

GAMMA IRRADIATED ELECTRON PARAMAGNETIC RESONANCE RESPONSE OF CARBONATE ION IMPLANTED HYDROXYAPATITE

by

**Bitā BAGHALZADEH¹, Farhood ZIAIE^{2*}, Fatemeh DOWLATSHAH³,
and Majid Mojtahedzadeh LARIJANI³**

¹Central Tehran Branch, Islamic Azad University, Tehran, Iran

²Radiation Application Research School, Nuclear Science & Technology Research Institute, Tehran, Iran

³Agricultural, Medical and Industrial Research School, Nuclear Science & Technology Research Institute, Karaj, Iran

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In this work, synthetic nano-structure hydroxyapatite samples were doped by carbonate ions with 80 keV of energies during different times of 4, 8, 16, and 24 minutes using an ion implantation device. All the samples were irradiated with the ⁶⁰Co gamma ray source at different absorbed doses of 5, 10, 20, and 50 kGy and subjected to electron paramagnetic resonance measurements, subsequently. The electron paramagnetic resonance signal intensities were constructed as a function of radiation dose and were compared with the results of non-implanted one, and were studied from dosimetric point of view. The obtained results show a considerable increment in electron paramagnetic resonance signal intensity of the samples which were implanted for 24 minutes.

Key words: electron paramagnetic resonance spectrometer, hydroxyapatite, gamma-ray, carbon doping, ion implantation technique

INTRODUCTION

Electron paramagnetic resonance (EPR) spectroscopy is an extremely sensitive method for detection and measurement of free radicals. EPR has been widely used in radiation dosimetry, control of irradiated food, polymers and medical physics. EPR biodosimetry is a physical method based on the measurement of stable radiation induced radicals in the calcified tissues of human body [1-5]. The individual dose can be best reconstructed using probes that are close to, or part of the exposed individual [6, 7].

Hydroxyapatite (HAP) with the chemical formula of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is a suitable probe for dose reconstruction due to containing stable radiation induced radicals that are a diagnostic signature of radiation exposure [6]. The research shows that the biological HAP contains carbonate groups and a small amount of other elements. During the formation of HAP as the hard part of the bones and teeth, over the time, some organic groups such as carbonate (CO_3^{2-}) replace hydroxyl groups (OH^-) or phosphate (PO_4^{3-}) at their positions in HAP crystals. Therefore, they have differences in terms of physical, chemical, mechanical properties as well as their crystallinity, and solubility in comparison to the artificial HAP [8, 9].

Ion implantation is one of the ways to change the physical structure of thin films. Replacement of ion in

the network structure will change the chemical composition of the substrate material, thus other properties of material could be changed subsequently. In this method, high-energy carbonate ions produced by an ion implantation device in a perfect vacuum, penetrate into the substrate material.

In this work the CO_2 ions entered into the HAP crystal structure at different bombardment times and were irradiated at different doses and subjected to the EPR measurement, subsequently. The results were compared with those of non-bombarded HAP samples.

EXPERIMENTAL PROCEDURE

Sample preparation

The HAP samples were obtained from Merck Company, Germany. The HAP powder samples were spread on the surface of an alumina sample holder to form a thin layer. Then the sample holders containing the HAP were subjected to carbonate ions bombardment.

Ion implantation procedure

A device of ion implantation system model MBM100, made in China was used in this experiment. The sample holders were transferred to the special

* Corresponding author; e-mail: fziaie@aeoi.org.ir

sample place in the ion implantation system. Before each implanting operation, the chamber was scoured out with alcohol and acetone. When the vacuum pressure reached $7 \cdot 10^{-5}$ Torr, the valve connected to the CO₂ gas capsule was opened till the vacuum reached the desired values. Then the appropriate voltage and current were applied to produce CO₂ ion beam with 80 keV of energy to bombard the samples. The samples were exposed to the ion beam in different time periods of 4, 8, 16, and 24 minutes. The system parameters during the implantation were ~18 mA ion beam current, 80 kV beam voltage, and 0.5 μA beam current on sample.

Characterization

Fourier transmission infrared spectroscopy (FTIR) was carried out on the samples in the wave number range of 400-4000 cm⁻¹ using a Perkin Elmer, series 100 spectrometer. Transmission electron microscopy (TEM) system EM208S series, made by Phillips Company was utilized to study and determine the size and morphology of the particles. X-ray diffraction (XRD) analysis was performed by a Philips Analytical X-Ray B.V., with the use of CuKα radiation (1.5456 Å* wavelength), in the 2θ range of 20°-60°. The grain size of the prepared powder products was measured using the Scherer's equation

$$t = \frac{0.89\lambda}{B \cos \theta} \quad (1)$$

where t [nm] is the grain size, λ [nm] – the wavelength of the X-ray, B [rad] – the full width at half maximum of a peak in X-ray pattern, and θ – the Bragg's angle.

Irradiation

Irradiation was carried out using a ⁶⁰Co gamma-ray source facility, PX-30, made in Russia. The samples were irradiated at doses of 5, 10, 20, and 50 kGy.

EPR measurement

The samples were put into the quartz thin-wall EPR tubes (4 mm diameter) and measured with a Bruker EMS-104 spectrometer operating in X-band. The EPR signal intensities were measured as peak height for the most intense EPR lines (first derivative of the absorption spectra) per sample mass. The used EPR spectrometer parameters for this study were 0.285 mT modulation amplitude, 100 kHz modulation frequency, 3.0 mT scan width, 1024 point field resolution, 164 m/s time constant, 21 s sweep time and 50 dB receiver gain.

* 1Å = 10⁻¹⁰ m

RESULTS AND DISCUSSION

XRD patterns of the HAP samples before and after the carbonate ion implantations were measured and demonstrated in fig.1. Evaluation and comparison of the sample diffraction patterns indicate the existence of the peaks in all samples which are fully in accordance with the standard cards of HAP (card no. 00-0350-0180). The XRD patterns show that the peak positions before and after implantation have not changed and no new peaks appeared afterward. Considering the intensity of the peak in position of 25.9° with Miller indices of (002), it is obvious that an increase in implantation time (carbon increase), decreases the peak height and increases the peak width. This result is in accordance with those reported in some references [10-15].

Figure 2 shows the FTIR analysis results for the samples before and after the implantation process. All of the observed bands are related to the carbon apatite which can be arranged in three types of phosphate, carbonate, and hydroxyl groups. The bands were observed in positions of 885 cm⁻¹ and 1417 cm⁻¹, while 1570 cm⁻¹ were associated with carbon compounds that became more intense due to the carbonate ion implantation. This means that the carbons have entered into the structure of HAP samples via this method.

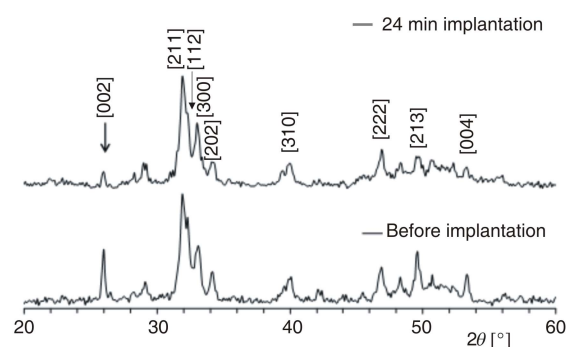


Figure 1. XRD patterns of the carbonate ions implanted HAP sample in comparison to the non-implanted one

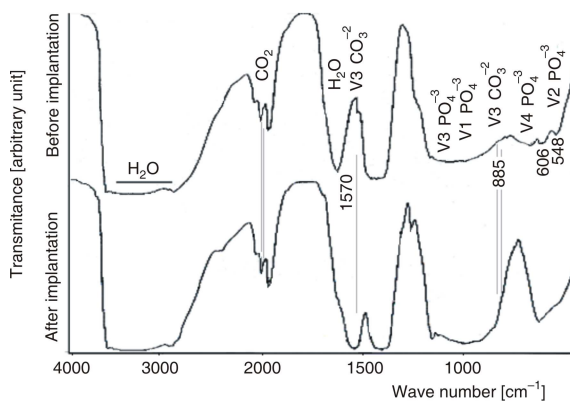


Figure 2. FTIR spectrum of carbonate ions implanted sample in comparison to the non-implanted one

Table 1. Average particle sizes of the HAP samples bombarded in different times

Bombardment time [min]	Average particle size [nm]	Standard deviation
0	22.24	3.17
4	21.19	3.51
8	19.22	2.61
16	18.66	2.51
24	17.98	2.82

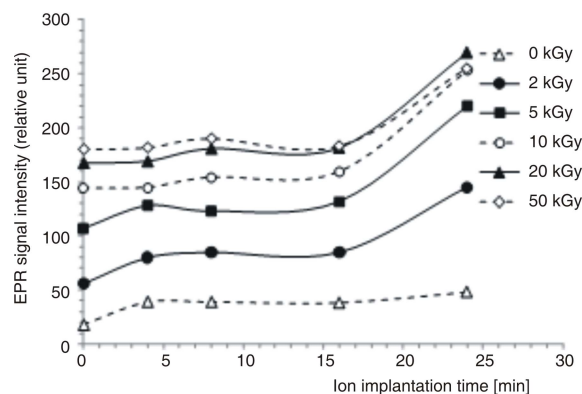
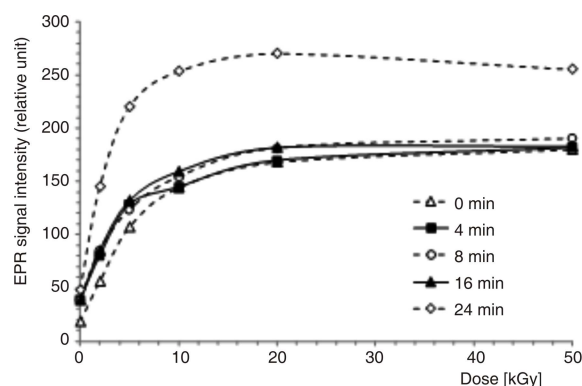
The grain sizes of the HAP samples were calculated by eq. 1 using the data extracted from the XRD patterns for the main XRD peaks. The average values over the same implantation time are reported in tab. 1. The results demonstrate that the average grain size decreases as the ion implantation time increases. In the author's view the decreasing of sample grain sizes is associated with the sputtering of grains due to the hitting of accelerated CO_2 ions. In fact, an increase in implantation time causes more sputtering and a smaller particle size.

TEM micrographs of the HAP samples are demonstrated in fig. 3. The particle sizes in the samples are obvious in TEM associated image which confirms the obtained results indicated in tab. 1.

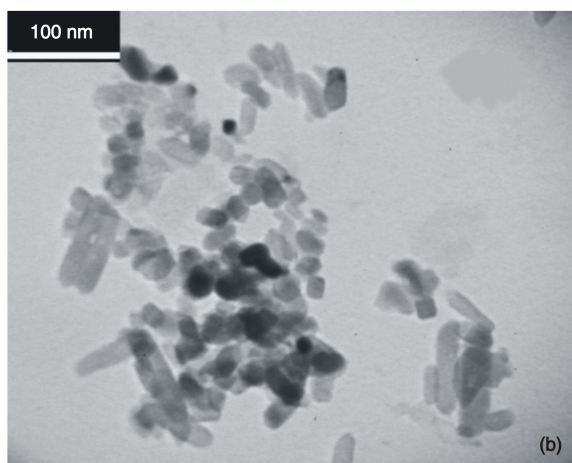
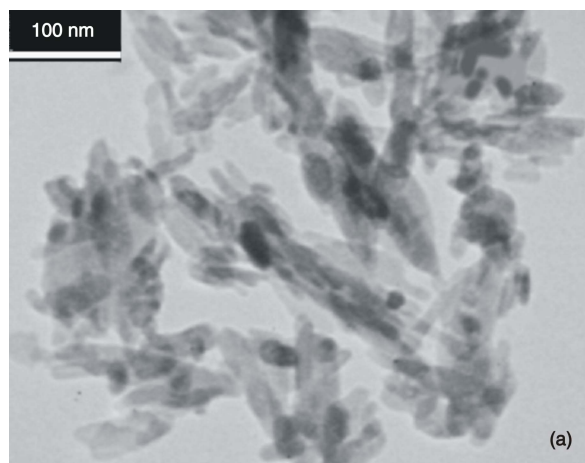
Figure 4 shows the EPR signal intensity variation as a function of carbonate ion implantation time at different radiation absorbed dose for the HAP samples. This figure clearly indicates that the EPR signal intensities remained approximately constant up to 16 minutes and increased afterwards.

Figure 5 shows the EPR signal intensity variation as a function of absorbed dose for the samples that were implanted by carbonate ions at the different times in comparison to the non-implanted samples.

It is obvious from the figure that EPR response trends of the implanted and non-implanted samples are almost the same in different dose intervals. For instance, all of the curves have acceptable response to be

**Figure 4. EPR signal intensity variations of HAP samples against the CO_2 ions implantation time****Figure 5. EPR response of HAP samples implanted with CO_2 ions in different bombardment times**

used as calibration curve at the dose lower than about 20 kGy. It means that the saturation occurs near the same dose for all the samples. On the other hand, the curve associated with the HAP samples implanted for 24 minutes with CO_2 ions, shows a very high EPR response in comparison to the others. This phenomenon could be associated with the differences in percentage

**Figure 3. TEM provided microstructure of HAP samples: (a) before implantation and (b) after 24 min implantation**

of carbon contents, particle sizes and the morphology of the samples. The carbonated impurities are incorporated into, or attached to the surface of HAP crystal during formation, and are converted to radicals through absorption of ionizing radiation. The contribution of the radiation induced radicals is mostly due to the attached carbonated impurities on the surface of HAP crystals. Thus, increasing the carbonate ion implantation time and decreasing the HAP particle size, causes the increase of the free radical population and EPR response, consequently [16-18].

CONCLUSIONS

The XRD and FTIR analysis indicate that carbonate ions have entered into the structure of HAP and carbon apatite was formed using the ion implantation method. The obtained results from the XRD and TEM analyses demonstrate that the average grain size decreases as the ion implantation time increases. The EPR response of the HAP samples implanted by carbonate ions in 24 minutes shows the higher intensity in comparison to the other samples. At a final conclusion, the ion implantation technique is the physical method to improve the EPR signal intensity of the HAP samples due to the increasing the carbonate radicals attached to the crystal surface and decreasing the particle size.

AUTHOR CONTRIBUTIONS

The research idea and the theoretical analysis were carried out by F. Ziaie, and the experiments were carried out by B. Baghalzadeh and F. Dowlatshah. The ion beam implantation process was carried out under supervision of M. M. Larijani. The manuscript was written by F. Ziaie, and the figures were prepared by F. Ziaie.

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**Бита БАГАЛЗАДЕХ, Фархад ЗИАИЕ, Фатемех ДОВЛАТШАХ,
Маџид Мојтахедзадех ЛАРИЏАНИ**

**ЕПР ОДЗИВ НА ГАМА ОЗРАЧИВАЊЕ ХИДРОКСИАПАТИТА
ИМПЛАНТИРАНОГ ЈОНИМА КАРБОНАТА**

У овом раду проучавани су узорци синтетичке наноструктуре хидроксиапатита, који су коришћењем уређаја за јонску имплантацију допирани јонима карбоната енергија 80 keV, током временских интервала од 4, 8, 16 и 24 минута. Сви узорци озрачени су извором гама зрачења ^{60}Co до нивоа апсорбованих доза од 5, 10, 20 и 50 kGy, и потом подвргнути ЕПР мерењима. Јачине ЕПР сигнала, представљене као функција дозе зрачења и упоређене са резултатима процеса без имплантације, проучаване су са дозиметријског становишта. Резултати показују значајан пораст јачине сигнала код узорака који су имплантирани 24 минута.

*Кључне речи: ЕПР спектрометрија, хидроксиапатит, гама зрачење, доирање уљеником,
јонска имплантација*
