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Paper

Al^{3+} Doped Nano-Hydroxyapatites and their Sintering Characteristics

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Pure and Al^{3+} doped nano-hydroxyapatites (HA) were synthesized by a precipitation method to investigate their densification and thermal stability after the air sintering at 1100°C and 1300°C. Second phases were formed after increasing the Al^{3+} content from 2.5% to 7.5% in HA and increasing the sintering temperature from 1100°C to 1300°C. Al^{3+} addition into HA resulted in change in the hexagonal lattice parameters from the pure HA. When the sintering temperature was increased from 1100°C to 1300°C, densification was improved, which was verified by SEM micrographs. Al^{3+} addition resulted in smaller grain size after the sintering at 1300°C.

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1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has been widely used as a bulk implant in non-load bearing areas of body and as coatings on implant metals. Structure of the inorganic part of the bone is similar to that of the pure HA. Some of the elements present in natural apatite are Mg^{2+}, F^-, CO_3^{2-}, etc.[1)]

Doping of HA with various elements was previously studied by many researchers. For example, Ergun et al.[2)] investigated the structure of HA doped with Mg^{2+}, Zn^{2+} and Y^{3+}. It was proposed that Y^{3+} ions completely substituted in HA. This was verified by a decrease in the hexagonal lattice volume of doped HA. Moreover, Y^{3+} doped HA had an improved osteoblast adhesion than pure HA. In addition to this study, osteoblast response to HA doped with Mg^{2+}, Zn^{2+}, La^{3+}, Y^{3+}, In^{3+}, and Bi^{3+} was done by Webster et al.[3)] It was proposed that these cations might have substituted for calcium in the HA. It was found that osteoblasts differentiated on HA doped with La^{3+}, Y^{3+}, In^{3+}, and Bi^{3+} cations faster than pure HA or HA doped with Mg^{2+} and Zn^{2+}.[3)]

Trace amount of Al^{3+} cations are present in the natural apatite.[4)] It was reported that a combination of Al^{3+} and F^- had an inhibitory effect on dissolution of bovine enamel powder.[5)] Moreover, it was suggested that Al^{3+} was adsorbed on the mineral surface.[5),6)] During the synthesizing process, the uptake of Al^{3+} into HA was almost complete at pH 7 and near to 60% at pH 9.[6)] Al^{3+} containing HA prepared at pH 7 and heated up to 700°C, transformed partially to β-tri calcium phosphate (TCP).[6)] No information was available about the amount of transformation from HA to β-TCP.

In this study, Al^{3+} doped HAs were synthesized by a precipitation method at pH 11. Pure HA and Al^{3+} doped HA were sintered in air at 1100°C and 1300°C. Structure of the apatite and transformation from HA to TCP were determined by X-ray diffraction (XRD). The grain sizes were measured with scanning electron microscope (SEM).

2. Experimental procedure

Bulk ceramic compounds used in this research are pure HA and Al^{3+} doped HA made by a precipitation method.[7)]

For the HA synthesis, 0.5 M $Ca(NO_3)_2 \cdot 4H_2O$ (300 ml) and 0.3 M $(NH_4)_2HPO_4$ (100 ml) were dissolved in distilled water separately. The Ca/P ratio should be 1.67 when these solutions are mixed to produce stoichiometric HA. NH_4OH was added to both of these solutions to bring the pH to 11. Then calcium nitrate solution was added drop wise into the continuously stirred ammonium phosphate solution. After stirring the HA solution at RT for 2–3 h, it was heated up to 90°C for 1 h during stirring. Then the solution was stirred for one more day at RT. In the next step, the solution was washed repeatedly and then filtered using a fine filter paper. The filtered wet cake was dried in an oven at 90°C overnight. Finally the dried cake was sintered at 1100°C or 1300°C for 1-h; it was heated and cooled in the furnace.

Al^{3+} doped HA samples were synthesized by a precipitation method. Aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) was dissolved in distilled water and the pH was brought to 11. Then this solution was added drop wise into an ammonium phosphate solution. Finally, calcium nitrate solution was added drop wise into this solution. Ca/P ratio was kept at 1.67 same as in stoichiometric HA synthesis. All the other steps were the same as for HA synthesis. 0.25, 0.5 and 0.75 moles of $Al(NO_3)_3$ ($9H_2O$ was added into the solution for every 10 mole of Ca $(NO_3)_2 \cdot 4H_2O$. Samples designations are given in **Table 1**.

The samples were characterized by XRD to determine which phases were present in the synthesized compounds. XRD was performed on all of the samples with Cu Kα radiation at 50 kV/30 mA with a Scintag XRD diffractometer (Sunnyvale, CA) and each sample was scanned in 2 θ interval of 10° and 80° with a speed of 1 degree/min. The patterns were compared with JCPDS files to identify each phase. The relative amounts of phases were determined from the most intense XRD peaks of the phases present (HA, α and β TCP).[8)] It is assumed that the concentrations (wt%) of HA and TCP phases are proportional to their peak heights in the mixtures. First, the ratio R_O of the peak heights of HA to that of α or β TCP was determined for mixtures of known concentrations of HA and α or β TCP. It was found that the ratio R_O did not depend on the relative amounts of HA and TCP; the values of R_O found were 1.755 for $R_O = I_H/I_\beta$ and $R_O = I_H/I_\alpha = 2.217$, where I_H, I_β and I_α are the XRD peak heights for HA, β-TCP and α-TCP, respectively, in mixtures of known concentrations. Then for mixtures of HA and β-TCP:

$$\frac{W_H}{W_\beta} = \frac{R}{R_O} \quad (1)$$

where W_H and W_β are the weight fractions of HA and β-TCP, respectively. A similar formula for mixtures of HA and α-TCP, with W_α substituted for W_β, was used. XRD angle positions were used to calculate the hexagonal unit lattice parameters of the pure and Al^{3+} doped HA by an iteration method. The volume of the each unit cell was calculated by the

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Table 1. Pure and Al^{3+} Doped Hydroxyapatites

Sample Designation	Description
HA	100 % hydroxyapatite
2.5Al	0.25 mole of $Al(NO_3)_3 \times 9H_2O$ for every 10 mole of $Ca(NO_3)_2 \cdot 4H_2O$ in HA.
5Al	0.5 mole of $Al(NO_3)_3 \times 9H_2O$ for every 10 mole of $Ca(NO_3)_2 \cdot 4H_2O$ in HA.
7.5Al	0.75 mole of $Al(NO_3)_3 \times 9H_2O$ for every 10 mole of $Ca(NO_3)_2 \cdot 4H_2O$ in HA.

Table 2. Relative Density of Pure HA, 2.5Al, 5Al, and 7.5Al

Mixture	1100°C	1300°C
HA	98.7	98.2
2.5Al	94.7	97.6
5Al	91.4	99.7
7.5Al	93.2	92.9

following formula $V = 2.589 \cdot a^2 \cdot c$.[2)]

The Archimedes method was used to determine the density (ρ) of the materials. The following formula was used to calculate the density of the samples.[9)]

$$Density(\mathrm{gm/cm^3}) = \frac{Wt(\mathrm{air})}{Wr(\mathrm{air}) - Wt(\mathrm{water})} \times \rho_{\mathrm{water}} \quad (2)$$

The theoretical density of the pure and Al^{3+} doped HA's were assumed same ($3.156\ \mathrm{g/cm^3}$).

A JOEL (JSM-840) scanning electron microscope at a voltage of 15 kV was used to examine the samples. Samples were etched with a 0.15 M lactic acid for 10 sec. They were coated with gold under vacuum before the characterization in SEM. Grain size was determined by the intercept method. The following formula was used to determine the grain sizes from the SEM micrographs.[10)]

$$G_{\mathrm{ave}} = \frac{L}{N*M} \quad (3)$$

where, G_{ave}: average grain size, L: circumference of the circle (20 cm), N: number of intersections along 20 cm circumference line, M: magnification

3. Results and discussion

Relative density of pure HA and Al^{3+} doped HA is given in **Table 2**. There was an increase in the density for 2.5Al and 5Al when the sintering temperature increased from 1100°C to 1300°C. Addition of Al^{3+} ions to the HA resulted in increased porosity, especially at 1100°C. The sinterability of Al^{3+} doped HAs was decreased at 1100°C. When the sintering temperature was increased to 1300°C, Al^{3+} doped HA showed better densification.

The average grain size of the pure HA and 5Al determined from the micrographs (**Figs. 1** and **2**) are given in **Table 3**.

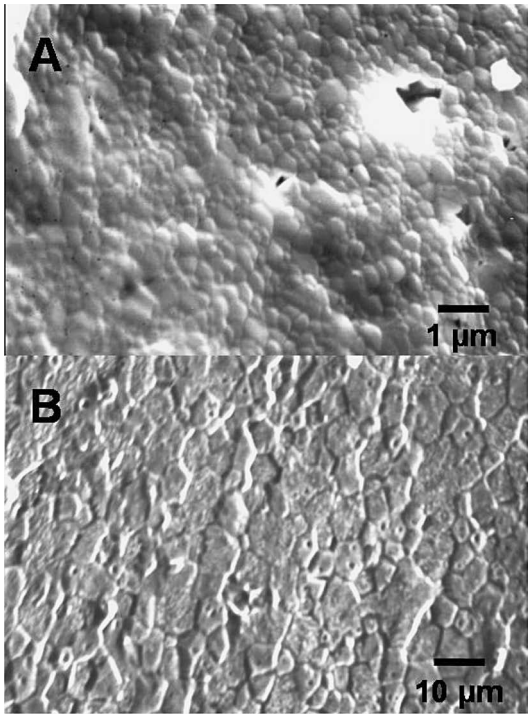

Fig. 1. SEM images of HA sintered at 1100°C for 1 h (A) and 1300°C for 1 h (B).

For sintering at 1100°C, the grain size of pure HA was smaller than that of 5Al. However, after the sintering at 1300°C, 5Al had substantially decreased grain size comparing with pure HA.

The main purpose of this study was to investigate thermal stability of Al^{3+} doped HAs after high sintering temperatures. The phases present for different Al^{3+} concentrations and sintering temperatures can be deduced from the XRD patterns in **Fig. 3**. When pure HA was sintered at 1100°C (Fig. 3(A)), there was no evidence for decomposition of the HA. Moreover, pure HA decomposed to TCP only 2% after the sintering at 1300°C (Fig. 3(B) and **Table 4**). However, when 2.5Al, 5Al, and 7.5Al were sintered at 1100°C, the HA phase partially transformed to the TCP phase (Fig. 3, patterns: C-H), which had the β structure, whereas for sintering at 1300°C it had α-structure. The amounts of HA in the pure and doped HA as calculated from the intensities of the XRD lines and Eq. (1) are given in Table 4. The decomposition of HA

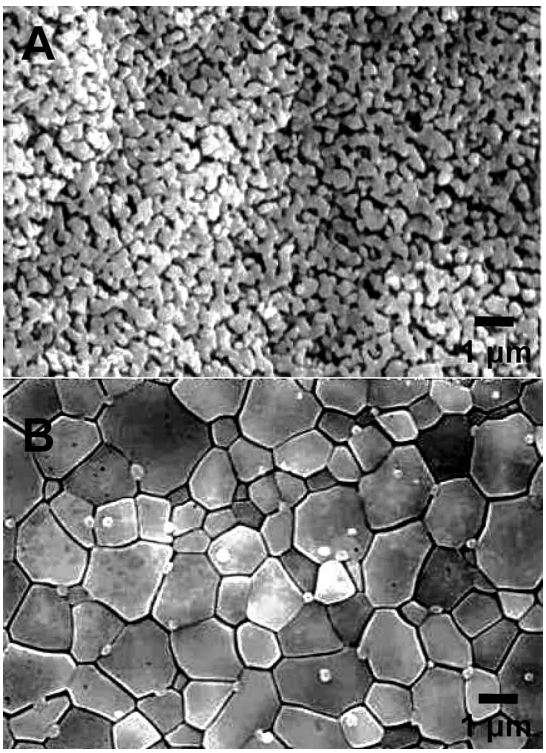

Fig. 2. SEM images of 5Al: after the sintering at 1100°C for 1 h (A) and at 1300°C for 1 h (B).

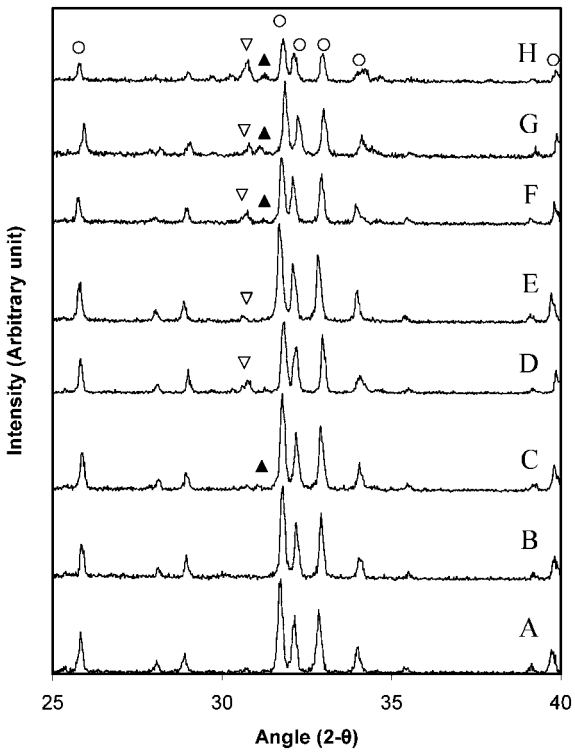

Fig. 3. XRD patterns of pure HA sintered at 1100°C-1 h (A), pure HA sintered at 1300°C-1 h (B), 2.5Al sintered at 1100°C-1 h (C), 2.5Al sintered at 1300°C-1 h (D), 5Al sintered at 1100°C-1 h (E), 5Al sintered at 1300°C-1 h (F), 7.5Al sintered at 1100°C-1 h (G), and 7.5Al sintered at 1300°C-1 h (H). (Phases: ○ HA, ▽ α-TCP, ▲ β-TCP)

Table 3. Average Grain Sizes of Pure HA and 5Al, as Measured from SEM Micrographs Shown in Figs. 1 and 2

	Average Grain size (μm)	
Mixture	**1100°C**	**1300°C**
HA	0.26 ± 0.04	4.44 ± 0.72
5% Al	0.59 ± 0.06	1.59 ± 0.08

Table 4. Weight Fraction W_H of HA in the Samples after Sintering, from the Intensities of X-ray Lines and Eq. (1)

	W_H	
Sample ID	**1100°C**	**1300°C**
HA	1	0.98
2.5Al	0.96	0.72
5Al	0.90	0.67
7.5Al	0.75	0.53

was greater at 1300°C than at 1100°C, especially for the higher Al^{3+} concentrations. It was found that Al^{3+} ions promoted the formation of TCP. No X-ray peaks were observed for aluminum oxides. Therefore, Al amount should be kept less than 5 mole% of the total Ca present in HA to minimize second phase formations especially α-TCP or β-TCP because it promotes the formation of TCP greatly.

The exchange of Al^{3+} ions for Ca^{2+} ions in the HA structure explains the increased tendency of the exchanged HA to decompose. The Al^{3+} ion introduces strain into the HA network structure, making the decomposition of HA (Eq. 4) more favorable.

$$Ca_{10}(PO_4)_6(OH)_2 \longrightarrow 3Ca_3(PO_4)_2 + CaO + H_2O \quad (4)$$

The increased tendency of decomposition of HA with reaction with Al^{3+} ions can be explained as resulting from removal of calcium from the HA and its dissolution into TCP and CaO. It is proposed that the removal of calcium ions from HA involves an exchange reaction with Al^{3+} ions. The radius of Ca^{2+} is about 0.1 nm; that of Al^{3+} is about 0.039 nm.[11),12)] Thus when the Al^{3+} ion is substituted for Ca^{2+}, the volume of the hexagonal unit cell of the HA is expected to be decreased as seen in **Table 5**. Moreover, the presence of vacancies created by OH^- removal from HA increased by the exchange of Ca^{2+} and Al^{3+} ions.

The increased porosity of the sintered HA with the addition of Al^{3+} ions probably resulted because of the water generated by decomposition of the HA (reaction 4). This water is held in pores formed during sintering, and must diffuse out of the HA matrix to form dense HA.

Table 5. Hexagonal Lattice Parameters for HA in Al^{3+} Doped HAs and Volume and Volume Changes of the Unit Cell

Mixture	Lattice Parameters in Å			
	a, 1100°C	**c,** 1100°C	**a,** 1300°C	**c,** 1300°C
HA	9.4264	6.8884		
2.5Al	9.4248	6.8812	9.4140	6.8916
5Al	9.4252	6.8920	9.4136	6.9013
7.5Al	9.4218	6.8807	9.4078	6.8937

Mixture	Volume ($Å^3$)		ΔVol. ($Å^3$)	
	1100°C	1300°C	1100°C	1300°C
HA	1584.7		0	
2.5Al	1582.5	1581.2	-2.2	-3.4
5Al	1585.1	1583.3	0.4	-1.3
7.5Al	1581.4	1579.7	-3.3	-5.0

4. Conclusions

Al^{3+} ions reduced the grain size of the HA after the sintering at 1300°C. Doping of Al^{3+} ions into HA accelerated the decomposition of HA into TCP and CaO. Increasing the sintering temperature of the Al^{3+} doped HAs from 1100°C to 1300°C improved their densification. Finally, mole% Al^{3+} ions in the HA should be kept less than the 5% of the Ca^{2+} ions present in HA.

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