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Multi-methodological characterization of Eu-doped polycrystalline hydroxyapatite, and comparison between low and high temperature synthesis

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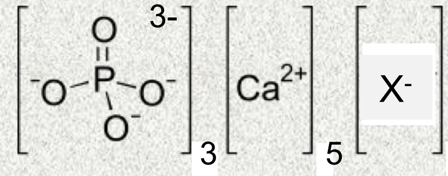
crystals MDPI

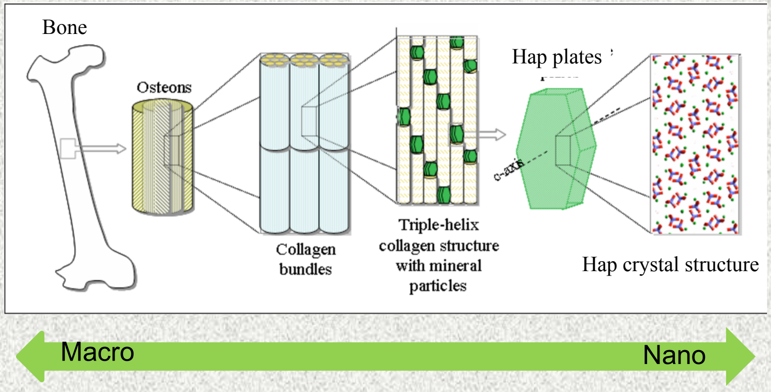
Apatite

$Ca_5(PO_4)_3(X)$ (X = F, Cl, OH) apatite are minerals largely spread all over igneous and sedimentary rocks (phosphorites).



Apatite framework allows many substitutions, both cationic and anionic, giving rise to apatite 'supergroup' made up by more of 40 species, of which the most known are $Ca_5(PO_4)_3F$ fluorapatite (FAp), $Ca_5(PO_4)_3Cl$ chloroapatite (ClAp), and $Ca_5(PO_4)_3OH$ hydroxyapatite (HAp)

HAp is the main mineral component of bones and teeth.

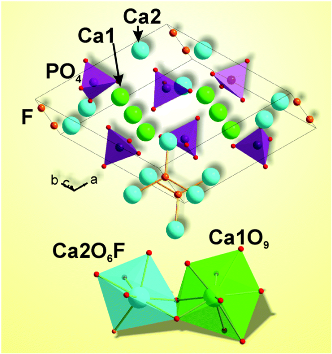


Synthetic apatite is largely employed in many technological and biomedical applications.

$Ca_5(PO_4)_3$(F, Cl, OH) Apatite: a very extended family

Apatite group

Clorapatite	$Ca_5(PO_4)_3Cl$
Fluorapatite	$Ca_5(PO_4)_3F$
Hydroxyapatite	$Ca_5(PO_4)_3OH$
Alforsite	$Ba_5(PO_4)_3Cl$
Johnbaumite	$Ca_5(AsO_4)_3OH$
Mimetite	$Pb_5(AsO_4)_3Cl$
Pieczkaite	$Mn_5(PO_4)_3Cl$
Pyromorphite	$Pb_5(PO_4)_3Cl$
Stronadelphite	$Sr_5(PO_4)_3F$
Svabite	$Ca_5(AsO_4)_3F$
Turneaureite	$Ca_5(AsO_4)_3Cl$
Vanadinite	$Pb_5(VO_4)_3Cl$



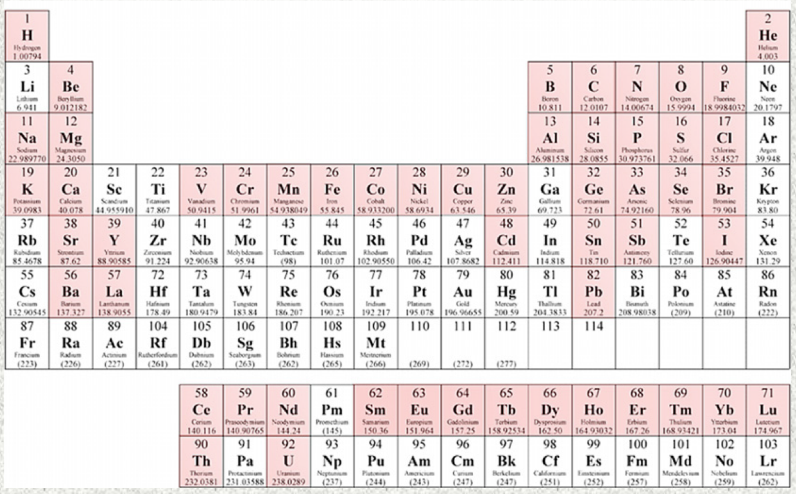
Belovite group -----> $(RE)^{3+}$

Britholite group -----> $(SiO_4)^{4-}$

Ellestadite group -----> $(SO_4)^{2-}$

Hedyphane group -----> Na^+, $(SO_4)^{2-}$

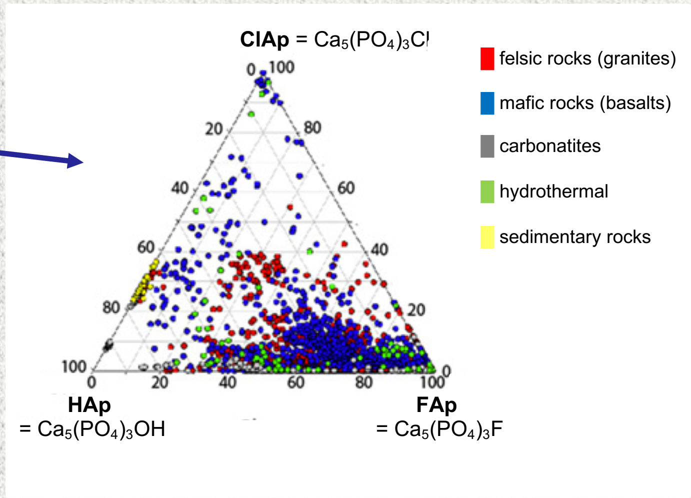
(RE = rare earths)

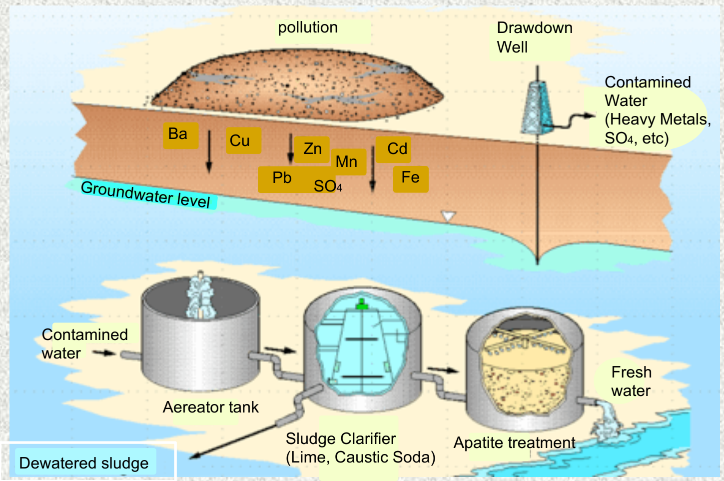


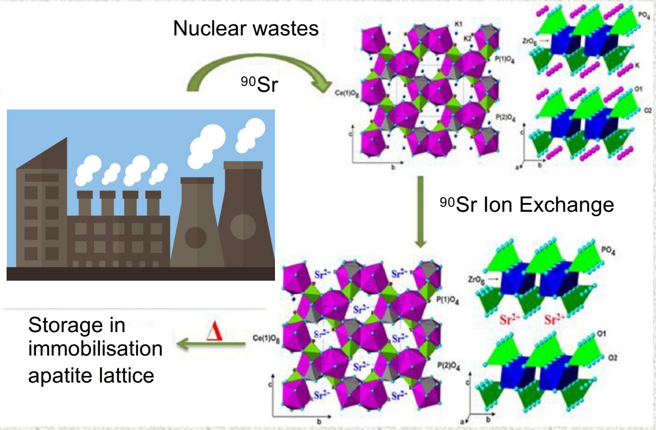
Pink-marked chemical species retrieved in natural apatites

Apatite: a very versatile material part 1

	Application	Employed properties
Geology	Petrogenetic indicator	Major- and trace-element composition
Environment	Solid nuclear waste storage	Thermal / chemical stability annealing temperature elemental affinity
	Water treatment	Elemental affinity







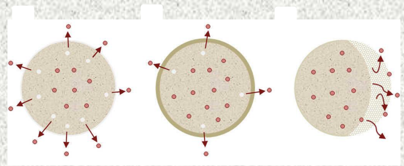
Apatite: a very versatile material part 2

	Application	Employed properties
Biomedical sciences	Orthopedics/Bone and teeth prosthesis	Natural constituent of bone
	Dentistry	Natural constituent of teeth
	Drug delivery agent	Size, morphology, structure, biocompatibility
Materials	Phosphors	Optical emission
	Laser	Optical emission and laser behavior
	Gems	Color, transparency

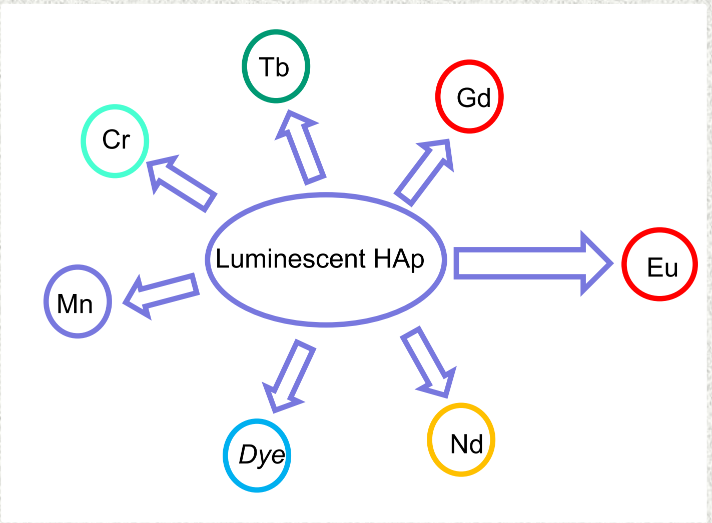
Commercial HAp, in disks, blocks and powders

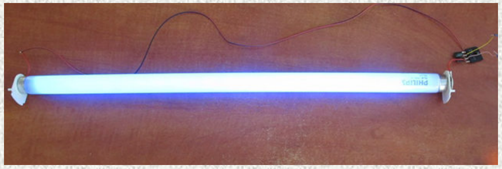
Coatings for dental prosthesis

Coatings for bone prosthesis



Nano-HAp: drug carrier agent



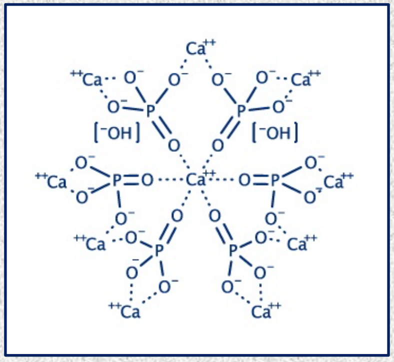


Fluorescent light bulb with coating of Mn-Sb apatite

apatite gem

Phosphors: materials that absorb incident energy, transforming it in visible radiation (Luminescence)

Hydroxyapatite $Ca_5(PO_4)_3OH$, THE biomaterial



PROPERTIES

- Biocompatibility
- Bioactivity
- Osteoconductivity
- Non toxicity
- Anti-inflammatory
- Luminescence (when doped with REE)

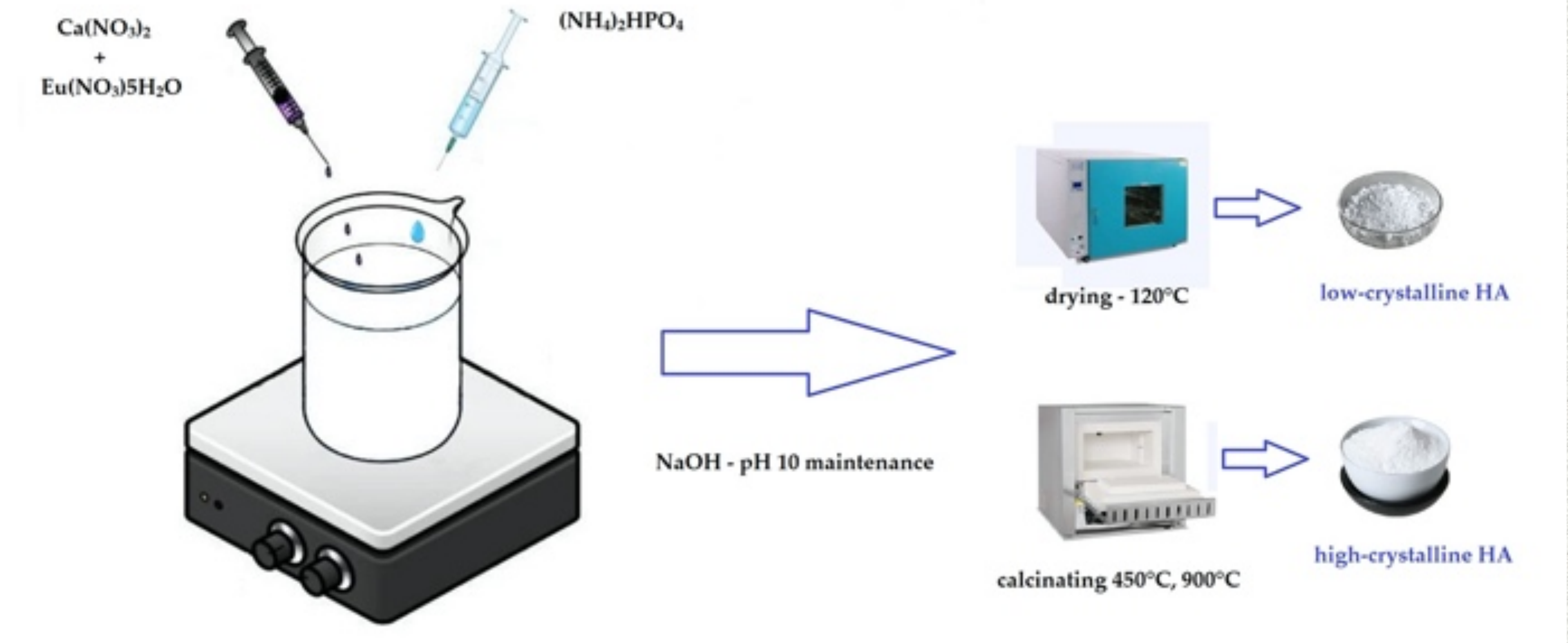
(some of the) APPLICATIONS

- Bone tissue engineering
- Bone void fillers
- Orthopedic/dental implant coating
- Restoration of periodontal defects
- Mineralizing agent in toothpastes
- Biomedical Imaging

Multi-methodological characterization of Europium-doped polycrystalline hydroxyapatite synthesized by chemical precipitation at room temperature

- Eu-doped hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (3% mol) powders were synthesized by an optimized chemical precipitation method at 25 °C, followed by drying at 120 °C and calcination at 450 °C and 900 °C.
- The obtained nanosized crystallite samples were investigated by means of a combination of inductively coupled plasma (ICP) spectroscopy, powder X-ray diffraction (PXRD), Fourier Transform Infrared (FTIR), Raman and photoluminescence (PL) spectroscopies.
- The Rietveld refinement in the hexagonal $P6_3/m$ space group showed Eu ordered at Ca2 site at high T (900 °C), and at Ca1 site for lower T (120 °C and 450 °C).
- FTIR and Raman spectra showed slight band shifts and minor modifications of the (PO_4) bands with increasing annealing T.
- PL spectra and decay curves revealed significant luminescence emission for the phase obtained at 900 °C and highlighted the migration of Eu from Ca1 to Ca2 site for increasing calcinating T.

HAp preparation



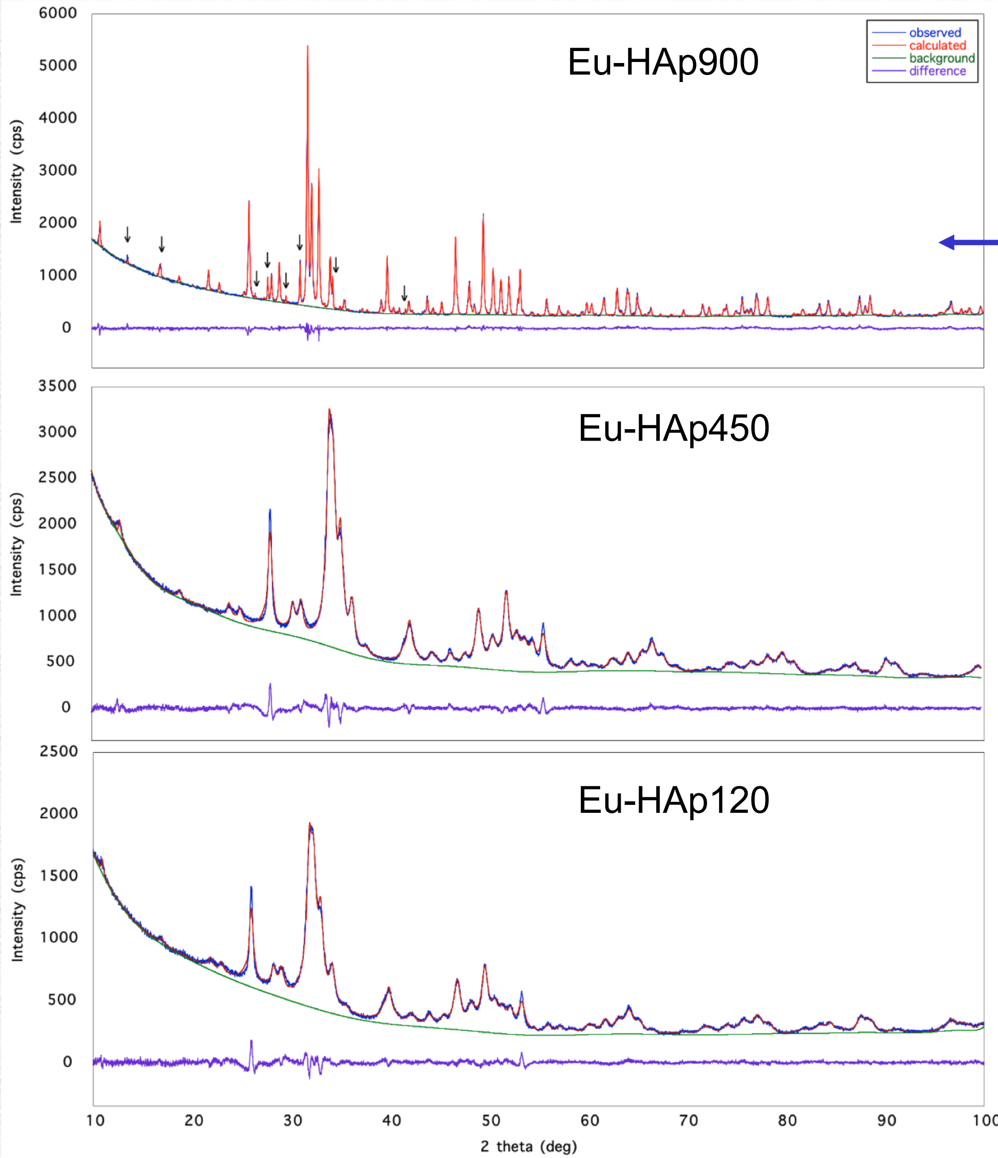
Samples:

Eu-HAp120 dried at 120 °C = $Ca_{9.76}Eu_{0.16}(PO_4)_6(OH)_2$; **Eu-HAp450** calcinated at 450° = $Ca_{9.82}Eu_{0.08}(PO_4)_6(OH)_2$; **Eu-HAp900** calcinated at 900° = $Ca_{9.92}Eu_{0.08}(PO_4)_6(OH)_2$; **HAp-900** calcinated at 900° = $Ca_{10}(PO_4)_6(OH)_2$

Sample	Ca (wt %)	P (wt %)	Eu (wt %)	(Ca + Eu)/P	Eu/(Ca + Eu)
HAp900	37.85	17.84	0.00	1.66	0.00
Eu-HAp120	32.84	15.74	3.70	1.66	0.03
Eu-HAp450	33.84	17.15	3.68	1.57	0.03
Eu-HAp900	36.22	18.75	4.03	1.54	0.03

Contents (wt %) and molar ratios of Ca, Eu and P for the synthesized HAp, obtained by ICP OES.

Powder XRD



Arrowed peaks correspond to arising of $Ca_3(PO_4)_2$ TCP phase at high synthesis temperature.

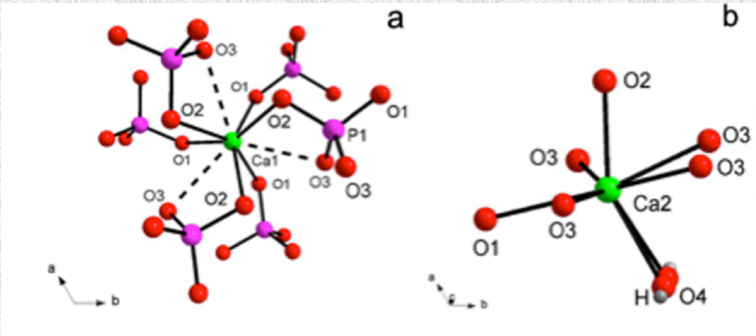
Good crystallinity (%) was observed for HT phases, unlike LT phases with amorphous behavior.
Size (nm) increased according to annealing temperature.

HAp900	Eu-HAp120	Eu-HAp450	Eu-HAp900
56 nm	25 nm	26 nm	148 nm
81%	3%	7%	87%

Structure and Rietveld refinement parameters for HAp samples.

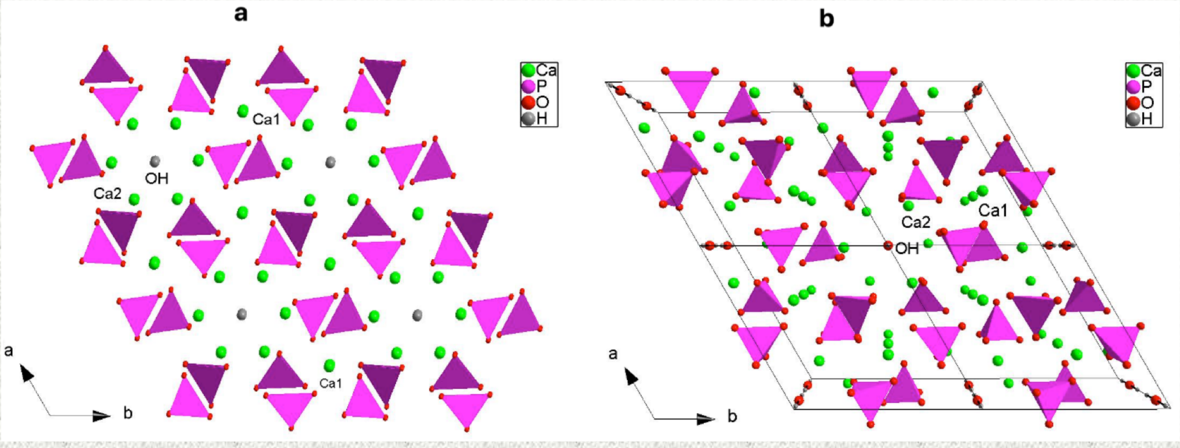
Crystal Formula	HAp900	Eu-HAp120	Eu-HAp450	Eu-HAp900
System, space group	Hex., $P6_3/m$	Hex., $P6_3/m$	Hex., $P6_3/m$	Hex., $P6_3/m$
$a = b$ (Å)	9.4145(4)	9.4108(13)	9.3952(11)	9.4147(4)
c (Å)	6.8758(5)	6.868(2)	6.8652(17)	6.8760(5)
V (Å^3)	527.77(5)	526.75(19)	524.80(16)	527.81(5)
Z; Density$_{calc.}$ (Mg·m^{-3})	1, 3.161	1, 3.226	1, 3.229	1, 3.208
Bragg refl., parameters	615, 57	205, 57	191, 58	615, 59
R_p; R_{wp}; R_{exp} (%)	2.55, 3.61; 4.33	2.03, 2.78 4.30	1.97, 2.71, 3.57	2.17, 3.00, 4.33

X-ray structure



*Detail of Ca1 (**a**) and Ca2 (**b**) coordination environments*

- Analysis of site occupancy showed that Eu^{3+} ions occupy, in the doped samples, the Ca1 positions for LT samples Eu-HAp120 (s.o.f.: $Ca_{0.96}Eu_{0.04}$) and Eu-HAp450 (s.o.f.: $Ca_{0.97}Eu_{0.03}$).
- This is in agreement with Fleet et al. (2000), although differently for the HT samples (Eu-HAp900), where Eu occupies Ca2 (s.o.f.: $Ca_{0.98}Eu_{0.02}$), in agreeement for most Eu-doped HAps (Aquilano et al., 2014).
- The shortening of Ca2-O distances for increasing annealing temperature, may induce the migration of Eu^{3+} from Ca1 up to Ca2 site, as observed in many HAp structures found in Inorganic Crystal Structure Database.

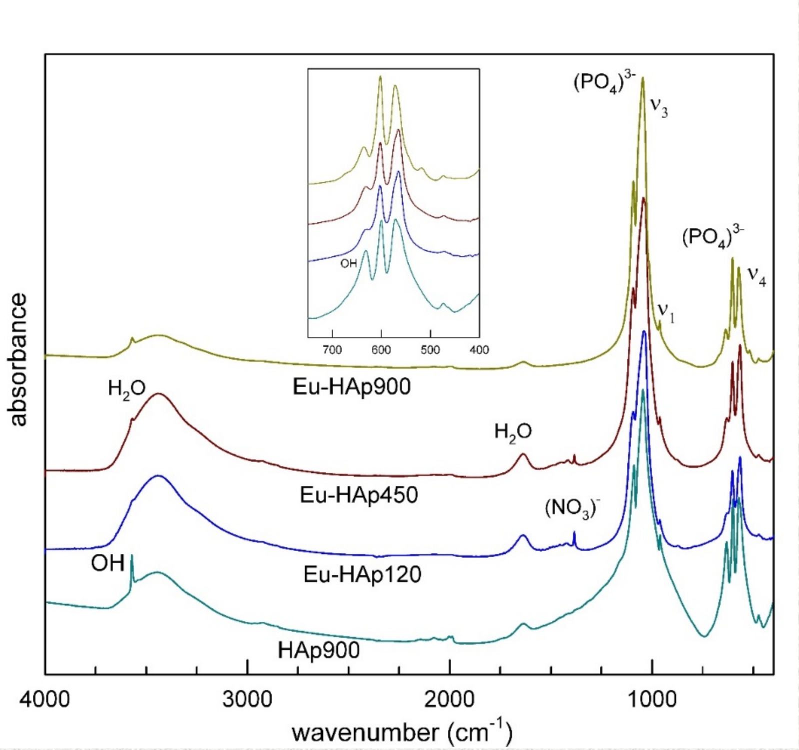


*Representation, down c, of the three-dimensional framework of HAp; (**a**) detail of the hexagonal tunnel, and clinographic view of the supercell 2 × 2 (**b**).*

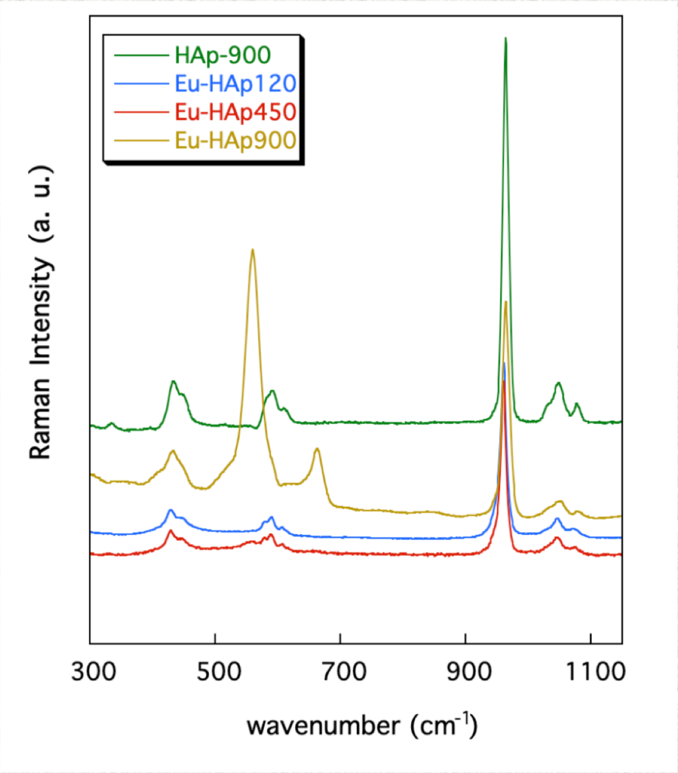
Fleet et al. Site Preference of Rare Earth Elements in Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$]. *Journal of Solid State Chemistry* **2000**, *149*, 391–398.

Aquilano et al. Low Symmetry Polymorph of Hydroxyapatite. Theoretical Equilibrium Morphology of the Monoclinic $Ca_5(OH)(PO_4)_3$. *Crystal Growth & Design* **2014**, *14*, 2846–2852

FTIR and Raman spectroscopies



FTIR spectra of Eu-doped HAp samples compared to pure Hap.



Raman spectra of Eu-doped HAp samples compared to pure Hap.

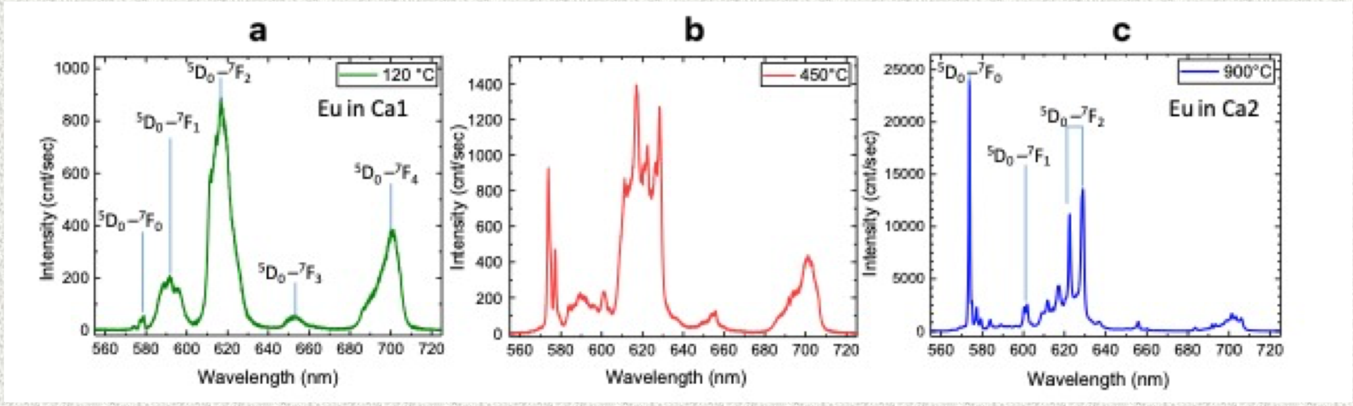
FTIR: in Eu-HAp900 of a weak peak at 518 cm^{-1} that can be assigned to the RE-O bonding, in agreement with Get'man et al. (2010), for HT phases.

Raman: Eu-HAP900 exhibits a band centered at 664 cm^{-1} which may be associated to vibrational modes of the $[PO_4]^{3-}$ groups bonded to the Eu ions (Zavala-Sanchez et al., 2015).

Get'man et al. Isomorphous substitution of samarium and gadolinium for calcium in hydroxyapatite structure. *Russ. J. Inorg. Chem.* **2010**, *55*, 333–338.

Zavala-Sanchez et al.. Distribution of Eu^{2+} and Eu^{3+} Ions in Hydroxyapatite: A Cathodoluminescence and Raman Study. *ACS Biomater. Sci. Eng.* **2015**, *1*, 1306–1313.

Photoluminescence spectroscopy



*PL spectra of Eu-doped HAp samples after thermal treatments at 120 °C (**a**), 450 °C (**b**) and 900 °C (**c**).*

The emissions from Eu at Ca1 are mainly observed for sample at 120°C (Figure 6a) and at 450°C (Figure 6b), while the sample annealed at 900 °C shows typical transition of Eu at Ca2 site (Figure 6c), in agreement with Garcia-Dominguez (2019).

Emissions of the $^5D_0-^7F_0$, transition at 573 nm of Ca2-Eu^{3+} is more than 10 times higher than the emission at 592 nm of Ca1-Eu^{3+}, indicating the almost complete substitution for this element at the Ca2 sites of HAp host matrix.

This behavior can be explained by a thermal energy that at the same time promotes process of crystallization and diffusion of the europium ions within the apatite structure and substitution of the Eu^{3+} ions in Ca2 sites, in according with structural results from XRD.

Garcia Dominguez et al. Structural and luminescent properties of europium-doped and undoped hydroxyapatite powders sintered by spark plasma. *Ceramics - Silikaty* **2019**, 100–109.

Conclusions

The multi-methodological characterization achieved through XRD and PL techniques, showed that the Eu entered in Ca1 site in the doped samples dried (120 °C) and calcinated (450 °C) at low temperature: these samples show low crystallinity (3% and 7%, respectively), good luminescence and very low crystallite size (around 25 nm).

Eu-doped sample calcinated at 900°C showed very high crystallinity (87%), with a crystallite size of 148 nm, while PL spectroscopy suggested that this sample presents the highest and narrowest emission bands. PL results showed the complete migration of Eu^{3+} ions in the Ca2 sites.

All results show that HAp phases obtained at 120° and 450°, displaying low crystallinity, could be employed as luminescent drug carriers, while HAp phases annealed at 900°, displaying good crystallinity, can be suitable biomaterials for biological system imaging.

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Reference: Baldassarre et al. Crystal-Chemistry and Luminescence Properties of Eu-Doped Polycrystalline Hydroxyapatite Synthesized by Chemical Precipitation at Room Temperature. *Crystals* **2020**, 10, 250.