Thermal stability of a modified sol-gel derived hydroxyapatite nanopowders

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Abstract. Hydroxyapatite Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{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\textsubscript{4}OH 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\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{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\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}OH\textsubscript{2} has a network structure formed by the chains of Ca(I)O\textsubscript{9} and Ca(II)O\textsubscript{6}OH polyhedral interconnected by discrete PO\textsubscript{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\textsubscript{4}\textsuperscript{3-}, groups by HPO\textsubscript{4}\textsuperscript{2-}, and CO\textsubscript{3}\textsuperscript{2-} and OH\textsuperscript{-} by F\textsuperscript{-}, 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.

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].

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.
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$^{-1}$ which 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 $\beta$-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$^{-1}$ which belongs to triply degenerate $\nu_4$ O-P-O bending mode in the phosphate group. As shown in Figure 4, the characteristic peaks of $\beta$-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 $\beta$-TCP at 750°C.

![Figure 4. FTIR spectra of as-dried and furnace heated powders.](image)

![Figure 5. FTIR spectra of as-dried and microwave heated powders.](image)
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 $\beta$-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.

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