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# A new iron oxophosphate $\text{SrFe}_3(\text{PO}_4)_3\text{O}$ with chain-like structure

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## Abstract

A new strontium iron oxophosphate  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  was synthesized by the solid state method and its structure was studied by single-crystal X-ray and electron diffraction, high-resolution electron microscopy, Mössbauer and IR spectroscopy. The compound crystallizes in a monoclinic system (space group  $P2_1/m$ ) with unit-cell parameters:  $a = 7.5395(7)$ ,  $b = 6.3476(7)$ ,  $c = 10.3161(13)$  Å,  $\beta = 99.740(9)^\circ$ . The structure of  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  represents a new structural type and is made up of isolated  $\text{PO}_4$  tetrahedra and  $\text{FeO}_n$  polyhedra connected via common vertices and edges to form a 3D framework. Iron cations occupy three crystallographically independent sites with different oxygen environment: Fe1 and Fe2 occupy two octahedral sites, and Fe3 is five-coordinated. Two particularities of this structure are remarkably mentioned: the isolated  $\{\text{FeO}_6\}_n$  octahedral chains along the  $b$  direction and the five coordinated environment for the Fe3 position. Mössbauer spectroscopy confirmed the presence of only high-spin  $\text{Fe}^{3+}$  cations in two types of coordination environment. The IR-data show the presence of only  $\text{PO}_4^{3-}$  groups.

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## 1. Introduction

Open framework phosphates containing transition elements are of particular interest because of their high chemical activity and thermal stability. The chemical activity of these compounds is a result of the ability of transition metals to realize more than one oxidation state, which facilitates reversible redox reactions.

Mixed metal phosphates with alkali-earth and iron cations have been shown to possess a rich structural chemistry due to the ability of iron to adopt different oxidation states (+2/+3) [1, 2] as well as different coordination environments. These structures are based on complex frameworks built of  $\text{FeO}_n$  and  $\text{PO}_4$  polyhedra sharing vertices and/or edges.

Various examples of such alkali-earth and iron (+3) compounds with different phosphate groups ( $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and known. Tang et al. [3] described the pillared-layered structure of  $\text{Ba}_3\text{Fe}_2(\text{HPO}_4)_6$ . The layers are formed of  $\text{FeO}_6$  octahedra and  $\text{HPO}_4^{2-}$  tetrahedra-

sharing corners. The whitlockite-type  $M_9\text{Fe}^{3+}(\text{PO}_4)_7$  ( $M = \text{Ca}$  [4],  $\text{Sr}$  [5]) compounds are made up of  $\text{PO}_4^{3-}$  tetrahedra, which connect the  $MO_n$  polyhedra into a 3-D framework via common vertices. The basic structural fragments of  $M\text{Fe}_2(\text{P}_2\text{O}_7)_2$  ( $M = \text{Ba}$  [6],  $\text{Sr}$  [7]) are columns of alkali-earth atoms located in a 3D framework formed by the  $\text{P}_2\text{O}_7^{4-}$  groups with  $\text{FeO}_6$  octahedra. Moreover, compounds with mixed anion composition ( $\text{Ba}_2\text{Fe}_3\text{H}(\text{PO}_4)_2(\text{P}_2\text{O}_7)_2$  [8]) and different oxidation states of iron cations ( $\text{SrFe}_3(\text{PO}_4)_3$  [2]) are known.

In this work we describe the synthesis, X-ray diffraction, electron microscopy, Mössbauer and IR spectroscopy of the new double iron and strontium oxophosphate  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$ .

## 2. Experimental

### 2.1. Synthesis and elemental analysis

Single crystals of  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  were grown by slow cooling a mixture of  $\text{Fe}_2\text{O}_3$  (99.5%),  $\text{SrCO}_3$  (99.99%) and  $\text{NH}_4\text{H}_2\text{PO}_4$  (99.99%) for initial composition

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“ $\text{Sr}_3\text{Fe}_4(\text{PO}_4)_6$ ” ( $\text{Fe}_2\text{O}_3:\text{SrCO}_3:\text{NH}_4\text{H}_2\text{PO}_4 = 1:1.5:3$ ) from 1373 to 1073 K with a cooling rate of 5 K/h. The red plate-like crystals were mechanically separated from the melt. The crystals were crushed into microcrystalline powder and their composition was studied by EDX analysis performed inside a Philips CM20 transmission electron microscope. Analysis of different crystallites from different zones led to practically the same elemental composition (Fe— $42.2 \pm 0.4$  at%; Sr— $15.4 \pm 0.4$  at%; P— $42.4 \pm 1.0$  at%). The oxygen content could not be quantified by EDX analysis.

For Mössbauer, IR spectroscopy and second-harmonic generation experiments pure powder samples of  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  were synthesized from a stoichiometric mixture of  $\text{Fe}_2\text{O}_3$ ,  $\text{SrCO}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  at 1173 K for 120 h.

## 2.2. Second-harmonic generation study

The second-harmonic generation (SHG) response of powder samples was measured with a Q-switched YAG:Nd laser at  $\lambda_{\omega} = 1064$  nm, in the reflection mode. The experimental set-up and arrangement have been described elsewhere [9]. The intensity of the SHG signal,  $I_{2\omega}$  from the sample and that from the reference sample (polycrystalline  $\alpha\text{-SiO}_2$ ) were registered. The insignificant value of the SHG signal for  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  ( $I_{2\omega} \approx 0.2 I_{2\omega}(\text{SiO}_2)$ ) indicates a centrosymmetric space group.

## 2.3. Electron diffraction and high-resolution electron microscopy (HREM)

Electron diffraction (ED) and high-resolution electron microscopy (HREM) were performed on crushed  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  samples deposited on holey carbon grids. EDX analysis and ED patterns were obtained using a Philips CM20 microscope equipped by a LINK-2000 EDX attachment; HREM observations were performed using a JEOL 4000 EX microscope. The Scherzer resolution of the microscope is 1.7 Å. Simulations of the HREM images were performed using the MacTamapas software.

## 2.4. X-ray diffraction

A red plate-like crystal ( $0.18 \times 0.13 \times 0.04$  mm) of  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  was used for single crystal X-ray data collection. The data were collected at room temperature on a Siemens P4 diffractometer equipped with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å) using  $\omega$ - $2\theta$  scanning mode. A total of 2463 reflections within the range  $2.74^\circ \leq \theta \leq 31.82^\circ$ , and  $-11 \leq h \leq 1$ ,  $-9 \leq k \leq 1$ ,  $-15 \leq l \leq 15$  were measured.

## 2.5. Mössbauer spectroscopy

$^{57}\text{Fe}$  Mössbauer spectroscopy experiments were performed in transmission geometry at 300 and 80 K using a constant acceleration Mössbauer spectrometer coupled with a 1024 multichannel analyzer. A  $^{57}\text{Co}/\text{Rh}$   $\gamma$ -ray source was used. The velocity scale was calibrated relative to  $\alpha\text{-Fe}$ . All isomer shift values ( $\delta$ ) given hereafter are referred to as  $\alpha\text{-Fe}$ . Experimental data were resolved into symmetric doublets with Lorentzian lineshapes using an iterative least-squares fit program.

## 2.6. IR-spectroscopy

IR-spectra were recorded at room temperature using a Nicolet Magna-750 Fourier-spectrometer in the wavenumber range  $400\text{--}4000$   $\text{cm}^{-1}$ . Powdered samples for IR data collection were mixed with KBr and pressed into pellets. The analysis of the IR spectrum was carried out in the areas of  $\text{OH}^-$  and  $\text{PO}_4^{3-}$  group oscillations. The IR-spectrum of  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  does not contain bands between  $3200\text{--}3600$  and  $710\text{--}760$   $\text{cm}^{-1}$  corresponding to the O–H stretching of the  $\text{OH}^-$  group and the P–O–P stretching of the  $\text{P}_2\text{O}_7^{4-}$  group, respectively.

# 3. Results and discussion

## 3.1. Electron diffraction

The  $[100]^*$ ,  $[010]^*$  and  $[001]^*$  ED patterns for  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  were obtained at room temperature (Fig. 1). The diffraction patterns were completely indexed in a *P*-monoclinic unit cell with lattice parameters:  $a = 7.54$ ,  $b = 6.35$ ,  $c = 10.33$  Å,  $\beta = 99.7^\circ$ .

The angle between rows of  $h00$  and  $00l$  reflections for  $[010]^*$  indicate a monoclinic distortion with  $\beta \approx 99.7^\circ$ . The  $[100]^*$  and  $[001]^*$  ED patterns exhibit the  $0k0$  reflections with  $k$ -odd. However, the  $0k0$  spots with  $k$ -odd disappear when the crystallite is tilted around the  $0k0$  row so as to avoid double-diffraction conditions (Fig. 1). The  $0k0$  spots with  $k$ -odd therefore are attributed to double diffraction. These diffraction conditions and the results of SHG investigation are consistent with the space group  $P2_1/m$ .

## 3.2. Mössbauer spectroscopy

Mössbauer spectra of  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  at 80 and 300 K are shown in Fig. 2 and the parameters corresponding to the fits are given in Table 1. The spectra at different temperatures indicate the presence two paramagnetic doublets with isomer shift (IS)  $\delta \approx 0.28\text{--}0.40$  mm/s in a 2:1 ratio.

According to Menil [10] the isomer shift values for all components are characteristic of high-spin  $\text{Fe}^{3+}$ . Two

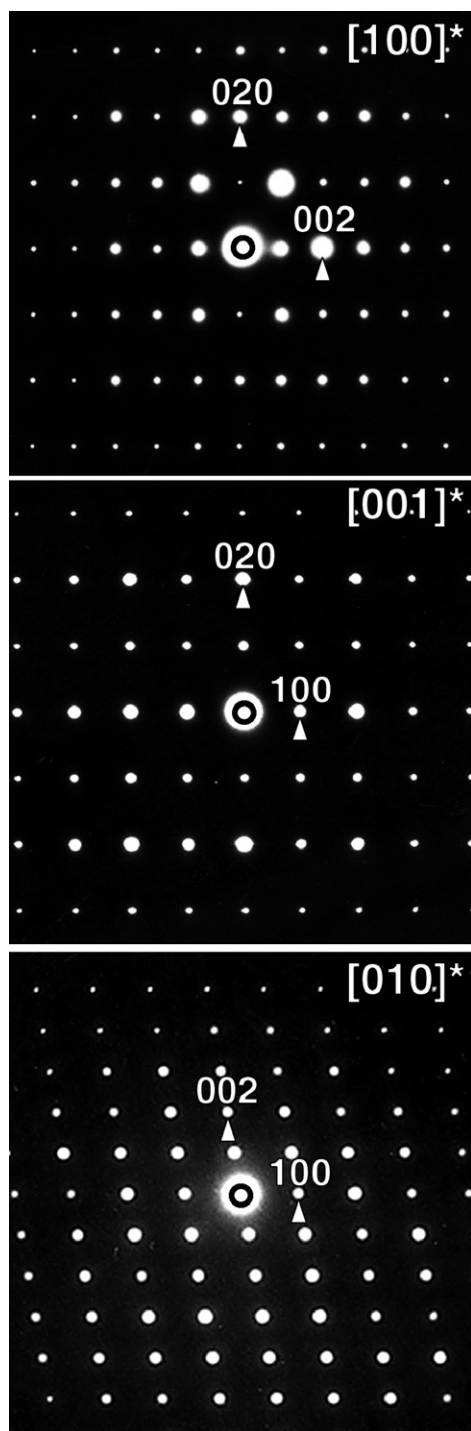


Fig. 1. Electron diffraction patterns along the main zone axes for  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$ .

doublets with different quadruple splitting indicate two different coordinations for iron cations.

### 3.3. Crystal structure determination

The structure determination and refinement were carried out in the space group  $P2_1/m$  using the Shelxtl-

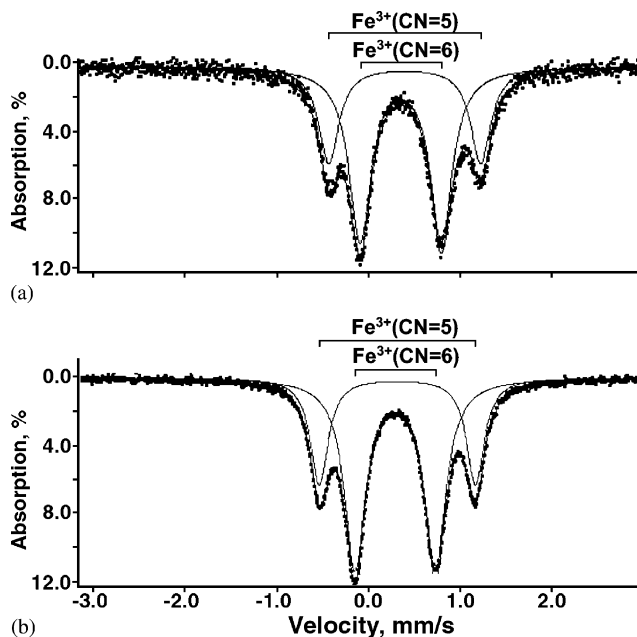


Fig. 2. Mössbauer spectra of  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  at (a) 77 K and (b) 300 K.

Table 1  
Parameters of Mössbauer spectra for  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$

T K	$\delta^a$ (mm/s)	$\Delta E_Q^b$ (mm/s)	FWHM <sup>c</sup> (mm/s)	S <sup>d</sup> (%)
80	0.40(1)	1.65(1)	0.27(1)	34
	0.36(1)	0.88(1)	0.29(1)	66
300	0.30(1)	1.69(1)	0.23(1)	32
	0.28(1)	0.87(1)	0.87(1)	68

<sup>a</sup> Isomer shift (CS):

<sup>b</sup> Quadruple splitting (QS):

<sup>c</sup> Full-width at half maximum:

<sup>d</sup> Area.

plus program package [11]. A direct method was used to obtain the initial atomic positions for Sr and Fe. Full-matrix least-squares refinement and subsequent difference Fourier maps were used to locate phosphorous and oxygen atoms. The final refinement cycles converged with  $R_1 = 0.0557$ ,  $wR_2 = 0.0908$ ,  $\text{Goof} = 1.04$  for all data. The highest peak and deepest hole in the final residual electron density were  $1.224$  and  $-1.189 e \text{ \AA}^{-3}$ , respectively. The main crystallography data are given in Table 2. Atomic positions, bond distances and angles are given in Tables 3 and 4, respectively.

### 3.4. Crystal structure description

The compound  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  crystallizes in a new structure type. A polyhedral representation of the structure along the [010] direction is shown in Fig. 3. The structure is made up of  $\text{PO}_4$  tetrahedra, that connect  $\text{FeO}_n$  polyhedra into a 3D framework via

Table 2  
Crystal and Structure Refinement Data for SrFe<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>O.

Formula	SrFe <sub>3</sub> (PO <sub>4</sub> ) <sub>3</sub> O
Formula weight (g)	556.08
Temperature	293(2) K
Radiation (λ, Å)	MoKα (0.71073)
Crystal habit	Red
Crystal system	Monoclinic
Space group	<i>P2<sub>1</sub>/m</i>
<i>a</i> (Å)	7.5395(7)
<i>b</i> (Å)	6.3476(7)
<i>c</i> (Å)	10.3161(13)
β (°)	99.740(9)
Volume (Å <sup>3</sup> )	486.59(9)
Z	2
Calculated density (g cm <sup>-3</sup> )	3.795
Absorption coefficient (cm <sup>-1</sup> )	104.08
<i>F</i> (0 0 0)	530
Crystal size (mm)	0.18 × 0.13 × 0.04
Data range θ(°); <i>h, k, l</i>	2.74–31.82; -11 ≤ <i>h</i> ≤ 1, -9 ≤ <i>k</i> ≤ 1, -15 ≤ <i>l</i> ≤ 15
Scan type	ω-2θ
Total reflections/unique	2463/1805
<i>R</i> <sub>int</sub> <sup>a</sup>	0.0367
Number of variables	113
Extinction coefficient	0.0133(12)
Max./min. residual $\bar{e}$ density (e Å <sup>-3</sup> )	1.224/-1.189
<i>R</i> <sub>1</sub> <sup>b</sup> / <i>wR</i> <sub>2</sub> <sup>c,d</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0399/0.0850
<i>R</i> <sub>1</sub> <sup>b</sup> / <i>wR</i> <sub>2</sub> <sup>c,d</sup> (for all data)	0.0557/0.0908
Goof <sup>e</sup> (Goodness of fit)	1.040

$$^a R_{\text{int}} = \frac{\sum |F_o^2 - F_o^2(\text{mean})|}{\sum F_o^2}$$

$$^b R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^c wR_2 = \frac{[\sum (w(F_o^2 - F_c^2))^2]}{[\sum (wF_o^2)]^{1/2}}$$

$$^d \text{Weighting scheme } w^{-1} = \sigma^2(F_o^2) + (0.0270P)^2 + 7.61P \quad \text{where } P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3.$$

$$^e \text{Goof} = \frac{[\sum (w(|F_o| - |F_c|)^2)]}{(\text{No. of refl.} - \text{No. of params.})^{1/2}}$$

common vertices and edges. Sr<sup>2+</sup> cations are located in the cavities of the structure. Iron cations occupy three crystallographically independent sites Fe1, Fe2, and Fe3 with different oxygen environment (Fig. 4a). Fe1 and Fe2 are located in a strongly distorted octahedral environment with (*d*<sub>Fe1-O<sub>6</sub></sub> = 1.987(3)–2.122(3) Å) and (*d*<sub>Fe2-O</sub> = 1.867(4)–2.265(4) Å) while Fe3 is coordinated by five oxygen atoms (*d*<sub>Fe3-O</sub> = 1.874(5)–1.987(3) Å) in a coordination geometry that can be described as square pyramid or trigonal bipyramid (Table 2).

Each Fe1O<sub>6</sub> octahedron shares two oxygen atoms with two Fe2O<sub>6</sub> octahedra, and the four remaining oxo-ligands are shared with four tetrahedra, two P1O<sub>4</sub> and two P2O<sub>4</sub> in a trans fashion (Fig. 4b). The Fe2O<sub>6</sub> octahedron shares one oxygen with Fe1O<sub>6</sub>, and is connected to P2O<sub>4</sub> and P3O<sub>4</sub> tetrahedra via common vertices and with P1O<sub>4</sub> tetrahedra via a common edge. The Fe3O<sub>5</sub> square pyramid shares its edge with P3O<sub>4</sub> and a corner with the P1O<sub>4</sub>- and P2O<sub>4</sub> tetrahedra. The phosphate tetrahedra have P–O bond lengths (⟨P1–O⟩ = 1.532 Å, ⟨P2–O⟩ = 1.534 Å and ⟨P3–O⟩ = 1.529 Å) similar to those found in other phosphates.

Table 3  
Fractional Atomic Coordinates and Thermal Parameters of SrFe<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>O

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U <sub>iso</sub> (Å <sup>2</sup> × 10 <sup>3</sup> )
Sr	2e	0.6693(1)	0.25	0.7017(1)	9(1)
Fe1	2c	0.0	0.0	0.5	6(1)
Fe2	2e	0.6523(1)	0.25	0.3019(1)	5(1)
Fe3	2e	0.2119(1)	0.25	0.0600(1)	8(1)
O1	2e	-0.1221(6)	0.25	0.4093(4)	7(1)
P1	2e	0.3141(2)	0.25	0.3856(2)	5(1)
O2	4f	0.2098(4)	0.0524(5)	0.4104(3)	9(1)
O3	2e	0.3492(6)	0.25	0.2417(4)	8(1)
O4	2e	0.5072(6)	0.25	0.4601(4)	9(1)
P2	2e	0.2545(2)	0.25	0.7385(2)	5(1)
O5	4f	0.3688(4)	0.0612(5)	0.7126(3)	9(1)
O6	2e	0.0767(6)	0.25	0.6344(4)	9(1)
O7	2e	0.2019(7)	0.25	0.8738(5)	15(1)
P3	2e	-0.2163(2)	0.25	0.0193(2)	6(1)
O8	4f	-0.2480(5)	0.0598(5)	-0.0746(3)	12(1)
O9	2e	-0.3486(7)	0.25	0.1130(4)	14(1)
O10	2e	-0.0236(6)	0.25	0.0958(5)	15(1)

In the trigonal bipyramidal description, two oxygen atoms O8 are located in the apical position, subtending an angle of 163.4°, while O3, O7 and O10 lie in the equatorial plane (Fig. 5a). Alternatively, in the square pyramidal description, O10 is located in the axial position and forms the shortest bond (Fe3–O10 = 1.874(5) Å), while O3, O7 and two O8 form long bonds at the basal positions (Table 2, Fig. 5b). It is difficult to choose between these two polyhedral descriptions on the base is of bond lengths and angles analysis. But, in our opinion, a description of the Fe3O<sub>5</sub> polyhedron as a square pyramid is preferable because the iron cation lies practically in the basal plane of the pyramid (formed by four oxygen atoms).

The main particularity of this structure is the {FeO<sub>4</sub>}<sub>*n*</sub> chain along the *b* direction; Fe1O<sub>6</sub> octahedra are connected to each other via common edges O1–O6 (Fig. 6). The equatorial oxo-ligands O1 and O6 are also shared with Fe2O<sub>6</sub> octahedra and P2O<sub>4</sub> tetrahedra, respectively. The apical oxo-ligands O2 and O2' are shared with P1O<sub>4</sub> tetrahedra. O2–O2' edges of these tetrahedra join the apical vertices of two neighboring Fe1O<sub>6</sub> octahedra, which leads to bending of the chains. The angle between equatorial planes of neighboring Fe1O<sub>6</sub> octahedra is about 20°. The {Fe1O<sub>4</sub>}<sub>*n*</sub> chains are linked by Fe2O<sub>6</sub> octahedra, P1O<sub>4</sub> and P2O<sub>4</sub> tetrahedra to form {Fe<sub>2</sub>P<sub>2</sub>O<sub>10</sub>}<sub>*n*</sub> layers perpendicular to the *c* direction (Fig. 4b). These layers are connected by Fe3O<sub>5</sub> and P3O<sub>4</sub> to form the 3D framework. The framework is rather strained as evidenced by the strongly distorted iron polyhedra, especially Fe2O<sub>6</sub>, in which the Fe2–O1 distance (1.867(4) Å) is about 17.6% shorter than the Fe2–O3 distance (2.265(4) Å). This strong distortion is presumably due to the edge O3–O4 shared by P1O<sub>4</sub> and Fe2O<sub>6</sub>. In comparison, the Fe1O<sub>6</sub>

Table 4  
Bond lengths (Å) and angles (°) for SrFe<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>O

<i>Fe1O<sub>6</sub>-octahedron</i>						
Fe1	O1	O1 <sup>8</sup>	O2	O2 <sup>8</sup>	O6	O6 <sup>8</sup>
O1	1.987(3)	180.0	89.37(15)	90.63(15)	76.33(13)	103.67(13)
O1 <sup>8</sup>		1.987(3)	90.63(15)	89.37(15)	103.67(13)	76.33(13)
O2			1.990(3)	180.0	91.61(15)	88.39(15)
O2 <sup>8</sup>				1.990(3)	88.39(15)	91.61(15)
O6					2.122(3)	180.0
O6 <sup>8</sup>						2.122(3)
<i>Fe2O<sub>6</sub>-octahedron</i>						
Fe2	O17	O3	O4	O51	O52	O97
O1 <sup>7</sup>	1.867(4)	159.84(17)	94.59(18)	95.64(9)	95.64(9)	116.3(2)
O3		2.265(4)	65.25(16)	85.11(9)	85.11(9)	83.85(18)
O4			2.113(4)	90.70(9)	90.70(9)	149.10(19)
O5 <sup>1</sup>				1.985(3)	168.49(18)	86.47(9)
O5 <sup>2</sup>					1.985(3)	86.47(9)
O9 <sup>7</sup>						2.122(3)
<i>Fe3O<sub>5</sub>-pyramida</i>						
Fe3	O3	O710	O811	O812	O10	
O3	1.982(4)	151.3(2)	83.43(10)	83.43(10)	100.0(2)	
O7 <sup>10</sup>		1.909(5)	93.31(10)	93.31(10)	108.7(2)	
O8 <sup>11</sup>			1.987(3)	163.4(2)	96.16(10)	
O8 <sup>12</sup>				1.987(3)	96.16(10)	
O10					1.874(5)	
<i>P1O4-tetrahedron</i>						
O2	O2	O23	O3	O4		
O2	1.525(3)	110.7(2)	109.70(15)	112.98(15)		
O2 <sup>3</sup>		1.525(3)	109.70(15)	112.98(15)		
O3			1.551(4)	100.3(2)		
O4				1.527(4)		
<i>P2O4-tetrahedron</i>						
O5	O5	O53	O6	O7		
O5	1.526(3)	103.5(2)	108.83(16)	113.90(17)		
O5 <sup>3</sup>		1.526(3)	108.83(16)	113.90(17)		
O6			1.570(4)	107.7(3)		
O7				1.515(5)		
<i>P3O4-tetrahedron</i>						
O8	O8	O83	O9	O10		
O8	1.540(3)	103.2(3)	110.80(17)	110.88(17)		
O8 <sup>3</sup>		1.540(3)	110.80(17)	110.88(17)		
O9			1.502(5)	110.1(3)		
O10				1.532(5)		
<i>Sr–O –coordination</i>						
2 × Sr–O(2) <sup>1,2</sup>	2.492(3)	2 × Sr–O(3)1,6	3.2344(9)	Sr–O(4)	2.584(4)	
2 × Sr–O(5) <sup>0,3</sup>	2.582(3)	2 × Sr–O(8)4,5	2.586(3)	Sr–O(6)7	3.262(4)	

Symmetry codes: <sup>1</sup>  $-x+1, -y, -z+1$ ; <sup>2</sup>  $-x+1, y+1/2, -z+1$ ; <sup>3</sup>  $x, -y+1/2, z$ ; <sup>4</sup>  $x+1, -y+1/2, z+1$ ; <sup>5</sup>  $x+1, y, z+1$ ; <sup>6</sup>  $-x+1, -y+1, -z+1$ ; <sup>7</sup>  $x+1, y, z$ ; <sup>8</sup>  $-x, -y, -z+1$ ; <sup>9</sup>  $x-1, y, z$ ; <sup>10</sup>  $x, y, z-1$ ; <sup>11</sup>  $-x, -y, -z$ ; <sup>12</sup>  $-x, y+1/2, -z$ ; <sup>13</sup>  $-x, y+1/2, -z+1$ ; <sup>14</sup>  $x, y, z+1$ ; <sup>15</sup>  $x-1, y, z-1$ .

and Fe3O<sub>5</sub> polyhedra are less distorted with a difference between short and long distances of 6.4% and 5.7%, respectively.

### 3.5. High-resolution electron microscopy

Fig. 7 shows a [100] view of the SrFe<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>O corresponding to the diffraction patterns of Fig. 1a. A view along the [100] direction is most representative for

this structure because of the direct correspondence to the cation and anion columns. The images in the very thin part consist of a square grid of bright dots separated by a row of less bright dots. Under the appropriate conditions of thickness and defocus the two sublattices of heavy atom columns are imaged differently. Based on calculated images it was found that the Sr atoms are imaged as dark dots whereas Fe1 cations show up as a less bright dots. The brighter dots in

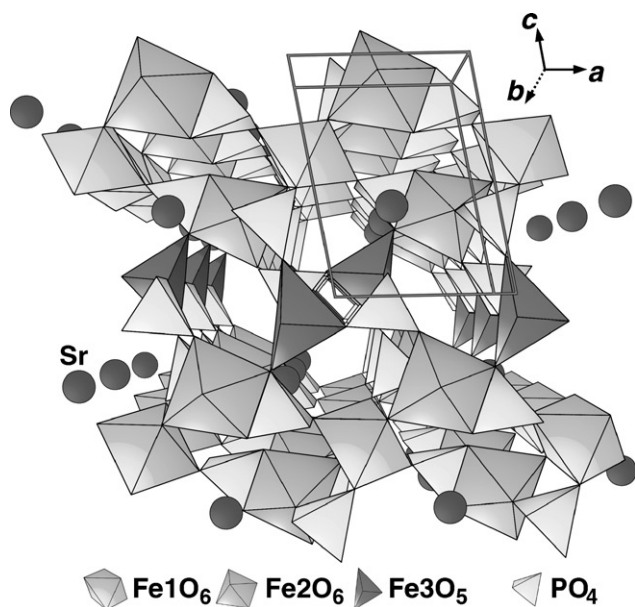


Fig. 3. Polyhedral view of the  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  structure along the  $[010]$  direction.

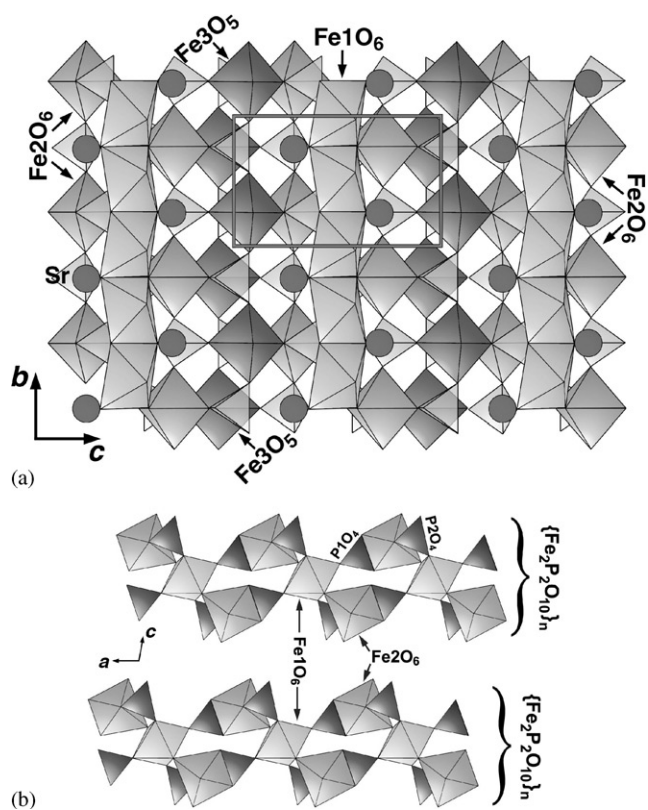


Fig. 4. (a) View of the iron polyhedra and strontium cation distribution in the crystal structure of  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  along the (a)  $[100]$  direction and (b) projection of the  $\{\text{Fe}_2\text{P}_2\text{O}_{10}\}_n$  layers along the  $b$  direction.

square arrangement correspond to the channels. Image simulations were based on the  $P2_1/m$  model (see Tables 2 and 3) and show a good agreement with the

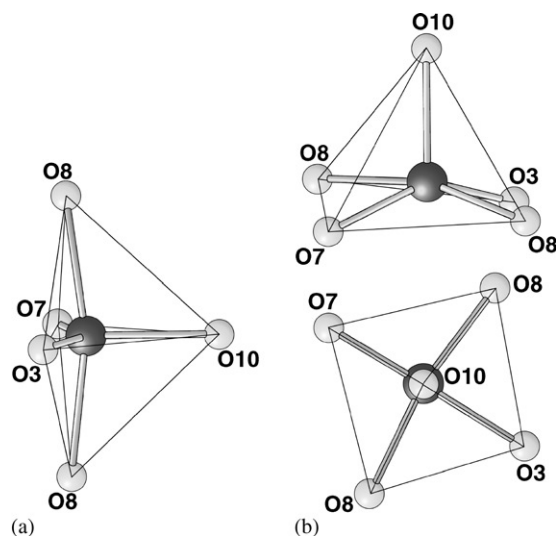


Fig. 5. Presentation of the  $\text{Fe}_3\text{O}_5$  polyhedron as a (a) trigonal bipyramid and a tetragonal pyramid

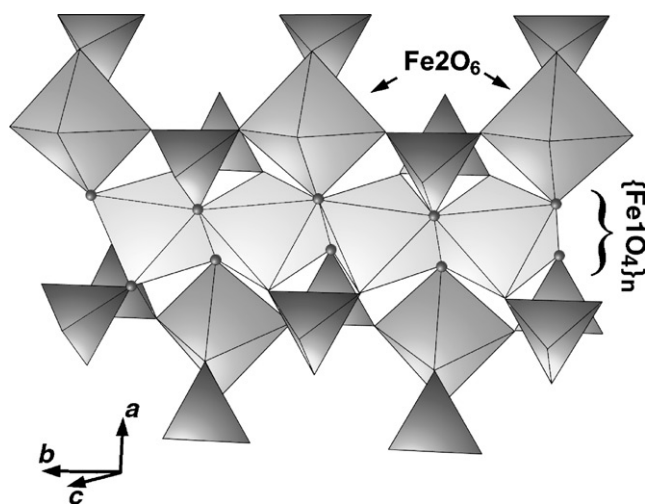


Fig. 6. Presentation of the  $\{\text{Fe}_1\text{O}_4\}_n$  chains along the  $c$  direction.

experimental images. One of them for a defocus value ( $\Delta f$ ) of  $-70$  nm and thickness ( $t$ ) of  $2.1$  nm are given as an inset in Fig. 7.

#### 4. Conclusion

A new complex strontium iron oxophosphate  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  was synthesized by a solid state method and studied by X-ray and electron diffraction, Mössbauer and IR spectroscopy and high-resolution electron microscopy. The structure of  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  represents a new structural type. It is made up of  $\text{PO}_4$  tetrahedra and  $\text{FeO}_n$  polyhedra connected into a 3D framework via common vertices and edges

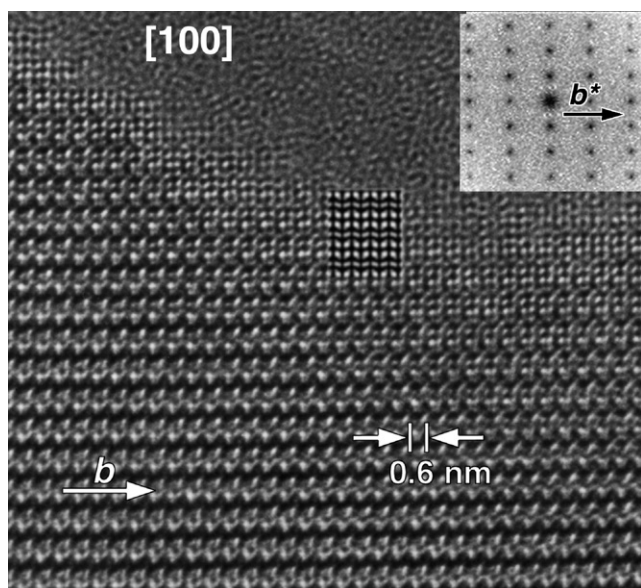


Fig. 7. HREM image of  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  along [100]; optical diffraction pattern given as inset and the corresponding diffraction pattern is shown in Fig. 1a.

In the  $\text{SrFe}_3(\text{PO}_4)_3\text{O}$  structure iron occupies three crystallographically independent sites with different oxygen environments: one five-coordinated and two octahedral sites. The Mössbauer study shows the presence of high-spin  $\text{Fe}^{3+}$  in two types of coordination environments. The ratio between the areas of Mössbauer spectra components ( $\sim 2:1$ ) is in accordance with the number of  $\text{FeO}_6$  and  $\text{FeO}_5$  polyhedra (4:2) obtained during the structure determination.

Two interesting particularities of this structure should be mentioned: (1) the  $\{\text{FeO}_4\}_n$  octahedral chains along the  $b$  direction; and (2) the 5-coordinated square pyramidal environment for  $\text{Fe}^{3+}$ . Similar chains were observed for  $\text{VO}_6$  octahedra in the series  $A\text{V}_2(\text{PO}_4)_2\text{O}$  ( $A = \text{Cd}, \text{Ca}, \text{Sr}$ ) [12]. Moreover 5-coordinated environment for  $\text{Fe}^{3+}$  was observed for  $\text{Fe}_3\text{PO}_7$  [13],  $\text{FeAsO}_4$  [14] and groups of compounds with the magnetoplumbite-type [15] and the  $\text{Mn}_2\text{HoO}_5$ -type [16] structure.

For  $\text{Fe}_3\text{PO}_7$  and the magnetoplumbite-type compounds [17] a trigonal bipyramidal environment is observed for  $\text{Fe}^{3+}$  while in the  $\text{FeAsO}_4$  [14] and  $\text{FeTiRO}_5$  ( $R = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$ ) compounds [18] with the  $\text{Mn}_2\text{HoO}_5$ -type structures square pyramidal  $\text{Fe}^{3+}$  is present.

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