

Crystal Structure of $\text{Pb}_{0.5}\text{Ti}_2(\text{PO}_4)_3$

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Abstract

$\text{Pb}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ has been prepared from solutions of the corresponding elements. Its crystal structure has been determined in $R\bar{3}$ space group, from X-ray powder diffraction data by Rietveld method. $R_p = 0,10$, $R_{wp} = 0,13$; $R_B = 0,06$. The parameters of the equivalent hexagonal cell are $a_h = 8.298 \pm 0.004 \text{ \AA}$ and $c_h = 22.70 \pm 0.06 \text{ \AA}$. The structure is formed by a 3D network of TiO_6 octahedra and PO_4 tetrahedra linked by corners. Pb^{2+} occupies half of the M1 site in an ordered manner. The Pb – O distance is 2.57 Å. TiO_6 octahedra are slightly distorted with Ti-O distances of 1.85; 1.87, 1.95 and 2.00 Å. PO_4 tetrahedra are normal, the P-O distances vary from 1.52 to 1.56; angles vary from 105 to 113°.

INTRODUCTION

$\text{M}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ phosphates (M = Mg, Ca, Co, Ni, Cu, Cd, Sr, Ba., Pb) have been extensively studied because of their low thermal expansion, catalytic and optical properties^{1,2,3,4} $\text{Pb}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ has been previously reported^{4,5} but no precise structural information has been given. The present paper reports on its crystal structure, refined by the Rietveld method from X-ray powder diffraction data.

EXPERIMENTAL

$\text{Pb}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ powder has been prepared from dilute solutions of $\text{Pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (I), $(\text{NH}_4)_2\text{HPO}_4$ (II) and TiCl_4 in ethanol (III) as reported for $\text{Co}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ ⁶. After addition of (III) in a (I + II) mixture at room temperature and slow evaporation at about 80°C, the resulting amorphous powder was heated at 200°C for 24h, at 600°C for 48h, and finally at 950°C for 48h. The X-ray diffraction data were collected at room temperature with a diffractometer using a graphite monochromator. The experimental conditions are given in table 1.

STRUCTURE ANALYSIS OF $\text{Pb}_{0.5}\text{Ti}_2(\text{PO}_4)_3$

At room temperature, the XRD pattern of $\text{Pb}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ can be indexed assuming a hexagonal cell ($a_h = 8.298 \pm 0.004 \text{ \AA}$; $c_h = 22.70 \pm 0.06 \text{ \AA}$). The observed reflections are compatible with the $R\bar{3}$ space group. The structural model was refined with the full profile Rietveld method using the program Fullprof⁷ and the whole angular range 10 – 120° (2 θ). The initial atomic coordinates were those of $\text{Ca}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ ^{4,8}. 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, 3 parameters U, V, W to

describe the angular dependence of the FWHM, 1 asymmetric parameter, 2 unit cell parameters, 1 zero point shift parameter, 19 fractional atomic coordinates, 8 isotropic temperature factors. The fit with these 42 refined parameters led to satisfactory profile factors ($R_p = 0.10$, $R_{wp} = 0.13$) and crystal structure model indicators ($R_B = 0.06$, $R_F = 0.05$). Details of the final refinement and atomic parameters are given in Tables 1 and 2. A comparison between the experimental and calculated X-ray diffraction data is presented in Figure 1. Table 3 collects selected bonds and distances.

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

Diffractometer	Philips PW 3040 / 00
Wavelength (Å)	$\lambda_{K\alpha 1}=1.5406$; $\lambda_{K\alpha 2}=1.5444$
Angular range (°) and Step width (°2 θ)	10 -120 and 0.02
Pseudo-Voigt function $PV=\eta L+(1-\eta)G$	$\eta = 0.71$
Caglioti law parameters	$U = 0.0128$; $V = -0.0051$; $W = 0.0039$
Number of reflections	927
Number of refined parameters	42
System	rhombohedral
Space group	$R\bar{3}$
a (Å); c (Å)	8.298 ; 22.70
d_{exp} ; d_{calc} (g/cm ³)	3.52; 3.56
R_F ; R_B	0.05; 0.06
R_p ; R_{WP}	0.10; 0.13
χ^2	2.5

The structure of $Pb_{0.5}Ti_2(PO_4)_3$ (Figure 2) can be described as a three-dimensional framework of PO_4 tetrahedra and TiO_6 octahedra sharing corners. The Pb^{2+} ions occupy half of the M(1) site with an ordered Pb^{2+} - vacancy along c axis. The Pb – O distance (2.57 Å) is very close to the sum of the ionic radii⁹ ($r_{Pb^{2+}} = 1.18\text{Å}$, $r_{O^{2-}} = 1.40\text{Å}$).

TABLE 2: Final positional and thermal parameters of $Pb_{0.5}Ti_2(PO_4)_3$

Atom	site	x	y	z	Biso(Å ²)	Occupancy
Pb	3a	0	0	0	2.3	0.5
Ti1	6c	0	0	0.1492	0.5	1
Ti2	6c	0	0	0.6461	0.8	1
P	18f	0.2837	-0.0002	0.2513	0.9	1
O1	18f	0.1795	0.1851	0.0916	1.1	1
O2	18f	0.1457	0.2123	0.3990	0.5	1
O3	18f	0.1743	0.9794	0.1944	0.5	1
O4	18f	0.9217	0.1332	0.3011	2.0	1

TABLE 3: Selected bond lengths (Å) and angles (°) for $\text{Pb}_{0.5}\text{Ti}_2(\text{PO}_4)_3$. The M-O distances are in bold, O-O distances are given below the diagonal and O-M-O angles are given above

Ti1	O1	O1	O1	O3	O3	O3
O1	2.00	2.62	2.62	3.83	2.70	2.87
O1	81.91	2.00	2.62	2.70	2.87	3.83
O1	81.91	81.91	2.00	2.87	2.83	2.70
O3	170.90	88.99	96.68	1.85	2.66	2.66
O3	88.99	96.68	170.90	92.27	1.85	2.66
O3	96.68	170.90	88.99	92.27	92.27	1.85
Ti2	O2	O2	O2	O4	O4	O4
O2	1.87	2.70	2.70	2.76	3.81	2.66
O2	92.77	1.87	2.70	3.81	2.66	2.76
O2	92.77	92.77	1.87	2.66	2.76	3.81
O4	92.53	174.51	88.39	1.95	2.66	2.66
O4	174.51	88.39	92.53	86.19	1.95	2.66
O4	88.39	92.53	174.51	86.19	86.19	1.95
Pb	O1	O1	O1	O1	O1	O1
O1	2.57	2.62	4.42	5.14	4.42	2.62
O1	61.31	2.57	5.14	4.42	4.42	2.62
O1	118.69	179.98	2.57	2.62	2.62	2.42
O1	180.00	118.69	61.31	2.57	2.62	4.42
O1	118.69	118.69	61.31	61.31	2.57	5.14
O1	61.31	61.31	118.69	118.69	180.00	2.57
P	O1	O2	O3	O4		
O1	1.52	2.52	2.49	2.46		
O2	110.84	1.53	2.51	2.58		
O3	108.73	109.86	1.54	2.52		
O4	105.49	112.87	108.87	1.56		

The PO_4 tetrahedra are rather regular with a weak angular dispersion of the O-P-O angles between 105 and 113° around the ideal value of 109.45°. The P - O distances are between 1.52 and 1.56 Å. The two titanium octahedral sites are slightly distorted but the mean Ti - O distances of 1.925 and 1.91 Å agree fairly with those found for $\text{Ca}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ ^{4,8}

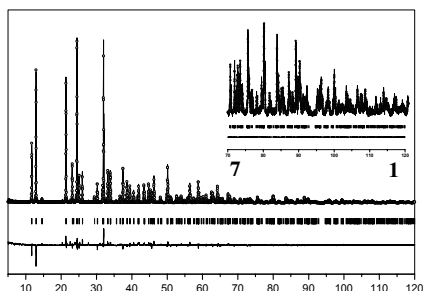


Figure 1: Experimental (points), calculated (solid line) and difference X-ray diffraction profiles of $Pb_{0.5}Ti_2(PO_4)_3$

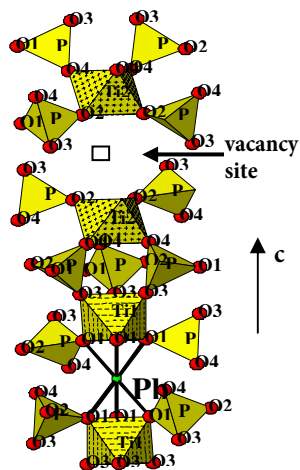


Figure 2: Fragment of the $Pb_{0.5}Ti_2(PO_4)_3$ structure

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