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Rare-earth (Eu^{3+}or Er^{3+}/Yb^{3+}) co-doped chlorapatite as downshifting and up-conversion materials for multimodal imaging

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Materials based on apatite have been extensively investigated in the literature due to their structural similarity to human bone, providing biocompatibility and bioactive properties that promote bone and tissue regeneration and repair [1]. The doping of rare-earth ions, such as Eu^{3+}, confers photoluminescence properties to these materials, opening avenues for photonics applications [2], such as fluorescent markers in biomedical imaging for medical diagnostics. Moreover, Er^{3+}/Yb^{3+} co-doped materials offer advantages for biological imaging. Their ability to convert NIR light into visible light enables deeper tissue penetration and eliminates background fluorescence, making them highly suitable for applications requiring high-resolution confocal analysis in biological systems. Besides, the chloride ions present in these materials can create an acidic environment on the bone surface that activates osteoclasts in bone resorption. This work aims at the synthesis, structural and spectroscopic properties of Eu^{3+} or Er^{3+}/Yb^{3+} doped chlorapatite ($Ca_5(PO_4)_3Cl$) nanoparticles for further application to monitor the process of bone resorption. The materials were synthesized by solid-state synthesis using $CaCl_2$, H_3PO_4 and $LnCl_3$ (Ln= Eu, Er and Yb) as precursors. The Eu^{3+} content was varied from 1 mol% to 5 mol% relative to calcium, while Er^{3+} and Yb^{3+} were fixed at 0.5 mol% and 3.0 mol% respectively. Crystallization of hexagonal and monoclinic phases with space group P63/m, for all samples, regardless of Eu^{3+} concentration was identified by X-ray diffraction analysis. The Raman spectra were recorded to obtain more detailed and confirm the structure of the doped and undoped samples. The vibrational modes of phosphate group in the Raman spectra confirmed the formation of crystalline chlorapatite without structural change as the Eu^{3+} ions doping. The Eu^{3+} emission spectra were obtained under excitation at different wavelengths, and the ${}^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3 and 4) electronic transitions were observed. An unusual ${}^5D_0 \rightarrow {}^7F_0$ transition was observed, confirming that the Eu^{3+} ions are incorporated into the $Ca_5(PO_4)_3Cl$ lattice [3]. Up conversion emission from 980 nm to visible range was observed for the Er^{3+} and Yb^{3+} co-doped chlorapatite. In summary, a well-crystallized lanthanide-doped chlorapatite was successfully synthesized herein, allowing for a systematic investigation on how the lanthanide ions influence their structural, morphological, and luminescent properties for further biological application.

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