Thermal stability of a modified sol-gel derived hydroxyapatite nanopowders

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Abstract. Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) powder was successfully synthesized by a modified sol-gel method using a solution of calcium nitrate in ethanol, along with a solution of diammonium hydrogen phosphate in water and NH_4OH as starting materials. The Ca/P molar ratio was maintained at 1.67. The powder was subjected to furnace and microwave heating to compare the decomposition of HA and study the crystallite sizes. It was found that microwave heated powders were pure HAP up to 230°C with absence of secondary phases. However, XRD patterns show that furnace heated powders convert completely to β-TCP when treated at 750°C and 1000°C. This result was confirmed by the absence of hydroxyl bands in the FT-IR spectra for these temperatures.

1. Introduction

Hydroxyapatite (HA) $[Ca_{10}(PO_4)_6(OH)_2]$ is a biocompatible polycrystalline ceramic material that has chemical composition and crystal structure similar to the human bone and teeth [1]. In addition, HA exhibits biocompatibility for bone bonding, osteoconductivity, and activity [2, 3-5], due to its ability to form strong chemical bonds [2] with host material/tissue/bones, and thus has been recognized as a potential graft material [2]. Hydroxyapatite $Ca_{10}(PO_4)_6 OH_2$ has a network structure formed by the chains of $Ca(I)O_9$ and $Ca(II)O_6OH$ polyhedral interconnected by discrete PO_4-tetrahedra. It is observed that the cation or anion substitution at Ca, P or OH sites, or variation in the stoichiometry, leads to significant differences in surface and bulk properties of HA [6]. Calcium substitution allows the addition of metallic sites to the material and the anion substitutions such as PO_4^{3-} groups by HPO_4^{2-} and CO_3^{2-} and OH^- by F^-, modify the surface properties and the thermal stability of the material [7].

Various chemical synthesis methods including hydrothermal [8], sol-gel [9], sonochemical [10], precipitation [11], microemulsion [12], microwave [13], mechanochemical [14] and surfactant-assisted approach [15] are available for the preparation of HA nanostructures. The sol-gel method is preferred due to its low synthesis temperature, high product purity, homogenous molecular mixing and the ability to generate nano sized particles compared to other alternatives [16]. Sol-gel method for the preparation of HA can usually form fine-grain microstructure containing a mixture of nano- to submicron particles with crystalline structure. It has been reported that these crystals are very efficient to improve the contact and stability at the artificial/natural bone interface observed in vitro and in vivo environments [17].

The present study reports the synthesis of HA done at room temperature, by a sol-gel method. Furthermore, this work reports thermal stability studies of HA particles in the given temperature range, so that one can choose between microwave and furnace heating for different purposes.

2. Materials and methods

2.1. Synthesis of HA nanopowders

Calcium nitrate (Ca(NO3)2·4H2O,LOBA Chimie) di-ammonium hydrogen phosphate (NH4H2PO4, FLOKA),), ethanol and ammonia solution (to adjust the pH) were the reagents used for the synthesis. Briefly, 1.67 M calcium nitrate solution in ethanol (pH=10) was added dropwise to 1M NH4H2PO4 (pH= 10) (stirring at room temperature, when the white precipitate solution was obtained, it was aged for 92 h at room temperature. The gel obtained after aging process was filtered and washed repeatedly with de-ionized water and acetone. The filtered cake was dried at 80°C for 12h in an oven, and then was crushed using mortar and pestle. The synthesized powders are then subjected to heat treatment in an electric furnace and a domestic microwave oven for 4 h and 20 min and at different temperatures viz. 200, 250, 300, 500, 750, 1000°C and 180, 220, 230°C respectively to study their effects on the decomposition of HA into other phases. Microwave heating of HA done at lower temperatures, ensures phase purity and is much suited for biomedical applications. Electric furnace treatment is time and energy consuming than the microwave. The procedure used to generate HA is depicted in the flow chart given in the Figure 1.
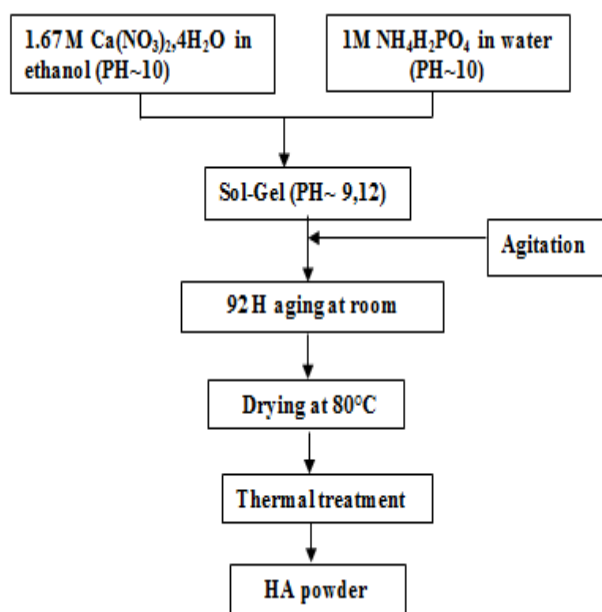

Figure 1. The flow chart of HA preparation.

2.2. Characterization of HA nanopowders

To investigate the phase composition and crystallinity of the sintered nano-HA, the X-ray diffraction (XRD) analysis was performed at a Discover model equipped with a monochromatized Cu-Kα radiation (λ= 1.5418 Å) in the 2θ range [10-80°] and a step size of 0.02° and a step duration of 2 s. Fourier transform infrared spectroscopy (FTIR: Bruker VERTEX 70 spectrometer) was used to analyze the functional group of the obtained powders. The spectra were recorded from 400 to 4000 cm^{-1} at 4 cm^{-1} resolution.

3. Results and discussion

The XRD patterns of the furnace and microwave heated powders are shown (in addition to the as-dried powder) in Figures 2 and 3 respectively. For the as-dried powder no characteristic peaks has been detected which means that the sample is amorphous while the furnace heated powders are of pure HA composition up to 500°C [2, 18-22]. However, it converts to β-TCP when treated at 750°C and 1000°C [22-24].
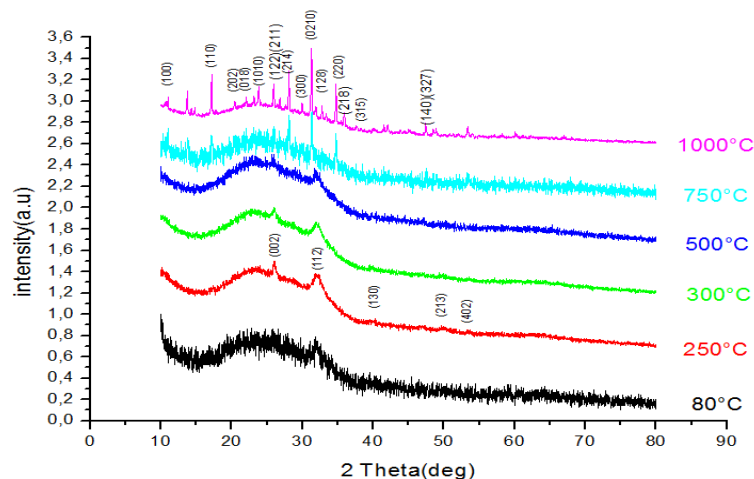

Figure 2. XRD pattern of as-dried and furnace heated powders.

Conversely, for microwave heated samples (Figure 3), it was conspicuously observed that, at all temperatures, there is no decomposition of HA into other secondary phases, and the sharp diffraction peaks indicate the high crystallinity of the heated samples. These results are confirmed by the FT-IR spectra of furnace and microwave heated samples as it is depicted at Figures 4 and 5 respectively. In fact, for the two samples the characteristic absorption bands at 3219 and 1649 cm^{-1} are attributed to adsorbed atmospheric water. The weak peak located at 3570 cm^{-1} corresponds to the vibrations of OH$^-$ ions in the HAP lattice [25]. The two weaker peaks, located at 771 cm^{-1} and 879 cm^{-1}, are associated with the carbonate group and clearly indicate its presence in the samples. The band at 1019-1023 cm^{-1} is assigned to triply degenerated (v_3) asymmetric stretching mode of P–O bond in hydroxyapatite structure. The characteristic doublet IR peaks around 1430 and 1471 cm^{-1} can be attributed to the vibrational frequencies of carbonate ions substituted at the phosphate site in apatite, so called B-type apatite [26, 27]. The band located at 559 cm^{-1} [28, 29] belong to triply degenerate v_4, O-P-O bending mode in the phosphate group.
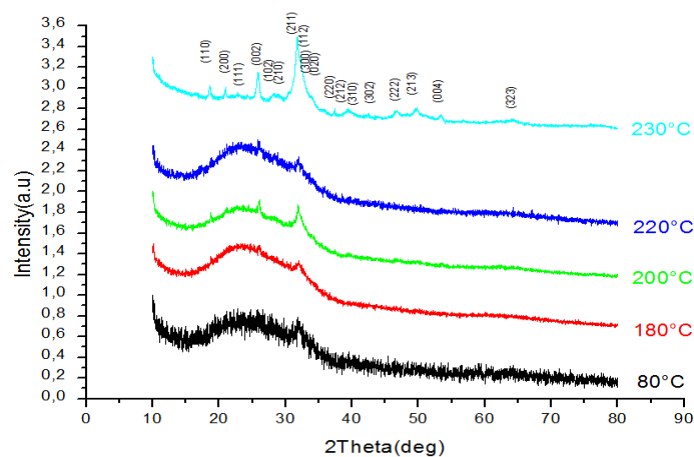

Figure 3. XRD pattern of as-dried and microwave heated powders.

Interestingly, for furnace heated samples, as the temperature increases, the OH^- peaks, at about 3418 cm^{-1}, disappears at 200°C, while the intensities of peaks at 3219 and 1649 cm^{-1} diminish indicating the removal of some amount of hydroxyl components such as crystalline water. We can also see that the peak of carbonate situated at 873°C disappear along with a diminution in intensity of the peaks located at 771, 1430 and 1471 cm^{-1} witch also indicate the removal of carbonate from the crystalline structure, this feature remains the same up to 500 °C. After heating at 750 °C, the OH^- absorption bands disappeared; Moreover, the spectrum of the sample treated at 750°C contains features from β-TCP, i.e. band shoulders around 1019, 1112 cm^{-1} [23], and also we note the presence of three bands situated at 490, 550 and 594 cm^{-1} witch belongs to triply degenerate v_4 O-P-O bending mode in the phosphate group. As shown in Figure 4, the characteristic peaks of β-TCP can be detected more obviously for the sample calcined at 1000°C, along with the absence of all peaks belonged to carbonate which means that we obtain a free carbonate structure at this temperature.

Contrarily, for microwave heated samples, it is conspicuously observed that there isn't removal of hydroxyl and carbonate components since all peaks relevant to them have the same feature for all microwave treated samples. Moreover, approximately no shift is observed for all peaks, which means that microwave heating is an outstanding technique since it converts the as-prepared apatite structure to hydroxyapatite rather than damaging it. Besides, microwave heating give us the hydroxyapatite structure in much shorter time (20 min) at a smaller temperature (180°C) compared to furnace heating (4h). To our knowledge, this is the first work that study phase stability of HA obtained by sol-gel process and heated by furnace and microwave oven. Furthermore, we report a total conversion of HA to β-TCP at 750°C.
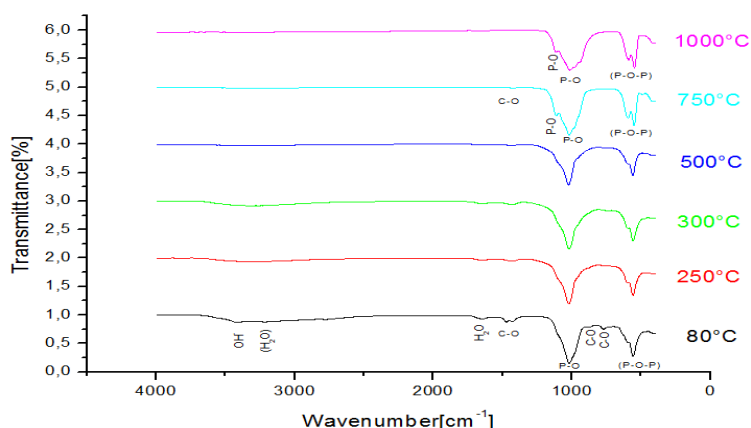

Figure 4. FTIR spectra of as-dried and furnace heated powders.
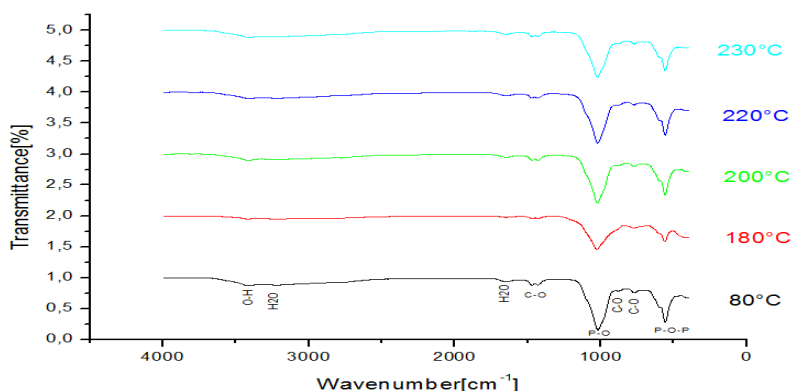

Figure 5. FTIR spectra of as-dried and microwave heated powders.

Another interesting point worthy to mention is that the amorphous structure obtained after drying process is of an apatitic structure (but not hydroxyapatite) since its XRD pattern show that it is amorphous whilst infra-red spectrum shows clearly the band of structural hydroxyl groups at 3570 cm^{-1} along with the other bands assigned to hydroxyapatite. Consequently, phase assertion come only after scrutinizing XRD patterns.

4. Conclusion
Thermal stability of synthesized HA was studied by furnace and microwave heating and it was found that microwave heated HA was pure with absence of secondary phases in all temperature, whilst, it was conspicuously observed that furnace heated HA convert to β-TCP when treated at 750°C and 1000°C. It is concluded that the microwave technique furnishes the product in much shorter time with high purity.

Acknowledgements

References
[1]   Suchanek W,Yashima M,Kakihana M and Yoshimura M 1996 Processing and mechanical properties of hydroxyapatite reinforced with hydroxyapatite whiskers *Biomaterials*17(17) 1715-23.
[2]   Bakan F,Laçin O and Sarac H 2013 A novel low temperature sol-gel synthesis process for thermally stable nanocrystalline hydroxyapatite Powder *Technol.* 233 295-302.
[3]   Bezzi G, Elotti G, Landi E, La Torretta T.M.G, Sopyan I and Tampieri A 2003 a novel sol-gel technique for hydroxyapatite preparation *Mater. Chem. Phys.*78 816-24.
[4]   Feng W, Sen L M, Peng L Y and Xin Q Y2005 A simple sol-gel technique for preparing hydroxyapatite nanopowders *Mater. Lett.* 59 916-19.
[5]   Lei L, Li L, Zhang L, Chen D and Tian W 2009 Structure and performance of nano-hydroxyapatite filled biodegradable poly((1,2-propanediol-sebacate)-citrate)elastomers *Polym. Degrad. Stab.* 4 1494-1502.
[6]   Cheikhi N, Kacimi M, Rouimi M, Ziyad M,Liotta L F,Pantaleo G and Deganello G 2005Direct synthesis of methyl isobutyl ketone in gas-phase reaction over palladium-loaded hydroxyapatite *J. Catal.* 232(2) 257-67.
[7]   Shimoda S,Aoba T, Moreno E C and Miake Y 1990 Effect of solution composition on morphological and structural features of carbonated calcium apatites *J. Dent. Res.*69(11) 1731-40.
[8]   Vázquez-Hernándeza F,Mendoza-Barrera C, Altuzar M, Meléndez-Lira M A,Santana-Aranda M, Olvera M andde la Olvera L 2010 Synthesis and characterization of hydroxyapatite nano particles and their application in protein adsorption *Mater. Sci. Eng. B.* 174 290-95.
[9]   Fathi M H and Hanifi A 2007 Evaluation and characterization of nanostructure hydroxyapatite powder prepared by simple sol-gel method *Mater. Lett.*61(18) 3978-83.
[10]   Giardina M A and Fanovich M A 2010 Synthesis of nanocrystalline hydroxyapatite from Ca(OH)$_2$ and H$_3$PO$_4$ assisted by ultrasonic irradiation *Ceram. Int.* 36 1961-69.
[11]   Li Z,Wang P and Wu Z 2005 Preparation of nano sized hydroxyl apatite particles at low temperatures *J. Mater. Sci.* 40 6589-91.
[12]   Bose S and Saha S K 2003 Synthesis and characterization of hydroxyapatite nano powders by emulsion technique *Chem. Mater.* 15 4464-649.
[13]   Mishra V K,Srivastava S K, Asthana B P andKumar D J 2012 Structural and spectroscopic studies of hydroxyapatite nanorods formed via microwave-assisted synthesis route *J. Am. Ceram. Soc.* 95 2709-15.

[14]   Nasiri-Tabrizi B, Honarmandi P, Ebrahimi-Kahrizsangi R and Honarmandi P 2009 Synthesis of nanosize single-crystalhydroxyapatite via mechanochemical *method Mater. Lett.* 63 543-46.

[15]   Coelho J M,Moreira J A,Almeida A and Monteiro F J 2010 Synthesis and characterization of HAP nanorods from a cationic surfactant template method*J. Mater. Sci. - Mater. Med.*21 2543-9.

[16]   Eshtiagh-Hosseini H, Housaindokht M R and Chahkandi M 2007 Effects of parameters of sol-gel process on the phase evolution of sol-gel-derived hydroxyapatite *Mater. Chem. Phys.* 106 310.

[17]   Li P and de Groot K 1994 Better bioactive ceramics through sol-gel process *J. Sol-Gel Sci. Technol.* 2 797.

[18]   Jadalannagari S,More S,Kowshik M andRamanan S R 2011 Low temperature synthesis of hydroxyapatite nano-rods by a modified sol-gel technique *Mater. Sci. Eng., C*31(7) 1534-8.

[19]   Santhosh SandPrabu S B 2013 Thermal stability of nano hydroxyapatite synthesized from sea shells through wet chemical synthesis *Mater. Lett.* 97 121-4.

[20]   Kuriakose T A,Kalkura S N,Palanichamy M,Arivuoli D,Dierks K,Bocelli G andBetzel C 2004 Synthesis of stoichiometric nano crystalline hydroxyapatite by ethanol-based sol-gel technique at low temperature *J. Cryst. Growth* 263(1) 517-23.

[21]   Anee T K,Ashok M,Palanichamy M andKalkura S 2003 NA novel technique to synthesize hydroxyapatite at low temperature *Mater. Chem. Phys.* 80(3) 725-30.

[22]   Rangavittal N, LandaCánovas A R,González Calbet J M andVallet Regí M 2000 Structural study and stability of hydroxyapatite and β-tricalcium phosphate: Two important bioceramics*J. Biomed. Mater. Res.*51(4) 660-8.

[23]   Sanosh K P,Chu M C, Balakrishnan A,Kim T N andCho S J 2010 Sol-gel synthesis of pure nano sized β-tricalcium phosphate crystalline powders *Curr. Appl. Phys.*10(1) 68-71.

[24]   Pan H B and Darvell B W 2009 Solubility of TTCP and β-TCP by solid titration *Arch. Oral. Biol.*54 671-7.

[25]   Poinern G J E,Brundavanam R L X T,Djordjevic S,Prokic M and Fawcett D 2011 Thermal and ultrasonic influence in the formation of nanometer scale hydroxyapatite bioceramic *Int. J. Nanomedicine* 6 2083.

[26]   Manjubala I and Sivakumar M 2001 In-situ synthesis of biphasic calcium phosphate Ceramics using microwave irradiation *Mater. Chem. Phys.*71 272-8.

[27]   Ito A, Nakamura S,Aoki H,Akao M,Teraoka K,Tsutsumi S andTateishi T 1996 Hydrothermal growth of carbonate-containing hydroxyapatite single crystals *J. Cryst. Growth* 163(3) 311-7.

[28]   Fowler B O 1974 Infrared studies of apatites. Vibrational assignments for calcium, strontium, and barium hydroxyapatites utilizing isotopic substitution *Inorg. Chem.*13 194.

[29]   Klee W E and Engel G 1970 Infrared spectra of the phosphate ions in various apatites*J. Inorg. Nucl. Chem.* 32 1837.