



## Thermally stimulated luminescence of $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_9\text{Ln}(\text{PO}_4)_7$ (Ln = Pr, Eu, Tb, Dy, Ho, Er, Lu)

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### ABSTRACT

The series of whitlockite compounds  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Ca}_9\text{Ln}(\text{PO}_4)_7$  (Ln = Pr, Eu, Tb, Dy, Ho, Er, Lu) was studied in radioluminescence (RL) and thermally stimulated luminescence (TSL) excited by X-rays. f-f emission lines of  $\text{Ln}^{3+}$  were observed in RL for  $\text{Ca}_9\text{Ln}(\text{PO}_4)_7$  (Ln = Pr, Eu, Tb, Dy, Ho, Er) whereas d-d emission band of the impurity  $\text{Mn}^{2+}$  was observed in  $\text{Mn}:\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Mn}:\text{Ca}_9\text{Lu}(\text{PO}_4)_7$  at 655 nm. In TSL, the Eu, Ho and Er compounds did not show any signal. As  $\text{Eu}^{3+}$ ,  $\text{Ho}^{3+}$  and  $\text{Er}^{3+}$  present the highest  $\text{Ln}^{3+}/\text{Ln}^{4+}$  ionization potential (IP) of the series, this was interpreted as the inability of these lanthanides to trap a hole. On the contrary  $\text{Pr}^{3+}$  in  $\text{Ca}_9\text{Pr}(\text{PO}_4)_7$ ,  $\text{Tb}^{3+}$  in  $\text{Ca}_9\text{Tb}(\text{PO}_4)_7$ ,  $\text{Dy}^{3+}$  in  $\text{Ca}_9\text{Dy}(\text{PO}_4)_7$ ,  $\text{Mn}^{2+}$  in  $\text{Mn}:\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Mn}:\text{Ca}_9\text{Lu}(\text{PO}_4)_7$  were identified as hole traps and radiative recombination centers in the TSL mechanism.  $\text{Ca}_9\text{Tb}(\text{PO}_4)_7$  was found to be a high intensity green persistent phosphor whereas  $\text{Mn}:\text{Ca}_9\text{Lu}(\text{PO}_4)_7$  is a red persistent phosphor suitable for *in vivo* imaging application.

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### 1. Introduction

Tricalcium phosphate (TCP)  $\text{Ca}_3(\text{PO}_4)_2$  is one of the best biocompatible material. Its composition is present in bones and teeth and therefore TCP is widely used for bones repair in dentistry or orthopaedics (Dorozhkin and Epple, 2002). Its structure offers a wide range of possible cationic substitutions as calcium occupy five inequivalent sites displaying a wide range of sizes and coordination spheres. Ca(5) presents by far the smallest Ca–O distance whereas Ca(4) is peculiar since it is 3-fold oxygen coordinated and half-occupied (Yashima et al., 2003). In case of  $\text{Ca}^{2+}$  substitution by heterovalent cations, more or less Ca(4) vacancies can compensate for local charge defects. In particular it was shown that  $\text{Ln}^{3+}$  can be incorporated in TCP according to the scheme  $3\text{Ca}^{2+} \rightarrow 2\text{Ln}^{3+} + \square$  and up to the limit composition  $\text{Ca}_9\text{Ln}(\text{PO}_4)_7$ , i.e.  $x = 3/7$  in  $\text{Ca}_{3-x}\text{Ln}_{2x/3}(\text{PO}_4)_2$  (Lazoryak, 1996). As TCP is a perfect model for human bones, the material is an excellent candidate for dosimetry applications (Fukuda et al., 1994) and thermally stimulated luminescence (TSL) above room temperature (RT) was reported with

$\text{Ln}^{3+}$  doping (Mizuguchi and Fukuda, 1999; Nakashima et al., 2005; Madhukumar et al., 2007). On the other hand, because of its high biocompatibility, TCP also appears as a candidate for red persistent phosphors for *in vivo* imaging (le Masne de Chermont et al., 2007). With this new and very promising application of persistent luminescence, the red persistent phosphors synthesized as nanoparticles in a solution are excited *ex vivo* with UV or X-rays for several minutes. The solution is then injected to the mouse and persistent red light is emitted for hours by the particles in the blood flow. This enables high contrast and longitudinal images of the mouse vasculature. As persistent luminescence is actually a thermally stimulated process, we present here a TSL study of Ln-substituted TCPs namely  $\text{Ca}_9\text{Ln}(\text{PO}_4)_7$  (Ln = Pr, Eu, Tb, Dy, Ho, Er, Lu) compared to the reference compound  $\text{Ca}_3(\text{PO}_4)_2$ . TSL was carried out from 30 K to 650 K in order to gain insight into the mechanism of TSL in TCP and  $\text{Ca}_9\text{Ln}(\text{PO}_4)_7$ .

### 2. Experimental

The materials were synthesized by solid state reaction. The starting powders were calcium carbonate  $\text{CaCO}_3$  (Merck, 99%), calcium hydrogen phosphate  $\text{CaHPO}_4$  (Prolabo, 97%), and rare-earth oxides  $\text{Ln}_2\text{O}_3$  (Ln = Eu, Dy, Ho, Er, Lu)/ $\text{Pr}_6\text{O}_{11}/\text{Tb}_4\text{O}_7$ . The stoichiometric mixtures were intimately grinded for 30 min in an agate mortar and heated up at 400 °C for 6 h to eliminate the volatile  $\text{H}_2\text{O}$

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and CO<sub>2</sub>. The powders were then carefully grinded again and calcinated between 1100 °C and 1200 °C, depending on to the rare earth, for 12 h to complete the reaction.

Radioluminescence (RL) and TSL measurements were conducted under vacuum on 13 mm diameter and 1 mm-thick pellets made of the powder samples. The pellet is silver glued on the cold finger of a closed cycle helium cryostat. X-rays irradiation is performed through a thin beryllium window of the cryostat at 45° angle from a molybdenum tube operating at 50 kV and 20 mA. Luminescence is detected through a quartz window of the cryostat at 45° angle by an optical fiber connected to a CCD camera coupled with a monochromator. In TSL the sample is firstly irradiated for 10 min. Then luminescence is detected while a heating rate of 10 K/min from 30 K to 650 K is being applied.

### 3. Results and discussion

X-ray diffraction (XRD) showed that TCP and Ca<sub>9</sub>Ln(PO<sub>4</sub>)<sub>7</sub> (Ln = Pr, Eu, Tb, Dy, Ho, Er, Lu) were pure whitlockite phases with space group R3c. Fig. 1 shows their X-ray excited RL spectra at 30 K as black full lines. When the spectrum was found different at RT, it has been rescaled and shown as a red full line. At 30 K, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> as well as Ca<sub>9</sub>Lu(PO<sub>4</sub>)<sub>7</sub> present a broad band between 300 and 550 nm. A structure can be distinguished implying the superimposition of at least three bands peaking respectively around 345, 410 and 485 nm. At RT, these blue bands vanish in Ca<sub>9</sub>Lu(PO<sub>4</sub>)<sub>7</sub>. They may be attributed to emissions from trapped excitons. A second broad band peaks at 655 nm and corresponds to the <sup>4</sup>T<sub>1</sub> → <sup>6</sup>A<sub>1</sub> d-d transition of Mn<sup>2+</sup> substituting Ca(5) [Mayer et al., 2006]. Mn comes most probably as an impurity from the calcium reactants and therefore appears as a substituting ion for Ca<sup>2+</sup> in the TCP structure.

The spectra of Ca<sub>9</sub>Ln(PO<sub>4</sub>)<sub>7</sub> (Ln = Pr, Eu, Tb, Dy, Ho, Er) show Ln<sup>3+</sup> f-f transitions as indicated in Fig. 1. Note that the intensity scale indicates the relative intensity. For Ca<sub>9</sub>Eu(PO<sub>4</sub>)<sub>7</sub>, an additional band is observed at 425 nm, corresponding to Eu<sup>2+</sup> 5d-4f transition. As it is weak while the transition is fully allowed, only a low amount of Eu<sup>2+</sup> relative to Eu<sup>3+</sup> should be present in the compound. Note that this Eu<sup>2+</sup> fluorescence vanished at RT, a phenomenon probably related to energy transfer. In Ca<sub>9</sub>Er(PO<sub>4</sub>)<sub>7</sub> Tm<sup>3+</sup> was found as an unavoidable impurity coming from Er<sub>2</sub>O<sub>3</sub> as f-f transitions of Tm<sup>3+</sup> can be distinguished at 457 and 476 nm. As far as the RL intensity is concerned (see Fig. 1), Ca<sub>9</sub>Tb(PO<sub>4</sub>)<sub>7</sub> presents a very high light output, considering that the monochromator slit widths were half-reduced for its spectrum relative to the other compounds. Then, the undoped compound as well as Pr, Eu, Dy and Lu compounds show similar weaker intensity when integrated over the observed wavelength range. Er and Ho compounds show respectively roughly 10 and 50 times less intense RL than the undoped compound. This may be explained by small energy differences between Er<sup>3+</sup> and Ho<sup>3+</sup> energy levels that favor non-radiative deexcitation and in general lead to near-infrared emission for these cations. As far as the application of persistent phosphors for *in vivo* imaging is concerned, Mn<sup>2+</sup>, Pr<sup>3+</sup> and Eu<sup>3+</sup> dopants which emit red and intense luminescence in TCP appear as suitable luminescent centers.

The TSL glow curve of TCP for the overall studied spectral range (300–800 nm) is presented as a green line in Fig. 2 (right axis). It is composed of four main peaks named A, B, C and D peaking respectively at 132 K, 165 K, 185 K and 220 K and a small shoulder at 252 K named E. The TSL intensity at two particular wavelengths (406 nm and 663 nm) is also displayed on a separate scale (left axis). The 406 nm TSL glow curve is mainly composed of peaks A, B and C. The 406 nm emission represents excitonic emission of the

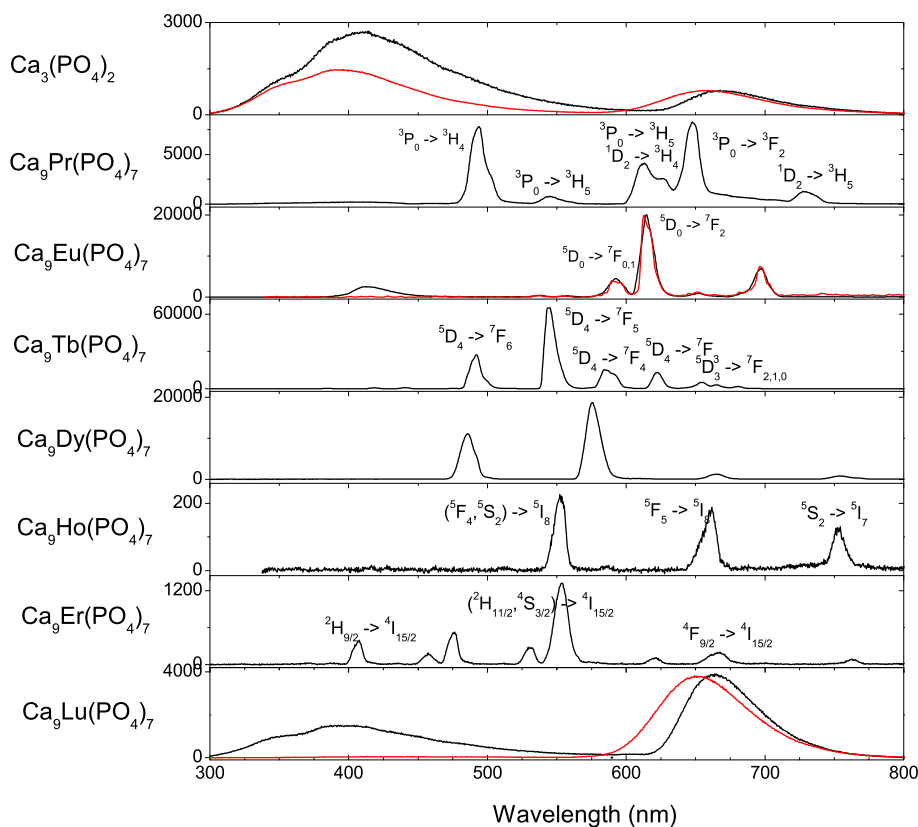
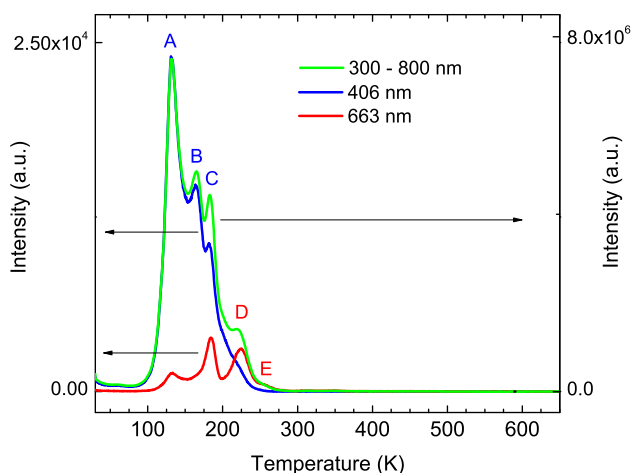


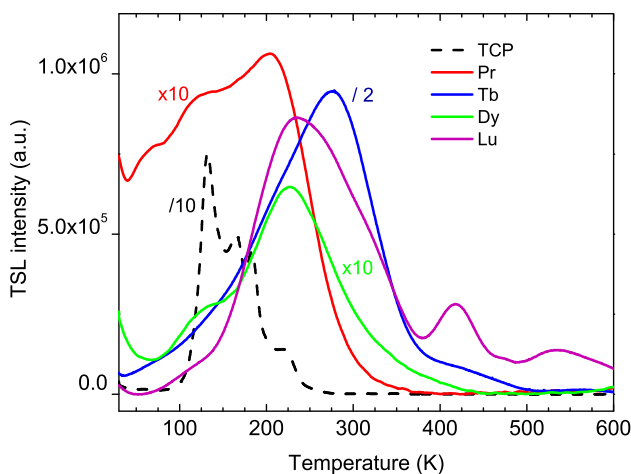
Fig. 1. RL spectra of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Ca<sub>9</sub>Ln(PO<sub>4</sub>)<sub>7</sub> at 30 K (black line) and 293 K (red line). All full lines intensities can be compared except for the Tb compound for which the monochromator slitwidths were half-reduced due to very high intensity. Red lines have been rescaled. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



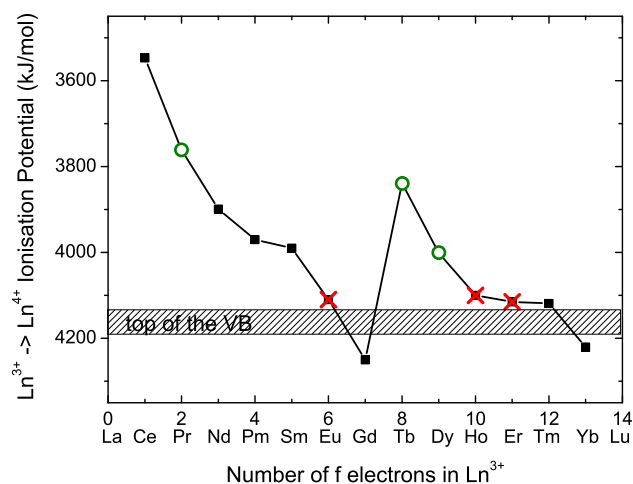
**Fig. 2.** Mn:Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> TSL intensity integrated from 300 to 800 nm (green curve), at 406 nm (blue curve) and at 663 nm (red curve). Arrows indicate the intensity scale for each glow curve. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

host. Therefore the TSL peaks A, B and C are most probably related to defects of the host. The 663 nm glow curve is composed of peaks A, C, D and E. The peaks D and E therefore appear as related to the presence of Mn<sup>2+</sup> in the host. The trap relative to C, and in a lesser extent the one relative to A, contributes to Mn<sup>2+</sup> luminescence whereas the one relative to B does not at all, indicating a possible spatial correlation between the C and A defects and Mn<sup>2+</sup>. Let us notice that around 5 times more light is emitted through excitons than through Mn<sup>2+</sup>. Indeed Mn is only present as a trace in the studied material. Finally the TSL glow curves show only very weak intensity above 300 K, indicating that both TCP and TCP:Mn<sup>2+</sup> would not present persistent luminescence at RT, nor would be suitable as dosimetry materials and that other codopants/defects should be incorporated for that purpose.

The TSL glow curves over the full spectral range (300–800 nm) realized on the Ca<sub>9</sub>Ln(PO<sub>4</sub>)<sub>7</sub> compounds are shown in Fig. 3 as full lines together with the one of TCP as a dotted line for comparison sake. The TSL peaks observed for TCP and described above are suppressed for all the shown Ca<sub>9</sub>Ln(PO<sub>4</sub>)<sub>7</sub>. Instead broad features of



**Fig. 3.** TSL intensities integrated over 300–800 nm for Mn:Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (TCP) and Ca<sub>9</sub>Ln(PO<sub>4</sub>)<sub>7</sub> (Ln = Pr, Tb, Dy, Lu as reported on the figure). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** Suggestion of Ln<sup>3+</sup> energy levels position relative to the top of the valence band (VB) in Ca<sub>9</sub>Ln(PO<sub>4</sub>)<sub>7</sub>. Green circle and red cross are relative to respectively presence and absence of TSL signal. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lower intensity and extending at higher temperatures appear. As in radioluminescence spectra, the Tb compound presents a significantly higher intensity than the rest of the Ca<sub>9</sub>Ln(PO<sub>4</sub>)<sub>7</sub> series. Pr and Dy compounds show somehow less intensity than Lu. These intensity features could not yet be explained in detail. More strikingly the Pr, Tb, Dy, and Lu compounds showed TSL whereas the Eu, Ho and Er ones did not present any detectable signal over the whole range of temperature. If we correlate this information with the Ln<sup>3+</sup>/Ln<sup>4+</sup> ionization potential (IP) (Emsley 1989) shown in Fig. 4, it appears that only the compounds with the lowest IP for Ln<sup>3+</sup> showed TSL. The ones with an IP superior to 4100 kJ/mol did not present any TSL. This tends to show that in Ca<sub>9</sub>Ln(PO<sub>4</sub>)<sub>7</sub> TSL of Ln<sup>3+</sup> occurs via hole trapping on Ln<sup>3+</sup> according to the scheme Ln<sup>3+</sup> + h → Ln<sup>4+</sup>. For lanthanide cations with a high IP, their energy levels might be too close to or even inside the valence band as suggested by Fig. 4, hence explaining their inability to trap a hole. At this point let us notice that Eu<sup>3+</sup> which appeared hereinabove as a potential efficient red emitter in Ca<sub>9</sub>Eu(PO<sub>4</sub>)<sub>7</sub> will therefore not be suitable for the application of persistent phosphor as it is unable to trap a hole.

Considering that Ln<sup>3+</sup> in the case of Ca<sub>9</sub>Ln(PO<sub>4</sub>)<sub>7</sub> and Mn<sup>2+</sup> in the case of Ca<sub>9</sub>Lu(PO<sub>4</sub>)<sub>7</sub> act as a hole trap, the TSL bands peaking at 204 K for Pr, 276 K for Tb, 226 K for Dy and 235 K for Lu in Fig. 4 should be related to electron traps. The TSL glow curves for Ca<sub>9</sub>Ln(PO<sub>4</sub>)<sub>7</sub> are strongly modified relatively to TCP and, for all Ln excepted Pr, display bands shifted to higher temperatures than TCP. Hence, the introduction of Ln<sup>3+</sup> (excepted Pr<sup>3+</sup>) induces additional electron traps deeper than in pure TCP. The TSL bands are quite broad obviously because a high percentage of Ln is introduced in the structure (14%) which provokes a large distortion of the structure and therefore probably a wide energetic distribution of traps. However the effect is clearly different depending on the introduced lanthanide ion and this might be due to differences in the site occupation according to the Ln<sup>3+</sup> size. A Rietveld (1969) study should enable us to properly locate Ln<sup>3+</sup> in the structure as it was done for Ca<sub>9</sub>Eu(PO<sub>4</sub>)<sub>7</sub> showing that Eu<sup>3+</sup> was occupying Ca (1), Ca(2) and Ca(3) (Ait Benhamou et al., 2009). Mn:Ca<sub>9</sub>Lu(PO<sub>4</sub>)<sub>7</sub> and Ca<sub>9</sub>Tb(PO<sub>4</sub>)<sub>7</sub> appear as the most favorable compound to present TSL with high intensity between 320 K and 400 K and therefore persistent luminescence at RT. Ca<sub>9</sub>Tb(PO<sub>4</sub>)<sub>7</sub> appears as a very good persistent phosphor but unfortunately emits in the green whereas Mn:Ca<sub>9</sub>Lu(PO<sub>4</sub>)<sub>7</sub> is the best red emitting persistent phosphor of the series.

#### 4. Conclusion

We have investigated the RL and TSL properties of the whitlockite family compounds  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Ca}_9\text{Ln}(\text{PO}_4)_7$  (Ln = Pr, Eu, Tb, Dy, Ho, Er, Lu) under X-rays. In RL all the  $\text{Ca}_9\text{Ln}(\text{PO}_4)_7$  compounds excepted  $\text{Ca}_9\text{Lu}(\text{PO}_4)_7$  showed  $\text{Ln}^{3+}$  f-f emissions whereas Mn:  $\text{Ca}_3(\text{PO}_4)_2$  and Mn:  $\text{Ca}_9\text{Lu}(\text{PO}_4)_7$  showed at 655 nm the d-d emission band of  $\text{Mn}^{2+}$  present as an impurity. In TSL glow curves, one finds that  $\text{Ln}^{3+}$  played the role of hole trap in  $\text{Ca}_9\text{Ln}(\text{PO}_4)_7$  (Ln = Pr, Eu, Tb, Dy, Ho, Er) and that only  $\text{Ln}^{3+}$  with the lowest IP could trap holes deeply enough to observe TSL above 30 K. Among them only  $\text{Ca}_9\text{Tb}(\text{PO}_4)_7$  showed very intense TSL between 320 and 400 K, implying very good persistent luminescence at RT. On the other hand Mn:  $\text{Ca}_9\text{Lu}(\text{PO}_4)_7$  showed intense TSL through the red emission of  $\text{Mn}^{2+}$  in the range 320–400 K. This compound is therefore suitable for red persistent luminescence for *in vivo* imaging. A sample with composition  $\text{Ca}_3(\text{PO}_4)_2:x\%\text{Mn}^{2+},y\%\text{Ln}^{3+}$  with careful control of the Mn and Ln contents should be now designed in order to optimize the red persistent luminescence properties.

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