

Eu-doped hydroxyapatite obtained by hydrothermal-microwave method

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Abstract – Eu-doped hydroxyapatite (HA) samples were obtained by hydrothermal-microwave method (HTMW). This method is a promising route for studying the crystallization process of HA using Eu^{3+} as marker. It was observed that the Eu^{3+} ion activator allows the characterization of the order-disorder states in a short range limit into the HA network.

Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is a bioceramic material, which is the principal constituent of the bone mineral phase. In the literature, the substitution of Ca^{2+} for rare earth ions in HA was studied by means of solid state reaction at high temperatures [1]. Trivalent europium (Eu^{3+}) has been used as a tool to probe the local symmetry and occupancy at the cationic sites in the structure of oxyapatites and fluorapatites [2]. Recently, Eu^{3+} ion has been proposed as a biological probe in Eu-doped calcium-deficient apatite, $\text{Ca}_9(\text{PO}_4)_5(\text{HPO}_4)(\text{OH})$ synthesized in hydroalcoholic medium [3].

In this work $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2:\text{Eu}$ (HA:Eu) was obtained by means of coprecipitation route and processed by HTMW method at 140°C for 0, 1, 20 and 40 minutes. The additive concentration was fixed in 1 mol% of Eu^{3+} . These samples were characterized by powder X-ray diffraction (XRD), Raman spectroscopy, and room temperature absorption and emission photoluminescence measurements. The characterizations in a long-range order of the HA:Eu structure has been observed by XRD (Figure 1). Figure 1 shows the formation of HA single phase in all synthesis conditions. It was also verified that the HTMW treatment favors the crystallization process of HA if compared with the sample obtained at room temperature. The absence of secondary phase, such as carbonate, was confirmed by Raman results. In order to make a short-range analysis of the HA:Eu system, the Eu^{3+} ions served as a probe to identify the structural organization in the HA matrix. From photoluminescence (PL) results it was observed that HA broad band occurs due to disorder in the HA lattice. In this way, the sample obtained at room temperature presents the biggest PL intensity. The HTMW treatment promotes a better definition of the Eu^{3+} transitions, while the HA broad band intensity decreases. It was observed in Figure 2 that 20 minutes is the best time for HTMW treatment in these conditions. For superior treatment times the broad photoluminescence band decreases. In other way, the Eu^{3+} transitions are better defined as the HTMW treatment time increases, indicating that the order in a short range of the HA lattice is increased. This order is undetected by XRD measurements, as Figure 1 shows.

In conclusion, the photoluminescence is a complementary technique for XRD on characterization of short- and long-range orders in solid arrangements. Visible HA broad band and the appearance of Eu^{3+} emissions are efficient to monitor the order-disorder during the HTMW treatment process, thus allowing the short and intermediate structural range order analysis.

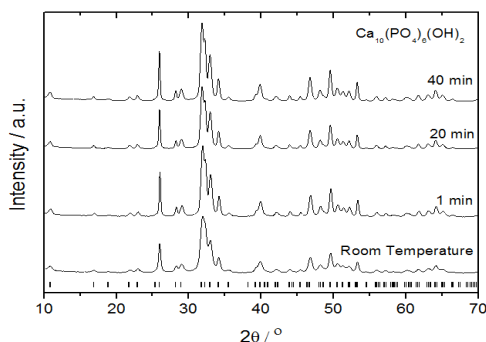


Figure 1: XRD patterns for the HA:Eu powders.

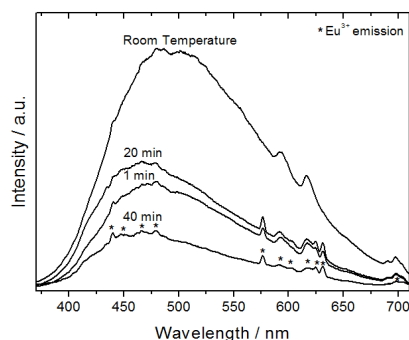


Figure 2: Room temperature PL spectrum of the HA:Eu samples.

References

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