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Elaboration and Characterisation of two new Iron Titanium Phosphates $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$ and $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$

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Abstract

Two new phosphates $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$ and $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ have been prepared and characterised by X-ray diffraction, Mössbauer spectroscopy and magnetic measurements. $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$ is isostructural to the oxyphosphate $\text{Ni}_{0.5}\text{TiO}(\text{PO}_4)$ while $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ belongs to the Nasicon family. Their structures are formed by a 3 D framework of TiO_6 octahedra and PO_4 tetrahedra linked by corners. Fe^{2+} ions occupy isolated octahedral cavities situated between two TiO_6 octahedra. The magnetic and Mössbauer parameters are typical of Fe^{2+} ions in octahedral sites with high spin configuration $t_{2g}^4 e_g^2$.

INTRODUCTION

The study of phosphates with octahedral $[\text{TiO}_6]$ and tetrahedral $[\text{PO}_4]$ groups has been intensive since the discovery of the Nasicon¹ (Na super ionic conductor) and the KTP² (KTiOPO_4) materials. In the course of our investigation on these phosphate families we discovered two new phases: $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$ and $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$. The present paper describes their preparation and characterisation by X-ray diffraction, Mössbauer spectroscopy and magnetic measurements.

EXPERIMENTAL

The powders of $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$ and $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ were prepared by conventional solid state reaction techniques in silica tubes sealed under vacuum. Stoichiometric proportions of Fe_2O_3 , TiO_2 , TiP_2O_7 and Fe have been mixed, ground and heated progressively up to 800°C for $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$ and 950°C for $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$. These phosphates can also be obtained by exchange reaction.

The X-ray diffraction data were collected at room temperature with Philips PW 3040 (θ - θ) diffractometer using a graphite monochromator. The magnetic susceptibility determination was performed from 4.2 to 300 K in an applied magnetic field ($0 < H < 3\text{T}$), using a SQUID magnetometer (MPMS-S2, Quantum Design). Mössbauer measurements were performed using a constant acceleration HALDER-type spectrometer, with a $^{57}\text{Co}(\text{Rh})$ source in transmission geometry. Isomer shift values refer to α -Fe at 293 K. The spectra at 4.2 K and 293 K were recorded using a variable temperature cryostat.

RESULTS AND DISCUSSION

The structure of $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$ and $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ have been determined from powder X-ray diffraction data, by Rietveld refinement using Fullprof program³. Here we give a summary of this study, details of which will be published elsewhere. $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$ is isostructural to $\text{Ni}_{0.5}\text{TiO}(\text{PO}_4)$ ⁴. It crystallizes in the monoclinic system, space group $P2_1/c$ (No.14), with $a = 7.4039(3)$ Å, $b = 7.3838(3)$ Å, $c = 7.4083(3)$ Å, $\beta = 120.366(1)$, $Z = 4$. $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ is isostructural to $\text{Co}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ ⁵. At room temperature its XRD pattern can be indexed assuming a hexagonal cell with the following parameters: $a_h = 8.509 \pm 0.003$ Å and $c_h = 21.015 \pm 0.004$ Å.

The structures of these phosphates (Figures 1, 2) are formed by a tridimensional framework of TiO_6 octahedra and PO_4 tetrahedra linked by corners. The TiO_6 octahedra are rather regular and isolated from each other in $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$, while in $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$ they are linked together by corners and form $-\text{Ti}-\text{O}-\text{Ti}-\text{O}-$ infinite chains with alternating short and long Ti-O bonds. In both phases, Fe^{2+} ions occupy isolated octahedral sites located between two TiO_6 octahedra and sharing with them two faces.

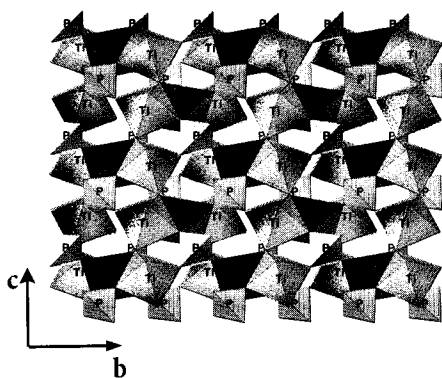


Figure 1: Structure of $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$

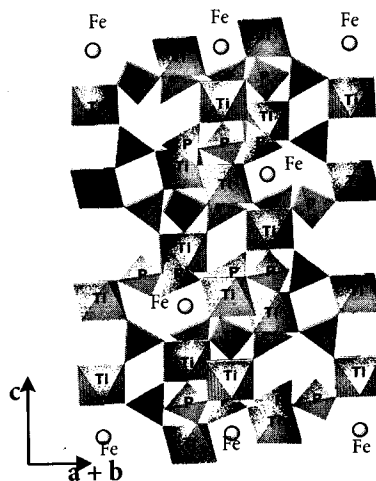


Figure 2: Structure of $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$

The thermal variation of the reciprocal magnetic susceptibility (Figure 3) between 4 and 300 K is linear. This paramagnetic behaviour shows that there is no magnetic interactions between divalent iron ions as expected from the structural study. Indeed the FeO_6 octahedra are isolated from each other and the $\text{Fe}^{2+}-\text{Fe}^{2+}$ distances are longer than 5 Å. The effective magnetic moment $\mu_{\text{eff}} = 5.13$ μB confirms the oxidation state (+II) of iron in octahedral sites with high spin configuration ($\text{Fe}^{2+}: t_2g^4 e_g^2$).

Figure 4 shows the Mössbauer spectra of $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$ and $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ measured at 4.2 K and 293 K. The values of isomer shift (δ), quadruple splitting (Δ) and width at half maximum (Γ) (Table I) are in agreement with the structural and magnetic results.

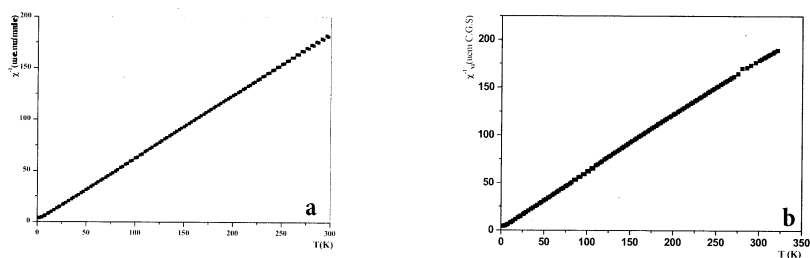


Figure 3: Thermal variation of the reciprocal susceptibility of $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$ (a) and $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ (b)

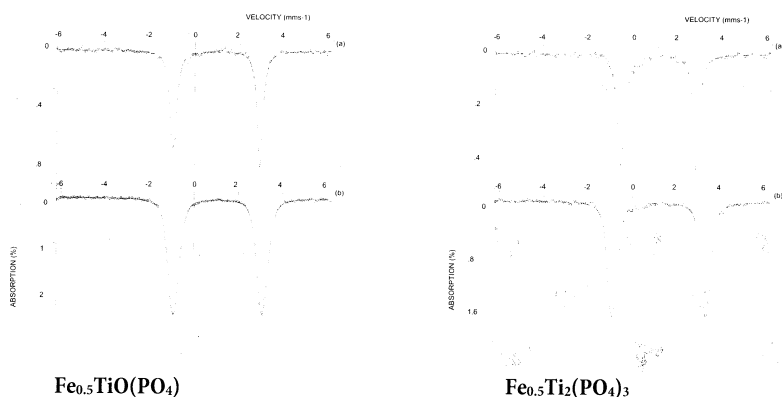


Figure 4: ^{57}Fe Mössbauer spectra of $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$ and $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ measured at 4.2 K (a) and 293 K (b)

Table 1: Mössbauer parameters of $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$ and $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$

Compound	T (K)	$\delta \pm 0.01$ (mm.s^{-1})	$\Delta \pm 0.01$ (mm.s^{-1})	$\Gamma_2 \pm 0.01$ (mm.s^{-1})	$\Gamma_1 \pm 0.01$ (mm.s^{-1})
$\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$	293	1.11	3.85	0.28	0.38
$\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$	4.2	1.24	4.02	0.30	0.30
$\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$	293	1.26	3.32	0.38	0.32
$\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$	4.2	1.36	4.21	0.30	0.30

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