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Thermoluminescent characteristics of synthetic hydroxyapatite (SHAp)

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HIGHLIGHTS

- Dosimetric characteristics of SHAp under gamma irradiation effect were analyzed
- SHAp powders were obtained by Sol–Gel method
- Fading anomalous of HAp was performed showing 15% during 90 days
- SHAp showed good dosimetric characteristics.
- Dosimetric characteristics of SHAp have not been reported yet in the literature before this paper

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ABSTRACT

This paper presents the experimental results of the thermoluminescent (TL) characteristics of synthetic hydroxyapatite (SHAp) obtained by the sol–gel method. For preparation of the SHAp powders, phosphorus pentoxide (P_2O_5) and calcium nitrate tetrahydrated ($Ca(NO_3)_2$–$4H_2O$) were used. The powders obtained were submitted at different temperatures. The structural and morphological characterization were carried out using X-ray diffraction (XRD) and scanning electron microscopy techniques. TL glow curve exhibited two peaks centered at around 200 °C and 300 °C. TL response of SHAp as a function of gamma absorbed dose was linear over a wide dose range. Fading of the storage information in the samples irradiated was also studied. The experimental results show that the synthetic hydroxyapatite obtained by the sol–gel method may have used in gamma radiation dosimetry applications.

1. Introduction

Thermoluminescence (TL) is thermally stimulated emission of light from a semiconductor or insulator, following the previous absorption of energy from ionizing radiation such as X-rays, gamma rays, high energy electron beam, etc. Thermoluminescent materials exhibit differences in dose response between sparsely ionizing radiation (high energy photons like X-rays and gamma rays) (Chen and McKeever, 1997, Furetta, 2003, McKeever, 1985). Thermally stimulated luminescence or better known as thermoluminescence (TL) is one of the most used techniques extensively used of ionizing radiation dosimetry, which makes use of materials commonly divided in two groups (the first one includes tissue equivalent phosphors) which generally exhibit low sensitivity to ionizing radiations whereas the second one is formed by systems with high sensitivity but poor equivalence to organic tissue (Azorín, 1990; McKeever et al., 1995). For many years the most commonly used TLDs were LiF detectors doped with Mg and Ti (Vij, 1993). Azorín and co-workers reported on the preparation method of high sensitivity of new material, calcium sulfate doped with dysprosium ($CaSO_4$:Dy), and its dosimetric properties (Azorín et al., 1993). Recently in our group has been born the idea to develop new materials as radiation dosimeter. In this order several material as well as biomaterial has been suggested to this purposes. One of the most popular materials constituted of human bone is the hydroxyapatite; for that reason our group has interest in this material. In order to synthetize and characterize of hydroxyapatite, it is necessary to take into account, beside the above, that differences in structure and composition of apatites also depend on the different processing techniques, as well as temperature and atmosphere in which are made (Brinker and Scherer, 1990). Among the main areas of application of calcium phosphates, and particularly the HAp, we have all areas of orthopedics and orthodontics, where they have to replace, partially or totally, parts of bone tissue (Elkayar et al., 2009, Elliot et al., 1973; Saikia et al., 2008). Other application is as a coating of metallic

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prostheses, which is done to give at the tissues a better suited and recognizable surface, given their characteristics and biocompatibility. Currently work is being done to improve the different techniques to achieve coatings with adequate stoichiometry and thickness. Among these techniques can find: physical and chemical deposition, elecro-deposition, radiation treatments on surfaces, plasma spray, electrophoresis, etc. (Kay et al., 1964). In the literature SHAp has been used as radiation dosimetry by electron paramagnetic resonance (EPR) technique (IAEA, 2002, Ranby and Rabek, 1997, Ziaie et al., 2009).Therefore, it is anticipated that synthesized HAP can be used for radiation dosimetry purposes by means of the thermoluminescence method.

In this work, synthetic hydroxyapatite (SHAp) samples were prepared the by sol–gel method and the samples were irradiated under gamma radiation dose and subsequently subjected to the TL measurement for its application as gamma radiation dosimeter.

2. Experimental details

The samples used in this investigation were obtained by the sol–gel method which were synthetized using calcium nitrate tetrahydrated ($Ca(NO_3)_2$–4 H_2O) and phosphorous pentoxide (P_2O_5) as well as described in a previous paper (Guzman Vázquez et al., 2005, Meza et al., 2011). The synthesis process consisted following steps: (a) solution, (b) mixture, (c) drying and (d) calcination (Agrawal et al., 2011, Cengiz et al., 2008, Hsieh et al., 2001). The final solution was kept under magnetic stirring for 1 h at room temperature. After this, the temperature was increased up to 56 °C for 48 h. The crystals obtained were ground and calcinated from 600 °C to 1200 °C at intervals of 300 °C, for 1 h. For each sintering procedure, the influence of the gamma irradiation dose was also investigated, as well as the sintering effects on the material characteristics. The formation of the compound was confirmed by studying the XRD patterns using a Siemens D-5000 X-ray source which emits a radiation of λ=0.15406 nm from a Cu target. X-ray diffraction (XRD) analysis was performed by a Philips Analytical X-Ray B.V., using Ni-filtered CuKα radiation, in the 2θ range of 5–80°. A scanning electron microscope (SEM) XL-30 series, made by Phillips Company, was used to investigate the SHAp particle size. The magnification of the system was obtained using the LaB6 filament ranging from 5kX as pointed in Fig. 2. The sample surfaces were coated with a thin gold layer prior to the SEM analysis.

The samples were packed in plastic cover and weighted. Irradiation was carried out with ^{60}Co γ-ray source facility. The irradiation was done under electronic equilibrium in Plexiglas with approximately 3% of uncertainty. The correction for the decay of ^{60}Co radionuclide and the subsequent decrease of the dose rate was performed. The samples were irradiated under gamma radiation source varying dose intervals from 25 Gy to 1 kGy. Previously to performing the gamma radiation measurements SHAp powder samples were submitted to a thermal treatment at 300 °C during 30 min in order to erase any undesirable information. Thermoluminescent readings were made using a Harshaw 3500 TL analyzer coupled to a personal computer in order to process and analyze the glow curves data. The heating rate of the TL analyzer was kept at 10 °C/s for all readings. The TL emission was integrated from room temperature (RT) up to 350 °C. In order to reduce the thermal noise, resulting from the heating planchet of the TL reader, readings were made under nitrogen atmosphere.

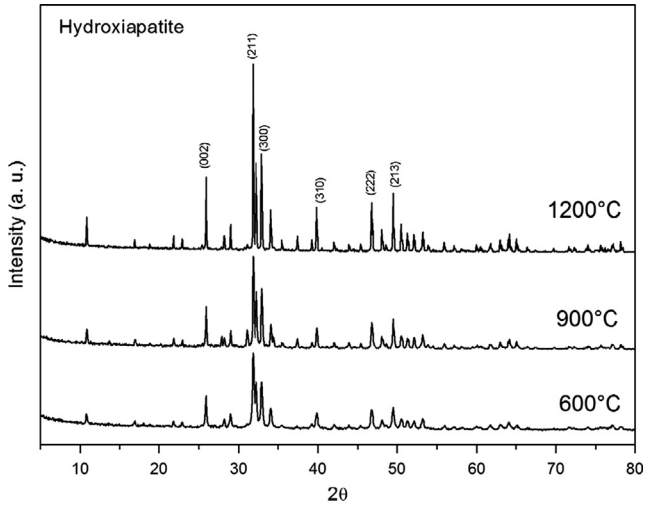

Fig. 1. X-ray diffraction patterns of SHAp synthetic powder submitted to three different thermal treatments.

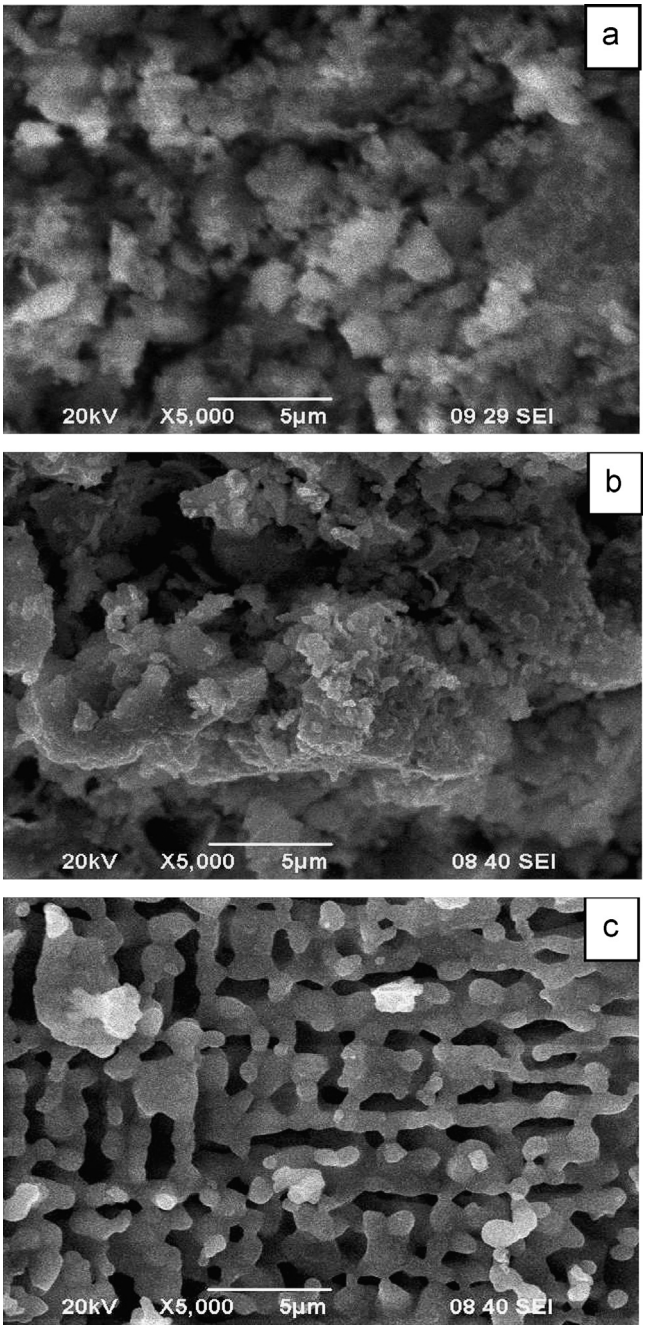

Fig. 2. Micrographs of SHAp synthetic powder submitted to three different thermal treatments.

3. Results and discussion

Samples obtained by this method were characterized to confirm the presence of HAp. Elementary analysis (EDS) results show an average Ca/P atomic ratio of 1.67 and it can be observed the presence of other elementary components in a smaller scale. Crystalline characteristics of SHAp powder are shown in Fig. 1. Fig. 1 shows the X-ray diffraction patterns of SHAp powder obtained by the sol–gel method and submitted to thermal treatment at 600, 900 and 1200 °C for 1 h in air. The diffraction patterns suggested a hexagonal phase of the hydroxyapatite. Hexagonal hydroxyapatite structure is confirmed to be predominant when the material is annealed at 1200 °C. The strongest peak appeared always at around angle $2\theta = 32.98°$ corresponding to the (211) hexagonal reflection. Except for the peak at around $2\theta = 33.5$ the other peaks with relatively weak intensities are described to the diffractions from the hexagonal structure. The only crystalline phase present corresponds to afore mentioned stoichiometric SHAp; the data bank from the International for Diffraction Data (ICDD 9-432) was used in a search/match program for phase identification.

Scanning Electron Micrograph of the surface of SHAp is shown in Fig. 2. The micrographs were obtained at 5kX for the calcinated powder at 600 °C, 900 °C and 1200 °C, respectively. As it can be seen in Fig. 2a samples were almost spherical form, this form is confirmed as well as increasing temperature. Samples calcinated at 1200 °C particles size are shown to be compact and agglomerated particles formed by smaller particles (see Fig. 2C); this behavior indicates that particles size grows with the thermal treatment. Thus, the particle size must be measured depending on the scale and resolution of the measure instrument; in this case the particle size must be determined with more accuracy if a scanning electron micrograph is used.

Fig. 3 shows the glow curve of SHAp powders exposed to gamma radiation of ^{60}Co. For each sintering procedure, the influence of the gamma irradiation dose in the samples is observed. TL glow curve of SHAp obtained at temperature lower than 900 °C is not well defined. However, this TL glow curve is performed when thermal treatment temperature is increased at 1200 °C. This glow curve exhibited two peaks centered at 200 °C and 300 °C respectively. The most TL intensity peak was centered at 300 °C, meanwhile as gamma radiation dose was increased the first peak was appeared at 200 °C. All TL experimental results were obtained for SHAp samples calcinated at 1200 °C. The thermoluminescence response was linear in the range from 25 to 100 Gy. This range was studied in order to use the material for high dose, and could be used in gamma radiation industrial dosimetry.

The reproducibility is very important when measuring gamma absorbed dose values. This parameter was determined by irradiating 10 samples, during 10 times, at the same experimental conditions.

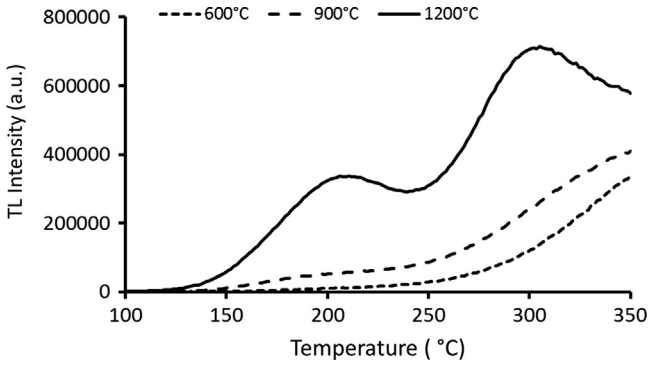

Fig. 3. TL glow curve of SHAp submitted to three different thermal treatments.

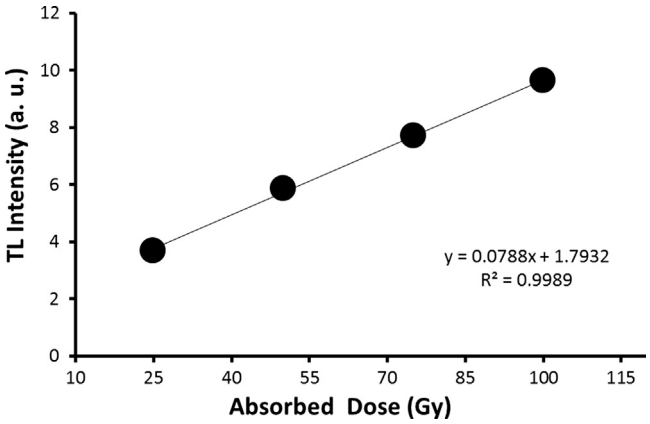

Fig. 4. TL response as a function of gamma absorbed dose in SHAp.

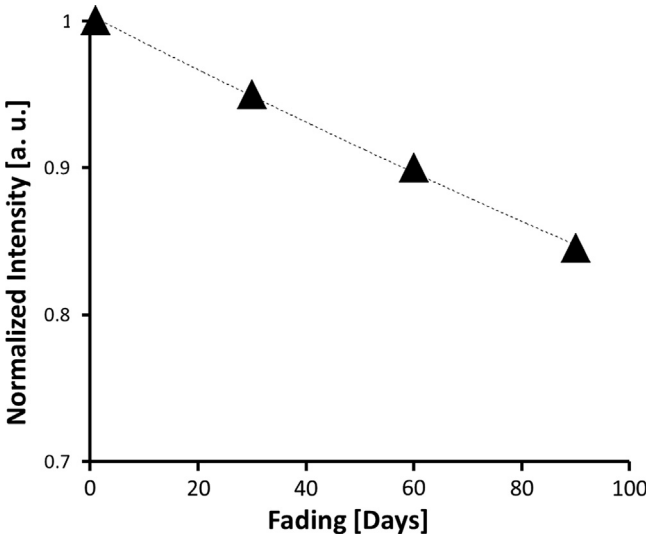

Fig. 5. Fading of SHAp as a function of storage time.

The reproducibility of TL readings of SHAp irradiated by gamma radiation was $\pm 3.5\%$.

Fig. 4 shows TL response of SHAp as a function of gamma absorbed dose. As it can be seen in this figure SHAp showed linearity in the range from 25 to 100 Gy. Other TL characteristics are fading, this is the TL response remaining in the phosphor at different post irradiation time. A group of set of powders were irradiated at an absorbed dose of 50 Gy with gamma irradiation and the readout procedure was performed each different day from 2 to up to 90 days after irradiation. Between irradiations, the dosimeters were stored at typical room conditions. After 90 days fading of the powders showed a fading value of 15% compared with that value obtained just after irradiation. This behavior was an improvement compared with that determined by others authors (Oliveira et al., 2012) reported in the literature. This behavior is showed in Fig. 5.

4. Conclusion

Considering the purpose of developing materials that is TL dosimetry of ionizing radiation, the SHAp is useful in determining this type of radiation in the range studied (0025–100 Gy). The energy of the ionizing radiation, stored in the SHAp after its irradiation can be maintained for a 3 months period, with a fading value of 15%. The wide linearity range (from 25 up to 100 Gy) and its good reproducibility value are the main advantages of the SHAp

powders, which speak in favor of their application in gamma radiation dosimetry.

Acknowledgments

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