# HIGH-TEMPERATURE SYNTHESIS, STRUCTURAL AND LUMINESCENT PROPERTIES OF Mn-DOPED α-TRICALCIUM PHOSPHATE

Lauryna Sinusaite[1], Diana Griesiute[1], Andris Antuzevics[2], Arturas Katelnikovas[1], Aleksej Zarkov[1]

[1]Institute of Chemistry, Vilnius University, Naugarduko st. 24, LT-03225, Vilnius, Lithuania
[2]Institute of Solid State Physiscs, University of Latvia, Kengaraga st. 8, LV-1063 Riga, Latvia
lauryna.sinusaite@gmail.com

Tricalcium phosphate polymorphs (α- and β-TCP) are alloplastic bone substitutes that belong to the class of calcium phosphate ceramics (CPCs). Due to their injectability, nontoxicity, bioactivity, osteoconductivity and biocompatibility, CPCs are promising biomaterials for bone tissue engineering applications and are commonly used as scaffolds and carriers to deliver stem cells, drugs and growth factors [1, 2]. α- and β-TCP possess same chemical composition, but due to having different structure, density and solubility, more reactive α-TCP is usually used as powder component of various bone cements while β-TCP – as biodegradable ceramics. The main advantages of α -TCP are that it can be used on its own and under physiological conditions with minimal heat release (meaning having no damage to human organism) it hydrates and sets into the biggest mineral component of natural bone – calcium deficient hydroxyapatite (CDHAp) [3].

Partial substitution of Ca ions by other biologically active cations is assumed to be a promising tool to superior biological properties of synthetic CPs. It is well known that presence of foreign ions in CP matrix can modify significantly physicochemical, mechanical and anti-bacterial properties of materials, to promote changes in morphology, solubility and kinetics of ion release. Additionally, doping elements open new possibilities for application of CPs as multifunctional materials. Optically active and paramagnetic ions make it possible to use these materials for bioimaging applications including fluorescence, magnetic resonance or multimodal imaging.

Manganese is an essential element in human organism that plays important role for normal bone formation and development. Studies have revealed that $Mn^{2+}$ enhances the ligand binding affinity of integrin, activates cell adhesion and increases osteoblast adhesion. However, high levels of $Mn^{2+}$ in human body may cause neurological disorder – manganism [4, 5]. At the same time, Mn is also known for its optical properties and was incorporated into different hosts for the preparation of luminescent materials. $Mn^{2+}$-doped materials after excitation can exhibit broad band emission in the red region and therefore can be used as photoluminescent materials [6].

The main aim of this study was to investigate feasibility of the synthesis of Mn-doped α-TCP and to study its photoluminescent and structural properties. In order to do that, a series of α-TCP powders doped with different amounts of $Mn^{2+}$ ions (from 0.2 to 1.0 mol%) were synthesized by wet precipitation method followed by high temperature synthesis using $Ca(NO_3)_2 \cdot 4H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ as starting materials. Metals to phosphorous ratio was kept 1.5. Obtained precipitates were vacuum filtered, washed with deionized water and ethanol afterwards dried in oven at 50 °C overnight and annealed at 1250 °C. Thermal quenching was used in order to stabilize α-TCP structure.

The crystal structure and purity were evaluated by X-ray powder diffraction (XRD), electron paramagnetic resonance (EPR) and Fourier-transform infrared (FTIR) spectroscopy. Scanning electron microscopy (SEM) was used to determine the morphological features of the synthesized products. Optical properties of the synthesized specimens were investigated in terms of photoluminescence (PL), excitation and emission spectra were recorded. ICP-OES analysis was performed in order to determine elemental composition of the products.

The results of XRD, FTIR and elemental analysis confirmed that proposed synthetic approach is suitable for the synthesis of Mn-doped TCP with a good phase purity and controllable chemical composition. It was demonstrated that Mn-containing powders under excitation at 408 nm revealed red emission centered at 630 nm. Emission intensity was found to be dependent on concentration of $Mn^{2+}$ ions.

[1] H. Xu, P. Wang, L. Wang et al, Calcium phosphate cements for bone engineering and their biological properties, Bone Research **5**, 17056 (2017).
[2] A. Lasckus, J. Kolmas, Ionic Substitutions in Non-ApatiticCalcium Phosphates, International Journal of Molecular Sciences **18**, 2542 (2017).
[3] R. G. Carrodeguas, S. De Aza, α-Tricalcium phosphate: Synthesis, properties and biomedical applications, Acta Biomaterialia **7**, 3536-3546 (2011).
[4] T. Wu, H. Shid, Y. Liang et al, Improving osteogenesis of calcium phosphate bone cement by incorporating with manganese doped β-tricalcium phosphate, Materials Science & Engineering C **109**, 110481 (2020).
[5] R. Singh, M. Srivastava, N. K. Prasad, Structural analysis and magnetic induced hyperthermia of $Fe^{3+}$ and $Mn^{2+}$ substituted β-$Ca_3(PO_4)_2$, New Journal of Chemistry **41**(21), 12879-12891 (2017).
[6] Q. Zhou, L. Dolgov, A. M. Srivastava et al, $Mn^{2+}$ and $Mn^{4+}$ red phosphors: synthesis, luminescence and applications in WLEDs. A review, Journal of Materials Chemistry C **6**, 2652 (2018).