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Ferroelectric phase transition in the whitlockite-type Ca₉Fe(PO₄)₇; crystal structure of the paraelectric phase at 923 K

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Abstract

A newly discovered phase transition in Ca₉Fe(PO₄)₇ is studied by high-temperature X-ray powder diffraction (XRD) and electron diffraction (ED), high-resolution electron microscopy, second-harmonic generation (SHG), differential scanning calorimetry, dielectric and electrical conductivity measurements. The phase transition temperature, T_c , is 890 ± 10 K. Dielectric measurements reveal the ferroelectric nature of the phase transition. A spontaneous polarization of about 2–3 μ C cm⁻² is estimated from SHG. The phase transition from a polar ferroelectric form β (space group R_{3c}), to a centrosymmetric paraelectric form β' (space group R_{3c}), is reversible and of first order. The evolution of the crystal structure and lattice parameters is studied by high-temperature XRD and ED. The structural parameters of β' -Ca₉Fe(PO₄)₇ are refined by the Rietveld method from XRD data at 923 K in the space group R_{3c} (Z = 6) with lattice parameters a = 10.3878(2) Å and c = 37.8387(4) Å ($R_{wp} = 1.48\%$ and $R_I = 2.16\%$). Both β - and β' -Ca₉Fe(PO₄)₇ are related to the whitlockite-type structure. The $\beta \rightarrow \beta'$ phase transition in Ca₉Fe(PO₄)₇ is accompanied by a disordering of the Ca²⁺ ions at the Ca₃ sites and orientational disordering of the P1O₄ tetrahedra.

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1. Introduction

Calcium orthophosphate, Ca₃(PO₄)₂, and its variations have been extensively studied as bioceramic [1] and luminescent [2] materials. Solid solutions Ca_{3-x}M_x(PO₄)₂ (M = Ni [3], Co [4] and Cu [5]) with the β -Ca₃(PO₄)₂-type structure (space group *R*3*c*, *Z* = 21) have catalytic activity, e.g., in propan-2-ol [4] and butan-2-ol [5] dehydrogenation. Reversible redox reactions without destroying the fundamental structure occur in Ca₉Fe(PO₄)₇ [6,7], Ca_{9.5}Cu(PO₄)₇ [8] and Ca₉Na_{1.5}Fe_{0.5}(PO₄)₇ [9] (*Z* = 6). Materials in which redox reactions do not cause destruction of their structure can be used as sensor materials [10], intermediators for two-

* Corresponding author. *E-mail address:* lebedev@ruca.ua.ac.be (O.I. Lebedev). stage oxidation of hydrogen [11] and materials for purification of gas mixtures by removing O_2 or H_2 [12].

Calcium orthophosphate at room temperature (T_R) can be obtained in two forms, α - and β -Ca₃(PO₄)₂. β -Ca₃(PO₄)₂ [13] has the whitlockite-type structure [14,15]. α -Ca₃(PO₄)₂ [16] has the distorted glaserite or β -K₂SO₄-type structure [15]. β -Ca₃(PO₄)₂ is a thermodynamically stable phase below 1408 K [17,18]. α -Ca₃(PO₄)₂ is thermodynamically stable between 1408 and 1703 K, but it is quenchable from high temperatures (ca. 1500 K) to T_R . The equilibrium temperature for the $\beta \leftrightarrow \alpha$ transformation is estimated to be (1408 ± 5) K [18]. The temperature of the $\beta \leftrightarrow \alpha$ phase transition strongly depends on the kind and amount of impurities. Divalent cations with a radius less than ca. 0.8 Å (e.g., Zn²⁺, Ni²⁺ and Co²⁺) or Sr²⁺ raised the temperature of the $\beta \leftrightarrow \alpha$ phase transition up to 1623–1723 K [19]. The

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replacement of Ca^{2+} or PO_4^{3-} for Ba^{2+} , Cd^{2+} or SiO_4^{4-} results in a decrease of the phase transition temperature.

α'-Ca₃(PO₄)₂, stable above 1703 K and with a structure closely related to α-Ca₃(PO₄)₂ [20], and α''-Ca₃(PO₄)₂, obtained from α-Ca₃(PO₄)₂ above 485 K [21], have been discovered and characterized. We have recently found a new modification, β', of Ca₃(PO₄)₂ in the temperature range from 1190 to 1400 K [22]. β'-Ca₃(PO₄)₂ is structurally very similar to β-Ca₃(PO₄)₂. A polar-to-centrosymmetric phase transition at ca. 770 K is detected by infrared spectroscopy in β-Ca₃(PO₄)₂ stabilized by Ni²⁺ and Cr³⁺ ions [23]. There is experimental evidence for a low-temperature phase transitions in Ca₃(PO₄)₂ [24–26]. A high-pressure form of Ca₃(PO₄)₂ is also described in the literature [27].

Solid solutions $Ca_{10.5-1.5x}Fe_x(PO_4)_7$ has been prepared in a composition range of $0 \le x \le 1$ [28] and structure parameters of $Ca_9Fe(PO_4)_7$ has been refined from X-ray powder diffraction (XRD) data measured at T_R [7]. $Ca_9Fe(PO_4)_7$ and the solid solutions $Ca_{10.5-1.5x}Fe_x(PO_4)_7$ were found to be isotypic with β - $Ca_3(PO_4)_2$ at T_R .

Earlier we have discovered and studied a new hightemperature ferroelectric phase transition in Ca₉In(PO₄)₇ with $T_c = 902$ K [29]. The present work is devoted to the study of a high-temperature phase transition in whitlockitetype calcium–iron phosphate and the refinement of the structure parameters of Ca₉Fe(PO₄)₇ at 923 K. Using a variety of physicochemical methods, we have clarified the nature of the phase transition and found it to be first order and to have an order–disorder ferroelectric type.

2. Experimental

2.1. Synthesis

 $Ca_9Fe(PO_4)_7$ is synthesized by the solid state method from stoichiometric mixtures of Fe_2O_3 , $CaCO_3$ and Ca_2P_2 - O_7 at 1273 K for 100 h with several intermediate grindings. After annealing, the sample is cooled in the furnace. XRD data show the resultant light-red product to be monophasic [30].

2.2. X-ray diffraction (XRD) experiments and structure refinements

High-temperature XRD patterns were obtained with a SIEMENS D500 powder diffractometer (Cu-K_{α} radiation) equipped with a BRAUN position-sensitive detector. For lattice-parameter refinements, XRD data were collected in a 2 θ range from 20° to 80° with a step interval of 0.02°. For structure refinements, XRD data were collected at 923 K in a 2 θ range between 10° and 110° with a step interval of 0.02°. The powdered sample was mixed with cellulose nitrate varnish and pasted on a Pt plate. The Pt plate was used as a sample heater. Structure and lattice-parameter refinements were performed by the Rietveld method [31]

with RIETAN-2000 [32]. The split pseudo-Voigt function of Toraya was fit to each reflection profile, and an 8th order Legendre polynomial was fit to the background. Coefficients for an analytical approximation to atomic scattering factors for Ca, Fe, P and O were taken from Ref. [33]. 2θ regions containing reflections from the Pt plate were excluded from the refinement. Preferred orientation was corrected with the March–Dollase function on the assumption of a (001) cleavage plane. The preferred-orientation parameter, *p*, was 0.790(2).

2.3. Second-harmonic generation (SHG)

A Q-switch pulsed Nd:YAG laser operated at a wavelength, λ_{ω} , of 1064 nm was used as a radiation source with a repetition rate of 4 pulses per second and a duration of about 12 ns. The laser beam was split into two beams to excite the radiation at half the wavelength $\lambda_{2\omega} = 532$ nm, simultaneously in the sample under investigation and in a reference sample (polycrystalline α -SiO₂). The peak power of the incident beam was about 0.1 MW on a spot 3 mm in diameter on the surface of the sample. SHG signals were measured between $T_{\rm R}$ and 1200 K. Intensities of the SHG signals from the sample, $I_{2\omega}$, and those from α -SiO₂, $I_{2\omega}$ (SiO₂), were registered in a reflection mode in order to make the signals independent of the thickness of the sample.

Both α -SiO₂ and Ca₉Fe(PO₄)₇ were prepared with one and the same crystalline particle size, *L*, of ca. 3000 nm. The small size of the crystalline particles made it possible to eliminate the influence of the coherence length, *l*_c, on the second-harmonic intensities, *I*_{2 ω} and *I*_{2 ω}(SiO₂), because *L* appeared to be less than *l*_c (in oxides, *l*_c is usually larger than 3000–5000 nm). Therefore, *L* represented the only spatial limitation for the $\omega + \omega = 2\omega$ nonlinear conversion process [34,35]. Under such conditions, the secondharmonic intensity ratio, *I*_{2 ω}/*I*_{2 ω}(SiO₂), became a numerical quantity for the direction-averaged optical nonlinearity coefficient, $\langle d \rangle$:

$$\langle d \rangle = A d_{11} (\text{SiO}_2) \frac{(n+1)^3}{(n_{\text{SiO}_2}+1)^3} \sqrt{I_{2\omega}/I_{2\omega}(\text{SiO}_2)}$$

where *n* and n_{SiO_2} are the refractive indices for the sample and α -SiO₂, respectively, and *A* is a geometrical factor. In the present study, we assumed $n = n_{\text{SiO}_2}$ and A = 1. Therefore, the ratio $I_{2\omega}/I_{2\omega}(\text{SiO}_2)$ directly represented the $\langle d \rangle$ value squared. Being intimately related to any changes of the crystal noncentrosymmetry, variations in $\langle d \rangle$ and $I_{2\omega}/I_{2\omega}(\text{SiO}_2)$ give reliable information about the crystal structure evolution in early stages of polar-to-centrosymmetric phase transformation.

2.4. Differential scanning calorimetry (DSC), dielectric and electrical conductivity measurements

Specific heat capacities, c_p , were measured with a Setaram DSC-111 difference-scanning calorimeter from 293 to 1088 K at a heating rate of 5 K min⁻¹. To measure the electrical conductivities, σ , we used samples in the form of pellets 4 to 5 mm in length and 5 to 6 mm in diameter. The pellets were obtained by pressing at 1 kbar and sintering at 1320 K for 10 h (cooling rate: 4 K min⁻¹). The densities of the resultant pellets rose up to 90% of theoretical densities. Pt electrodes were put on the flat surfaces of the pellets. All the conductivities were measured by the impedance spectroscopy method in a frequency range from 1 to 10^{6} Hz with a Solatron 1260 frequency response analyzer. In order to characterize the dielectric properties of $Ca_9Fe(PO_4)_7$, we used the same ceramic samples. We measured the dielectric constant, ε , the dielectric losses tangent, tan δ , and the specific electrical conductivity between 293 and 1000 K with computer-controlled ac-bridges R5083 and E7-12 at electric field frequencies of 10 kHz, 100 kHz and 1 MHz. Good reproducibility of the σ versus T curves in heating–cooling cycles served as an indicator of quasi-equilibrium conditions during our measurements.

2.5. Electron diffraction (ED) and high-resolution electron microscopy (HREM)

ED and HREM investigations were made on crushed $Ca_9Fe(PO_4)_7$ samples deposited on holey carbon grids. ED patterns in the temperature range from 293 to 1123 K were obtained with a Philips CM20 microscope equipped with a double-tilt heating holder. Energy Dispersion X-ray (EDX) spectra were registered with a LINK-2000 attachment. EDX measurements were obtained using beam probe diameters varying between 60 and 300 nm. HREM was performed on a JEOL 4000 EX microscope operating at 400 kV. The Scherzer resolution of the microscope was ca. 1.7 Å. Simulations of the HREM images were performed with the MacTampas software.

3. Results

3.1. Determination of local composition

The local chemical composition in Ca₉Fe(PO₄)₇ crystallites is evaluated by EDX analysis performed inside the electron microscope. EDX measurements show that the Ca/Fe ratio for different crystallites is 9.5 ± 0.5 (the ideal ratio is 9.0). The elemental analysis gives 5.2 ± 0.3 at% for Fe, 49.3 ± 0.3 at% for Ca and 45.4 ± 0.4 at% for P. This measurement deviates from the theoretical 5.9, 52.9 and 41.2 at% for Fe, Ca and P, respectively. Therefore, the element content in calcium phosphate, Ca₅(PO₄)₃OH (ALDRICH, 99.9%), has been studied as a standard. We found experimentally 57.95 ± 0.63 at% for Ca and $42.05 \pm$ 0.63 at% for P, different from the nominal 62.5 at% Ca and 37.5 at% P. This deviation is of the same order of magnitude as our findings for Ca₉Fe(PO₄)₇. We can, therefore, believe that we have prepared the nominal composition. An important measure is the Ca/Fe ratio. Measurements of the Ca/Fe ratio vary from 8.9 to 10.1 for a probe diameter of 200–300 nm. However, when the probe diameter is decreased in the range 60–90 nm, the Ca/Fe ratio is found to vary from 8.9 to 13.1. This variation in composition may be explained in terms of formation of a solid solution Ca_{10.5–1.5x}Fe_x(PO₄)₇ ($0 \le x \le 1$) [28]. Note that in Ca₉In(PO₄)₇ isotypic with Ca₉Fe(PO₄)₇, the ideal Ca/In ratio equal to 9 was observed without any significant deviation from this value [29].

3.2. Phase transition

Fig. 1a shows the temperature dependence of the SHG signal for Ca₉Fe(PO₄)₇. Disappearance of the SHG signal during heating indicates the presence of a polar-tocentrosymmetric phase transition. This phase transition is reversible because the SHG signal reappears during cooling. A temperature hysteresis in the $I_{2\omega}/I_{2\omega}(SiO_2)$ versus T curve is clearly observed for $Ca_9Fe(PO_4)_7$. This fact suggests a first-order phase transition. Slight differences in the SHG signals before and after heating-cooling cycles are caused by different thermal treatments of the samples. For example, Fig. 1a (curve 1) presents the temperature dependence of the SHG signal for Ca₉Fe(PO₄)₇ quenched from 873 K to $T_{\rm R}$. This sample shows a step-like increase of the SHG signal at ca. 770 K and then a sharp decrease of the SHG signal near the phase transition temperature, $T_{\rm c}$, of ca. 890 K.

Fig. 1b displays the results of the DSC measurements. The shape of the c_p versus T curve for Ca₉Fe(PO₄)₇ also indicates a first-order phase transition with $T_c = 886$ K. The weak peak at ca. 770 K coincides with the beginning of the sharp changes of the SHG signal (Fig. 1a, curves 1 and 2). Apparently the anomalies detected in the $c_p(T)$ curve are responsible for the restructuring of the domain structure preceding the polar-to-centrosymmetric phase transition.

The phase transition in Ca₉Fe(PO₄)₇ is also accompanied by step-like changes in the electrical conductivity (Fig. 1c). Jumps on the temperature dependence of the electrical conductivities are observed during heating and cooling with a temperature hysteresis.

The ε versus *T* curve for Ca₉Fe(PO₄)₇ (Fig. 1d) clearly demonstrates sharp maxima at 900 K on heating (curve 1) and at 880 K on cooling (curve 2) for all the frequencies. Such electric-field frequency behavior is characteristic of proper or pseudo-proper ferroelectrics [36]. The less distinct maximum on the tan δ versus *T* curve just below *T*_c obviously reflects the increase of mobility of the polar domain structure, thus being in accordance with the ferroelectric nature of the phase transition. According to the dielectric measurements, the phase transition in Ca₉Fe(PO₄)₇ has a ferroelectric nature and, therefore, only a phase transition from space group *R*3*c* to *R*3*c* is possible [37]. The unit-cell dimensions should not change in this type of phase transition (see Section 4).



Fig. 1. Evidence of the phase transition in Ca₉Fe(PO₄)₇: (a) temperature dependence of the SHG signal; (b) specific heat capacity, c_p , versus *T*; (c) temperature dependence of the dc electrical conductivity, $\lg \sigma$; (d) temperature dependence of the dielectric constant, ε , and loss tangent, tan δ , at 1 MHz. (1) and (3): heating curves; (2): cooling curve.

3.3. High-temperature XRD study

Fig. 2 shows the XRD patterns of Ca₉Fe(PO₄)₇ at different temperatures and the disappearance of reflections with *l* odd. Reflections of Ca₉Fe(PO₄)₇ at temperatures between 293 and 1273 K can be indexed on the basis of space groups *R*3*c* and *R*3*c* (*Z* = 6) with lattice parameters $a \approx 10$ Å and $c \approx 37$ Å. However, examination of the list of the observed



Fig. 2. Temperature dependence of the XRD patterns for Ca₉Fe(PO₄)₇. (*hkl*) reflections with l = 2n + 1 in the space group *R*3*c* ($a \approx 10$ Å and $c \approx 37$ Å) are marked by arrows.

reflections reveals that all *l* indices were even for the XRD patterns taken above T_c . This fact allows us to halve the *c* parameter of the high-temperature phase. The lattice transformation a' = -a, b' = -b and 2c' = c gives supergroup $R\bar{3}m$ (Z = 3) with lattice parameters $a \approx 10$ Å and $c \approx 19$ Å of the space group $R\bar{3}c$ (see a group–subgroup diagram in Fig. 3). Because of the close similarity of the two forms of Ca₉Fe(PO₄)₇ to the whitlockite-type β -Ca₃(PO₄)₂, the high-temperature and low-temperature forms will be referred to as β' -Ca₉Fe(PO₄)₇ and β -Ca₉Fe(PO₄)₇, respectively. Note that the observed reflection conditions of -h + k + l = 3n for hkil, h + l = 3n for $h\bar{h}0l$, and l = 3n for $hh2\bar{h}l$ (hexagonal axes, obverse setting) allow possible space groups $R\bar{3}$ and $R\bar{3}m$ with $a \approx 10$ Å and $c \approx 19$ Å for β' -Ca₉Fe(PO₄)₇.

Fig. 4 displays the temperature dependence of the lattice parameters for Ca₉Fe(PO₄)₇. The phase transition is accompanied by a discontinuity in the temperature dependence of the *a*, c/Z and V/Z parameters.

3.4. Electron diffraction study

ED patterns at $T_{\rm R}$ for Ca₉Fe(PO₄)₇ along [0001]*, [1100]*, [1101]* and [1120]* are shown in Fig. 5. Reflec-



i-s: isomorphic subgroups of lowest index

Fig. 3. Group–subgroup diagram for β - and β' -Ca₉Fe(PO₄)₇. Arrows present subgroups.



Fig. 4. Temperature dependence of the lattice parameters a, c/Z and V/Z for Ca₉Fe(PO₄)₇. Z is the number of formula units per unit cell.

tions on the ED patterns can be indexed in space group *R3c* with the lattice parameters determined from XRD data [7].



Fig. 5. Electron diffraction patterns along the main zone axes for β -Ca₉Fe(PO₄)₇ at room temperature.

Spots on the [0001]* pattern obey the reflection condition of -h + k = 3n imposed by the space group R3c. The $[1\overline{1}00]^*$ pattern exhibits the 000*l* reflections with l = 3n(n odd) forbidden in space group R3c. Intensities of these reflections, however, are systematically lower than those of the 000*l* reflections with l = 6n. The appearance of these forbidden reflections has been attributed to double diffraction. On tilting the specimen around the (000l) axis, intensities of the 000*l* reflections with l = 3n (*n* odd) further weaken and finally vanish. The 000*l* reflections with l = 3n(*n* odd) are absent in the $[11\overline{2}0]^*$ zone since the conditions for double diffraction are absent in this zone. The $[11\overline{2}0]^*$ diffraction pattern exhibits a rhombohedral shift of the spot rows along c^* by $hc^*/3$. Thus, the observed reflection condition, -h + k + l = 3n for *hkil*, with the extra condition l = 6n for 000l leads to only one space group, R3c, for β -Ca₉Fe(PO₄)₇ (taking into account the results of SHG).

Heating of the sample from 293 to 1133 K does not change the ED patterns. Intensities of the $hh\overline{2hl}$ reflections with l = 3n (*n* odd) only decrease but these reflections do not disappear with increasing temperature between 778 and 1133 K (Fig. 6) in contrast to the XRD data, where all reflections with *l* odd were not observed above T_c . In the case of a phase transition from space group R3c to $R\overline{3}m$ with halving the *c* parameter from ~ 38 to ~ 19 Å, all $hh\overline{2hl}$ reflections on these ED patterns with l = 3n (*n* is odd) should disappear. Thus, the ED data evidenced that only a phase transition from space group R3c to $R\overline{3}c$ was possible because space groups R3c and $R\overline{3}c$ have the same reflection conditions. These findings are in good agreement with the dielectric data but in contradiction with the XRD data.



Fig. 6. $[1\overline{1}00]^*$ electron diffraction patterns of Ca₉Fe(PO₄)₇ at different temperatures.

3.5. HREM studies

HREM studies have been performed at T_R along [0001] and [1100]. The structure of β -Ca₉Fe(PO₄)₇ can be interpreted in terms of cation and oxygen columns in these directions. The contrast interpretation of the HREM images is based on a comparison between the experimental images and the calculated ones. We calculated the HREM images using fractional coordinates for β -Ca₉Fe(PO₄)₇ in the space groups *R*3*c* [7], *R*3*m* and *R*3 (see Fig. 3). Images calculated on the basis of space groups *R*3*m* and *R*3 did not differ from each other. As mentioned above, the bulk β -Ca₉Fe(PO₄)₇ crystallizes in the space group *R*3*c*.

Fig. 7 shows the [0001] HREM image. The brighter dots in the HREM image correspond to columns of Fe atoms while the less bright dots represent Ca atoms. The calculated image shows a good agreement with the experimental one. The calculated images along this zone are similar to each other for different structure models (space groups R3c and R3m), which makes it impossible to discern them.

In the [1100] HREM images of Fig. 9 clearly regions with a different contrast can be discerned; the two images are taken from the same crystallite, but at different places. When compared with the calculated images of this section (Fig. 8); the contrast in Fig. 9a can be associated with a R3c symmetry, while the contrast in Fig. 9b can be explained assuming a R3m symmetry. In the latter the (1210) planes are straight, in the former they are wavy. This waviness appears for all focus values for a model with R3c symmetry and never for a R3m symmetry (Fig. 8). In the Fourier transform (FT) of Fig. 9a, given as an inset, the 000l reflections with l = 3n (n is odd) forbidden in



Fig. 7. HREM image of β -Ca₉Fe(PO₄)₇ along [0001] at $T_{\rm R}$. A calculated image for the $\Delta f = -65$ nm and t = 11.1 nm is shown as inset.



Fig. 8. Matrix of simulated [1100] high-resolution images for different defocus (Δf) and thickness (*t*) values assuming the *R*3*c* and *R*3*m* structure models of β -Ca₉Fe(PO₄)₇, respectively.

*R*3*c* are only weakly observed. The periodicity along the *c*-axis is ≈ 6 Å in Fig. 9a but 12 Å in Fig. 9b. This 12 Å periodicity is related to the presence of the (0003) reflection. We, therefore, have to assume that in the room temperature phase of β -Ca₉Fe(PO₄)₇ both (closely related) structures with symmetries the *R*3*c* and *R*3*m* occur within the same crystallite. Note that the *R*3*m* symmetry was not found in Ca₉In(PO₄)₇ (where the Ca/In ratio is ideally equal to 9) [29].

A similar phase transition ($\beta \leftrightarrow \beta'$) has been detected in Ca₉In(PO₄)₇ using almost the same experimental techniques [29]. Intensities of reflections with *l* odd dropped



Fig. 9. [1100] HREM images of different regions in β -Ca₉Fe(PO₄)₇. (a) shows the *R*3*c* symmetry while (b) shows the *R*3*m* symmetry. The calculated images for the *R*3*c* ($\Delta f = -50$ nm and t = 2 nm) and *R*3*m* ($\Delta f = -50$ nm and t = 10 nm) models are presented in inset in the corresponding images. The Fourier transform is given in the left upper corner.

noticeably on the XRD patterns at T_c , but these reflections did not disappear in Ca₉In(PO₄)₇. The invisibility of reflections with *l* odd in β' -Ca₉Fe(PO₄)₇ can be because of their very small intensities related to the worse signal-tonoise ratio for Ca₉Fe(PO₄)₇ compared to Ca₉In(PO₄)₇. We analyzed the intensities of the *l* odd reflections calculated with RIETAN-2000 (Table 1). In Ca₉Fe(PO₄)₇, the intensities of these reflections decreased largely in the β' -phase. In Ca₉In(PO₄)₇, the intensities of these reflections also decreased but to a less extent. Because ED is more sensitive in comparison with XRD, these weak reflections are observed on the ED patterns of β' -Ca₉Fe(PO₄)₇ but not on the XRD patterns. The apparent contradiction between the XRD and ED data is, therefore, related to the sensitivity of both methods. Table 1

Intensities	(counts) of	some separate	ely located	reflections	with l	=2n	+1
for β - and	β' -Ca ₉ $R(P$	$O_4)_7 \ (R = Fe$	and In)				

hkl		Ca ₉ Fe(PO ₄) ₇				Ca ₉ In(PO ₄) ₇			
	300	0 K	923	3 K	300) K	973	3 K	
	Iobs	Ical	Iobs	<i>I</i> _{cal}	Iobs	<i>I</i> _{cal}	Iobs	<i>I</i> _{cal}	
211	3345	3254	372	376	2506	2581	698	692	
119	2828	2814	17	17	1898	1961	472	470	
223	4590	4700	751	757	3718	3724	157	158	
131	2598	2652	91	92	2078	2072	299	299	

All the intensities were calculated with RIETAN-2000 [32]. $I_{obs} = 100000$ counts for the 100% reflection (0210).

3.6. Structure of β' -Ca₉Fe(PO₄)₇ at 923 K

For the initial fractional coordinates in the Rietveld analysis of β' -Ca₉Fe(PO₄)₇, we used those of β -Ca₉Fe(PO₄)₇ at $T_{\rm R}$ (space group *R*3*c*, a = 10.339 Å and c = 37.130 Å) [7]. In the structure of β -Ca₉Fe(PO₄)₇, the Fe³⁺ ions occupy the M5 site of the β -Ca₃(PO₄)₂ structure, Ca²⁺ ions occupy the M1–M3 sites, while the M4 and M6 sites are vacant (Fig. 10a and 10b).

The arrangement of the majority of the atoms in β -Ca₉Fe(PO₄)₇ is close to centrosymmetric with pseudocenters of symmetry at the M3 and M5 sites. Only the P1O₄ tetrahedra and, therefore, cavities M4O₁₅ and M6O₁₃ are not connected by the pseudocenters of symmetry (Fig. 10a and 10b). To introduce centers of symmetry in β -Ca₉Fe-(PO₄)₇, half of the P1O₄ tetrahedra should change their orientation (Fig. 11). In that way, half of the M4O₁₅ cavities are transformed into M6O₁₃ cavities and vise versa. The ideal centrosymmetric structure (see also Fig. 3) should have two types of M3 sites and two types of M5O₆ polyhedra surrounded by two M4O₁₅ cavities or by two M6O₁₃ cavities.

In the $R\bar{3}c$ model, the Ca1 (= M1) and Ca2 (= M2) sites and the P2O₄ and P3O₄ tetrahedra of the β -Ca₉Fe(PO₄)₇ structure are equivalent, while the Fe5 (= M5; 6b) and Ca3 (= M3; 18d) sites are situated at centers of symmetry; the P1 atom lies at site 6a; the O11 and O12 atoms are located at sites 12c and 36f, respectively, with g = 1/2, where g is occupancy. The Rietveld refinements with these atomic arrangements lead to unreasonably large isotropic atomic displacement parameters, B, for Ca3 (B = 7.4(2) Å²), P1 (B = 6.7(2) Å²) and O11 (B = 35(2) Å²) atoms. A displacement of these atoms from their ideal positions to split ones (from 18d to 36f for Ca3, from 6a to 12c for P1, and from 12c to 36f for O11) lowered their B parameters considerably.

Table 2 lists experimental and refinement conditions, lattice parameters, *R* factors and so forth. Table 3 gives the final fractional coordinates and *B* parameters and Table 4 presents the main bond lengths. Fig. 12 displays observed, calculated, and difference XRD patterns for β' -Ca₉Fe(PO₄)₇.

The *B* parameters for the Ca1, Ca3, Fe5, P2, O21, O22, O23 and O24 atoms are enlarged ($B = 0.9-3.1 \text{ Å}^2$) due to the high-temperature XRD experiments. The *B* parameters



Fig. 10. (110) projections of the structure of (a, b) β -Ca₉Fe(PO₄)₇ (space group *R*3*c*) and (c) β' -Ca₉Fe(PO₄)₇ (space group *R*3*c*): Layer I (a) and Layers II (b, c). Columns *A* and *B* are indicated by thick marks. β - and β' -Ca₉Fe(PO₄)₇ have the same Layer I. Arrows present elements of the structure of β -Ca₉Fe(PO₄)₇ connected by pseudocenters of symmetry.

Table 2

Conditions of the XRD experiment and part of refinement results for β' -Ca₉Fe(PO₄)₇

Temperature (K)	923	Space group	<i>R</i> 3 <i>c</i> (No. 167)
2θ range (deg)	10-110	Lattice parameter	ers:
2θ step width (deg)	0.02	a (Å)	10.3878(2)
Imax (counts)	63036	<i>c</i> (Å)	37.8387(4)
Variables:		Ζ	6
Structural	39	$R_{\rm wp}$	1.48%
Background	9	Rp	1.14%
Profiles	10	R _I	2.16%
Lattice parameters	2	$R_{\rm F}$	2.32%
Zero shifts + scale + text	ure $3 + 1 +$	1 <i>S</i>	1.45

for the P1, O11 and O12 atoms are about 2–3 times larger than for the other atoms due to their disordering. Similar, *B* parameters were obtained in the structure analysis of β' -Ca₉In(PO₄)₇ at 973 K [29].



Fig. 11. Columns A in (a) polar (space group R3c) and (b) ideal centrosymmetric (space group $R\overline{3}$) whitlockite-type structures.

Table 3
Fractional coordinates and isotropic atomic displacement parameters for β' -
$Ca_9Fe(PO_4)_7$

	47.7					
Atom ^a	Site	g	x	у	z	$B({\rm \AA}^2)$
Ca1	36 <i>f</i>	1	0.7099(2)	0.8554(9)	0.43467(5)	2.19(8)
Ca3	36 <i>f</i>	1/2	0.1441(27)	0.2853(6)	0.32868(12)	1.90(14)
Fe5	6b	1	0.0	0.0	0.0	1.26(11)
P1	12c	1/2	0.0	0.0	0.2572(5)	3.9(5)
P2	36 <i>f</i>	1	0.6498(3)	0.8340(10)	0.03123(8)	1.91(9)
011	36 <i>f</i>	1/6	0.937(18)	0.057(18)	0.2878(9)	5.3(1.4)
012	36 <i>f</i>	1/2	0.030(2)	0.895(2)	0.2650(3)	3.7(7)
O21	36 <i>f</i>	1	0.7337(6)	0.864(3)	0.1742(1)	3.1(2)
O22	36 <i>f</i>	1	0.7434(15)	0.7514(16)	0.1208(3)	2.5(4)
O23	36 <i>f</i>	1	0.7270(15)	0.9859(16)	0.1152(3)	0.9(4)
O24	36 <i>f</i>	1	0.5049(5)	0.748(2)	0.13207(9)	2.2(2)

^a Atom numerations retain the same as those in β -Ca₉Fe(PO₄)₇ [7]. In β' -Ca₉Fe(PO₄)₇: M1=M2=Ca1, M3=Ca3, M5=Fe5, P2=P3, O21=O34, O22=O32, O23=O31 and O24=O33. In oxygen numeration, the first number is for the P atom and the second number is for the O atom in the tetrahedron.

Disordering of cations at the M3 sites and orientational disordering of the P1O₄ tetrahedra is also observed in other structurally related compounds, Sr₉Fe_{1.5}(PO₄)₇ [38], Sr_{9.1}Cu_{1.4}(PO₄)₇ [39] and β' -Ca_{5/7}Sr_{16/7}(PO₄)₂ (refined

Table 4 Bond lengths (Å) in β' -Ca₉Fe(PO₄)₇

Bonds	<i>d</i> (Å)	Bonds	<i>d</i> (Å)
Ca1–O21	2.403(5)	Ca3-O22	2.39(2)
-O23	2.42(2)	-O22a	2.39(2)
-011	2.43(3)	-O21	2.47(3)
-O23a	2.50(2)	-O21a	2.50(3)
-O24	2.51(2)	-O23	2.57(2)
-O22	2.54(1)	-O23a	2.60(2)
-O12	2.54(2)	-O11	2.69(15)
-O24a	2.60(2)	-O11a	2.75(16)
-O12a	2.60(2)	-O12	2.79(1)
-O22a	2.70(1)	-O21b	3.04(4)
		-O21c	3.12(4)
Fe5–O24 (×6)	2.025(5)	Ca3–Ca3a ^a	0.934(9)
P1011	1.60(4)	P2-O21	1.539(5)
-O12 (×3)	1.52(2)	-O22	1.55(2)
P1–P1a ^a	0.55(4)	-O23	1.46(1)
		-O24	1.618(6)

^a Distances between split positions.

from XRD data) [22], Sr_{9.2}Co_{1.3}(PO₄)₇ (refined from single crystal X-ray diffraction data) [40] and Sr_{9.3}Ni_{1.2}(PO₄)₇ (refined from neutron powder diffraction data and studied by a MEM-based pattern fitting of synchrotron XRD data) [41]. Their structure parameters were refined with space group $R\overline{3}m$ and lattice parameters $a \approx 11$ Å and $c \approx 19$ Å. In all the above-mentioned compounds, the *B* parameter for disordered atoms is 2–5 times larger than for the other atoms.

4. Discussion

Using XRD, ED, HREM, SHG, DSC, dielectric and electrical-conductivity measurements, we have found a high-temperature ferroelectric phase transition in Ca₉Fe(PO₄)₇ with $T_c = (890 \pm 10)$ K. β - and β' -Ca₉Fe(PO₄)₇ are both based on the whitlockite-type structure. β' -Ca₉Fe(PO₄)₇ is stable only at temperatures above T_c and cannot be obtained by quenching to T_R . The DSC, SHG, dielectric and electrical-conductivity data indicate that the phase transition in Ca₉Fe(PO₄)₇ is first order. The $\beta \rightarrow \beta'$ phase transition is accompanied by a disordering of Ca²⁺ ions at the Ca₃ sites and orientational disordering of the P1O₄ tetrahedra as revealed by the structure refinements independent of the structural model used. According to the obtained structural data the $\beta \rightarrow \beta'$ phase transition should be classified as an order–disorder ferroelectric phase transition [36].

The (110) projection of the structures of β - and β' -Ca₉Fe(PO₄)₇ are shown in Fig. 10. The structures can be constructed from two types of layers, termed I and II (Fig. 10a and 10b) [15]. Layer I consists of *B* columns (Fig. 10a), while layer II consists of *A* and *B* columns (Fig. 10b). The *B* and *A* columns have a different alternation of cations and PO₄ tetrahedra. Layers I are almost similar for β - and β' -Ca₉Fe(PO₄)₇. The main differences between them are in layer II (Fig. 10b and 10c) and in column *A*. The observed disordering of the P1O₄



Fig. 12. Observed, calculated and difference XRD patterns for β' -Ca₉Fe(PO₄)₇ at 923 K. Bragg reflections are indicated by thick marks. Short thick marks present reflections with *l* odd. 2θ regions containing reflections from the Pt plate were excluded from the refinement.

tetrahedra in β' -Ca₉Fe(PO₄)₇ can be explained by the fact that columns *A* in the ideal centrosymmetric whitlockite structure (Fig. 11b), [P1O₄–M4O₁₅–M5O₆–M4O₁₅–P1O₄–M6O₁₃–M5'O₆–M6O₁₃–]_{∞}, are not located according to the translation symmetry of a *R*-centered lattice, (1/3, 2/3, 2/3)+ and (2/3, 1/3, 1/3)+.

The transition from β -Ca₃(PO₄)₂ (space group R3c) [13] to α -Ca₃(PO₄)₂ (space group $P2_1/a$) [16] is also a phase transition of the 'polar-to-centrosymmetric' type. In contrast to the $\beta \rightarrow \beta'$ transition in Ca₉Fe(PO₄)₇, the $\beta \rightarrow \alpha$ transition in $Ca_3(PO_4)_2$ is accompanied by significant shifts of cations and anions in the whitlockite-type structure to form a β -K₂SO₄-type one [42]. Because the structure of β - $Ca_9Fe(PO_4)_7$ has many features common to K_2SO_4 -related compounds, it is interesting to compare the dielectric properties of Ca₉Fe(PO₄)₇ with those of K₂SO₄ and its analogues. An aptitude of SO_4^{2-} tetrahedra for rotation produces a remarkable number of related structures [43]. Nevertheless, little is known to date about the ferric behavior in the K₂SO₄ family. β -K₂SO₄ undergoes a distortion-type phase transition at 56 K, which was shown to be nonferroelectric or ferroelastic [44]. K₂SeO₄ demonstrates two phase transitions at 129.5 and 93 K. The phase transition at 93 K leads to ferroelectricity with a very small spontaneous polarization, P_s , of 0.06 μ C cm⁻² [45,46]. P_s is larger by an order of magnitude $(0.6 \ \mu C \ cm^{-2})$ in NH₄KSO₄ below its ferroelectric phase transition with $T_c = 223$ K [47]. A weak anomaly in ε at T_c, a temperature hysteresis of 10 K, and the Curie– Weiss constant, C_{C-W} , as small as 40 K were observed in NH₄KSO₄. Submillimeter spectra of NH₄KSO₄ contained a relaxor mode due to rotation movements of the SO_4^{2-} tetrahedra [47].

Structures of ferroelectric phosphates $A^{I}A^{II}PO_{4}$ ($A^{I} =$ Na, K, Rb and Cs and $A^{II} =$ Co, Zn, Ca, Sr, Ba and Pb) [48,49] in some aspects are close to that of Ca₉Fe(PO₄)₇. In $A^{I}A^{II}PO_{4}$, P_{s} and anomalies in ε did not exceed several units, e.g., ε changed from 4 to 6 near T_{c} in CsZnPO₄ [48]. A phase transition in NaPbPO₄ with $T_{c} = 1063$ K led to $P_{s} = 3.4 \ \mu\text{C} \text{ cm}^{-2}$ at T_{R} [49] which is less by an order of magnitude than the P_{s} value expected from the Abrahams–Kurtz–Jamieson formalism [50] for proper ferroelectrics with the same T_{c} . On the other hand, a consistent classification of ferroelectrics as a 'pseudo-proper' ferroelectric implies special relationships between the symmetry of ferroelectric (below T_{c}) and paraelectric (above T_{c}) phases.

The symmetry of a ferroelectric phase must be related to the symmetry of a paraelectric phase by imposing the spontaneous polarization vector symmetry [37]. This condition is fulfilled for Ca₉Fe(PO₄)₇ with its symmetry transformation from *R*3*c* to *R*3*c* in the $\beta \rightarrow \beta'$ phase transition. Moreover, since the vector symmetry does not affect the translation symmetry, unit-cell dimensions should not change in this type of phase transitions. Unit-cell dimensions do not change in Ca₉Fe(PO₄)₇ during the $\beta \rightarrow \beta'$ phase transition. Taking into account a small *P*_s value of 2–3 µC cm⁻², estimated from the SHG data [35], and the small anomalies in ε near T_c for Ca₉Fe(PO₄)₇, we have enough arguments to consider Ca₉Fe(PO₄)₇ as a new pseudo-proper ferroelectric with a high Curie temperature and a small spontaneous polarization.

Supplementary material

Supplementary material has been sent to the Fachinformationzentrum Karlsruhe, Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany, as supplementary material No. 413447 (5 pages) and can be obtained by contacting the FIZ (quoting the article details and the corresponding SUP number).

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References

- (a) Z. Zyman, J. Weng, X. Liu, X. Li, X. Zhang, Biomaterials 15 (1994) 151;
 - (b) T. Kitsugi, T. Yamamura, T. Nakamura, O. Masanori, Biomaterials 16 (1995) 1101;
 - (c) S. Langstaff, M. Sayer, T.J.N. Smith, S.M. Pugh, S.A.M. Hesp, W.T. Thompson, Biomaterials 20 (1999) 1727;
 - (d) A. Bigi, E. Foresti, M. Gandolfi, M. Gazzano, N. Roveri, J. Inorg. Biochem. 66 (1997) 259.
- [2] (a) V. Pelova, K. Kynev, G. Gochev, Mater. Sci. Lett. 14 (1995) 330;
 (b) H. Donker, W.M.A. Smit, G. Blasse, J. Electrochem. Soc. 136 (1989) 3130.
- [3] (a) G.E. Vrieland, The Dow Chemical Co., US patent 3,935,126, 1974;
 (b) H.O. Krabbenhoft, General Electric Co., US patent 4,346,249, 1981;
 - (c) H.O. Krabbenhoft, General Electric Co., US patent 4,366,089, 1981;
- (d) G.R. Strickler, The Dow Chemical Co., US patent 4,471,146, 1983.[4] A. Legrouri, S.S. Romdhane, J. Lenzi, M. Lenzi, G. Bonel, J. Mater.
- Sci. 31 (1996) 2469.
 [5] A. Benarafa, M. Kacimi, G. Coudurier, M. Ziyad, Appl. Catal. A 196 (2000) 25.
- [6] B.I. Lazoryak, V.A. Morozov, M.S. Safonov, S.S. Khasanov, Mater. Res. Bull. 30 (1995) 1269.
- [7] B.I. Lazoryak, V.A. Morozov, A.A. Belik, S.S. Khasanov, S.Sh. Shekhtman, J. Solid State Chem. 122 (1996) 15.
- [8] B.I. Lazoryak, N. Khan, V.A. Morozov, A.A. Belik, S.S. Khasanov, J. Solid State Chem. 145 (1999) 345.
- [9] T.V. Strunenkova, V.A. Morozov, S.S. Khasanov, K.V. Pokholok, A.N. Zhdanova, B.I. Lazoryak, Crystallogr. Rep. 42 (1997) 64 (in Russian).

- [10] B.I. Lazoryak, Fundamental Study of New Material and Processes in the Substance, Moscow State Univ. Press, Moscow, 1994, p. 54.
- [11] M.S. Safonov, B.I. Lazoryak, S.S. Pozharskii, S.V. Dashkov, Dokl. Acad. Nauk Russ. 358 (1994) 663.
- [12] B.I. Lazoryak, V.A. Morozov, A.N. Zhdanova, RF patent 95100507/ 26, 1995.
- [13] B. Dickens, L.W. Schroeder, W.E. Brown, J. Solid State Chem. 10 (1974) 232.
- [14] C. Calvo, R. Gopal, Am. Mineral. 60 (1975) 120.
- [15] B.I. Lazoryak, Russ. Chem. Rev. 65 (1996) 287.
- [16] M. Mathew, L.W. Schroeder, B. Dickens, W.E. Brown, Acta Crystallogr. B 33 (1977) 1325.
- [17] W. Fix, H. Heymann, R. Heinke, J. Am. Ceram. Soc. 52 (1969) 346.
- [18] H. Monma, M. Goto, J. Ceram. Soc. Jpn. 91 (1983) 473.
 [19] (a) J. Ando, Bull. Chem. Soc. Jpn. 31 (1958) 196;
 (b) J.F. Sarver, M.V. Hoffman, F.A. Hummel, J. Electrochem. Soc. 108
- (1961) 1103.
- [20] R.W. Nurse, J.H. Welch, W. Gutt, J. Chem. Soc. (1959) 1077.
- [21] L.J. Ruan, X.R. Wang, L.T. Li, Mater. Res. Bull. 31 (1996) 1207.
- [22] A.A. Belik, F. Izumi, S.Yu. Stefanovich, A.P. Malakho, B.I. Lazoryak, I.A. Leonidov, O.N. Leonidova, S.A. Davydov, Chem. Mater. 14 (2002) 3197.
- [23] G.N. Kustova, E.N. Yurchenko, E.B. Burgina, M.M. Andruschkevich, P.A. Buyanov, Zh. Strukt. Khim. 20 (1979) 1019 (in Russian).
- [24] A.L. Mackay, D.P. Sinha, J. Phys. Chem. Solids 28 (1967) 1337.
- [25] H. Koelmans, J.J. Engelsman, P.S. Admiraal, J. Phys. Chem. Solids 11 (1959) 172.
- [26] S.S. Romdhane, G. Bonel, G. Bacquet, Mater. Res. Bull. 18 (18) (1983) 559.
- [27] P. Roux, D. Louer, G. Bonel, C. R. Acad. Sci. 286 (1978) 549.
- [28] B.I. Lazoryak, S.Yu. Oralkov, V.N. Golubev, A.N. Zhdanova, Russ. J. Inorg. Chem. 35 (1989) 1710 (in Russian).
- [29] V.A. Morozov, A.A. Belik, S.Yu. Stefanovich, V.V. Grebenev, O.I. Lebedev, G. Van Tendeloo, B.I. Lazoryak, J. Solid State Chem. 165 (2002) 278.
- [30] Powder Diffraction File, Card 45-338, JCPDS, International Center for Diffraction Data, 1601 Park Lane, Swarthmore, PA, 1981.

- [31] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65.
- [32] F. Izumi, T. Ikeda, Mater. Sci. Forum 321-324 (2000) 198.
- [33] E.M. Maslen, A.G. Fox, M.A. O'Keefe, International Tables for Crystallography, vol. C, Kluwer, Dordrecht, 1999, pp. 572–574.
- [34] S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798.
- [35] S.Yu. Stefanovich, Lasers and electro-optics (CLEO-Europe'94), in: Proc. Eur. Conf., Amsterdam, The Netherlands, 1994, p. 249.
- [36] J. Ravez, C. R. Acad. Sci. Paris, Ser. IIc: Chem. 3 (2000) 267.
- [37] M.E. Lines, A.M. Glass, Principles and Applications of Ferroelectrics and Related Materials, Clarendon Press, Oxford, 1977.
- [38] A.A. Belik, B.I. Lazoryak, K.V. Pokholok, T.P. Terekhina, I.A. Leonidov, E.B. Mitberg, V.V. Karelina, D.G. Kellerman, J. Solid State Chem. 162 (2001) 113.
- [39] A.A. Belik, A.P. Malakho, B.I. Lazoryak, S.S. Khasanov, J. Solid State Chem. 163 (2002) 121.
- [40] A.P. Malakho, A.A. Belik, P.S. Salamakha, B.I. Lazoryak, Mater. Res. Bull., submitted for publication.
- [41] A.A. Belik, F. Izumi, T. Ikeda, V.A. Morozov, R.A. Dilanian, S. Torii, E.M. Kopnin, O.I. Lebedev, G. Van Tendeloo, B.I. Lazoryak, Chem. Mater. 14 (2002) 4464.
- [42] M.T. Robinson, J. Phys. Chem. 62 (1958) 925.
- [43] B.V. Beznosikov, Ferroelectrics 144 (1993) 179.
- [44] S. Schmits, H.-J. Weber, 10th Crystallogr. Meeting, in: Proc. Eur. Conf., Wroclaw, Poland, 1986, p. 355.
- [45] M. Izumi, J.D. Axe, G. Shirane, K. Shimaoka, Phys. Rev. B 15 (1977) 4392.
- [46] C. Gonzalez-Silgo, X. Soains, C. Ruiz-Perez, M.L. Martinez-Sarrion, S. Mestres, Ferroelectrics 177 (1996) 191.
- [47] A.A. Volkov, Y.G. Goncharov, G.V. Kozlov, S.P. Lebedev, O.I. Sirotinskii, J. Petzelt, B. Winke, Fiz. Tverd. Tela 30 (1988) 1773 (in Russian).
- [48] D. Blum, J.C. Peusin, J.Y. Henry, Ferroelectrics 61 (1984) 265.
- [49] B. Elouadi, L. Elammari, J. Ravez, Ferroelectrics 56 (1984) 17.
- [50] S.C. Abrahams, S.K. Kurtz, P.B. Jamieson, Phys. Rev. 172 (1968) 551.