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Physico-chemical characterization of new rare earths doped calcium phosphates

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Calcium phosphate

Due to the abundance in nature as phosphate ores, in living organisms as bones and teeth, and in the majority of various pathological calcifications, calcium phosphates are inorganic compounds of special interest for human being.

There are a large variety of calcium phosphates, which are differentiated by the type of phosphate anion.

Namely:

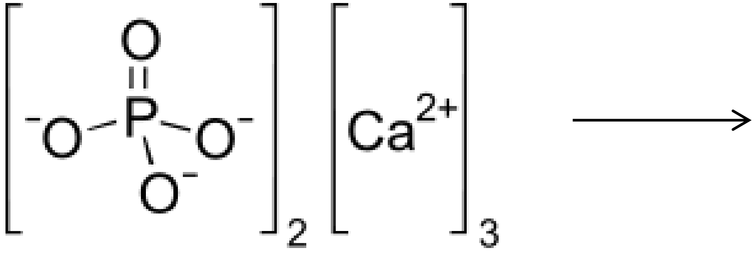
ortho- (PO_4^{3-}), meta- (PO_3^{-}), pyro- ($P_2O_7^{4-}$) and poly- $(PO_3)_n^{n-}$

Dorozkhin. Ceramics International **41** (2015) 13913–13966

Tricalcium phosphate (TCP) biomaterial

Of great interest are tricalcium phosphates $Ca_3(PO_4)_2$ (TCP), a synthetic phosphate material known for well reproducing human bone density.

It is naturally retrieved in human dental calculi, salivary stones, arthritic cartilage, soft-tissue deposits*.



TCP has three polymorphs

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Tricalcium phosphate (TCP) polymorphs

β-TCP polymorph
High-temperature phase, prepared at temperature above ~ 800° C. Stable and bioresorbable, is isotypic with *whitlockite* mineral $Ca_9(Mg,Fe^{2+})(PO_4)_6(PO_3OH)$

α-TCP polymorph
At temperature above ~ 1200° C, **β-TCP** is transformed into the high-temperature phase **α-TCP.**
Unstable in water, reacts to form $Ca_{10}(PO_4)_6(OH)_2$ hydroxyapatite (HA)

γ-TCP polymorph
Synthesized from **β-TCP** at temperature above ~ 1000° C, and at pressure above ~ 4 Gpa.
Also found in meteorite samples (*tuite*)

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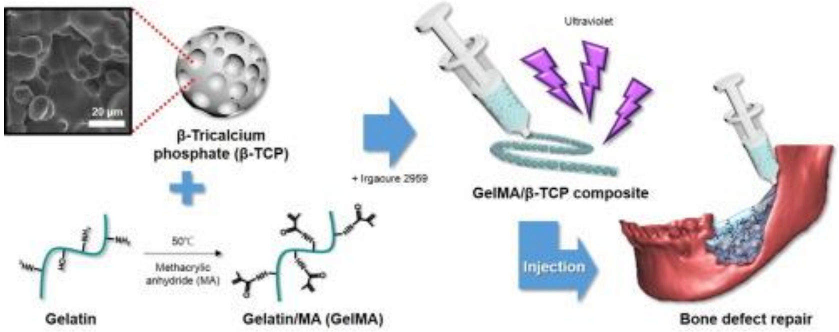
Applications of TCPs…

bone tissue ingrowth: although TCP is not the primary mineral component of human bones (made up by hydroxyapatite), it is widely used as material in the treatment of bone defects and to help bone tissue ingrowth.

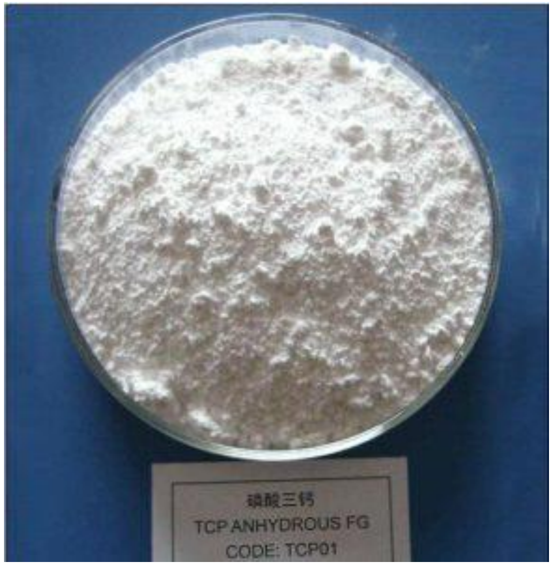
TCP is used in bone cements and fillers, low load bearing implants, aiming to provide a degradable coating on metallic implants, to induce a favourable biological response, and to increase osteointegration of the implant.



As bone graft substitute, TCP is able of hardening Ca-deficient hydroxyapatite (CDHA) and remodeling at similar rate to bone.

TCP shows wet compressive strength slighlty less than natural cancellous bone.

Applications of TCPs…



In food production
Widely used as Calcium supplements in food industries in order to promote bone growth; as nutrition supplements, in milk, condiments and meat products to regulate acidity, enhance flavor and nutrition; as anti-caking agent in flour products.

In beverage
Widely used as nutrition supplements and anti-caking agent in beverages.

In pharmaceutical/cosmetical
Used in toothpastes as gentle polishing agent.

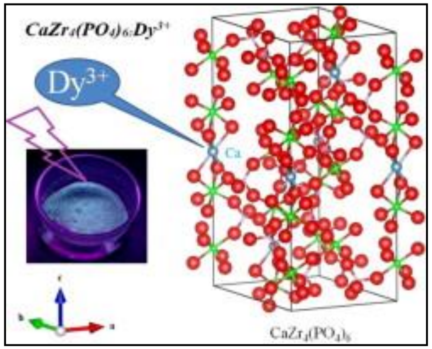
In agriculture
Widely used as Ca-supplement in fertilizers.

TCP is also widely employed as thermoluminescent dosimeter for X-rays devices, owing to its density human bone – like. The material absorbs X-rays in the way human tissues would do, and stores charges before emitting light when thermally activated.

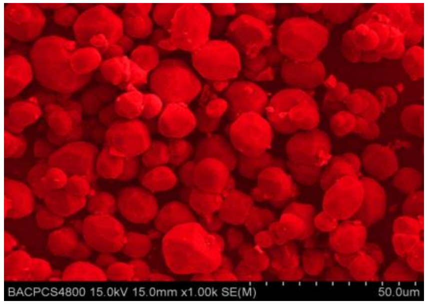
Doped TCPs…

TCP can be doped by rare earth (RE) cations, acting as **optical materials**.

Interactions between the electronic band states of the host crystal and the RE ion's localized at $4f^{N}$ and $4f^{N-1}$-5d states, influence the material's optical properties.



TCP have been proposed as materials for bio-imaging*, storing charges and emitting fluorescence, *i.e.* red long-lasting phosphors, used in biomedical applications, such as optical imaging, but also bioassays, drug delivery and therapy.



*Ait Benhamou et al. *Journal of Solid State Chemistry* **182** (2009) 2319–2325.

Doped TCPs…

To this aim, a set of new rare-earth doped β-tricalcium phosphates **$Ca_9\mathit{RE}(PO_4)_7$ (*RE* = La, Pr, Nd, Eu, Gd, Dy, Tm, Yb, Lu)** has been subjected to crystal-chemical characterization aimed at understanding their properties and simulate their biological activity.

The knowledge of dopant distribution is crucial as optical properties depend on dopant–dopant distances and on dopant–defect interactions. A careful control of the dopant distribution in β-TCP would be required for appropriate applications.

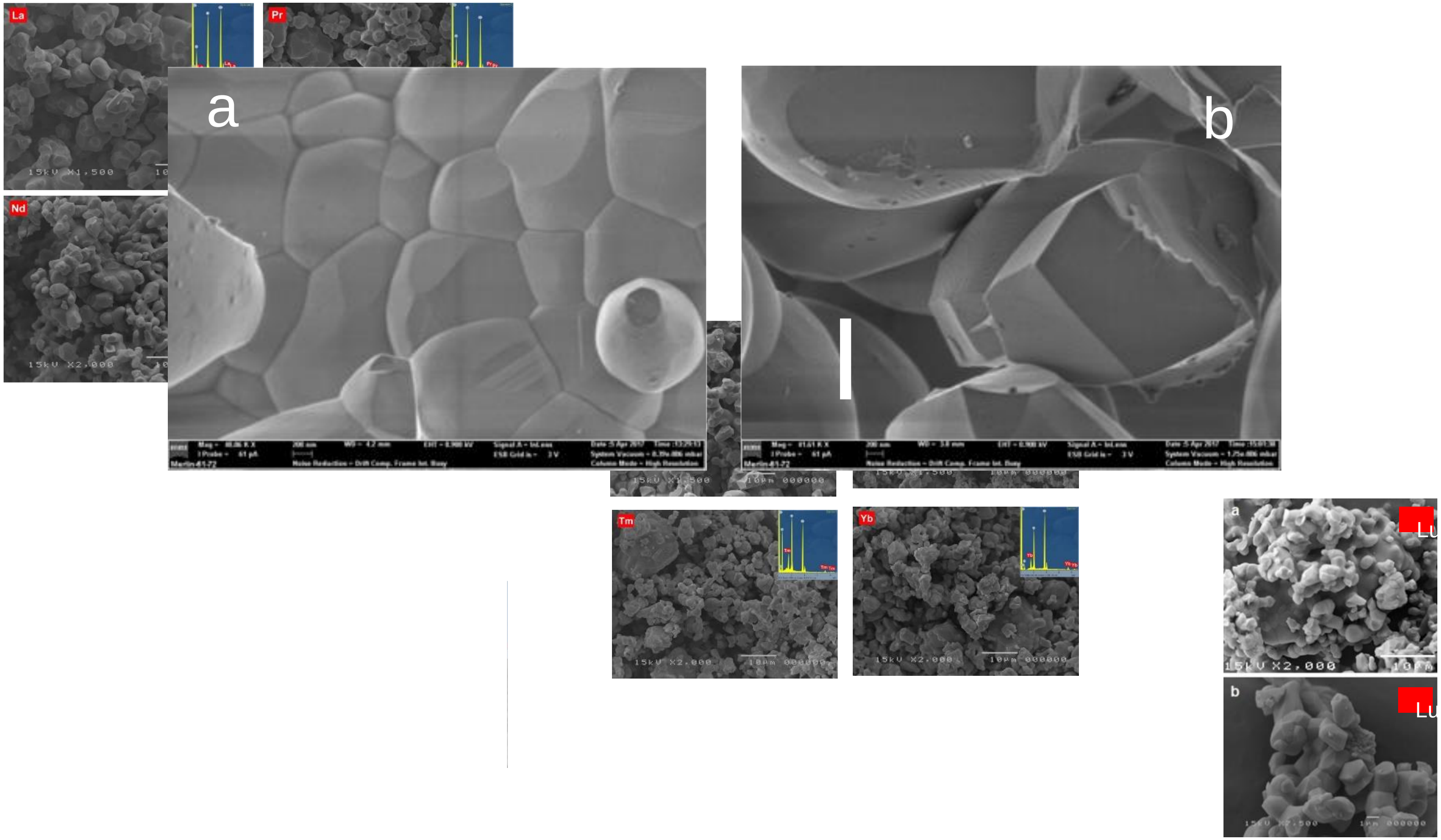
- *Synthesis:* $Ca_9\mathit{RE}(PO_4)_7$ (*RE* = La, Pr, Nd, Eu, Gd, Dy, Tm, Yb, Lu) TCP phosphates were synthesized by solid state reaction from a mixture of reagent-grade $CaCO_3$, $CaHPO_4$, and rare-earth oxides REE_2O_3*.

- After a heating cycle at 400° C, in order to remove H_2O and CO_2, the different powder mixtures were grinded in an agate mortar, pressed and annealed in an alumina crucible at 1200° C for 48 hours in a furnace.

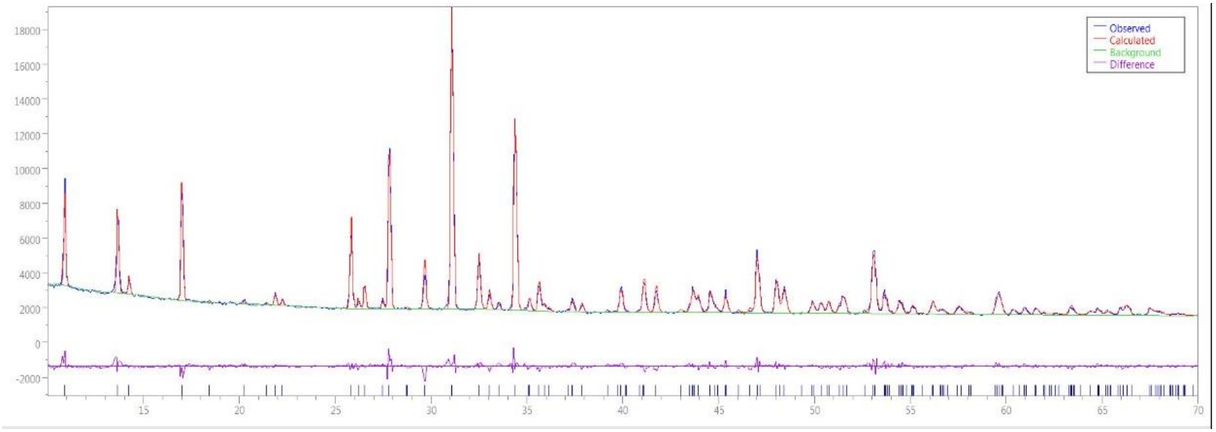
*Ait Benhamou et al. *Journal of Solid State Chemistry* **182** (2009) 2319–2325.

SEM morphology: *RE* - TCP powders consist of aggregates of sub-spherical micro-crystals with sizes from 10 to < 1 µm.

Aggregates with triple-point junctions (Fig. a) are common, suggesting a high degree of sintering; grains with trigonal shapes (Fig. b) are also observed. Morphologies are repeated for all phases.



Rietveld refinements show that all *RE*-TCP compounds crystallize with a derived β-$Ca_3(PO_4)_2$ structure (rhombohedral space group $R3c$, a=b=10.4352(2) Å, c=37.4029(5) Å, V=3527.26 $Å^3$), in turn derived from the mineral whitlockite $Ca_9(Mg,Fe^{2+})(PO_4)_6(PO_3OH)$

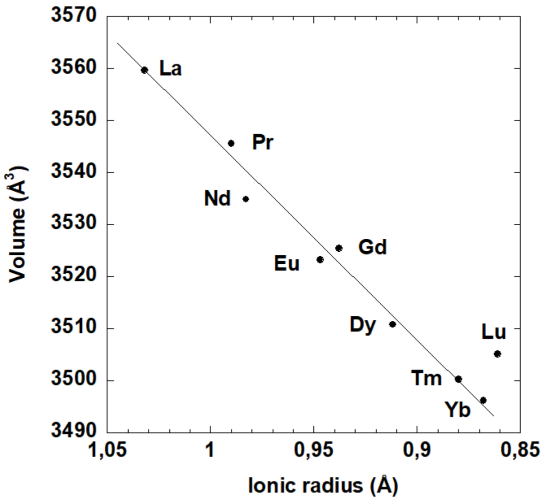


Refined unit cell parameters range from:

a = b = 10.4695(3) Å, c = 37.500(3) Å and V=3559.7(2) $Å^3$ (La)

up to:

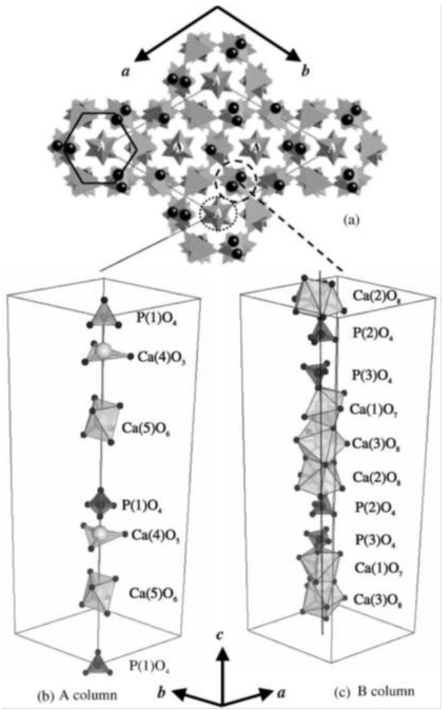
a = b = 10.4164(1) Å, c = 37.302(1) Å, V = 3505.1(1) $Å^3$ (Lu).

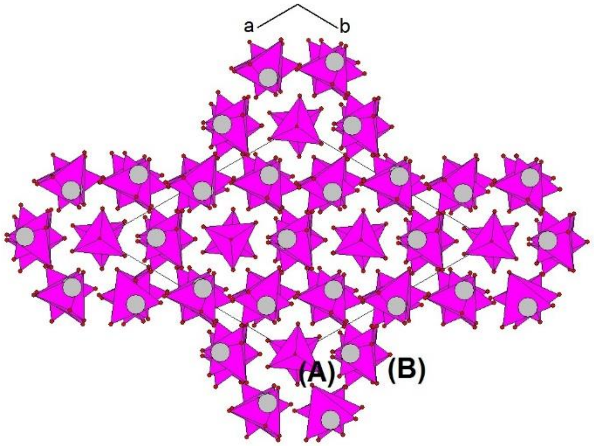


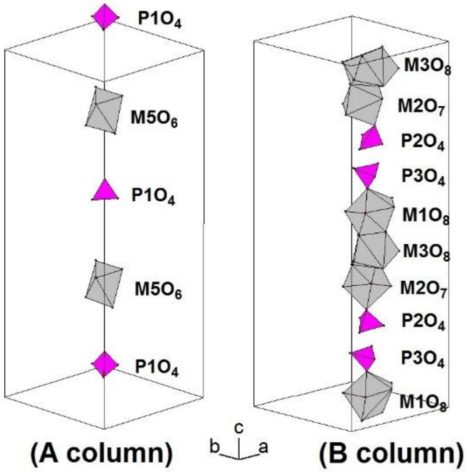
Cell volume of RE β–TCP phases as a function of RE ionic radius

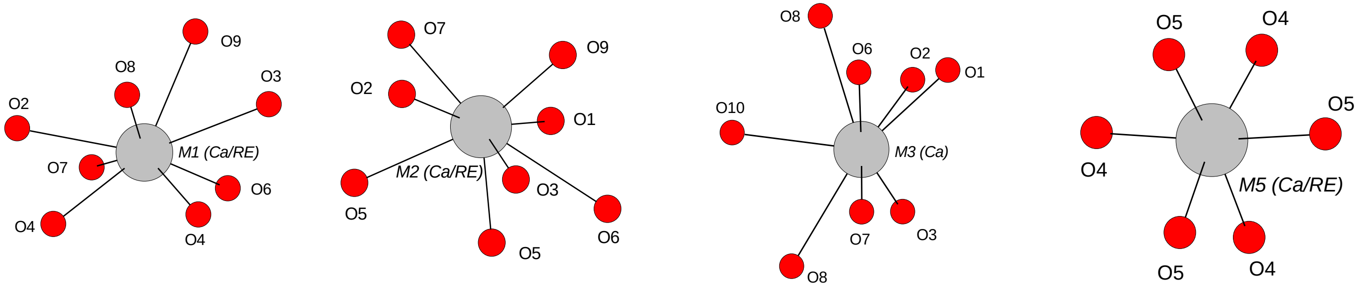
Three-dimensional framework of pure β-$Ca_3(PO_4)_2$ (whitlockite structure)

When a trivalent cation enters the structure, the M4 site disappears.









Ca/RE and Ca cationic environments.*

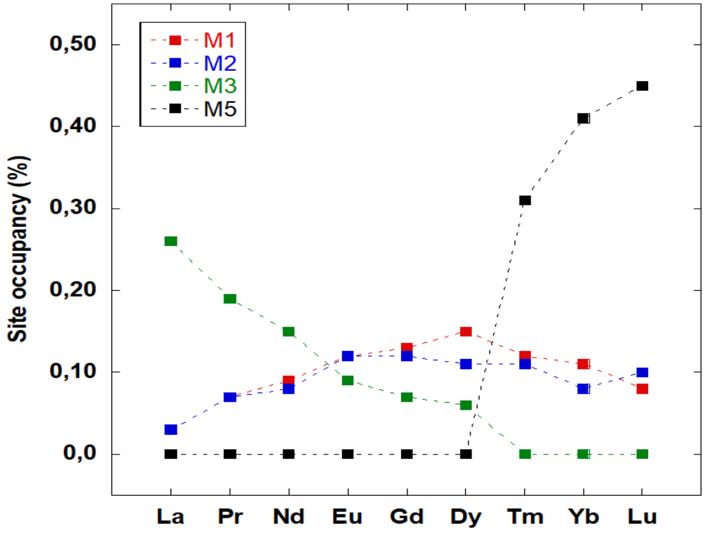
<RE–RE> distance in RE β-TCP phosphates is 3.60 Å, enough to limit the RE–RE energy transfer. Then high light yield is expected in such compounds.*

*El Khouri et al. *Ceramics International* **43** (2017) 15645-15653

RE	**site 1**	**site 2**	**site 3**	**site 5**	***RE*-apfu**	**Ca-apfu**	**Charge**
La	0.13	0.10	0.00	0.32	1.01	8.99	21.0
Pr	0.19	0.11	0.00	0.22	1.12	8.88	21.1
Nd	0.20	0.11	0.00	0.22	1.15	8.85	21.2
Eu	0.21	0.15	0.00	0.19	1.27	8.73	21.3
Gd	0.35	0.09	0.00	0.06	1.38	8.62	21.4
Dy	0.33	0.09	0.00	0.14	1.40	8.60	21.4
Tm	0.19	0.10	0.00	0.39	1.26	8.74	21.3
Yb	0.11	0.08	0.00	0.51	1.08	8.92	21.1
Lu	0.16	0.10	0.00	0.40	1.18	8.82	21.2

Refinement of RE occupancies in TCP sites. Site 4: empty. Charge: valence units

RE occupancy values found describe evident trends in function of the RE atomic number: decreasing and increasing respectively in M3 and M5 sites; increasing in both M1 and M2 for Low-RE and slightly decreasing for High-RE*.



Sites occupancies in present RE β-TCP phases

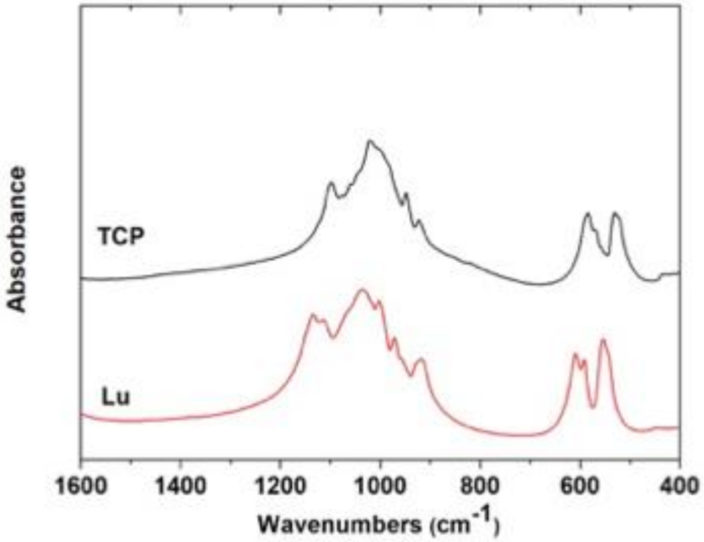
*Capitelli et al. *Journal of Rare Earths* (2018) in press.

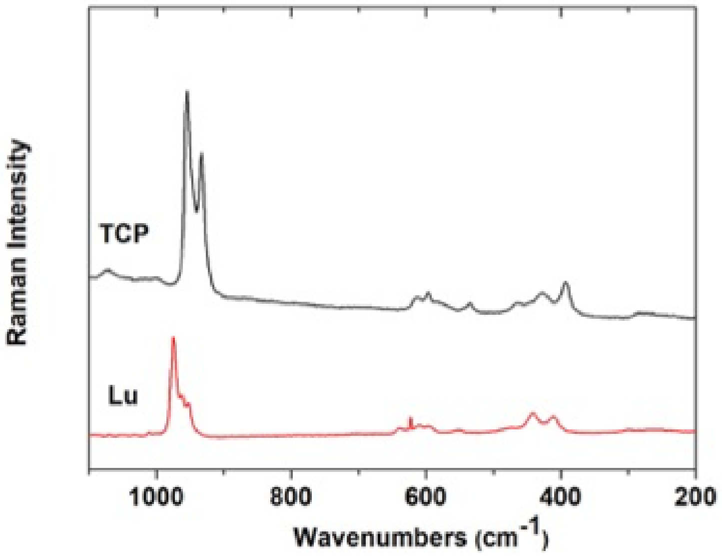
Vibrational spectroscopy

FTIR and Raman spectra of *RE* – TCP*, are quite similar to pure $Ca_3(PO_4)_2$ (TCP), as compared here for Lu phase.

The internal P-O antisymmetric stretchings is in the 1200-1000 cm^{-1} range (IR), while the symmetric P-O stretchings are the most intense peaks in the Raman pattern.

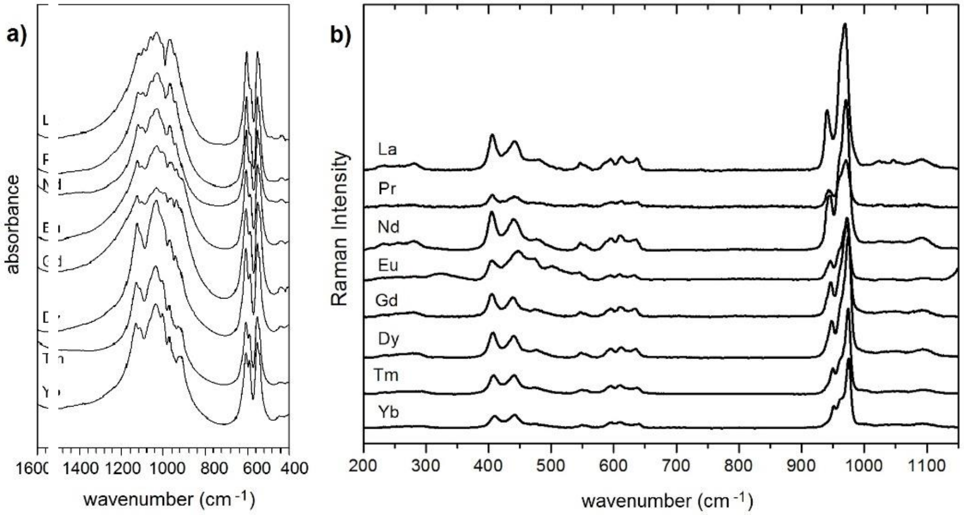
The P-O bending in the range 600-400 cm^{-1} are intense in the IR pattern (antisymmetric) while being weak in the Raman pattern



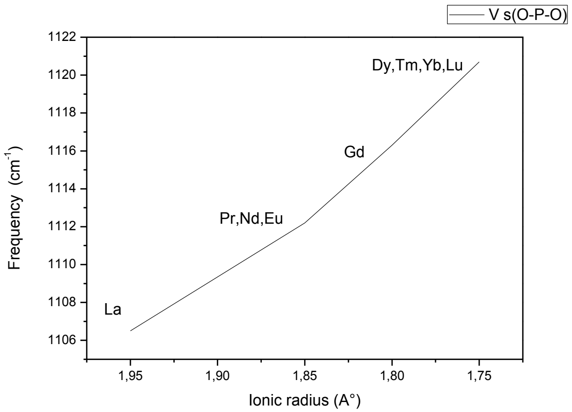


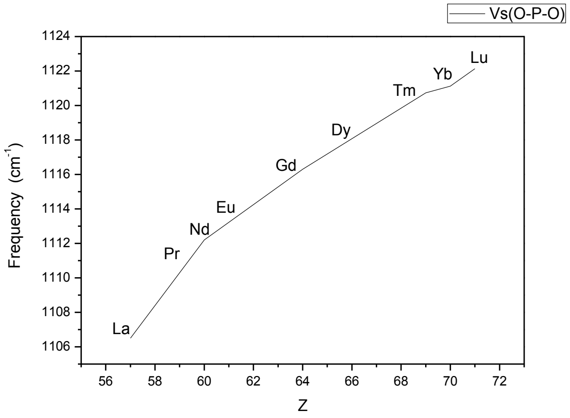
*El Khouri et al. *Ceramics International* **43** (2017) 15645-15653

The substitution of *RE* into TCP structure does not induce major modifications in the spectra, in agreement with the fact that all *RE*-TCPs have the same symmetry; a P-O band shift is however observed indicating slight modifications in the P-O bond lengths.



Worthy of note the increasing of (O-P-O) stretching frequencies values at the increasing of *RE* ionic radius and Z.





Conclusion

Distribution of RE within structural sites implies long RE-RE distances even at high concentration and therefore weak quenching of RE^{3+} luminescence, making $Ca_9RE(PO_4)_7$ promising phosphor materials.

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