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The effects of Ni-addition on the crystal structure, thermal properties and morphology of Mg-based hydroxyapatites synthesized by a wet chemical method

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ABSTRACT

Four Mg-based hydroxyapatites (HAps) doped with Ni at various amounts of 0, 0.6, 1.2 and 1.8 at% were prepared at the temperature of 870 °C by a wet chemical synthesis. The crystallite size, lattice parameters and crystallinity percent dramatically decreased with adding of Ni. The amount of HAp phase for all the Ni-containing samples is smaller than that of the Ni-free MgHAp. Furthermore, the lattice strain, stress and anisotropic energy density values were affected by the amount of Ni. The differential thermal analysis (DTA) measurements taken in the temperature range from 25 to 1000 °C showed that all the samples are thermally stable. No significant change in the morphology was observed. It was observed that the gradual introduction of Ni caused the Ca-deficiency.

1. Introduction

Hydroxyapatite (HAp) with the chemical formula of $Ca_{10}(PO_4)_6(OH)_2$ is one of the most-used members of the calcium orthophosphates [1]. The crystal structure of HAp is hexagonal having the $P6_3/m$ space group symmetry with lattice parameters $a = b = 0.9418$ nm and $c = 0.6884$ nm [2,3]. Since HAp is a bioactive, biocompatible, osteoconductive and non-toxic material, its structure and chemical composition are very similar to that of the natural bone, and it has been used as a bone substitute material in medical applications [4–9].

Cationic (e.g., Li^+, Na^+, K^+, Ag^+, Mg^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Sr^{2+}, Pb^{2+}, Ce^{3+}, Ti^{4+} and W^{6+}) and anionic substitutions (e.g., F^-, Cl^-, CO_3^{2-} and SiO_4^{4-}) have been widely used by many authors to investigate their effects on the apatitic structure and to make HAp more useful than its pure form [10–18]. Undoubtedly, Mg, which is the fourth most-found element in the human body (the order of the first three is as follows: Ca > K > Na), is one of the most popular dopants and is a biocompatible, osteoconductive, osseointegrable and lightweight material. The mechanical properties of Mg are quite similar to bone tissue [19–22]. As a result of human and animal studies, a very close association between osteoporosis and Mg-deficiency has been reported [23].

As far as we know, there are only a few articles about Ni-substituted HAps, and some of these studies can be summarized as mentioned below. Neelakandeswari et al. [24] prepared Ni-HAp using the microwave-assisted Henry reaction and observed the formation of calcium nickel phosphate and nickel oxide phases. Ni-doped HAps were synthesized by Priya et al. [25] using wet chemical precipitation method using cetyltrimethylammonium bromide (CTAB) and it was emphasized that all the as-prepared samples are bone cell compatible and osteoconductive. Guerra-Lopez et al. [26] reported that the amount of the amorphous calcium phosphate and dicalcium phosphate dihydrate (known as the Brushite) phases increases with increasing Ni/Ca ratio.

In the literature, there are many studies on Mg-substituted HAps, whereas there are only a few articles about Ni-substituted HAps, as mentioned above. In addition, we have not been able to find any work related to HAps containing both dopants in the literature. We found only one publication about Mg and Ni co-doped silicate HAps prepared by the microwave assisted wet precipitation method, and in the mentioned study, it was reported that Ni^{2+} containing silicate HAps showed good antibacterial activity against *E. coli* and *P. aeruginosa* [27].

In this study, we synthesized a series of Mg-based HAps with different amounts of Ni (e.g, 0, 0.6, 1.2 and 1.8 at%) using the wet chemical method and characterized their crystal structure, morphology and thermal properties using the experimental methods, including X–ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy, energy dispersive X–ray

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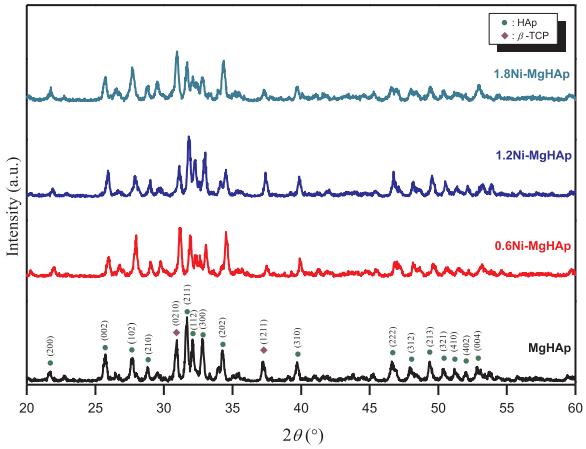

Fig. 1. XRD patterns of Ni-free and Ni-doped Mg-based HAps.

spectroscopy, differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Using the above-mentioned results, we have present a report on the effects of Ni content on the crystal structure, thermal properties and morphology of Mg-based HAps, in more details.

2. Materials and method

Mg-based HAps doped with Ni at various amounts of 0, 0.6, 1.2 and 1.8 at% were synthesized by the means of the wet chemical method following the steps below: Firstly, an appropriate amount of diammonium hydrogen phosphate (DAP, $(NH_4)_2{\cdot}HPO_4$) was dissolved in the distilled water using a magnetic stirrer. Secondly, the appropriate amounts of calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$), magnesium nitrate tetrahydrate ($Mg(NO_3)_2{\cdot}4H_2O$) and nickel (II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, Merck) were dissolved in one beaker and then as-prepared solution was slowly added to the DAP solution. The new solution was stirred at 80 °C for 5 h and converted into a gel. The gel was dried in an oven at 170 °C for 18 h. Finally, the as-dried gel was calcined at 870 °C for 1 h and a white powder was obtained. For all the samples, Mg content was kept at the constant value of 0.6 at%, and (Ca + Mg + Ni)/P molar ratio was fixed to 1.67.

For all the samples, X–ray diffraction (XRD) data were collected by a Rigaku RadB-DMAX II diffractometer operated at 40 kV and 40 mA using CuKα radiation with the wavelength (λ) of 0.15406 nm. Fourier transform infrared (FTIR) investigations within the spectral range from 400 to 4000 cm^{-1} were carried out using a PerkinElmer Spectrum One spectrometer, using potassium bromide (KBr) pellets. A scanning electron microscope (SEM, LEO EVO 40xVP) equipped with an energy dispersive X–ray (EDX, Bruker XFlash detector 4010) operated at 20 kV was used for investigating the morphology with the elemental analysis. Using the differential thermal analysis (Shimadzu DTA 50) and thermogravimetric analysis (Shimadzu TGA 50) techniques, the thermal properties of the as-produced samples in the temperature range from 25 to 1000 °C at a heating rate of 10 °C min^{-1} were studied.

Table 1
The detailed XRD characterization result for each sample.

Sample	Miller indices			Observed values		Calculated values	
	h	*k*	*l*	2*θ* (°)	*d* (nm)	2*θ* (°)	*d* (nm)
MgHAp	2	0	0	21.660	0.409660	21.719	0.408859
	0	0	2	25.740	0.345828	25.737	0.345873
	2	1	0	28.800	0.309742	28.864	0.309068
	2	1	1	31.680	0.282210	31.683	0.282184
	3	0	0	32.800	0.272824	32.831	0.272573
	3	1	0	39.720	0.226743	39.711	0.226794
	2	1	3	49.360	0.184480	49.265	0.184815
	3	2	1	50.400	0.180915	50.357	0.181057
	0	0	4	52.840	0.173121	52.901	0.172937
0.6Ni-MgHAp	2	0	0	21.840	0.406622	21.779	0.407749
	0	0	2	25.960	0.342947	25.843	0.344476
	2	1	0	28.920	0.308484	28.944	0.308229
	2	1	1	31.780	0.281344	31.779	0.281355
	3	0	0	32.920	0.271857	32.923	0.271833
	3	1	0	39.760	0.226524	39.823	0.226178
	2	1	3	49.480	0.184061	49.453	0.184156
	3	2	1	50.540	0.180446	50.509	0.180549
	0	0	4	53.060	0.172455	53.132	0.172238
1.2Ni-MgHAp	2	0	0	21.880	0.405887	21.788	0.407577
	0	0	2	25.840	0.344512	25.844	0.344456
	2	1	0	28.840	0.309321	28.957	0.308099
	2	1	1	31.820	0.281000	31.791	0.281253
	3	0	0	32.960	0.271537	32.937	0.271718
	3	1	0	39.800	0.226305	39.841	0.226083
	2	1	3	49.520	0.183921	49.463	0.184121
	3	2	1	50.540	0.180446	50.531	0.180478
	0	0	4	53.100	0.172334	53.135	0.172228
1.8Ni-MgHAp	2	0	0	21.880	0.405887	21.808	0.407204
	0	0	2	25.920	0.343467	25.895	0.343749
	2	1	0	29.020	0.307443	28.984	0.307817
	2	1	1	31.840	0.280828	31.826	0.280949
	3	0	0	33.000	0.271217	32.968	0.271469
	3	1	0	39.860	0.225978	39.879	0.225876
	2	1	3	49.540	0.183852	49.545	0.183834
	3	2	1	50.520	0.180513	50.584	0.180300
	0	0	4	53.240	0.171914	53.246	0.171897