

Ab initio determination and Rietveld refinement of the crystal structure of Ni_{0.50}TiO(PO₄)

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(Received 12 March 1998; accepted 30 March 1998)

The structure of the oxyphosphate Ni_{0.50}TiO(PO₄) has been determined *ab initio* from conventional X-ray powder diffraction data by the "heavy atom" method. The cell is monoclinic (space group $P2_1/c$, $Z=4$) with $a=7.3830(5)$ Å, $b=7.3226(5)$ Å, $c=7.3444(5)$ Å, and $\beta=120.233(6)^\circ$. Refinement of 46 parameters by the Rietveld method, using 645 reflexions, leads to $cR_{wp}=0.152$, $cR_p=0.120$, and $R_B=0.043$. The structure of Ni_{0.50}TiO(PO₄) can be described as a TiOPO₄ framework constituted by chains of tilted corner-sharing TiO₆ octahedra running parallel to the c axis, crosslinked by phosphate tetrahedra and in which one-half of octahedral cavities created are occupied by Ni atoms. Ti atoms are displaced from the center of octahedra units in alternating long (2.231) and short (1.703 Å) Ti–O bonds along chains. © 1999 International Centre for Diffraction Data. [S0885-7156(98)00303-0]

Key words: Ni_{0.50}TiO(PO₄), *ab initio* structure determination, Rietveld refinement, powder diffraction, titanyl oxyphosphate compounds

I. INTRODUCTION

Interest in titanium phosphates, both in glass and crystalline form, for their properties as ionic conductor or non-linear optical material, has led to a large number of studies. Two major types of structures can be encountered: Nasicon type structure (Hagman and Kierkegaard, 1968; Krimi *et al.*, 1993; El Jazouli *et al.*, 1997) and potassium titanyl phosphate (KTP) structure (Tordjman *et al.*, 1974; Stucky *et al.*, 1989; Bierlein and Vanherzeele, 1989).

Recently some of us, studying thermal stability of Nasicon type compounds with formula Ni_{0.50}Ti₂(PO₄)₃ in the NiO–TiO₂–P₂O₅ ternary diagram, have shown the existence of a new phase as a product of decomposition (El Jazouli *et al.*, 1998). Its chemical composition was determined as Ni_{0.50}TiO(PO₄).

The present paper reports the synthesis of Ni_{0.50}TiO(PO₄) and an *ab initio* determination of crystal structure from the X-ray powder diffraction pattern.

II. EXPERIMENTAL

The oxyphosphate Ni_{0.50}TiO(PO₄) was synthesized by the following techniques:

- (i) Solid state with stoichiometric amounts of NiO, (NH₄)₂HPO₄, and TiO₂ previously dried at 600 °C; mixture ground and heated at 300 °C for 24 h, at 600 °C for 48 h, and finally at 950 °C for 48 h;
- (ii) Coprecipitation with diluted solutions of NiCl₂·6H₂O (I), (NH₄)₂HPO₄ (II), and TiCl₄ in ethanol (III) as starting materials. A slow addition of (III) in (I+II) mixture at room temperature induces a precipitation. After drying at about 100 °C, the resulting amorphous powder was progressively heated up to 800 °C for

24 h. The final green products have been controlled by X-ray powder diffraction analysis using CuK α radiation.

Efforts to grow single crystals have been performed by chemical vapor transport (Glaum and Gruehn, 1990; Glaum *et al.*, 1990; Reinauer *et al.*, 1994). Ni_{0.50}TiO(PO₄) powder was introduced with NH₄Cl as transport agent in a silica ampoule which was evacuated and sealed. The silica ampoule was then placed in a two-zone furnace (1000 → 900 °C) for 2 weeks. Single crystals have been obtained but they are heavily twinned and not usable for structural determination as shown by a film analysis (Buerger and Weissenberg cameras).

Consequently, the structural determination was undertaken from the powder data. Diffraction data were collected at room temperature on a Philips PW 3040 (θ - θ) diffractometer: Bragg-Brentano geometry; diffracted-beam graphite monochromator; CuK α radiation (40 KV, 40 mA); Soller slits of 0.02 rad on incident and diffracted beams; divergence slit of 1°; antiscatter slit of 1°; receiving slit of 0.05 mm; holder surface dusted with 20 μ m sieve and corrected with a razor blade; sample spinner used; steps of 0.02° (2θ) over the angular range 10–140° (2θ) with a fixed counting time of 30 s.

TABLE I. Monoclinic unit cell parameters of Ni_{0.50}TiO(PO₄) at 295 K.

$a=7.3830(5)$ Å	$V=343.05(3)$ Å ³
$b=7.3226(5)$ Å	$M_r=188.226$
$c=7.3444(5)$ Å	$Z=4$
$\beta=120.233^\circ(6)$	$D_m=3.62\pm 0.02$ g.cm ⁻³
$M_{20}=34$	$D_x=3.64$ g.cm ⁻³
$F_{30}=44.0(0.0110;35)$	

TABLE II. Powder diffraction data of $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$ ($\text{CuK}\alpha_1$; $\lambda = 1.54056 \text{ \AA}$).

$2\theta_{\text{obs}}$	$100/I_0$	d_{obs}	hkl	$2\theta_{\text{cal}} - 2\theta_{\text{obs}}$	$\pm 2\theta_{\text{obs}}$	$100/I_0$	d_{obs}	hkl	$2\theta_{\text{cal}} - 2\theta_{\text{obs}}$
13.884	18	6.373	100	-0.012	51.921	3	1.760	$14\bar{1}$	-0.002
18.439	17	4.808	110	-0.007				140	0.002
18.493	10	4.794	011	-0.006	53.123	2	1.7227	$4\bar{1}\bar{3}$	-0.012
24.288	4	3.662	020	0.002				$4\bar{1}\bar{1}$	0.018
27.040	13	3.295	$2\bar{1}\bar{1}$	-0.012	53.311	2	1.7170	$3\bar{3}\bar{1}$	0.003
27.154	100	3.281	$1\bar{1}\bar{2}$	-0.010	53.486	4	1.7118	$1\bar{1}\bar{4}$	-0.015
			111	0.010				$1\bar{3}\bar{3}$	0.004
27.952	31	3.189	$2\bar{0}\bar{2}$	-0.025				113	0.011
			200	0.001	55.975	10	1.6415	$2\bar{2}\bar{4}$	0.008
28.103	41	3.173	$1\bar{2}\bar{1}$	-0.031	56.026	7	1.6401	222	0.000
			120	-0.025	56.117	2	1.6376	141	-0.016
			002	0.000	57.390	7	1.6043	$3\bar{3}\bar{3}$	0.009
			021	0.012	57.431	8	1.6033	330	0.000
30.527	4	2.926	$2\bar{1}\bar{2}$	-0.003	57.608	3	1.5987	033	0.011
30.687	2	2.911	012	-0.001	57.697	3	1.5965	$4\bar{0}\bar{4}$	0.015
34.475	15	2.599	$2\bar{2}\bar{1}$	-0.001	57.768	14	1.5947	$4\bar{2}\bar{3}$	-0.035
34.569	14	2.593	$1\bar{2}\bar{2}$	-0.002				$4\bar{2}\bar{1}$	-0.007
			121	0.014				400	0.000
37.175	6	2.417	$3\bar{0}\bar{2}$	0.002	58.048	7	1.5877	$2\bar{4}\bar{2}$	-0.016
37.352	4	2.406	$2\bar{2}\bar{2}$	-0.009				124	0.025
			220	0.011				240	-0.001
37.462	3	2.399	102	-0.012	58.123	13	1.5858	004	-0.022
			022	0.017				$0\bar{4}\bar{2}$	0.007
39.246	8	2.294	$3\bar{1}\bar{2}$	-0.018	59.183	2	1.5599	414	0.016
			$3\bar{1}\bar{1}$	-0.004	59.581	1	1.5504	014	0.002
39.367	5	2.287	$2\bar{1}\bar{3}$	0.000	63.097	1	1.4722	$4\bar{3}\bar{2}$	0.001
39.421	5	2.284	211	-0.016	63.325	1	1.4675	234	0.009
39.515	19	2.279	112	-0.027	63.731	2	1.4591	$3\bar{4}\bar{2}$	-0.005
			$1\bar{3}\bar{1}$	-0.022				$3\bar{4}\bar{1}$	0.005
			130	-0.017	63.913	1	1.4554	142	-0.003
			031	0.011	64.774	1	1.4381	$5\bar{1}\bar{2}$	0.007
44.327	15	2.042	$3\bar{1}\bar{3}$	-0.040	64.972	4	1.4342	$4\bar{3}\bar{3}$	-0.009
			310	-0.001				$4\bar{3}\bar{1}$	0.017
44.546	11	2.032	$1\bar{3}\bar{2}$	-0.010	65.065	2	1.4324	$3\bar{1}\bar{5}$	0.010
			131	0.003	65.156	3	1.4306	312	-0.011
45.061	7	2.010	$2\bar{2}\bar{3}$	-0.028	65.303	8	1.4277	$1\bar{3}\bar{4}$	-0.023
			221	0.006				$1\bar{5}\bar{1}$	0.014
45.140	1	2.007	122	0.001				133	0.001
46.817	1	1.939	$2\bar{3}\bar{2}$	-0.002	67.447	1	1.3875	340	0.009
49.330	4	1.846	$4\bar{0}\bar{2}$	0.003	67.592	1	1.3848	104	0.003
49.596	3	1.837	204	0.015	68.921	5	1.3613	$2\bar{5}\bar{1}$	0.002
49.761	7	1.831	023	-0.018	69.307	2	1.3547	$2\bar{2}\bar{5}$	0.008
			040	0.006	72.453	3	1.3034	524	0.013
50.980	2	1.790	$4\bar{1}\bar{2}$	0.005	72.676	9	1.3000	$4\bar{4}\bar{2}$	0.014
51.244	4	1.781	214	0.012	72.926	3	1.2961	242	0.022
51.652	3	1.768	$3\bar{0}\bar{4}$	0.014					

III. POWDER DIFFRACTION PATTERN ANALYSIS

A. Indexing and cell refinement

The indexing of the X-ray powder diffraction pattern of $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$ was performed by means of the computer program DICVOL (Boultif and Louër, 1991). The first 20 peaks' positions, with a maximal absolute error of 0.03° (2θ) were used as input data. One primitive monoclinic cell was found [$M(20) = 57$] very close to a B -centered orthorhombic lattice [$M(20) = 15$].

The peaks' positions were obtained after α_2 -stripping by means of the PROFILE program of the DIFFRAC-AT package (Socabim-Siemens). The data were calibrated externally with the refined zero shift of the Rietveld refinement process. The unit cell parameters were refined (Table I) with the complete powder diffraction data set (Table II). Intensities given in

Table II are obtained from the "observed intensities" of the Rietveld refinement.

B. Structure determination

The crystal structure of $\text{LiTiO}(\text{PO}_4)$ has been found (Nagorny *et al.*, 1991) in the orthorhombic $Pnma$ space group with the cell parameters: $a = 7.394(2)$, $b = 6.371(2)$, $c = 7.228(1) \text{ \AA}$. For $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$, three similar double cells (with $b_0 = 2b$) can be derived from this monoclinic cell. Figure 1 illustrates these three possibilities leading to three very close C -centered orthorhombic lattices,

$$a_{o1} = 7.383 \text{ \AA}, \quad b_{o1} = 12.691 \text{ \AA}, \quad c_{o1} = 7.323 \text{ \AA},$$

$$\gamma_{o1} = 89^\circ.94,$$

$$a_{o2} = 7.344 \text{ \AA}, \quad b_{o2} = 12.758 \text{ \AA}, \quad c_{o2} = 7.323 \text{ \AA},$$

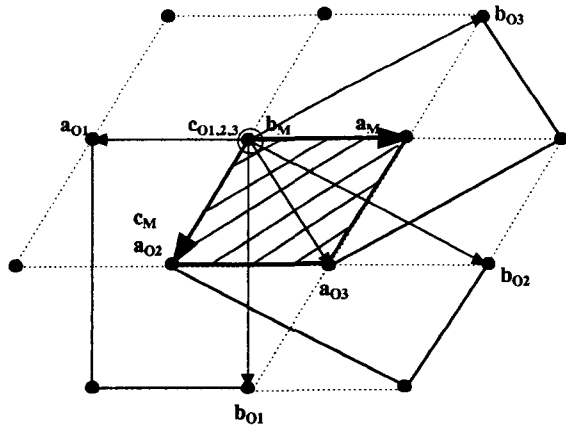


Figure 1. Pseudo *C*-orthorhombic lattices derived from the *P*-monoclinic cell.

$$\begin{aligned} \gamma_{02} &= 90^\circ.41, \\ a_{03} &= 7.338 \text{ \AA}, \quad b_{03} = 12.769 \text{ \AA}, \quad c_{03} = 7.323 \text{ \AA}, \\ \gamma_{03} &= 89^\circ.65. \end{aligned}$$

First, searches were done for a structural model of orthorhombic symmetry derived from $\text{LiTiO}(\text{PO}_4)$. Trials of Patterson-function deconvolution with the SHELXS86 program (Sheldrick, 1986) and with structure factors obtained with the ‘‘pattern matching’’ option of the FULLPROF program (Rodríguez-Carvajal, 1990) in the Laue class *mmm*, were unsuccessful.

Further attempts were done in the monoclinic Laue class *2/m*. A starting file of 146 structure factors of resolved reflexions selected in the range $10\text{--}90^\circ(2\theta)$ because they had no neighboring reflexion at less than $0.25 \times \text{FWHM}$ (full

TABLE III. Details of Rietveld refinement for $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$ in $P2_1/c$ space group.

Wavelength (Å)	$\lambda K_{\alpha 1} = 1.54060; \lambda K_{\alpha 2} = 1.54442$
Step scan increment ($^\circ 2\theta$)	0.02
2θ range ($^\circ$)	10–140
Program	FULLPROF
Zero point ($^\circ 2\theta$)	0.046(2)
Pseudo-Voigt function [$PV = \eta L + (1 - \eta)G$]	$\eta_0 = 0.62(2)$
Caglioti law parameters	$U = 0.013(2)$ $V = -0.001(2)$ $W = 0.0031(2)$
No. of reflections	645
No. of refined parameters	46
R_F	0.033
R_B	0.043
R_p	0.089
cR_p	0.122
cR_{wp}	0.120
χ^2	0.152
	2.04

Note: The *R* factors are defined as:

$$\begin{aligned} R_p &= \frac{\sum_i |y_i(\text{obs}) - y_i(\text{calc})|}{\sum y_i(\text{obs})}; \quad R_{wp} = \left[\frac{\sum_i w_i (y_i(\text{obs}) - y_i(\text{calc}))^2}{\sum_i w_i (y_i(\text{obs}))^2} \right]^{1/2}, \\ cR_p &= \frac{\sum_i |y_i(\text{obs}) - y_i(\text{calc})|}{\sum |y_i(\text{obs}) - y_i(\text{back})|}; \quad cR_{wp} = \left[\frac{\sum_i w_i (y_i(\text{obs}) - y_i(\text{calc}))^2}{\sum_i w_i (y_i(\text{obs}) - y_i(\text{back}))^2} \right]^{1/2}, \\ R_B &= \frac{\sum_k |I(\text{‘‘obs’’}) - I(\text{calc})|}{\sum_k I(\text{‘‘obs’’})}; \quad R_F = \frac{\sum_k |I(\text{‘‘obs’’})^{1/2} - I(\text{calc})^{1/2}|}{\sum_k I(\text{‘‘obs’’})^{1/2}}, \\ \chi^2 &= \frac{\sum_i w_i (y_i(\text{obs}) - y_i(\text{calc}))^2}{N - P}. \end{aligned}$$

width at half maximum) was constituted. A trial structure was found for Ni and Ti atomic sites in the space group $P2_1/c$. Successive difference Fourier syntheses using the SHELXL93 program (Sheldrick, 1993), and structure factor

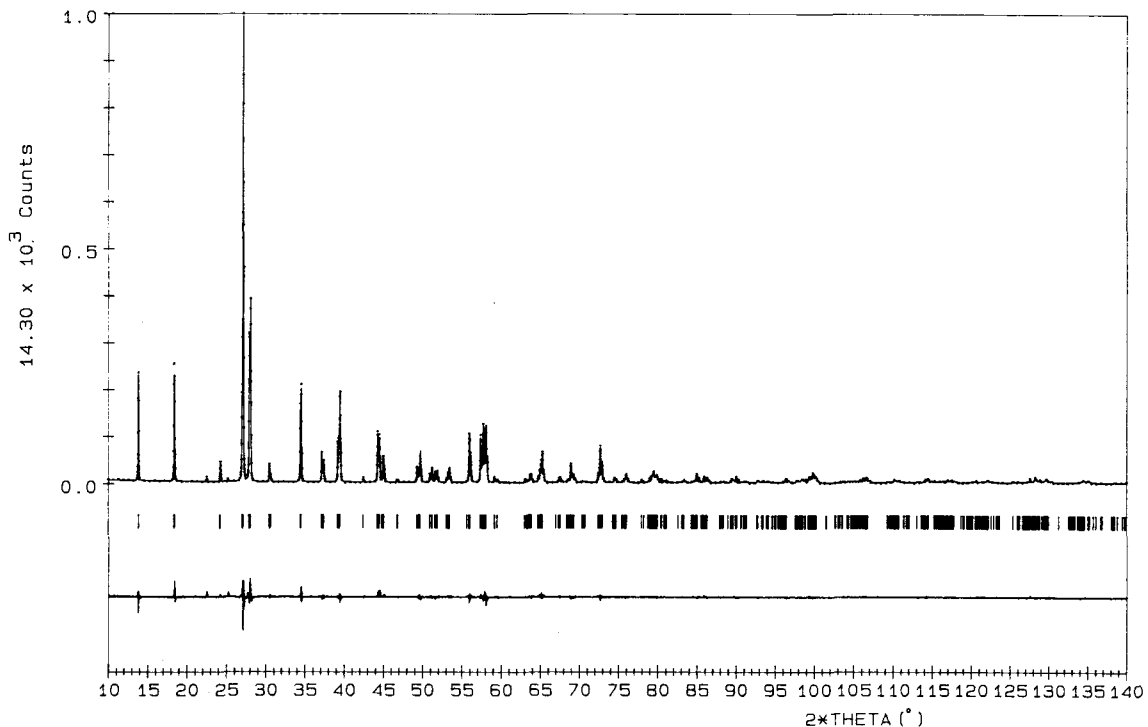


Figure 2. Final Rietveld plot of $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$. The upper trace illustrates the observed data (dots) and the calculated pattern (solid line). The vertical markers show positions calculated for Bragg reflections.

TABLE IV. Atomic coordinates and isotropic temperature factors with their estimated standard deviation (e.s.d.).

	Wyckoff site	Site symmetry	x	y	z	$B_{iso}(\text{\AA}^2)$
Ti	4e	1	0.7348(5)	0.2203(5)	0.5301(5)	0.37(7)
Ni	2a	$\bar{1}$	0	0	0	0.63(11)
P	4e	1	0.2462(9)	0.1237(9)	0.7508(8)	0.49(8)
O(1)	4e	1	0.7640(18)	0.1589(16)	0.7671(17)	0.2(2)
O(2)	4e	1	0.7766(20)	0.0031(16)	0.0939(21)	0.6(3)
O(3)	4e	1	0.4400(15)	0.2415(17)	0.8716(17)	0.2(3)
O(4)	4e	1	0.2579(17)	0.0086(17)	0.5816(18)	0.4(3)
O(5)	4e	1	0.0578(17)	0.2481(18)	0.1452(19)	0.3(3)

values improved by Rietveld calculations during structure determination progress, allowed us to locate P and O atoms ($R=0.15$).

C. Rietveld refinement

The structural model was further refined with the full profile Rietveld method using the program FULLPROF and the whole angular range 10–140°(2 θ). The following parameters were refined: 1 scale factor; 6 coefficients for the polynomial function describing the angular variation of the background; 1 parameter for the pseudo-Voigt shape function (with the value obtained the contribution of each peak 2 θ_k was considered inside the range 2 $\theta_k \pm 16$ FWHM); 3 parameters U , V , W to describe the angular dependence of the FWHM (Caglioti *et al.*, 1958); 1 asymmetric parameter; 4 unit-cell parameters; 1 zero point shift parameter; 21 fractional atomic coordinates; 8 isotropic temperature factors. The fit with these 46 refined parameters led to satisfactory profile factors ($R_p=0.089$; $R_{wp}=0.122$) and crystal structure model indicators ($R_B=0.043$; $R_F=0.033$).

TABLE V. Selected interatomic distances (Å) and angles (°).

P–O(2)	: 1.545(15)	O(2)–P–O(3)	: 109.4(1.6)
P–O(3)	: 1.517(14)	O(2)–P–O(4)	: 109.8(1.6)
P–O(4)	: 1.539(14)	O(2)–P–O(5)	: 109.5(1.6)
P–O(5)	: 1.527(15)	O(3)–P–O(4)	: 111.3(1.5)
		O(3)–P–O(5)	: 107.3(1.5)
		O(4)–P–O(5)	: 109.5(1.6)
Ti–O(1)	: 1.703(12)	O(1)–Ti–O'(1)	: 166(6)
Ti–O'(1)	: 2.231(13)	O(1)–Ti–O(2)	: 95.7(1.0)
Ti–O(2)	: 2.066(12)	O(1)–Ti–O(3)	: 100.4(1.0)
Ti–O(3)	: 1.902(13)	O(1)–Ti–O(4)	: 101.2(1.1)
Ti–O(4)	: 1.879(13)	O(1)–Ti–O(5)	: 94.8(1.1)
Ti–O(5)	: 2.103(15)	O'(1)–Ti–O(2)	: 74.9(7)
		O'(1)–Ti–O(3)	: 89.5(9)
		O'(1)–Ti–O(4)	: 86.5(8)
		O'(1)–Ti–O(5)	: 73.8(7)
		O(2)–Ti–O(3)	: 89.4(9)
		O(2)–Ti–O(4)	: 160(4)
		O(2)–Ti–O(5)	: 78.0(8)
		O(3)–Ti–O(4)	: 98.0(1.1)
		O(3)–Ti–O(5)	: 161(5)
		O(4)–Ti–O(5)	: 89.9(9)
		Ti–O(1)–Ti'	: 139.7(1.5)
Ni–O(1)	: 2×2.077(12)	O(1)–Ni–O(2)	: 77.9(8)
Ni–O(2)	: 2×2.083(16)	O(1)–Ni–O(5)	: 78.4(7)
Ni–O(5)	: 2×2.040(13)	O(2)–Ni–O(5)	: 79.0(9)

TABLE VI. Bond valence calculations for $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$ (calculated from Brese and O'Keeffe (1991), $S_i = \sum_j \exp((R_{ij} - d_{ij})/b)$ with $b=0.37$ Å and R_{ij} relative to O^{2-} : 1.815 Å for Ti^{4+} , 1.654 Å for Ni^{2+} , and 1.604 Å for P^{5+}).

	Ti	P	Ni	S_i	Σ_{theo}
O1	1.35		0.32*2	2.00	2
O1'	0.33				
O2	0.51	1.17	0.31*2	1.99	2
O3	0.79	1.27		2.06	2
O4	0.84	1.19		2.03	2
O5	0.46	1.23	0.35*2	2.04	2
S_i	4.28	4.86	1.96		
Σ_{theo}	4	5	2		

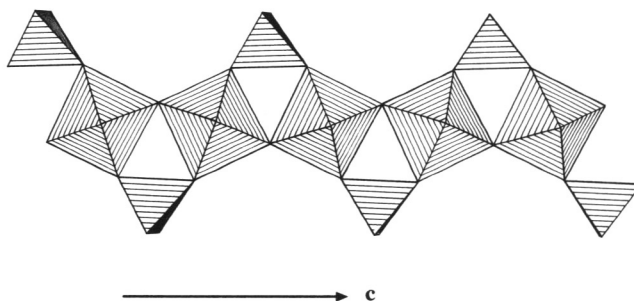


Figure 3. Chain of TiO_6 octahedra and PO_4 tetrahedra along c axis.

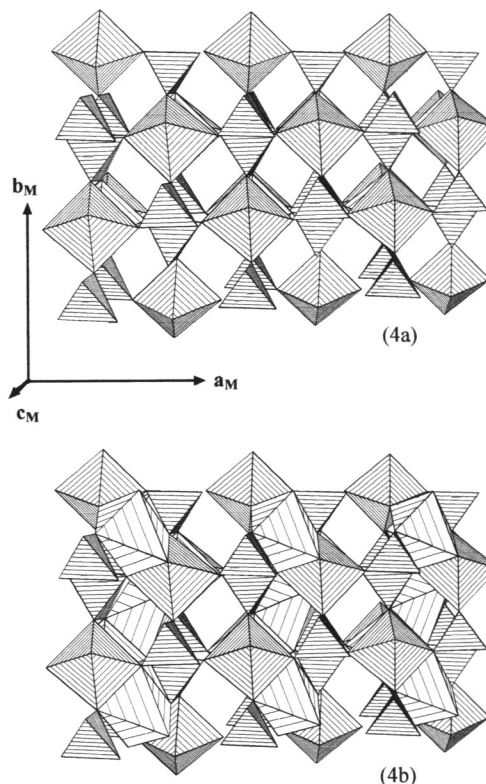


Figure 4. Three dimensional framework of TiPO_5 (a) and arrangement of the NiO_6 octahedra (b) in the structure of $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$.

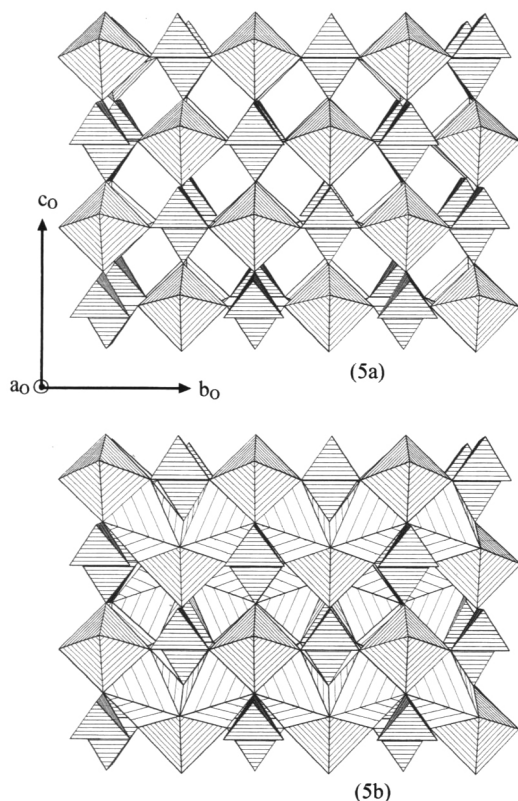


Figure 5. Three dimensional framework of TiPO_5 (a) and arrangement of the LiO_6 octahedra (b) in the structure of $\text{LiTiO}(\text{PO}_4)$.

The main crystallographic details of the Rietveld refinement are summarized in Table III. Figure 2 displays the agreement obtained between observed and calculated profiles. The final atomic parameters are given in Table IV and selected bond distances and angles in Table V. Standard deviations have been multiplied by 1.70 to correct local correlations (Berar and Lelann, 1991).

Valence bond sums (Table VI) based on bond-strength analysis (Brown and Altermatt, 1985; Brese and O'Keeffe, 1991) are in good agreement with the expected formal oxidation state of Ni^{2+} , Ti^{4+} , P^{5+} , and O^{2-} ions.

IV. DISCUSSION OF THE STRUCTURE

The dominant structural units in $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$ are chains of tilted corner-sharing TiO_6 octahedra running parallel to the c axis (Fig. 3). The O(1) oxygen atoms of the shared corners, not implied in (PO_4) tetrahedra, justify the oxyphosphate designation. Titanium atoms are displaced from the geometrical center of the octahedra resulting in alternating long (2.231) and short (1.703 Å) Ti–O(1) bonds. The four remaining Ti–O bond distances have intermediate values ranging between 1.879 and 2.103 Å. In one chain, the off-center displacement of Ti atoms induces creation of electric moments. As the space group $P2_1/c$ is centrosymmetric, there is compensation of antiparallel moments of adjacent chains, so $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$ is antiferroelectric.

Chains are linked by phosphate tetrahedra to constitute sheets parallel to (100). Isolated octahedral cavities of these

sheets (2a site), between two faces of two TiO_6 octahedra, are occupied by Ni atoms. Each PO_4 tetrahedron shares two oxygen atoms [O(2) and O(4)] with two TiO_6 consecutive octahedra of one chain and one oxygen atom O(5) with a neighboring parallel chain of the sheet. Links of sheets by remaining oxygen atom O(3) of phosphate tetrahedron lead to three-dimensional framework with empty channels parallel to the c axis [Fig. 4(b)].

The structure has to be compared with that of the orthorhombic LiTiPO_5 compound [Fig. 5(b)], which shows a similar framework-building TiPO_5 based on TiO_6 octahedra and PO_4 tetrahedra [Figs. 4(a) and 5(a)].

The $P2_1/c$ monoclinic deformation ($\mathbf{a}_M = -\mathbf{a}_0/2 + \mathbf{b}_0$, $\mathbf{b}_M = \mathbf{c}_0$, $\mathbf{c}_M = \mathbf{a}_0$) split the four Li atomic positions (4a site in $Pnma$) into: two positions of the 2a site occupied by Ni atoms, two other positions between 2b and 2d sites. The size of these two last sites is not compatible with insertion of cations. Particularly the 2d site leads to an octahedral environment (six O atoms between 2.06 and 2.27 Å), but the distance with two Ti atoms is too short (2.30 Å) (compared to the observed Ni–Ti length value 2.92 Å).

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