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Determination and Rietveld refinement of the crystal structure of $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ from powder X-ray and neutron diffraction

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The structure of the oxyphosphate $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ has been determined from conventional X-ray and neutron powder diffraction data. The parameters of the monoclinic cell (space group $P2_1/c$, $Z=4$), obtained from X-ray results, are: $a=6.3954(6)$ Å, $b=7.2599(6)$ Å, $c=7.3700(5)$ Å, and $\beta=90.266(6)^\circ$; those resulting from neutron study are: $a=6.3906(7)$ Å, $b=7.2568(7)$ Å, $c=7.3673(9)$ Å, and $\beta=90.234(7)^\circ$. Refinement by the Rietveld method using whole profile, leads to satisfactory reliability factors: $cR_{wp}=0.128$, $cR_p=0.100$, and $R_B=0.038$ for X-ray and $cR_{wp}=0.110$, $cR_p=0.120$, and $R_B=0.060$ for neutrons. The structure of $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ can be described as a TiOPO_4 framework constituted by chains of tilted corner-sharing TiO_6 octahedra running parallel to the c axis and cross linked by phosphate tetrahedra. In this framework, there are octahedral cavities occupied by Li and Ni atoms: Li occupies the totality of the 2a sites and Ni occupies statistically half of the 2b sites. Ti atoms are displaced from the center of octahedra units in alternating long (2.242 Å) and short (1.711 Å) Ti–O bonds along chains. © 2002 International Centre for Diffraction Data. [DOI: 10.1154/1.1515299]

Key words: $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$, titanyl oxyphosphate, structure determination, Rietveld refinement, powder diffraction, X-rays, neutrons

I. INTRODUCTION

Interest in titanium phosphates, both in glass and crystalline forms, for their properties as ionic conductors or non-linear optical materials, has led to a large number of studies. The structure of $\text{LiTiO}(\text{PO}_4)$ has been determined from single crystal (Nagorny *et al.*, 1991) and from powder (Robertson *et al.*, 1994) X-ray diffraction data. Recently we determined the structure of $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$ (Gravereau *et al.*, 1999). The existence of a solid state solution between these two compounds was envisaged in the way to create cation deficiency in $\text{LiTiO}(\text{PO}_4)$: $\text{Li}_{(1-2x)}\text{Ni}_x\text{TiO}(\text{PO}_4)$. We have shown that the compounds with $0 \leq x \leq 0.10$ crystallize in the orthorhombic system with $Pnma$ space group ($\text{LiTiO}(\text{PO}_4)$ type), whereas the compounds with $0.10 < x \leq 0.25$ crystallize in the monoclinic system with $P2_1/c$ space group. For $0.25 < x < 0.5$ the two phases $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ and $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$ are obtained simultaneously.

The present paper reports on the determination of $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ crystal structure from X-ray and neutron diffraction powder patterns.

II. EXPERIMENTAL

The oxyphosphate $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ was synthesized from aqueous solutions of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (I) and $(\text{NH}_4)_2\text{HPO}_4$

(II), Li_2CO_3 dissolved in dilute nitric acid solution (III), and solution of TiCl_4 diluted in ethanol (IV) as starting materials. The mixture (precipitate + solution) obtained by slow addition of (IV) in (I+II+III) at room temperature was dried at about 100 °C to remove the volatile compounds. The reaction is completely achieved after several thermal treatments of 24 h at 200, 500, 800, and 880 °C, respectively. The powder is ground before being submitted to each thermal treatment. The final product is green.

Efforts to grow single crystals have been performed by adding Li_3PO_4 or LiPO_3 as a flux to the prepared phase $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$. The mixture was heated at high temperatures up to 1300 °C. After cooling down the melting powder, at the rate of 5 °C/h, only single crystals of Li_3PO_4 and LiPO_3 were obtained. The X-ray pattern does not show the existence of $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$.

Consequently the structural determination was undertaken from the powder data. Both X-ray and neutron diffraction were used, in order to obtain advantages of the differences of scattering amplitudes for the two techniques.

X-ray diffraction data have been collected at room temperature on a Philips PW 3040 (θ – θ) diffractometer, with subsequent experimental conditions: Bragg–Brentano geometry; diffracted-beam graphite monochromator; $\text{Cu K}\alpha$ 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 corrected with a razor blade; sample spinner used; steps of $0.02^\circ(2\theta)$ over the

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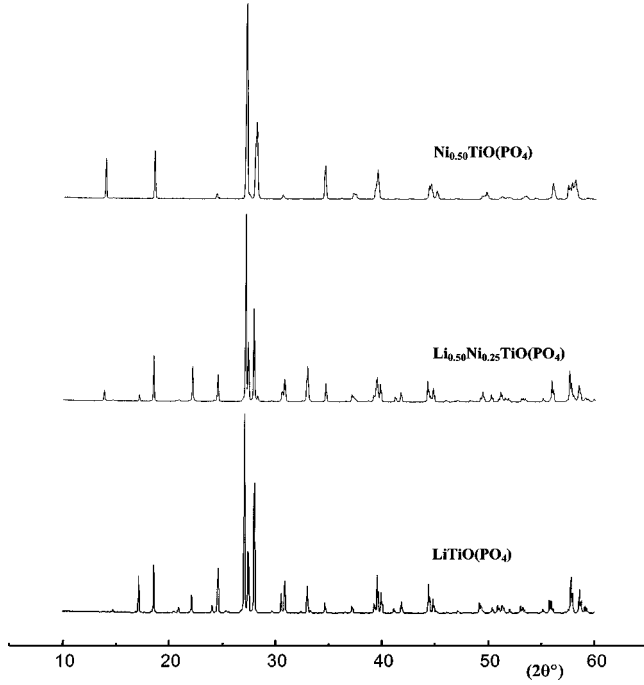


Figure 1. X-ray spectra of $\text{LiTiO}(\text{PO}_4)$, $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$, and $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$.

angular range 12° – 120° (2θ) with a fixed counting time of 30 s.

Neutron diffraction data have been collected at room temperature on the high resolution powder diffractometer 3T2 in Saclay (LLB, Orphée Reactor), with: $\alpha_1 = 10'$; focusing (335) Ge monochromator; $\lambda = 1.2251 \text{ \AA}$; 6° – 125.70° angular range of measurement (2θ), 0.05° step; 20 He^3 detectors, $\alpha_3 = 10'$.

III. STRUCTURE DETERMINATION

A. Powder diffraction pattern analysis

Figure 1 shows that the X-ray spectra of $\text{LiTiO}(\text{PO}_4)$ and $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ are close. The crystal structure of $\text{LiTiO}(\text{PO}_4)$ has been found (Nagorny *et al.*, 1991) orthorhombic with $Pnma$ space group and $a = 7.394(2) \text{ \AA}$, $b = 6.371(2) \text{ \AA}$, $c = 7.228(1) \text{ \AA}$ cell parameters at $T = 300 \text{ K}$. In a first step, for $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$, searches were done in an orthorhombic symmetry starting from $\text{LiTiO}(\text{PO}_4)$ as a structural model. The peak observed in the X-ray pattern around $2\theta \approx 13.86^\circ$ is not compatible with $Pnma$ space group and it was then attributed to $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$ as an impurity. Refinement of 35 parameters in this case (orthorhombic structural model of $\text{LiTiO}(\text{PO}_4)$ and $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$ for impurity) led to nonsatisfactory indicator values ($R_p = 0.161$, $R_{wp} = 0.213$, $cR_p = 0.224$, $cR_{wp} = 0.272$, $R_B(\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)) = 0.103$, and $R_B(\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)) = 0.235$). The presence of $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$ is found to about 4 percentage molar. In addition, a very deep analysis of the observed and calculated patterns of $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ shows some shift between calculated and observed peaks (e.g., around $2\theta \approx 22.14^\circ$). These problems led us to reconsider the starting hypothesis for this new compound.

TABLE I. X-ray powder diffraction data of $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ ($\lambda\alpha_1$, $\text{Cu} = 1.5406 \text{ \AA}$).

$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	d_{obs}	d_{calc}	$100/I_0$	hkl
13.86	13.85	6.389	6.395	7	100
17.14	17.14	5.173	5.172	4	011
18.48	18.49	4.801	4.799	25	110
22.14	22.07	4.015	4.028	19	11-1
	22.14		4.015		111
24.14	24.15	3.687	3.685	1	002
24.52	24.52	3.630	3.630	15	020
27.12	27.14	3.288	3.286	100	012
27.38	27.39	3.257	3.256	32	021
27.88	27.89	3.200	3.199	50	10-2
	27.90		3.198		200
28.24	28.27	3.160	3.157	3	120
30.52	30.53	2.929	2.928	6	11-2
	30.55		2.926		210
30.60	30.64	2.922	2.918	6	112
30.80	30.79	2.903	2.904	12	12-1
	30.84		2.900		121
32.86	32.88	2.726	2.724	12	21-1
32.96	32.98	2.718	2.716	19	211
34.66	34.69	2.588	2.586	10	022
37.12	37.14	2.422	2.421	4	20-2
37.30	37.32	2.411	2.410	3	202
37.44	37.47	2.402	2.400	2	12-2
	37.48		2.400		220
38.68	38.69	2.328	2.327	1	013
39.18	39.18	2.299	2.299	4	031
	39.23		2.296		21-2
39.44	39.40	2.285	2.287	12	212
	39.45		2.284		22-1
39.52	39.54	2.280	2.279	13	221
39.80	39.83	2.265	2.263	10	130
41.20	41.22	2.191	2.190	3	11-3
41.28	41.35	2.187	2.184	2	113
41.76	41.73	2.163	2.165	5	13-1
	41.77		2.163		131
44.26	44.28	2.046	2.045	11	310
44.48	44.53	2.037	2.035	4	023
44.80	44.80	2.023	2.023	7	032
45.96	45.99	1.975	1.973	2	31-1
46.80	46.80	1.941	1.941	1	12-3
47.06	47.08	1.931	1.930	1	13-2
	47.09		1.930		230
48.26	48.27	1.886	1.886	1	21-3
48.44	48.44	1.879	1.878	1	213
49.24	49.28	1.850	1.849	3	30-2
49.44	49.47	1.843	1.843	6	004
	49.49		1.842		302
49.56	49.59	1.839	1.838	3	320
50.24	50.27	1.816	1.815	4	040
50.92	50.97	1.793	1.792	2	31-2
51.12	51.15	1.787	1.786	6	014
	51.17		1.785		32-1
	51.17		1.785		312
51.26	51.27	1.782	1.782	4	321
51.54	51.56	1.773	1.773	2	10-4
51.66	51.69	1.769	1.768	2	104
51.86	51.88	1.763	1.762	2	041
53.08	53.12	1.725	1.724	2	033
53.24	53.19	1.720	1.722	2	11-4
	53.27		1.720		22-3
53.42	53.47	1.715	1.714	2	223
53.96	53.95	1.699	1.700	1	14-1
	53.98		1.699		141
55.12	55.13	1.666	1.666	2	13-3
55.92	55.97	1.644	1.643	11	024
	55.99		1.642		322
57.58	57.56	1.601	1.600	16	20-4
	57.57		1.600		330
	57.61		1.599		400
58.00	58.02	1.590	1.590	4	124
58.48	58.46	1.578	1.579	9	142
	58.47		1.578		240
	58.53		1.577		142
59.10	59.14	1.563	1.562	3	21-4
	59.14		1.562		331
	59.17		1.561		410
59.34	59.39	1.557	1.556	2	214
59.88	59.90	1.545	1.544	2	24-1
	59.96		1.543		241

TABLE II. Details of Rietveld refinement conditions for $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ — $P2_1/c$ space group.

	X-ray diffraction	Neutron diffraction
Wavelength (Å)	$\lambda K\alpha_1 = 1.54060$ $\lambda K\alpha_2 = 1.54442$	$\lambda = 1.22510$
Step scan increment ($^\circ 2\theta$)	0.02	0.05
2θ range ($^\circ$)	12–120	6–125.7
Program	FULLPROF	FULLPROF
Zero point ($^\circ 2\theta$)	−0.011 (2)	−0.025 (2)
Pseudo-Voigt function	$\eta = 0.59$ (1)	$\eta = 0.20$ (3)
$PV = \eta L + (1 - \eta)G$		
Caglioti parameters	$U = 0.045$ (3) $V = -0.010$ (3) $W = 0.005$ (1)	$U = 0.31$ (4) $V = -0.38$ (5) $W = 0.195$ (14)
No. of reflections	1021	1098
No. of refined parameter	44	52
Space group	$P2_1/c$	$P2_1/c$
a (Å)	6.3954(6)	6.3906 (7)
b (Å)	7.2599 (6)	7.2568 (7)
c (Å)	7.3700 (5)	7.3673 (9)
β ($^\circ$)	90.266 (6)	90.234 (9)
V (Å ³)	342.19(7)	341.7(1)
d_m	3.40	3.40
d_{calc}	3.44	3.44
Z	4	4
Atom number	9	9
R_F	0.021	0.036
R_B	0.036	0.060
R_p	0.074	0.049
R_{wp}	0.100	0.062
cR_p	0.102	0.110
cR_{wp}	0.128	0.120
χ^2	1.76	8.6

B. Indexing and cell refinement

The indexing of the X-ray powder diffraction pattern of $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ was performed by means of the computer program DICVOL (Boulton and Louër, 1991). The first 19 peak positions used were obtained after α_2 -stripping by means of the profile program of the Diffrac-AT package (Socabim–Siemens), with a maximal absolute error of $0.03^\circ(2\theta)$. There were no solutions in the orthorhombic system but a good monoclinic cell was found: $a = 7.360$ Å, $b = 7.247$ Å, $c = 6.386$ Å, and $\beta = 90.31^\circ$: $M(19) = 34.2$ and $F(19) = 46.3$ (0.0093; 44).

All observed reflections in neutron pattern (in particular peak at $2\theta \approx 13.86^\circ$) are compatible with this monoclinic solution, so a single phase has to be considered.

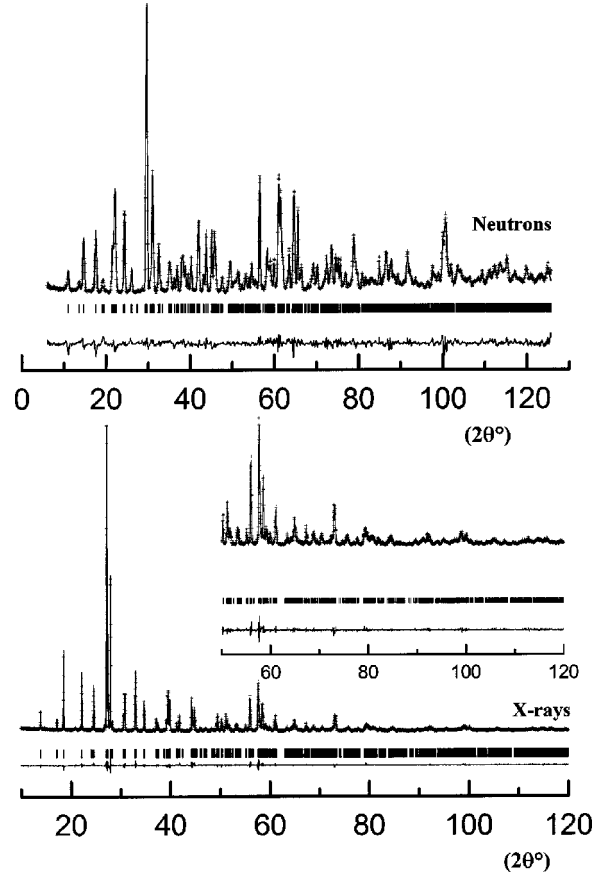


Figure 2. Final Rietveld plot of $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$. The upper symbols illustrate the observed data (cross) and the calculated pattern (solid line). The vertical markers show calculated positions of Bragg reflexions. The lower curve is the difference diagram. Some peaks of very low intensity, observed at about 14.8° , 21.5° , and 30° , in X-ray diagram are attributed to $\text{LiTi}_2(\text{PO}_4)_3$.

So further attempts were done in the monoclinic Laüe class $2/m$. After a global profile refinement using “Profile matching” option of FULLPROF program (Rodriguez-Carvajal, 1993), the examination of hkl reflections (reflection conditions: $(h01) h = 2n$; $(0k0) k = 2n$) leads to $P2_1/a$ space group. To work in the standard $P2_1/c$ space group we reverse a and c parameters. The final unit cell parameters of $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ are $a_m = 6.3954(6)$ Å, $b_m = 7.2599(6)$ Å, $c_m = 7.3700(5)$ Å, and $\beta_m = 90.266(6)^\circ$. These parameters are very close to $\text{LiTiO}(\text{PO}_4)$ ones ($a_o = 7.402$ Å, $b_o = 6.376$ Å, $c_o = 7.235$ Å, and $\gamma_o = 90^\circ$) with

TABLE III. Atomic coordinates and isotropic temperature factors with their estimated standard deviation (e.s.d.) in $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ (from neutron diffraction results).

	Wyckoff site	x	y	z	B_{iso} (Å ²)	Site occ
Ti	4e	0.762(3)	0.220(2)	0.332(2)	0.1(1)	1
Li	2a	0.000	0.000	0.000	2.7(5)	1
Ni	2b	0.500	0.000	0.000	1.9(2)	0.5
P	4e	0.249(2)	0.128(1)	0.374(2)	0.3(1)	1
O(1)	4e	0.748(2)	0.154(1)	0.111(1)	0.7(1)	1
O(2)	4e	0.261(2)	0.001(1)	0.206(1)	0.7(1)	1
O(3)	4e	0.252(2)	0.010(1)	0.548(1)	0.7(1)	1
O(41)	4e	0.446(3)	0.249(2)	0.876(2)	0.7(1)	1
O(42)	4e	0.055(2)	0.249(2)	0.366(2)	0.7(1)	1

TABLE IV. Selected interatomic distances (Å) and angles (°) in XO_6 ($X=Ti, Ni, Li$) octahedra and PO_4 tetrahedra from neutron diffraction: X–O distances are given in bold, O–O distances are given above the diagonal, and O–X–O angles are below.

TiO ₆	O1	O1	O2	O3	O41	O42
O1	1.696(14)	3.937(13)	2.853(13)	2.780(13)	2.838(20)	2.798(20)
O1	170.8(1.0)	2.253(14)	2.613(13)	2.838(13)	2.680(18)	2.765(20)
O2	98.3(8)	73.9(8)	2.062(15)	3.890(13)	2.678(20)	2.775(18)
O3	100.3(1.0)	85.9(8)	158.8(1.0)	1.895(15)	2.765(18)	2.796(18)
O41	97.6(1.3)	76.6(1.0)	81.0(1.0)	88.5(1.0)	2.062(15)	3.897(9)
O42	102.0(1.3)	83.0(1.0)	88.8(1.3)	94.9(1.3)	159.1(6)	1.901(13)
NiO ₆	O1	O1	O2	O2	O41	O41
O1	2.104(11)	4.208(13)	2.597(13)	3.382(20)	2.680(20)	3.176(18)
O1	180.0(1.0)	2.104(11)	3.382(20)	2.597(13)	3.176(18)	2.680(20)
O2	75.0(5)	105.0(1.0)	2.160(11)	4.320(13)	2.678(20)	3.251(18)
O2	105.0(1.0)	75.0(5)	180.0(1.0)	2.160(11)	3.251(18)	2.678(20)
O41	80.3(8)	99.7(8)	78.9(8)	101.1(8)	2.051(15)	4.102(15)
O41	99.7(8)	80.3(8)	101.1(8)	78.9(8)	180.0(8)	2.051(15)
LiO ₆	O1	O1	O2	O2	O42	O42
O1	2.129(11)	4.258(13)	2.597(13)	3.528(20)	2.798(20)	3.203(18)
O1	180.0(1.0)	2.129(11)	3.528(20)	2.597(13)	3.203(18)	2.798(20)
O2	72.7(5)	107.3(1.0)	2.250(11)	4.500(10)	2.775(18)	3.356(18)
O2	107.3(1.0)	72.7(5)	180.0(1.0)	2.250(11)	3.356(18)	2.775(18)
O42	81.6(8)	98.4(8)	79.2(8)	100.8(8)	2.102(15)	4.204(13)
O42	98.4(8)	81.6(8)	100.8(8)	79.2(8)	180.0(1.0)	2.102(15)
PO ₄	O2	O3	O41	O42		
O2	1.554(13)	2.520(10)	2.501(18)	2.522(18)		
O3	109.5(1.0)	1.540(13)	2.493(18)	2.522(18)		
O41	108.0(1.3)	107.9(1.3)	1.544(20)	2.495(23)		
O42	110.9(1.5)	111.3(1.3)	109.2(18)	1.516(20)		

$a_m \approx b_o$, $b_m \approx c_o$, $c_m \approx a_o$, $\beta_m = 90.266 \approx 90^\circ$. The difference is that some peaks in the orthorhombic system split into more peaks in the monoclinic system, e.g., the reflection (121)- $Pnma$ split into (211) and (21-1)- $P2_1/c$.

Because of this approach of all parameters, the starting atomic positions were those of $LiTiO(PO_4)$ with the following circular permutation:

$LiTiO(PO_4)-Pnma$	$Li_{0.50}Ni_{0.25}TiO(PO_4)-P2_1/c$
x_o	$x_m = y_o$
y_o	$y_m = z_o$
z_o	$z_m = x_o$

Let us note that the $Pnma$ -(4a) sites (0,0,0) are split into $P2_1/c$ -(2a) (0,0,0) and (2b) (1/2,0,0) sites, while $Pnma$ -(8d) sites $[x_o, y_o, z_o]$ are split into two $P2_1/c$ -(4e) sites: $[x_m, y_m, z_m]$ and $[1/2 - x_m, y_m, z_m]$.

C. Rietveld refinement

The above-described structural $P2_1/c$ model was refined, using X-ray data, with the full profile Rietveld method using the FULLPROF program and the whole angular range $12^\circ - 120^\circ$ (2θ). The following parameters were refined: scale factor; coefficients for the polynomial function describing the angular variation of the background (6 parameters); parameters U , V , W describing the full width of half maximum (FWHM) angular dependence (Caglioti *et al.*, 1958); parameter (η) for pseudo-Voigt shape function (the contribution of

the $2\theta_k$ Bragg peak was considered inside the range $2\theta_k \pm 16$ FWHM); 1 asymmetry parameter; unit-cell parameters a , b , c , β ; zero point shift parameter; fractional atomic coordinates (21 parameters), and isotropic temperature factors (9 parameters, a constrained model has been used for the refinement of B_{iso} of oxygen ions). The fit with these 44 refined parameters led to satisfactory profile ($R_p = 0.074$; $R_{wp} = 0.100$, $cR_p = 0.102$; $cR_{wp} = 0.128$) and crystal structure model indicators ($R_B = 0.036$; $R_F = 0.021$).

Refinements of the structure using neutron diffraction were done to confirm the distribution of Li and Ni in (2a) and (2b) $P2_1/c$ sites ($b_{Li} = -0.19 \times 10^{-12}$ cm, while $b_{Ni} = 1.03 \times 10^{-12}$ cm). The results are quite similar to those obtained using X-ray diffraction inside 2 e.s.d. for x , y , z parameters.

The X-ray powder diffraction data are presented in Table I. Main crystallographic details of the Rietveld refinement are summarized in Table II for the two powder diffraction techniques. Figure 2 displays the agreement obtained between observed and calculated profiles. The final atomic parameters are given in Table III and selected bond distances and angles in Table IV. Standard deviations have been multiplied by the Berar factor to correct local correlations (Bérar and Lelann, 1991).

IV. DISCUSSION OF THE STRUCTURE

The dominant structural units in the oxyphosphate $Li_{0.50}Ni_{0.25}TiO(PO_4)$ are chains of tilted corner sharing TiO_6 octahedra running parallel to the c axis (Figure 3). Titanium

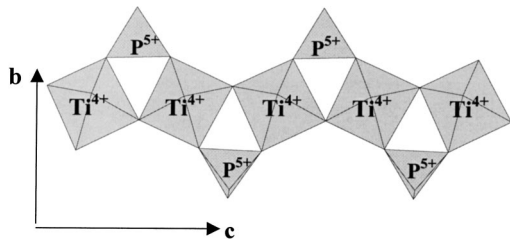


Figure 3. Ti–O–Ti–O– chain and PO₄ tetrahedra in Li_{0.50}Ni_{0.25}TiO(PO₄).

atoms are displaced from the geometrical center of the octahedra resulting in alternating long (2.242 Å) and short (1.711 Å) Ti–O1 bonds. The four remaining Ti–O bond distances have intermediate values ranging between 1.914 and 2.050 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 Li_{0.50}Ni_{0.25}TiO(PO₄) is antiferroelectric.

Titanium octahedra chains are linked by phosphate tetrahedra to constitute sheets parallel to (100). In this framework, there are octahedral cavities occupied by Li and Ni atoms: Li occupies the totality of the 2a sites and Ni occupies statistically half of the 2b sites. LiO₆ and NiO₆ octahedra share edges and form chains running parallel to *a* axis (Figure 4). Each PO₄ tetrahedron shares 2 oxygen atoms with two TiO₆ consecutive octahedra of one chain and one oxygen atom with a neighboring parallel chain of the sheet. Links of sheets by the remaining oxygen atom of phosphate tetrahedron lead to [TiOPO₄]ⁿ⁻ three-dimensional framework (Figure 5). The LiO₆ octahedra are distorted: four Li–O distances (Li–O(42): 2×2.120 Å and Li–O(1): 2×2.146 Å) are close to the calculated ones (2.14 Å) (Shannon and Prewitt, 1969); the two other distances (Li–O(2): 2×2.277 Å) are longer than the sum of ionic radii. NiO₆ octahedra are distorted; the Ni–O distances vary from 2.030 to 2.154 Å. The Ni–O(1) distances (2×2.090 Å) are very close to the calculated ones (2.10 Å); the Ni–O(41) and Ni–O(2) distances are, respectively, 2×2.030 Å and 2×2.154 Å.

Valence bond sums, $S_i = \sum \exp[(R_{ij} - d_{ij})/b]$ with $b = 0.37$ Å, based on bond-strength analysis (Brown and Altermatt, 1985; Brese and O’Keeffe, 1991) are in good agreement with the expected formal oxidation states of Li⁺ (0.88), Ni²⁺ (1.86), Ti⁴⁺ (4.21), P⁵⁺ (4.87), and O²⁻ (2.09) ions.

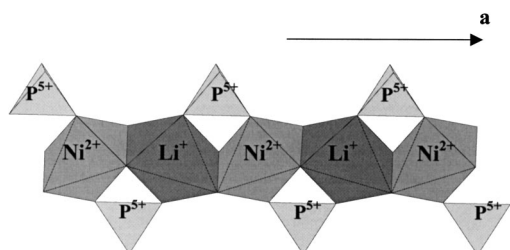


Figure 4. NiO₆–LiO₆–NiO₆–LiO₆– chain and PO₄ tetrahedra in Li_{0.50}Ni_{0.25}TiO(PO₄).

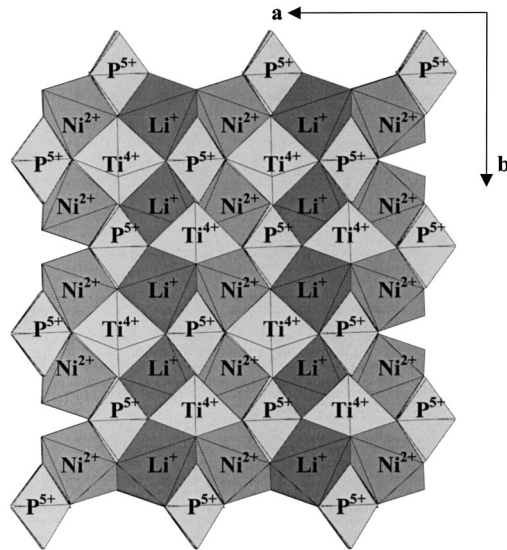


Figure 5. Structure of Li_{0.50}Ni_{0.25}TiO(PO₄).

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