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Rapid synthesis of thermally stable hydroxyapaptite

Rabia Nazir [a], Nida Iqbal [a], Abdul S. Khan [a], Aftab Akram [b], Anila Asif [a], Aqif A. Chaudhry [a], Ihtesham ur. Rehman [c], Rafaqat Hussain [d,*]

[a] *Interdisciplinary Research Centre in Biomedical Materials, COMSATS Institute of Information Technology, Lahore, 56000, Pakistan*
[b] *School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan*
[c] *The Kroto Research Institute, Department of Materials Science and Engineering, University of Sheffield, Sheffield, S3 7HQ, United Kingdom*
[d] *Department of Chemistry, University Teknologi Malaysia, 81310 UTM Skudai, Johor Darul Ta'zim, Malaysia*

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Abstract

We have optimized the wet precipitation synthesis of hydroxyapaptite to obtain thermally stable powder in the short time span of 3 min. Exposure of the reaction mixture to 1000 W microwave for 3 min furnished hydroxyapatite, which was thermally stable at temperatures up to 1200 °C. Powders were analyzed for phase purity using X-ray crystallography; chemical composition was studied using Fourier transform infrared spectroscopy while particle morphology was analyzed using scanning electron microscopy.

Keywords: Microwave; Rapid synthesis; Hydroxyapatite; Biomaterial

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1. Introduction

Calcium phosphate (CP) family has been the focus of attention of surgeons and clinicians through many years due to its use as synthetic bone replacement materials [1]. Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is the most extensively explored member of the CP family due to its similar composition as the mineral component of human hard tissue and superior biocompatibility [2,3]. With the passage of time, HA (Ca/P = 1.67) has found its way to numerous applications in the field of medicine especially as a bone substitute [4,5]. It has been used as porous beds (bone in-growth applications) [6–9], dense sintered forms (for semi-load bearing sites) [6,9,10] and surface coating agent on metallic implants [11–13]. HA ceramics tend to exhibit inferior mechanical strength, especially in wet environment under physiological condition, which makes them unsuitable for load bearing applications [6,10]. While non stoichiometric HA ($Ca/P \neq 1.67$) is thermally unstable giving rise to other CP phases at elevated temperatures resulting in poorly dense compacts. Therefore, considerable attention has been focused towards the synthesis of thermally stable HA for load bearing application [14].

A variety of techniques have been reported for the synthesis of stoichiometric HA [14] e.g. wet chemical methods [2,15], hydrothermal processes [1,3], solid-state reaction [6,16] and sol–gel synthesis [17]. However, these methods suffer from drawbacks such as long reaction times, use of toxic and expensive chemicals and incorporation of impurities and other CP phases [18,19]. Microwave technology has evolved over the last few years and now offers promising energy source for synthesis of various kinds of materials such as organic compounds, conventional ceramics, polymers and composites [20,21]. It is also being utilized in the processing of biomaterials [20–22] as well as ionic substitution of Ag [15,23], Zn [6,24], CO_3 [25] and many other minor ionic substitutions [26] of appetites and sintering of bioceramics [25]. Microwave radiations have been frequently applied to synthesize products with tailored properties (biphasic mixtures [2,5], nanosized particles [20,26] with varying morphologies [18,26]). There are certain advantages of this advance technology that make it to be used successfully as an ideal source of energy. The greatest advantage of utilizing microwave radiation is that it enables volumetric heating hence ensuring uniform heating with almost no thermal gradient, which allows

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* Corresponding author. Tel.: +60 755 34316, fax: +60 755 66162.
E-mail address: rafaqat@kimia.fs.utm.my (R. Hussain).

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higher heating rates and shorter processing times [27]. The rapid heating and the accelerated rate of crystallization might favor the development of the thermodynamically stable phase reducing the probability of intermediate metastable phases formation (e.g. tricalcium phosphates in case of HA synthesis) [1,15,20]. Moreover, this technique has inherent flexibility towards scale up for bulk production and processing of materials [26].

Microwave assisted wet synthesis of phase pure HA has been presented in literature with varying synthesis parameters such as precursors, pre-exposure aging period, exposure time and power input. A large spectrum of Ca and P precursors have been used extensively [1,20,24], similarly power input-exposure time relationship has been optimized but with long exposure time to achieve required particle size and degree of crystallinity [6].

In the present work, we have optimized microwave-accelerated wet synthesis of HA using $Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_2HPO_4$ as Ca and P precursor respectively with the aim of synthesizing thermally stable phase pure HA in a matter of minutes. The scope of the present study was to investigate the effect of microwave power (W) and reaction time on the synthesis of phase pure HA, which is thermally stable at temperatures as high as 1200 °C.

2. Materials and methods

Calcium nitrate ($Ca(NO_3)_2{\cdot}4H_20$) (UniChem) and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) (AppliChem) were used as precursors for the synthesis of HA. All necessary calculations were based on Ca/P ratio 1.67. Diammonium hydrogen phosphate (0.6 M) and Calcium nitrate (1 M) solutions were prepared separately in 400 ml distilled water. pH of both solutions were adjusted above 10 by adding ammonium hydroxide (BDH) before mixing. Diammonium hydrogen phosphate solution was added drop wise to the calcium nitrate solution at a dropping rate of 2 ml per minute. After the completion of addition the reaction mixture was stirred for 30 min (pH was maintained above 10) before refluxing in a domestic microwave oven (Samsung MW101P) Fig. 1 for 1, 3, 5 and 10 min (30 s ON, 30 s OFF) at 600 W, 850 and 1000 W. After microwave exposure the resulting reaction mixture was filtered, washed with distilled water, dried at 80 °C for 2 h in an oven followed by drying in a box furnace at 200 °C for 2 h. The resulting powder was heat treated at 1200 °C for 2 h (ramp rate: 5 °C/min) and cooled down to room temperature (ramp rate: 30 °C/min). Resulting products were isolated and characterised using XRD, FTIR and SEM.

2.1. Sample characterisation

X-ray diffraction (XRD) technique was used to evaluate phase purity of HA powders. Analysis was carried out on diffractometer system PERT-PRO using Goniometer geometry (PW3050/60) at room temperature with Cu K-alpha radiation. XRD pattern was recorded continuously with 2θ from 20° to 80° with a step size of 0.02. Characteristic functional groups were identified using Fourier transform infrared (FTIR, Nicolet 6700) spectroscopy. Photoacoustic cell was used as a sampling accessory. Spectra were collected over the region 4000–400 cm^{-1} at resolution of 4 cm^{-1} averaging 256 scans. Powder morphology and particle size was investigated by scanning electron microscope (JEOL JSM6490A, Japan). Samples for SEM analysis were gold plated with coating thickness 250A using coating unit JFC 1500 Ion sputtering device. Energy dispersive X-ray (EDX) spectrometer attached to the scanning electron microscope (SEM) was used to analyze chemical composition.

Fig. 1. Experimental set up for microwave assisted synthesis of HA in our laboratory: (a) interior view and (b) exterior view.

3. Results and discussion

High temperature phase stability of HA powder is very important for its applications. Therefore, the synthesized powders were heat treated at 1200 °C for 2 h, in a high temperature programmable furnace, in air. After the heat treatment, the powders were analyzed for their phase composition using FTIR and XRD techniques, while the particle morphology was studied using SEM.

3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of HA heat treated at 1200 °C. Fig. 2a showed characteristic peaks of crystalline HA. The peak at 3573 cm^{-1} was assigned to the O–H stretching mode (υ_s) of the hydroxyl group. A band observed in the range 1418–1564 cm^{-1} was attributed to the C–O stretching of carbonate group in HA. The peak observed in the range 1071 and 1103 cm^{-1} was due to the υ_3 asymmetric stretching of P–O bond of phosphate group in HA. The peak at 963 cm^{-1} was assigned to the P–O symmetric stretching. The peak at 637 cm^{-1} corresponded to the υ_L vibration mode of the hydroxyl group. Peaks at 606 and 582 cm^{-1} were assigned to the O–P–O bending modes. The sharpness of the bands at 637, 602 and 582 cm^{-1} indicated the formation of a crystalline HA. While the FTIR spectra (Fig. 2b) of reaction mixture unexposed to the microwaves showed majority of the characteristic peaks of HA but peaks were not well defined especially in the range 1071 and 1103 cm^{-1} corresponding to the υ_3 asymmetric stretching of P–O bond of phosphate group indicating the formation of non-stoichiometric amorphous HA. Similarly, FTIR spectra for both batches (650 W and 1000 W) are shown in Fig. 3, the peak at 963 cm^{-1} and the range 1071 and 1103 cm^{-1} gradually increased in intensity with increase in exposure time and became narrower when the power of microwave radiations was increased from 650 to 1000 W indicating the formation of stoichiometric HA.

3.2. X-ray diffraction (XRD)

Phase evaluation of synthesized powder showed characteristics peaks of prepared HA corresponding to specific crystallographic planes located at 25.91°, 28.94°, 31.78°, 32.19°, 32.93°, 34.1°, 39.80°, 46.71° and 49.49°. Peak analysis were performed using ICDD Powder Diffraction File No. 00-009-0432 and ICDD Powder Diffraction File No. 00-009-169 for HA & β-TCP respectively and the results are listed in Table 1.

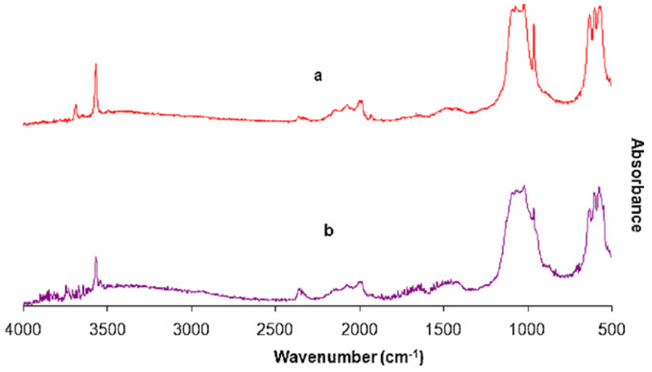

Fig. 2. FTIR spectra of HA (a) exposed to 1000 W for 5 min microwaves followed by heat treatment at 1200 °C and (b) synthesized under unexposed conditions.

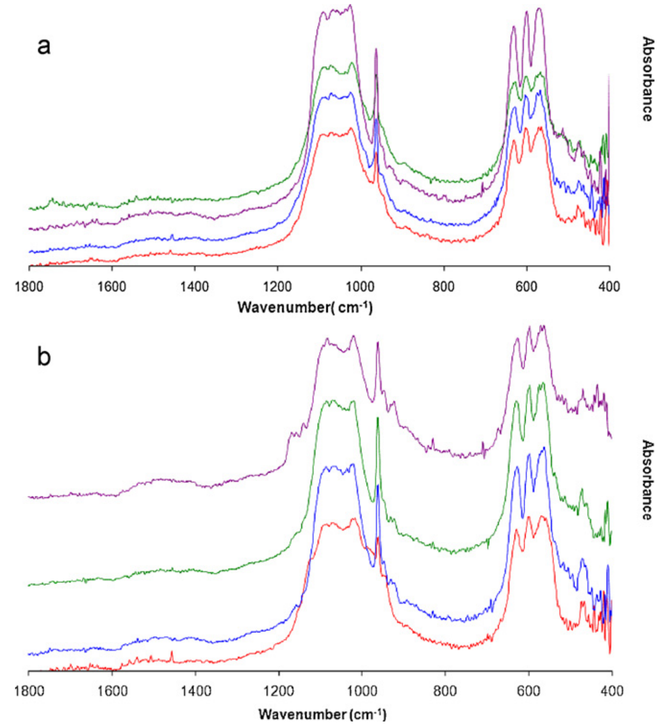

Fig. 3. FTIR spectra of HA exposed to microwaves for 1, 3, 5 and 10 min (from lower to upper curve). (a) 600 W and (b) 1000 W.

It was observed that all the reaction mixtures exposed to 600 W microwave radiations furnished biphasic mixtures of HA and TCP. Reaction mixtures exposed to 800 W microwaves for 1 and 3 min also furnished biphasic mixture of HA and TCP, while all other reaction mixtures exposed to microwaves furnished phase pure HA powders.

XRD pattern of the powder synthesized without microwave irradiation (Fig. 4a) indicated the formation of secondary phase

Table 1
Phase composition of calcium phosphates prepared using microwave irradiation method. HA: TCP ratios are calculated on the basis of relative intensities of peaks of HA & TCP.

Sample ID	Power input (W)	Exposure time (min)	Phase analysis HA:TCP
D	0	0	85:15
A-1	600	1	85:15
A-2	600	3	90: 10
A-3	600	5	90:10
A-4	600	10	95:05
B-1	850	1	85:15
B-2	850	3	90:10
B-3	850	5	100:0
B-4	850	10	100:0
C-1	1000	1	80:20
C-2	1000	3	100:0
C-3	1000	5	100:0
C-4	1000	10	100:0

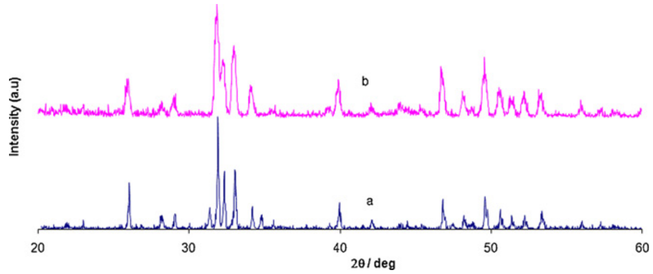

Fig. 4. XRD pattern of (a) synthesized under unexposed conditions and (b) synthesized under exposed conditions (1000 W for 5 min).

of β-TCP which was confirmed by the presence of the characteristic peak of TCP at 31°. While the XRD pattern (Fig. 4b) of HA synthesized by exposing the reaction mixture to 1000 W of microwaves for 3 min showed no peaks for the secondary phases and hence confirming the formation of phase pure HA.

All reaction mixtures exposed to microwaves for 1 min furnished biphasic mixtures of HA and β-TCP (Fig. 5a). We believe that the effective exposure time of 1 min is too short for microwaves to have any positive effect on the reaction kinetics. However, all reaction mixtures exposed to microwave radiation for 10 min yielded phase pure HA (Fig. 5b), in addition to the phase purity, gradual increase in crystallinity of HA powders was also observed when the power output of the microwave was increased from 600 W to 1000 W. XRD patterns (Fig. 6a, b) of reaction mixtures exposed to 650 W show that the full width at the half maximum of the characteristic peak of HA centered at 32θ gradually decreased when the exposure of reaction mixture to microwaves increased from 1 to 10 min, indicating that the prolonged exposure to microwaves enhanced the crystallite size, while the same peak also increased in intensity when the reaction mixture was exposed to 1000 W microwaves for 1, 3, 5 and 10 min, indicating the formation of highly crystalline HA with a larger crystallite size.

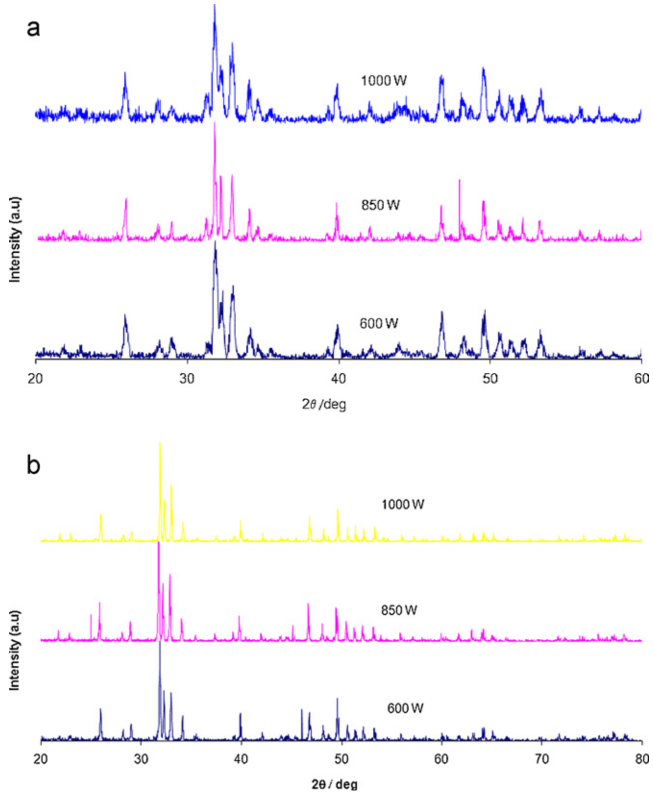

Fig. 5. Effect of increasing power output from 600 W to 1000 W: (a) for 1 min and (b) for 10 min.

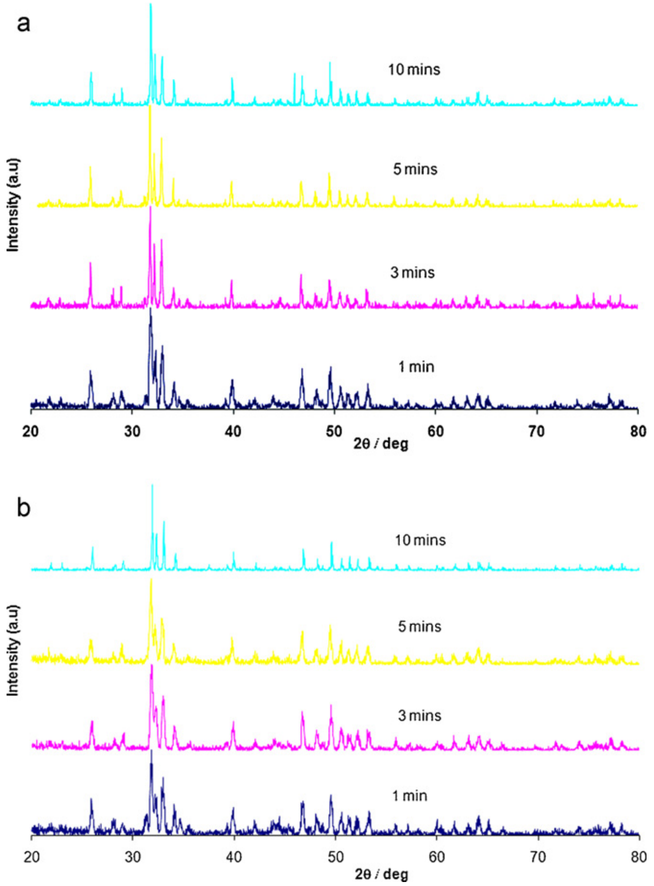

Fig. 6. Effect of increase in exposure time from 1 to 10 min (from lower to upper curve) at (a) 600 W, (b) 1000 W.

The electromagnetic energy at 2.45 GHz was applied to the reaction mixture in this study, the energy at this frequency diminishes the strength of the bonds between the calcium and its hydration sphere, thus facilitating the deaquation step which is one of the pre-requisites for the formation of apatite in aqueous solutions [28,29]. The dipole moment of the hydroxyl ions in HA structure has been linked to the dielectric nature of hydroxyapatite, resulting in the absorption of more microwave radiation and hence ensuring the formation of HA phase [30–33,1].

3.3. Scanning electron microscopy (SEM)

SEM analysis of samples revealed that the synthesized HA powder exist as spherulites agglomerates with narrow size distribution. However there is a slight increase in size of these agglomorates ranging from 0.75 μm ± 0.28 μm (S.D. = standard deviation) at 600 W to 0.80 μm ± 0.25 μm (S.D.) at 1000 W. The power of microwave radiations and exposure time

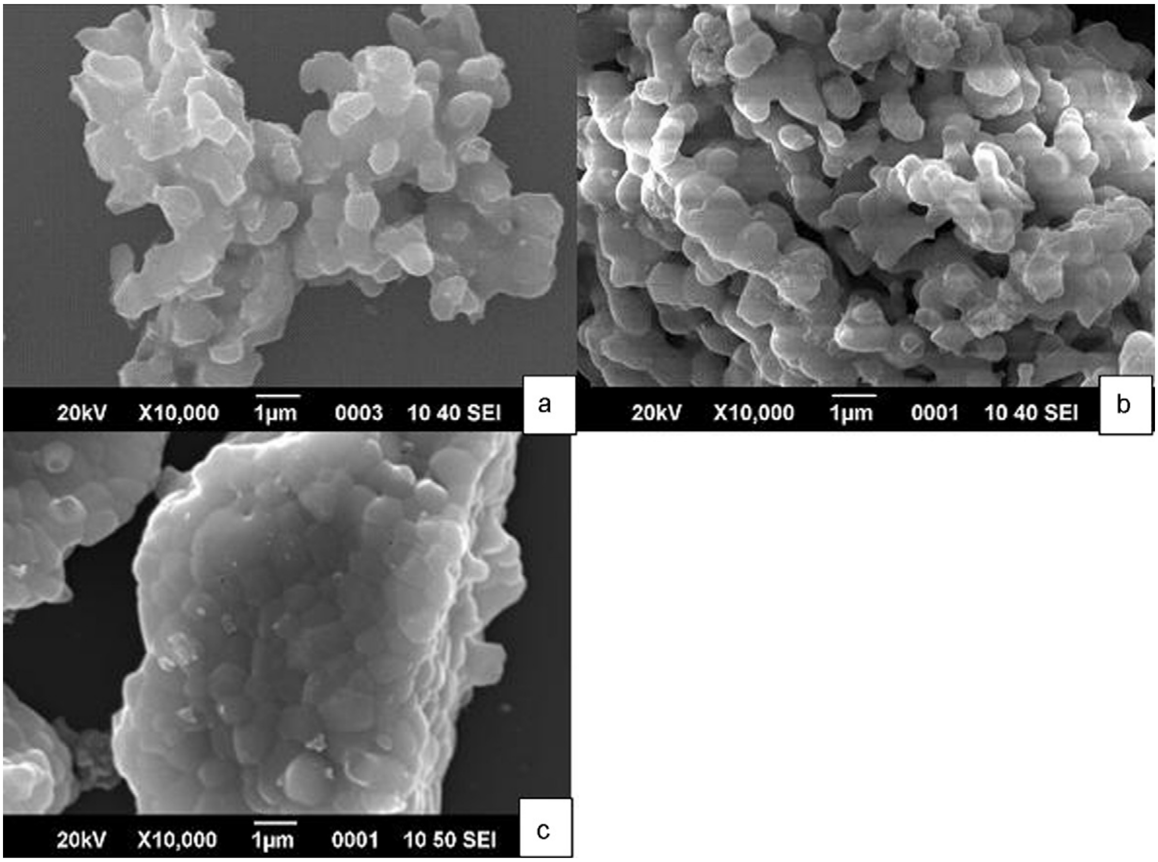

Fig. 7. SEM micrographs of HA particles synthesized via microwave radiation (a) 600 W for 10 min, (b) 850 W for 10 min, (c) 1000 W for 10 min.

did not have much effect on the morphology as shown in Fig. 7a–c.

4. Conclusion

In this study we have demonstrated that thermally stable phase pure HA can be rapidly synthesized from concentrated solution of calcium nitrate (1 M) and diammonium hydrogen phosphate (0.6 M) using microwaves. Degree of crystallinity and particle size can be controlled by altering microwave power output and exposure time to furnish hydroxyapatite with desired properties.

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