Supplementary Information

Luminescent lanthanide-doped calcium phosphate from oyster shell waste: an example of bright recycling

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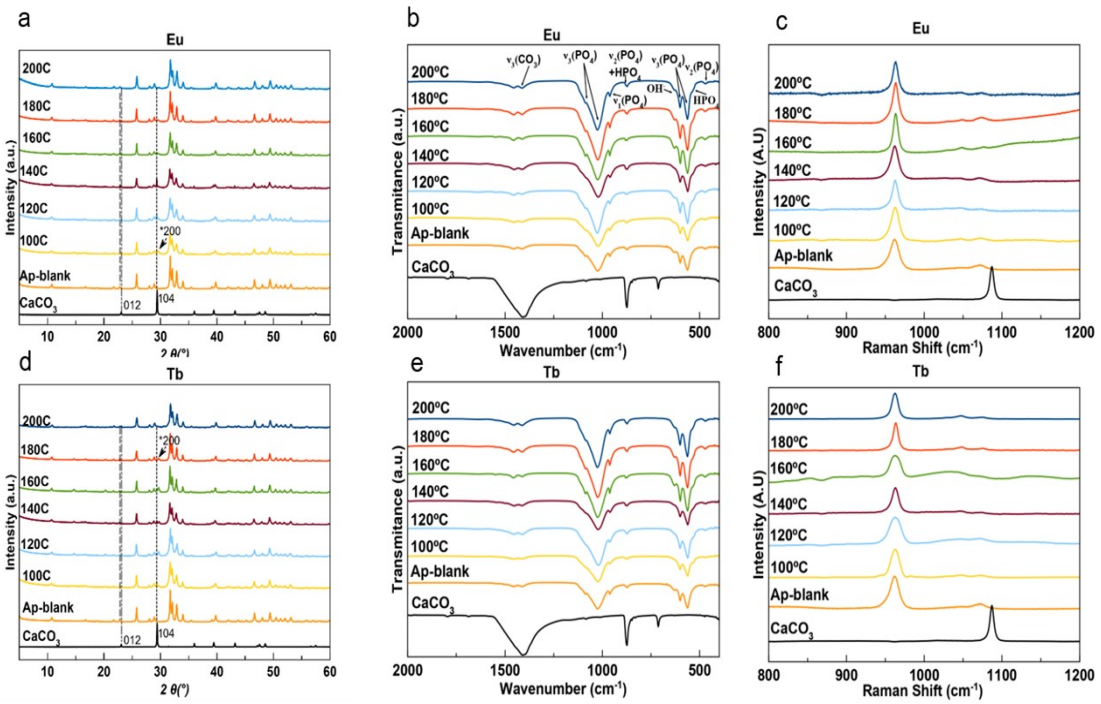

Figure S1. Conversion of bCC powder to Eu- and Tb-doped apatites at temperatures between 100 °C and 200 °C for 7 days analyzed by XRD (a, d), FTIR (b, e) and Raman spectroscopy (c, f).

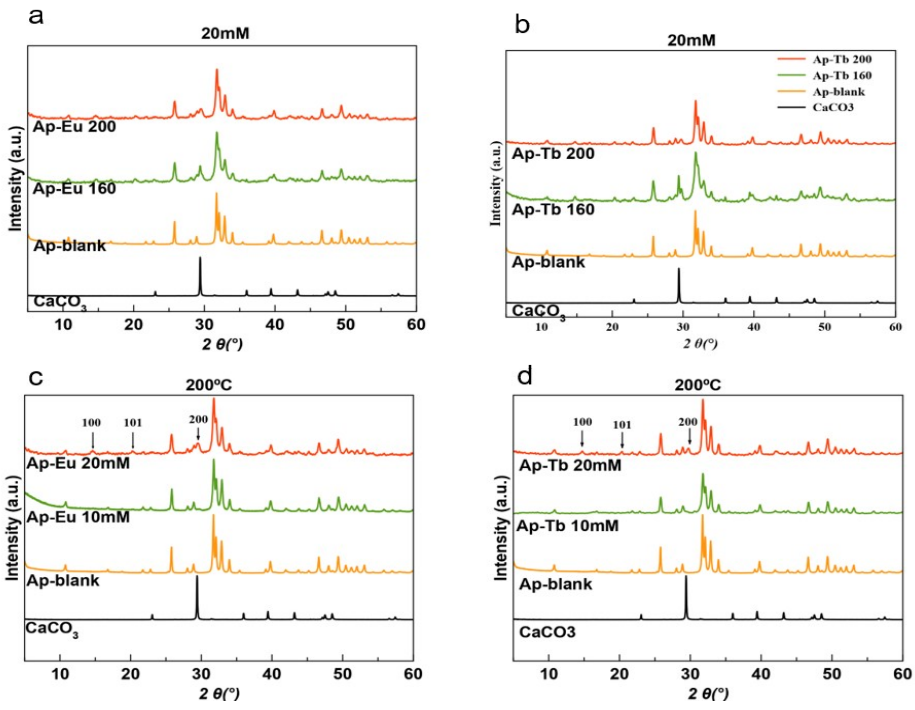

Figure S2. XRD patterns corresponding to the conversion of bCC powder to Eu- and Tb-doped apatites at 160°C and 200 °C for 7 days in presence of 20mM Eu^{3+}(a) and 20 mM Tb^{3+}(b), and at 200 ºC in presence of 10 and 20 mM Eu^{3+} (c), and 10 and 20 mM Tb^{3+}.

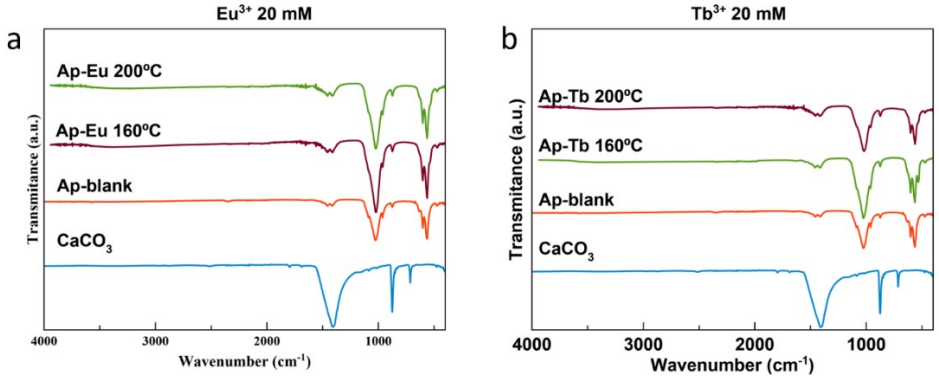

Figure S3. FTIR spectra corresponding to the conversion of bCC powder to Eu- and Tb-doped apatites at 160°C and 200 °C for 7 days in presence of 20mM Eu^{3+}(a) and 20 mM Tb^{3+}(b).

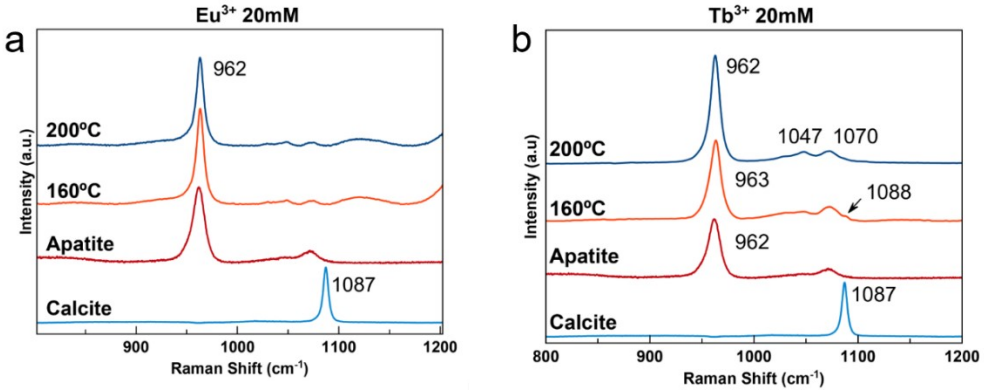

Figure S4. Raman spectra corresponding to the conversion of bCC powder to Eu- and Tb-doped apatites at 160°C and 200 °C for 7 days in presence of 20mM Eu^{3+}(a) and 20 mM Tb^{3+}(b).

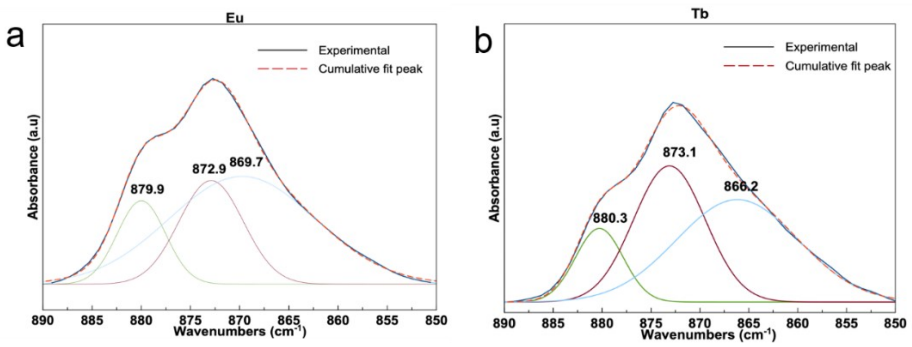

Figure S5. Deconvolution of the FTIR 875 cm^{-1} band of samples prepared in presence of 10 mM Eu^{3+} (a) and 10 mM Tb^{3+} (b) into three sub-bands attributed from left to right to A-type (CO_3^{2-} replacing OH^-), B-type (CO_3^{2-} replacing PO_4^{3-}) and labile CO_3^{2-} species located at the surface of the particles.

Table S1. Element composition determined by ICP

Sample (T ºC, Conc Ln mM)	**Eu (ppm)**	**Tb (ppm)**	**Ca (ppm)**	**P (ppm)**	**(Ln+Ca) /P**
Ap-Eu (160,10)	21,57		289,30	132,50	1.72
Ap-Eu (200,10)	26,74		291,00	127,40	1.81
Ap-Eu (160,20)	48,33		273,30	117,40	1.88
Ap-Tb (160,10)		35,32	274,90	130,30	1.68
Ap-Tb (200,10)		20,07	293,20	132,70	1.74
Ap-Tb (160,20)		34,04	257,00	103,20	1.99
Ap (160,0) (Blank)			297,80	114,70	2.00
Ap (200,0) (Blank)			297,20	127,10	1.80

Eu and Tb determined by ICP-MS and Ca and P by ICP-OES

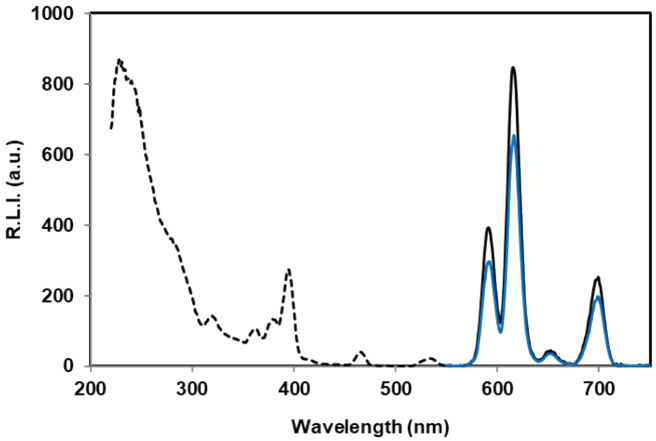

Figure S6. Uncorrected excitation (dashed lines) and emission (solid lines) spectra of Eu-doped particle prepared with 20 mM Eu and at 200ºC using a λ_{exc}=230 nm (black line) and λ_{exc}=395 nm (blue line). Slit-widths$_{exc/em}$ = 10/10 nm, t_d = 120 µs, t_g = 5 ms and voltage detector = 480v.

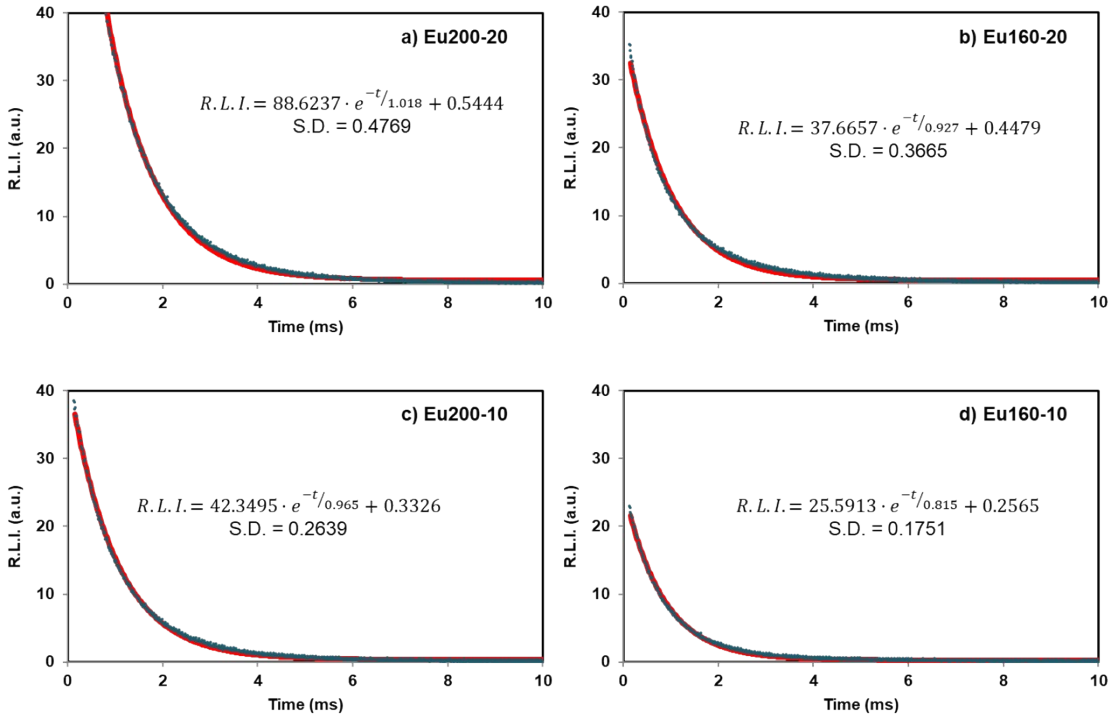

Figure S7**.** Luminescence decay curve of Eu-doped particles. $\lambda_{exc/em}$ = 395/616 nm, slit-widths$_{exc/em}$ = 10/10 nm, and detector voltage = 700 V. Circles correspond to experimental data and lines to the fitting equation.

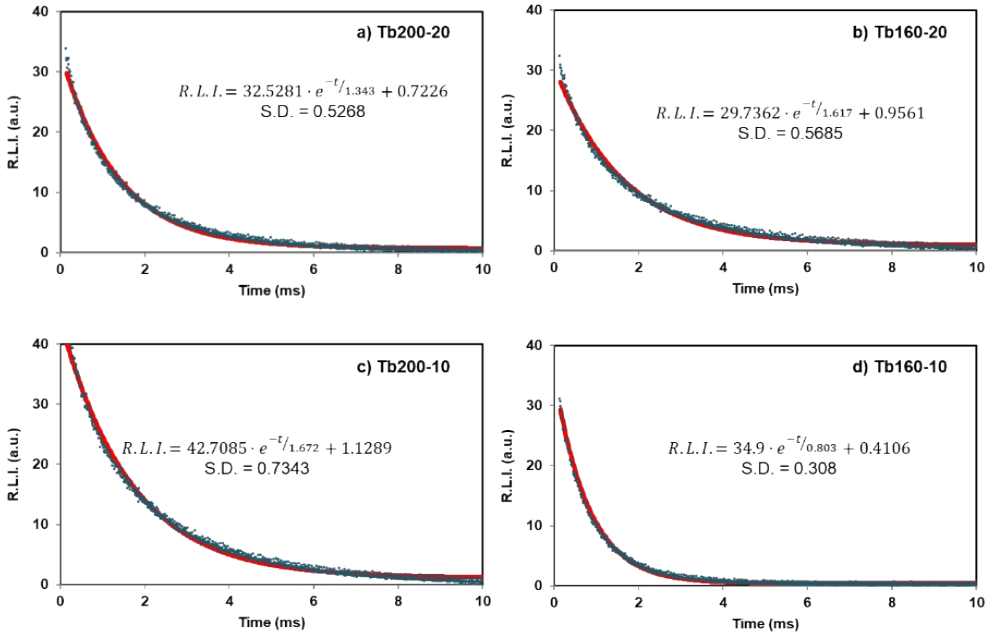

Figure S8. Luminescence decay curve of Tb-doped particles. $\lambda_{exc/em}$ = 372/543 nm, slit-widths$_{exc/em}$ = 20/20 nm, and detector voltage = 800 V. Circles correspond to experimental data and lines to the fitting equation.

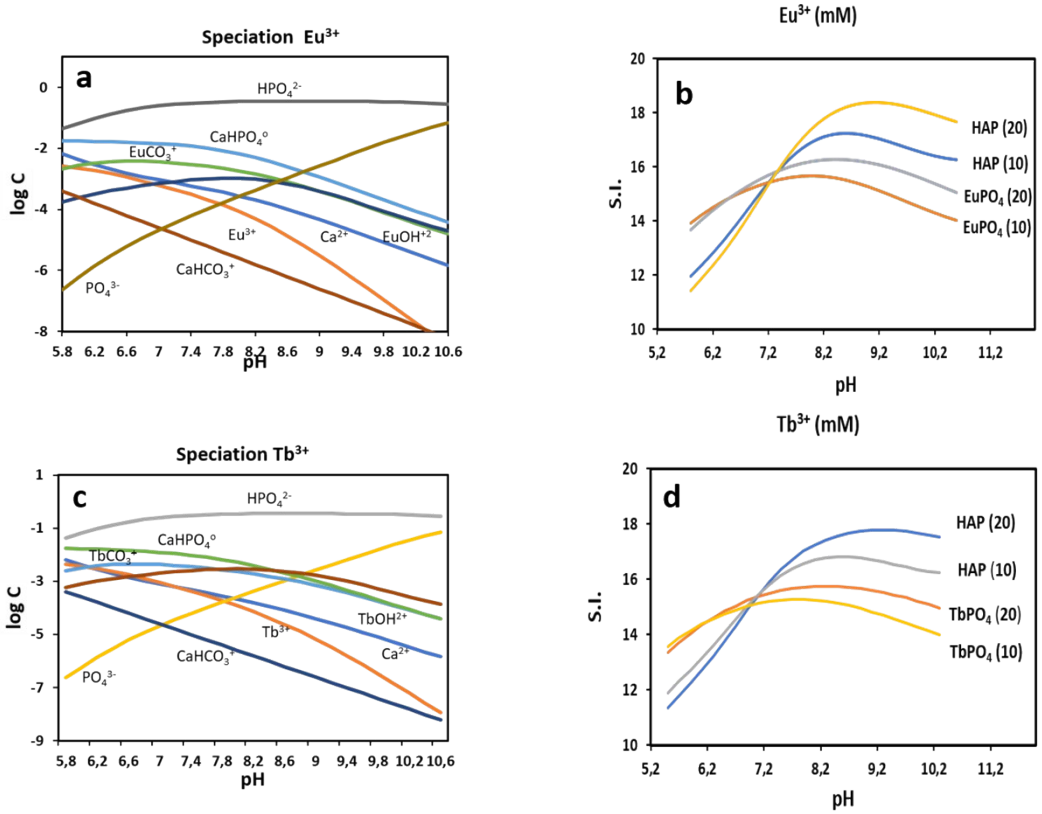

Figure S9. Speciation (a,c) in the system calcite/($H_2PO_4^-$/HPO_4^{2-}/PO_4^3)/Ln^{3+} as a function of pH using 10 mM Ln^{3+} and saturation index (S.I.) (b, d) using 10 and 20 mM Ln^{3+}