



Solution combustion synthesis and characterization of strontium substituted hydroxyapatite nanocrystals

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ABSTRACT

In the present study, synthesis of monophasic Sr-HAp nanocrystals using a single step Solution Combustion Synthesis (SCS) process is reported. Effects of important process parameters on the formation of monophasic Sr-HAp nanocrystals were investigated to optimize the process for cost effective synthesis. X-ray Diffraction (XRD) and transmission electron microscopy (TEM) studies of as-synthesized powders (Sr ranging from 0 to 30%) revealed close packed hexagonal structure, with individual primary particle sizes ranging from 15 to 70 nm length and 5 ± 1 nm diameter. Scanning Electron Microscopy (SEM) studies showed that Sr substitution in HAp increased the aspect (L/D) ratio of primary nanorod and reduced the secondary agglomerate coarsening. Fourier Transform-Infrared (FTIR) and Energy Dispersive Spectroscopy (EDS) studies confirmed the presence of appropriate concentrations of phosphates and hydroxyl groups along with small amounts of carbonates in the as-synthesized Sr-HAp. Differential Scanning Calorimetry (DSC) studies up to 400 °C and XRD patterns of powders calcined at 1100 °C proved that Sr addition in HAp enhances the stability by suppressing the phase transformation during further consolidation. In effect, nano Sr-HAp powders synthesized using SCS process resembled the structural and chemical nature of bone mineral and could be used as a possible candidate material for hard tissue replacement and drug delivery systems.

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1. Introduction

Research on modification of composition in engineering alloys and compounds is being carried out continuously to improve the properties and surface characteristics for enhancing their service life. In particular, it is required for biomaterials to achieve fast recovery and to minimize subsequent surgical treatments in patients [1–3]. Hydroxyapatite $\{Ca_{10}(PO_4)_6(OH)_2\}$ is considered to be an important bioactive ceramic material, since it resembles the biological apatite and can be prepared as a dense or porous body as well as a thin film with excellent biocompatibility and osteoconductivity [4–7]. Synthetic nanohydroxyapatite is preferred for bio applications, since their functional properties are similar to natural apatite and better than that of their micro counterparts [5,8]. Synthetic hydroxyapatite is a non-stoichiometric compound and metal cations like Na^+ , K^+ , Zn^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+} and Fe^{3+} can be readily substituted in calcium positions. The substitutions improve the mechanical properties and bioactivity of HAp for normal functioning of living organisms inside the body. Strontium can be substituted in the crystal lattice of synthetic HAp without any solubility limit. However, low dosages are preferred because of their beneficial effects in local delivery of Sr^{2+} for osteoporotic bone treatments and enhancement of bone regeneration during hard tissue replacements by preventing the

undesirable bone resorption [9–16]. In addition, Sr substitution also stabilizes the HAp phase against any phase transformation as well as crystal growth during high temperature sintering, during the manufacture of the implant parts [12].

Several research works on synthesis of Sr-HAp using sol–gel process [1,4–9,11–13,17,18], precipitation method [10,14,19], hydrothermal method [20], solvothermal method [21], microwave processing [7], mechanical alloying [9] and biomimetic synthesis [22] have been reported. However, these processes are time-consuming and require high-temperature calcination to get pure Sr-HAp. In recent times, combustion synthesis has emerged as a simple, versatile and cost-effective exothermic reaction method, initiated by a fuel (e.g. urea or glycine) at low ignition temperature (T_{ig}). This exothermic reaction produces a high flame temperature (T_f) ranging from 700 to 1500 °C depending on the nature of reactants used for the synthesis of advanced metallic alloys, ceramics and composites in nanosizes, allowing uniform and homogeneous substitution of dopants in these materials [23–26].

Although several investigators have worked on SCS of pure HAp [25–27], reports on the synthesis of (i) Sr-HAp and (ii) nanocrystalline Sr-HAp by SCS process, are very rare. This paper reports the synthesis of nanocrystalline Sr-HAp by SCS process using calcium acetate, strontium chloride and diammonium phosphate as precursors. Effects of time, temperature and pH of the solution on the formation of monophasic Sr-HAp are also discussed. The reason behind the usage of acetate precursors for combustion technique is that, it is more environment-friendly than the

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conventional nitrate precursors which release NO_x gases into the atmosphere during combustion. Moreover, acetate precursors may also substitute carbonates in the HAp lattice for phosphate (B-type) or hydroxyl (A-type) group so that it performs as an effective natural bone mineral substitute with improved properties for biomedical applications. Several authors have reported the formation of stable biphasic calcium phosphates (HAp along with tricalcium phosphates (TCP)) during the synthesis [10–12], whereas this work attempts to produce a pure nanocrystalline Sr-HAp in a single step process. This paper also reports the structure, morphology and chemical characteristics of the as-synthesized powders as a function of Sr substitution (0 to 30 mol%) using XRD, FTIR, SEM, TEM equipped with EDS and DSC studies. Sr substitution was limited to 30 mol% because high dosages may induce improper bone mineralization during service and are not preferred for bioapplications [10].

2. Materials and methods

Sr substituted HAp designed as $\text{Ca}_{10-x}\text{Sr}_x(\text{PO}_4)_6(\text{OH})_2$, where the compositional parameter 'x' ranges from 0 to 3 (0 to 30 mol%) were combustion synthesized using aqueous precursors. Initially, pure HAp was prepared at an ignition temperature of 500 °C by varying the synthesis time to get HAp without any impurities. Then, 15 mol% Sr-HAp powders were synthesized using the same procedure over a range of time, temperature and pH for optimizing the parameters for the combustion synthesis of Sr-HAp. Using this optimized procedure, 0 to 30 mol% Sr substituted HAp powders were produced.

2.1. Synthesis of pure HAp and Sr-HAp

A wet paste containing 69 mM calcium acetate and 41.5 mM diammonium phosphate was prepared and its pH was adjusted to 7.4 by adding appropriate amounts of tris hydroxyl methyl amino methane. Finally, urea ($\text{CH}_4\text{N}_2\text{O}$) was added as a fuel for combustion. This urea decomposes into cyanuric acid (HCNO) and ammonia (NH_3), when heated above 300 °C. This gaseous mixture spontaneously ignites at 500 °C in an aqueous medium and raises the local temperature of the solution. Hence the prepared solution was kept at the ignition temperature of 500 °C for 3, 5, 10, 20 and 30 min in a muffle furnace for combustion to occur, keeping all the other parameters constant. Then the crucible was taken out and spongy mass obtained was crushed to obtain fine powders. To study the influence of process parameters on Sr substitutions during combustion process, optimal 15 mol% Sr-HAp was synthesized following the same procedure at different synthesis times (20, 30 and 40 min), at different temperatures from 300 °C to 600 °C by an increment of 100 °C with three different pH values as 5 (acidic), 7.4 and 10 (basic). In all these experiments, one parameter was changed keeping other two parameters constant. Further trials for Sr substitutions (5, 10, 15, 20, 25 to 30 mol%) were carried out using optimized parameters. The (Ca + Sr)/P ratio was maintained at 1.67 to get 100% Sr-HAp with controlled solubility and optimum bioactivity. To study the thermal stability during sintering at higher temperatures, calcination of pure HAp and 15 mol% Sr-HAp samples was performed in air at 1100 °C for 2 h.

2.2. Characterization

XRD analysis was carried out using SHIMADZU LabX-6000 model X-Ray Diffractometer for obtaining the diffraction pattern of the synthesized samples with a scan speed of $2^\circ/\text{min}$. using Cobalt ($K\alpha$) radiation ($\lambda = 1.78897 \text{ \AA}$). The phases present, crystal structure, change in lattice parameters as well as crystallite sizes of synthesized powders were characterized using XRD. FTIR spectra were obtained using SHIMADZU FTIR system with 20 scans in the range of $400\text{--}4000 \text{ cm}^{-1}$ using KBr as beam splitter. Secondary electron images of representative samples were taken using JEOL-JSM 6360 model SEM equipment

at 25 kV. High resolution (HRTEM) images, Selected Area Diffraction (SAD) patterns and elemental analysis of the synthesized powders were obtained using TEM/EDS (JEOL) at 200 kV and X-ray detector facility. Thermal analysis was carried out at a heating rate of 4° per minute using a Perkin-Elmer DSC to obtain information about the thermal stability of synthesized powders.

3. Results and discussion

Structure and properties of as-synthesized and calcined Sr-HAp powders studied from XRD, FTIR spectroscopy, SEM, TEM and DSC investigations are discussed in the following sections.

3.1. Phase analysis of as-synthesized pure HAp

The minimum time required for the formation of crystalline hydroxyapatite at 500 °C during combustion reaction was studied using XRD. Fig. 1A shows the XRD patterns of five HAp samples prepared with different synthesis times, ranging from 3 to 30 min at 500 °C. XRD patterns indicated the presence of partially crystalline calcium phosphates in the sample synthesized for 3 min, while fine crystalline pure HAp was found in the sample synthesized for 30 min. Thus it was concluded that the degree of crystallinity increased with the increased time of combustion.

XRD patterns were analyzed for the presence of any unreacted precursors like calcium acetate, calcium or ammonium phosphates and impurity phases like oxides. XRD patterns of samples synthesized

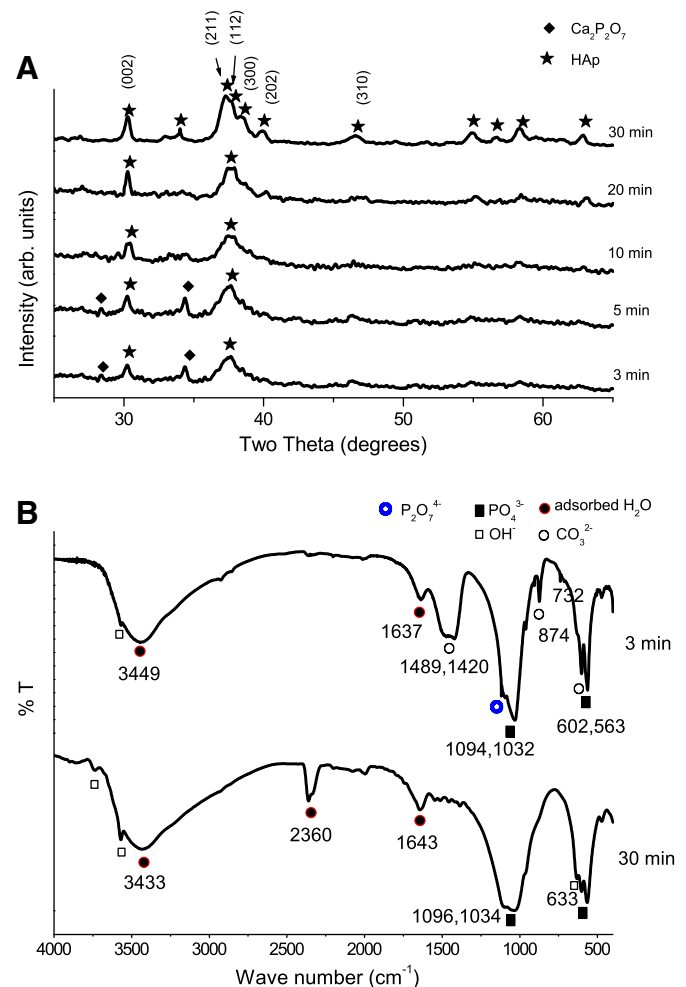


Fig. 1. Results of pure HAp samples synthesized at 500 °C with 7.4 pH (A) XRD patterns, (B) FTIR spectra of selected samples.

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