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The effects of duration of ultrasonication on the morphology and structural properties of Ni-doped hydroxyapatite structure

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ABSTRACT

This work aims to explain the effects of sonication periods, ranging from 0 to 4 h with a step of 1 h, on the morphology and structural properties of Ni-doped hydroxyapatites (at a constant amount of 0.4 at.%). The sonication time affected the lattice parameters, crystallinity, and crystallite size. Among the sonicated samples, it was observed that the increasing sonication period reduced the *c*/*a* ratio. It was also found that the morphology was affected by the ultrasonication duration.

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1. Introduction

Hydroxyapatite (HAp), which is one of the most used bioceramics and a member of the calcium orthophosphates, is a significant material used in medical applications such as bone and tooth repairing and possesses high biocompatibility and osteoconductivity [1, 2]. It can be prepared by using different methods such as microwave, sol-gel, hydrothermal, sonochemical, emulsion, wet chemical route, combustion, and pyrolysis [3-6]. Sometimes it can be synthesized with the use of these methods together. HAp can also be obtained from natural sources such as mammalian bones, eggshells, and fishbone [7].

The effects of the sonication period on the characteristic properties of the HAp structure were reported by some researchers [8,9]. Edwin and Wilson [10] investigated the effects of ultrasonication period on Sr-doped HAp structures and noted that the increase in the ultrasonication time caused a decrease in the aspect ratio. Hartatiek et al. [11] studied nano-HAp/SiO_2 composites and showed that the porosity decreased with the increasing sonication period.

The synthesizing of HAp using the dopant(s) can have some advantages or disadvantages compared to its pure form. Usually, a high amount of the dopant(s) does not prefer since it may cause some adverse conditions, such as toxicity in the HAp structure [12-14]. To avoid this situation, a low amount of the dopant of Ni was used in the present study. In the literature, the average amount of Ni for a healthy individual was reported as approximately 10 mg [15]. The current work focuses on the effects of the duration of sonication on the structural and morphologic properties of Ni-based HAp samples.

2. Materials and Method

All the samples doped with Ni at a constant amount were prepared by a wet chemical route followed by ultrasonication at different periods. In the synthesis,

calcium nitrate tetrahydrate, nickel (II) nitrate hexahydrate, and diammonium hydrogen phosphate were used. All these chemicals were purchased from Sigma-Aldrich. For dissolving all the chemicals, distilled water (DW) was used. For all the samples, 100 mL of the solution of 49.8 mmol calcium nitrate tetrahydrate and 0.2 mmol nickel (II) nitrate hexahydrate was prepared in a flask. In another flask, 100 mL of 30.0 mmol of diammonium hydrogen phosphate solution was prepared, poured drop wisely into the first solution, and the pH was adjusted to 10.0 by adding an ammonia solution. This solution was mixed in a magnetic stirrer for 90 min. at room temperature. This final mixture was ultrasonicated for the different times of 0, 1, 2, 3, and 4 h in the stainless steel ultrasonic bath filled with the DW. These samples were named NiHAp0, NiHAp1, NiHAp2, NiHAp3, and NiHAp4, considering the above-mentioned times. Each mixture was put in an oven at 120 °C for 18 h to dry, and this dried powder was heated in an electrical furnace at 900 °C for two h.

3. Results and Discussions

Fig. 1 illustrates the as-obtained XRD patterns of Ni-based HAps prepared with different ultrasonication periods. For all the samples, the formation of the main phase of the HAp (PDF No: 09–0432) and minor phase of the β-TCP (PDF No: 09–0169) is observed. The sonication time affects the intensities of both the (3 0 0) plane of the main phase and the (0 2 10) plane of the minor phase.

To obtain more detail from the XRD data, the lattice parameters (a and c), and unit cell volume (V) were calculated by using the following expressions [16]

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

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

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

The average crystallite size (t) and crystallinity percent (X_C%) values were computed by using the Scherrer equation and relation reported by Landi et al. [17], respectively.

$$t = \frac{0.9\lambda}{B_{1/2}\cos\theta} \quad (3)$$

$$X_C\% = \left(1 - \frac{V_{112/300}}{I_{300}}\right) \times 100 \quad (4)$$

where λ is the wavelength of the incident X–rays, $B_{1/2}$ is the full width at half maximum, θ is the diffraction angle, $V_{112/300}$ is the peak intensity of the pit between (112) and (300) planes and I_{300} is the peak intensity of the (300) plane. Table 1 gives the detailed XRD calculation results for the parameters of the t, a, c, V and X_C%, and it is seen that the sonication duration affects these parameters of the samples having the same chemical composition. In the results reported by Edwin and Wilson [10], it was observed that the sonication time significantly affected the lattice parameters of the Sr-doped HAps. Additionally, the c/a ratio is significantly affected by sonication time. Among the sonicated samples, it is found that the increasing sonication time decreases the c/a ratio.

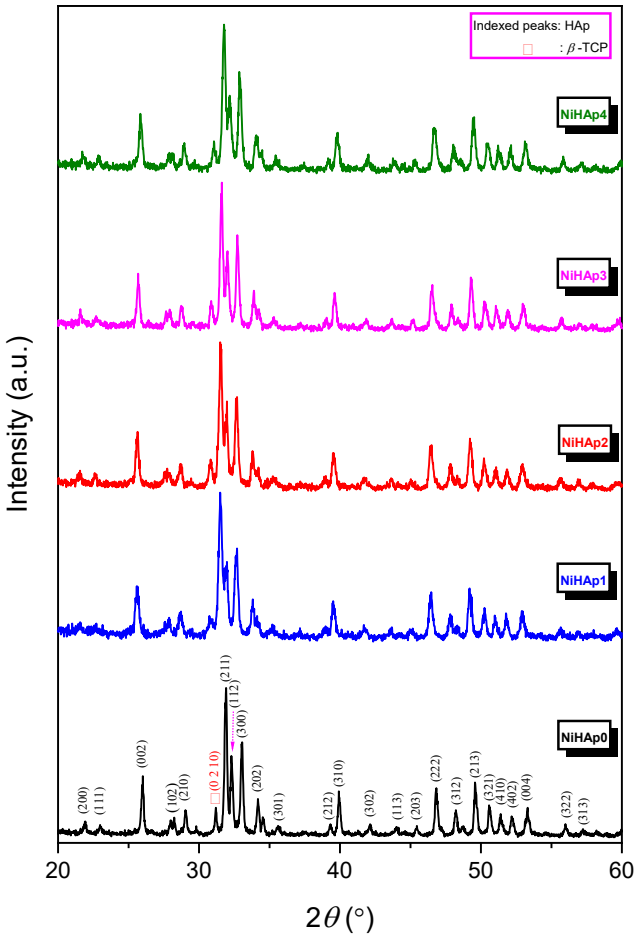

Fig. 1. XRD graphs of the samples

Table 1. XRD calculation results of the samples

Sample	t (nm)	a (nm)	c (nm)	c/a	V (nm)^3	Xc (%)
NiHAp0	46.0	0.9379	0.6844	0.72972	0.5214	88.4
NiHAp1	35.6	0.9485	0.6948	0.73253	0.5413	81.0

NiHAp2	32.0	0.9479	0.6943	0.73246	0.5402	81.2
NiHAp3	37.7	0.9473	0.6932	0.73176	0.5387	88.2
NiHAp4	33.2	0.9423	0.6890	0.73119	0.5298	83.3

Fig. 2 shows the FTIR spectra of the samples. The bands at 1086 (anti-symmetric stretching mode of P–O, υ_3), 1024 (υ_3), 962 (symmetric stretching mode of P–O, υ_1), 598 (bending mode of O–P–O, υ_4), and 562 cm^{-1} (bending mode of O–P–O, υ_4) are related to the phosphate group [18-21]. The bands observed at 633 and 3572 cm^{-1} are associated with the vibrational modes of the hydroxyl group [22].

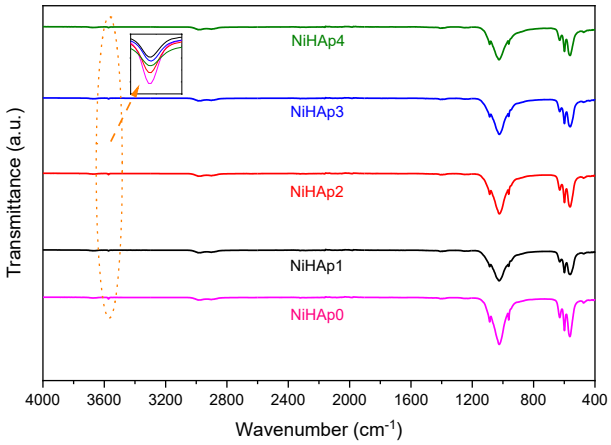

Fig. 2. FTIR results of the samples

Fig. 3 shows the samples' SEM images, which imply that the NiHAp structure's morphology is significantly affected by the sonication periods. The (Ca+Ni)/P molar ratio was found to be 1.60, 1.76, 1.74, 1.85, and 1.57 for NiHAp0, NiHAp1, NiHAp2, NiHAp3, and NiHAp4, respectively from the EDX results. These ratios differ from the theoretical value of 1.67 reported for the HAp structure. These variations may be due to the duration of the sonication process. Additionally, it is also seen that every sample includes the elements of Ca, Ni, P, and O.

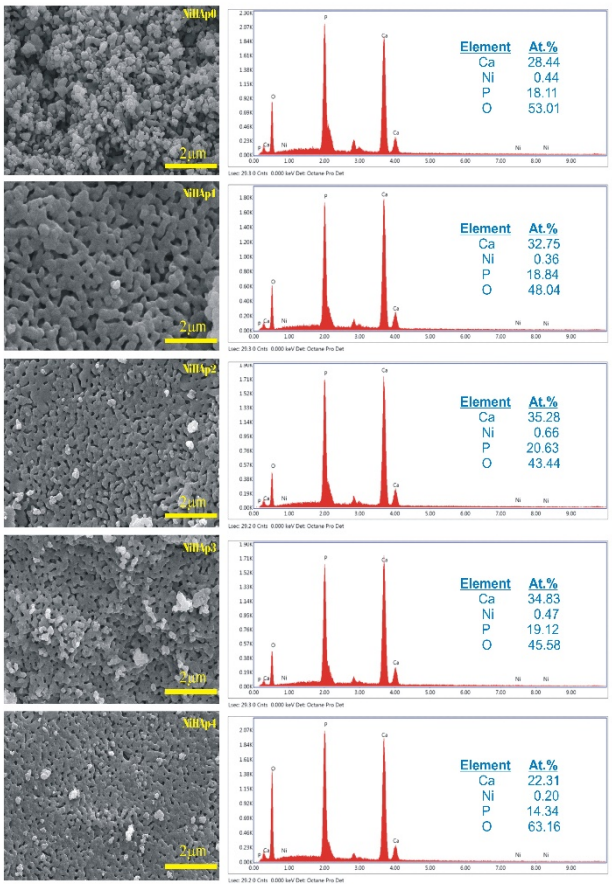

Fig. 3. SEM and EDX results of the as-synthesized samples

4. Discussion

In this study, Ni-doped HAp samples were prepared at various sonication periods and the effects of these periods on the structural properties and morphology. It was found that the sonication time affected the lattice parameters, crystallinity, and crystallite size. Considering all the sonicated samples, a gradual decrease in the *c*/*a* ratio was found with an increasing sonication period. Additionally, it was observed that this period affected the morphology significantly.

Competing interests

The authors declare that they have no competing interests.

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