

Hydroxyapatites of marine origin as sustainable candidates for implantology

L. Duta¹, G.E Stan², V. Grumezescu¹, G. Dorcioman¹, E. Matei², I. Zgura², O. Gherasim^{1,3}, G. Popescu-Pelin¹, F.N. Oktar^{4,5}

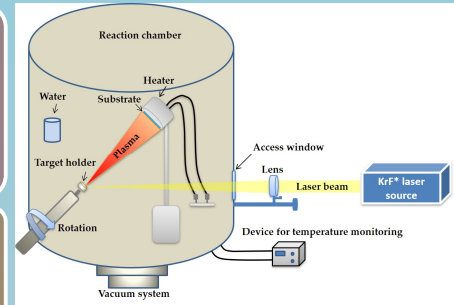
¹National Institute for Lasers, Plasma and Radiation Physics, Lasers Department, Magurele, Romania; liviu.duta@infpr.ro; ²National Institute of Materials Physics, Magurele, Romania; ³Department of Science and Engineering of Oxide Materials and Nanomaterials, Faculty of Applied Chemistry and Materials Science, Politehnica University of Bucharest, Bucharest, Romania; ⁴Department of Bioengineering, Faculty of Engineering, University of Marmara, Istanbul, Turkey; ⁵Advanced Nanomaterials Research Laboratory (ANRL), University of Marmara, Istanbul, Turkey

Motivation

- Development of implants easily integrated into the living body by using biomaterials.
- Route to obtain a material with a bone-like architecture and composition → fabricate it from sustainable resources, of biological origin, such as waste products (i.e., HA derived from fish bones, FB, or sea-shells).
- Synthesis by PLD of bio-hydroxyapatite thin films (doping with 0.5, 1 and 2 wt.% of Li_3PO_4 , MgF_2 and Ag).
- Detailed morphological, structural, compositional and mechanical investigations → beneficial influence of doping agents on the characteristics of the synthesized structures.

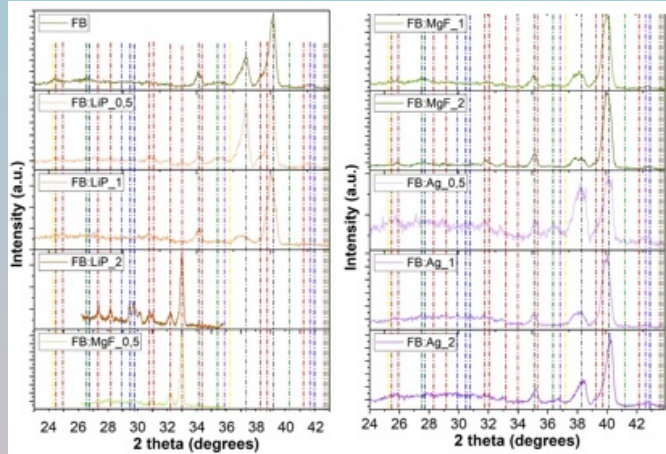
Materials and Methods

- PLD experiments, KrF* excimer laser source ($\lambda = 248\text{nm}$, $T_{\text{FWHM}} \leq 25\text{ns}$, $\nu = 10\text{Hz}$), deposition parameters ($p \approx 50\text{ Pa}$, H_2O vapors, $d = 5\text{ cm}$, $E = 360\text{ mJ}$, $T = 500^\circ\text{C}$, $F = 3.5\text{ J/cm}^2$, $N = 5000$).
- Simple (FB) and doped (with 0.5, 1 and 2 wt.% of Li_3PO_4 , MgF_2 and Ag → FB:LiP, FB:MgF and FB:Ag).

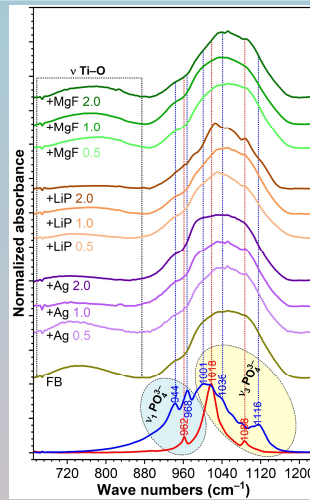


PLD experimental set-up

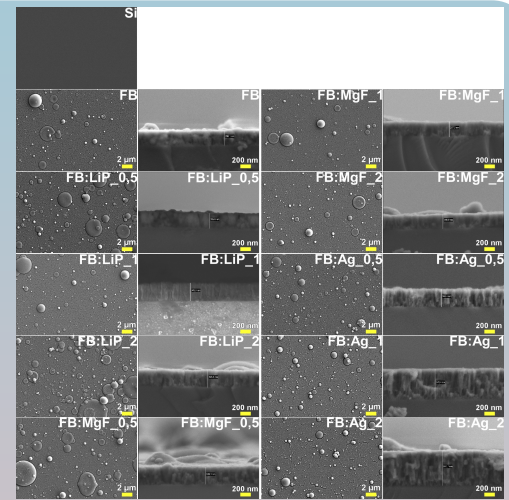
Results



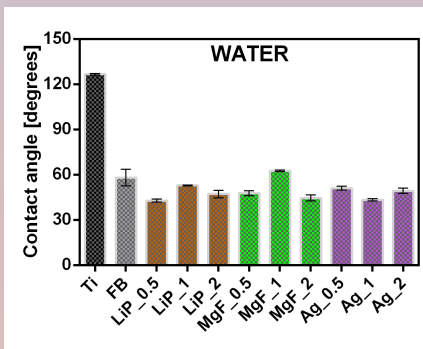
XRD diffractograms of simple and doped bio-hydroxyapatite thin films. Peaks were highlighted as following: Ti (grey), TiO_2 rutile (green), TiO_2 anatase (yellow), TiO (violet), $\text{Ca}_3(\text{PO}_4)_2$ whitlockite (blue) and $\text{Ca}_9(\text{PO}_4)_6(\text{OH})_3$ (red).



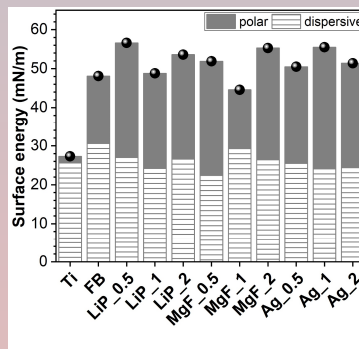
FT-IR spectra of simple and doped bio-hydroxyapatite thin films.



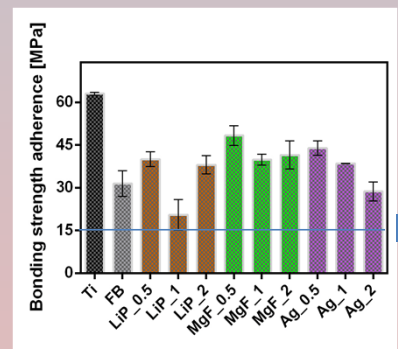
Top-view and cross-view SEM micrographs of simple and doped bio-hydroxyapatite thin films. Magnification bars: 2 μm (top-view) and 200 nm (cross-view).



Contact angle values inferred for simple and doped bio-hydroxyapatite coatings.



Surface free energy values inferred for Ti, and simple and doped bio-hydroxyapatite thin films (γ_d – hatched region, γ_p – grey region).



Pull out bonding strength adherence values measured in the case of simple and doped bio-hydroxyapatite thin films.

Conclusions

- Structural investigations → synthesis of films with different degrees of crystallinity, mainly influenced by the nature of the dopant/concentration and by the source material;
- Morphological examination → fabrication of films with rough surfaces, made of droplets, ideal for the good adhesion of cells and anchorage of implants *in situ*;
- Contact angle measurements → hydrophilic behaviour → rapid bone regeneration;
- Bonding strength adherence → values more than three times higher than the threshold imposed by ISO standard regulating the load-bearing implant coatings (>15 MPa);
- Preliminary results → incorporation of dopants into BioHA thin films can provide a delivery system for bioactive agents able to promote osseointegration, in correlation with an improved anchorage of bone metallic implants for suitable use in implantology.

Acknowledgements

This work was supported by a grant of Ministry of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE2019-1449 (TE 189/2021) and Core Programme 16N/2019.