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Synthesis of hydroxyapatite using phosphate-rich glasses in the system $CaO–P_2O_5–H_2O$ and acoustic waves

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Phosphate-rich glass powders in the $CaO–P_2O_5$ system were prepared by the sol–gel method using aqueous solutions of $Ca(NO_3)_2 \cdot 4H_2O$ and H_3PO_4. Glass powders were subjected to reaction with $Ca(OH)_2$ and water under varied experimental conditions, such as temperature (25–90 °C), particle size (1–5 and 40 µm), and ultrasound waves (20 kHz). Parallel experiments were also conducted without ultrasound for comparison. The reaction products were composed of $Ca(H_2PO_4)_2 \cdot H_2O$ (monocalcium phosphate monohydrate), $CaHPO_4$ (monatite), $CaHPO_4 \cdot 2H_2O$ (brushite), $Ca_5(PO_4)_3OH$ (hydroxyapatite) and amorphous calcium phosphate. It is interesting to note that hydroxyapatite and brushite were obtained at a low temperature of 60 °C in a very short period of time (30 min). All samples were characterized by X-ray diffraction and scanning electron microscopy.

1. Introduction

Hydroxyapatite, $Ca_5(PO_4)_3OH$(HAp) is an important constituent of bones and teeth. Recently, it has attracted much attention as a substitute material for damaged teeth and bones. HAp has spread to the fields of electronics and surface science (or adsorption chemistry), where sintered or powder HAp is expected to function as gas sensors, catalysts and chromatographic adsorbers [1]. HAp has been synthesized in the form of a powder by solid state reaction or by solution routes using Ca and P bearing precursors; these powders were sintered to a dense polycrystalline body by high temperature heat-treatment by conventional sintering, HIP and very recently by microwave sintering [2–4]. Single crystals of HAp have also been grown by a hydrothermal method [5, 6]. However, no effort has been made so far to synthesize HAp from glasses. Here we describe the results of our current research using acoustic energy to accelerate the existing reactions or cause new reactions in the $CaO–P_2O_5–H_2O$ system; an area which has been virtually unexploited so far in materials research. Recently, we reported [7] the effect of ultrasound on the reactivity of Al_2O_3 with water and H_3PO_4, in which we observed a substantial increase in reactivity as well as new reactions.

The effect of sonic energy on the reactivity of chemical systems is termed sonochemistry, and has been thus far mainly confined to the area of organic reactions. It is well recognized [8] that the effects caused by ultrasound are mainly attributed to: (i) rapid movement of fluids due to variation of sonic pressure; (ii) formation and collapse of microbubbles (cavitation) creating localized high temperature and high pressure conditions; and (iii) microstreaming in which a large amount of vibrational energy is put into small volumes with little heating. In most cases two or more mechanisms may be operating simultaneously, and which of them dominates in a particular system depends on experimental conditions, such as exposure time, nature of the system, particle size, viscosity of liquid phase, etc.

In this paper we describe the synthesis of hydroxyapatite and brushite from P_2O_5-rich calcium phosphate glasses, and the effect of ultrasound on the reactivity at low temperature (< 90 °C). Glasses were prepared from a dry gel, calcined at 800 °C and crushed to 1–5 µm size and then allowed to react with water and $Ca(OH)_2$ in the presence of ultrasound for a few minutes. This process is very different from the one in which tetra calcium phosphate (TCP), $Ca_4(PO_4)_2O$, is reacted with other phosphates to form HAp [9], because TCP is first formed at a very high temperature (~ 1500 °C) and completion of the reaction takes a long time (2–5 days).

2. Experimental procedure

The glass powders were prepared by the sol–gel method using aqueous solutions of $Ca(NO_3)_2$ (J. T.

Abbreviations used in text: CH, calcium hydroxide, $Ca(OH)_2$; NF, sodium hydroxide, NaF; MCPA, monocalcium phosphate anhydrous, $Ca(H_2PO_4)_2$; MCPM, monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2 \cdot H_2O$; DCPA, dicalcium phosphate anhydrous (monatite), $CaHPO_4$; DCPD, dicalcium phosphate dihydrate (brushite), $CaHPO_4 \cdot 2H_2O$; HAp, hydroxyapatite, $Ca_5(PO_4)_3OH$; g, calcium phosphate (1:2) glass, glass powder; Am, calcium phosphate, amorphous phase.

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TABLE I X-ray diffraction results of glass (80 wt %) + $Ca(OH)_2$ (20%) + H_2O system

Particle size (μm)	Time	Temperature		
		Room temp.	60°C	90°C
1–5	5 min		DCPD, MCPM, Am	
	10 min		DCPD, MCPM, Am	
	1 h	MCPA, Am	DCPD, MCPM, Am	
	3 h	MCPA, Am		
	1 day	DCPD, MCPM, Am		
40	1 day	No reaction	DCPA, MCPA, Am	DCPA, Am
	3 days	No reaction	DCPA, MCPA, Am	DCPA, Am
	7 days	No reaction	DCPA, Am	MCPM

Baker Chemical Co., Phillipsburg, NJ) and H_3PO_4 (E. M. Science, Cherry Hill, NJ) as precursors. The solutions were mixed at room temperature with a Ca/P mole ratio of 1:4 and heated at 70 °C for 5–7 h on a hot plate with a magnetic stirrer. The gel thus obtained was dried at 80 °C for 16 h, calcined at 700 °C for 2 h, ground to − 325 mesh and melted at 80 °C in platinum crucibles. The melts were quenched to room temperature and ground to 40 μm (−325 mesh), and part of it was further sized ultrasonically to 1–5 μm. The reactivity of the glass powder was studied at temperatures ranging from room temperature to 90 °C, with and without ultrasound.

The reaction mixture contained glass powder, $Ca(OH)_2$ and H_2O; sometimes a small amount of NaF (about 4%) was also added as a catalyst. The amounts of glass and $Ca(OH)_2$ were in the proportions 1:1 or 1:1.26 by weight. About 2 g of solid material was added to 35 ml of deionized water. To provide the sonic energy, an ultrasonificator (Branson Sonic Power Co., model 350 Sonifier) producing acoustic waves at a frequency of 20 kHz with a maximum power of 350 W was used. A sonic probe made of Ti (tapered microtip, 5 mm dia.) and driven by a PZT transducer was dipped into the reacting system to be exposed to the ultrasound. The intensity of sonification could be controlled by altering the power input to the transducer. We normally optimized the settings in our experiments to provide maximum power output. In the present study, one set of samples was exposed to acoustic waves for periods ranging from 5 min to 1 h. It was noted that the temperature of the mixture had risen to about 60 °C after typically 10 min of ultrasonification. Another set of samples was treated without ultrasound at different temperatures ranging from room temperature to 90 °C, and for various time periods ranging from 5 min to 7 days. The product obtained in each experiment was characterized by X-ray diffractometry and scanning electron microscopy for phase identification and powder morphology, respectively.

3. Results and discussion

The results of glass powder + $Ca(OH)_2$ + H_2O (without ultrasound) reactions showed that the formation of HAp takes place after several intermediate compounds had formed sequentially as the reaction temperature and time were raised. The compounds were formed in the following sequence: $Ca(H_2PO_4)_2$, $Ca(H_2PO_4)_2 \cdot H_2O$, $CaHPO_4$, $CaHPO_4 \cdot 2H_2O$ and finally $Ca_5(PO_4)_3OH$. The results under various experimental conditions are summarized in Table I for the samples containing glass (80 wt %) + $Ca(OH)_2$ (20 wt %). It is evident from these data that irrespective of glass particle size and with 20% $Ca(OH)_2$, the reactivity was very low regardless of operating temperature. The fine glass powder was obviously more reactive even at room temperature. No HAp was observed under these conditions. This is attributed to the insufficient amount of Ca^{2+} present in the system. In subsequent experiments the amount of CH was increased to 50%, which was just enough to provide HAp stoichiometry, and only fine glass powder (1–5 μm size) was utilized, since it was found (Table I) to be more reactive. Table II gives the results of the experiments performed on these samples at 37 °C without ultrasound. From XRD analyses it was determined that all samples contained HAp, the amount increasing with increasing reaction time. The addition of a small amount of NaF increased the reactivity and resulted in more crystalline HAp (Table II). However, without ultrasound it still needed about 1 h to form single phase hydroxyapatite.

TABLE II X-ray diffraction results of glass (50 wt %) + $Ca(OH)_2$ (50%) + H_2O + (NaF) system treated at 37 °C

System	Reaction time (min)	Phase(s) present
g + CH + H_2O	10	DCPD, HAp, CH, Am
g + CH + H_2O	30	Same as above
g + CH + H_2O + (NF)	10	HAp, CH, Am
g + CH + H_2O + (NF)	30	HAp, Am
g + CH + H_2O + (NF)	60	HAp, Am

An effort was made to compare the results of experiments conducted at 60 °C with and without acoustic wave stimulation (AWS) (Table III). With ultrasound, we were able to synthesize HAp single phase material in 10 min at 60 °C in the presence of NaF. On the other hand, without AWS, the reaction did not complete even after 1 h soaking, there was still unreacted CH present in the mixture.

Figs 1, 2 and 3 show the typical XRD patterns of selected samples. From these patterns it is evident that the X-ray peaks of the sonicated material are stronger

TABLE III X-ray diffraction results of glass (50 wt %) + $Ca(OH)_2$ (50 %) + H_2O + (NaF) system treated at 60 °C with and without AWS

System	Without AWS		With AWS	
	Time (min)	Phase(s)	Time (min)	Phase(s)
g + CH + H_2O			5	DCPD, CH, Am
g + CH + H_2O	10	HAp, DCPD, Am	10	HAp, DCPD, CH, Am
g + CH + H_2O	60	HAp, CH, Am	60	HAp
g + CH + H_2O + NF	5	HAp, CH, Am	5	HAp, CH
g + CH + H_2O + NF	10	HAp, CH, Am	10	HAp

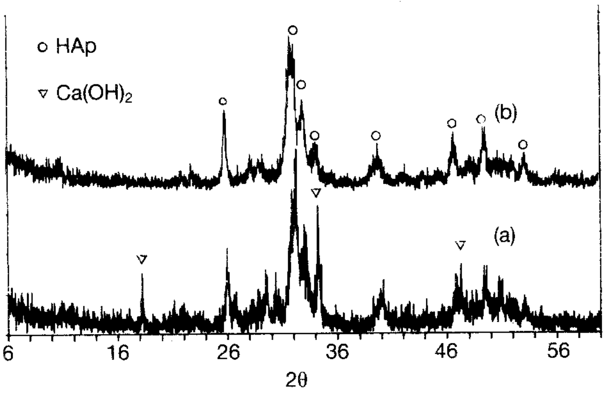

Figure 1 X-ray diffraction patterns of the samples of the glass + $Ca(OH)_2$ + H_2O system heated at 60 °C for 1 h: (a) without ultrasound; (b) with ultrasound.

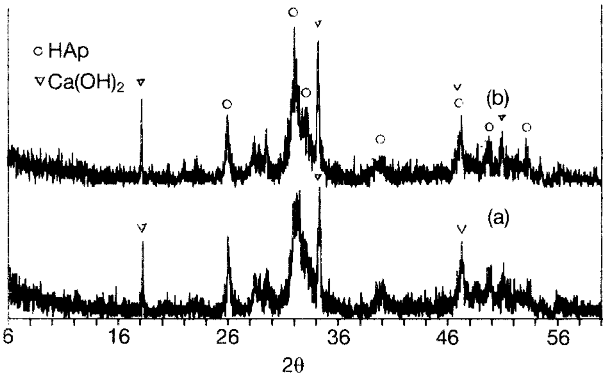

Figure 2 X-ray diffraction patterns of the samples of glass + $Ca(OH)_2$ + H_2O + (NaF) heated at 60 °C for 5 min: (a) without ultrasound; (b) with ultrasound.

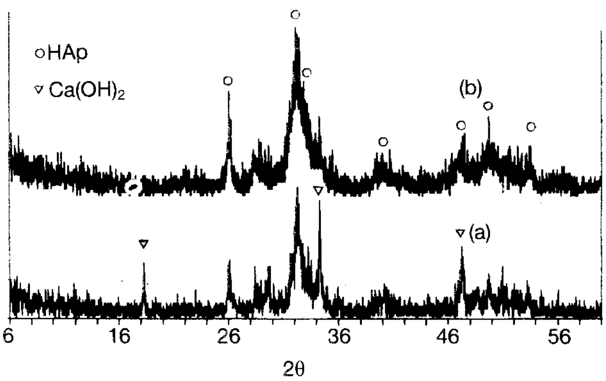

Figure 3 X-ray diffraction patterns of the samples of glass + $Ca(OH)_2$ + H_2O + (NaF) heated at 60 °C for 10 min: (a) without ultrasound; (b) with ultrasound.

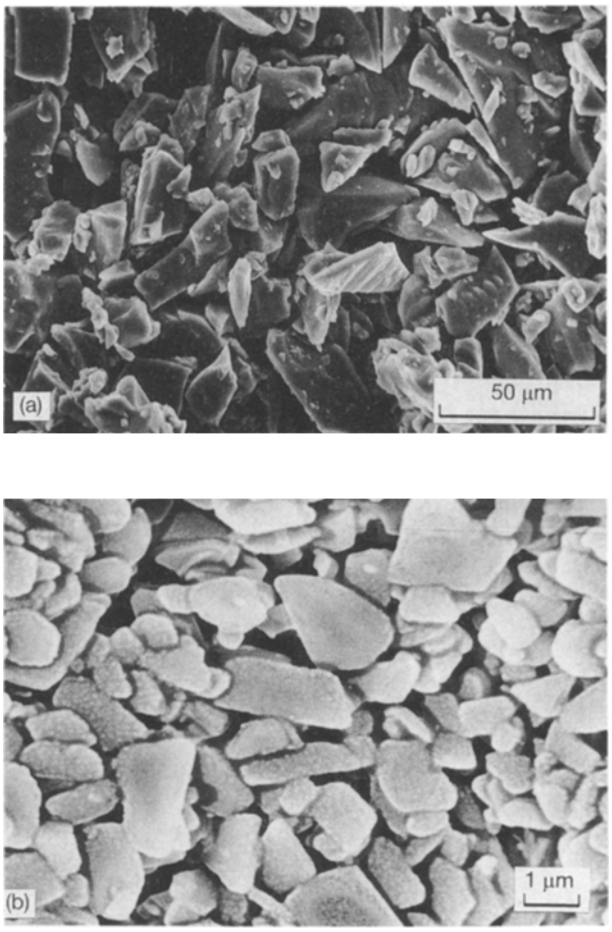

Figure 4 Morphology of the starting glass powders of different sizes: (a) 40 μm; (b) 1–5 μm.

and sharper than those of unsonicated samples, indicating the influence of ultrasound in accelerating the reactivity. In this study the morphology of the HAp synthesized (with and without AWS) is different from the HAp formed at high temperatures, which mainly consists of fine crystals with distinct shape and size. Fig. 4 gives the morphology of the starting glass powders. The hydroxyapatite formed in this study was usually fine-grained with an irregular shape and mixed with an amorphous phase (Fig. 5).

Based on the above results, following sequence of reactions can be suggested:

$$\text{glass} + H_2O \rightarrow \text{MCPA} + \text{Am}$$

$$\text{MCPA} + Ca(OH)_2 + \text{Am} + H_2O \rightarrow \text{MCPM} + \text{Am}$$

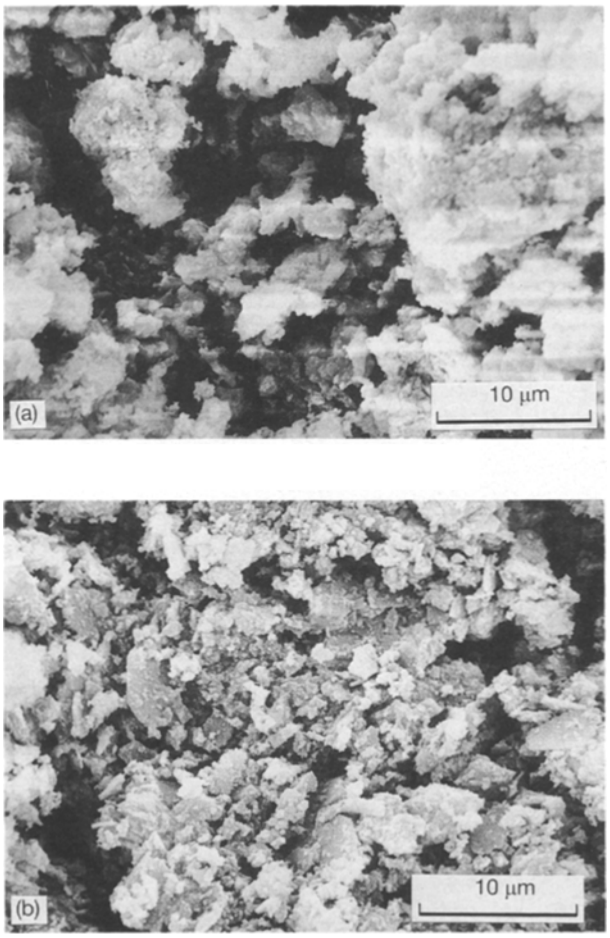

Figure 5 Scanning electron micrographs of the hydroxyapatite powders prepared in this study using phosphate rich glasses: (a) without ultrasound; (b) with ultrasound.

$$\mathrm{MCPM} + \mathrm{Ca(OH)_2} + \mathrm{Am} + \mathrm{H_2O} \rightarrow \mathrm{DCPA} + \mathrm{Am}$$

$$\mathrm{DCPA} + \mathrm{Am} + \mathrm{Ca(OH)_2} + \mathrm{H_2O} \rightarrow \mathrm{DCPD} + \mathrm{Am}$$

$$\mathrm{DCPD} + \mathrm{Am} + \mathrm{Ca(OH)_2} + \mathrm{H_2O} \rightarrow \mathrm{HAp}$$

It is clearly evident that by using acoustic waves of 20 kHz, the reactivity of phosphate-rich glass in water has been enhanced. This can be attributed to the crushing and dispersion of solid particles due to high energy ultrasound, and to the phenomenon of cavitation [10]. These effects are important for glass reactions. The cavitation creates high temperature and high pressure conditions in the localized regions, which aid in accelerating the existing reactions or causing new reactions.

4. Conclusions

Hydroxyapatite powder was prepared, by using a mixture of phosphate-rich glasses in a $CaO-P_2O_5$ system and $Ca(OH)_2$ in water at 60 °C using acoustic energy, within a few minutes. The use of ultrasound of 20 kHz accelerated the reactivity substantially and produced fine grained (1–5 μm) crystalline hydroxyapatite powder.

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