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Crystal Structure of $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$

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Abstract

$\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ has been obtained by the conventional solid state reaction technique. Its crystal structure has been refined from X-ray powder diffraction data by the Rietveld method in $P2_1/c$ space group ($R_B=0.08$, $R_F=0.05$, $R_p=0.13$ and $R_{wp}=0.18$). The monoclinic unit cell parameters are: $a_m=6.400\pm0.001\text{\AA}$, $b_m=7.279\pm0.001\text{\AA}$, $c_m=7.385\pm0.001\text{\AA}$, $\beta=90.36\pm0.02^\circ$, $Z=4$. The structure is formed by a three dimensional framework of TiO_6 octahedra and PO_4 tetrahedra. TiO_6 octahedra form $-\text{Ti}-\text{O}-\text{Ti}-\text{O}-$ infinite chains parallel to the c axis. In these chains, very short $\text{Ti}-\text{O}$ bonds ($\sim 1.68\text{\AA}$) and very long ones ($\sim 2.26\text{\AA}$) are alternating. The cobalt and lithium atoms occupy octahedral cavities which form infinite chains of edge-sharing octahedra running parallel to the a axis.

INTRODUCTION

Titanium oxyphosphates $\text{M}^i\text{TiO}(\text{PO}_4)$ ($\text{M}^i = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{Tl}$) have been extensively studied for their nonlinear optical and electrooptical properties^{1, 2, 3, 4, 5, 6, 7}. The substitution of a monovalent ion by a divalent one led us to a new series of titanium oxyphosphates. Recently we determined the structure of $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$ ^{8,9} and $\text{Li}_{0.5}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$ ¹⁰. The present paper reports on the determination of $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ crystal structure from X-ray diffraction powder pattern.

EXPERIMENTAL

The powder of $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ was obtained from stoichiometric mixture of Li_2CO_3 , CoO , TiO_2 and $(\text{NH}_4)_2\text{HPO}_4$ heated respectively at 300°C , 600°C , 800°C and 1000°C with intermediate regrindings. The final product is pink. Diffraction data were collected at room temperature on a Philips PW 3040 (θ - θ) diffractometer using a graphite monochromator [$\text{CuK}\alpha$ radiation (40 kV, 40 mA)], the experimental conditions are presented in table 1.

STRUCTURAL DETERMINATION

The structure of $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ was refined by the Rietveld method using the Fullprof program¹¹. The initial atomic coordinates used for the refinement were those of the isostructural compound $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)$. After the refinement of 46 parameters (1 scale factor, 21 atomic parameters, 4 unit cell parameters, 1 zero shift error, 6 background parameters, 4 parameters of line profiles u , v , w and x ; 1 parameter of the Pseudo-Voigt function η ; linear combination of the Gaussian and Lorentzian functions, 2 asymmetrical

parameters, 5 isotropic temperature factors and the microabsorption coefficient), the conventional reliability factors were: $R_B=0.08$, $R_F=0.05$, $R_p=0.13$, $R_{wp}=0.18$, $CR_p=0.17$, and $CR_{wp}=0.22$. The cell parameters are: $a_m=6.400\pm0.001\text{\AA}$, $b_m=7.279\pm0.001\text{\AA}$, $c_m=7.385\pm0.001\text{\AA}$, $\beta=90.36\pm0.02^\circ$, $Z=4$. The atomic positions and the principal interatomic distances are given in tables 2 and 3, respectively. Figure 1 shows good agreement between observed and calculated patterns.

Table 1: Structural data and X-ray Rietveld refinement parameters

| | |
|--|---|
| Diffractometer | Philips PW 3040 |
| Wavelength (\AA) | $\lambda_{K\alpha 1} = 1.54060\text{\AA}$, $\lambda_{K\alpha 2} = 1.54442\text{\AA}$ |
| Step scan increment ($^\circ 2\theta$) | 0.02 |
| 2θ range ($^\circ$) | 10-120 |
| Zero point ($^\circ 2\theta$) | -0.0331 |
| Pseudo-voigt function | $PV = \eta L + (1-\eta)G$, $\eta = 0.49(2)$ |
| Caglioti law parameters | $U=0.0326(7)$; $V=0.0027(1)$; $W=0.0030(3)$ |
| No. of reflections | 1023 |
| No. of refined parameters | 46 |
| System; Space group | Monoclinic; $P2_1/c$ |
| a (\AA); b (\AA); c (\AA); β ($^\circ$) | 6.400; 7.279; 7.385; 90.36 |
| Volume (\AA^3); Z | 344.03; 4 |
| R ; R_B ; R_p ; R_{wp} ; CR_p ; CR_{wp} | 0.05; 0.08; 0.13; 0.18; 0.17; 0.22 |

Table 2: Atomic coordinates and isotropic temperature factors (\AA^2)

| Atom | Site | Sym site | x | y | z | Biso(\AA^2) | Occupancy |
|------|------|-----------|------------|------------|------------|------------------------|-----------|
| Li | 2a | $\bar{1}$ | 0.0000 | 0.0000 | 0.0000 | 0.49(2) | 1.00 |
| Co | 2b | $\bar{1}$ | 0.5000 | 0.0000 | 0.0000 | 0.38(3) | 0.50 |
| Ti | 4e | 1 | 0.7580(9) | 0.2205(7) | 0.3339(8) | 0.30(4) | 1.00 |
| P | 4e | 1 | 0.2512(6) | 0.1270(10) | 0.3743(12) | 0.40(3) | 1.00 |
| O(1) | 4e | 1 | 0.7538(1) | 0.1551(4) | 0.1146(3) | 0.29(2) | 1.00 |
| O(2) | 4e | 1 | 0.7362(12) | 0.0028(10) | 0.7968(9) | 0.29(2) | 1.00 |
| O(3) | 4e | 1 | 0.2491(13) | 0.4886(1) | 0.0528(5) | 0.29(2) | 1.00 |
| O(4) | 4e | 1 | 0.4514(10) | 0.2487(5) | 0.8696(2) | 0.29(2) | 1.00 |
| O(5) | 4e | 1 | 0.9548(1) | 0.7453(8) | 0.1324(15) | 0.29(2) | 1.00 |

The structure of $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ is similar to that of $\text{Li}_{0.50}\text{Ni}_{0.25}\text{TiO}(\text{PO}_4)^{10}$. It is formed by a three dimensional framework of TiO_6 octahedra and PO_4 tetrahedra. PO_4 groups are isolated each from other and connected to TiO_6 octahedra by corners. Each TiO_6 octahedron shares four corners of its basic plan with four PO_4 tetrahedra and the two other corners with two TiO_6 . TiO_6 octahedra form infinite chains $\text{Ti}-\text{O}-\text{Ti}-\text{O}$ parallel to the c axis (Figure 2). In these chains, a very short $\text{Ti}-\text{O}$ bonds (1.68\AA) and very long one (2.26\AA) are alternating. Lithium atoms fully occupy the site 2a, whereas cobalt atoms occupy statistically half of the site 2b. The cobalt and lithium octahedra form infinite chains of edge-sharing octahedra running parallel to the a axis (Figure 3). Each TiO_6 shares two adjacent faces with LiO_6 and CoO_6 .

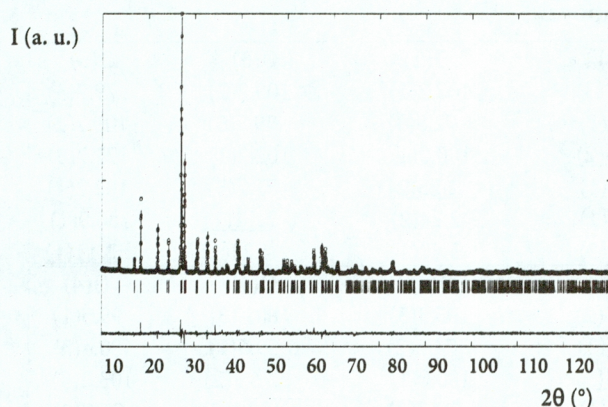


Figure 1: Observed (circle), calculated (solid line) and difference X-ray profiles of $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$

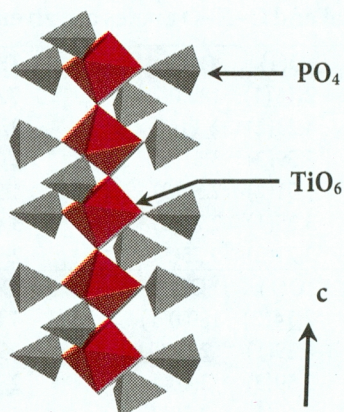


Figure 2: Chain of TiO_6 octahedra running parallel to the c axis and linked by PO_4 tetrahedra

The average P–O distance (1.57 Å) is close to those generally observed for isostructural oxyphosphates. Angles O–P–O vary from 106.3 to 110.6°. The distances of the equatorial Ti–O bonds, implying oxygens of PO_4 groups $[\text{Ti}-\text{O}(\text{PO}_4)]$ are fairly uniform with a mean of 1.94 Å. The distances Li–O and Co–O vary respectively from 2.11 to 2.25 Å and 2.07 to 2.14 Å. CoO_6 octahedra are isolated each from others ($d_{\text{Co}-\text{Co}} = 5.18 \text{ Å}$).

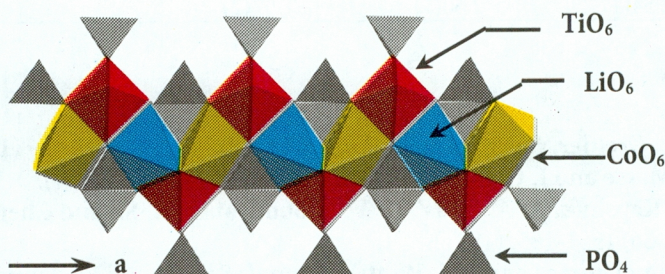


Figure 3: Chains of LiO_6 and CoO_6 octahedra running parallel to the a axis

Table 3: Interatomic distances (Å) and angles (°) for $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$

X-O (X = Li, Co, Ti, P) distances are underlined. O-O distances are given below the diagonal and O-X-O angles are given above

| LiO_6 | O(1) | O(1') | O(2) | O(2) | O(5) | O(5) |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| O(1) | <u>2.11(1)</u> | 180.0(1) | 72.8(3) | 107.2(1) | 100.2(2) | 79.7(3) |
| O(1') | 4.23(2) | <u>2.11(1)</u> | 107.2(1) | 72.8(3) | 79.7(3) | 100.2(2) |
| O(2) | 2.59(3) | 3.51(2) | <u>2.25(2)</u> | 180.0(1) | 102.2(1) | 77.7(3) |
| O(2) | 3.51(2) | 2.59(3) | 4.50(1) | <u>2.25(2)</u> | 77.7(3) | 102.2(1) |
| O(5) | 3.25(1) | 2.71(2) | 3.40(1) | 2.74(2) | <u>2.11(1)</u> | 180.0(1) |
| O(5) | 2.71(2) | 3.25(1) | 2.74(2) | 3.40(1) | 4.23(1) | <u>2.11(1)</u> |
| CoO_6 | O(1) | O(1') | O(2) | O(2) | O(4) | O(4) |
| O(1) | <u>2.14(2)</u> | 180.0(1) | 74.6(2) | 105.3(3) | 80.4(3) | 99.5(1) |
| O(1') | 4.29(1) | <u>2.14(2)</u> | 105.3(3) | 74.6(2) | 99.5(1) | 80.4(3) |
| O(2) | 2.59(3) | 3.40(1) | <u>2.13(3)</u> | 180.0(1) | 76.7(2) | 103.2(3) |
| O(2) | 3.40(1) | 2.59(3) | 4.27(1) | <u>2.13(3)</u> | 103.2(3) | 76.7(2) |
| O(4) | 2.72(2) | 3.22(1) | 2.61(1) | 3.30(2) | <u>2.07(1)</u> | 180.0(1) |
| O(4) | 3.22(1) | 2.72(2) | 3.30(2) | 2.61(1) | 4.14(1) | <u>2.07(1)</u> |
| TiO_6 | O(1) | O(1') | O(2) | O(3) | O(4) | O(5) |
| O(1) | <u>1.68(2)</u> | 172.6(3) | 98.5(1) | 99.9(2) | 98.5(2) | 99.5(1) |
| O(1') | 3.94(1) | <u>2.26(1)</u> | 74.1(2) | 87.2(2) | 79.4(3) | 81.7(3) |
| O(2) | 2.83(1) | 2.59(3) | <u>2.03(3)</u> | 160.6(4) | 80.8(1) | 89.3(3) |
| O(3) | 2.73(2) | 2.87(1) | 3.86(3) | <u>1.88(1)</u> | 90.8(2) | 93.1(2) |
| O(4) | 2.79(2) | 2.72(2) | 2.61(1) | 2.76(2) | <u>1.99(1)</u> | 160.5(3) |
| O(5) | 2.71(1) | 2.71(3) | 2.74(2) | 2.72(1) | 3.80(1) | <u>1.86(2)</u> |
| PO_4 | O(2) | O(3) | O(4) | O(5) | | |
| O(2) | <u>1.58(1)</u> | 110.6(3) | 106.3(2) | 110.3(2) | | |
| O(3) | 2.58(3) | <u>1.56(2)</u> | 109.8(3) | 108.0(1) | | |
| O(4) | 2.52(1) | 2.56(2) | <u>1.56(3)</u> | 111.5(2) | | |
| O(5) | 2.59(1) | 2.54(1) | 2.60(1) | <u>1.57(2)</u> | | |

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