Turkish Journal of Engineering

Turkish Journal of Engineering (TUJE)
Vol. 2, Issue 1, pp. 1-6, January 2018
ISSN 2587-1366, Turkey
DOI: 10.31127/tuje.327822
Research Article

CHARACTERIZATION OF HYDROTHERMALLY SYNTHESISED HYDROXYAPATITE BIOCERAMIC

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Received: 11/07/2017 Accepted: 14/09/2017

ABSTRACT
In this study, hydroxyapatite (HAP) was synthesized by hydrothermal method. The structural analysis, thermal analysis and electrical characteristics of HAP sample have been investigated. The structural analysis was performed to determine the crystal structure and to observe the surface morphology of the sample. The thermal analysis was made from room temperature to 925 ˚C, to determine the mass loss according to temperature and phase transitions or decomposition in the sample and also TG-DTA analysis was done to determine the thermal stability. The compositional analysis was done by EDX. I-V analysis was made to calculate the electrical conductivity value of the sample and electrical conductivity of the sample was obtained to be$1.2x10^{-10}$ S/cm.

Keywords: *Hydroxyapatite (HAP), Hydrothermal Method, Electrical Conductivity*

1. INTRODUCTION

With the developing technology, the depth of material properties can be reached. In this respect, it is possible to find a faster solution to the needs of mankind. Nanotechnology is a new trend in today's technology. In the transition from macro structure to micro structure, unanswered questions began to be answered gradually. Materials that have been obtained in very small sizes have been a source of inspiration for a lot of work such as nanotube, nanowire etc. At the same time, thanks to the material structure, it has been well understood how to synthesize the materials as well as how the existing materials can be developed. Developments in bio ceramic materials, which have a different place in materials, are important for human anatomy (Brown *et al.*, 1994; Gümüşderelioğlu, 2002; Orlovskii *et al.*, 2002). Today, the issue of biocompatibility of materials becomes increasingly important (Pasinli, 2004). Determination should be made as to the purpose of use in the between materials with direct contact with blood and other materials, and this biocompatibility should be assessed within its own environment (Gümüşderelioğlu, 2002; Park *et al.*, 2002). Semi-biological body parts used in medical interventions that are necessary after the diseases or accidents must meet the requirements as mechanical properties at the same time.

Hydroxyapatite (HAP) in these materials constitutes the main mineral components of materials such as teeth, bones. Hydroxyapatite is a biologically dynamic calcium phosphate ceramic that can be used in surgical operations. Although HAP powder bioactivity has a large hold on bone development along its surface, it is insufficient to withstand severe load in terms of mechanical properties. Hydroxyapatite is a biological apatite as it is in the living bone component. The biological apatite weighs 70% of the bone (Singh *et al.*, 2014). Hydroxyapatite is a biologically dynamic calcium phosphate ceramic that can be used in surgical operations. Although HAP powder bioactivity has a large hold on bone development along its surface, it is insufficient to withstand severe load in terms of mechanical properties (Singh and Sidhu, 2014). Hydroxyapatite is a biological apatite as it is in the living bone component. Almost 70% of the bone forms biological apatite (Singh and Sidhu, 2014). Besides, the HAP in bone is found with other ions such as impure fluoride, magnesium and sodium (Sadat-Shojai *et al.*, 2013). The HAP is chemically represented as $Ca_{10}(PO_4)_6(OH)_2$ and its crystal structure is shown in Fig. 1.

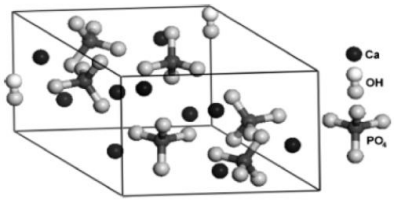

Fig. 1. Crystal structure of hydroxyapatite (Zhang, 2007).

The HAP materials can be synthesized in many different methods (Sadat-Shojai *et al.*, 2013) and uses. HAP also can be coated by stronger materials lie zirconium and aluminum oxide to provide high mechanical properties. That uses make more successful operations in clinical practice (Hench *et al.*, 1993; Brown and Constantz, 1994; Orlovskii *et al.*, 2002). In our study we have synthesized Hydroxyapatite bio ceramic material. The developed HAP characterization has been made and results are discussed.

2. MATERIALS AND METHOD

The nanostructured hydroxyapatite bio ceramic (10mmol) calcium nitrate tetrahydrate $Ca(NO_3)_2\,4H_2O$ is dissolved in 30mL distilled water than solution mixed by magnetic stirrer for 30 mins. at 60°C, and 6mmol ammonium hydrogen phosphate $(NH_4)_2HPO_4$ is dissolved in 30mL distilled water, was added to the solution. Both solutions separately sonicated for 10 min. After the addition of 40 mg of cetyltrimethyl ammonium bromide to the solution and sonicated 60 mins., the ratio of Ca/P in the solution was maintained 1.67. Also, put hydrothermal 24 hours at 180°C and at 140°C in 100 mL water in an autoclave. After 24 hours filtering, the solution cleaned then dried in the oven. Then calcinated at 700°C in a furnace evaporate the nitrates and hydrates from the structure. In addition, the detailed sample preparation procedure and the crystalline phases of synthesised nanostructured hydroxyapatite bio ceramic were determined by X-ray diffraction (XRD) analysis on the Rigaku RadB-DMAX II diffractometer with CuKα radiation at room temperature. Morphological features of hydroxyapatite bio ceramic coatings were observed by scanning electron microscopy (SEM) executed on a scanning electron microscope JEOL-7001 and EDX performed on Energy Dispersive X-ray analysis JEOL-7001. Fourier transform infrared (FTIR) spectroscopy was taken (Thermo scientific Nicole IS 5) and we to used Keithley 4200 semiconductor characterization system for current-voltage (I-V) analysis. The weight loss measurements made by thermogravimetric analysis (TGA) and the phase transitions occurred in the sample was analysed by differential thermal analysis (DTA) by SHIMADZU DTG-60AH equipment.

2.1. Results and Discussions

Analyzes and results have been individually assessed within themselves.

2.1.1. X-Ray Analysis

XRD spectra of the HAP taken within a 2θ range of 20-80° are shown in Fig. 2. The mean crystallite size D of the sample was computed by analyzing the XRD data using the Debye - Scherrer formula:

$$\mathbf{D} = \frac{\mathbf{k\lambda}}{\boldsymbol{\beta}\,\mathbf{cos}\,\boldsymbol{\theta}} \qquad (1)$$

where D represents average crystalline size, λ is the wavelength of X-ray (0.1540559 nm), θ is the peak angle of diffraction degree (Bragg's angle) and β is the full width of the peak at the half-maximum intensity in radian (FWHM), also Scherrer constant defined as the crystallite shape and is around equal to 0.9. Sharp peaks appeared in the XRD patterns of the calcined HAP powders revealed good crystallinity. The characteristic peak of the sample appears at 2θ = 29.08, corresponding to (210) plane of

HAP, which confirms the presence of HAP crystallite. The average crystalline size of all samples scaffold were estimated using Debye-Scherer equation confirming the nanostructure of the nano-composite and was found to be 12.2 nm, this range confirms that all the studied composites are nanostructured materials (Padiyan *et al.*, 2003; Badran *et al.*, 2017).

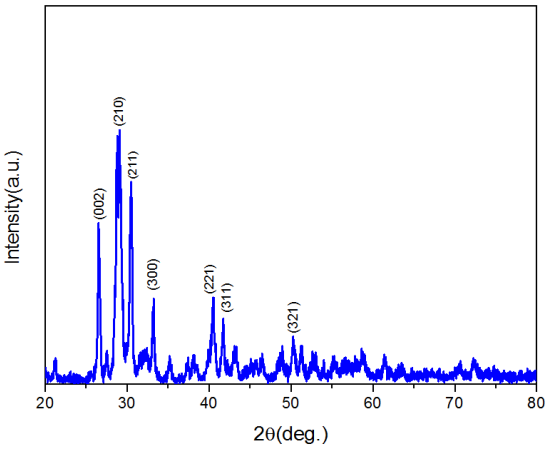

Fig. 2. XRD patterns of HAP powder in the sample

2.1.2. FTIR Analysis

FTIR is a way utilised for chemical identification, principled on the actuality that the selective absorption of material happens in the infrared domain. The molecule of chemical substance vibrates in numerous modes later absorption of infrared giving fourier transform infrared spectroscopy absorption spectrum, above broad wavelength scope. FTIR analyses helped us to reveal the chemical bonding characteristics with the powder samples. FTIR spectra of the HAP are shown in Fig. 3. All the bands corresponding to HAP structure were observed in FTIR spectrums. The observed bands correspond to the bands of hydroxyl and absorbed water phosphate species (Sato *et al.*, 2006). Characteristic bands for phosphate stretching vibrations and phosphate banding appeared in the region (950 cm^{-1} -1250 cm^{-1}). The bands at (903 cm^{-1}–962 cm^{-1}) correspond to ν_1 stretching mode of PO_4^{3-} group while the bands at (1032cm^{-1}–1092 cm^{-1}) correspond to ν_3 stretching mode(Stanić *et al.*, 2010; Zhang *et al.*, 2010). PO_4 bands at (1091cm^{-1}–962 cm^{-1}) confirm the formation of HAP structure. The most intense peak among the phosphate group was observed in the region of ~720cm^{-1} (Sato *et al.*, 2006; Al-Hazmi, 2016). The obtained all FTIR bands are in good agreement by the bands of HAP (Sato *et al.*, 2006). The appearance of the sharp peaks associated with the stretching vibration in investigated samples indicates to the formation of crystalline HAP.

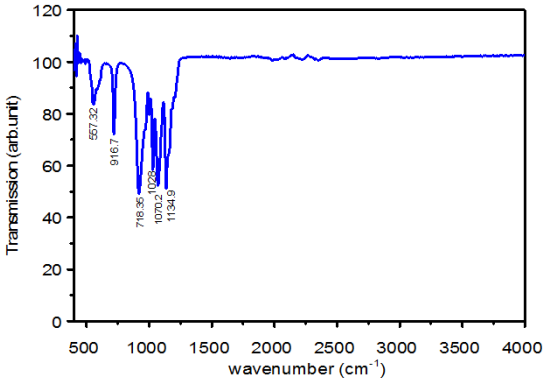

Fig. 3. FTIR spectra of HAP in the sample

2.1.3.SEM and EDX Analysis

Scanning electron microscopy instrument has been used to obtain the morphology of HAP. The SEM images of the HAP in the range microparticle are shown in Figs. 4-7. The morphology of HAP sample exhibits plate-like structure with a smooth surface 6000X magnification. The elemental analysis with the HAP sample was performed by X-ray Energy Dispersive spectroscopy (EDS). The phosphorus, calcium and oxygen were observed in EDS spectra of report which presented in Table 1. The elemental composition and homogeneity of particles have major effects on biocompatibility and bioactivity properties of bio ceramic materials. To know the inter relationship between materials properties, the composition of the material should be known. This technique was utilised to analyses of HAP specimen. Organic reactions of a HAP sample are powerfully depending on its chemical composition, energy dispersive spectroscopy (EDS), result uncovers that HAP specimen contains Ca, P and O. The best Ca/P ratio for synthesised specimen was observed to be 1.65, which is somewhat smaller than 1.67 theoretical worth and the similar was usually reported (Jagadale *et al.*, 2016).

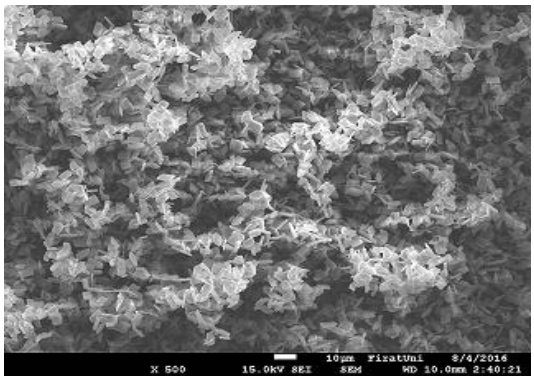

Fig. 4. SEM (10µm) of HAP in the sample at 500x magnification.

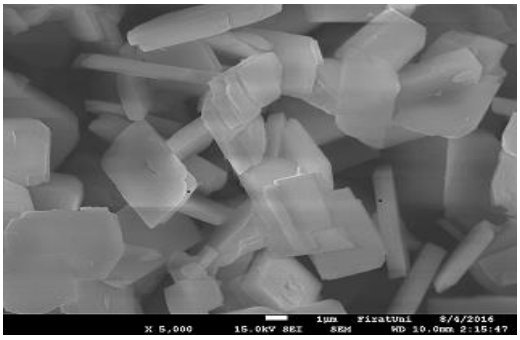

Fig. 5. SEM (1µm) of HAP sample at 6000x magnification.

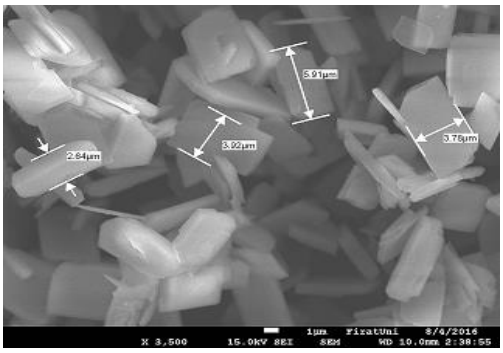

Fig. 6. SEM (1µm) of HAP in the sample at 3500x magnification

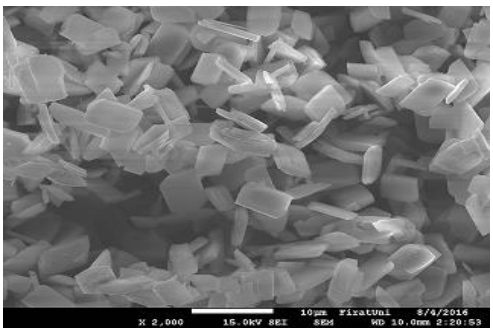

Fig. 7. SEM (10µm) of HAP in the sample at 2000x magnification

Table 1. This is the example for table formatting

Element	Weight%	Atomic%
O	11.49	22.63
P	33.66	34.24
Ca	54.85	43.12

2.1.4. TGA/DTA Analysis

Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) for hydroxyapatite sample was made from room temperature to 925°C. Thermal stability of HAP sample was examined by thermal decomposition of the powder. The TGA/DTA results are shown in Fig. 8. The TGA (thermogravimetric analysis) demonstrates total weight loss is 8.583% in the temperature range from room temperature to 925°C that the decomposition of HAP sample due to evaporation of physically adsorbed water is given in Fig. 9. DTA (differential thermal analysis) curve shows that thermal decomposition of HAP sample at 290.76°C with an endothermic peak and this peak is alone due to degradation of residual water from the sample shown in Fig. 10. The result of thermal decomposition is useful for optimization of conditions to obtain monophasic biomaterial.

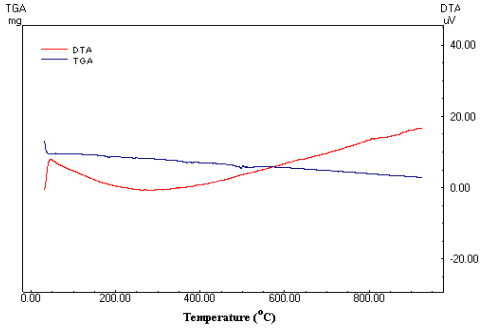

Fig. 8. TG/DTA curves of the sample

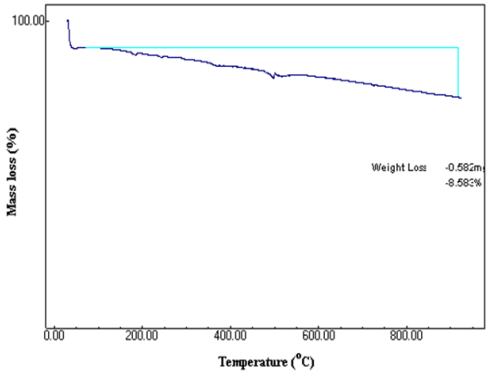

Fig. 9. TG curve of the sample

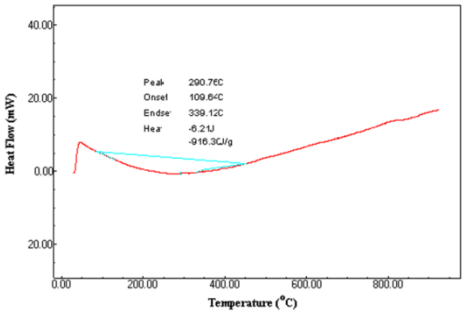

Fig. 10. DTA curve of the sample

2.1.5. I-V Characterization

In I-V characterization the current slope of the sample according to the voltage value was provided. So the graph of current versus voltage value can be drawn. In this graph, the resistivity of the sample was found. From this point, the slope (3.9756×10^{-10}S) of the sample as seen in

Fig. 11 was found, and then the slope of the graph to calculate the electrical conductivity was used by the help of the following equation:

$$\boldsymbol{\sigma = \frac{I}{V} . \frac{d}{A}} \qquad (2)$$

where (I) am current, (V) is the voltage, (d) is the thickness of the sample and (A) is the surface area of the sample. As the electrical conductivity as $1.2x10^{-10}$ S/cm was calculated. The electrical conductivity value calculated for sample has good values for HAP as compared in literature. Also it can be said that insulators are materials having an electrical conductivity σ $<10^{-8}$ S/cm.

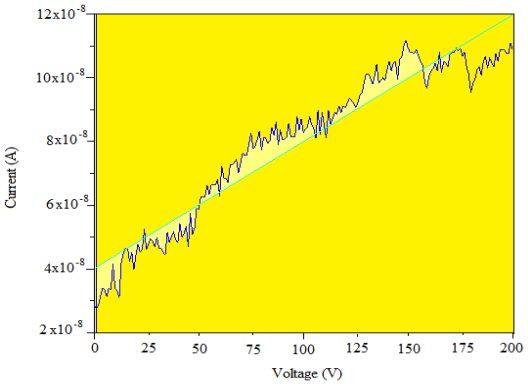

Fig. 11. I-V Characterization curve of the sample

5. CONCLUSION

In this work, hydroxyapatite was prepared via the hydrothermal method. Also characterised of sample determine by XRD, FTIR, I-V, TG-DTA, EDS, SEM, chemical and thermal analyses were used to investigate the structure, morphology, and composition of the obtained product. XRD is used to analyse the structural properties of material, the crystallite size obtained from XRD was found to be 12.2 nm. In I-V characterization of the sample, the electrical conductivity of the sample was obtained as $1.2x10^{-10}$ S/cm and that the electrical conductivity value has importance for HAP considering the literatures. TG-DTA analysis was done to determine the thermal stability, the thermal analysis demonstration the confirm construction of stability compound of the material. Also by used the TGA (thermogravimetric analysis) demonstrates the total weight loss 8.583% in the temperature range from room temperature to 925°C. FTIR is a way used for chemical identification, based on the fact that the selective absorption of material occurs in the infrared region. The most intense peak among the phosphate group was observed in the region of ~720cm^{-1}. SEM has been used to of the obtained HAP. The morphology of HAP sample exhibit shape plate-like structure with a smooth surface.The elemental analysis of the sample was performed by X-ray Energy Dispersive spectroscopy (EDS). The phosphorus, calcium, and oxygen were observed only in obtained EDS spectra of the HAP sample.The best Ca/P ratio for synthesised sample was found to be 1.65.

ACKNOWLEDGEMENTS

This work is financially supported by FÜBAP, Project No: FF.16.14.

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