Kazan Federal University
Zavoiskii Physical-Technical Institute
Russian Academy of Sciences
Bruker Ltd (Moscow)
"Dynasty" Foundation
Russian Foundation for Basic Reserch

ACTUAL PROBLEMS OF MAGNETIC RESONANCE AND ITS APPLICATION

XV International Youth Scientific School

ACTUAL PROBLEMS OF MAGNETIC RESONANCE AND ITS APPLICATION
KAZAN

Program
Lecture Notes
Proceedings

Kazan
22 - 26 October 2012

Kazan Federal University
Zavoiskii Physical-Technical Institute
Russian Academy of Sciences
Bruker Ltd (Moscow)
“Dynasty” Foundation
Russian Foundation for Basic Reserch

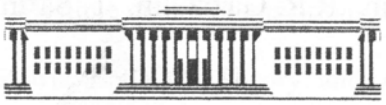
ACTUAL PROBLEMS OF MAGNETIC RESONANCE AND ITS APPLICATION

XV International Youth Scientific School

Program
Lecture Notes
Proceedings

Kazan
22 – 26 October 2012

KAZAN UNIVERSITY



2012

Proceedings of the XV International Youth Scientific School “Actual problems of magnetic resonance and its application”, 22 – 26 October 2012, Kazan. Edited by professor M.S. Tagirov (Kazan Federal University) and professor V.A. Zhikharev (Kazan State Technological University). – Kazan: Kazan Federal (Volga Region) University, 2012. – 210 p.

The reports of young scientists submitted on XV International Youth Scientific School “Actual problems of magnetic resonance and its application” carry out by Kazan Federal (Volga Region) University and Zavoiskii Physical-Technical Institute are included in the present collection.

ISBN 978-5-905787-85-0

Double doping nanoparticles of hydroxyapatite

M.R. Gafurov[1], G.V. Mamin[1], S.B. Orlinskii[1], G.A. Tokarev[1],
E.S. Kovaleva[2], V.I. Putlyaev[2]

[1]Kazan (Volga region) Federal University, Kremlevskaya st. 18, Kazan, 420008, Russia.
[2]Lomonosov Moscow State University, GSP-1, Leninskie Gory, Moscow, 119991, Russia.
e-mail: grigoryat@yandex.ru

Inroduction

Synthetic hydroxyapatite (HAP) $Ca_{10}(PO_4)_6(OH)_2$ – widespread material that used in medicine for treatment of damaged bone tissue due to chemical and stage similarity with inorganic components of bone tissue [1, 2]. For enhancement of efficiency of bioresorbable implants as substitutes of bone tissue it is possible to use a material bases on carbonized hydroxyapatite $Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2$, in which PO_4 group partially replaced by CO_3 group. It is more precisely reproduce the structure of bone in comparison with not modified hydroxyapatite.

The process of synthesis of hydroxyapatite according to the following mechanism [2]:

$$(10\text{-}x)Ca(NO_3)_2 + (6\text{-}x)(NH_4)_2HPO_4 + xNaHCO_3 + 8NH_4OH \rightarrow$$
$$\rightarrow Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2\downarrow + (20\text{-}2x)NH_4NO_3 + 6H_2O.$$

In this case, the nanocrystals are precipitated from a colloidal solution and have a size equal to 30 nm, that is the optimal particle diameter for the process of bioresorption [3]. As we can see, in the synthesis of nitrogen-containing NO_3 and NH_4 groups are used, which can be trapped by falling out particles of hydroxyapatite. These compounds are highly toxic and prevent the use of hydroxyapatite in medicine [3].

There are two different mechanisms to capture nitrogen compounds by hydroxyapatite nanoparticles:

1. NO_3 and NH_4 groups replace PO_4 and OH groups in the crystal lattice of hydroxyapatite.

2. On the surface of hydroxyapatite held a mother solution containing NO_3 and NH_4 groups.

In the first case, it is very difficult to remove nitrogen compounds from the drug. In the second case, there is drug wash with distilled water used, followed by removal of water by annealing the powder of HAP with temperatures over 100 °C. The water evaporates and grab NO_3 and NH_4 groups, thereby reducing their concentration in the final preparation.

Thus, there is need for detecting the presence of nitrogen-containing compounds in the hydroxyapatite, the definition of localization and verification mechanism for the HAP by annealing treatment with EPR method.

Results and discussion

In the experiments, we investigated samples of carbonated hydroxyapatite and HAP doped with manganese. In these samples we can observe the EPR signal of manganese centers. In order to detect the other impurity centers, hydroxyapatite samples were irradiated by X-ray. After the irradiation spectrum was observed (fig.1). It consists of three lines of equal integrated intensity, which suggests that the observed spectrum is determined by the hyperfine interaction of the magnetic moment of the unpaired electron of paramagnetic center

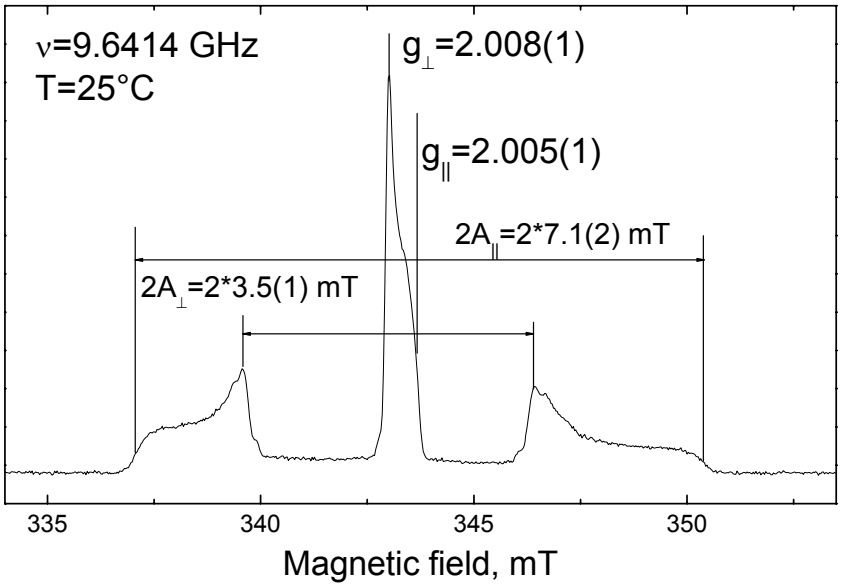


Fig.1. The EPR spectrum of NO_3^{2-} complexes in HAP

with the magnetic moment (I=1) of the nitrogen nucleus ^{14}N. The values of the g-factors and hyperfine constants proves that we have observed the spectrum of NO_3^{2-} complexes.

To check the effect of HAP synthesis technique, we compared the spectrum of the NO_3^{2-} groups in the carbonated HAP and hydroxyapatite doped with manganese (fig.2). The

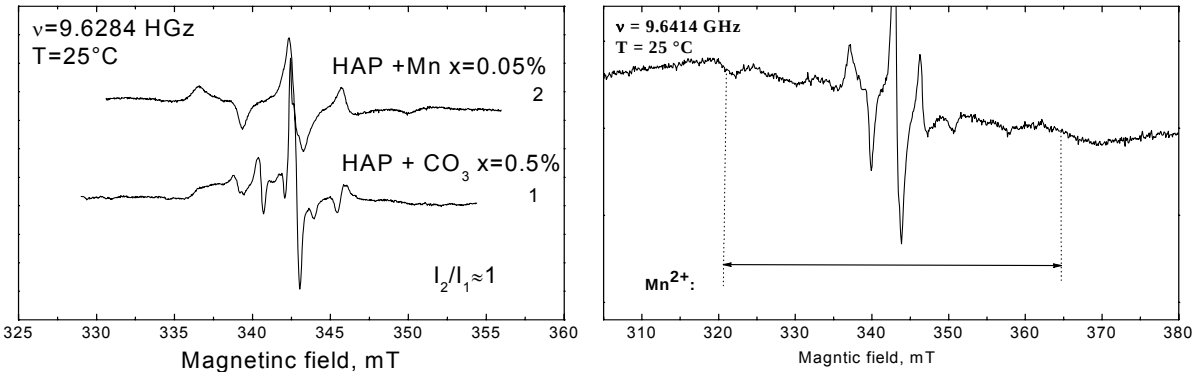


Fig.2. The EPR spectra of NO_3^{2-} complexes in the carbonized hydroxyapatite and HAP doped with manganese

line width of the spectrum for hydroxyapatite doped with manganese is larger than that of carbonated HAP, but the value of the integrated intensity of the EPR spectra are almost equal, which means almost the same concentration of NO_3^{2-} complexes in these samples.

The particles of hydroxyapatite powder might be doped either only manganese ions or CO_3 groups ions or the both. To determine are the particles of HAP co-doped or not, we measured the time of spin-spin relaxation of the NO_3^{2-} groups in the carbonated hydroxyapatite and HAP doped with manganese (fig.3). As we can see, the addition of even very small amount of manganese reduces T_2 to 30 times. Therefore Mn and CO_3 ions co-doped in the particles of powder. But also this prevented the investigations of EPR spectra of NO_3^{2-} groups in HAP doped with manganese by ELDOR methods.

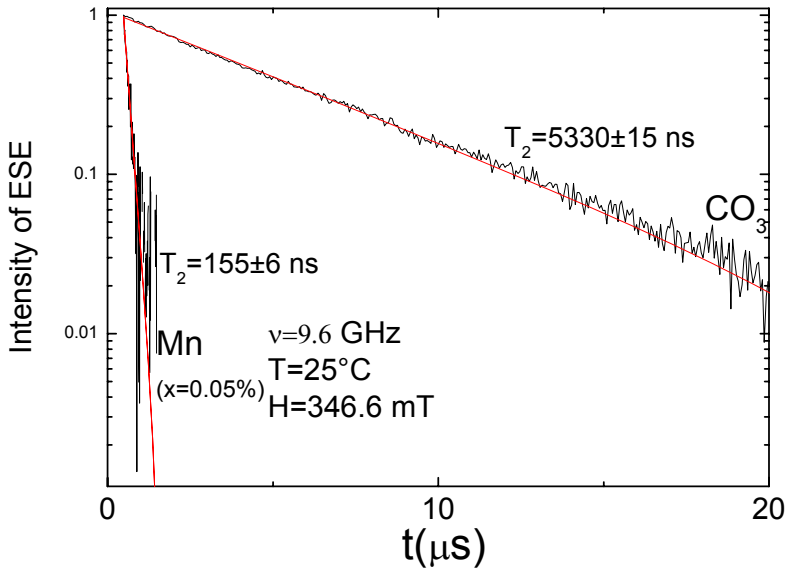


Fig.3. T_2 of NO_3^{2-} complexes in the carbonated HAP and HAP doped with manganese

Conclusion

The CW X-band EPR spectra of carbonized and doped with manganese hydroxyapatite were measured and interpreted, their spectroscopic and relaxation characteristics were obtained.

Measurements showed that the concentration of complexes NO_3^{2-} is equal in the samples of carbonated hydroxyapatite and HAP dopes with manganese. The study of samples of hydroxyapatite doped with manganese ions showed higher probability of complex formation of manganese ions and NO_3 groups within the crystal structure of hydroxyapatite. The results can be useful for the modernization of the synthesis of nanocrystalline hydroxyapatite.

References

[1] Lafon, J. P. Preparation and characteristics of nanosized carbonated apatite by urea addition with coprecipitation method / J. P. Lafon, E. Champion, D. Bernache-Assollant // J. Eur. Cer. Soc. -2008. –V.28. -P.139–147.

[2] LeGeros, R.Z. Properties of osteoconductive biomaterials: calcium phosphates / R.Z. LeGeros // Clin. Orthop. Relat. Res. -2002. –V. 395. –P.81–98.

[3] Kovaleva, E.S. Bioresorbable carbonated hydroxyapatite $Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2$ powders for bioactive materials preparation / E.S. Kovaleva, M.P. Shabanov, V.I. Putlyaev, Y.D. Tretyakov, V.K. Ivanov, N.I. Silkin // Cent. Eur. J. Chem. 2009. –V.7(2). –P. 168