



Structural investigation of calcium phosphates.

Francesco Capitelli,^{a,*} Rosanna Rizzi,^b Angela Altomare,^b Dritan Siliqi,^b Francesco Baldassarre,^b Giancarlo Della Ventura,^c Abdelouahad Zegzouti,^d Manuela Rossi,^e Veronica Paterlini.^f

Calcium phosphates (CaP) materials, employed in different biomedical applications because of their density very close to those of CaP mineralized phases of human bones, are largely investigated in many scientific fields.¹ The most known CaP are tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ (TCP) and hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (HAp). TCP is the synthetic analogue of mineral whitlockite $\text{Ca}_9\text{Mg}(\text{PO}_4)_6[\text{PO}_3(\text{OH})]$ and, owing to its density similar to that of human bones, is a material widely used in biomedical applications. In the present work, we investigated two sets of substituted β -TCP materials, coming from solid-state reactions at $T = 1200^\circ$, respectively with rare earths cations (*RE*),² and with divalent transition metals (Mn, Ni, Cu).³ All TCP were subject to a multi-methodological crystal chemical investigation based on SEM-EDS microscopy, powder X-ray diffraction (PXRD), FTIR, Raman and luminescence spectroscopies. Investigation was completed with the structural refinement (Rietveld method). SEM morphological analyses revealed the presence of subspherical microcrystalline aggregates. Refinement of site occupancies showed the tendency of *RE* cations to replace Ca in the largest structural sites; in the smaller octahedral M5 site, low *RE* (La→Gd) are not present, contrary to high *RE* (Dy→Lu) present in this site, while divalent cations showed a strong tendency to occupy this energetically favourable site. FTIR and Raman spectra show slight band shifts of the phosphate modes correlated to the evolving size of the replacing element, as well as strong luminescence properties were found in many *RE*- TPC (Eu and Gd phases) and in Mn-TCP. Distribution of RE within TCP structural sites was deeply investigated.

HAp is the primary mineral component of human bones and teeth. We investigated HAp, coming from high-temperature syntheses, doped with different cations at different concentrations, e.g. bismuth-HAp as possible bio-material,⁴ and *RE*-HAp as phosphor materials.^{5,6} Multi-methodological characterization was completed by dielectric measurements for Bi-HAp: morphological analysis revealed a decrease in crystallite size by bismuth-addition in HAp lattice, while the relative permittivity, dielectric loss and alternating current conductivity change with increasing frequency, the alternating conductivity gradually decreases with the addition of Bi. For (Eu, Gd)-HAp, FTIR spectra showed slight band shifts of the phosphate modes correlated to the evolving size of the replacing cation, while significant luminescence properties were found for Eu- and Gd-phases.

References

- 1 S. V. Dorozhkin, Calcium orthophosphate bioceramics, *Ceramics International* 41 (10, Part B) (2015) 13913 – 13966. doi:10.1016/j.ceramint.2015.08.004.
- 2 F. Capitelli, M. Rossi, A. ElKhouri, M. Elaattmani, N. Corriero, A. Sodo, G. D. Ventura, Synthesis, structural model and vibrational spectroscopy of lutetium tricalcium phosphate $\text{Ca}_9\text{Lu}(\text{PO}_4)_7$, *Journal of Rare Earths* 36 (11) (2018) 1162 – 1168. doi:10.1016/j.jre.2018.02.014.

^a CNR - Istituto di Cristallografia, Montelibretti (RM), Italy

^b CNR - Istituto di Cristallografia, Bari, Italy

^c Dipartimento di Scienze, Università Roma Tre, Rome, Italy

^d Faculté des Sciences Semlalia, Université Cadi Ayyad, Marrakech, Morocco

^e Dipartimento di Scienze della Terra dell'Ambiente e delle Risorse, Università di Napoli Federico II, Naples, Italy

^f Luminescent Materials Laboratory, Università di Verona, Verona, Italy

Creative Commons Attribuzione - Non commerciale - Condividi allo stesso modo 4.0 Internazionale

† oral communication at 1 st Conference on Crystallography, Structural Chemistry and Biosystems, (Catania) 04-06/10/2021

- 3 A. Altomare, R. Rizzi, M. Rossi, A. El Khouri, M. Elaatmani, V. Paterlini, G. Della Ventura, F. Capitelli, New $Ca_{2.90}(Me^{2+})_{0.10}(PO_4)_2$ β -tricalcium Phosphates with $Me^{2+} = Mn, Ni, Cu$: Synthesis, Crystal-Chemistry, and Luminescence Properties, *Crystals* 9 (6) (2019) 288. doi:10.3390/cryst9060288.
- 4 A. El Khouri, A. Zegzouti, M. Elaatmani, F. Capitelli, Bismuth-substituted hydroxyapatite ceramics synthesis: Morphological, structural, vibrational and dielectric properties, *Inorganic Chemistry Communications* 110 (2019) 107568. doi:10.1016/j.inoche.2019.107568.
- 5 F. Baldassarre, A. Altomare, N. Corriero, E. Mesto, M. Lacalamita, G. Bruno, A. Sacchetti, B. Dida, D. Karaj, G. D. Ventura, F. Capitelli, D. Siliqi, Crystal chemistry and luminescence properties of eu-doped polycrystalline hydroxyapatite synthesized by chemical precipitation at room temperature, *Crystals* 10 (4) (2020) 250. doi:10.3390/cryst10040250.
- 6 V. Paterlini, M. Bettinelli, R. Rizzi, A. El Khouri, M. Rossi, G. Della Ventura, F. Capitelli, Characterization and luminescence of eu³⁺- and gd³⁺-doped hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, *Crystals* 10 (9) (2020) 806. doi:10.3390/cryst10090806.