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## Lattice distortions in hydroxyapatites with size as follows from the electronic relaxation time measurements

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**Abstract.** Pure and substituted hydroxyapatites ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , HAp) have been recently gaining special importance in catalysis for selective reactions where the synergetic functioning of acid–base active site pair facilitates the molecular transformations. Transition to the nanostructured HAp materials and ion incorporation can cause lattice distortions and influence physicochemical properties of HAp. We have investigated powders of HAp synthesized by wet techniques from the nitrogen-containing solutions with the average particle sizes of 30 (nanosized) and 1000 nm (microsized) with pulsed electron paramagnetic resonance (EPR). Electronic relaxation times ( $T_{1e}$ ) for the stable impurity paramagnetic  $\text{NO}_3^{2-}$  centers were measured in the temperature range of 10–300 K. It is revealed that  $T_{1e}$  shortens with the size reduction of factor two in the whole temperature range. The results are discussed in the framework of the modified Debye model taking into account non-Debye HAp phonon density. The obtained results show the feasibility of pulsed EPR techniques for characterization HAp based materials.

### 1. Introduction

Hydroxyapatite (HAp,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) belongs to the apatite family. It is one of the most usual forms of calcium phosphates (CaP) materials, more commonly known and studied as biomaterial being a major constituent of teeth and bones [1], [2]. The special attribute of HAp is its ability to form solid solutions and to accept a large number of anionic and cationic substituents exhibiting both acid ( $\text{PO}_4^{2-}$  ion) and base ( $\text{Ca}^{2+}$  ion) active sites together. In addition to its various medical and biological applications, HAP is applied such as fluorescent markers, material for fuel cell, or an adsorption and stabilization matrix for radioactive waste and harmful metals [1]–[6].

Since recently, due to their mentioned ion-exchange capacity, acid base adjustability, adsorption capacity, non-toxicity, thermal stability, ability to synthesize species with a controlled size and porosity, substituted by various cations and anions, HAP based materials attract scientific attention as heterogeneous catalysts for biodiesel production and natural gas-methane- $\text{C}_2$  hydrocarbon conversion [7]–[16]. Aside from economic considerations, another driving reason for the development of heterogeneous catalysis is its ecological impact forcing to develop manufacturing processes that release



the minimum amount of possible waste. In this context, HAp (that can be derived also from the natural sources such as eggshell, animal bone, mollusk shells, etc. and is a renewable one) is considered as a cost-effective catalyst.

Adsorption and incorporation of impurity ions can manifest itself in HAp lattice distortion. It could be also expected that size reducing (necessary for increasing surface-to-volume ratio) can lead to the changes in the vibrational spectrum of a crystal lattice. Changes in crystal lattice, in their turn, often cause changes in crystallinity, thermal stability, solubility and other physicochemical properties of the material [1], [3]. Intrinsic natural or artificially created / incorporated paramagnetic centres can serve as sensitive probes to follow these changes. Investigation of temperature dependence of the longitudinal (spin-lattice) electronic relaxation time,  $T_{1e}$ , is the most informative for these purposes [4], [17]. However, to the best of the authors' knowledge, there are no convincing experimental proofs of the size effect on the spin lattice relaxation (SLR) rate of paramagnetic centres. In this work we present study of temperature dependence of  $T_{1e}$  for  $\text{NO}_3^{2-}$  stable radicals in the micro-sized and nano-sized powders of HAp.

## 2. Materials and Methods

Two samples of hydroxyapatite – micro-sized (with the crystallites of about 1  $\mu\text{m}$ ) and nano-sized (30 nm) were studied. The  $\text{NO}_3^-$  species in the trace amounts were incorporated into the structure of hydroxyapatite powder with the chemical formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  to obtain the crystallites according to the equation



by dropwise addition of 0.3 M stock solution of  $(\text{NH}_4)_2\text{HPO}_4$  (99.9%, Labteh, Russia) to 0.5 M stock solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (99.9%, Labteh, Russia).

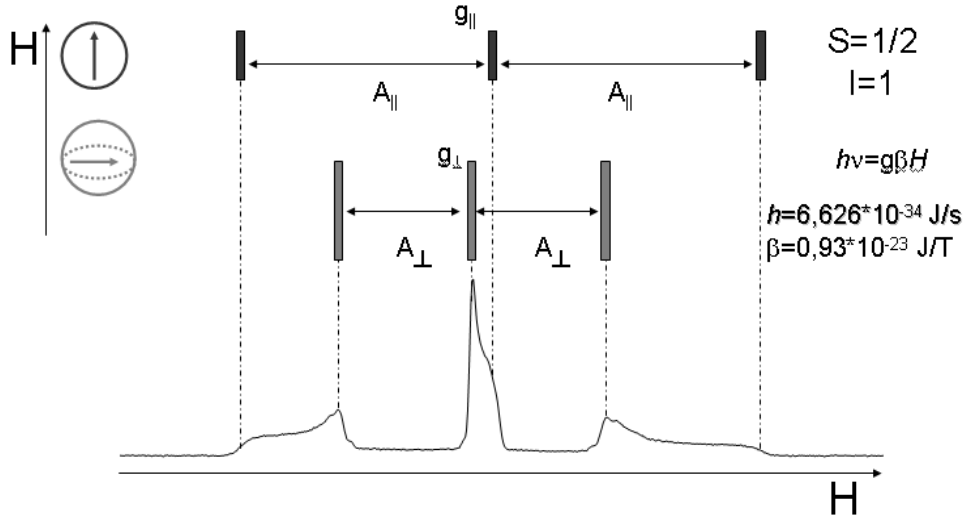
The obtained samples were characterized by infrared spectroscopy, X-ray diffraction technique, electron microscopy, elemental analysis. Details of the synthesis, post-synthesis treatments and analytical characterization of HAp powders are given in paper [3].

X-ray irradiation of the synthesized nanopowders was performed using a URS-55 tube ( $U = 55 \text{ kV}$ ,  $I = 16 \text{ mA}$ ; W-anticathode) at room temperature (RT) with an estimated dose of 5 kGy to create stable paramagnetic centers. Pulsed and continuous wave (cw) electron paramagnetic resonance (EPR) measurements were done using X-band (9 GHz) Bruker Eleksys 580 spectrometer equipped with the liquid helium temperature controller. Electron spin echo (ESE) EPR spectra were recorded by means of field-swept two-pulse echo sequence (FS ESE)  $\pi/2 - \tau - \pi$  by sweeping the external magnetic field  $B_0$  with the pulse length of  $\pi$  pulse of 32 ns and time delay  $\tau = 300 \text{ ns}$ . To extract the spin-lattice (longitudinal) relaxation times  $T_{1e}$  the Inversion-Recovery pulse sequence  $\pi - T_{\text{delay}} - \pi/2 - \tau - \pi$  with the  $T_{\text{delay}}$  varied was applied.

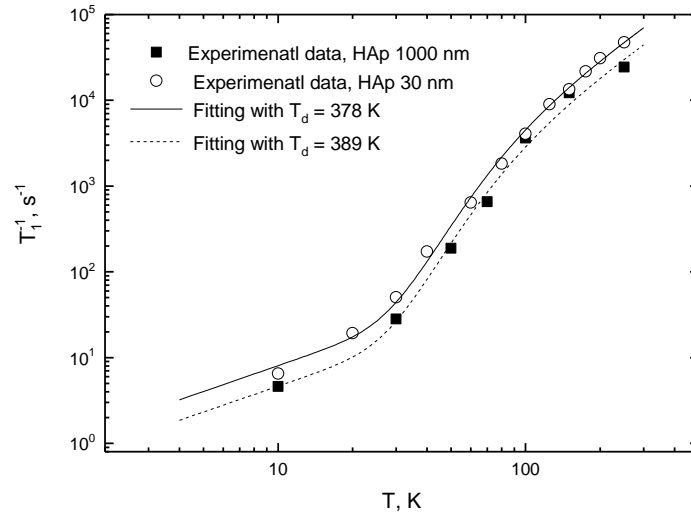
## 3. Results and Discussion

The synthesized HAp powders at RT are EPR silent. ESE EPR spectrum of the micro-sized HAp after irradiation is shown in Figure 1. No significant changes in EPR spectrum is observed with the size decrease. The obtained stable paramagnetic centres are due to the  $\text{NO}_3^{2-}$  of axial symmetry with  $S = 1/2$ ,  $g_{\parallel} = 2.0015(5)$ ,  $g_{\perp} = 2.0055(5)$ ,  $A_{\parallel} = 6.65(40) \text{ mT}$ ,  $A_{\perp} = 3.35(40) \text{ mT}$  caused by the near planar symmetry of radical and  $I = 1$  for  $^{14}\text{N}$  nuclei [18]. No other paramagnetic impurities were detected within the limits of sensitivity of our setup.

We have checked the difference in  $T_{1e}$  along the spectrum in the magnetic fields corresponding to the three local maxima in ESE signal (Figure 1). Our  $T_{1e}$  measurements did not show anisotropy within the acquisition accuracy. Therefore, the results for the central peak ( $g_{\perp}$ ) are presented. Experimental data for the inverse for  $T_{1e}$  value (relaxation rate) along with the corresponding fittings discussed below are drawn in Figure 2.



**Figure 1.** EPR spectrum for the micro-sized HAp sample and its schematic explanation for the  $\text{NO}_3^{2-}$  centre of the axial symmetry.



**Figure 2.** Experimental  $T_{1e}$  data for the micro-sized (solid squares) and the nano-sized (open circles) HAp powders and their approximations with  $T_D = 378$  K (solid line) and  $T_D = 389$  K (dashed line) by using Eq. (5).

The observed temperature dependences of the relaxation rates  $1/T_{1e}$  can be fitted as a sum of direct and two-phonon processes [19], [20]:

$$T_{1e}^{-1} = T_{dir}^{-1} + T_{Raman}^{-1} = C_{dir} T + C_{Raman} T^9 f\left(\frac{\Theta_D}{T}\right), \quad (2)$$

where the first term is responsible for the direct process of relaxation at low temperatures, the second one defines the Raman spin-lattice relaxation process with Debye approximation for lattice vibrations,

$\Theta_D$  is a Debye temperature,  $C_{dir}$  and  $C_{Raman}$  are coefficients which values were fitted,  $f(\frac{\Theta_D}{T}) \equiv f(z) \equiv I_8(z)/I_8(\infty)$ ,  $I_8(z) = \int_0^z x^8 e^x / (e^x - 1)^2 dx$ .

HAp are non-Debye solids, i.e. the HAp phonon density does not obey Debye law [21]. Taking into account the last one calculated in the previous work of our group [19], we have fitted the experimental data by using Eq. (2). The best approximations are achieved for  $\Theta_D = 389(5)$  K for the micro-sized sample and  $\Theta_D = 378(5)$  K for the nano-sized one. The first value is in a good correspondence with the data derived from the heat capacity measurements [19], [21]. For the micro-sized sample  $C_{dir} = 0.46$ ;  $C_{Raman} = 6.13$  while for the nano-sized one  $C_{dir} = 0.81$ ;  $C_{Raman} = 9.70$ . Analysis of the fitting coefficients is a matter of the separate research.

We have to note that the size reduction leads to the increase of the relaxation rate of up to 2.5 times in the whole temperature range that was hardly foreseen *a-priori*. Indeed, with the reducing crystal size to the nanometer scale in one, two or three dimensions, because of the absence of translational symmetry, periodicity can no longer be used in analysing the dynamics of lattice vibrations. As a result, first of all, the waves with  $\lambda/2 > d$  are not realized (here  $d$  is the smallest characteristic size of the system and  $\lambda$  is a vibrational wavelength). In this case, certain frequencies fall from the spectrum of the lattice vibrations, which leads to a change in the Debye formula. Therefore, it can be expected that a decrease in particle size should shift the phonon spectrum into the high-frequency region making  $T_{1c}$  longer (or relaxation rate less) than for the bulk sample. Experimentally, from the comparison of the specific heats of massive single-crystal samples and nanopowders of palladium, Si, MgO, etc., a decrease of the Debye temperature was observed with the sample size [22].

It could be speculated that the surface and the surface paramagnetic centres rather than bulk paramagnetic species could play a significant role in the case of the nanomaterials. But as we have already mentioned, no significant changes in EPR spectra and  $T_{2e}$  values for stable  $\text{NO}_3^{2-}$  complexes were found with the size or HAp surface treatment in a series of our previous papers (see [18] and references therein). Therefore, we suppose that for the both types of the investigated species we have deal with the intrinsic (bulk)  $\text{NO}_3^{2-}$  radicals.

#### 4. Conclusions and Perspectives

Rational design of heterogeneous catalysts requires application of various theoretical and analytical tools for their study and characterization. Electron paramagnetic resonance spectroscopy, which includes continuous wave and pulsed methods, is frequently used in the study of catalytically active systems. The role of EPR in these studies varies considerably from, on the one hand, a comprehensive description of the electronic states of the paramagnetic active site in the catalytic cycle to, on the other hand, a simple analytical confirmation that a radical centre is present [23]-[26]. In this paper we show some abilities of pulsed EPR for investigation and analysis of HAp based materials to encourage the specialists in different scientific and industrial branches to use different EPR approaches in their studies and routine analyses.

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