



Original Research Paper

Effect of salt concentration on the electrical and morphological properties of calcium phosphates obtained via microwave-induced combustion synthesis



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ABSTRACT

Calcium phosphates (CaP) have been widely used in biomedical applications. One of the most versatile techniques for obtaining CaP is auto-combustion synthesis. This technique stands out because of its low cost and high efficiency; however, the difficulty of controlling the size and morphology of the product is its principal disadvantage. The aim of this study was to synthesize calcium phosphates through microwave-induced and salt-assisted solution combustion synthesis. The initial ratio of Ca/P was 1.5, employing urea as fuel and potassium chloride as an additive. The morphology and the electrical properties of CaP in relation to the amount of salt added were evaluated using scanning electron microscopy (SEM) and impedance spectroscopy, respectively. It was found that the inclusion of salt during the synthesis affects the morphology of calcium phosphates, creating whisker-like structures, with lengths approximately between 500 nm and 1 μm and widths between 30 nm and 300 nm, which depend on the salt concentration. Calcium pyrophosphate was the major phase of the synthesized product without the addition of salt, and hydroxyapatite (HAP) and chlorapatite (CAP) when salt was included. The dielectric constant exhibited lower values for the samples rich in calcium pyrophosphate and values between 16 and 32 for HAP and CAP at 1 kHz.

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1. Introduction

Calcium phosphates are biomaterials of great interest for biomedical applications such as bone replacement, tissue engineering, dental materials, and drug delivery agents [1–7], principally because of their high degree of biocompatibility and their composition, which is similar to natural bone. Various methods, such as solid state synthesis [8,9], chemical methods, sol-gel [10,11], coprecipitation [12,13], hydrothermal [14], hydrothermal assisted by templates [15,16], combustion [17–22], and other techniques [23] have been reported for obtaining CaP. Synthesis by combustion has been of great interest for obtaining different oxides. This technique stands out because of its low cost and high efficiency. Self-combustion allows obtaining large quantities of material, opening the possibility of scaling it to the industrial level for high value-added products. However, the difficulty of control-

ling the size and the morphology of the synthesized products is its principal disadvantage. Self-combustion is a technique that involves exothermic and redox reactions at high temperatures between a fuel and an oxidizing agent. Most of the materials obtained using the self-combustion technique exhibit grains of micrometric and even nanometric sizes with granular or spherical morphologies, but they are generally highly aggregated. Over the last decade, research studies have been conducted in order to find ways of controlling the morphology and decreasing the aggregation level of materials synthesized through combustion techniques. These studies are focusing on the control of the variation of some thermodynamic parameters and the use of chemical compounds such as surfactants, cosurfactants, and others [21,22]. A methodology that has shown promising results in controlling the morphology is synthesis via microwave-induced and salt-assisted solution combustion [24]. With this technique, various structures have been obtained with a high degree of dispersion and whisker-like morphology [23,25]. Furthermore, the method of synthesis has a great influence on the electrical properties of the

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materials obtained. The dielectric properties of calcium phosphates are important in some applications such as the process of bone repair [26–33]. Fracture healing can be improved through the presence of electric fields, because bone growth increases with negative charge and decreases with positive charge. In calcium phosphates, this mechanism seems to involve adsorption of Ca^{2+} ions, which can act as nucleation centers [33]–[38]. Hydroxyapatite (HAP) can be polarized. This calcium phosphate can help the osteobonding and growth of new bone via charge accumulation [34,35]. Moreover, biocompatible systems can be used in the manufacture of biosensors. The aim of the present study is to identify the effect of KCl concentration used as an additive during combustion synthesis on the morphology of the powders obtained and their dielectric properties.

2. Materials and methods

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ -MERCK), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$ -Scharlab) Urea ($\text{CO}(\text{NH}_2)_2$ -MERCK), nitric acid (HNO_3 -MERCK), and potassium chloride (KCl-Merck) were used as raw materials. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ were mixed in 15 ml of distilled water under constant stirring with a constant ratio of $\text{Ca}/\text{P} = 1.57$ (in 100 ml beakers). Afterward, sufficient HNO_3 was added to the mix to dissolve the precipitate previously formed. To assure the addition of the right amount of fuel (urea) and reach the maximum combustion temperature, the parameter ϕ was defined in Eq. (1) [36], setting the stoichiometric ratio oxidizer-combustible $\phi = 1$. During this stage, the solution remained under constant stirring for one hour.

$$\phi = \frac{\sum \text{Coefficient. Reducing elements} \times \text{Valence}}{\sum \text{Coefficient. Oxidant elements} \times \text{Valence}} \quad (1)$$

In order to control the amount of salt added, the parameter γ was defined as the ratio of CaP to be prepared to the amount of added salt. Solutions were prepared with γ values of 0, 0.07, 0.11, 0.16, 0.33, and 1 and renamed as γ_0 , γ_1 , γ_2 , γ_3 , γ_4 , and γ_5 . 10 ml of additional water was added in cases of a large amount of KCl. The mixtures were placed separately on a plate heated to 60°C with vigorous stirring, and each one remained on the plate until the solvent was almost totally evaporated. The beaker with each solution was taken separately to a microwave oven (LG brand) of 2.4 GHz. There they were placed between alumina refractories, maintaining microwave irradiation on all samples for 1 minute 30 s, until combustion. Each system was left in the microwave for 20 min in order to avoid thermal shock of the reactor. Subsequently, each sample was washed three times using vacuum filtration with hot water in order to remove the excess of KCl present. The recovered material was dried in an electric oven for 30 min at 70°C . The powders obtained were suspended in 80 ml of isopropyl alcohol and then ultrasonicated in 500 W Cole Palmer equipment with different amplitudes for 1 h. Finally, the powders were dried for 2 h at 90°C .

The structure of the obtained materials was evaluated using X-ray diffraction with a double circle multipurpose diffractometer (Xpert-Pro, PAN analytical) with Cu-K α radiation ($\lambda = 0.15406$ nm) and diffraction angles between 10° and 50° (2θ). Raman spectroscopy measurements were obtained with a confocal Raman spectrometer (Labram, Horiba) using a laser of 532 nm and 5 mW. For the morphological analysis, samples were prepared via ultrasonication in isopropyl alcohol on a Cole Parmer instrument of 500 W with 80% amplitude for 1:20 h. SEM images were obtained with a scanning electron microscope (Carl Zeiss, EVO MA10), and then image analysis and statistical analysis were performed with GNU and InfoStat software, respectively. For

dielectric measurements, the powders were pressed uniaxially at 15000 KPa to form discs of 0.8 cm in diameter and 0.2 cm in thickness. Afterward, they were tested on an LCR meter (HIOKI 3522-50) within a frequency range of 0.1–200 kHz at room temperature.

3. Results and discussion

3.1. Structure of the obtained samples

Fig. 1 shows the XRD patterns for samples γ_0 , γ_1 , and γ_5 , respectively. The predominant phase without the addition of KCl was calcium pyrophosphate $\text{Ca}_2\text{P}_2\text{O}_7$ (JCPDS 01-073-0440), with a minority phase of calcium phosphate hydrate $\text{Ca}(\text{PO}_3)_2 \cdot 2\text{H}_2\text{O}$ (JCPDS 00-003-0331). With the presence of KCl, apatite phases, such as the hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (JCPDS 01-074-0566) and chlorapatite $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ (JCPDS 01-70-1454), were formed. On increasing the concentration of KCl, more chlorapatite and $\text{Ca}_2\text{P}_2\text{O}_7$ formation was detected (sample γ_5), with decreased HAP.

Fig. 2 shows Raman spectra between 300 and 1500 cm^{-1} at 25°C . Internal vibration modes of tetrahedral group PO_4^{3-} at 960 cm^{-1} correspond to a symmetric stretching of the P–O bond. The vibrational band centered at 429 cm^{-1} can be attributed to bending modes of the O–P–O bond. Bands present at 1046 cm^{-1} and 1074 cm^{-1} are related to the asymmetrical stretching of the P–O bond from the group PO_4^{3-} [37,38]. These results agree with the results obtained via X-ray diffractograms of the samples γ_1 ,

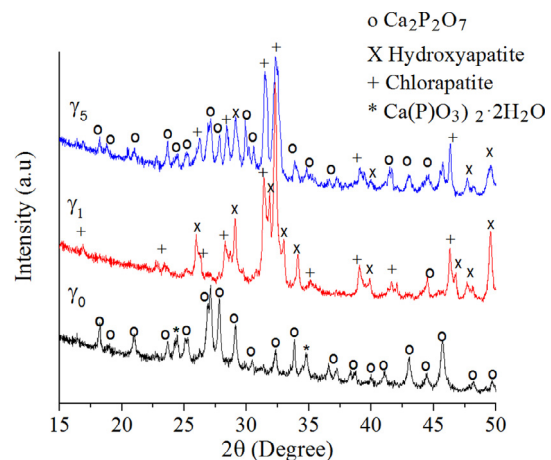


Fig. 1. X-ray spectrum for samples γ_0 , γ_1 , and γ_5 .

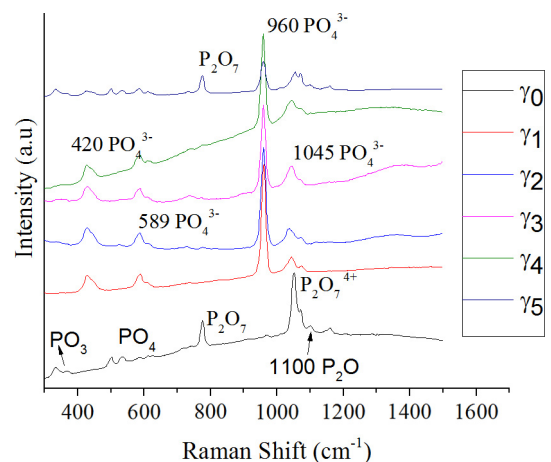


Fig. 2. Raman spectrum for samples depending on the salt content (γ).

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