

The effects of high amounts of Al and Zn on the structural properties of hydroxyapatite prepared by sol-gel method

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In the present study, the effects of high amounts of Al and Zn additives on the crystal structure, phase composition and microstructure of hydroxyapatite (HAp) samples synthesized by sol-gel route were investigated by X-ray diffraction (XRD), Fourier transformation infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) techniques. The values of the crystallinity percent, crystallite size, lattice parameter of a and volume of the unit cell decrease gradually with increasing amount of the co-additives. The formation of the new phases is observed and these phases become dominant with increasing amount of Al and Zn. The morphology of HAp, shape and size of the particles are also affected by the amount of Al and Zn. As expected, a gradual decrease in the Ca/P molar ratio is observed.

Key words: Hydroxyapatite, Crystal Structure, Crystallinity Percent, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD).

Introduction

Undoubtedly, calcium phosphates (CaPs) are some of the most popular bioceramics. Hydroxyapatite (HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is a member of CaPs, and there is a great interest in it for biomedical applications since it is a non-toxic, chemically stable, osteoconductive, bioactive, non-allergenic and biocompatible material. Furthermore, the chemical composition of HAp is similar to the inorganic components of bones and teeth [1-11]. There are a lot of methods used to synthesize HAp such as sol-gel, hydrothermal, sonochemical, solid state reactions, mechanochemical, combustion, surfactant template, microwave irradiation and spray pyrolysis. Among these techniques, sol-gel is one of the most-preferred methods because this method has a lot of advantages such as the high product purity and lower costs for preparing the nanosized HAp having high purity and crystallinity [12-17]. Several elements such as Zn, Mg, Al, Sr and Fe have frequently been used as the additives to improve or control the structural properties of HAp or HAp based ceramic materials [18-22]. There is no doubt that Zn is one of the most-preferred elements used for the above-mentioned aim. Furthermore, Zn is an essential trace element in human bone and plasma [23]. Contrary to Zn, trivalent Al is not an essential trace element in body but still it has been used as a dopant for preparing HAp to understand its biological effects in more detail [24].

Even though the effects of low or high concentrations

of Al and Zn on the characteristic properties of HAp such as crystal structure, morphology and biocompatibility have been investigated and reported by many researchers, no studies could be found related to the effects of high concentrations of these two elements as co-additives on the structural properties of HAp. Taking this into account, we prepared Al and Zn containing HAp-based ceramic samples, and characterized these using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy.

The main objective of this study is to present a detailed report related to the effects of high concentrations of Al and Zn co-additives on the structural properties of HAp.

Materials and Method

All the starting chemicals including calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, CN), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$, DAP), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, AN) and nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, CN) were obtained from Sigma-Aldrich and used without further purification. As a reference sample, the pure hydroxyapatite (HAp) was synthesized as follows. 0.5 M CN and 0.3 M DAP solutions were prepared using distilled water as a solvent. The DAP solution was added drop-wisely to the CN solution, and an opaque mixture was obtained. This mixture was continuously stirred at 85 °C for 5 h, and dried in an oven at 160 °C for 16 h. The dried sample was heated in an electric furnace at 900 °C for 1.5 h, and the HAp powder was obtained. To prepare Al and Zn containing calcium phosphate samples, the AN and ZN were dissolved in the CN solution. The same experimental procedure with the above-mentioned processes was used to synthesize Al and Zn containing calcium

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phosphate ceramics. For all the samples, the values of the molarities were (0.5-2x) M CN, x M AN, x M ZN and 0.3 M DAP. The x values were chosen as 0, 0.0375, 0.0750 and 0.1125, and the as-prepared samples were named as AZ1, AZ2, AZ3 and AZ4, respectively. The (Ca + Al + Zn)/P molar ratios were adjusted to the value of 1.67.

X-ray diffraction (XRD) patterns of the as-synthesized samples were recorded using a Bruker D8 Advance diffractometer operated at 40 kV and 40 mA. Using the KBr pellet method, Fourier transform infrared (FTIR) spectra were collected by a Perkin Elmer Spectrum One spectrometer in the spectral range of 400-4000 cm⁻¹. The morphological observations were done by using a JEOL JSM 7001F scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX, Oxford Instruments INCA energy 350) spectrometer.

Results and Discussion

Fig. 1 presents XRD patterns of the as-prepared samples. For the pure HAp (AZ1) sample, the major phase of the standard hydroxyapatite (JCPDS card No: 09-0432) and minor phases of β -tricalcium phosphate (β -TCP, JCPDS card No: 09-0169) and calcium oxide (CaO, JCPDS card No: 37-1497) were observed. While the HAp remained as the major phase, the minor phase of CaO disappeared with the addition of Al and Zn for the rest samples (AZ2, AZ3 and AZ4). The formation of minor phases of aluminum phosphate (AlPO₄,

JCPDS card No: 72-1161) and calcium zinc phosphate (Ca₁₉Zn₂(PO₄)₁₄, JCPDS card No: 48-1196) was also detected. From the third sample (AZ3), the formation of zinc phosphate (Zn₃(PO₄)₂, JCPDS card No: 76-0604) phase was started. As expected, the proportion of zinc and aluminum-based phases increased with increasing amounts of the additives of Zn and Al.

The average crystallite size (*D*) is calculated using the following Scherrer equation [25].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of the X-rays ($\lambda = 0.15406$ nm for CuK α radiation), β is the full width at half maximum (FWHM) and θ is the diffraction angle. Using XRD data, the crystallinity percent (X_C %) is computed from the following relation [15]:

$$X_C \% = \frac{\sum A_C}{\sum A_C + \sum A_A} \times 100 \quad (2)$$

where $\sum A_C$ is the total area under crystal peaks, and $\sum A_A$ is the total area under amorphous peaks. The lattice parameters (*a* and *c*) and volumes of the unit cell (*V*) are estimated using the following relations, respectively [25]:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (3)$$

$$V = 0.866a^2c \quad (4)$$

where *d* is the distance for two adjacent planes and *h*, *k* and *l* are the Miller indices.

The calculated values of the above-mentioned parameters are listed in Table 1. All the parameters are affected by the amount of the co-additives. With increasing amount of the co-additives, a gradual decrease in the values of the average crystallite size, both lattice parameters, volume of the unit cell and crystallinity percent is seen from Table 1, except for the *c* value of AZ2 sample. This is an expected result since there is a significant imbalance among the ionic radii of Ca²⁺ (0.099 nm), Zn²⁺ (0.074 nm) and Al³⁺ (0.051 nm). Since there is a decrease in the calculated values of both lattice parameters, Al and/or Zn ions may probably occupy both Ca²⁺ and OH⁻ sites [21]. These findings are in very good agreement with the earlier

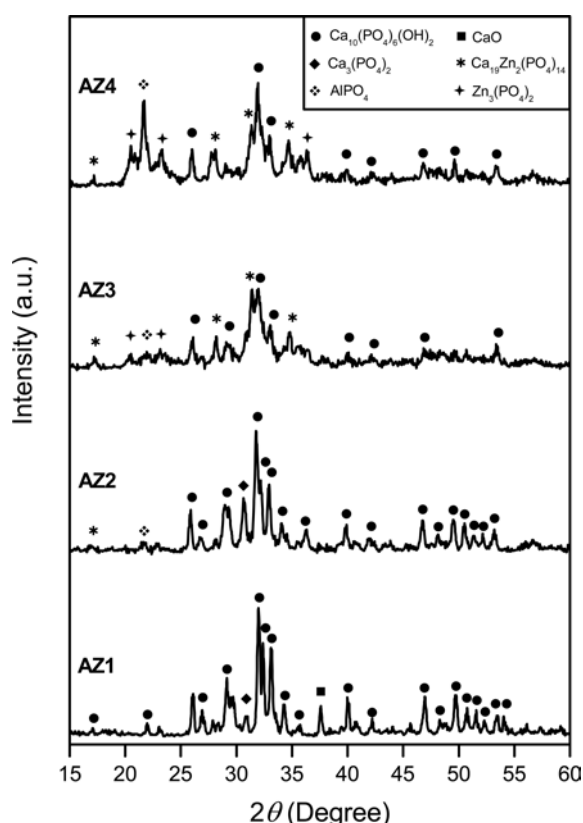


Fig. 1. X-ray diffraction (XRD) patterns of the as-synthesized samples.

Table 1. The calculated values of crystallite size (*D*), crystallinity percent (X_C %), lattice parameters (*a* and *c*) and volume of unit cell for all samples.

Sample	<i>D</i> (nm)	X_C %	<i>a</i> (nm)	<i>c</i> (nm)	<i>V</i> (nm ³)
AZ1	25.84	74.2	0.9419	0.6874	0.5281
AZ2	18.93	69.3	0.9412	0.6880	0.5278
AZ3	17.89	45.8	0.9400	0.6843	0.5236
AZ4	15.27	30.7	0.9384	0.6823	0.5203

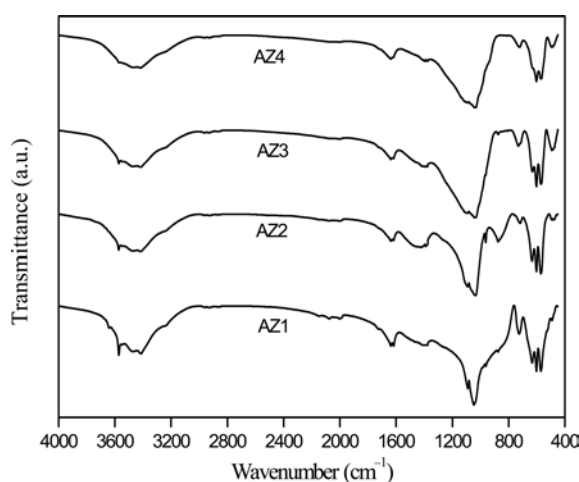


Fig. 2. FTIR spectra of the as-synthesized samples.

reports [18, 20, 24, 26, 27]. Additionally, for the AZ3 and AZ4 samples the secondary phases are dominant.

The crystallite size calculated for these phase is 15.51 nm for AZ3 and 12.36 nm for AZ4. These are so close to the average values computed using the peaks belonging to the apatitic structure and confirm the decrease in the crystallite size.

For each sample, the bands belonging to the functional groups of hydroxyl and phosphate, as well as the adsorbed water are detected from the FTIR spectra given in Fig. 2. The observed bands on the FTIR spectra of the as-synthesized samples and their assignments are as follows. The bands related to the phosphate group are observed at 570, 602 and 1034 cm^{-1} . The bands associated to the vibrational modes of the hydroxyl group are detected at 634 and 3571 cm^{-1} . The very broad band centered at 3411 cm^{-1} and a narrow one at 1640 cm^{-1} are due to the presence of adsorbed water [28-31]. A wide band centered at about 1425 cm^{-1} is related to the carbonate group, which is a common impurity for both synthetic and natural HAp [32]. The intensity and

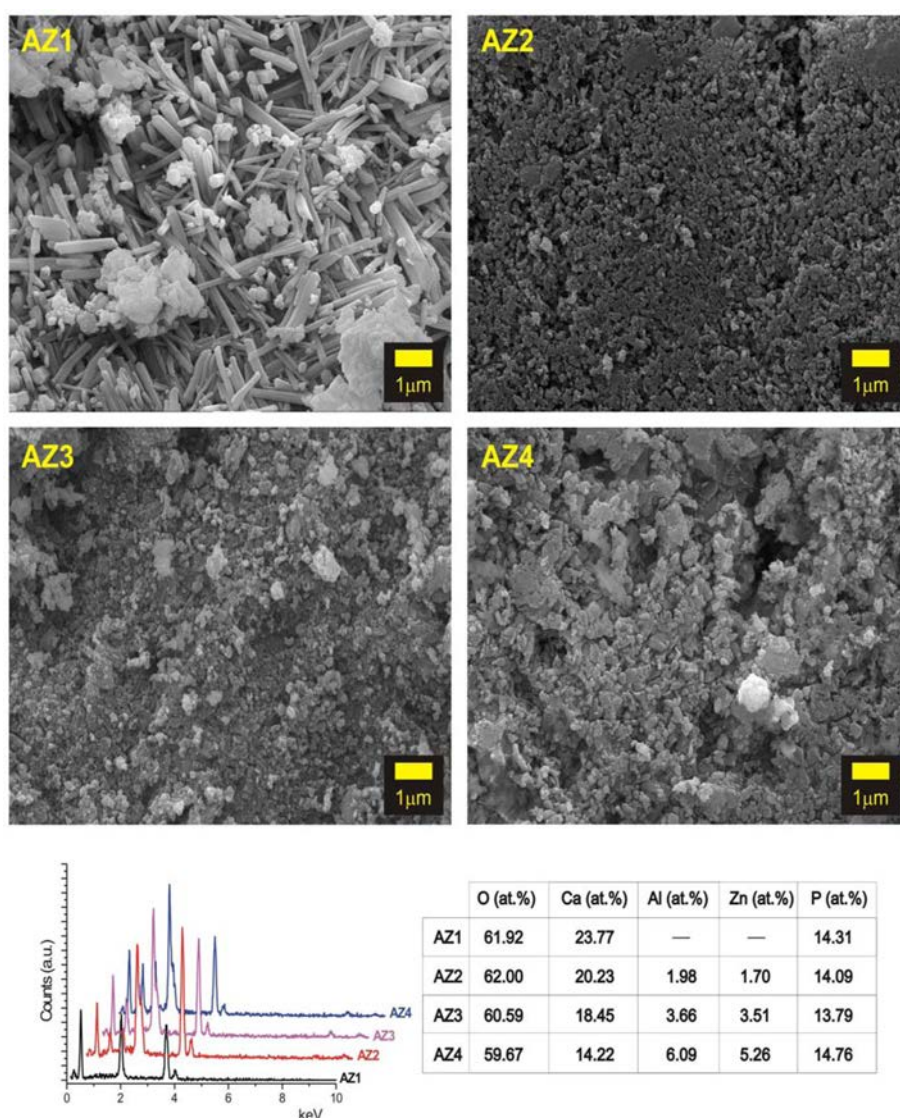


Fig. 3. SEM images at 10,000X magnification and EDX analysis reports of the as-synthesized samples.

sharpness of the bands observed at 3571, 1034 and 634 cm^{-1} decrease gradually with increasing amount of the co-additives. Since it was reported that the sharpness of these bands is affected by the changes in the crystallinity, this finding supports the XRD results.

Fig. 3. shows the SEM images of the samples, as well as the EDX spectra and analysis report. As seen in Fig. 3, while AZ1 sample (or pure HAp) is composed of the randomly oriented rods and agglomerated tiny particles, the samples of AZ2, AZ3 and AZ4 are composed of tiny particles smaller than microns and have a very similar morphology to each other. The morphology of the HAp is significantly affected by high contents of Al and Zn, as expected. Al and Zn contents detected from EDX analysis increase with increasing amounts of them, while the amount of P remains almost the same. The influence of Al is slightly higher than that of Zn. Since the ionic radius of Al is smaller than that of Zn, this is a quite reasonable result. The Ca/P molar ratio is found to be 1.66, 1.44, 1.34 and 0.96 for AZ1, AZ2, AZ3 and AZ4, respectively, and calcium deficiency is observed as expected. The (Ca + Al + Zn)/P molar ratio is 1.91, 1.88 and 1.73 for AZ2, AZ3 and AZ4, respectively, and this ratio is higher than that of the stoichiometric value of 1.67. Both molar ratios decrease gradually with the addition of Al and Zn.

Conclusions

It is possible to achieve the following evaluations as a result of this study. The stoichiometric HAp and HAp-based new ceramic samples containing Al and Zn can be easily prepared by the sol-gel technique. Higher amounts of Al and Zn affect the structural properties of the HAp namely, all the as-investigated parameters change with the addition of these. With increasing amount of the co-additives, both the average crystallite size and crystallinity degree gradually decrease from 25.84 nm to 15.27 nm, and from 74.2% to 30.7%, respectively. The values of the lattice parameters and volume of the unit cell are also affected by Al and Zn contents. The formation of the new phases with the addition of Al and Zn is detected. The morphology of the HAp varies significantly with the addition of the high amounts of Al and Zn. Besides the Ca-deficiency, the introduction of Al and Zn is observed.

Acknowledgments

This work was supported by Management Unit of Scientific Research projects of Firat University (FÜBAP) (Project Number: FF.14.26).

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