Synthesis and X-ray characterization of Li(1–2x)NixTiO(PO4) (0

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Synthesis and X-ray characterization of $Li_{(1-2x)}Ni_xTiO(PO_4)$ $(0 \leqslant x \leqslant 0.50)$

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$Li_{(1-2x)}Ni_xTiO(PO_4)$ oxyphosphate powders were prepared from dilute solutions of $NiCl_2.6H_2O$, Li_2CO_3, $(NH_4)_2HPO_4$, and $TiCl_4$ in ethanol. The final temperature was 850 °C. $Li_{(1-2x)}Ni_xTiO(PO_4)$ oxyphosphates with $0 \leqslant x \leqslant 0.10$ crystallize in the orthorhombic system with space group Pnma, while those with $0.10 < x \leqslant 0.25$ crystallize in the monoclinic system with space group $P2_1/c$.

Key words: oxyphosphates, X-ray diffraction, $Li_{(1-2x)}Ni_xTiO(PO_4)$

I. INTRODUCTION

Interest in titanium phosphates, both in glassy and crystalline forms, as ionic conductors or nonlinear optical materials, has led to a large number of studies. The structures of $Ni_{0.50}TiO(PO_4)$ ($P2_1/c$ space group), $Li_{0.50}Ni_{0.25}TiO(PO_4)$ ($P2_1/c$ space group) and $LiTiO(PO_4)$ (Pnma space group) have been determined using powder X-ray diffraction for all three compounds (Gravereau *et al.*, 1999; Manoun *et al.*, 2002; Robertson *et al.*, 1994; Manoun *et al.*, 2003, in progress) and using single crystal XRD for $LiTiO(PO_4)$ (Nagornyi *et al.*, 1991). Solid solution between $LiTiO(PO_4)$ and $Ni_{0.50}TiO(PO_4)$ was envisaged as a way to create cation deficiency in $LiTiO(PO_4)$: $Li_{(1-2x)}Ni_xTiO(PO_4)$. A structural study of this series showed a limited solid solution between these two compounds. Our aim in this paper is to describe the preparation and characterization by X-ray diffraction of $Li_{(1-2x)}Ni_xTiO(PO_4)$ materials.

II. EXPERIMENTAL

$Li_{(1-2x)}Ni_xTiO(PO_4)$ oxyphosphate powders were prepared from dilute solutions of $NiCl_2.6H_2O$ (I), Li_2CO_3 (II), $(NH_4)_2HPO_4$ (III), and $TiCl_4$ in ethanol (IV). The slow addition of (IV) in a (I)+(II)+(III) mixture (with stirring) at room temperature induced precipitation. After drying at about 100 °C, the resulting amorphous powder was progressively heated up to 850 °C for 48 h. The final products were analyzed by XRD. The diffraction data were collected at room temperature on a Phillips PW 3040 (θ–θ) diffractometer: Bragg–Brentano geometry; diffracted-beam graphite monochromator; CuKα 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 was corrected with a razor blade; sample spinner used; using steps of 0.02° (2θ) over the large angular range 10–120° (2θ) with a fixed counting time of 20 or 30 s. Rietveld's profile analysis method was employed for refinements using the program FULLPROF (Rodriguez-Carvajal, 1990).

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III. RESULTS AND DISCUSSION

Figure 1 shows the X-ray powder diffraction patterns of $Li_{(1-2x)}Ni_xTiO(PO_4)$ $(0 \leqslant x \leqslant 0.25)$. For the composition $x = 0.10$, the pattern is similar to that of $LiTiO(PO_4)$. In $Li_{0.60}Ni_{0.20}TiO(PO_4)$, the peak observed at $2\theta \approx 13.85°$ is not compatible with the Pnma space group. This peak is more intense in the pattern for $Li_{0.50}Ni_{0.25}TiO(PO_4)$. Structural refinements of $Li_{(1-2x)}Ni_xTiO(PO_4)$ $(0 \leqslant x \leqslant 0.50)$ were undertaken on the powder data by the Rietveld method (Manoun *et al.*, 2003, in progress). They showed a solid solution in the domain $0 \leqslant x \leqslant 0.25$, with orthorhombic symmetry for $0 \leqslant x \leqslant 0.10$ and with monoclinic symmetry for $0.10 < x \leqslant 0.25$. $Li_{0.50}Ni_{0.25}TiO(PO_4)$ is the limit of the solid solution. Compositions with $0.25 < x < 0.50$ gave a mixture of $Li_{0.50}Ni_{0.25}TiO(PO_4)$ and $Ni_{0.50}TiO(PO_4)$. Table I shows the results obtained from the Rietveld profile analysis method for $Li_{(1-2x)}Ni_xTiO(PO_4)$.

Indexing of X-ray powder diffraction patterns for these compositions was performed by means of the computer program DICVOL (Boultif and Louër, 1991). The first 20 peak positions [25 peaks for $Li_{0.60}Ni_{0.20}TiO(PO_4)$], with a maximal absolute error of 0.03° (2θ), were used as input data. The unit cell parameters were refined (Table I) using the complete powder diffraction data sets (Tables II, III, IV, V). Intensities given in Tables II, III, IV, and V were obtained from the ''observed intensities'' of the Rietveld refinement.

All the observed reflections for the compositions $x \leqslant 0.10$ could be indexed in the space group Pnma (No. 62) in which phosphorous cations were located on the tetragonal sites (4c), the titanium cations were located on the octahedral sites (4c), and nickel and lithium cations were located on the octahedral sites (4a).

All the observed reflections for the compositions $0.10 < x \leqslant 0.25$ could be indexed in the space group $P2_1/c$ (No. 14). Phosphorous cations were located on the tetragonal sites (4e), titanium cations were located on the octahedral sites

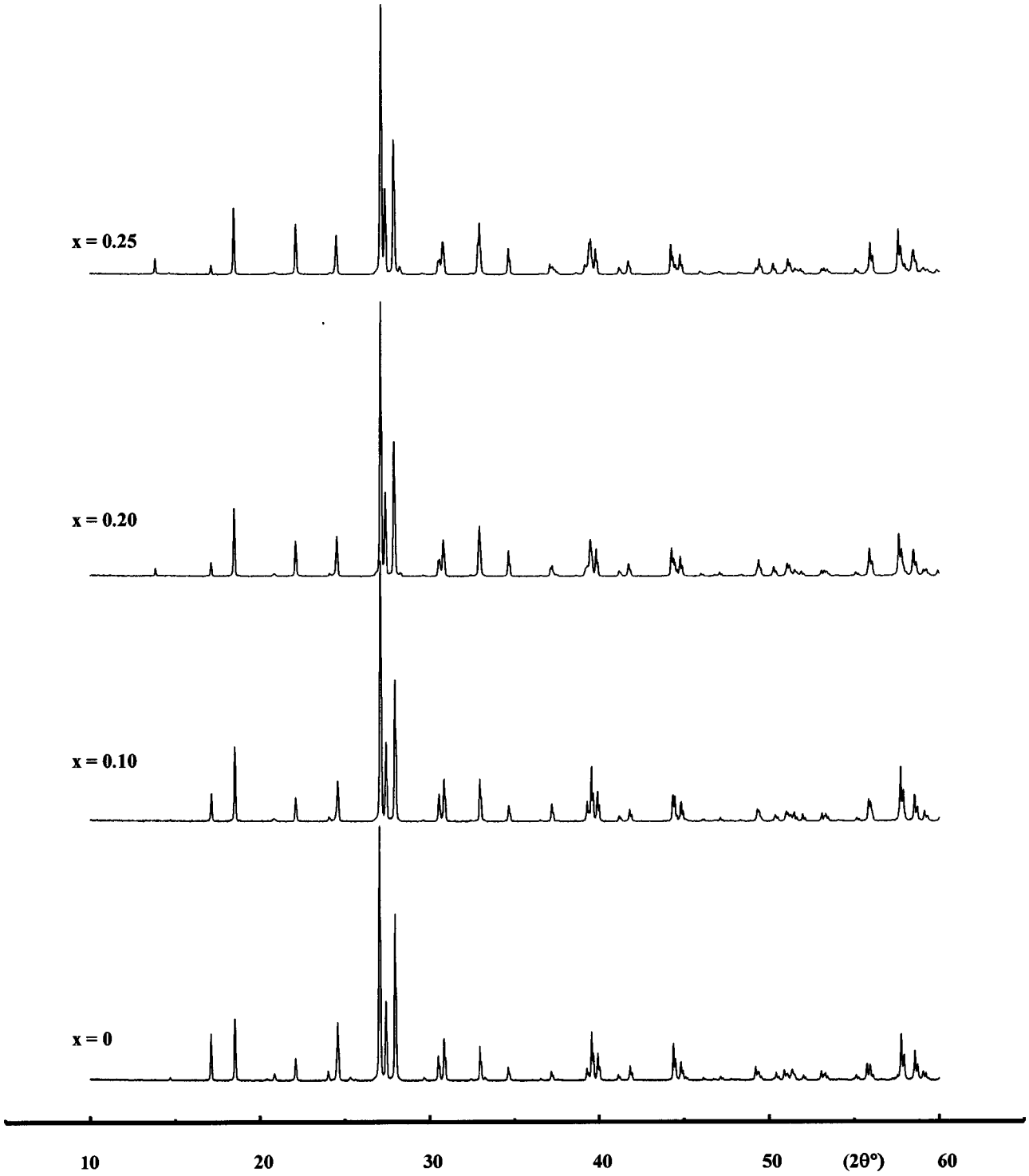

Figure 1. X-ray powder diffraction patterns of $Li_{(1-2x)}Ni_xTiO(PO_4)$ ($x=0;0.10;0.20;0.25$).

(4e), and nickel and lithium cations were located on the octahedral sites (2b) and (2a).

The structure of the compositions $0 \leqslant x \leqslant 0.25$ is based on a three-dimensional anionic framework constructed of chains of alternating TiO_6 octahedra and PO_4 tetrahedra, with the lithium and nickel atoms, distributed randomly except for $x=0.25$, in cavities in the framework. The dominant structural units in the compositions are chains of tilted corner-sharing TiO_6 octahedra running parallel to one axis. The parameters of the compositions $0 \leqslant x \leqslant 0.10$ are very close to those of the compositions $0.10 < x \leqslant 0.25$ ($a_m \approx b_o$, $b_m \approx c_o$, $c_m \approx a_o$, $\beta_m \approx 90°$). Figure 2 shows the cell parameter variations as a function of x for $Li_{(1-2x)}Ni_xTiO(PO_4)$ ($0 \leqslant x \leqslant 0.25$), where progressive substitution of lithium by nickel provokes a decrease of $a_o(c_m)$ and an increase of $b_o(a_m)$ and $c_o(b_m)$. The decrease of $a_o(c_m)$ is due to the substitution of Li ($r_i = 0.76$ Å) by Ni ($r_i = 0.69$ Å) (Shannon, 1976). Figure 3 shows the structure of $Li_{0.60}Ni_{0.20}TiO(PO_4)$, the substitution of Li by Ni is taking

TABLE I. Results obtained from Rietveld's profile analysis method for $Li_{(1-2x)}Ni_xTiO(PO_4)$. Figures of merit M and F of the DICVOL program are also given.

Nominal composition	Orthorhombic phase %	Monoclinic phase $Ni_{0.50}TiO(PO_4)$ %	**Orthorhombic phase formula and corresponding M and F factors**	Unit cell parameters
$LiTiO(PO_4)$	100	0	$LiTiO(PO_4)$ $M_{20}=92.3$, $F_{20}=112.8(0.0047; 38)$	$a_o=7.4015\ (2)$ Å $b_o=6.3756\ (2)$ Å $c_o=7.2350\ (3)$ Å
$Li_{0.80}Ni_{0.10}TiO(PO_4)$	100	0	$Li_{0.80}Ni_{0.10}TiO(PO_4)$ $M_{20}=45.8$, $F_{20}=62.8(0.0084; 38)$	$a_o=7.3892\ (2)$ Å $b_o=6.3832\ (2)$ Å $c_o=7.2429\ (2)$ Å
Nominal composition	Monoclinic phase %	Monoclinic phase $Ni_{0.50}TiO(PO_4)$ %	**Monoclinic phase formula and corresponding M and F factors**	
$Li_{0.60}Ni_{0.20}TiO(PO_4)$	100	0	$Li_{0.60}Ni_{0.20}TiO(PO_4)$ $M_{25}=51.4$, $F_{25}=85.9(0.0057; 51)$	$a_m=6.3904\ (2)$ Å $b_m=7.2532\ (2)$ Å $c_m=7.3759\ (3)$ Å $\beta_m=90.154\ (2)°$
$Li_{0.50}Ni_{0.25}TiO(PO_4)$	100	0	$Li_{0.50}Ni_{0.25}TiO(PO_4)$ $M_{20}=60.1$, $F_{20}=93.6(0.0051; 42)$	$a_m=6.3954\ (2)$ Å $b_m=7.2599\ (2)$ Å $c_m=7.3700\ (3)$ Å $\beta_m=90.266\ (2)°$
$Li_{0.33}Ni_{0.33}TiO(PO_4)$	68.67	31.33	$Li_{0.50}Ni_{0.25}TiO(PO_4)$	
$Li_{0.20}Ni_{0.40}TiO(PO_4)$	38.42	61.58	$Li_{0.52}Ni_{0.24}TiO(PO_4)$	

place in the sheet parallel to (100) plan for the orthorhombic phases and parallel to the (001) plan for the monoclinic phases; the $b_o(a_m)$ and $c_o(b_m)$ parameters increase with the strength of the $Ni^{2+}-Ni^{2+}$, $Ni^{2+}-Li^{+}$, $O^{2-}-O^{2-}$ electrostatic repulsions.

TABLE II. Powder diffraction data of $LiTiO(PO_4)$ ($\lambda k\alpha_1=1.5406$ Å).

$2\theta_{obs}$	$2\theta_{calc}$	d_{obs}	d_{calc}	$100I/I_0$	h k l
17.131	17.125	5.1719	5.1737	14	1 0 1
18.531	18.534	4.7842	4.7834	21	0 1 1
22.111	22.109	4.0170	4.0174	9	1 1 1
24.031	24.027	3.7002	3.7008	3	2 0 0
24.591	24.589	3.6172	3.6175	20	0 0 2
27.051	27.041	3.2936	3.2948	100	2 0 1
27.411	27.420	3.2512	3.2501	32	1 0 2
27.971	27.967	3.1873	3.1878	62	0 2 0
30.511	30.516	2.9275	2.9271	10	2 1 1
30.851	30.856	2.8960	2.8956	17	1 1 2
32.971	32.977	2.7145	2.7140	14	1 2 1
34.631	34.647	2.5881	2.5869	6	2 0 2
37.191	37.196	2.4156	2.4153	4	2 2 0
39.291	39.259	2.2912	2.2930	5	1 0 3
	39.295		2.2910		2 2 1
39.571	39.568	2.2756	2.2758	21	1 2 2
39.931	39.936	2.2559	2.2557	12	0 1 3
41.131	41.134	2.1929	2.1927	3	3 1 1
41.831	41.832	2.1578	2.1577	7	1 1 3
44.391	44.392	2.0391	2.0390	14	0 3 1
	44.410		2.0383		3 0 2
44.811	44.821	2.0209	2.0205	9	2 0 3
45.091	45.099	2.0090	2.0087	1	2 2 2
46.131	46.139	1.9661	1.9658	1	1 3 1
46.751	46.752	1.9415	1.9415	1	3 1 2
47.151	47.147	1.9260	1.9261	2	2 1 3
49.191	49.201	1.8508	1.8504	7	4 0 0
49.411	49.413	1.8430	1.8430	3	2 3 0

The difference between the orthorhombic and monoclinic phases is that some calculated peaks in the orthorhombic system split into more peaks in the monoclinic system, for example, 121(Pnma) split into 211 and 21-1 ($P2_1/c$). As

TABLE III. Powder diffraction data of $Li_{0.80}Ni_{0.10}TiO(PO_4)$ ($\lambda k\alpha_1=1.5406$ Å).

$2\theta_{obs}$	$2\theta_{calc}$	d_{obs}	d_{calc}	$100I/I_0$	h k l
17.127	17.129	5.1731	5.1725	9	1 0 1
18.507	18.513	4.7903	4.7888	24	0 1 1
22.107	22.102	4.0177	4.0186	9	1 1 1
24.067	24.068	3.6948	3.6946	2	2 0 0
24.567	24.562	3.6207	3.6214	16	0 0 2
27.067	27.072	3.2917	3.2911	100	2 0 1
27.407	27.405	3.2516	3.2519	30	1 0 2
27.947	27.933	3.1900	3.1916	52	0 2 0
30.547	30.536	2.9241	2.9252	11	2 1 1
30.827	30.834	2.8982	2.8976	18	1 1 2
32.947	32.951	2.7164	2.7161	18	1 2 1
34.647	34.657	2.5869	2.5862	7	2 0 2
37.207	37.197	2.4146	2.4152	7	2 2 0
39.287	39.225	2.2914	2.2949	7	1 0 3
	39.291		2.2912		2 2 1
39.527	39.532	2.2781	2.2778	22	1 2 2
39.887	39.89	2.2583	2.2582	13	0 1 3
41.187	41.181	2.1900	2.1903	3	3 1 1
41.787	41.794	2.1599	2.1596	6	1 1 3
44.327	44.337	2.0419	2.0414	13	0 3 1
	44.447		2.0366		3 0 2
44.807	44.809	2.0211	2.0210	10	2 0 3
45.087	45.084	2.0092	2.0093	1	2 2 2
46.087	46.091	1.9679	1.9676	1	1 3 1
46.787	46.782	1.9401	1.9403	1	3 1 2
47.127	47.13	1.9269	1.9268	2	2 1 3
48.307	48.298	1.8825	1.8829	1	3 2 1
49.287	49.289	1.8474	1.8473	7	4 0 0
49.427	49.388	1.8425	1.8438	3	2 3 0

TABLE IV. Powder diffraction data of $Li_{0.60}Ni_{0.20}TiO(PO_4)$ ($\lambda k\alpha_1 = 1.5406$ Å).

$2\theta_{obs}$	$2\theta_{calc}$	d_{obs}	d_{calc}	$100I/I_0$	h k l
13.851	13.847	6.3885	6.3902	2	1 0 0
17.131	17.132	5.1720	5.1716	4	0 1 1
18.491	18.489	4.7945	4.7950	22	1 1 0
22.071	22.073	4.0242	4.0238	1	1 1 −1
22.111	22.114	4.0171	4.0165	14	1 1 1
24.111	24.112	3.6882	3.6880	1	0 0 2
24.531	24.527	3.6260	3.6265	14	0 2 0
27.111	27.103	3.2865	3.2874	100	0 1 2
27.391	27.383	3.2535	3.2544	29	0 2 1
27.891	27.877	3.1963	3.1979	51	1 0 −2
	27.901		3.1952		2 0 0
28.271	28.272	3.1542	3.1541	1	1 2 0
30.531	30.526	2.9257	2.9261	5	1 1 −2
	30.587		2.9204	4	1 1 2
30.811	30.792	2.8997	2.9014	9	1 2 −1
	30.822		2.8987	7	1 2 1
32.951	32.896	2.7161	2.7205	11	2 1 −1
	32.953		2.7159	15	2 1 1
34.671	34.663	2.5852	2.5858	10	0 2 2
37.151	37.151	2.4181	2.4181	4	2 0 −2
	37.253		2.4117	3	2 0 2
37.471	37.465	2.3982	2.3986	1	1 2 −2
	37.483		2.3975		2 2 0
	37.516		2.3954		1 2 2
38.631	38.637	2.3288	2.3285	1	0 1 3
39.231	39.18	2.2946	2.2974	3	0 3 1
	39.241		2.2940		2 1 −2
39.351	39.339	2.2879	2.2885	10	2 1 2
	39.467		2.2814		2 2 −1
39.511	39.516	2.2790	2.2787	10	2 2 1
39.831	39.832	2.2614	2.2613	12	1 3 0
41.191	41.196	2.1898	2.1895	3	1 1 −3
41.271	41.266	2.1870	2.1860	1	1 1 3
41.751	41.734	2.1617	2.1625	5	1 3 −1
	41.757		2.1614		1 3 1
44.291	44.283	2.0435	2.0438	14	3 1 0
44.491	44.484	2.0347	2.0350	4	0 2 3
44.791	44.787	2.0218	2.0220	9	0 3 2
	45.024		2.0119		2 2 −2
46.011	46.013	1.9710	1.9709	1	3 1 −1
46.071	46.078	1.9686	1.9683	1	3 1 1
46.771	46.781	1.9407	1.9403	1	1 2 −3
46.851	46.844	1.9376	1.9379	1	1 2 3
47.091	47.083	1.9283	1.9286	1	1 3 −2
	47.098		1.9280		2 3 0
	47.125		1.9270		1 3 2
49.371	49.306	1.8444	1.8467	7	3 0 −2
	49.384		1.8440		0 0 4
	49.429		1.8424		3 0 2

TABLE V. Powder diffraction data of $Li_{0.50}Ni_{0.25}TiO(PO_4)$ ($\lambda k\alpha_1 = 1.5406$ Å).

$2\theta_{obs}$	$2\theta_{calc}$	d_{obs}	d_{calc}	$100I/I_0$	h k l
13.831	13.836	6.3976	6.3953	5	1 0 0
17.131	17.131	5.1719	5.1719	2	0 1 1
18.471	18.474	4.7996	4.7988	21	1 1 0
22.051	22.05	4.0278	4.0280	1	1 1 −1
22.111	22.122	4.0170	4.0150	19	1 1 1
24.131	24.132	3.6851	3.6850	1	0 0 2
24.511	24.504	3.6289	3.6299	13	0 2 0
27.111	27.116	3.2865	3.2858	100	0 1 2
27.371	27.366	3.2558	3.2564	30	0 2 1
27.871	27.864	3.1985	3.1993	50	1 0 −2
	27.879		3.1976		2 0 0
27.951	27.979	3.1896	3.1864	1	1 0 2
28.251	28.246	3.1564	3.1569	3	1 2 0
30.511	30.51	2.9275	2.9276	5	1 1 −2
30.591	30.615	2.9201	2.9178	4	1 1 2
30.751	30.761	2.9052	2.9043	9	1 2 −1
30.811	30.814	2.8997	2.8994	7	1 2 1
32.851	32.856	2.7241	2.7237	12	2 1 −1
32.951	32.954	2.7161	2.7159	17	2 1 1
34.651	34.66	2.5866	2.5860	11	0 2 2
37.111	37.11	2.4206	2.4207	5	2 0 −2
37.291	37.287	2.4094	2.4096	3	2 0 2
37.431	37.44	2.4007	2.4001	1	1 2 −2
	37.451		2.3994	1	2 2 0
38.651	38.662	2.3277	2.3270	1	0 1 3
39.151	39.149	2.2991	2.2992	2	0 3 1
39.191	39.198	2.2968	2.2964	3	2 1 −2
39.411	39.368	2.2845	2.2869	11	2 1 2
	39.422		2.2839		2 2 −1
39.511	39.506	2.2790	2.2792	10	2 2 1
39.791	39.795	2.2636	2.2633	12	1 3 0
41.191	41.19	2.1898	2.1898	4	1 1 −3
	41.312		2.1837		1 1 3
41.691	41.693	2.1647	2.1646	6	1 3 −1
	41.733		2.1626		1 3 1
44.251	44.246	2.0452	2.0454	14	3 1 0
44.491	44.496	2.0347	2.0345	4	0 2 3
44.771	44.768	2.0227	2.0228	9	0 3 2
	44.975		2.0140		2 2 −2
45.951	45.957	1.9734	1.9732	2	3 1 −1
46.071	46.069	1.9686	1.9686	1	3 1 1
46.771	46.766	1.9407	1.9409	1	1 2 −3
	46.876		1.9366		1 2 3
47.051	47.046	1.9298	1.9300	1	1 3 −2
	47.055		1.9297	1	2 3 0
	47.119		1.9272		1 3 2
48.231	48.227	1.8853	1.8855	1	2 1 −3
49.251	49.242	1.8486	1.8490	6	3 0 −2
	49.427		1.8425		0 0 4
	49.454		1.8415		3 0 2
49.551	49.549	1.8381	1.8382	1	3 2 0

described by Manoun *et al.* (Manoun *et al.*, 2002), the atomic positions of the monoclinic phases are close to those of the orthorhombic phases with the following circular permutation:

$LiTiO(PO_4)$, $Li_{0.80}Ni_{0.10}TiO(PO_4)$ Pnma	$Li_{0.60}Ni_{0.20}TiO(PO_4)$, $Li_{0.50}Ni_{0.25}TiO(PO_4)$ $P2_1/c$
x_0	$z_m \approx y_0$
y_0	$x_m \approx z_0$
z_0	$y_m \approx x_0$

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

IV. CONCLUSION

$Li_{(1-2x)}Ni_xTiO(PO_4)$ oxyphosphates have been prepared and characterized by X-ray diffraction. This study shows the existence of a solid solution in the domain $0 \leqslant x$

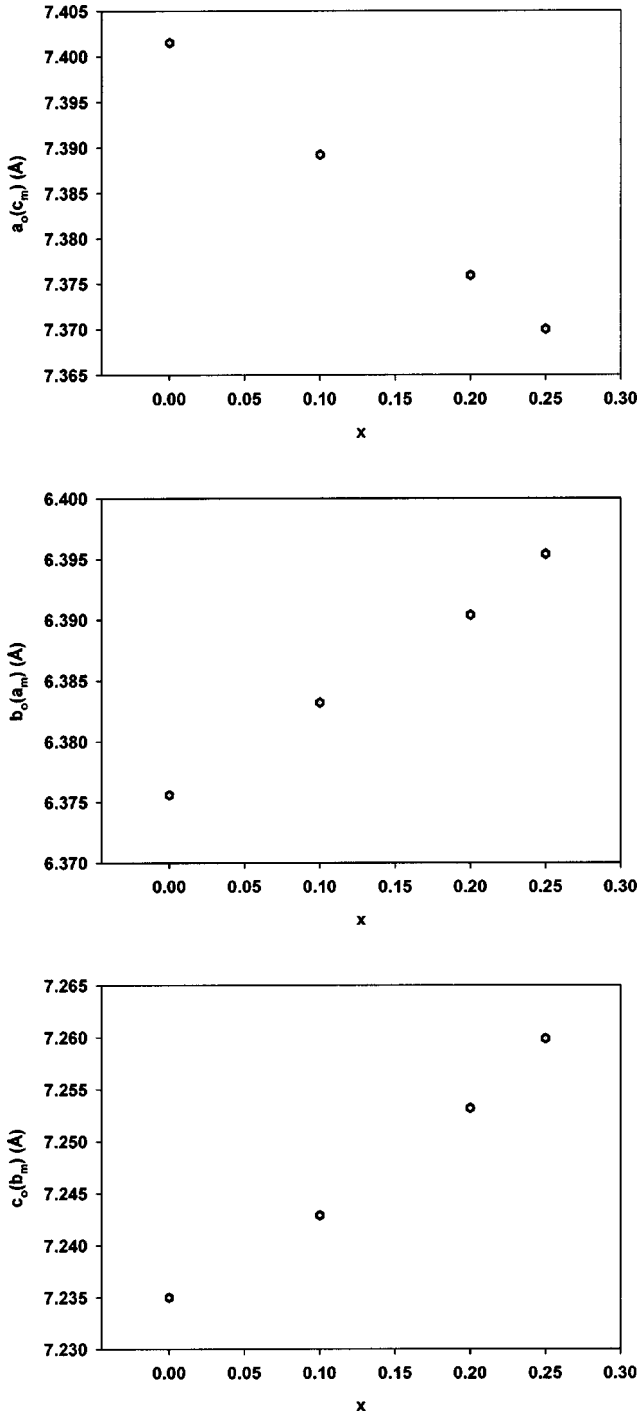

Figure 2. Cell parameter variations as a function of x for $Li_{(1-2x)}Ni_xTiO(PO_4)$ $(0 \leqslant x \leqslant 0.25)$, where progressive substitution of lithium by nickel provokes a decrease of $a_o(c_m)$ and an increase of $b_o(a_m)$ and $c_o(b_m)$.

$\leqslant 0.25$, with the orthorhombic symmetry for $0 \leqslant x \leqslant 0.10$ and with monoclinic symmetry for $0.10 < x \leqslant 0.25$. Compositions with $0.25 < x < 0.50$ give a mixture of $Li_{0.50}Ni_{0.25}TiO(PO_4)$ and $Ni_{0.50}TiO(PO_4)$.

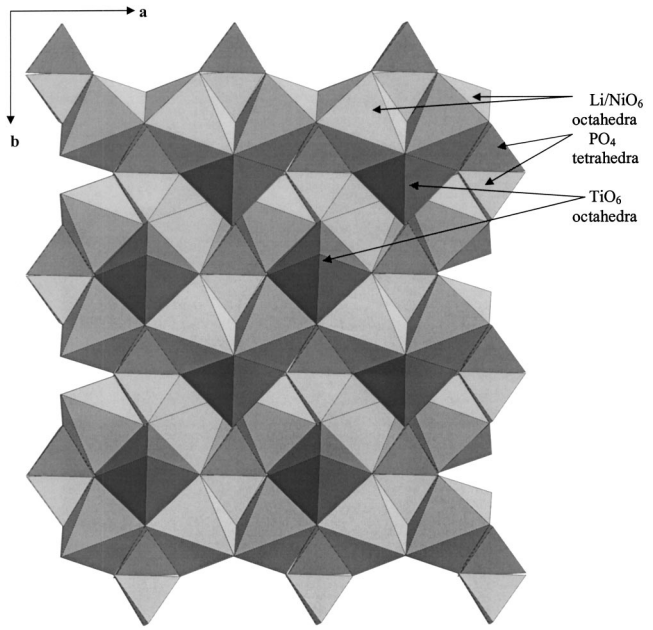

Figure 3. Structure of $Li_{0.60}Ni_{0.20}TiO(PO_4)$, Li^+, and Ni^{2+} are distributed randomly. The substitution of Li by Ni is taking place in the sheet parallel to (100) for the orthorhombic phases and parallel to (001) for the monoclinic phases.

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