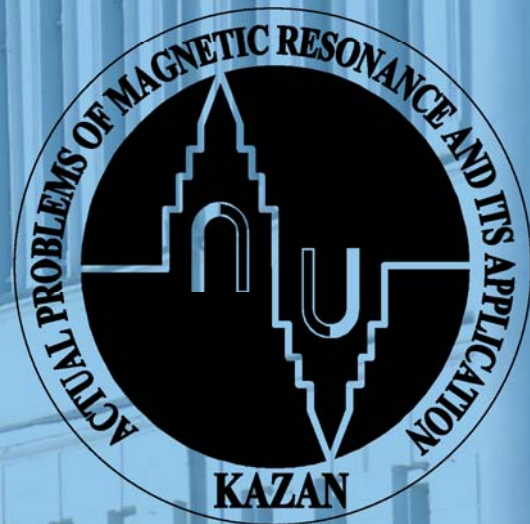


**Kazan Federal University
Zavoiskii Physical-Technical Institute
“Dynasty” Foundation
Bruker Ltd (Moscow)**

**ACTUAL PROBLEMS
OF MAGNETIC RESONANCE
AND ITS APPLICATION**

**XIII International
Youth Scientific School**



**Program
Lecture Notes
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**KAZAN UNIVERSITY
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EPR/ENDOR of hydroxyapatite nanocrystals doped by lead ions

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Introduction

Hydroxyapatite — $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ — is one of the intensively studying materials in contemporary inorganic materials science. The interest in a hydroxyapatite researches is dictated not only by the number of its applications, e.g. bone tissue repairing[1], radionuclide sorption[2], but also by its complex structure that allows a lot of anionic and cationic substitutions. The important feature of the hydroxyapatite structure is the presence of the two nonequivalent calcium positions called Ca-1 and Ca-2. The distances between Ca-1 and the nearest phosphorous is 3.2Å and is 5.4Å for distance between Ca-1 and hydrogen; for Ca-2 these distances are 3.0Å and 2.8Å respectively. In this work authors studied hydroxyapatite doped by lead ions — $\text{Ca}_{10-x}\text{Pb}_x(\text{PO}_4)_6(\text{OH})_2$ (PbHAP) and determined characteristics of Pb^{3+} paramagnetic centers and their localization within crystal.

Materials

Two powder samples with one hour and seven days synthesis time were studied. The average nanocrystal sizes were evaluated from X-ray diffraction spectra (fig.1a) at 20nm and 1µm, respectively.

The activation process is the isovalent substitution of Ca^{2+} ions for Pb^{2+} , but this valence state of lead ions isn't paramagnetic for the outer 6s electronic shell has two electrons with the opposite spins. To produce paramagnetic centers samples were treated by X-ray and

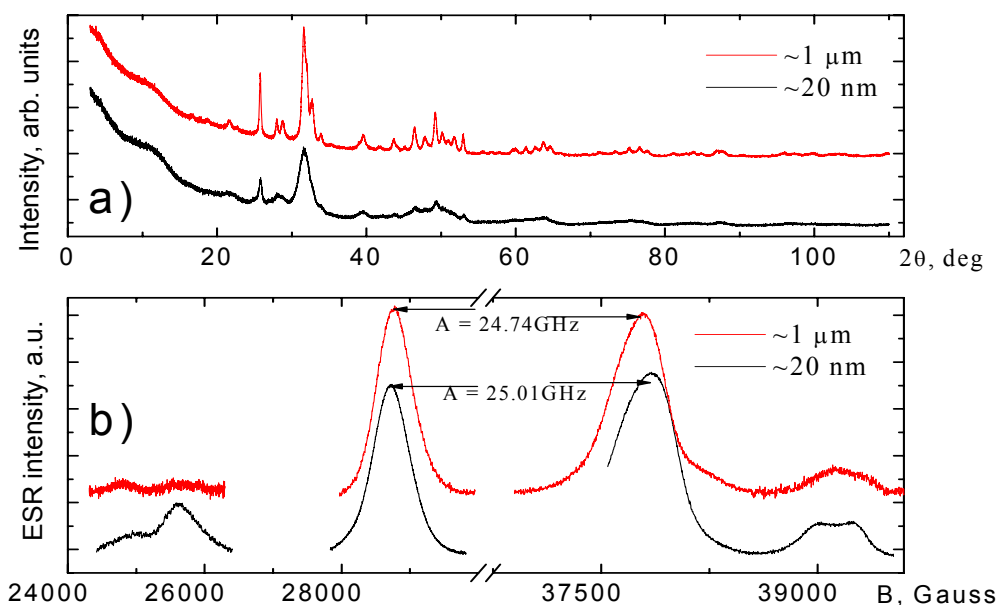


Fig.1. X-ray diffraction spectra (a) and EPR spectra (b) of nanocrystalline and microcrystalline lead doped hydroxyapatite.

eventually some amount of Pb^{2+} converted into Pb^{3+} with the electronic spin $S = 1/2$. It is important to note that the lead ions have the electronic spin as well as the nuclear spin. Only one of the natural isotopes, Pb-207, with natural abundance 21.6% has nuclear spin $I = 1/2$, whereas even isotopes with mass number 204,206 and 208 have no nuclear spin.

Methods

Samples were studied by high-frequency (94GHz) pulsed electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) with Bruker Elexsys 680 spectrometer. For low-temperature experiments helium-flow cryostat made by Oxford Instruments was used. EPR spectra were recorded by means of two-pulse echo sequence, ENDOR spectra were detected by Mims technique. X-ray irradiation of the samples were carried out in the URS-55 ($U = 55\text{kV}$, $I = 16\text{mA}$, W - anticathode) at room temperature, dose of radiation was assessed at 10kGy.

Results and summary

The EPR spectra of the non-irradiated hydroxyapatite samples activated by the lead ions did not show the presence of the paramagnetic centers within the nanocrystals.

The EPR spectrum of the PbHAP after X-ray exposure was composed of two lines, nonoverlapping with the g -factor~2 region, which is typical for the systems with $S = 1/2$, $I = 1/2$. The splitting between these two lines is proportional to the hyperfine structure parameter. Characteristics of the paramagnetic centers are evaluated from EPR spectra and are represented as follows: $A_{1\mu\text{m}} = 24.74(5)\text{GHz}$, $A_{20\text{nm}} = 25.01(5)\text{GHz}$ and $g = 1.982(2)$ for both samples. One can see that the strength of the hyperfine interaction increases with decreasing of the nanocrystal sizes. Typical EPR spectrum is shown in fig.1b. The EPR lines with low intensity, which were recorded at low and high magnetic fields, arise from Pb ions in the growth solution, i.e. these ions are not embedded within hydroxyapatite crystal lattice. This assumption was proved because these lines disappeared from the EPR spectrum of PbHAP samples after annealing at 400°C.

In the theoretical work[3] authors claimed that Pb ions can substitute Ca only in the Ca-2 site. In the present paper the ENDOR method is used to determine the substitution position experimentally. The ENDOR spectra of phosphorous and hydrogen are shown in fig.2a and fig.2b, respectively. The more is the strength of the superhyperfine interaction, the less is the distance between paramagnetic electron and neighboring nuclei. The strength of the

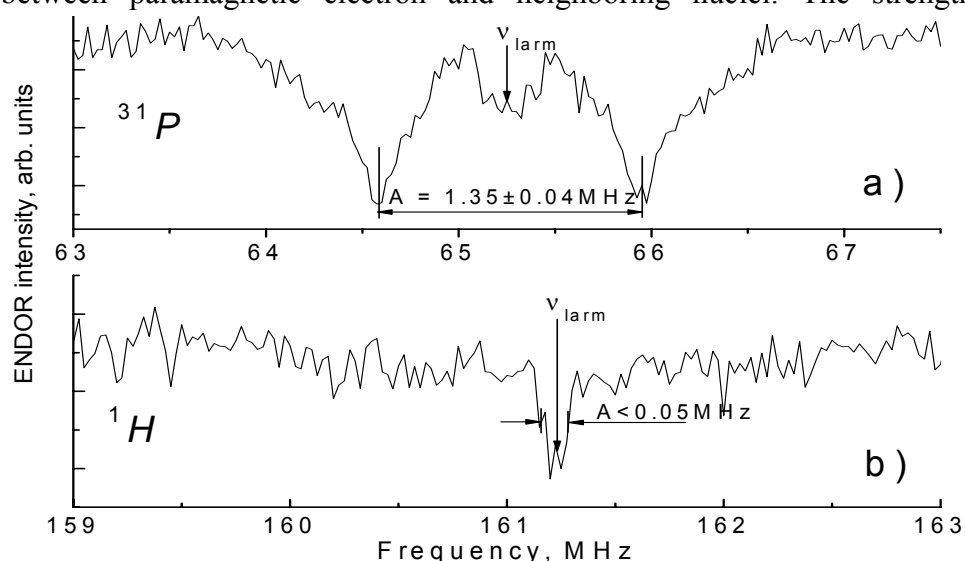


Fig.2. ENDOR spectra near to Larmor frequencies of phosphorous (a) and hydrogen (b) of nanocrystalline sample.

superhyperfine interaction is maximal for phosphorous nuclei, see fig.2a. From the hydroxyapatite structure analysis one can conclude that Pb substitutes Ca in Ca-1 position.

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