OSL STUDY OF ION SUBSTITUTED HYDROXYAPATITES

Timor Grego[1,2], Ina Erceg[2], Božana Čolović[3], Maja Dutour Sikirić[2], Nadica Maltar-Strmečki[2]

[1]University Hospital Centre Zagreb, Kišpatićeva 12, Zagreb, Croatia
[2]Division of Physical Chemistry, Ruđer Bošković Institute, Bijenička c. 54, Zagreb, Croatia
[3]Vinča Institute of Nuclear Sciences, Mike Petrovića Alasa 12-14, Belgrade, Serbia

tgrego@kbc-zagreb.hr, ierceg@irb.hr , bozana@vin.bg.ac.rs, msikiric@irb.hr, nstrm@irb.hr

INTRODUCTION

Calcium phosphates (CaPs) constitute the main mineral component of the hard tissues of vertebrates, therefor their synthetic analogues are the most commonly used materials in orthopedics and stomatology.

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is a CaP which due to its similarity to mineral part of hard tissue is best known as biomaterial for hard tissue regeneration[1]. As HA substituted with different ions is the one occurring in biological systems, ion-substituted HA are increasingly attracting attention as hard tissue biomaterials[2,3]. However, HA has also been among the most studied dosimetric materials in the high dose and retrospective dosimetry, by the EPR (electron paramagnetic resonance) spectroscopy. They could as well be used as OSL (optically stimulated luminescence) dosimeters[4].

Influence of Mg and Si substitution on structure and morphology of HA were determined by powder X-ray diffraction (Panalytical Aeris Research Edition) and scanning electron microscopy (FE-SEM (JEOL JSM-7000F microscope).

The gamma radiation induced radical were used as probes to follow and control the changes in relation with substituted ions by EPR spectroscopy.

SYNTHESIS AND MATERIALS

Synthesis of Mg,Si-substituted HA

Calcium nitrate ($Ca(NO_3)_2{\cdot}4H_2O$), diammonium hydrogenphosphate ($(NH_4)_2HPO_4$) and magnesium nitrate ($Mg(NO_3)_2{\cdot}6H_2O$) were used as Ca, P and Mg precursors while SiO_2 sol was used as Si precursor. Needed amounts of precursors were dissolved in Milli Q water. To this solution, $(NH_4)_2HPO_4$ solution was added dropwise with constant stirring. To the formed reaction urea was added. Obtained reaction mixture was heated under reflux at 100°C for 5 h. Formed precipitates were dried at 200 °C.

Characterization

The composition of synthetised Mg, Si-substituted HA was detremined by powder X-ray diffraction (PXRD), while morphology was assesed by scanning electron microscopy (SEM).

EPR measurements

EPR spectra were recorded on a Varian E109 X-band EPR spectrometer equipped with a Bruker ER 041 XG microwave bridge, operating at 9.5 GHz with 100 kHz modulation, at room temperature.

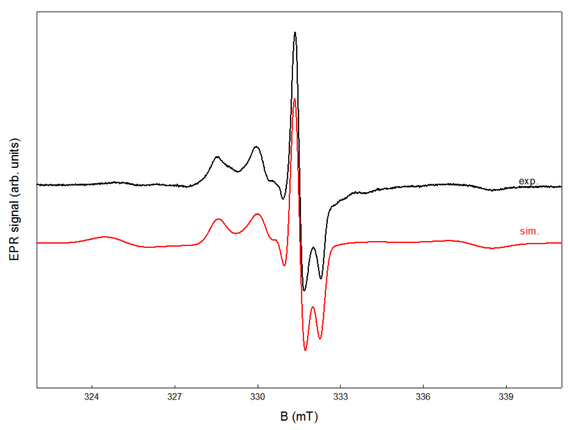
OSL measurements

The samples were irradiated with radiation to a dose of 100 Gy and 1000 Gy from the gamma source. OSL measurements have been performed on the SUERC Portable OSL reader by blue light stimulation at room temperature.

RESULTS

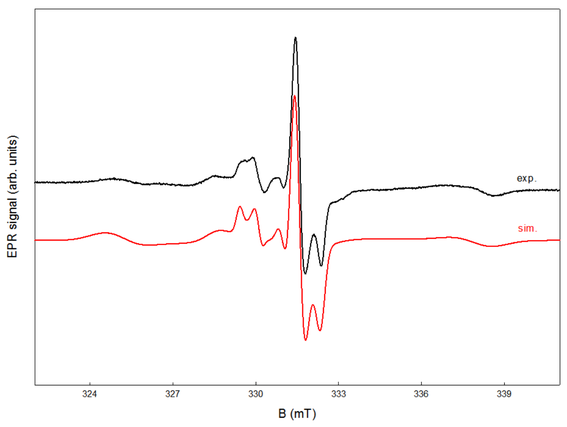
EPR

0.4% Si 2% Mg



Radical	g_x	g_y	g_z	A_{II} (mT)	$A_\perp$ (mT)
CO_2^-	2.0031	1.9972	2.0017		
O_3^-	2.0036	2.0199	2.0090		
SO_2^-		2.0054			
NO_3^{2-}	2.0057	2.0057	2.0017	6.61	3.27

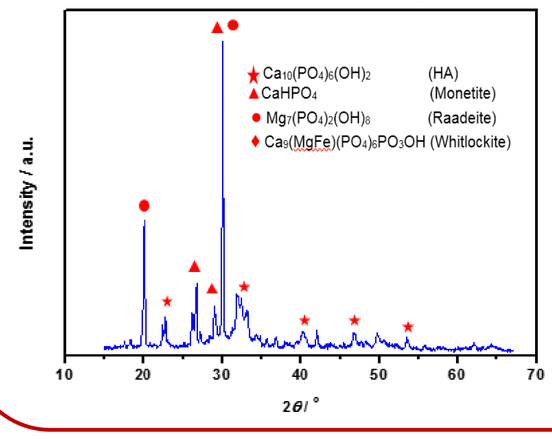
1.25% Si 2% Mg



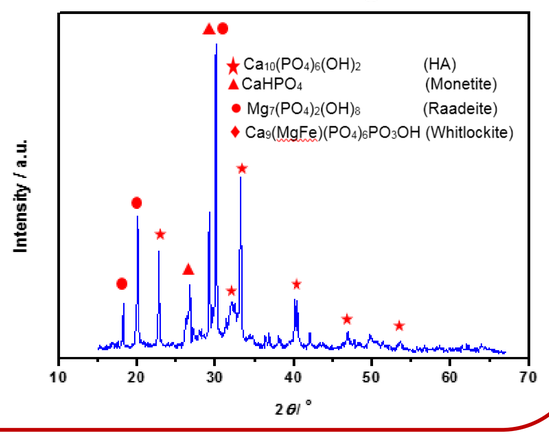
Radical	g_x	g_y	g_z	A_{II} (mT)	$A_\perp$ (mT)
CO_2^-	2.0031	1.9972	2.0017		
O_3^-	2.0039	2.0150	2.0108		
CO_3^-	2.0036	2.0199	2.0090		
SO_2^-		2.0054			
NO_3^{2-}	2.0057	2.0057	2.0017	6.61	3.27

PXRD

0.4% Si 2% Mg

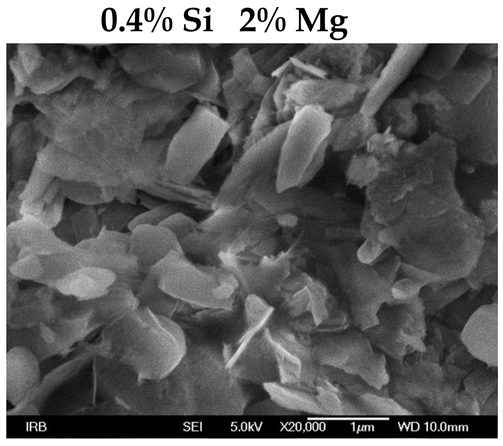


1.25% Si 2% Mg

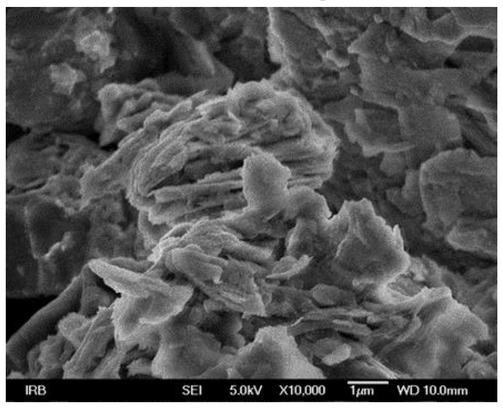


SEM

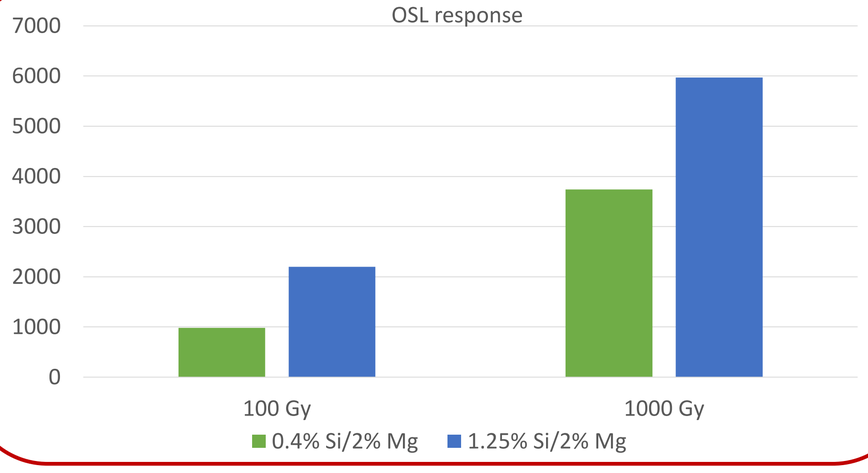
0.4% Si 2% Mg



1.25% Si 2% Mg



OSL



- Synthesis of Mg, Si - substituted HA resulted in formation of mixture of hydroxyapatite, monetite, whitlockite and raadeite was formed.
- Different ion-substitutions affected morphology of obtained precipitates.
- The analysis by EPR spectroscopy confirm the influence of Mg and Si on short range ion arrangement in synthetic HA.
- The OSL signal when stimulated by blue light is significantly higher (~1.6x) in the HAP samples doped with a higher percentage of silicium, for the same value of Mg (2%).

CONCLUSIONS

Obtained results imply possibility for application of investigated synthetic Mg and Si substituted hydroxyapatite as dose indicator materials using OSL techniques. However, a detailed study of the synthetic ion substituted hydroxyapatite features is necessary in specific regarding to the ion concentration, the dose value and the fading characteristics in order to confirm their applicability as OSL dosimeters.

REFERENCES

1. Dorozhkin S.V. Calcium Orthophosphate-Based Bioceramics and Biocomposites: Wiley-VCH, Weinheim, Germany; 2016.
2. Boanini E, Gazzano M, Bigi A. Ionic substitutions in calcium phosphates synthesized at low temperature. Acta biomaterialia. 2010; 6(6):1882-94. Epub 2009/12/31.
3. Szurkowska K, Kolmas J. Hydroxyapatites enriched in silicon – Bioceramic materials for biomedical and pharmaceutical applications. Progress in Natural Science: Materials International. 2017;27(4):401-9.
4. International Atomic Energy Agency (IAEA) Use of electron paramagnetic resonance dosimetry with tooth enamel for retrospective dose assessment. Vienna: IAEA-Tecdoc-1331; 2002.
5. Majer, M., Roguljić, M., Knežević, Ž., Starodumov, A., Ferenček, D., Brigljević, V., Mihaljević, B., 2019. Dose mapping of the panoramic 60Co gamma irradiation facility at the Ruđer Bošković Institute – Geant4 simulation and measurements. Appl. Radiat. Isotopes 154, 108824.

ACKNOWLEDGMENT

The Croatian Science Foundation under the project No. HRZZ-IP-2018-01-1493 (CaPBiomimNanocomp): Mechanisms of Calcium Phosphate formation on Inorganic Nanomaterials. A Biomimetic synthesis for multifunctional Nanocomposites for Hard Tissue regeneration.

NATO Science for Peace and Security (SPS) Project No. G5684: Novel biological and physical methods for triage in radiological and nuclear (R/N) emergencies (BioPhyMeTRe).

Croatian-Serbian bilateral Project: Ion-substituted Hydroxyapatites for Bone Tissue Enginering