# 57-Fe Mössbauer and magnetic studies of a new diphosphate $Zn_5Fe_2(P_2O_7)_4$



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#### Abstract

Fe<sup>2+</sup> ions in Fe<sub>7</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>4</sub> were substituted by Zn<sup>2+</sup>and the magnetic properties and Mössbauer spectra of the new material were studied. The obtained sample of Zn<sub>5</sub>Fe<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>4</sub> is isostructural with the parent Fe<sub>7</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>4</sub>, which is orthorhombic with a C222<sub>1</sub> space group. Magnetometry shows that the Néel temperature is T<sub>N</sub> = 15.4(1) K, which is in accordance with Mössbauer measurements performed at RT and 4.2 K.

Keywords Diphosphate · Mössbauer spectrometry · Magnetometry

## **1** Introduction

Phosphates exhibit various useful properties for industrial applications. However, according to the World Health Organization, the current processes in the phosphate industry generate significant amounts of solid waste containing dangerous substances that are known to be very harmful for the environment and health [1]. The need for novel phosphate-based materials and

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new production techniques that might reduce the environmental and health impact is therefore well recognized worldwide. Morocco is one of the major producers of phosphates worldwide, and the present investigation is in line with the national strategic plan for the valorization of phosphates [2]. These aspects render phosphates in general worthy of scientific studies. Different types of zinc-iron phosphates have shown interesting magnetic properties [3, 4], so that further investigations of their magnetism are desirable. In the present work, we have focused on  $[Zn^{II}{}_{5}Fe^{III}{}_{2}(P_{2}O_{7})_{4}]$ , a  $Zn^{2+}$  compound belonging to the pyrophosphate (diphosphate) family of compounds, for which the mixed-valence iron species  $Fe^{II}{}_{5}Fe^{III}{}_{2}(P_{2}O_{7})_{4}$  (or, in a simplified way,  $Fe_{7}(P_{2}O_{7})_{4}$ ) can be considered the parent species, in which the Fe<sup>II</sup> is replaced by  $Zn^{II}$ .

## 2 Experimental

The sample was prepared by a solid-state reaction route at high temperature in air [5]. The socalled "dry way" method followed the following procedures: Stoichiometric amounts of ZnO,  $Fe_2O_3$  and  $(NH_4)HPO_4$  were used as starting materials. After milling for one hour, the solid mixture was heat-treated at temperatures up to 850 °C for 24 h. The heat treatment was interrupted periodically for grinding to ensure the homogeneity of the sample.



Fig. 1 Crystal structure of Zn<sup>II</sup><sub>5</sub>Fe<sup>III</sup><sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>4</sub>: Fe in yellow, Zn in grey, P in violet and O in red

	IS (mm/s)	QS (mm/s)	B (T)	WID (mm/s)	%
RT	0.43(1)	0.73(2)	_	0.35(1)	95.1(2)
	0.43(1)	1.39(1)	_	0.20(1)	3.7(2)
	1.26	2.39	_	0.63(1)	1.2(2)
4.2 K	0.53(1)	-0.028(1)	52.8(1)	0.65(15)	92.8(2)
	0.60(1)	0.46(1)	-	1.85(1)	7.2(2)

Table 1 Mössbauer parameters resulting from the fits to the spectra shown in Fig. 2

IS Isomer shift relative to metallic iron at room temperature, QS Electric quadrupole splitting or quadrupole shift, respectively, B Hyperfine magnetic field, WID Line width at half maximum, % Site intensity in percent. Last digit errors are given in parentheses, except when the parameters were kept constant during the fit

*X-ray diffraction* (XRD) was used to structurally characterize the powder sample at room temperature, using Cu-K $\alpha$  radiation (1.541874 Å). The refinement of the lattice parameters was carried out by the Rietveld method using the HighScore Plus software [6]. The crystallite size (Dsc) was calculated from the full-width-at-half-height (FWHM) of the diffraction peaks, using the Scherrer equation [7].

*Magnetometry measurements* were done in a vibrating sample magnetometer (VSM) equipped with a cryogen-free Physical Properties Measurement System (Dynacool PPMS) and operating at a vibration frequency of 40 Hz and an amplitude of 2 mm in the central area of the coils, where the powder sample was placed in a rod-shaped Perspex sample holder.

*Mössbauer spectra* were recorded at room temperature (RT) and 4.2 K in a transmission geometry *WissEL* spectrometer, using a source of <sup>57</sup>Co in a Rh matrix with an activity of about 20 mCi. The samples were in powder form in sample holders made of Perspex. The measurements at RT were carried out in a spectrometer operating with a triangular velocity waveform. For the analysis at 4.2 K spectra were recorded with a sinusoidal velocity waveform. In this case, the measurements were performed in a liquid helium bath cryostat with the source kept at the same temperature as the absorber. All spectra were fitted by the least squares method, with a set of Lorentzian lines determined using the *NORMOS* program distributed by *WissEL GmbH*. Isomer shifts are given relative to  $\alpha$ -Fe at RT.



Fig. 2 Temperature dependence of the inverse magnetic susceptibility of the  $Zn_5Fe_2(P_2O_7)_4$  sample. On the right side the low-temperature part of the curve is shown with an expanded temperature scale

## 3 Results and discussion

X-ray diffraction patterns revealed an orthorhombic structure with a C222<sub>1</sub> space group. The sample is thus isostructural with the parent  $Fe_7(P_2O_7)_4$  [8]. The obtained average value of the crystallite size (Dsc = 24.30 nm) confirms that the prepared diphosphate material is nanometric. Figure 1 shows that  $Zn^{II}_5Fe^{III}_2(P_2O_7)_4$  structure is formed by  $ZnO_6$  and  $FeO_6$  octahedra and  $PO_4$  tetrahedra belonging to 2 types of  $P_2O_7$  groups.

Figure 2 shows the thermal variation of the inverse of magnetic susceptibility for the  $Zn_5Fe_2(P_2O_7)_4$  sample. The anomaly observed near 15 K can be ascribed to an antiferromagnetic-paramagnetic transition with  $T_N = 15.4(1)$  K, smaller than that of  $Fe_7(P_2O_7)_4$  which has  $T_N = 25$  K [9]. This smaller value indicates that the magnetic exchange interactions



Fig. 3 Mössbauer spectra taken at RT and 4.2 K for the sample Zn<sub>5</sub>Fe<sub>2</sub>(P<sub>2</sub>O<sub>7)4</sub>

involved in the ordering are weaker in  $Zn_5Fe_2(P_2O_7)_4$  than in  $Fe_7(P_2O_7)_4$  [9], presumably because the magnetic interactions are related to the iron content in the compound, which is smaller in the case of  $Zn_5Fe_2(P_2O_7)_4$ .

In Fig. 3 Mössbauer spectra taken of the sample at room temperature (RT) and 4.2 K are shown. In the RT spectrum one can observe that the substitution of  $Fe^{2+}$  ion sites was largely successful, but a small percentage (1.2%) of Fe<sup>2+</sup> still remains. The ferric iron in the RT spectrum is composed of a major Fe<sup>3+</sup> doublet and an additional weak Fe<sup>3+</sup> doublet with a higher quarupole splitting (QS), probably due to ferric Fe sitting in the ZnO<sub>6</sub> octahedra [9]. Since the left line of the weak Fe<sup>2+</sup> doublet is practically invisible below the dominant Fe<sup>3+</sup> doublets, this doublet was fitted with the parameters restrained to the values of the most intense Fe<sup>2+</sup> doublet found in RT spectrum of Fe<sub>7</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>4</sub> [9]. At 4.2 K a small Fe<sup>3+</sup> doublet with a small QS is found together with a dominant sextet whose hyperfine parameters are close to the ones of  $Fe_7(P_2O_7)_4$ , but with a smaller hyperfine magnetic field of B = 52.8 T instead of B = 54.6 T for  $Fe_7(P_2O_7)_4$  [9]. The weak ferric doublet can be ascribed to a small impurity that does not take part in the magnetic ordering. This doublet does not describe the same environment as the weak Fe<sup>3+</sup> doublet found at RT, and it belongs to a phase that is not magnetically ordered at 4.2 K. This rules out the spinel ZnFe<sub>2</sub>O<sub>4</sub>, which orders magnetically at 4.2 K even when in the form of nanoparticles [10]. A pure iron oxide phase should also order magnetically at 4.2 K. even in its nanosized form. Most probably, this doublet represents iron in a phosphate that does not order at 4.2 K. This phase is not seen at RT because such a weak doublet is not observable under the dominant doublet of  $Zn_5Fe_2(P_2O_7)_4$ . On the other hand, the ferric doublet with a large QS seen at RT should split at 4.2 K or it would be seen as a remaining doublet of about 4% area. It must be magnetically split and hidden below the main magnetic component. This would agree with the assumption that this component is  $Fe^{3+}$  on Zn sites in  $Zn_5Fe_2(P_2O_7)_4$ . The Fe<sup>2+</sup> doublet seen at RT must also split at 4.2 K but as it is weak it stays bellow the main magnetic pattern of Fe<sup>3+</sup>.

#### 4 Conclusions

The sample of  $Zn_5Fe_2(P_2O_7)_4$  is isostructural with the parent  $Fe_7(P_2O_7)_4$ , being orthorhombic with a C222<sub>1</sub> space group. Magnetometry shows that the Néel temperature is  $T_N = 15.4(1)$  K, which is in accordance with Mössbauer measurements at RT and 4.2 K. The substitution of  $Fe^{2+}$  ion sites by Zn was successful, but a small percentage (1.2%) of  $Fe^{2+}$  still remains. The present Mössbauer results complete the structural study of  $Zn_5Fe_2(P_2O_7)_4$  diphosphate made in ref. [5].

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