

## SYNTHESIS AND CHARACTERIZATION OF TERBIUM DOPED HYDROXYAPATITE AT DIFFERENT PERCENTAGES BY WEIGHT

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This work focuses on the study of the effect of doped Hydroxyapatite (Hap) with different percentages by weight of Terbium by the Sol-Gel method. The synthesized materials showed a significant effect on the morphology and the crystalline structure, presenting circles on the surface of the Hydroxyapatite which increased in size depending on the amount of terbium used. The synthesized materials showed the characteristic peaks of hydroxyapatite with the hexagonal crystalline structure. The FTIR studies expressed the characteristic stretches of the Hydroxyapatite. The emission spectra showed the typical emission of Terbium ions with a main signal at 544 nm.

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### 1. Introduction

Today there is a wide diversity and sophistication of biomaterials that are commonly used in medical science, giving rise to a new interdisciplinary field between medicine, biology, toxicology, pharmacology, chemistry, materials science, and engineering, called nanomedicine. In this area of nanomedicine multifunctional nanoparticles are being developed with the aim that they may function as theranostics [1]. In the development of these theranostic nanoparticles (TNP) several medical imaging systems are involved, including Magnetic Resonance Imaging (MRI), X-Ray Computed Tomography (CT), Positron Emission

Tomography (PET), Single-photon emission computed tomography (SPECT), Bioluminescence Imaging (BLI), Fluorescent Images (FLI) and ultrasound (US) [2,3]. To take advantage of these imaging systems offer, TNP are developed with magnetic, radio-luminescent, phosphorescent, bioluminescent and fluorescent properties, or a combination of these properties depending on the medical imaging form used [4-6]. In the case of ceramic nanoparticles, Hydroxyapatite is a biomaterial that offers advantages such as: a deep penetration into tissues for image acquisition, a low cost, a relatively easy way to synthesize, stability and high biocompatibility [7]. Having the same composition as the minerals in bones and human teeth, Hydroxyapatite nanoparticles [HAp,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] have non-toxic, non-inflammatory, bioactive and osteoconductive properties [8,9]. Furthermore, they may be kinetically stable in bodily fluids [10]. HAp has a porous surface that can be used to load a treatment by applying pressure; this allows the drug to remain intact during loading and release. It also has a high specific surface and  $\text{OH}^-$  groups that can be used to functionalize specific ligands, therapeutic or

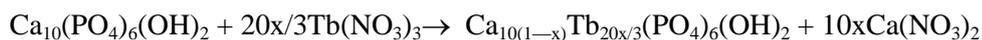
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contrast agents [11,12]. HAp nanoparticles, it can be used as a platform for the nanostics, allow the replacement of calcium ions in the molecule for different elements with specific characteristics, for example, ions of the lanthanide series. By replacing the  $\text{Ca}^{2+}$  ions for trivalent ions such as  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Tb}^{3+}$ , HAp nanoparticles can exhibit strong fluorescence under a source of electromagnetic radiation [13]. The use of lanthanides as triggers for the substitution of calcium ions displays advantages such as high luminescence efficiency, thermal and chemical stability, and low resonance energy. This indicates a lower use of excitation energy, a long emission and low toxicity [14-16]. At the present time, there is no previous report about the study of hydroxyapatite doped with Terbium using different percentages by weight. That is why the effect of doped Hydroxyapatite at different percentages by weight of Terbium via the sol-gel method, for possible uses in medicine, is reported in this study. The materials were characterized with respect to morphology, structural and luminescent properties.

## 2. Experimental

HAp:Tb synthesis via the sol-gel method, in this method of synthesis, reagents are dissolved in an acidic medium and the reaction is assisted by tartaric acid, which acts as a chelating agent [17]. The stoichiometric amounts of the reagents were obtained based on the following chemical equation:



The stoichiometric amounts of reactants are dissolved in a nitric acid solution at 14%. Then to this first solution a second solution of tartaric acid is added while maintaining the system under constant stirring. The molar ratio of the tartaric acid and the metal ions was of 2:1. This mixture was kept under constant stirring for a period of 24 h at room temperature. After said time, the temperature was increased to 80 °C where it remained for 2h. Immediately thereafter, the temperature was increased to 120 °C for the purposes of evaporating the solvent. It is worth mentioning that this synthesis procedure was performed in a fume hood due to the generation of corrosive vapors. Up to this stage of the synthesis process, solids with white and brown regions and sticky consistencies were obtained. Finally, a heat treatment was performed at 800 °C for 2 h to favor the formation of crystalline solids. After heat treatment, a homogeneous white solid powder was obtained. The 4 samples prepared at 0, 1, 2, 3, and 4% by weight of terbium were labeled Mo, M1, M2, M3 and M4. The material characterization was performed by means of a Jeol JSM-5300 SEM for the study of morphology. Fourier transformed infrared spectrometry was used to determine the vibrations of the functional group. The crystalline structure was analyzed via X-ray diffraction (XRD). The photoluminescence spectrum of the sample was recorded with a Fluorescence Spectrophotometer.

## 3. Results and discussion

Fig. 1 shows the studies of the morphology of the Hydroxyapatite doped with terbium was performed by scanning electron microscopy (SEM). In Figure 1(a), one can observe the characteristic form of Hydroxyapatite in the shape of cauliflower, with different sizes and lengths ranging from 10 to 25  $\mu\text{m}$ . In Figure 1(b), one can see the surface of the Hydroxyapatite with 5000 x magnification, where the material has the morphology of stacked flakes with a size of 10  $\mu\text{m}$ . Figure 1(c) shows the Hydroxyapatite material doped with Terbium to 1 %, where one can observe small agglomerations of particles in all directions, and that, with an increase in Terbium, these particles begin to form small circles on the material surface which have a non-uniform distribution of different diameters. This type of morphology is more evident (Figure 1d) for higher percentages by weight. On the sample with 0.4 % of Terbium, the circles on the surface can be seen to have a diameter of about 1 to 2  $\mu\text{m}$ . The Analysis of the crystal structure of the doped Hydroxyapatite

with different percentages by weight of Terbium is found in Figure 2, where the presence of several diffraction peaks are observed at a  $2\theta$  angle of 25.88, 31.76, 32.19 and 32.89 for the (002), (211), (112) and (300) planes corresponding to the Hydroxyapatite hexagonal phase (JCPDS:74-0565)[18]. Also, the peak intensity decreases with the increase of Terbium; this may be due to the interactions that were performed in the synthesis process, where, Terbium ions are interacting with the crystal structure of HAp. The Analysis of the intermolecular interactions was performed by means of Fourier transform infrared spectroscopy (FTIR) shown in Figure 3. The analysis of samples was carried out in a frequency range of 500-4000  $\text{cm}^{-1}$

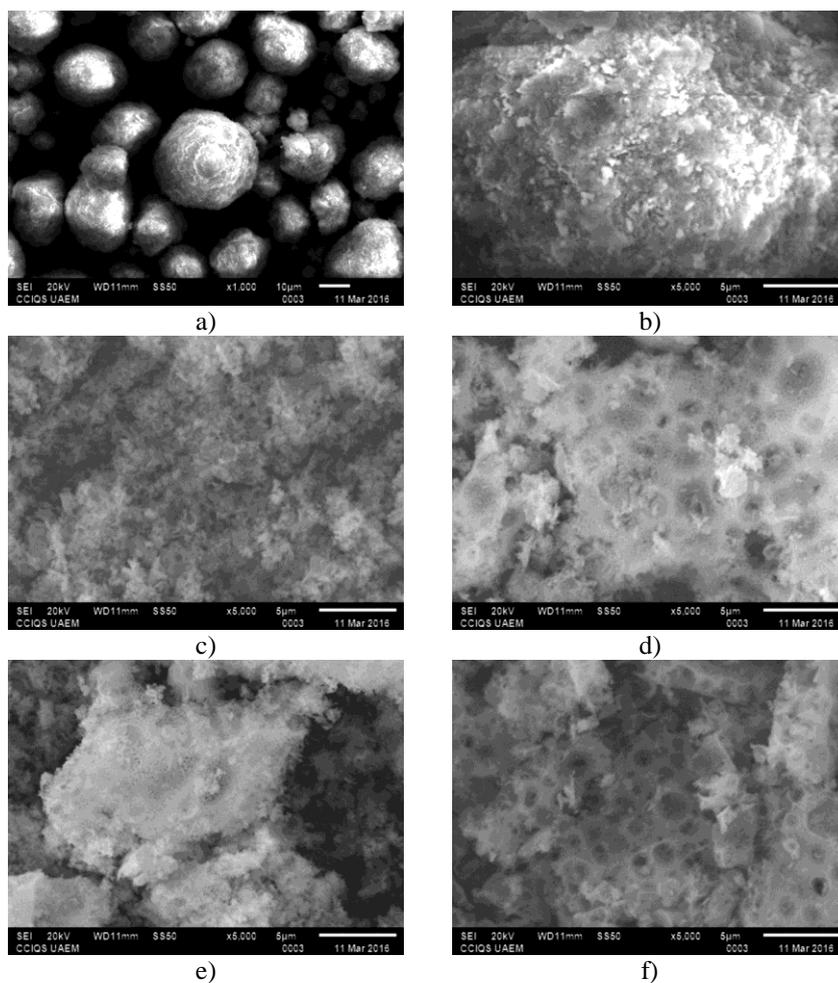


Fig. 1. Morphology of Terbium doped HAp at different percentages by weight.

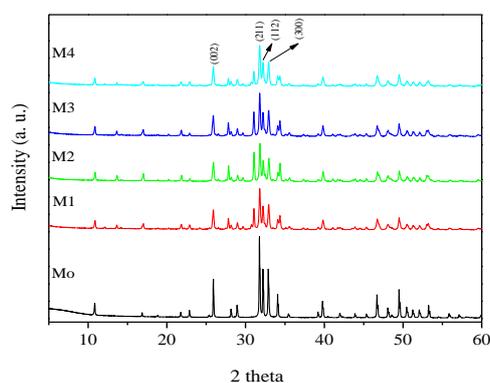


Fig. 2. X-Ray diffraction patterns of Tb doped Hydroxyapatite.

The FTIR spectra shows a very weak interaction at around  $450\text{-}500\text{ cm}^{-1}$ , this interaction is due to the vibration of the  $(\text{PO}_4)^{-3}$  ion. A more pronounced interaction is also observed at around  $500\text{-}600\text{ cm}^{-1}$ , which is also related to the  $(\text{PO}_4)^{-3}$  ions. A much stronger interaction can be appreciated at  $1000\text{ cm}^{-1}$  that results from the two other interactions. These analyses confirm the HAp structure. These results are very similar to those reported by Li *et al.* [19].

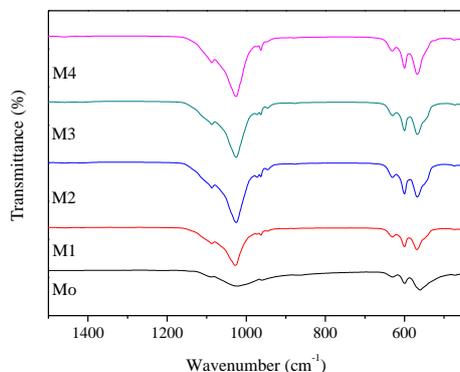


Fig. 3. FTIR spectra of the HAp:Tb samples.

In Fig. 4, the emission spectra of Terbium doped hydroxyapatite at different percentages by weight is shown. It can be seen that hydroxyapatite presents no emissions. The samples showed the typical emissions of terbium ions with a main signal at 544 nm (green) [20]. A tendency is observable: the higher concentration of ions, the greater signal strength. Sample M4, which had a higher concentration of Tb ions, had a more intense signal than the others. Excitation spectra showed absorption at a wavelength at 219 nm (not shown here) which is a characteristic signal for rare earths.

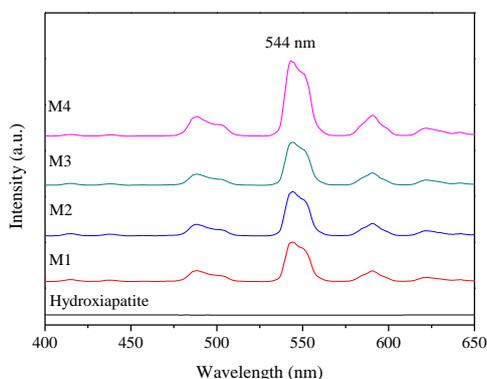


Fig. 4. Emission spectra of Hap at different percentages by weight of Terbium.

#### 4. Conclusions

The Hydroxyapatite with different percentages by weight of Terbium by the Sol-Gel method was successfully realized. The surface of the material shows a clear modification of the surface depending on the amount of Terbium. The effect of Terbium on HAp morphology was very remarkable at 4% of terbium, where well-defined circles with a diameter of about  $1\text{ }\mu\text{m}$  were present. This may be related to the interaction of Terbium with the hydroxyapatite. These results indicate that the synthesized materials could be used as markers for easy common laser excitation.

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