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Synthesis of hydroxyapatite through a solid-state reaction method and study of its thermoluminesence dosimetric properties against gamma rays

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Abstract
In this research work, powder hydroxyapatite samples were synthesized using a solid-state reaction method to investigate the annealing effect. The crystal structure was carried out by XRD system produced data, and the Rietveld method using MAUD software. The samples were irradiated in different radiation absorbed doses up to 1500Gy and their thermoluminescence properties including glow curve, response, fading effect and reproducibility were investigated from dosimetry point of view. The results showed that the annealing temperature significantly affects the crystal structure and thermoluminescence dosimetry response of hydroxyapatite samples, consequently. It was concluded that high temperature annealing process can lead to formation of β-TCP crystal phase during the synthesis of hydroxyapatite. Percentage of this formed phase increases with rising the temperature, and finally leads to increasing of the thermoluminescence response.
Keywords: Hydroxyapatite; Solid state; Thermoluminescence dosimetry; Rietveld refinement

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, etc. TL application in high radiation dosimetry, dating techniques in archaeology and geology and as well as the study of lattice defects continues to attract a wide attention of researchers [1]. Biomaterials are the most well-known proposals for TL dosimetry. One of these known materials is in the bones of the human body which its main content is hydroxyapatite [2]. In our previous work, HAP was synthesized through hydrolysis and hydrothermal method to investigate the effect of phase structure of HAP on TL response. It was observed that an extra β-TCP phase is formed during synthesis of HAP, which leads to an increase in the TL response [3]. In the present work, HAP powder was synthesized via solid-state reaction method to investigate the effect of annealing temperature on the phase structure of HAP and also on its TL properties.

Experimental: Preparation of the materials
In this method, $Ca(NO_3)_2{\cdot}4H_2O$ (99% Merck), $(NH_4)_2HPO_4$ (99% Merck) and $NaHCO_3$ (99% Merck) were used as the starting materials, which were combined according to the following chemical equation at room temperature:

$$6(NH_4)_2HPO_4+10Ca(NO_3)_2{\cdot}4H_2O+8NaHCO_3=Ca_{10}(PO_4)_6(OH)_2+12\,NH_4NO_3+8NaNO_3+8CO_2+10H_2O$$

Ca/P ratio was 1.67. The reactants were ground and then blended. Grinding was continued until a foamy white liquid formed. After 24hr aging, the resultant products were washed several times with ethanol and de-ionized water to complete removal of the by-products and then dried in an oven at 80°C for 6 hr. The dried sample was termed as As-prepared HAP and annealed HAP at 400, 500, 600, 700, 800 and 900°C (for 3hr) are termed HAP-400, HAP-500, HAP-600, HAP-700, HAP-800 and HAP-900, respectively.

Results and discussion
XRD and Rietveld analysis
Figure 1 shows the diffraction pattern of samples in 2θ range 20–60. Rietveld refinement was performed using MAUD software to calculate the percentage of formed crystal phases. It was found that samples are a combination of hexagonal and monoclinic and an extera β-TCP phase. CIF files required for MAUD came from the website of (http://crystallography.net/) with COD ID 7217892, 2300273, and 1517238 for the monoclinic, hexagonal and β-TCP phases, respectively. The obtained phase percentages are given in Table 1.

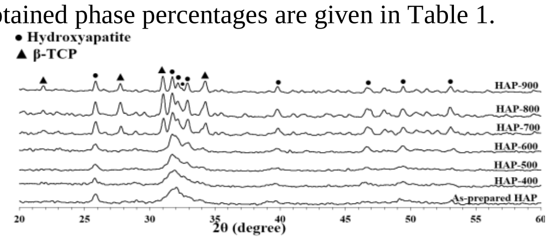

Figure 1. XRD patterns of final products.

Table 1. Formed phase percentages (%).

sample	Monoclinic	Hexagonal	β- TCP
As-prepared	19.12	80	0.88
HAP-400	15.11	84	0.89
HAP-500	9.37	90	0.63
HAP-600	0.25	98	1.75
HAP-700	7	57	36
HAP-800	1	50	49
HAP-900	1	50	49

As it can be seen from Fig. 1 and Table 1, all of the samples are a combination of different crystal phases with a high percentage of hexagonal phase. Also, the HAP decomposes to β-TCP at 700°C. β-TCP percentage increases with increasing temperature up to 800°C and then remains constant. This study showed that the final products never contained less than 50wt% hexagonal HAP. A similar result was obtained by Morgan et al. for the monoclinic HAP [4].

Glow curve

Figure 2 demonstrates the effect of annealing temperature on TL glow curves of samples irradiated at 800Gy using Cobalt-60 gamma-cell 220. The results showed that the HAP-900 have the highest area under curve with a main peak at 230°C.

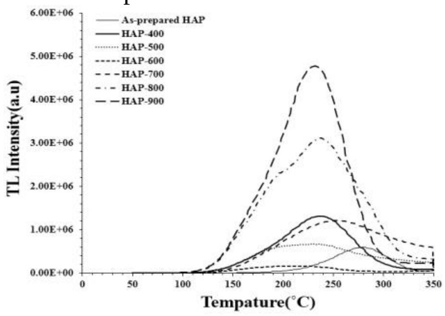

Figure 2. TL glow curves of the samples at 800 Gy.

TL response

In this experiment, the TL response was assumed as the area under the glow curve. Figure 3 shows the mass normalized response-dose curves for synthesized samples. The tests were repeated three times for each irradiation dose. Error bars are also given in terms of standard deviation in the figure.

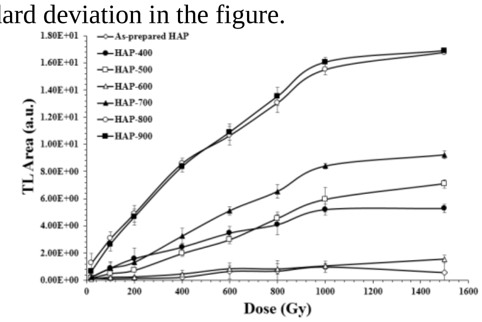

Figure 3. TL response of the samples at 800 Gy.

According to the Figures 2 and 3, HAP-900 sample has the highest area under the glow curve and consequently the highest TL response. It means that in solid-state synthesis method high annealing temperature and also existence of β-TCP phase are effective in improving the TL response. Also, the response is linear up to 1000Gy and then saturated at 1500Gy that means HAP synthesized in this study is appropriate for dosymetric purposes up to 1000Gy.

Fading

To study the fading effect, samples irradiated to 800 Gy. The fading effects of samples were studied during 30 days after irradiation. It was observed that the TL response of the HAP-900 decreases by about 19% during two weeks after irradiation and then remains constant for two next weeks. This sample has the lowest fading during 30 days. The optimal time between irradiation and reading is 30 days for HAP-900. The As-prepared HAP has the highest fading and loses about 90% of its initial response during 30 days. Thus, HAP-900 is optimal sample in this study.

Reproducibility

Reproducibility test was done for optimal sample (i.e. HAP-900). The average TL responses along with their standard deviations after 7 successive cycles of thermal treatment at 400 °C, irradiation at 800 Gy and readout are presented in Fig. 4. The reproducibility of TL response was estimated less than ±5%.

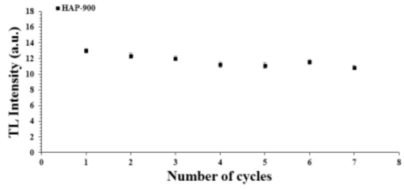

Figure 4. Reproducibility of HAP-900.

According to Fig. 4, the TL response is aproximatly stable. Therefore, HAP-900 is appropriate from dosymetric point of viwe.

Conclusions

In this study, the HAP samples synthesized via solid-state method to investigate the annealing effect on HAP structure and TL properties. It was concluded from Rietvel analysis that the synthesized samples consisted of HAP and an extera β-TCP phases. Finally, the TL properties of the samples were studied. The TL response of the HAP-900 was higher than others. It was concluded that in the solid-state method it is better to synthesis of HAP at high temperatures.

The linearity, fading effect and reproducibility of the samples were investigated and HAP-900 sample was determined as optimal sample and it was suitable for TL dosimetry up to 1000 Gy.

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