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Structural and mechanical investigations of magnesium and fluoride doped nanosize calcium phosphates

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Pure and Mg^{2+} and F^- doped nano-calcium phosphates (CaP), which were synthesized by a precipitation method to investigate their microstructural and mechanical properties. After the drying and calcination processes, the samples were sintered at 1100 °C for 1 hour. High densities were achieved except for the 7.5% mole Mg doped samples. Due to the Mg^{2+} substitution, β -TCP phase was detected besides HAp, resulting in the formation of HAp/ β -TCP biphasic composites with different compositions. The substitutions of the ions have been verified by the decrease in the hexagonal unit cell volumes of the doped CaPs. FTIR spectra revealed the characteristic absorption bands of HAp, β -TCP and the ones that were resulted from the F-OH bonds. In general, the microhardness and diametral tensile strength tests revealed that Mg^{2+} ions in large amounts (7.5% mole) had negative effects on the micro hardness of the samples, while substitution of the F⁻ ions had a positive effect on their mechanical properties.

Key words: Biomaterials, Sintering, X-ray Diffraction, Mechanical Properties.

Introduction

Calcium phosphates (CaP) are the salts, which are generally used as hard tissue implants such as coatings on metal prosthesis or in composites. The compounds with $H_2PO_4^$ ions normally are not found in biological systems because they form under acidic conditions. However, both HPO_4^{2-} and PO_4^{3-} can occur in the mineral of bone and teeth. The hydrated CaPs contain OH⁻ ions and they belong to the basic apatatic CaP family [1].

Hydroxyapatite (HAp, Ca₁₀(PO₄)₆(OH)₂) has been widely used as an implant material for hard tissues owing to its excellent biocompatibility to human tissues because it has similar structure with the mineral part of bone [2-4]. Nevertheless, its poor mechanical properties such as strength, hardness and toughness limit the applications of HAp in load-bearing areas [5]. Therefore, it has been used in nonload bearing fields such as ossicles in the middle ear [2, 5].

HAp has Ca and P elements in its hexagonal structure. These elements are present in the inorganic part of the bone. Therefore, strong bonds are generated on the bone and implant surface [6]. There have been many attempts to improve the various properties of synthetic HAp [7-11]. The special attention was on nano crystalline HAp to achieve improvements both biologically and mechanically.

Biological HAp crystals contain many ionic impurities such as; K⁺, Mg²⁺, Na⁺, CO₃²⁻ and F⁻ [12-14]. Substi-

tution of these ions enhances the biological, mechanical and chemical properties of nano HAp [12]. Among the dopants of 5 wt.% Mg²⁺, Zn²⁺, La³⁺, Y³⁺, In³⁺ and Bi³⁺, the following ions (Zn²⁺, In³⁺, Bi³⁺) were reported as the best effective dopants enhancing the osteoblast attachment to HAp [12]. It is reported that doping of HAp with 2 mol% of Zn²⁺ or 2 mol% Mg²⁺ increased the osteoblast adhesion significantly [14].

Magnesium is one of the most important bivalent ions, which affects the bone fragility. It can substitute for Ca sites in HAp. In bone tissue, Mg stimulates the transformation of immature (amorphous) bone into a more crystalline form. The translocation of Mg into mineral tissues prevents fractures by increasing the bone elasticity [15, 16]. Its deficiency effects all stages of skeletal metabolism, causing cessation of bone growth, decreasing of osteoblastic and osteoclastic activities. Therefore, Mg incorporation into the HAp structure is of great interest for developing of artificial bone substitutes [17].

β-TCP, is a slow degrading, bioresorbable calcium phosphate ceramic [18]. It is reported that β-TCP is stable below 1125 °C and above this temperature it undergoes a phase transition to β-TCP leading to an expansion in the crystal lattice. Therefore, at sintering temperatures above this transition temperature densification problems occur [19]. Mg²⁺ ions stabilize the β-TCP upon heating above 800 °C along with the formation of HAp and improve the thermal stability of TCP [16, 20]. Also Mg²⁺ ions improve the densification behavior of TCP, stabilize the cell-material interface, improve the cell attachment and growth and also reduce the resorption and solubility of TCP [20, 21].

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Fluoride doping is also frequently used in order to improve the thermal stability and biological properties of HAp. It can substitute for the OH⁻ sites in HAp. Fluoride is known to be important in suppressing dental caries [22, 23]. It stimulates the proliferation and differentiation of bone cells [24]. Moreover, it has been used in treatment of osteoporosis [25]. Because the structural energy of F⁻ is much lower than that of other atoms, F is very stable in the lattice sites and doping F⁻ ions can stabilize the crystal structure of HAp [26]. The presence of F⁻ ions also has a reducing effect on the acid dissolution of HAp [1]. It has also been reported that doping low amounts (0.5-0.05 wt%) of either Mg²⁺ or F⁻ increased the in vivo stability of HAp [27].

HAp decomposes to TCP at about 1300 °C [28] and it is also reported that HAp has poor biodegradation characteristics. For this reason, various researchers have proposed HAp/ β -TCP biphasic ceramics for excellent bioactivity of HAp and bioresorbability of β -TCP [19].

Among the studies about Mg²⁺ doped HAp and F⁻ doped HAp powders, only a few studies about both Mg²⁺ & F⁻ substituted HAps have been published up to date [16, 26]. In this study, CaPs doped with Mg^{2+} and/or F⁻ were synthesized by a novel precipitation method and sintered at 1100 °C for 1 hour. Mg^{2+} and F^- ions were doped in different mole % amounts and in different Ca/P ratios for the first time. The densities of the materials were determined by the Archimedes method. The presence of phases in sintered samples was investigated by X-ray diffraction (XRD). Hexagonal lattice parameters of the samples were calculated from XRD results. The FTIR method was used to investigate the presence of the bonds in the samples. SEM was used to determine the grain size of the samples. Microhardness measurements were taken to study the mechanical properties of HAp, β-TCP and HAp/β-TCP biphasic composites.

Experimental Procedure

Pure-HAp was synthesized by a precipitation method [29-31]. Calcium nitrate tetra hydrate (Ca(NO₃)₂·4H₂O) and di-ammonium hydrogen phosphate ((NH₄)₂HPO₄) were mixed into each other to obtain pure HAp. 0.5 M Ca(NO₃)₂·4H₂O and 0.3 M (NH₄)₂HPO₄ was separately prepared in distilled water. The Ca/P ratio was kept at 1.67 to obtain the correct stoichiometry of HAp. Ammonia solution was added into both solutions to bring the pH to the 11-12 level. Calcium nitrate solution was added drop wise into the continuously stirring di-ammonium hydrogen phosphate solution. During stirring, the mixture was initially heated until boiling in order to increase the reaction rate and it was left stirring overnight at room temperature (RT). After the stirring, the mixture was filtered using a fine filter paper to obtain a wet cake. It was dried overnight in an oven at 200 °C. After the drying, calcination was performed at 600 °C for 10 minutes. Next, the sintering was performed at 1100 °C for 1 h.

For doped HAp, the main precursors were the same. Additionally, magnesium nitrate $(Mg(NO_3)\cdot 6H_2O)$ and ammonium fluoride (NH_4F) were used. Magnesium nitrate was added into calcium nitrate solution in 1, 2.5 and 7.5 moles% of calcium nitrate. Ammonium fluoride was added into di-ammonium phosphate solution in the compositions of 2.5 and 7.5 moles% of di-ammonium phosphate. The procedure used in the preparation of pure HAp was performed to prepare doped HAp. The proportions of elements additions were adjusted according to mole percentage of the precursors. After the solutions were mixed, the products were stirred, filtered, calcined and sintered similar to pure HAp.

The list of the samples produced and their designations are given in Table 1. The samples were classified in 5 different groups according to their Ca/P ratios and the amount of doped Mg^{2+} and F^- ions.

The densities of the discs were measured by a geometrical method. Powders were cold-pressed after the calcination at 600 °C for 15 minutes. 10 disks were prepared for each sample. After measuring the average green densities, the disks were air-sintered in a furnace at 1100 °C for 1 h and they were cooled in the furnace to RT. After the sintering, the bulk densities of the samples were measured and the average value was taken as the sintered density. Volume and densities of the samples were determined by the formulae below:

$$V = \left(\pi \cdot \frac{D^2}{4}\right) \cdot t \tag{1}$$

Table 1.	List of the synthesiz	zed products
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Group No	Sample ID	Ca/P	Mg	F
	2Mg0F0	2.00	-	-
1	1.67Mg0F0	1.67	-	-
1	1.5Mg0F0	1.50	-	-
	1.2Mg0F0	1.20	-	-
	1.95Mg2.5F2.5	1.95	2.5	2.5
r	1.625Mg2.5F2.5	1.625	2.5	2.5
2	1.463Mg2.5F2.5	1.463	2.5	2.5
	1.17Mg2.5F2.5	1.17	2.5	2.5
	1.65Mg1F2.5	1.65	1	2.5
3	1.625Mg2.5F2.5	1.625	2.5	2.5
	1.542Mg7.5F2.5	1.542	7.5	2.5
	1.65Mg1F0	1.65	1	-
4	1.625Mg2.5F0	1.625	2.5	-
	1.542Mg7.5F0	1.542	7.5	-
	1.625Mg2.5F0	1.625	2.5	-
5	1.625Mg2.5F2.5	1.625	2.5	2.5
	1.625Mg2.5F7.5	1.625	2.5	7.5

$$d = \frac{w}{V} \tag{2}$$

where;

V = disc volume; t = disc thickness; D = disc diameter; w = weight; d = density.

Additionally, in order to improve the densification of the samples during sintering, the as-dried samples were directly sintered at 1100 °C for 1 h without crushing to powder form. The density measurements of these pieces were taken by the Archimedes method and these samples were used for the microhardness measurements. The densities of the dried and sintered samples were measured by the following formula:

$$Density(g/cm^{3}) = \frac{Wt_{(air)}}{Wt_{(air)} - Wt_{(water)}} \times \rho_{(water)}$$
(3)

where;

 $\rho_{(water)}$: density of water; $Wt_{(air)}$: dry weight of the sample; $Wt_{(water)}$: wet weight of the sample.

The theoretical densities of HAp and β -TCP are 3.156 g/cm³ and 3.07 g/cm³, respectively. The theoretical densities (ρ_t) of the HAp/ β -TCP composites were calculated according to their weight percentages (wt% of HAp and wt% of β -TCP, which were calculated from the ratios of the most intense XRD peaks of the phases) in the samples by the following formulae [32]:

$$\rho_t = \frac{1}{\frac{W_{\beta-TCP}}{3.07} + \frac{W_{HAP}}{3.156}}$$
(4)

$$W_{HAp} + W_{\beta - TCP} = 1 \tag{5}$$

The relative densities (ρ) were calculated by dividing the measured bulk densities (ρ_{bulk}) by the theoretical densities (ρ_t).

XRD was performed to study the amounts of the phases and hexagonal lattice parameters of the samples. A Rigaku DMAX 2200 machine was used with Cu-K α radiation at 40 kV/ 40 mA and the samples were scanned from 10° to 80° in 20 angles with a scan speed of 2.0° minute⁻¹. The results were compared with the JCPDS files for HAp (#09-0432) [33] and β -TCP (#09-0169) [34].

FTIR measurements were performed to identify the presence of bonds in the samples. The CaP powders produced and potassium bromide (KBr) were mixed by a weight ratio of 1 to 300. In order to prepare the samples for the analysis, transparent pellets were produced by cold pressing. A FTIR spectrometer, BioRad FTS 175C was used and the spectra records were performed from 4000 cm⁻¹ to 500 cm⁻¹ using a 512 scan.

SEM analysis was performed to determine the average grain sizes of the sintered samples. A QUANTA 400F Field Emission SEM at a voltage of 20 kV was used. Firstly, the samples were coated with gold and platinum

under vacuum. Grain sizes of the samples were determined by the intercept method. The following formula was used to determine the average grain sizes [35]:

$$G_{av} = \frac{L}{N^*M} \tag{6}$$

where:

 G_{av} : Average grain size; L : circumference of the circle; N : number of the intersections along the intersection line; M : magnification.

Additionally, the microhardness measurements were determined by a Vickers micro hardness tester (HMV-2, Shimadzu, Japan). The surfaces of the samples were first ground step by step with SiC papers (Buehler Ltd., USA) from 600 to 1200 grades and finally polished with 1 μ m diamond paste. This procedure resulted in a removal of ~1 mm thick layer to avoid the "skin" effect on mechanical properties of the internal part of the sintered samples [36].

Approximately 20 measurements were performed on each sample with a diamond indenter with a 200 g load. The average microhardness was calculated by the formula below [37]:

$$HV = 0.001854 \frac{P}{d^2}$$
 (7)
where:

Where:

HV : Vickers hardness (GPa); P : Applied load (N); d : diagonal indent length (mm).

Results and Discussion

Green and sintered densities of the disc-shaped samples are presented in Table 2. The calculations were performed according to Equations 1, 2 and 4. Although a high green density was achieved for sample 2Mg0F0, its relative sintered density was lower than that of sample 1.67Mg0F0. The samples in Table 2 were calcined at 600 °C and then the cold pressed samples were air sintered at 1100 °C for 1 h.

By increasing the Mg content and therefore the amounts of β -TCP, the relative densities were decreased. It has been reported that the densities of the Mg²⁺ ion substituted CaPs were lower than those of the stochiometric CaPs [38]. However, by the addition of F⁻ ions, the densification behavior of the samples was increased significantly for all groups.

The relative densities of sintered samples measured by the Archimedes method are given in Table 3. The dried samples with irregular shapes were directly air sintered at 1100 °C for 1 h. Because the shrinkage in these samples was much more than that of the previous ones, higher densities were achieved and these samples were used for the microhardness measurements. Sample 1.625Mg2.5F2.5 exhibited the highest density among the doped samples.

Table 2. Green and sintered densities of the cold pressed disks

Group No	Sample ID	Bulk Density (Green) (g/cm ³)	Relative Density % (Green)	Bulk Density (Sintered) (g/cm ³)	Relative Density % (Sintered)
	2Mg0F0	1.72	54.4	2.76	87.5
1	1.67Mg0F0	1.61	51.1	2.87	90.8
1	1.5Mg0F0	1.41	45.6	2.79	90.1
	1.2Mg0F0	1.39	45.4	2.61	85.1
	1.95Mg2.5F2.5	1.63	51.6	-	-
n	1.625Mg2.5F2.5	1.55	49.4	2.85	90.5
2	1.463Mg2.5F2.5	1.39	45.0	2.79	90.1
	1.17Mg2.5F2.5	1.35	43.8	2.48	80.7
	1.65Mg1F2.5	1.52	48.2	2.88	91.3
3	1.625Mg2.5F2.5	1.55	49.4	2.85	90.5
	1.542Mg7.5F2.5	1.50	48.2	2.40	77.1
	1.65Mg1F0	1.53	48.6	2.83	89.6
4	1.625Mg2.5F0	1.53	48.6	2.80	89.2
	1.542Mg7.5F0	1.62	52.0	2.53	81.1
5	1.625Mg2.5F0	1.53	48.6	2.80	89.2
	1.625Mg2.5F2.5	1.55	49.4	2.85	90.5
	1.625Mg2.5F7.5	1.51	47.9	2.87	91.3
Table 3	. Densities of the s	intered pi	eces by th	e Archimed	les method

Group No	Sample ID	Bulk density (g/cm ³)	Theoretical density (g/cm ³)	% Density
	2Mg0F0	2.96	3.16	93.9
	1.67Mg0F0	3.00	3.16	95.0
1	1.5Mg0F0	3.01	3.10	97.1
	1.2Mg0F0	2.75	3.07	89.6
	1.95Mg2.5F2.5	3.00	3.16	95.2
2	1.625Mg2.5F2.5	3.03	3.14	96.4
2	1.463Mg2.5F2.5	2.81	3.09	91.0
	1.17Mg2.5F2.5	2.47	3.07	80.2
	1.65Mg1F2.5	3.02	3.16	95.8
3	1.625Mg2.5F2.5	3.03	3.14	96.4
	1.542Mg7.5F2.5	2.52	3.11	80.9
	1.65Mg1F0	2.91	3.16	92.1
4	1.625Mg2.5F0	2.92	3.14	93.0
	1.542Mg7.5F0	2.83	3.11	90.7
5	1.625Mg2.5F0	2.92	3.14	93.0
	1.625Mg2.5F2.5	3.03	3.14	96.4
	1.625Mg2.5F7.5	2.91	3.15	92.7

The improvement in the densification behavior between the groups 1 and 2 with the additions of Mg^{2+} and F^{-}

ions became more apparent above a Ca/P ratio of 1.67.

Group 3 shows the effect of the increase in the amounts of Mg²⁺ with a constant 2.5 mole% F⁻ addition and the group 4 shows the effect of an increase in the amount of Mg²⁺ on density. In group 3, bulk densities of the samples decreased sharply when compared with group 4 when the mole% of Mg^{2+} ions was increased from 2.5 to 7.5. The decrease in the density by the addition of Mg²⁺ ions has also been reported for Mg²⁺ ions substituted HAps [39]. The highest densities were achieved for the samples 1.65Mg1F2.5 and 1.65Mg1F0 in groups 3 and 4, respectively (Table 2). A similar observation was also reported for 1 wt% MgO addition to HAp/TCP composites (sintered at 1000-1100 °C for 12 h) and the optimum amount of MgO doping was found to be 1 wt%, which leads to a 99% relative density in HAp/ β -TCP composites [19]. It was also reported in the same study that the higher concentrations of MgO suppressed the grain growth of HAp/TCP composites and lowered the sinterability.

An enhancement in the relative densities was observed for the samples in group 5 with the F^- mole% 2.5 region with a constant 2.5 mole% Mg²⁺ amount. The relative density of sample 1.542Mg7.5F2.5 was reduced significantly in comparison to that of sample 1.542Mg7.5F0.

The theoretical densities of HAp and β -TCP are 3.156 and 3.07 g/cm³, respectively. Therefore, the densities should decrease as the wt% of β -TCP phase increases. In the samples 1.625Mg2.5F2.5 and 1.625Mg2.5F0 (~15 wt% β -TCP), the densities were slightly increased in both F⁻ doped and undoped samples with a constant amount of Mg²⁺ in comparison with samples 1.65Mg1F2.5 and 1.65Mg1F0. An enhancement in densification by the incorporation of F⁻ ions into the sample 1.625Mg2.5F2.5 was observed when compared with that of the sample 1.625Mg2.5F0 with no F⁻ addition.

The XRD spectra of the sintered samples in group 1 are presented in Fig. 1. The samples 2Mg0F0, 1.67Mg0F0, 1.5Mg0F0, 1.2Mg0F0 with Ca/P ratios of 2.00, 1.67, 1.50, 1.20 were compared with the JCPDS files of HAp and β -TCP.

For the sample 2Mg0F0, the CaO phase was detected in addition to HAp because the Ca/P ratio was higher than 1.67 [36, 40]. For this sample, an additional peak was observed at the 20-angle of 37.44° due to the presence of the CaO phase. For sample 1.67Mg0F0, the sintered products were pure HAp. For sample 1.5Mg0F0, a pure HAp/ β -TCP composite was obtained. For the Ca/P ratio of 1.20 (sample 1.2Mg0F0), the product was β -TCP. Narrow and sharp peaks were observed for all of the samples indicating the high crystallinity of these powders. The peaks for HAp and β -TCP were closely matched to their counterparts of the JCPDS files.

It has been reported that the structure of bone consists of amorphous phase β -TCP and crystalline phase of HAp in nano crystal sizes [41]. HAp/ β -TCP composites are generally produced from calcium deficient apatites at temperatures above 800 °C or by introducing Mg²⁺



Fig. 1. XRD results of a) standard HAp (JCPDS# 09-0432); b) standard β -TCP (JCPDS# 09-0169); c) 2Mg0F0; d) 1.67Mg0F0; e) 1.5Mg0F0; f) 1.2Mg0F0. All samples were sintered at 1100 °C for 1 h.

ions into the HAp structure [16]. In a study of HAp/TCP biphasic ceramics, it was observed that the phase composition was basically a function of the Ca/P ratio of the raw material and the use of porojen did not alter the HAp/TCP content, but induced changes in the relative content of the TCP phase (α or β phase) [42]. It has been reported that even small variations in the Ca/P ratios of the initial precipitates significantly affect the phase composition of the final CaP materials [40]. In Fig. 1, the increase in the β -TCP phase can be seen. The samples became more calcium deficient from sample 1.67Mg0F0 to 1.2Mg0F0.

In Fig. 2, the XRD patterns of the sintered samples (group 2) are presented. In this group, all the products were doped with 2.5 mole% Mg²⁺ and F⁻ and sintered at 1100 °C for 1 h. Although the Ca/P ratios were adjusted as in group 1, the Ca/P ratios were decreased as shown in Table 1 as a result of the substitution of Mg²⁺ ions for the Ca²⁺ sites in the samples. The increase in the β -TCP phase can be observed from the XRD patterns for this group. The peaks for HAp and β -TCP were also closely matched with the 2 θ angles of JCPDS patterns seen in Fig. 1. However, as a result of the substitution of Mg²⁺ and F⁻ ions, a slight shift to the



Fig. 2. XRD results of a) standard HAp (JCPDS# 09-0432); b) standard β -TCP (JCPDS# 09-0169); c) 1.95Mg2.5F2.5; d) 1.625Mg2.5F2.5; e) 1.463Mg2.5F2.5; f) 1.17Mg2.5F2.5. All samples were sintered at 1100 °C for 1 h.

left was observed.

Although Mg^{2+} ions are known to trigger β -TCP formation even at low sintering temperatures [16, 20, 21], a trace amount of HAp was formed in the sample 1.17Mg2.5F2.5. This could be attributed to the existence of F⁻ ions, which is known to make the structure of HAp more stable [43]. When compared with Fig. 1, the most intense peaks of β -TCP became narrower and higher in Fig. 2, which indicates better crystallinity in the samples. It was reported that the CaP materials can be combined with Mg²⁺ ions in order to improve crystallization of phosphate deposits and therefore its persistence and biocompatibility [44]. In sample 1.95Mg2.5F2.5, a dominant HAp was present and no β -TCP phase was observed. Moreover, the CaO phase was also observed for the sample 1.95Mg2.5F2.5 at a 20-angle of 37.46°. The presence of the CaO phase was also reported for the CaP ceramics with Ca/P ratios higher than 1.67 [36,40]. For the sample 1.625Mg2.5F2.5, the sintered product was HAp with a small amount of β -TCP. As the Ca/P ratio decreased, the β -TCP phase became dominant with a small amount of HAp in the sintered product for the sample 1.463Mg2.5F2.5.

Naturally, as the Ca/P ratio decreased, the amount of β -TCP increased as can be seen from Fig. 2. For sample

1.95Mg2.5F2.5, an additional peak at a 2θ -angle close to the one that was observed for sample 2Mg0F0, was also formed due to the increased Ca²⁺ ion content.

Fig. 3 presents the XRD patterns for the samples in group 3. No β -TCP formation was observed for the sample 1.65Mg1F2.5 (1 mole% Mg). In a study, HAp/β-TCP biphasic ceramics were produced by the co substitution of Na⁺, Mg²⁺ and F⁻ ions with 3 different HAp/ β -TCP ratios by adjusting the amount of the initial Ca/P ratios and the amount of the dopants [16]. It was shown that the elements incorporated played a crucial role in the thermal stability of the apatites up to 1400 °C and increased calcium deficiency led to the formation of a higher proportion of β -TCP in the biphasic ceramics [16]. As the Mg²⁺ ion content increased, β-TCP formation was also increased in group 3. The increase in the β -TCP content with the increase in the Mg²⁺ ion content was also reported elsewhere [38, 45]. From sample 1.625Mg2.5F2.5 to 1.542Mg7.5F2.5, a slight shift to higher 2 θ -angles was observed in β -TCP peaks with the increase in the Mg²⁺ ion content.

As a result of Mg^{2+} and F^- additions, slight shifts to the right were also observed for the HAp peaks with respect to the pure HAp (sample 1.67Mg0F0). As the amount of Mg^{2+}

ions was increased to 7.5 mole%, the diffraction peaks of HAp became broader for the sample 1.542Mg7.5F2.5 indicating the poor crystallinity.

Fig. 4 presents the XRD patterns of the samples in group 4 with increasing amounts of (1, 2.5, 7.5 mole%) Mg^{2+} content. No F⁻ ion was added into the samples for this group. No β -TCP formation was observed for the 1 mole% Mg doped sample 1.65Mg1F0. For the samples 1.625Mg2.5F0 and 1.542Mg7.5F0, β -TCP peaks were formed and peaks of \hat{a} -TCP get higher, respectively. By an increase in the Mg²⁺ content from 2.5 mole% to 7.5 mole%, a slight shift in the 20 values were also observed in the β -TCP peaks. These peak shifts were also reported for MgO addition into HAp/ β -TCP mixtures by Ryu *et al.* [19].

As the Mg²⁺ ion content increased to 7.5 mole% (sample 1.542Mg7.5F0), the diffraction peaks of HAp became broader similar to the sample 1.542Mg7.5F2.5, as seen in Fig. 3, showing the poor crystalline nature of this sample. Moreover, as a result of the substitution of Mg²⁺ ions, slight peak shifts were also observed for the HAp peaks with respect to the sintered pure HAp (sample 1.67Mg0F0).



Fig. 3. XRD results of a) standard HAp (JCPDS# 09-0432); b) standard β -TCP (JCPDS# 09-0169); c) 1.65Mg1F2.5; d) 1.625Mg2.5F2.5; e) 1.542Mg7.5F2.5. All samples were sintered at 1100 °C for 1 h.

Fig. 5 shows the XRD results of the group 5 samples



Fig. 4. XRD results of a) standard HAp (JCPDS# 09-0432); b) standard β -TCP (JCPDS# 09-0169); c) 1.65Mg1F0; d) 1.625Mg2.5F0; e) 1.542Mg7.5F0. All samples were sintered at 1100 °C for 1 h.

Fig. 5. XRD results of a) standard HAp (JCPDS# 09-0432); b) standard β -TCP (JCPDS# 09-0169); c) 1.625Mg2.5F0; d) 1.625Mg2.5F2.5; e) 1.625Mg2.5F7.5. All samples were sintered at 1100 °C for 1 h.

with the selective effect of an increase in the F content with a constant amount (2.5 mole%) of Mg dopant. In Fig. 5, well-crystallized samples were obtained. The intensity of β -TCP peaks was decreased with an increase in the F⁻ content. As can be seen from this fig as the F content increased from 2.5 to 7.5 mole%, the intensity of the peak from the (002) plane was also increased, indicating that the crystals were well crystallized and oriented in the c- axis direction of the apatite. Moreover, the crystallinity was increased with an increase in the F⁻ content [46, 47].

In order to control the phase content during the sintering for the samples in group 1, the phase transition temperature (1125 °C) from β to α -TCP [48] was taken as the threshold value and the highest optimum sintering temperature was taken as 1100 °C [49]. Additionally, the optimum sintering time was chosen as 1 h [29].

The amounts of HAp and β -TCP phases present in the samples are presented in Table 4. The phases were determined from the relative intensity measurements from the XRD patterns according to equations 4 and 5. The amount of β -TCP formation was increased with an increase in the Mg²⁺ content and decreased with an increase

Fable 4. Presence of HAp and β -TCP phases in the sample	able
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Groups	Sample ID	$W_{\beta\text{-TCT}}$ %	W_{HAP} %	Phase Formations
1	2Mg0F0	-	100.0	No TCP
	1.67Mg0F0	-	100.0	No TCP
	1.5Mg0F0	69.8	30.2	TCP
	1.2Mg0F0	100.0	-	TCP
2	1.95Mg1.5F2.5	-	100	No TCP
	1.6251.5F2.5	14.8	85.2	TCP
	1.4631.5F2.5	72.6	27.4	TCP
	1.171.5F2.5	97.5	2.5	TCP
3	1.65Mg1F2.5	-	100.0	No TCP
	0.625Mg1F2.5	-	85.2	TCP
	1.463Mg2.5F2.5	72.6	27.4	TCP
	1.17Mg7.5F2.5	97.5	2.5	TCP
4	1.65Mg1F0	-	100.0	No TCP
	1.625Mg2.5F0	14.6	85.0	TCP
	1.542Mg7.5F0	46.9	53.1	TCP
5	1.625Mg2.5F0	14.9	85.0	ТСР
	1.625Mg2.5F2.5	14.8	85.2	TCP
	1.625Mg2.5F7.5	12.5	87.5	TCP

in the F⁻ ion content in group 5, making the structure of the HAp more stable. It was reported that F tends to decrease the strain in the apatite lattice and thereby increases the stability of the apatite structure [50]. In a study that compares the fluoridated HAp with pure HAp, more β -TCP phase was detected in the HAp than in the fluoridated HAp at both 1300 °C and 1400 °C, which confirmed that the thermal stability of fluoridated HAp increased with an increase in the F⁻ ion content in the specimens [51]. It was also reported that as a result of the F⁻ ion substitution into the HAp lattice, peak shifts to higher 2θ values were observed in the positions of (211), (300) and (112) peaks in an increasing manner with an increase in the F⁻ ion content [52, 53]. Peak shifts in these positions due to the F⁻ ion substitution were also reported in another study [51]. However, the XRD patterns obtained from the fluoridated HAp samples with different F⁻ ion contents revealed the same systematic shift for these peaks (independent from the F⁻ ion contents) in contrast to previous reports by Okazaki et al. [52, 53]. Therefore, the form of the shifted peaks was interpreted as the convolution of the peaks from HAp and FAp [51].

In the XRD patterns of group 5, from sample 1.625Mg2.5F2.5 (2.5 mole% F^-) to 1.625Mg2.5F7.5 (7.5 mole% F^-), the positions of (211), (300) and (112) peaks were shifted significantly to higher 2 θ values. However, for the smallest amount of F^- addition (2.5 mole%), a significant shift could not be detected, suggesting that the findings of Okazaki *et al.* [52,53] might be more accurate compared to the study [51] mentioned above.



Although Mg²⁺ ions are known to trigger β -TCP formation, no β -TCP phase was observed for 1 mole% Mg²⁺ ions in the sample 1.95Mg2.5F2.5 (Fig. 2) and in the samples 1.65Mg1F2.5 and 1.65Mg1F0 (Figs. 3 and 4). As indicated in Table 4, no β -TCP formation was observed for samples 2Mg0F0 and 1.95Mg2.5F2.5. Some amount of CaO was present together with HAp for these samples because their Ca/P ratios exceeded the stochiometric ratio. However, since the main aim of this study was to compare the β -TCP and HAp amounts and to investigate their resulting structural and mechanical affects, CaO amounts are not taken into account in Table 4.

Hexagonal lattice parameters and unit cell volumes of all the samples are presented in Table 5. As seen from this table, hexagonal lattice parameters 'a' and 'c' were decreased for all sintered materials in comparison with the lattice parameters of the pure HAp (JCPDS #09-0432). As a result, unit cell volumes of the apatites were decreased.

The variations in the lattice parameter values "a" and "c" were not found to be in correlation with the decrease in the Ca/P ratios for HAp, in group 1 and the changes in the unit cell volumes were mainly due to the sintering, as there were no dopants in this group. Small irregular changes have been observed in "a" and "c" lattice parameters. On the other hand, both "a" and "c" lattice parameters of HAp were decreased gradually with the decrease in the Ca/P ratio as a result of the substitution of constant amounts of Mg²⁺ and F⁻ ion additions (2.5 mole%)

Table 5. HAp and β -TCP lattice parameters of the samples

in group 2. In a study with fluoridated HAp and Mgcontaining fluoridated HAps by Okazaki and coworkers, it was reported that the "a" lattice parameter was decreased with the increase in degree of fluoridation, which suggested the substitution of F^- ions into the apatite crystals [26, 53]. Additionally, for the Mg²⁺ ion containing fluoridated HAps, the "c" lattice parameter was also decreased as a result of the substitution of Mg²⁺ ions into the apatite crystals [26]. Therefore, this decrease in the lattice parameters of HAp should be attributed to the substitution of these ions within the samples in group 2.

Because ion sizes of both Mg^{2+} and $\mathrm{F}^{\scriptscriptstyle -}$ are smaller than those of Ca^{2+} and OH^{-} ions, it is expected that the addition of these ions results in the shrinkage of unit cell volumes (Table 5). The effective ionic radii of Mg^{2+} and Ca^{2+} ions are 0.72 Å and 1.0 Å and F⁻ and OH⁻ ions have an effective ionic radii of 1.33 Å and 1.37 Å, respectively [54]. In group 4, "a" lattice parameters were slightly increased by the addition of 1 mole% Mg²⁺ ion (sample 1.65Mg1F0) in comparison with the pure HAp sintered at 1100 °C (sample 1.67Mg0F0). Increasing the Mg²⁺ ion amount to 2.5 mole% did not change the "a" values, while for the 7.5 mole% Mg^{2+} ion, the "a" lattice parameter was increased in group 4. This change in the "a" lattice parameters may be due to the stresses introduced to the unit cell by the addition of Mg²⁺ ions. The "c" lattice parameter was decreased from sample 1.65Mg1F0 to sample 1.625Mg2.5F0 as the Mg content increased.

Groups	Sample IDs		HAP Lattice	e Parameter	s	Sample IDs		HAP Lattice	e Parameter	s
		a(Å)	c(Å)	$V(Å^3)$	$\Delta Va(Å^3)$		a(Å)	c(Å)	$V(Å^3)$	$\Delta Va(Å^3)$
	HAp (09-0432)	9.4180	6.8840	1580.9	0.0	β-TCP (09-0169)	10.4290	37.3800	3520.8	0.0
1	2Mg0F0	9.4132	6.8739	1576.9	-3.9	2Mg0F0	-	-	-	-
	1.67Mg0F0	9.4106	6.8720	1575.6	-5.3	1.67Mg0F0	-	-	-	-
	1.5Mg0F0	9.4118	6.8765	1577.0	-3.8	1.5Mg0F0	10.4289	37.5213	3534.1	13.2
	1.2Mg0F0	-	-	-	-	1.2Mg0F0	10.3938	37.3992	3498.9	-22.0
2	1.95Mg2.5F2.5	9.4090	6.8785	1576.6	-4.3	1.95Mg2.5F2.5	-	-	-	-
	1.625Mg2.5F2.5	9.4080	6.8758	1575.6	-5.3	1.625Mg2.5F2.5	10.3765	37.4024	3487.5	-33.3
	1.463Mg2.5F2.5	9.3615	6.875.3	1560.0	-20.9	1.463Mg2.5F2.5	10.3543	37.2940	3462.6	-58.3
	1.17Mg2.5F2.5	-	-	-	-	1.17Mg2.5F2.5	10.3798	37.2834	3478.7	-42.1
3	1.65Mg1F2.5	9.4100	6.8785	1576.9	-4.0	1.65Mg1F2.5	-	-	-	-
	1.625Mg2.5F2.5	9.4080	6.8758	1575.6	-5.3	1.625Mg2.5F2.5	10.3765	37.4024	3487.5	-33.3
	1.542Mg7.5F2.5	9.4100	6.8962	1580.9	0.1	1.542Mg7.5F2.5	10.3708	37.3296	3476.9	-43.9
4	1.65Mg1F0	9.4147	6.8787	1578.5	-2.3	1.65Mg1F0	-	-	-	-
	1.625Mg2.5F0	9.4147	6.8754	1577.8	-3.1	1.625Mg2.5F0	10.3711	37.7841	3519.5	-1.3
	1.542Mg7.5F0	9.4210	6.8766	1580.2	-0.7	1.542Mg7.5F0	10.3447	37.1974	3447.2	-73.6
5	1.65Mg2.5F0	9.4147	6.8754	1577.8	-3.1	1.65Mg2.5F0	10.3711	37.7841	3519.5	-1.3
	1.625Mg2.5F2.5	9.4080	6.8758	1575.6	-5.3	1.625Mg2.5F2.5	10.3765	37.4024	3487.5	-33.3
	1.542Mg7.5F7.5	9.3857	6.9464	1584.3	3.4	1.542Mg7.5F7.5	10.3470	37.5044	3477.2	-43.6

However, a further increase in the Mg content did not show the same effect on the "c" lattice parameter.

It has been reported that Mg substitution into the apatite crystals may occur to a limited extend whereas it was also suggested that the substitution of Mg²⁺ ions could be promoted by fluoride [26]. Therefore, it can be concluded that in the case of group 4, 2.5 mole% Mg could be substituted into the apatite structure as the limit value in the absence of F⁻ ions. It has been reported that F ions increase the crystal sizes of HAp along the c-axis direction [55]. In summary, Mg ions have a decreasing effect on the "c" lattice parameters, while F⁻ ions have an increasing effect. When the "c" lattice parameters of groups 3 and 4 are compared, it can be seen that the effect of the F ions on the "c" values is dominant. The "c" lattice parameter of sample 1.542Mg7.5F0 for 7.5 mole% Mg.

In group 3, the addition of F^- ions suppressed the increase in the "a" lattice parameters with respect to group 4 for the same variations of Mg²⁺ ions. Incorporation of F^- ions into the apatite structure causes a contraction of the "a" lattice [26, 53]. Therefore, it can be concluded that in group 3, an increase in the "a" value was not observed in sample 1.65Mg1F2.5 with 1 mole% Mg addition with respect to sample 1.65Mg1F0 in group 4.

In group 5; sample 1.625Mg2.5F7.5, the highest c/a ratio was obtained due to the gradual decrease in the "a" lattice parameters for both HAp and β -TCP and an increase in the "c" lattice parameter of HAp for the highest F^{-} amount. As a result of the substitution of F^{-} ions, with the addition of 7.5 mole% F- ion, an apparent increase in the "c" lattice parameter values were observed in both HAp and β -TCP phases for sample 1.625Mg2.5F7.5. Since all of the samples in group 5 were doped with a constant amount of Mg²⁺ ions (2.5 mole%) besides F⁻ ions, it is logical to attribute this increase to the high amount of F^- ion substitution. It was also reported that for 20%, 60% and 100% F⁻ ion substitution for OH⁻ groups, the crystallinity of the fluoridated HAps was increased graually with an increase in the F⁻ content. This indicated that the F⁻ concentration increased the driving force for the apatite crystal growth during precipitation [47].

Additionally, the slight shift to higher 20 values that was observed from sample 1.625Mg2.5F2.5 to 1.542Mg7.5F2.5 in the XRD patterns of group 3 (Fig. 3) indicated that the lattice parameters of β -TCP decreased by the increase in the Mg²⁺ content. This can also be verified from Table 5. A slight shift to higher 20 values was also observed from sample 1.625Mg2.5F0 to 1.542Mg7.5F0 similar to group 3 samples in Fig. 4. This shift also indicated the decrease in the β -TCP lattice parameters (Table 5) as was reported for the previous group. A similar observation was also reported by Ryu *et al.* [19] for a MgO addition into HAp/ β -TCP mixtures. The decrease in the lattice parameters of β -TCP occurs as a result of the lattice contraction due to the replacement of Ca²⁺ atoms with Mg²⁺ ions with smaller radii.

Mg²⁺ ions improve the densification behavior of β -TCP by shifting its phase transition temperature (~1125 °C) to higher values and prevent its transition to β -TCP, which leads to an expansion in the unit cell volume. The variation in the unit cell volumes (ΔV) of β -TCP in sample 1.542Mg7.5F0 with no F⁻ dopant, was significantly high for 7.5 mole% Mg²⁺. However, a high ΔV value was also obtained for sample 1.625Mg2.5F7.5 with 2.5 mole% Mg²⁺ and 7.5 mole% F⁻ dopants, which indicated that the change in the unit cell volumes were mainly due to the difference in the atomic radii of the dopants.

It has been reported that the amount of Mg^{2+} ions associated on the surface of HAp is usually much more than the Mg^{2+} ions incorporated into its crystalline structure [55]. As a result of the change in the lattice parameters (Table 5) of the Mg^{2+} and/or F⁻ doped HAps, it can be concluded that Mg^{2+} ions are actually incorporated into the unit cell structure of HAp. The variations in the lattice parameters and unit cell volumes of the doped samples with respect to their undoped counterparts can be interpreted as the incorporation of these ions into the unit cell structure of the samples.

In group 5, the F⁻ content was increased from 0 to 7.5 mole%, while the Ca/P ratio and the Mg content were kept the same. The "c" values of the samples were increased significantly and the "a" values were decreased in the HAp phase.

FTIR was employed to identify the functional groups of the sintered doped and undoped CaPs. All of the samples showed the characteristic bands for HAp and β -TCP as well as the bands that appeared due to the substitution of the dopants. For all of the samples sintered at 1100 °C, the spectra region for the presence of adsorbed water around 3300-3600 cm⁻¹ [16] was almost a flat line, indicating a minimum amount of adsorbed water in the samples.

The band at 962.59 cm⁻¹ is assigned to v_1 , the nondegenerate P-O symmetric stretching mode. The bands at 1048.4 and 1090.8 cm⁻¹ are assigned to the components of the triply degenerated v_3 antisymmetric P-O stretching mode and the bands at 573.89 and 599.93 were assigned to the components of the triply degenerate v_4 O-P-O bending mode [40]. The bands that are attributed to the v_2 O-P-O bending mode were out of range for the investigated frequency interval.

The spectra for the samples categorized in five groups are presented in Fig.s 6-10. In Fig. 6, the undoped CaP samples of group 1 were investigated for Ca/P ratios ranging from 2.00 to 1.20. In the spectra for pure HAp (sample 2Mg0F0, 1.67Mg0F0) and HAp/ β -TCP composite (sample 1.5Mg0F0), the bands for PO₄ groups and OH⁻ groups were easily observable, while for the pure β -TCP (sample 1.2Mg0F0) the OH⁻ stretching and librational modes of HAp had disappeared.

The characteristic OH⁻ absorption bands at 631.7 and 3571.6 cm⁻¹ of HAp [42] were present for the spectra of samples 2Mg0F0-1.5Mg0F0 and naturally disappeared



Fig. 6. FTIR patterns of the sintered CaP samples of group 1: a) 2Mg0F0; b) 1.67Mg0F0; c) 1.5Mg0F0; d) 1.2Mg0F0.

for sample 1.2Mg0F0, which was in good agreement with the findings of Slosarczyk et al. [40]. Therefore, the transmittance intensities of the OH⁻ groups for HAp were gradually decreased from sample 1.67Mg0F0 to 1.2Mg0F0 as the HAp content decreased. Additionally, the OH⁻ intensities were also decreased for sample 1, due to the decrease in the HAp wt % as a result of the presence of the CaO phase (Fig. 1). It has been reported that because of its reactivity against water, the presence of CaO could be very harmful for implantation materials and when stored in air, the sintered material can absorb water vapor with the formation of some amount of $Ca(OH)_2$ [40]. Since the spectral region assigned for the absorbed water at 3300-3600 cm⁻¹ was almost a flat line in all of the samples, it can be concluded that a transformation from the CaO phase to Ca(OH)2 did not occurr for the samples 2Mg0F0 and 1.95Mg2.5F2.5.

Therefore, the decrease in the intensities of OH⁻ bands in HAp can not be attributed to the excess amount of Ca ions in sample 2Mg0F0, forming bonds with the OH ions, but they could be rather as a result of the decrease in HAp by weight. This behavior suggests that the transmission intensities give us also quantitative information about the amount of HAp and β -TCP. A similar case with 2% CaO and 98% HAp (by weight) was reported by Slosarczyk et al. [40]. In that study, CaO existence was verified due to the surface hydroxyl ions at around 3642 cm⁻¹ that did not originate from HAp, suggesting a transformation of CaO to Ca(OH)₂. The absorbance band at \sim 3642 cm⁻¹ has been assigned to the surface hydroxyl ions [1]. However, this band was not observed for sample 2Mg0F0, verifying that the CaO phase did not transform to Ca(OH)₂. Additionally, some irregular fluctuations were observed in the FTIR spectra of the samples. These fluctuations may be due to the impurities present in the samples. Additionally, as the β -TCP content increased, broadening accompanied with the reduction in the intensities was observed in the bands assigned for the PO_4^{3-} groups. As the β -TCP phase occurred in sample 1.5Mg0F0 and totally in sample 1.2Mg0F0, additional peaks were detected at around



Fig. 7. FTIR patterns of the sintered CaP samples of group 2: a) 1.95Mg2.5F2.5; b) 1.625Mg2.5F2.5; c) 1.463Mg2.5F2.5; d) 1.17Mg2.5F2.5.

the infrared frequencies 1126 cm^{-1} and 971 cm^{-1} , which can be attributed to the β -TCP phase [42].

The FTIR spectra for the samples in group 2 are presented in Fig. 7. All of the samples were doped with 2.5 mole% Mg^{2+} and F⁻ ions with Ca/P ratios ranging from 1.95 to 1.17 as seen in Table 1. The bands assigned for the PO₄ groups and OH⁻ vibrational modes were also visible for this group. As is seen in Fig. 7(a-d), the broadening of the PO₄ groups were also gradually increased from sample 1.95Mg2.5F2.5 to 1.17Mg2.5F2.5 with an increase in the â-TCP content (Table 4) similar to the samples in group 1. In samples 1.95Mg2.5F2.5 and 1.625Mg2.5F2.5 the dominant phase was HAp, while for samples 1.463Mg2.5F2.5 and 1.17Mg2.5F2.5 the β -TCP phase was dominant. As a result, the characteristic bands of OH- groups for HAp disappeared for samples 1.463Mg2.5F2.5 and 1.17Mg2.5F2.5. In samples 1.95Mg2.5F2.5 and 1.625Mg2.5F2.5 additional peaks other than HAp were identified at frequencies 3544.6 cm⁻¹ [47] and \sim 720 cm⁻¹ [16], which were assigned to the incorporated F⁻ ions replacing by the OH⁻ groups of HAp. It should also be noted that as a result of the partial replacement of the F⁻ ions with the OH⁻ groups, the peaks corresponding to OH- were not as intense as the ones detected for the pure HAp (sample 1.67Mg0F0) with no additional phases. For the samples 1.95Mg2.5F2.5 and 1.625Mg2.5F2.5, the librational OH- peak at 631.7 cm⁻¹ for HAp was considerably shifted from its normal position to $\sim 640 \text{ cm}^{-1}$ due to the incorporation of F⁻ ions into the apatite unit structure. In a FTIR study for HAp/ β -TCP composites co-substituted with Na²⁺, Mg^{2+} and F^{-} ions, approximately the same amount of peak shift was also reported as a result of the Fincorporation [16].

It was reported that the presence of the CaO phase could be identified with FTIR by determining the existence of the surface hydroxyl ions due to the transformation of the CaO phase to Ca(OH)₂ [40]. The FTIR band at \sim 3642 cm⁻¹ has been assigned to the surface hydroxyl ions [1, 36]. This peak could not be detected also as in the case of sample 2Mg0F0. This might be also due



Fig. 8. FTIR patterns of the sintered CaP samples of group 3: a) 1.65Mg1F2.5; b) 1.625Mg2.5F2.5; c) 1.542Mg7.5F2.5.

to the presence of F^- ions forming a new peak at 3544.6 cm⁻¹ assigned to the F-OH bonding, interrupting a possible transformation from CaO to Ca(OH)₂. It should also be noted that the OH⁻ source for F-OH bond assignment was mainly at the OH stretching and librational modes of HAp, which was easily observed for the samples in group 5.

In Fig. 8, the FTIR patterns of the samples in group 3 are presented. The Ca/P ratios ranged from 1.65 to 1.542 as a result of the increase in the amount of Mg^{2+} ions replacing the Ca²⁺ ions. In all the samples, the F⁻ content was constant at 2.5 mole%, while the Mg content was 1, 2.5 and 7.5 mole% for the samples 1.65Mg1F2.5, 1.625Mg2.5F2.5 and 1.542Mg7.5F2.5, respectively. The characteristic vibration modes for the PO₄³⁻ groups and OH⁻ groups that were aroused from HAp and F-OH bonding were also visible for this group. Due to the incorporation of F⁻ ions, the same amount of peak shift was also observed at the OH⁻ librational mode for this group as in the previous one.

For the first two groups, broadening and a decrease in the intensities were observed for the PO_4^{3-} groups with the increase in the β -TCP and therefore the decrease in the HAp content (by weight). Although a decrease in the HAp content was also observed for group 3, the intensities of the PO_4^{3-} groups were increased significantly as the Mg²⁺ ion content increased from 1 mole% to 7.5 mole%. As a result of the Mg²⁺ ion addition, a slight shift of the 3571.6 cm⁻¹ absorbing bands was observed. Broadening of the phosphate bands and a slight shift of the 3571.6 cm⁻¹ bands was also reported for increasing amounts of Mg²⁺ ion substitution into HAp ceramics [38, 39].

The FTIR patterns of the samples in group 4 are presented in Fig. 9. In this group, Ca/P ratios were also ranged from 1.65 to 1.542 as a result of the increase in the amount of Mg^{2+} ions replacing the Ca²⁺ ions. The Mg^{2+} contents were 1, 2.5 and 7.5 mole% for the samples 1.65Mg1F0, 1.625Mg2.5F0 and 1.542Mg7.5F0 as in the previous group. However, no F⁻ was present within the samples of this group. As a result, the peaks due to F-OH⁻ bonding



Fig. 9. FTIR patterns of the sintered CaP samples of group 4: a) 1.65Mg1F0; b) 1.625Mg2.5F0; c) 1.542Mg7.5F0.

were not observed in these spectra. The infrared frequencies assigned for PO_4^{3-} groups and OH^- librational, stretching modes were almost at the same wave numbers in comparison with group 1. In particular for sample 1.542Mg7.5F0, an increase was also observed in the intensities of the PO_4^{3-} groups similar to group 3 due to the increased Mg²⁺ ion content. However, with the existence of 2.5 mole% F^- , this increase was quantitatively more accurate for group 3. Similar to groups 1 and 2, the intensities of the OH^- groups of HAp were also decreased with the decrease in the HAp content.

Finally, the FTIR patterns of group 5 are presented in Fig. 10. The effect of increase in the F content from 0 to 7.5 mole% was investigated for the CaP samples with a constant 1.625 Ca/P ratio and 2.5 mole% Mg²⁺. Apart from the vibrational modes of PO₄³⁻ groups and OH⁻ groups of HAp, the infrared frequencies assigned to the OH-F bonding were also observed in an increasing manner with the increase in the F⁻ content. Intensities of the librational and stretching modes of OH⁻ were gradually decreased forming a shoulder for the sample 1.625Mg2.5F7.5, while the intensities at around 720 cm⁻¹ and 3544.6 cm⁻¹ were gradually increased as a result of the F⁻ ions replacing OH⁻ ions. The presence of the peaks assigned for the OH⁻ librational and stretching modes



Fig. 10. FTIR patterns of the sintered CaP samples of group 5: a) 1.625Mg2.5F0; b) 1.625Mg2.5F2.5; c) 1.625Mg2.5F7.5.



Fig. 11. SEM images of: a) 2Mg0F0; b) 1.67Mg0F0; c) 1.5Mg0F0; d) 1.2Mg0F0; e) 1.95Mg2.5F2.5; f) 1.625Mg2.5F2.5; g) 1.463Mg2.5F2.5; h) 1.17Mg2.5F2.5; i) 1.65Mg1F2.5; j) 1.542Mg7.5F2.5; k) 1.65Mg1F0; l) 1.625Mg2.5F0; m) 1.542Mg7.5F0 and n) 1.625Mg2.5F7.5. The scale bars are 500 nm.

confirms that the F ions only partially replaced the OH⁻ ions, resulting in the formation of flouridated HAp. The peak shifts that were detected due to the incorporation of F⁻ ions in groups 2 and 3 were also observed for group 5. The amount of the peak shift was found to be increased (~670 cm⁻¹) with 7.5 mole% F⁻ content for sample 1.625Mg2.5F7.5.

SEM images of the pure and doped CaPs are given

in Fig. 11. All of the images were taken from the samples that were sintered at 1100 °C for 1 h. The average grain sizes of the samples according to their groups are presented in Table 6.

The SEM examinations revealed that the average grain sizes were generally increased with an increase in the β -TCP content. The presence of the CaO phase (in sample 2Mg0F0 and 1.95Mg2.5F2.5) increased the average grain

Group No	Sample ID	Auerage Grain size (nm)
1	2Mg0F0	267
	1.67Mg0F0	261
	1.5Mg0F0	213
	1.2Mg0F0	566
2	1.95Mg2.5F2.5	261
	1.625Mg2.5F2.5	222
	1.463Mg2.5F2.5	636
	1.17Mg2.5F2.5	740
3	1.65Mg1F2.5	197
	1.625Mg2.5F2.5	222
	1.542Mg7.5F2.5	600
4	1.6Mg1F0	256
	1.625Mg2.5F0	245
	1.542Mg7.5F0	453
5	1.625Mg2.5F0	245
	1.625Mg2.5F2.5	222
	1.625Mg2.5F7.5	208

 Table 6. Average grain sizes of the samples

sizes of these samples, suggesting that the phase purity could be a factor in reducing the grain sizes. In group 2, the average grain sizes were increased with a decrease in the Ca/P ratios and therefore an increase in the β -TCP content, except for sample 1.95Mg2.5F2.5 to sample 1.625Mg2.5F2.5 because of the presence of the CaO phase in sample 1.95Mg2.5F2.5.

In group 3, in which the Mg^{2+} ion content varied from 1 to 7.5 mole% with a constant amount of F^- ions, the smallest average grain size was achieved for 1 mole% Mg^{2+} and 2.5 mole% F^- (sample 1.65Mg1F2.5).

For very small concentrations of magnesia (MgO) substitutions (in the range of 0.25 to 3.00 wt%) into HAps, a gradual decrease in the average grain sizes has been observed with an increase in the Mg²⁺ content [39]. On the other hand, when the Mg²⁺ concentrations ranged from 1 to 7.5 mole%, a decrease in the average grain sizes of the samples did not occur. Therefore, the smallest grain size was achieved for sample 1.65Mg1F2.5 doped with 1 mole% Mg²⁺ and 2.5 mole% F⁻. However, for the sample 1.65Mg1F0 in group 4, which was doped with 1 mole% Mg, an increase was observed in the average grain size. Therefore, the decrease in the average grain size of sample 1.65Mg1F2.5 should not only be attributed to the presence of Mg²⁺ but also to the presence of F⁻ ions.

As the relative densities of the samples were decreased, a discontinuity in the pore distribution was observed for the samples in group 4 as the Mg^{2+} content was increased. It was previously shown that in Mg^{2+} doped HAps, large grains correspond to unsubstituted HAp while the substitution of Mg^{2+} for Ca²⁺ occurred in smaller grains [39]. In group 5, among the samples doped with a constant amount of Mg^{2+} , as the F⁻ content was increased from 0 to 7.5 mole%, the average grain size was gradually decreased.

In group 1, the highest microhardness value was obtained for a Ca/P ratio of 2.00 and as the Ca/P ratio was decreased, the microhardness was decreased gradually (Fig. 12). Jarcho *et al.* determined the hardness of dense polycrystalline HAp ceramics sintered in air by the Knoop method as equal to 4.8 GPa while the hardness of natural apatite reached to ~4.3 GPa [29].

In group 2, a gradual decrease in the microhardness values was also observed for the same variations of Ca/P ratios with 2.5 mole% Mg²⁺ and F⁻ additions as seen in Fig. 13. However, in group 2, the decrease in the microhardness values started from a smaller value and reached its minimum with a greater slope as a result of the Mg²⁺ addition. For the CaP precipitates with Ca/P ratios higher then 1.67 formed CaO phase besides HAp after the sintering at 1250 °C [36], which was also detected for the samples 2Mg0F0 and 1.95Mg2.5F2.5 in their XRD patterns. It was also reported that CaO can transform into Ca(OH)₂ in air and then partially to CaCO₃, which significantly decreases the hardness of the samples 2Mg0F0 and 1.95Mg2.5F2.5 were found to be the highest among



Fig. 12. Micro-hardness values of the samples in group 1: a) 2Mg0F0; b) 1.67Mg0F0; c) 1.5Mg0F0; d) 1.2Mg0F0. All samples were sintered at $1100 \text{ }^{\circ}\text{C}$ for 1 h.



Fig. 13. Micro-hardness values of the samples in group 2: a) 1.95Mg2.5F2.5; b) 1.625Mg2.5F2.5; c) 1.463Mg2.5F2.5; d) 1.17Mg2.5F2.5.

the groups 1 and 2 despite the presence of the CaO phase. This behavior should suggest that CaO to $Ca(OH)_2$ transformation did not occur for these samples, which was also confirmed by the FTIR patterns from these samples.

It has been reported that the addition of Mg^{2+} ions into HAp ceramics resulted in a reduction of both densities and the Vickers hardness values of the HAp ceramics [39]. In groups 3 and 4, the effect of an increase in the Mg^{2+} content with a constant amount of F dopant (2.5 mole%) and the effect of Mg^{2+} alone were investigated, respectively (Figs. 14, 15). The hardening effect of the F⁻ addition was confirmed by comparing the microhardness results for groups 3 and 4. The microhardness values showed the same characteristic slope in both groups.

In group 4, with no F^- addition, the decrease in the microhardness values due to the increase in the Mg²⁺ content started from a smaller value in comparison with group 3. Generally, it was observed that in the absence of F^- ions, the microhardness values of the samples became smaller.

Finally, the affect of an increase in the F^- content on to the microhardness values was investigated, for group 5 (Fig. 16). The hardening effect of the F^- ion was also confirmed by the measurements among the compositions in this group. As seen in Fig. 16, an increase in the microhardness values of the samples was proportional to the increase in the F^- amount.



Fig. 14. Micro-hardness values of the samples in group 3: a) 1.65Mg1F2.5; b) 1.625Mg2.5F2.5; c) 1.542Mg7.5F2.5.



Fig. 15. Micro-hardness values of the samples in group 4: a) 1.65Mg1F0; b) 1.625Mg2.5F0; c) 1.542Mg7.5F0.



Fig. 16. Micro-hardness values of the samples in group 5: a) 1.625Mg2.5F0; b) 1.625Mg2.5F2.5; (c) 1.625Mg2.5F7.5.

b

Sample ID

0

а

Conclusions

In this study, CaPs with ratios ranging from 1.17 to 2.00 were produced by a precipitation method. Mg^{2+} and/or F⁻ ions were doped into this material with varying amounts in order to investigate the effects on microstructural and mechanical properties. Additionally, with the addition of Mg^{2+} ions to HAp/β -TCP biphasic ceramics were produced with varying ratios, which are tailored both with the Ca/P ratios of the precursors and the Mg²⁺ contents. All the samples were sintered at 1100 °C for 1 h. The densities measured by the Archimedes method were higher compared to the ones measured by the geometrical method due to the difference in the preparation methods. High densities were achieved for the pure and doped HAps except for the ones doped with 7.5 mole% Mg²⁺. The XRD patterns revealed that the increase in the β -TCP phase was proportional to the increase in the Mg²⁺ content and inversely proportional to the decrease in the Ca/P ratios and the F content. The hexagonal lattice parameter measurements revealed the substitution of the ions into the apatite structure. The FTIR measurements revealed that all of the samples showed the characteristic bands for HAp and β -TCP. SEM images revealed that the grain sizes generally increased with an increase in the Mg²⁺ content and decreased with an increase in the F⁻ content. The microhardness values of the samples were also decreased with an increase in Mg²⁺ ions and therefore the amount of β-TCP and increased with an increase in the F⁻ content.

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