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Ceramics International 39 (2013) 2359–2363

CERAMICS INTERNATIONAL

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X-ray investigation of sintered cadmium doped hydroxyapatites

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Received 1 July 2012; received in revised form 27 August 2012; accepted 28 August 2012
Available online 3 September 2012

Abstract

Pure and cadmium (Cd) doped hydroxyapatites (HA, $Ca_{10}(PO_4)_6(OH)_2$) were synthesized by a precipitation method from aqueous solutions of $Ca(NO_3)_2 4 \cdot H_2O$ for the former and $Cd(NO_3)_2 4 \cdot H_2O$ for the latter, by using $(NH_4)_2HPO_4$ as the phosphate source, while pH was kept in the range of 11–12. The effect of incorporation of Cd^{2+} ions into the structure of HA was investigated after the air sintering at 1100 °C for 1 h. The results indicate that Cd^{2+} addition into HA yields nearly fully densified products with respect to pure stoichiometric HA. The XRD patterns showed that Cd doping increases the crystallinity of HA. The 2, 4.4, and 8.8 mol% Cd doped HAs had calcium oxide (CaO) impurity phase in their lattice. The CaO phase in the HA structure gradually disappeared with increasing Cd amount, and was replaced with cadmium oxide (CdO) in the CdHA doped with 11 mol% Cd. Cd^{2+} ion incorporation decreased the a- and c-axis lattice constants and unit cell volume of HA.

Keywords: A. Sintering; B. X-ray methods; D. Apatite; Cadmium

1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has been widely used in various biomedical applications. Calcium ions (Ca^{2+}) in HA can be substituted by heavy metals and metal toxicity in vertebrates mostly attacks hard tissues. Indeed, natural or synthetic apatite shows significant reactivity to the toxic metals. Metal ions either accumulate and bind with HA on its surface or go inside and substitute in the location of Ca^{2+} ions in the structure which results in changes in hexagonal lattice parameters of HA. Among these, cadmium (Cd) is highly toxic and is known to be a carcinogen. It can be taken into the human body via nutrition, drinking water, smoking, and even breathing [1]. Cd toxicity in body can cause ‘Itai itai’ disease, where Ca of bones was replaced with Cd, causing osteoporosis, osteomalacia and kidney damage [2]. On the other hand, the ion exchange ability of HA can be used for removal of this metal from waste water.

Removal of cadmium ions (Cd^{2+}) from aqueous solutions by HA with the influence of different sorption parameters were previously studied by various groups [1,3]. Moreover, removal characteristics of Cd from aqueous solution by a phosphate rock were determined by investigating various operating variables [4]. In order to remove the toxic heavy metal ions from waste water, aqueous solutions and contaminated soil, HA has been widely used [1,4,5]. The immobilization of Cd in filters of HA was also studied [6]. Moreover, it was shown that the phosphate group containing minerals are the controlling solids for Ca^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} in soils [7–9].

Cadmium hydroxyapatites (CdHA, $Cd_{10}(PO_4)_6(OH)_2$) were synthesized from various chemical sources and synthesis methods [2,10–16]. For example, CdHAs were synthesized from the aqueous solutions of Cd-nitrate, ammonium phosphate and acetamide [2]. Cd source chemicals could be listed as $Cd(OH)_2$, $(CdHPO_4)_3 \cdot 3(NH_3) \cdot 3(H_2O)$, $Cd_3(PO_4)_2$ and CdO etc. [10,11,13–15]. Various synthesis methods were previously used to synthesize the CdHAs, such as the wet chemical method,

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http://dx.doi.org/10.1016/j.ceramint.2012.08.087

hydrolysis method, and hydrothermal method [2,10–13,15–18]. It was shown that the pH value of the solution is very important in determining the final crystalline structure of CdHA [17,18]. It was proposed that a high pH is necessary to obtain CdHA. Otherwise, other Cd phosphates like $Cd_5H_2(PO_4)_4\cdot 4(H_2O)$ could be formed at low pH values [18]. However, in low pH, CdHA with a chemical formula of $Cd_{10}(PO_4)_6(OH)_2$ was synthesized which has a hexagonal crystalline structure with the unit cell parameters of $a=9.335$ Å and $c=6.664$ Å [16]. The volume of this unit cell is slightly smaller than that of pure HA.

In addition to Cd–HAs, the structure of various Cd-apatites ($Cd_5(VO_4)_3I$, $Cd_5(PO_4)_3Br$, $Cd_5(AsO_4)_3Br$, and $Cd_5(VO_4)_3Br$) was previously studied [19]. It was found that these compounds were close to isostructural similar to fluroapatite ($Ca_5(PO_4)_3F$) [19].

Cd doped strontium HAs or fluroapatites (FA) were synthesized with various chemical compositions and investigated by X-ray diffraction and IR methods [20]. Cd doped HAs were synthesized by a wet method using the chemicals of $Cd(CH_3COO)_2\cdot 2(H_2O)$, $Ca(CH_3COO)_2\cdot H_2O$ and ammonium phosphate [21]. Moreover, modeling hexagonal unit cell parameters of Cd doped HAs from pure HA to pure CdHA showed a satisfactory match with the experimental data [22].

In this study, the Cd–HA interaction and the structural effects of Cd incorporation into HA lattice were investigated. Pure and Cd^{2+} doped HAs were synthesized by a precipitation method at a pH of 11–12 for the first time. Samples were sintered in air at 1100 °C for 1 h. After the sintering, density of the samples was determined by the Archimedes method. Presence of phases and unit cell parameters of the samples were determined by X-ray diffraction (XRD).

2. Material and methods

In this study, pure HA and Cd^{2+} doped HAs were synthesized by a precipitation method [23,24]. For the synthesis of pure HA, 0.5 M calcium nitrate ($Ca(NO_3)_2\cdot 4H_2O$) and 0.3 M ammonium phosphate ($(NH_4)_2HPO_4$) were dissolved in distilled water, separately. The Ca/P ratio was adjusted to 1.67 when these solutions were mixed to synthesize stoichiometric HA. Ammonium hydroxide (NH_4OH) was added to both of these solutions to bring the pH level to 11–12. Then, calcium nitrate solution was poured dropwise into the continuously stirred ammonium phosphate solution. The solution was stirred at room temperature (RT) for 1 day. Then the solution mixture was washed repeatedly and then filtered by using a fine filter paper. The filtered cake was dried in an oven at 90 °C. Finally, the dried cake was sintered in air atmosphere at 1100 °C for 1 h.

Cd^{2+} doped HAs were also synthesized by the same precipitation method. Cadmium nitrate ($Cd(NO_3)_2\cdot 4H_2O$) was dissolved in distilled water and its pH level was brought to 11–12. Then, this solution was added dropwise into the ammonium phosphate solution. Finally, calcium nitrate solution was added dropwise into this solution. All other steps were the same as for pure HA synthesis. The sample compositions and designations are presented in Table 1.

Table 1
Sample designation of pure and Cd^{2+} doped hydroxyapatites synthesized in this study.

Sample designation	Description
HA	100% Hydroxyapatite
2CdHA	2 mol of $Cd(NO_3)_24\cdot H_2O$ for every 98 mol of $Ca(NO_3)_24\cdot H_2O$ in HA
4.4CdHA	4.4 mol of $Cd(NO_3)_24\cdot H_2O$ for every 95.6 mol of $Ca(NO_3)_24\cdot H_2O$ in HA
8.8CdHA	8.8 mol of $Cd(NO_3)_24\cdot H_2O$ for every 91.2 mol of $Ca(NO_3)_24\cdot H_2O$ in HA
11CdHA	11 mol of $Cd(NO_3)_24\cdot H_2O$ for every 89 mol of $Ca(NO_3)_24\cdot H_2O$ in HA

The densities of the samples sintered at 1100 °C for 1 h were determined by the Archimedes method as [25]:

$$Density(g/cm^3)=\frac{Wt_{air}}{Wt_{air}-Wt_{water}}\rho_{water} \qquad (1)$$

where ρ_{water} is the density of water, Wt_{air} and Wt_{water} are the weight of the sample in air and water, respectively. The relative density was calculated by taking the theoretical density of HA as 3.156 g/cm^3 [26].

The samples were characterized by XRD to determine the phases present in their structure. XRD studies were performed with Cu-K_α radiation at 50 kV/30 mA with a Scintag XRD diffractometer (Sunnyvale, CA). Each sample was scanned from 20° to 60° in 2θ with a speed of 1 degree/min.

XRD angle positions were used to calculate the hexagonal unit lattice parameters of the pure and Cd^{2+} doped HA by an iteration method [27]. The volume of the each unit cell was calculated by the following formula:

$$V=2.589a^2c \qquad (2)$$

3. Results and discussion

Cadmium is one of the heavy metals that are not involved in any physiological functions but rather have toxic effects on the human body. Although Cd can be found naturally in the environment, the excess amount released from industrial wastes is very hazardous for aquatic and soil life. Due to the remarkable ion exchange capacity of HA, it is considered as an effective Cd binding material which is a disadvantageous feature for the HA in the body. Therefore, it is important to understand the Cd–HA interaction for both the cases. The main purpose of this study was to investigate the substitution of Cd^{2+} ions into HA and the thermal stability of Cd^{2+} doped HAs after sintering at 1100 °C. The sintering temperature was chosen as 1100 °C in order to have a consistent temperature with other researchers in the field. The effect of the sintering on the mechanical properties of HA has been widely studied [24,28,29]. Jarcho et al. [24] have reported that the optimum sintering temperature is 1100 °C for 1 h sintering time in order to obtain pore-free, single-phase, translucent hydroxyapatite. They also demonstrated the presence of decomposition products at grain boundaries of HA sintered at higher temperatures (e.g., 1250 °C for 1 h). Rodriguez-Lorenzo et al. [30] also recommended the optimal heat-treatment temperature as 1100 °C for the development of appropriate microstructure that resulted in optimal mechanical properties. In comparison, the sintering behavior and mechanical properties of Cd doped hydroxyapatite have been hardly studied. Ergun et al. [31] synthesized HA doped with magnesium, zinc, cadmium, and yttrium, separately. Salts of these cations were added to precipitating HA and similarly the precipitates were sintered at 1100 °C for 1 h. They incorporated Cd into the apatite structure at a level of 2% added fraction of Ca in HA. At this sintering temperature, they obtained densities close to theoretical density for sintered samples, which is evidence for low bulk porosity.

The densities of the pure and Cd^{2+} doped hydroxyapatites synthesized in this study are given in Table 2. The densest sample was 2CdHA with a 99% relative density, which was more than the relative density of pure HA. However, the relative densities were slightly and almost linearly decreased from 97.5% for pure HA to 94.5% for 11CdHA. These levels of relative densities of all samples were regarded as high. It can be said that the increase in the amount of Cd^{2+} ions did not alter the relative densities very significantly. Under these sintering conditions (in air at 1100 °C for 1 h), almost fully densified pure and doped HAs were obtained.

The XRD patterns of the pure and Cd doped HA samples together with the standard patterns of HA and β-tricalcium phosphate (β-TCP) are given in Fig. 1. When pure HA (Fig. 1c) was sintered at 1100 °C, there was only HA present in the system corresponding to JCPDS #9-432, whose pattern is given in Fig. 1b. Furthermore, when Cd^{2+} doped HAs were sintered at 1100 °C, the HA phase was stable and there was no β-TCP (JCPDS#9-169, Fig.1a) present in the system. Moreover, increasing the amount of Cd^{2+} ions in the system resulted in an increase in the intensities of HA peaks. This could suggest that increasing the Cd amount resulted in a higher crystallinity in the system.

Table 2
Densities of the pure and Cd^{2+} doped hydroxyapatites sintered at 1100 °C for 1 h.

Sample I.D.	Density(g/cm^3)	Relative density (%)
HA	3.077	97.5
2CdHA	3.123	99.0
4.4CdHA	3.051	96.7
8.8CdHA	3.024	95.8
11CdHA	2.983	94.5

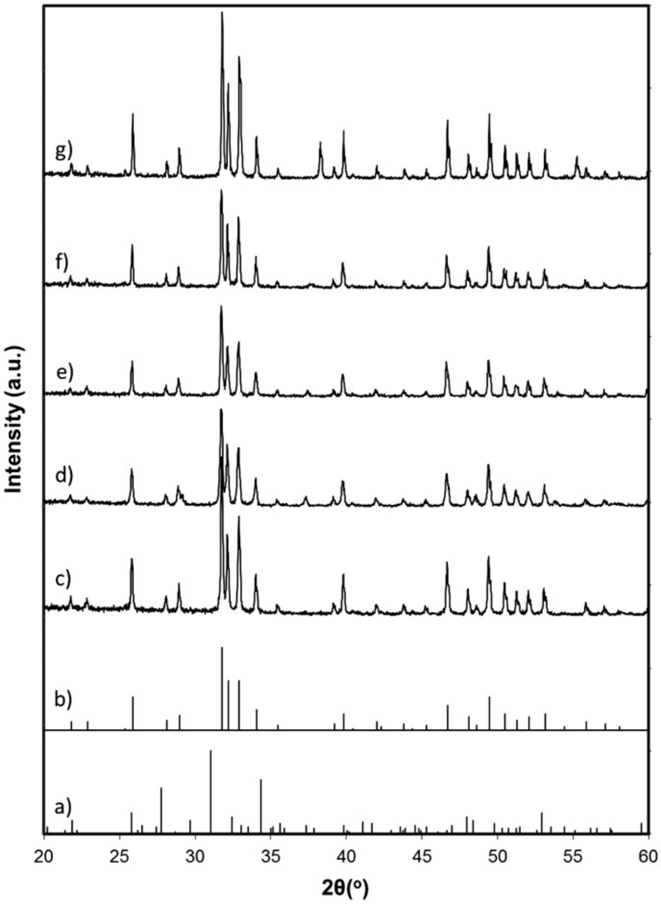

Fig. 1. XRD patterns of (a) standard β-TCP (JCPDS#9-169); (b) standard HA (JCPDS#9-432); (c) pure HA; (d) 2CdHA; (e) 4.4CdHA; (f) 8.8CdHA; and (g) 11CdHA.

Fig. 2 shows the expanded XRD patterns of the samples and the standard patterns of calcium oxide (CaO) and caldmium oxide (CdO) in the range from 35° to 39°. In Fig. 2d, the peak at $2\theta = 37.34°$ in the XRD pattern of 2CdHA was identified as CaO (JCPDS#37-1497, Fig. 2a). It is proposed that Cd^{2+} ions went into the hexagonal lattice of HA to substitute for Ca^{2+} and the remaining Ca^{2+} ions were present as CaO. The explanation for this might be the exchange of Cd^{2+} ions with Ca^{2+} ions in the HA structure might increase the tendency of the exchanged HA to decompose. The Cd^{2+} ion introduces strain into the HA network structure and could make the decomposition of HA (Eq. 3) more favorable.

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3Ca_3(PO_4)_2 + CaO + H_2O \qquad (3)$$

We can also observe a XRD peak shift toward higher angles with increasing amount of Cd. The peak at $2\theta = 37.34°$ in Fig. 2d (attributed to CaO) gradually shifted to $2\theta = 38.28°$ in Fig. 2g, which was identified as CdO (JCPDS#2–1102, Fig. 2b). As the Cd amount increases in the structure (from 2 to 11 mol%), CaO phase disappeared and was replaced with CdO, which confirms the full incorporation of Cd^{2+} ions into the Ca^{2+} sites. In

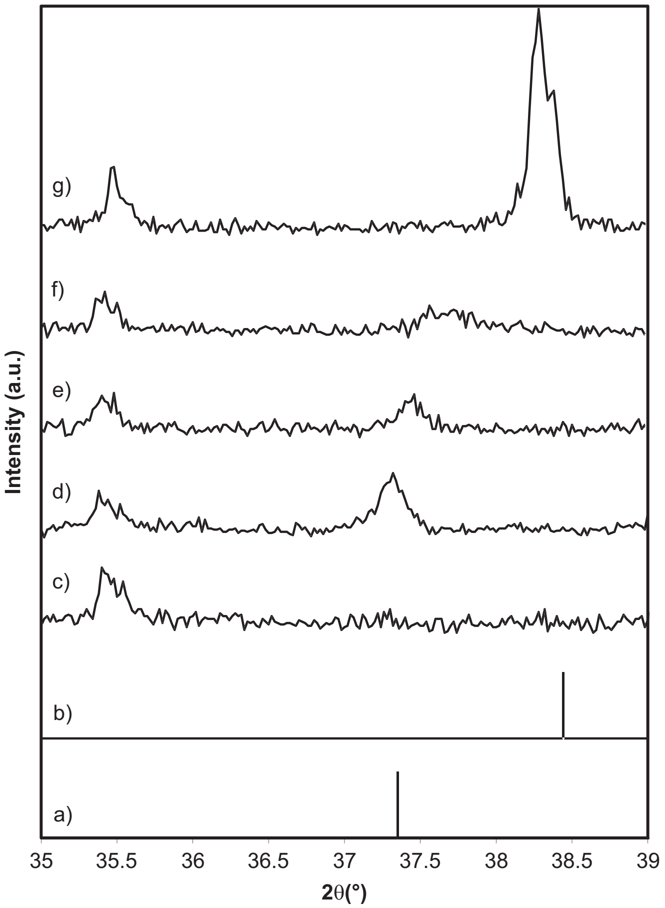

Fig. 2. The expanded XRD patterns of: (a) standard CaO (JCPDS#37–1497); (b) standard CdO (JCPDS#2–1102); (c) pure HA; (d) 2CdHA; (e) 4.4CdHA; (f) 8.8CdHA; (g) 11CdHA.

addition, the radius of Ca^{2+} ion is about 0.1 nm and that of Cd^{2+} is about 0.095 nm [32]. Therefore, it can also be thought that the incorporation of Cd^{2+} ions, which have smaller ionic radii than Ca^{2+} ions, reduced the lattice constant and hence the peak shifted toward a higher diffraction angle. Moreover, the XRD peak shift toward a higher angle indicates an improvement in the overall crystal structure and confirms the effectiveness of the Cd doping. The presence of CdO phase in the structure of 11CdHA can also be identified from the extra peak at $2\theta = 55.24^\circ$ in Fig. 1g, which is assigned to CdO (JCPDS#2-1102).

The lattice parameters *a* and *c* in the Cd^{2+} doped HAs and the volume changes of the unit cell are given in Table 3. It is supposed that the removal of Ca^{2+} ions from HA involves an exchange reaction with Cd^{2+} ions. As stated before, the radius of Cd^{2+} ion is smaller than the radius of Ca^{2+} ion. Thus, when the Cd^{2+} ion was substituted for Ca^{2+}, the lattice parameters and the volume of the hexagonal unit cell of the HA were expected to be decreased. From Table 3, it is seen that as the amount of Cd^{2+} ions in the structure of HA increases from 2 to 11 mol%, both lattice constants *a* and *c* and unit cell volume of CdHA decrease. The shrinking of bond lengths due to the substitutional Cd^{2+} ions was confirmed by the shift of the XRD peak toward a higher angle in Fig. 2. With the increasing amount of Cd^{2+} ions in the HA lattice, the decrease in density despite the decrease in the unit cell volume was thought to result from the fact that the water generated by the decomposition given in Eq. 3 leads to an increase of the porosity of the samples. As the decomposition is made more favorable with the additional Cd^{2+} ions, more water is generated and diffuses out of the HA matrix during sintering to form pores and accordingly, the density decreases.

Table 3
Lattice parameters *a* and *c* for HA in Cd^{2+} doped HAs and volume and volume changes of the unit cell.

Sample I.D.	Lattice parameters			
	a(Å)	*c*(Å)	Vol. (Å^3)	ΔVol. (Å^3)
HA	9.4322	6.9050	1590.5	
2CdHA	9.4387	6.9033	1592.3	1.8
4.4CdHA	9.4379	6.9005	1591.3	0.9
8.8CdHA	9.4357	6.8949	1589.3	−1.1
11CdHA	9.4250	6.8918	1585.0	−5.5

4. Conclusions

It is possible to incorporate cadmium into the structure of hydroxyapatite by the replacement of Ca^{2+} sites with the Cd^{2+} ions. In this study, 2, 4.4, 8.8 and 11 mol% Cd doped HA were synthesized successfully by precipitation of calcium nitrate and ammonium phosphate at pH 11–12. After sintering at 1100 °C for 1 h, the resulted Cd doped HAs were nearly fully densified with minimum 94.5% relative density of 11CdHA with respect to the theoretical density of stoichiometric HA. The densest sample was 2CdHA with 99% relative density which was also denser than the pure hydroxyapatite synthesized in this study. The XRD results suggested that the crystallinity increases with the increasing amount of Cd doping at constant sintering temperature of 1100 °C. The lattice parameters and the volume of the hexagonal unit cell of the HA decreased with the increasing incorporation of Cd^{2+}, which has a smaller ionic radius than Ca^{2+}. At low concentrations of Cd^{2+}, the presence of CaO was attributed to the decomposition of HA due to Cd doping. However, CaO phase gradually decreased and 11CdHA was lacking CaO phase; instead, it had CdO in its structure. From this, it is speculated that Cd was continuously incorporated into the HA lattice with increasing Cd concentration and the XRD patterns indicated that CdO phase was formed clearly at 11 mol% doping.

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