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Synthesis and characterization of phosphate and carbonate nanoparticles doped with manganese for applications as active centers in sunscreens

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Abstract – Phosphates and carbonates are biocompatible materials that can be used in the formulation of inorganic sunscreens. The sunscreen use is necessary extremely, because the exhibition in the sun long term can provoke skin cancer. In this work chemical precipitation method was used to produce nanocrystals of those materials. X-ray diffraction and energy dispersive X-ray measurements confirmed that the materials were in the expected crystalline structures without formation of species reactivate. Atomic force microscopy analyses showed the nanoparticle formation. The optical absorptions in the range of the ultraviolet radiation indicated that these materials have potential applications as active media in sunscreen.

It has been well known that ultraviolet (UV) rays in sunshine are very harmful to the human skin and deteriorates some organic materials. Hence many sunscreen materials for UV-shielding have been developed using synthetic organic and inorganic chemicals products. However, the organic sunscreens may pose a safety problem when they are used at high concentrations, because it has been suggested that some of the organic UV absorbers cause skin irritation for sensitive individuals and demonstrate estrogenic activities. On the other hand inorganic sunscreens constitute a safer way to protect the skin of the sun noxious effects. Hydroxyapatite (HAP), tricalcium phosphate (β-TCP) and calcite have excellent properties to be used as active ingredient for sunscreens: their biocompatibility and not toxicity, besides, their absorption of UVB (290-320 nm) to the UVA (320-400 nm) can be obtained producing these doped materials [1].

Thus, in the present work, Mn^{2+}-doped HAP and Mn^{2+}-doped β-TCP were chemically synthesized by precipitation method of $Ca(NO_3)_2.4H_20$ and $(NH_4)_2HPO_4$, while the Mn^{2+}-doped calcite was produced using a precipitation route of $CaCl_2$ with $(NH_4)_2CO_3$ adding the metal in the concentration 0,01M. The materials were characterized by powder X-ray Diffraction (XRD), Energy Dispersive X-ray (EDX), Atomic Force Microscopy (AFM) and UV-vis spectroscopy (AO). XRD analysis showed the formation of the wanted phases. Besides those phases, picks of HAP were identified in the sample of β-MnTCP. Using the Scherrer formula within the JADE Rigaku computer code and diffraction peaks, the crystallite sizes were estimated. The sizes are found to dependent of the dopant and are smaller than 43 nm. With the results of EDX it was possible to identify minority phases not revealed by XRD: MnO for calcite:Mn^{2+}, CaO for HAP and MnO and CaO for MnHAP and β-MnTCP. With AFM it was possible to verify that the produced powder are mainly formed by agglomerates, composed nanometric particles. These particles had elliptical shape, whose dimensions varied due the introduction of Mn^{2+} in the matrix of the materials. HAP varied its size of 15 for 19 nm, β-TCP of 25 for 35 nm and calcite of 25 for 15 nm. AO spectra were measured for pure materials and doped (figure 1) and the results confirmed that the Mn^{2+} ions we successfully incorporated in the HAP and β-TCP. Absorption spectra of the pure calcite and doped (figure 1c) it didn't produce any important absorption in UV, because the absorption intensity is small. MnHAP and β-MnTCP presented excellent absorption in UV and some absorption in the visible. The above results indicated that the material biocompatible host can be 'activated' with convenient doping ions generating a nanopowder with potential applications in sunscreens.

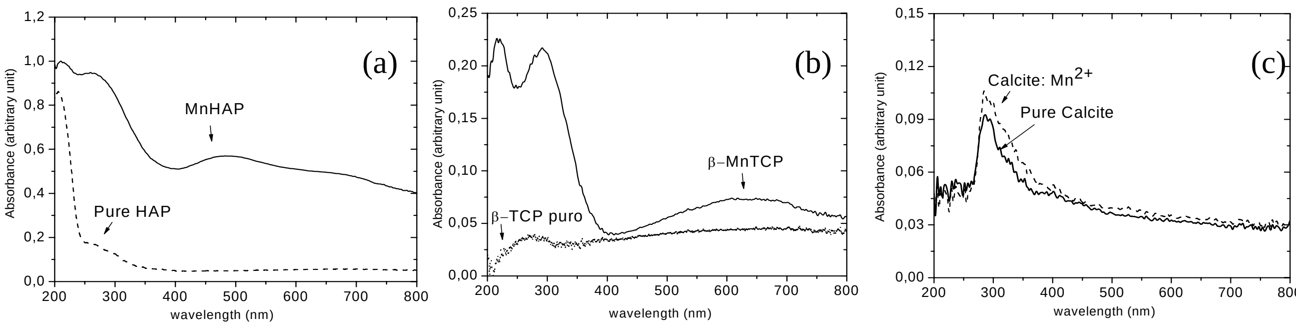

Figure 1: UV–Vis absorption spectra (a) Pure HAP and MnHAP (b) Pure β-TCP and β-MnTCP (c) Pure calcite and calcite: Mn^{2+}

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