

Summary of the doctoral dissertation

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„Development of functional phosphate-based luminescent nanoparticles for luminescence thermometry, thermal history and optical heating applications”

The research undertaken as part of the PhD thesis involved the synthesis of nanoparticles with phosphate residues ($(\text{PO}_4)^{3-}$ and $(\text{P}_5\text{O}_{14})^{3-}$). The selection of this group of compounds was motivated by their high potential in biological applications. They are characterized by high stability, insolubility in water, high resistance to different pH conditions, and a high refractive index. Modification and optimization of the synthesis of orthophosphate nanoparticles to obtain highly stable colloidal systems have been crucial in the application of these compounds in luminescence thermometry for potential biological applications. It should be emphasized that, although phosphates doped with lanthanide ions are very well studied, there are only few literature reports on transition metal ion doping of these materials at the nanoscale. Thus, optimization of the procedures for obtaining phosphors doped with TM^{3+} ions was essential to obtain efficient luminescence. Within the scope of the dissertation, hydro- and solvothermal methods were optimized. The hydrothermal method, possess the most advantages, as the nanoparticles thus obtained already after synthesis do not require additional modification and form highly stable colloidal systems in water. The solvothermal method, on the other hand, made it possible to obtain nanoparticles with different morphologies that exhibited specific thermometric properties depending on the obtained shape. Furthermore, an essential analysis of phosphate-based nanoparticles, obtained by the co-precipitation method, revealed that fundamental research on the relationship between the crystal structure, the covalence of metal-oxygen bonds, and the efficiency and resolution of luminescent thermometers were still need to be explored.

In addition, the use of rare earth orthophosphate nanoparticles as thermal history phosphors has been proposed for the first time. The unique structural properties of REPO_4 , which are revealed under specific synthesis conditions, were exploited. By using a hydrothermal procedure, $\text{REPO}_4 \cdot x\text{H}_2\text{O}$ was obtained, which undergoes a phase transition with increasing annealing temperature. The transformation of the crystal structure was observed using X-ray diffraction and spectroscopic studies. The introduction of the Eu^{3+} as dopant ions allowed to use the luminescence asymmetry parameter, which is the ratio between the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ electron transitions in the Eu^{3+} ions, as a luminescence structural probe. In addition, confirmation of the application potential of these materials was provided by a proof-of-concept experiment.

The exploited potential of phosphate nanoparticles doped with transition metal ions was furthermore deepened by their use as light-to-heat converters. Colloidal yttrium orthophosphate nanoparticles doped with Cr^{3+} ions were obtained by solvothermal synthesis. Their efficiency as light-to-heat converters was confirmed by a photo-thermo-induced methyl methacrylate polymerization experiment.

In conclusion, a systematic structural and spectroscopic study of ortho- and ultra-phosphate nanoparticles was completed with a view to their use as luminescent thermometers, light-to-heat converters, and thermal history phosphors.