Radiation Measurements 87 (2016) 49–55

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

EPR study of radiation-induced defects in carbonate-containing hydroxyapatite annealed at high temperature

I.P. Vorona [a, *], V.V. Nosenko [a], N.P. Baran [a], S.S. Ishchenko [a], S.V. Lemishko [a], I.V. Zatovsky [b], N.Yu. Strutynska [b]

[a] V. Lashkaryov Institute of Semiconductor Physics of NAS of Ukraine, Nauky Prospect, 45, 03028, Kyiv, Ukraine
[b] Taras Shevchenko National University of Kyiv, Volodymyrska Str., 64/13, 01601, Kyiv, Ukraine

HIGHLIGHTS

- High T_{ann} influences essentially the formation of radiation-induced defects in HAP.
- The main stable defects in the annealed HAP are CO_3^{3-}, O^- and oxygen vacancy $V_{\bar{O}}$.
- New O-related radical with the parameters $g_{||} = 2.002$, $g_{\perp} = 2.0135$ was detected.

ARTICLE INFO

Article history:
Received 6 November 2015
Received in revised form
14 January 2016
Accepted 7 February 2016
Available online 10 February 2016

Keywords:
Hydroxyapatite
EPR
Annealing
Paramagnetic defects

ABSTRACT

Radiation-induced (γ or UV) paramagnetic defects in carbonate-containing hydroxyapatite (HAP) annealed at high (600–950 °C) temperature were studied by EPR. The complex spectra reveal the presence of different paramagnetic species. Their contributions were found to be strongly dependent on the annealing temperature as well as microwave power, thus, by the adjustment of experimental conditions some of the components can be eliminated that allowed to record EPR spectra caused by no more than two types of paramagnetic defects. All experimental spectra were analyzed using computer simulation. The parameters of the paramagnetic defects detected were determined, and the centers models were discussed. It was found that high-temperature annealing influences essentially the formation of radiation-induced defects in HAP. The CO_3^{3-}, O^- centers and oxygen vacancy $V_{\bar{O}}$ were shown to be the main stable γ-induced defects in the HAP annealed at high temperatures. New paramagnetic defect with the parameters $g_{||} = 2.002$, $g_{\perp} = 2.0135$ was detected and tentatively identified as an O-related radical. The γ-induced EPR response from CO_3^{3-} radicals was found to be more intense than response from CO_2^- in non-annealed HAP. UV-irradiation was found to create smaller amounts of paramagnetic defects in comparison with γ-rays. Besides, oxygen vacancy $V_{\bar{O}}$ was not observed, while two other centers (CO_3^- and the center of unknown nature) appear in the UV-induced EPR spectra.

1. Introduction

The electron paramagnetic resonance (EPR) technique allows to identify lattice defects and to determine their structure at the atomic level. Due to high sensitivity of EPR method it can be used to study low defects concentration which often can not be detected by other methods. This is especially important in the case when defects significantly influence the properties of functional materials, or when they are the indicators of properties changes. In the case of carbonate-containing hydroxyapatite (HAP) the CO_2^- paramagnetic centers are the indicator of radiation exposure. They are widely used in EPR dosimetry for determining the doses of ionizing radiation (see for example, Fattibene and Callens, 2010; Ikeya et al., 1984; Hassan et al., 2004), as well as in EPR dating to define the fossil's age (Grun, 1989; Skinner et al., 2000). The CO_2^- radicals are the main stable radiation-induced defects in HAP (Ikeya, 1993). The stable CO_3^- centers (Brik et al., 2005; Callens et al., 1989; Callens, 1997), NO_3^{2-} (Baran et al., 2011; Gafurov et al., 2014a, 2014b; Nosenko et al., 2012), unstable CO_3^{3-} and O^- (Callens et al., 1989, 1998; Callens, 1997; Mengeot et al., 1975; Moens et al., 1994, 1996; Sadlo et al., 1998; Rudko et al., 2010), as well as some other centers were also identified in HAP.

* Corresponding author.
E-mail address: ip_vorona@yahoo.com (I.P. Vorona).

http://dx.doi.org/10.1016/j.radmeas.2016.02.020
1350-4487/

HAP is widely used in medical material science, in particular, as a coating for metallic implants. The important characteristic of such coatings is their high adhesion that is achieved by plasma or detonation spraying techniques. These technologies imply that during the production of coating the initial material is subjected to high temperatures that can influence the structure of HAP (Nosenko et al., 2015). As the physical properties of HAP depend on the defect structure, the information about the nature and amount of defects induced by high temperature treatment is extremely important. In this way radiation-induced defects as a paramagnetic probe can be useful tools to study the changes in the structure of HAP caused by thermal treatment. Biological and synthetic HAP annealed at moderate temperatures were studied in the following papers. γ-induced paramagnetic centers in the enamel annealed at $T_{ann} \leq 330^{o}C$ were studied in Vorona et al. (2005). Centers in the enamel annealed at $400^{o}C$ were investigated in Sadlo et al. (1998). Thermally induced centers in biological HAP were detected in Aldrich et al. (1992), Fattibene et al. (2000). The radiation defects in synthetic HAP annealed at $T_{ann} = 100–700\ ^{\circ}C$ were studied in Vorona et al. (2013), Zatovskii et al. (2013); it was found that O^- and CO_3^{3-} centers play an essential role at the annealing above 400 °C.

The effect of high temperature (above 600 °C) annealing on the formation of radiation-induced defects in the synthetic HAP was studied in a few works. In Ishchenko et al. (2009) the radiation defects in the enamel annealed in the range of 20–1000 °C were investigated. The EPR spectra of radiation defects in the annealed (up to 1200 °C) synthetic HAP were shown in Dowlatshah et al. (2012), however the signals were not identified. The paper (Brik et al., 2007) is devoted to carbonate defects (CO_2^-, CO_3^-, CO_3^{3-}) formed by γ- or X-irradiation of annealed (up to $1000^{o}C$) biogenic and synthetic HAP. The present study deals with a detailed analysis of the EPR spectra and identification of paramagnetic centers induced by γ- or UV-irradiation in synthetic carbonate-containing HAP annealed at high (600–950 °C) temperatures.

2. Materials and experimental details

HAP powder was synthesized from aqueous media by the wet precipitation method. The salts of $(NH_4)_2HPO_4$, $Ca(NO_3)_2$ and Na_2CO_3 were used as initial reagents. The molar ratio of Ca^{2+}/PO_4^{3-} in the initial reagents was 10/6. Precipitation of HAP was carried out at pH 7.5–7.7. The obtained precipitate was dried in air at 80 °C. The X-ray diffraction patterns of the initial and annealed samples were typical for an apatite with no admixture of any other phase.

Isochronous annealing was carried out in the muffle furnace in the temperature range $T_{ann} = 600–950$ °C in air. The annealing duration was 60 min at each selected temperature. The temperature was measured by a thermocouple with the accuracy of ±2 °C.

To create paramagnetic defects the annealed samples were irradiated by γ-rays or UV light. ^{60}Co source with exposure rate 2.58 10^{-2} C kg^{-1} s^{-1} (100 R/s) was used as a source of γ-rays. Absorbed dose was about 10 kGy. The high-pressure mercury lamp (DRT type) was used for UV-irradiation. The duration of the UV irradiation was 4 h. After the exposure the samples were stored at room temperature for one month in order to avoid the detection of short-living paramagnetic centers.

EPR measurements were carried out at room temperature using X-band EPR spectrometer Varian E12 (~9.5 GHz) equipped with TE_{011} cavity (E-233) with the quality factor 20 000. The samples of 10–30 mg were placed in quartz tubes of 4 mm inner diameter. Microwave power was varied in the range of 0.002–200 mW. 100 kHz modulation of the magnetic field with 0.05 mT amplitude was used. The error of the magnetic field measurements did not exceed 0.01 mT. The EPR spectra of the samples were recorded together with the spectrum of $MgO:Cr^{3+}$ reference sample with $g = 1.9800$ that allowed to determine the g-factor with accuracy ± 0.0002.

For the modelling of the powder EPR spectra, we used SimFonia program from the WINEPR package; the components of *g*-tensor, as well as width and shape of the initial EPR line, were taken as input parameters. The intensities of components of the EPR spectrum were fitted using the Separator program from the Visual EPR package (Grachev and Semenov, 1983).

3. Results and discussion

3.1. Determination of the parameters of paramagnetic centers and their identification

High-temperature annealing (600–950 °C) does not induce any intense EPR signals. After the irradiation by γ-rays or UV-light all HAP powders exhibit the complex EPR spectra that depend on the annealing temperature. In the spectrum of non-annealed powder after γ- or UV-irradiation the signals caused by CO_2^- and NO_3^{2-} centers were observed (see the details in (Vorona et al., 2013)); no other signals were detected. Fig. 1 shows the EPR spectra of γ-induced defects in HAP samples annealed in the temperature range of 600–950 °C and recorded at 0.2 and 2 mW. The spectra are the superposition of several signals and depend on the microwave power. In what follow we will show that some of these signals can be registrated in a “pure form” (i.e., avoiding the overlapping with other centers EPR signals) when the microwave power and annealing temperature are properly adjusted.

Fig.2 shows the simplest EPR spectra of HAP powders annealed at different temperatures. Slightly asymmetric γ-induced single EPR line is observed at low microwave power in HAP powders annealed at 600 °C. The line intensity saturates with increasing microwave power. This line in “pure form” with maximal intensity was detected at 0.002 mW (Fig. 2a) and well described by the parameters $g_x = 2.0044$, $g_y = 2.0033$, $g_z = 2.0019$ (Gaussian line with $\Delta B_{pp} = 0.3$ mT). These parameters and saturation behaviour allow to ascribe this line to CO_3^{3-} centers in the B position (Moens et al., 1994).

At 0.002 mW two single lines dominate in the γ-induced EPR spectrum of the powder annealed at 950 °C (see Fig. 2b). The first signal is caused by CO_3^{3-} centers discussed above. The second signal is the isotropic line with $g = 1.9990$. Similar signal has been previously observed in the γ-irradiated nanocrystalline HAP prepared by dry milling, but was not interpreted (Sadło et al., 2012). In (Fanovich et al., 2001) the signal at $g = 1.999$ was observed in modified hydroxyapatite HAP powders and assigned to $V_{\bar{O}}$ defects (electrons localized on the oxygen vacancies).

In γ-irradiated sample annealed at 650 °C the anisotropic signal dominates in the EPR spectrum at microwave power 20 mW (Fig. 2c). It is well described by the parameters $g_x = 2.0420$, $g_y = 2.0335$, $g_z = 2.0027$ that are characteristic for the surface O^- center (Callens et al., 1989, 1998; Callens, 1997). For this calculation we used the Voight lineshape with equal contributions of homogeneous and heterogeneous broadening expansion ($(\Delta B_{pp})_x = (\Delta B_{pp})_y = 0.63$ mT and $(\Delta B_{pp})_z = 0.2$ mT).

Fig.2d shows the spectrum of γ-induced defects in the powder annealed at 950 °C, the spectrum was recorded at 20 mW in the wide range of magnetic fields. Two anisotropic signals dominate. The first signal is well described by the parameters $g_x = 2.060$, $g_y = 2.058$, $g_z = 2.002$ (Gaussian line with $(\Delta B_{pp})_x = (\Delta B_{pp})_y = 0.3$ mT and $(\Delta B_{pp})_z = 0.25$ mT), which are close to the parameters of the O^- radical in A position (Moens et al., 1996; Callens et al., 1998). The best description of the second signal is achieved using Lorentzian lineshape ($\Delta B_{pp} = 0.4$ mT) with the parameters $g_\perp = 2.0135$, $g_{||} \sim 2.002$. This signal has been previously