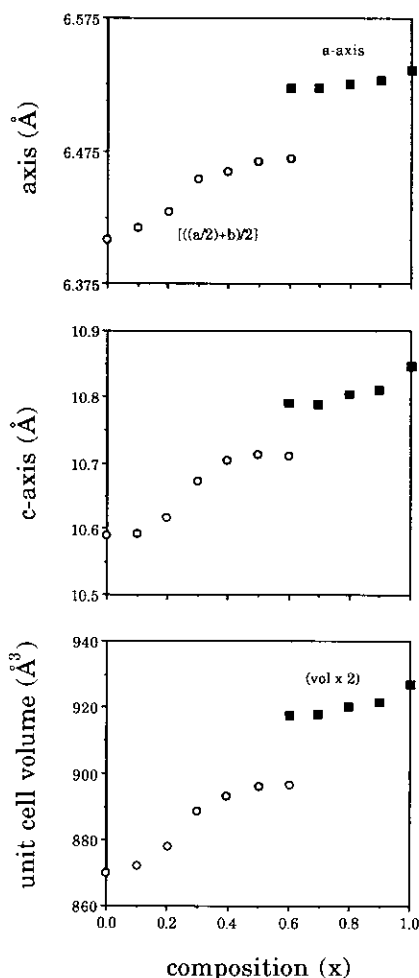

FIG. 2. Dramatic dropoff of SHG signal as a function of x for the $K[T_{1-x}(MN)_x]P$ system. SHG is referenced to α-SiO$_2$ = 1.

system are given in Table II. Figure 1 shows lattice constants and unit cell volume as a function of composition. SHG was measured using a powder technique (12) with a pulsed Nd : YAG laser ($\lambda = 1.064$ μm). Particle size was similar for all samples ($d_{90} \sim 50$ μm; $d_{50} \sim 25$ μm) and the SHG signal measured was normalized to α-quartz. The SHG results are given in Fig. 2.

Crystal Structure Determination

A summary of the crystallographic data for $K(Mg_{1/3}Nb_{2/3})PO_5$ is given in Table III. The structure was solved[2] by direct methods (MULTAN) in space group $P4_122$ (No. 91). The asymmetric unit consists of one (Mg/Nb) atom and one P atom on axial twofolds, one O atom on a diagonal twofold,

FIG. 1. Unit cell data for $K[T_{1-x}(MN)_x]P$ showing the discontinuity associated with the structural transition (○, orthorhombic and ■, tetragonal).
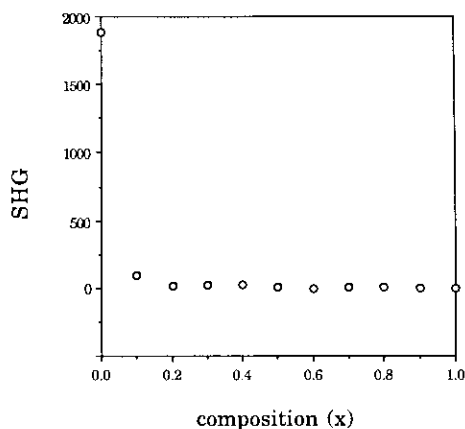
[2] All crystallographic calculations were performed on a DEC/CRAY computer network, using a system of programs developed by J. C. Calabrese. The package incorporates the ORTEP plot program (written by C. K. Johnson, 1971). Structure was obtained using MULTAN (written by P. Main, Univ. of York, England, 1980).

TABLE III

CRYSTALLOGRAPHIC DATA FOR K(Mg$_{0.33}$Nb$_{0.67}$)PO$_5$

formula	K(Mg$_{0.33}$Nb$_{0.67}$)PO$_5$
formula weight	220.12
symmetry	tetragonal
space group	P4$_3$22 (No. 95)
a (Å)	6.535(1)
c (Å)	10.841(2)
volume (Å^3)	463.0
Z	4
calculated density (mg/m^3)	3.157
crystal color	colorless
crystal shape	square pyramid
crystal size (mm)	0.08 x 0.19 x 0.19
crystal faces ((hkl), mm)	(014), 0.083; (10$\bar{1}$), 0.100;
	($\bar{1}$0$\bar{1}$), 0.093; (0$\bar{1}$$\bar{1}$), 0.087;
	(01$\bar{1}$),0.100
temperature (°C)	−70
μ(Mo) (cm^{-1})	29.44
diffractometer	Enraf-Nonius CAD4
radiation (graphite monochromator)	Mo K$_\alpha$
reflections centered	25
data collected	1524
min, max 2θ	3.8, 60.0
max h,k,l	9 9 15
data octants	+ + +, − + +
scan method	ω
scan width (°ω)	1.20 − 1.50
scan speed(°ω/min)	2.00 − 5.00
typical half-height peak width (°ω)	0.14
check reflections	2, 11 times
variation	1% fluctuation
absorption method	numerical integration
transmission factors, range	0.43 − 0.57
duplicates	669, 1.3% R-merge
no. of unique data (I ≥ 3σ(I))	668
solution method	direct methods (MULTAN)
refinement method	full-matrix least squares on F
anomalous dispersion	K, (Mg/Nb), P,
weighting scheme	biweight ($\propto$ [σ^2(I)+0.0009(I)^2]$^{-1/2}$)
atoms refined	anisotropic: all atoms
parameters varied	44
data/parameter ratio	15.00
R, Rw	3.79, 5.40
error of fit	2.97
max shift Δ/σ	0.36
max residual density (e/Å^3)	0.10

and two O atoms and the one K atom in general positions. Refinement of the multiplicity of the potassium position indicates

TABLE IV

FRACTIONAL COORDINATES ($\times 10^4$) AND ISOTROPIC THERMAL PARAMETERS

Atom	x/a	y/b	z/c	B_{eq} (Å^2)^a
K^b	7872(6)	7673 (7)	1975(3)	5.2(1)
Mg/Nb	5000	7400.3(9)	5000	1.0(1)
P	10000	6523 (2)	5000	0.7(1)
O(1)	5431(4)	5431	6250	1.1(1)
O(2)	8111(4)	7866 (4)	4785(2)	1.0(1)
O(3)	10269(4)	5135 (5)	3863(2)	1.4(1)

^{a} $B_{eq} = \frac{4}{3}\Sigma^3_{i=1} \Sigma^3_{j=1} (a_i \cdot a_j)\beta_{ij}$.
^{b} The K position is half-occupied (see text).

TABLE V

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES^a

(Mg/Nb)–O(1)	1.890(1)	O(1) –(Mg/Nb)–O(3)b	173.4°(1)
(Mg/Nb)–O(2)	2.069(3)	O(1)c–(Mg/Nb)–O(3)a	173.4°(1)
(Mg/Nb)–O(3)a	2.124(3)	O(2) –(Mg/Nb)–O(2)c	163.1°(2)
P–O(2)	1.533(3)	O(2)–P–O(2)d	110.1°(2)
P–O(3)	1.540(3)	O(2)–P–O(3)i	107.9°(2)
		O(2)–P–O(3)d	111.5°(1)
		O(3)–P–O(3)d	107.9°(3)
K–O(1)e	3.064(6)		
K–O(2)	3.053(5)		
K–O(2)f	2.820(5)		
K–O(3)	3.065(5)		
K–O(3)b	2.986(5)		
K–O(3)g	2.578(4)		
K–O(3)h	2.679(4)		

^{a} Symmetry operation codes: (a) y, 2 − x, $\frac{1}{4}$ + z; (b) 1 − y, 2 − x, $\frac{3}{4}$ − z; (c) 1 − x, y, 1 − z; (d) 2 − x, y, 1 − z; (e) 1 − x, 1 − y, −$\frac{1}{2}$ + z; (f) 2 − y, x, −$\frac{1}{4}$ + z; (g) x, 1 − y, $\frac{1}{2}$ − z; (h) 1 − y, x, −$\frac{1}{4}$ + z.

half-occupancy in the general position, which is consistant with a disorder of the potassium over two general sites separated by 1.582(7) Å. In addition, the (Mg/Nb) site is a composite of 1/3 Mg and 2/3 Nb as confirmed by least-squares refinement and is in excellent agreement with chemical analysis. No evidence for ordering (higher order diffraction peaks) of Mg and Nb could be detected from long-exposure axial photographs. The enantiomorphic space group $P4_3$22 was chosen over $P4_1$22 on the basis of lowest R-value ($R = 3.79(4_3) − 3.92(4_1)$; $R_w = 5.40(4_3) − 5.54(4_1)$). Atomic scattering factors, including anomalous terms for K, (Mg/Nb), and P, were taken from the "International Tables for X-ray Crystallography" (13).

The final positional parameters and selected bond lengths and angles are given in Tables IV and V, respectively. The asymmetric unit is shown in Fig. 3. Supplementary tables of all bond distances (within 3.7 Å) and angles, thermal parameters, and calculated and observed structure factors are also available.
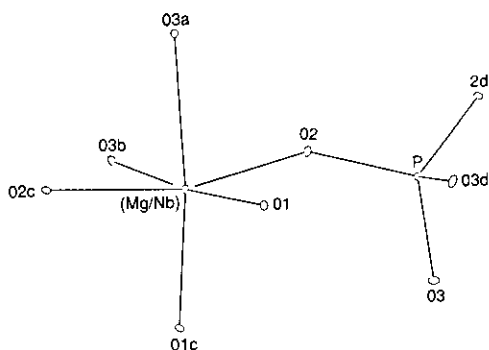
FIG. 3. Asymmetric unit of the $[(Mg_{1/3}Nb_{2/3})O_{6/2}PO_{4/2}]^{1-}$ framework of KMNP.

Results and Discussion

Not only is $K(Mg_{1/3}Nb_{2/3})PO_5$ an aliovalent analogue of $KTiOPO_4$, but also there exists a fortuitous lattice match between tetragonal ($\{P4_122 - P4_322\}$) KNMP and orthorhombic ($Pna2_1$) KTP such that

	KMNP		KTP
	a	$\sim$	$\frac{1}{2}a$
		$\sim$	b
and	c	$\sim$	$c.$

Hence, there is a strong similarity between the powder patterns of these two compounds. This coincidence most likely led to the erroneous report (*1*) that KMNP is isostructural with KTP. However, the change in space group noted above is indicative of a gross structural distinction between the two chemically related compounds. Figure 1 locates the structural discontinuity associated with the $K[T_{1-x}(MN)_x]P$ system at roughly $x = 0.6$.

Both KMNP and KTP (*3*) can be described as consisting of one-dimensional chains of $MO_{6/2}$ octahedra ($M = Mg_{1/3}Nb_{2/3}$ and Ti, respectively) linked by $PO_{4/2}$ tetrahedra to form a three-dimensional framework which, in turn, forms three mutually perpen-

dicular (along the major crystal axes), intersecting channels in which the potassium ions reside. Based on this description, if the $MO_{6/2}$ octahedral chains were equivalent, one could expect the structures to be analogous. However, the structural transition between KMNP and KTP involves a change in the linkage of the $MO_{6/2}$ octahedra from all-*cis* for KMNP to *cis-trans* for KTP (see Fig. 4). In particular, the all-*cis* linkage found in KMNP results in a chiral spiraling (left-handed screws for the $P4_322$ enantiomorph) of the $(Mg_{1/3}Nb_{2/3})O_{6/2}$ chains down the *c*-axis (see Figs. 5 and 6), whereas the *cis-trans* linkage found in KTP produces undulating $TiO_{6/2}$ chains propagating along [011] and [01$\bar{1}$] crystallographic directions (*3*). An all-*cis* $TiO_{6/2}$ octahedral linkage has been observed previously in the structure $Na_2Ti_2P_2O_{10}$ (*14, 15*). Furthermore, with respect to the individual $MO_{6/2}$ octahedra themselves, KMNP does not contain an

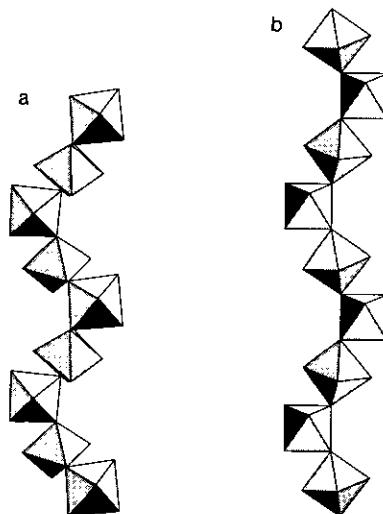FIG. 4. A comparison of (a) the all-*cis* configuration of the $MO_{6/2}$ octahedral chains in KMNP versus (b) the *cis-trans* arrangement of the $TiO_{6/2}$ chains in KTP.
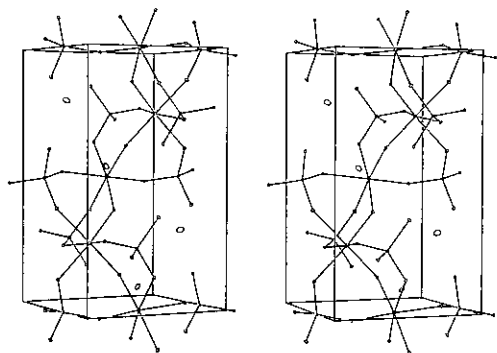
FIG. 5. Stereoscopic view of the unit cell of KMNP (half of the symmetry-related disordered K ions omitted for clarity (see text)).

(Mg, Nb)—O bond equivalent to the very short titanyl Ti=O bond found in KTP (see Fig. 7)—a situation similar to that found in KSnPO$_5$ (16, 17). Therefore, KMNP is properly written as K(Mg$_{1/3}$Nb$_{2/3}$)PO$_5$, whereas KTP is usually written as KTiOPO$_4$.

KTP has large nonlinear optical coefficients (18). KMNP, on the other hand, was reported (1) to exhibit ~0 SHG. Results obtained in this study have confirmed that observation. Therefore, based upon the KMNP structure discussed above, either the change in symmetry or the change in the coordination geometry of the $MO_{6/2}$ octahedral site or some combination of the two may be responsible for the loss of SHG relative to that of KTP. To differentiate, both phase stability and SHG were correlated with composition for the system K[T$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$]PO$_5$. It was found that the KTP structure is stable over the range $0 \leq x \leq$ ~0.5, while the KMNP structure is stable over a narrower range, ~0.7 $\leq x \leq$ 1. Two-phase behavior is observed in the intermediate range (see Fig. 1). In sharp contrast, the drop of SHG with x is remarkably rapid (see Fig. 2). This implies that aliovalent substitution into the titanyl chains

is a more important factor in determining nonlinear optical properties than is the phase change. This is not particularly surprising in light of the fact that numerous examples of dramatic SHG loss with complete iso- and aliovalent substitution for titanium have been noted (1) in cases where the KTP structure-type is maintained. However, the rapidity of the dropoff as a function of composition in the case of KMNP is without precedent and indeed noteworthy.

The structural implication is that local insertion of a relatively uniform (Mg$_{1/3}$Nb$_{2/3}$)O$_{6/2}$ octahedra for highly distorted TiO$_{6/2}$ causes a break in the continuity of the long–short O—Ti=O bonding. Furthermore, in cases where cationic substitution for Ti allows the long–short bonding O—(M/Ti)=O to be preserved, namely, M = V (19) and Nb (20), it has been reported that the substitution does not appreciably alter SHG. In fact, the substitution
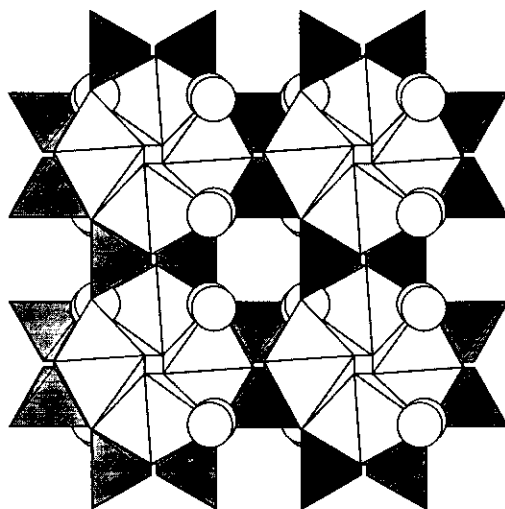

FIG. 6. Packing diagram of the KMNP structure viewed down the c-axis (fourfold left-handed screw) emphasizing the spiraling (Mg$_{1/3}$Nb$_{2/3}$)O$_{6/2}$ chains (light octahedra) and the disordered (doubled spheres; half-occupied) potassium ions (see text) within the channels; PO$_{4/2}$ (dark tetrahedra).
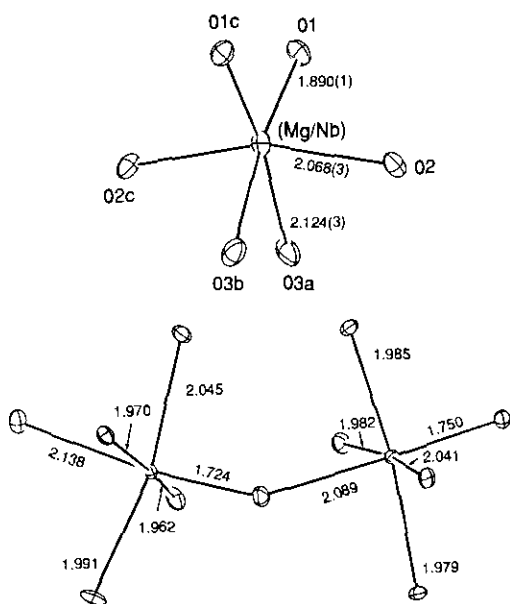
FIG. 7. A comparison of bond lengths for the $MO_{6/2}$ octahedra of (top) KMNP and (bottom) KTP (symmetry-related oxygen atoms shaded).

of charge-compensated Nb for Ti may even enhance SHG at low levels of substitution (21). This then would imply that the incorporation of a magnesium ion into the structure is primarily responsible for the loss of SHG. From Fig. 2 it can be seen that as little as 3% substitution of charge-compensated Mg for Ti lowers SHG by 2 to 3 orders of magnitude.

Finally, it remains only to address whether or not low-level substitution of a more regularly coordinated ion for titanium is sufficient to drastically affect nonlinear optical properties as seen in Fig. 2. In the case of the isovalent substitution of a more regularly coordinated Sn ion for Ti, i.e., $K(Ti_{1-x}Sn_x)OPO_4(K[T_{1-x}Sn_x]P)$, it was reported (22, 23) that SHG fell off systematically (roughly linearly (24)) with composition (x). Thus, while both iso- and aliovalent substitution degrade SHG, the degree differs substantially. Therefore, on the basis of a comparison with $K[T_{1-x}Sn_x]P$, the

precipitous drop in SHG observed for $K[T_{1-x}(MN)_x]P$ suggests that it cannot be attributed simply to a break in the integrity of the titanyl chains, but that electronic effects associated with aliovalent substitution are far more detrimental to the nonlinear optical properties of KTP than are those associated with isovalent substitution.

Acknowledgments

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