

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

S. BENMOKHTAR<sup>1</sup>, A. EL JAZOULI<sup>1</sup>, J.P.CHAMINADE<sup>2</sup>, P. GRAVEREAU<sup>2</sup>, A. WATTIAUX<sup>2</sup>, L. FOURNES<sup>2</sup> and J.C. GRENIER<sup>2</sup>

<sup>1</sup>LSMS, UFR Sciences des Matériaux Solides, Faculté des Sciences Ben M'Sik-UH2M, Boulevard Idriss El Harti, B.P. 7955 Casablanca, Morocco.

<sup>2</sup>Institut de Chimie de la Matière Condensée de Bordeaux, ICMCB CNRS, 87, Av. Dr. Schweitzer, 33608 Pessac, France.

### 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  $\text{TiO}_6$  octahedra and  $\text{PO}_4$  tetrahedra linked by corners.  $\text{Fe}^{2+}$  ions occupy isolated octahedral cavities situated between two  $\text{TiO}_6$  octahedra. The magnetic and Mössbauer parameters are typical of  $\text{Fe}^{2+}$  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 Nasicon<sup>1</sup> (Na super ionic conductor) and the KTP<sup>2</sup> ( $\text{KTiOPO}_4$ ) 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  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{TiP}_2\text{O}_7$  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 ( $\theta$ - $\theta$ ) diffractometer using a graphite monochromator. The magnetic susceptibility determination was performed from 4.2 to 300 K in an applied magnetic field ( $0 < H < 3T$ ), 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  $\alpha$ -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 program<sup>3</sup>. 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  $\text{Ni}_{0.5}\text{TiO}(\text{PO}_4)$ <sup>4</sup>. It crystallizes in the monoclinic system, space group  $\text{P}2_1/c$  (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  $\text{Co}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ <sup>5</sup>. 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  $\text{TiO}_6$  octahedra and  $\text{PO}_4$  tetrahedra linked by corners. The  $\text{TiO}_6$  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,  $\text{Fe}^{2+}$  ions occupy isolated octahedral sites located between two  $\text{TiO}_6$  octahedra and sharing with them two faces.

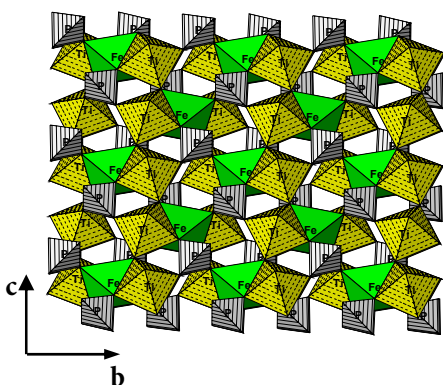


Figure 1: Structure of  $\text{Fe}_{0.5}\text{TiO}(\text{PO}_4)$

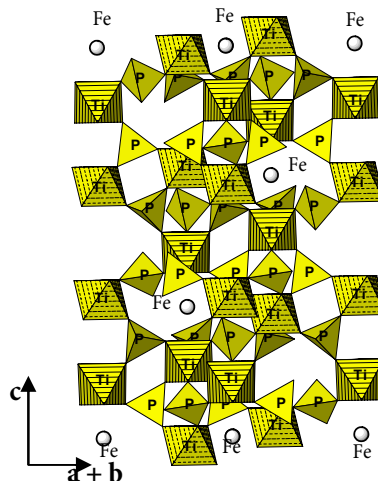


Figure 2: Structure of  $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$

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  $\text{FeO}_6$  octahedra are isolated from each other and the  $\text{Fe}^{2+}-\text{Fe}^{2+}$  distances are longer than  $5$  Å. The effective magnetic moment  $\mu_{\text{eff}} = 5.13$   $\mu\text{B}$  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 ( $\delta$ ), quadruple splitting ( $\Delta$ ) and width at half maximum ( $\Gamma$ ) (Table I) are in agreement with the structural and magnetic results.

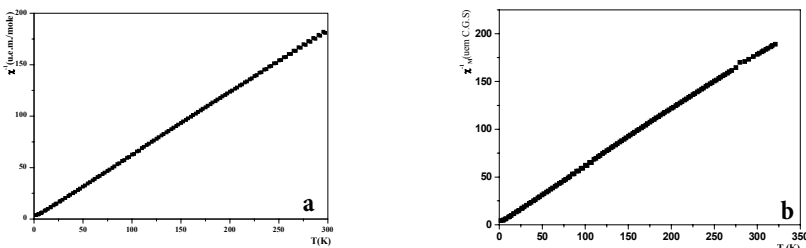


Figure 3: Thermal variation of the reciprocal susceptibility of  $Fe_{0.5}TiO(PO_4)$  (a) and  $Fe_{0.5}Ti_2(PO_4)_3$  (b)

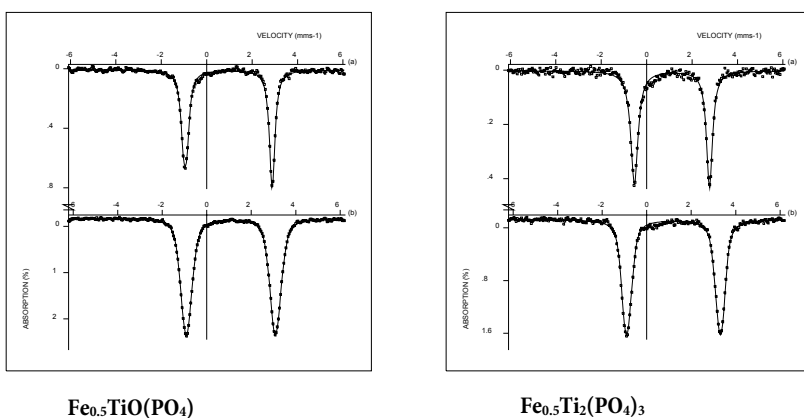


Figure 4:  $^{57}Fe$  Mössbauer spectra of  $Fe_{0.5}TiO(PO_4)$  and  $Fe_{0.5}Ti_2(PO_4)_3$ , measured at 4.2 K (a) and 293 K (b)

Table 1: Mössbauer parameters of  $Fe_{0.5}TiO(PO_4)$  and  $Fe_{0.5}Ti_2(PO_4)_3$

Compound	T (K)	$\delta \pm 0.01$ ( $mm.s^{-1}$ )	$\Delta \pm 0.01$ ( $mm.s^{-1}$ )	$\Gamma_2 \pm 0.01$ ( $mm.s^{-1}$ )	$\Gamma_1 \pm 0.01$ ( $mm.s^{-1}$ )
$Fe_{0.5}TiO(PO_4)$	293	1.11	3.85	0.28	0.38
$Fe_{0.5}TiO(PO_4)$	4.2	1.24	4.02	0.30	0.30
$Fe_{0.5}Ti_2(PO_4)_3$	293	1.26	3.32	0.38	0.32
$Fe_{0.5}Ti_2(PO_4)_3$	4.2	1.36	4.21	0.30	0.30

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