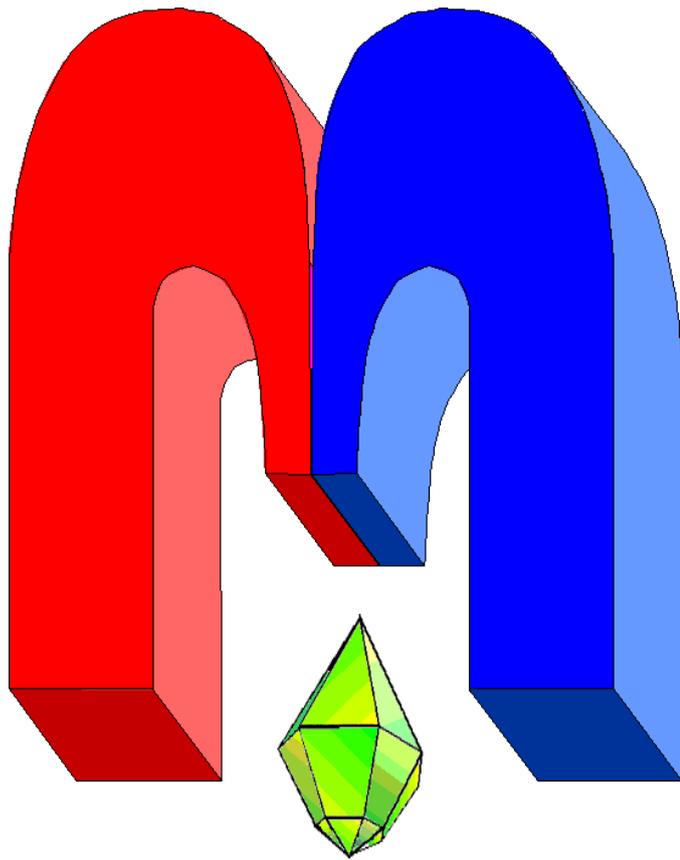


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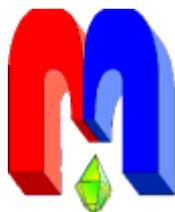
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† In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

The study of synthetic tricalcium phosphate by EPR and DFT methods

D.V. Shurtakova*, G.V. Mamin, M.R. Gafurov

Kazan Federal University, Kremlevskaya 18, Kazan 420008, Russia

*E-mail: darvshurtakova@kpfu.ru

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In this research, we propose a model of an impurity nitrogen center in tricalcium phosphate (TCP). This impurity was not intentionally added but was detected by electron paramagnetic resonance (EPR). It was shown that the EPR spectrum of the powder under study is due to two types of such impurity centers, which we attribute to the TCP phase and the admixed hydroxyapatite phase. The parameters of the spin Hamiltonian for the center in TCP obtained using Density Functional Theory (DFT) calculations are close to the experimental ones and allow us to propose a model of a nitrogen-containing center. The temperature dependence of the spin-lattice relaxation rate in the TCP phase is described by a process proportional to $T^{2.35}$ in the temperature range from 10 to 300 K.

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Keywords: electron paramagnetic resonance, g -factors, hyperfine interaction, tricalcium phosphate.

1. Introduction

Tricalcium phosphate (TCP) $\text{Ca}_3(\text{PO}_4)_2$ is actively used in medical preparations for the restoration and remodeling of bone and dental tissue, for the manufacture of biodegradable ceramics in the form of dense and macroporous granules, multivitamin complexes with TCP. Calcium ions released during the dissolution of TCP in the body are involved in the creation of new bone tissue [1]. To achieve the best medical effect in bone tissue remodeling, TCP-based preparations are added impurities or mixed with other materials, such as hydroxyapatite (HAp) [2].

TCP and HAp differ in their biological activity. TCP has a high absorption rate and high hydrophilicity, while HAp has poor absorption, high brittleness and poor mechanical properties. Biphasic calcium phosphate (β -TCP/HAp) can increase the mechanical strength of ceramic materials, ensure the stability of the scaffold material until new bone is formed [3].

The addition of impurities to the composition of calcium phosphates can affect the physicochemical and biological properties of crystals [4, 5]. In general, such crystals retain their structure. However, the presence of impurities can cause minor internal stresses in the crystal, which in turn can affect solubility, hardness, brittleness, heat resistance, etc. Different impurity ions and their location in the structure of calcium phosphates have various effects on the local deformation of the lattice. This, in turn, can affect the properties of the biomaterial [6, 7].

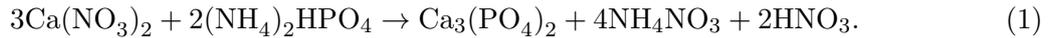
Apart from the targeted introduction of impurities into synthetic calcium phosphates, unplanned impurities can also be included in the structure (for example, nitrogen or carbonate complexes). Nitrogen complexes can get into the structure during the preparation of samples (as they are used in chemical reactions) [8]. Nitrogen oxides have an adverse effect on humans [9], therefore, such impurities require special control.

2. Materials and methods

2.1. Materials

The most well-known and stable modification of TCP is β -TCP (β -Ca₃(PO₄)₂, R3cH rhombohedral crystal structure). There is also a low symmetry α -TCP phase (chemical formula α -Ca₃(PO₄)₂, monoclinic crystal structure P2₁/a) and a γ -TCP phase (chemical formula γ -Ca₃(PO₄)₂, rhombohedral crystal structure R $\bar{3}$ m).

In this paper, we investigate the powder of tricalcium phosphate, which was synthesized at the A.A. Baikov Institute of Metallurgy and Materials Science by precipitation from colloidal solutions according to the following chemical reaction [10]:



According to powder X-Ray Diffraction (PXRD) [10], it was shown that this tricalcium phosphate powder was formed mainly in the β -TCP modification with an admixture of the hydroxyapatite phase (79% and 21%, respectively).

2.2. Methods

EPR (electron paramagnetic resonance) spectra were recorded on an ElexsysBruker 580/680 spectrometer in the X- and W-ranges in the temperature range from 10 to 300 K in the pulsed mode using the standard Hahn sequence $\pi/2 - \tau - \pi$. The length of the π -pulse was 16–48 ns, the time τ varied from 180 to 3000 ns. Paramagnetic centers were created by “URS-55” X-ray irradiation equipment (W-anticathode) for 1 hour with a accumulated dose of 10 kGy. Approximation of the EPR spectra was carried out in a program written by the Matlab environment using the EasySpin module. The Quantum Espresso program was used to calculate the EPR parameters by Density Functional Theory (DFT) calculations.

3. Experimental results and discussion

3.1. EPR spectra

The presence of an impurity nitrogen center in the structure due to the fact that calcium nitrate (chemical formula Ca(NO₃)₂) is used in the synthesis reaction of calcium phosphate powder. In this case, the nitrogen center has a charge of “-1”. The NO₃⁻ center is not paramagnetic, the EPR signal will not be observed regardless of the temperature. X-ray irradiation ionizes the impurity nitrogen center, and the EPR spectrum was observed. Calculations show that the replacement of the phosphorus group by the nitrogen group causes strong local deformation, and the electron added to the structure is localized at the NO₃ center. The EPR spectra of synthetic TCP appeared after X-ray irradiation with a dose of 10 kGy. At 300 K, the spectrum of TCP (Figure 1) in the X-band has 3 distinct lines with the parameters represented in the R₁^{HAp} row of Table 1. These parameters are close to those of the nitrogen center in hydroxyapatite; therefore, we can assume that this center belongs to the centers of the NO₃²⁻ impurity of the hydroxyapatite phase [8].

As the temperature decreases, the spectrum becomes more complex and new lines appear. This may indicate the presence of another center in the system, which can be attributed to the tricalcium phosphate phase. To determine the centers in tricalcium phosphate, the EPR spectra were measured at different times between first and second MW pulses τ (Figure 2).

To separate parts of the spectra from different phases of the sample, we used the technique described in [11]. The results are shown in Figure 3. Relative intensities of the spectra: 15% (R₁),

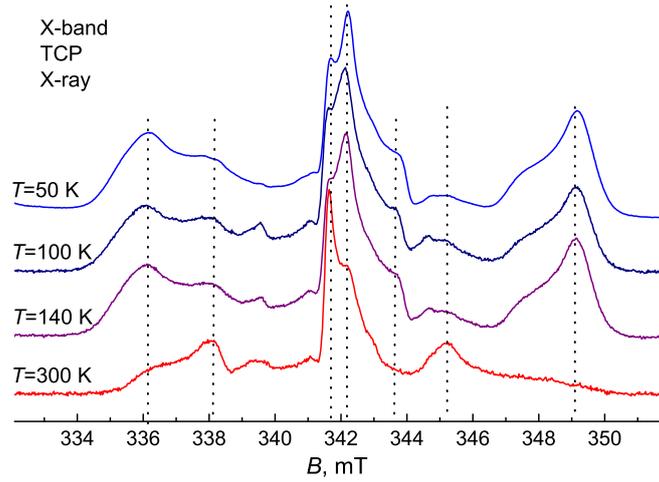


Figure 1. Temperature dependence of the EPR spectrum of impurity centers in TCP powder in the X-band.

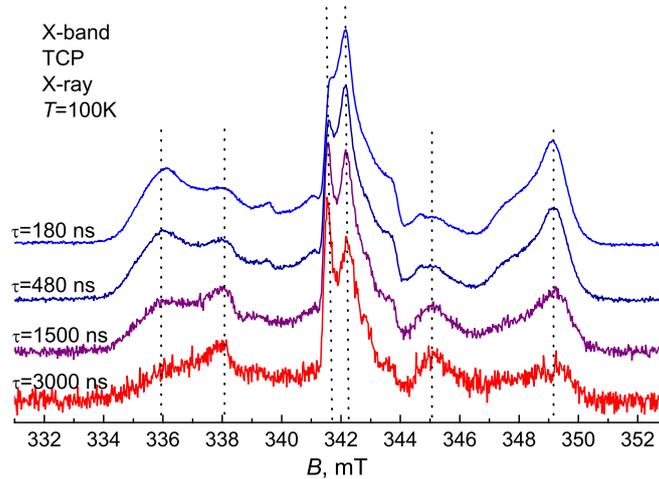


Figure 2. Dependence of the EPR spectrum of impurity centers in TCP powder in the X-band on the delay time between pulses τ

85% (R_2). According to PXRD, the proportion of HAp is 21%, and that of TCP is 79%, which means that the nitrogen complex enters more into the TCP phase. The first spectrum (Figure 3a), corresponding to slower spin-spin relaxation, has a shape and spectroscopic parameters close to the EPR spectrum at a temperature of 300 K and can be attributed to NO_3^{2-} centers in HAp. The second center also has 3 lines in the EPR spectrum (Figure 3b), which corresponds to a hyperfine interaction with the ^{14}N nucleus, so it can also be attributed to nitrogen-containing centers in β -TCP. Since β -TCP has trigonal symmetry, the Hamiltonian was used to model the center (II):

$$H = g_x \mu H_x S_x + g_y \mu H_y S_y + g_z \mu H_z S_z + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z. \quad (2)$$

It was also necessary to add one more structureless line ($g = 2.004$) of oxygen-containing centers, for example, the PO_3^{2-} group [12]. The main axis of the hyperfine structure constant

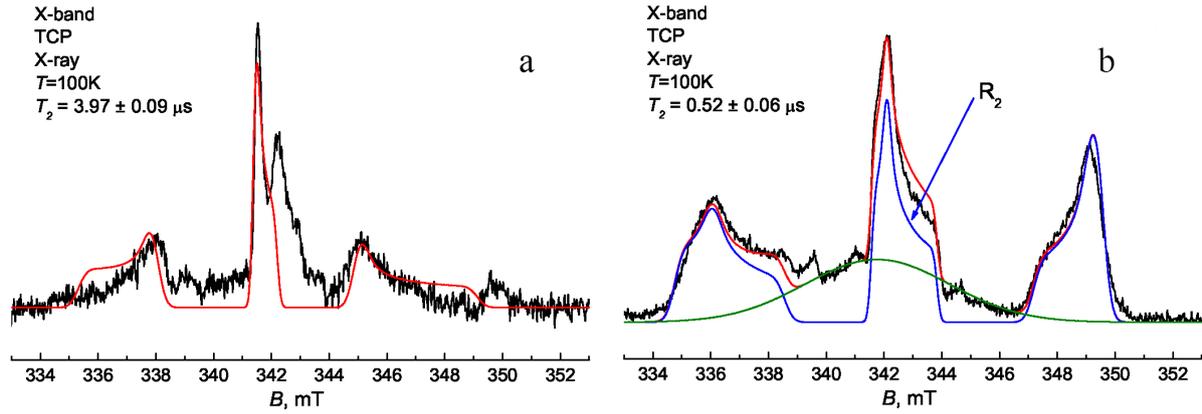


Figure 3. Description of powder EPR spectra of impurity nitrogen centers in TCP. Figure a shows the center related to the HAp phase, Figure b shows the center related to the TCP phase.

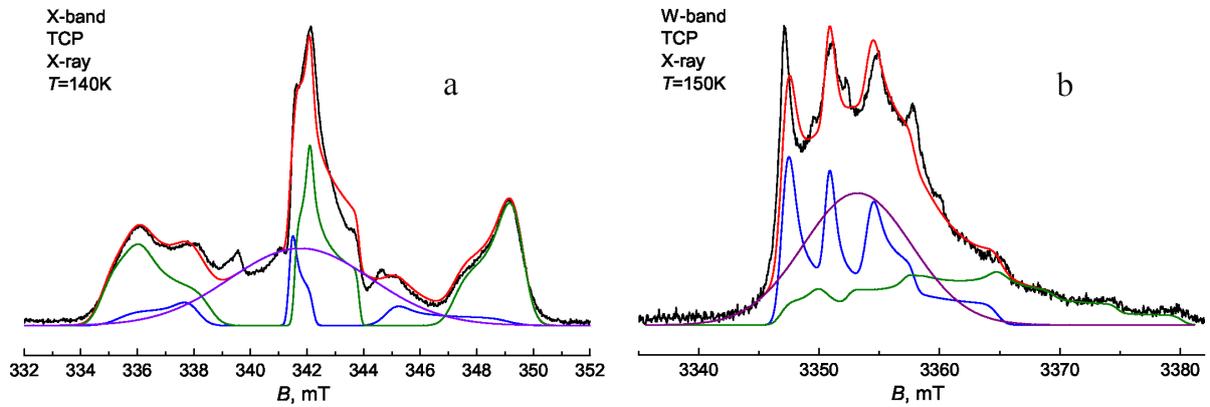


Figure 4. Description of the total EPR spectrum of TCP powder in the X- and W-bands (a and b respectively).

(HFS) tensor for the R_2^{TCP} center is directed along the c axis of the crystal for better agreement with the experimental data. This Hamiltonian describes well the R_2^{TCP} impurity center in the split EPR spectrum (Figure 3b).

The description of the initial experimental spectra of the TCP powder was carried out simultaneously in the X- and W-bands by the total spectrum from the three above-mentioned centers and is shown in Figure 4. The approximation parameters are in Table 1.

Table 1. Approximation parameters of the spin Hamiltonian impurity nitrogen centers in TCP.

| Complex | $R_1^{\text{HAp}}(\text{NO}_3^{2-})$ | $R_2^{\text{TCP}}(\text{NO}_3^{2-})$ | $R_{\text{calc}}(\text{NO}_3^{2-})$ |
|-------------|--------------------------------------|--------------------------------------|-------------------------------------|
| g_x | 2.0060 ± 0.0002 | 1.9919 ± 0.0003 | 1.9967 |
| g_y | 2.0060 ± 0.0001 | 2.0018 ± 0.0005 | 1.9993 |
| g_z | 2.0018 ± 0.0002 | 2.0048 ± 0.0004 | 2.0038 |
| A_x , MHz | 98 ± 5 | 155 ± 9 | 106 |
| A_y , MHz | 98 ± 5 | 148 ± 6 | 106 |
| A_z , MHz | 193 ± 3 | 207 ± 9 | 182 |

3.2. DFT calculations

To accurately identify the center, DFT calculations were carried out. According to previous calculations in HAp [8] the nitrogen center is a NO_3 complex, which occupies the position of the PO_4 phosphorus group. Due to the similar structure of HAp and TCP, a similar model was adopted for calculations. The parameters of the spin Hamiltonian (g -factor and hyperfine interaction constant A) for this center were calculated using the Quantum Espresso program.

Due to technical limitations, the calculation of these parameters was carried out for a simpler phase γ -TCP. This phase has 3 $\text{Ca}_3(\text{PO}_4)_2$ formula units per unit cell, has a triclinic $R\bar{3}m$ symmetry, and is a collection of PO_4 -Ca(2)-Ca(1)-Ca(2)- PO_4 “threads” displaced relative to each other. The β -TCP phase is a supercell, which is approximately 8 times larger in volume than γ -TCP, 7 times larger in composition (contains 21 formula units), consists of two types of “threads” A and B. “Thread” B corresponds to a “thread” in γ -TCP, and “thread” A - consists of half of the formula unit (PO_4 (1) – Ca (4) (50%) – ... – Ca (5) – ...) [13].

The calculation the spin Hamiltonian parameters of the nitrogen center in TCP were carried out for a “supercell” of 4 elementary cells of γ -TCP, where the PO_4 group was replaced by the NO_3 group. To save electrical neutrality, the neighboring Ca ion was removed from the structure [8]. At the first step, the positions of ions in an electrically neutral crystal were optimized without changing the cell parameters (calculation type “relax”). At the second step, it was taken into account that the EPR spectrum appears after irradiation, so an additional electron was added to the structure obtained at the first step. The result of calculating the parameters of the spin Hamiltonian is shown in Table 1 (R_{calc} row). The calculated values of the g -factor are close to the experimental values of the R_2^{TCP} center.

The calculated spin polarization is shown in Figure 5 (under the letter a, positive values of the spin polarization, under the letter b, negative values). The oxygen and nitrogen ions are located in the same plane parallel to the xy (ab) plane. It can be seen from the figure that the spin density is distributed to a greater extent along one of the oxygen ions. Since the spin polarization enters directly into the hyperfine interaction constant, the main axis of the hyperfine interaction tensor will also be turned into this plane.

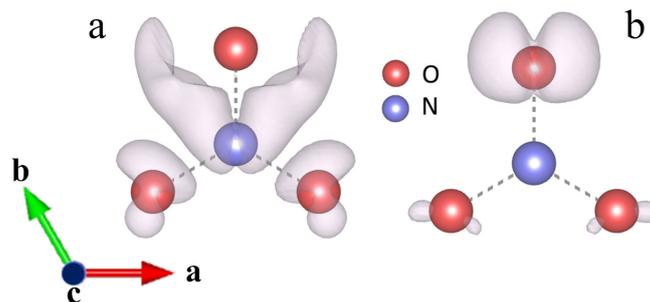


Figure 5. Positive (a) and negative (b) values of the spin polarization around the NO_3^{2-} center in the TCP structure.

3.3. Spin-spin and spin-lattice relaxation

The measured spin-spin relaxation in this sample is described by two exponential dependencies with spin-spin relaxation times $T_2(R_1^{\text{HAp}}) = 3.97 \pm 0.09 \mu\text{s}$ and $T_2(R_2^{\text{TCP}}) = 0.52 \pm 0.06 \mu\text{s}$ (at a temperature of 300 K), which indicates the presence of two paramagnetic centers. With de-

creasing temperature, the rate of spin-spin relaxation for the NO_3^{2-} center in TCP decreases (approximately 3 times for 100 K as compared to 300 K), while for the NO_3^{2-} center in hydroxyapatite it does not change.

Spin-lattice relaxation is also described by a two-exponential process with times $T_1(\text{R}_1^{\text{HAp}}) = 20.26 \pm 0.52 \mu\text{s}$ and $T_1(\text{R}_2^{\text{TCP}}) = 4.78 \pm 0.4 \mu\text{s}$ (at a temperature of 300 K). For both centers, with decreasing temperature, the rate of spin-lattice relaxation decreases (for both centers, approximately 18 times for 100 K as compared to 300 K). Spin-lattice relaxation does not affect spin-spin relaxation because it proceeds more slowly.

The temperature dependence of the spin-lattice relaxation rate in the β -TCP phase is shown in Figure 6. In the temperature range of 10–300 K, this dependence is described by a process proportional to $T^{2.35}$; it is impossible to distinguish the regions of one-phonon and two-phonon processes. In the region of 60 K, relaxation is slowed down. This behavior may be due to the complex shape of the phonon spectrum of the TCP crystal. For the HAp phase, the temperature dependence of the spin-lattice relaxation coincides with the previously obtained [14]. In the temperature dependence of the spin-lattice relaxation rate in the HAp crystal, one can single out the ranges of predominance of one- or two-phonon processes. The difference in rates indicates various phonon spectra in tricalcium phosphate.

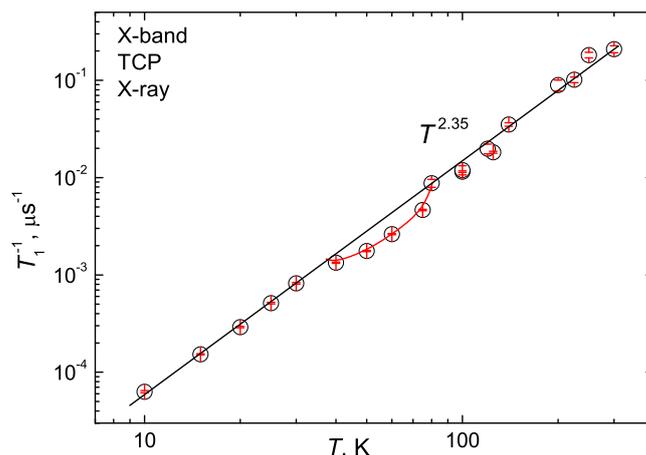


Figure 6. The temperature dependence of the spin-lattice relaxation rate in the β -TCP phase.

4. Summary

In this work, we established that the EPR spectrum of the powder under study is due to the admixture of the NO_3^{2-} complex, which is included in both HAp and TCP phases. The spin Hamiltonian parameters of the nitrogen-containing center in the TCP were determined. The parameters calculated using DFT show that the electron spin density (spin polarization) in the region of the impurity nitrogen center is distributed mainly along the bond with one of the oxygens; therefore, the main z axes of the hyperfine interaction tensor A is located in the ab plane. The TCP phase has shorter spin-spin and spin-lattice relaxation times. The temperature dependence of the spin-lattice relaxation rate in the temperature range 10–300 K is described by a process proportional to $T^{2.35}$.

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