

Hydrothermal Synthesis of nanocrystalline powders of alkaline-earth hydroxyapatites, $A_{10}(PO_4)_6(OH)_2$ (A = Ca, Sr and Ba)

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In the present work, we report a direct precipitation of nanocrystalline powders of alkaline-earth hydroxyapatites of the compositions, $A_{10}(PO_4)_6(OH)_2$ (A = Ca, Sr or Ba) from aqueous solutions containing Na_3PO_4 and MCl_2 (M = Ca, Sr or Ba) at 150°C for 2 days and autogeneous pressure under hydrothermal conditions. The products were characterized by X-ray powder diffraction, transmission electron microscopy and scanning electron microscopy. The paper also discusses a convenient and economical hydrothermal route for the extraction of nanocrystalline calcium hydroxyapatite, from fish bone waste. © 2006 Springer Science + Business Media, Inc.

1. Introduction

Hydroxyapatite (HAp), in particular, calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, (Ca-HAp) is one of the most attractive materials for bone implant due to its compositional and biological similarity to native bone tissues [1, 2]. Bone is an inorganic-bioorganic composite material consisting mainly of collagen proteins and HAp, and its properties depend intimately on its nano-scale structures, which are dictated specifically by the collagen template [3]. One of the contemporary themes is to assemble and design artificial HAp nano-structures that can interact with and replace natural biological materials. Synthesis of nano-size hydroxyapatites with controlled particle characteristics is a prerequisite for the formation of HAp-based nanocomposites. Synthesis of HAp has been attempted by various methods like solid state reaction [4], sol-gel [5, 6], hydrothermal [7, 8], emulsion and microemulsion [9, 10] methods. Hydrothermal reaction is currently a popular “soft chemistry” technique to obtain several nano-crystalline oxide materials. Though hydrothermal method has been successfully employed to prepare calcium HAp (Ca-HAp) at lower temperatures, various precursors employed so far have resulted only in poor powder

characteristics (particle size, morphology and size distribution) [11]. Recently, we have demonstrated a convenient microwave-mediated solid state metathesis route for the formation of alkaline-earth HAp using Na_3PO_4 and MCl_2 (M = Ca, Sr or Ba) as reactants [12, 13]. When we attempted hydrothermal treatment of these two salts in aqueous solution in the molar ratio Ca to P = 1.67, we observed the formation of monophasic M-HAp (M = Ca, Sr or Ba) powders with sub-micron size. Surprisingly, the method did not require any pH control unlike previous reports. To the best of our knowledge, there is no report on the formation of strontium and barium hydroxyapatite under mild hydrothermal conditions. A metathetic reaction between Na_3PO_4 and MCl_2 in aqueous solution is probably responsible for a facile hydrothermal synthesis of these hydroxyapatite phases. In addition, we also report an effective and economical hydrothermal route for nanocrystalline Ca-HAp from fish bone waste. Since natural hydroxyapatite is an excellent biocompatible inorganic substance, the animal resource will be ideal for the fabrication of practical products for advanced biomaterials. Fish bone which is a waste can be used for the extraction of hydroxyapatite by hydrothermal conditions. Such

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natural waste-originated hydroxyapatite represents a possible resource for future ceramics [14].

2. Experimental methods

Pure Na₃PO₄, CaCl₂, SrCl₂, BaCl₂ and distilled water were used for the preparation of the starting compounds. Preparation of calcium, strontium and barium hydroxyapatite powders were carried out by the hydrothermal method. Aqueous sodium phosphate and alkaline-earth chloride solution in the molar ratio 1.67 : 1 were taken in a Teflon lined acid digestion reactor (volume – 30 ml, degree of filling – 80%) and kept at 150°C for two days. pH was around 12 before and after hydrothermal treatment. No additional reagent was used to adjust pH of the solution. pH was essentially due to aqueous sodium phosphate. The products were isolated by centrifuging, subsequent washing in distilled water and dried at 80°C. Fish waste (fish bone from kitchen waste) was first soaked in 1 M NaOH for 12 h to eliminate all the proteins attached with the bone. After this the solid mass (big lumps) was washed with water and dried. The dried product was suspended in water and treated hydrothermally at 150°C for two days. Fine powders were obtained after filtration and drying in an oven at 80°C. We repeated this experiment with different kinds of fish (mostly from river sources) available from the market. The as-synthesized samples were characterized using Ni-filtered CuKα powder X-ray diffraction (XRD), thermal analysis (TGA and DTA), scanning electron microscopy (SEM), energy dis-

persive X-ray emission analysis (EDAX) and transmission electron microscopy (TEM).

3. Results and discussions

Fig. 1 shows powder X-ray diffraction patterns of M-HAPs synthesized by hydrothermal reaction.

In all the cases, EDAX analysis showed only the presence of Ca (or Sr or Ba as the case may be) and P with a composition close to a molar ratio of M/P~1.67. Powder XRD patterns were completely indexed on a hexagonal cell and the refined cell parameters and intensities (Table I) clearly confirm that all the samples belong to a hexagonal hydroxyapatite based crystal structure.

For comparison, we have also provided the cell parameters of alkaline-earth hydroxyapatites synthesized by microwave-mediated metathesis route [12, 13]. Powder XRD patterns of all the phases reported here match very well with phases reported in the powder diffraction database [15–17]. The powder pattern obtained from the hydrothermal treatment of fish-bone was close to that of Ca-HAP reported in the literature [15]. Incidentally, there is an earlier report on the formation of Ca-HAP from fish-bone waste [14]. Their method involves pretreatment of the waste followed by high temperature heating. Cell parameters and volume of HAP (Table I) show a strong correlation with radius of alkaline-earth ion suggesting the composition of the phases are close to A₁₀(PO₄)₆(OH)₂ [A = Ca, Sr and Ba]. Under our reaction, we could not

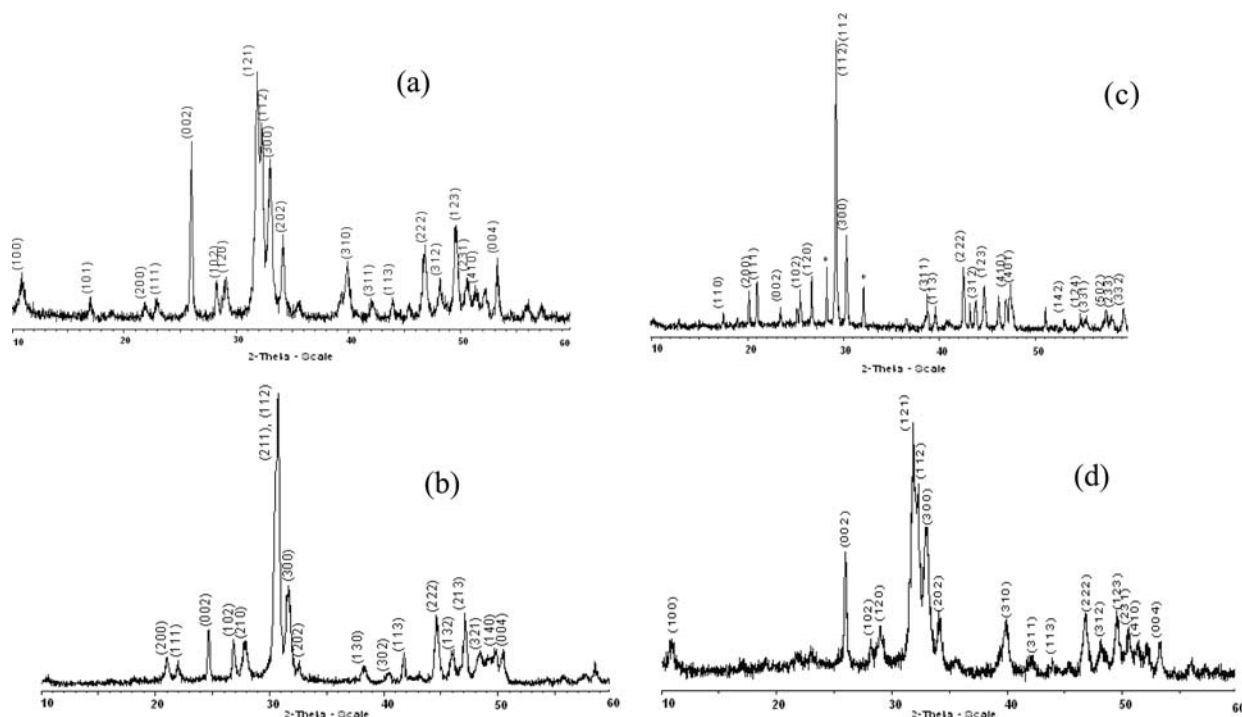


Figure 1 Powder XRD patterns of hydrothermally synthesized (a) Ca-HAP, (b) Sr-HAP powders, (c) Ba-HAP and (d) Ca-HAP obtained from fish waste. * correspond to unidentified reflections.

TABLE I Cell parameters and volume of $A_{10}(PO_4)_6(OH)_2$ [A = Ca, Sr and Ba]

Composition	Ionic radius* (C.N. IX) Å	Synthetic method	Cell Parameters (Å)		Volume (Å ³)	Reference
			<i>a</i>	<i>c</i>		
Ca ₁₀ (PO ₄) ₆ (OH) ₂	1.18	Hydrothermal	9.394	6.868	524.9	present work
		Metathesis	9.346	6.836	517.2	[12]
		Database	9.423	6.876	528.7	[15]
		Fishbone	9.407	6.686	512.3	present work
Sr ₁₀ (PO ₄) ₆ (OH) ₂	1.31	Hydrothermal	9.832	7.246	606.6	present work
		Metathesis	9.809	7.235	602.8	[13]
		Database	9.744	7.265	597.3	[16]
Ba ₁₀ (PO ₄) ₆ (OH) ₂	1.47	Hydrothermal	10.205	7.599	685.3	present work
		Metathesis	10.209	7.604	686.3	[13]
		Database	10.190	7.721	694.3	[17]

* See reference 18.

obtain a magnesium hydroxyapatite; the reaction invariably led to an amorphous product.

Fig. 2 shows the SEM images of the various M-HAPs prepared in this study. The morphologies of all hydrothermally synthesized M-HAPs appear to be similar with considerable agglomeration. Considering the size of individual M-HAP precursors, the re-crystallization process probably occurred during soak and then arranged in the same direction of the template, which was similar to the mineralization process of biological inorganic molecule. The property of M-HAP growing along the same orienta-

tion as the template could be of interest in the design of biomaterials, especially those used for bone tissue repair.

Fig. 3 shows TEM images of the M-HAPs. Hydrothermally synthesized M-HAP invariably occurred as nanorods; the average diameters varied between 20–50 nm with lengths in the range of 200–500 nm. Considering the average individual size of crystallite of M-HAP precursors estimated by XRD, the HAP inclined to grow in the *c*-axis of HAP lattice. Fig. 3a shows the TEM images of Ca-HAP. They are mainly elongated fibers with lengths up to 300 nm and diameter less than 10 nm. Fig. 3b shows

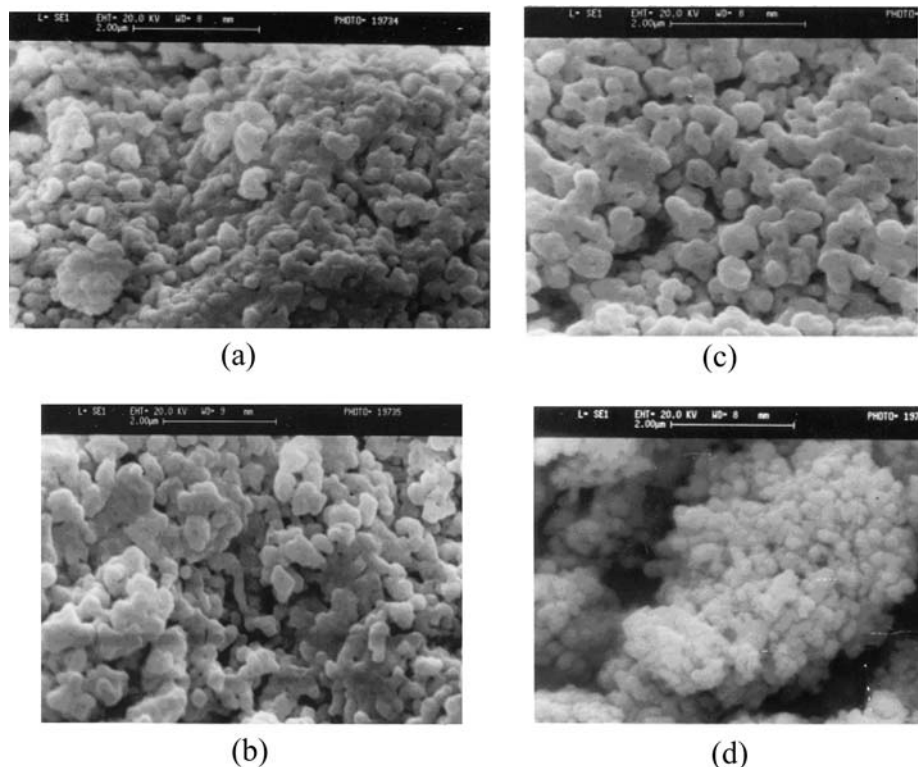


Figure 2 SEM images of hydrothermally synthesized (a) Ca-HAP, (b) Sr-HAP powders, (c) Ba-HAP and (d) Ca-HAP obtained from fish waste.

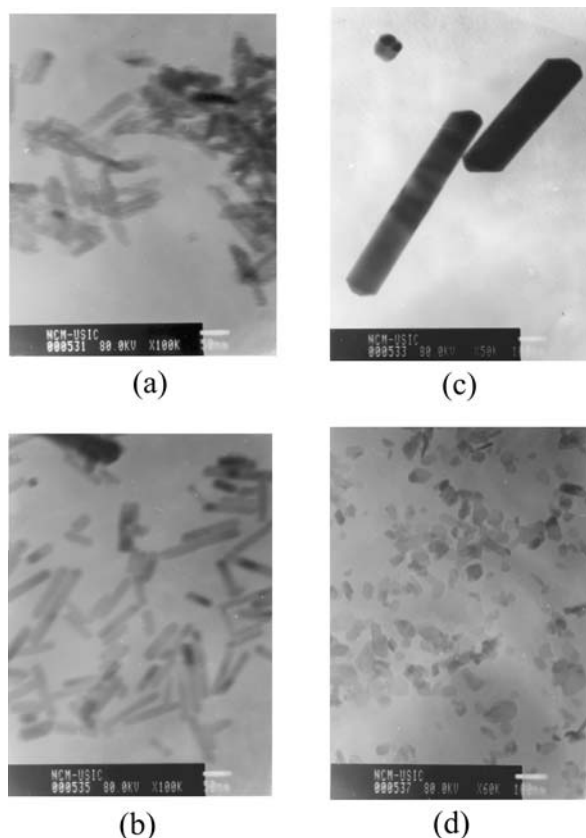


Figure 3 TEM images of hydrothermally synthesized (a) Ca-HAp, (b) Sr-HAp powders, (c) Ba-HAp and (d) Ca-HAp obtained from fish waste.

TEM images of Sr-HAp. They are mainly nanofibers with lengths upto 200 nm and diameter less than 10 nm. Sr-HAp nanofibers are well dispersed with uniform morphology. Fig. 3c shows TEM images of Ba-HAp with a very high aspect ratio. Their length is nearly 600 nm and diameter around 100 nm. Fig. 3d shows the TEM images of calcium hydroxyapatite extracted from fish bone. They are very small particles having irregular shape with particle size less than 100 nm. In the case of hydrothermally synthesized M-HAPs, the particles have regular shapes due to controlled nucleation whereas in the case of fish waste, the hydrothermal treatment only provides a medium to extract the Ca-HAp particles from the bone composite.

4. Conclusions

In conclusion, nanocrystalline powders of pure calcium, strontium and barium hydroxyapatite were synthesized via hydrothermal treatment and characterized with XRD,

TEM and SEM. These nanocrystalline oxides will be employed as starting materials for assembling nanocomposites to replace natural biological materials. Fish originated hydroxyapatite is a potential new ceramics resource in the coastal areas of Asia. The present result also suggests a possible materials-recycling technology for future waste management and ecology.

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References

1. L. L. HENCH, *J. Am. Ceram. Soc.* **74** (1991) 1487.
2. K. S. TENHUISEN, R.I. MARTIN, M. KLIMKIEWICZ and P.W. BROWN, *J. Biomed. Mater. Res.* **29** (1995) 803.
3. A. TISELIUS, S. HJERTEN and O. LEVIN, *Arch. Biochem. Biophys.* **65** (1956) 132.
4. B. O. FOWER, *Inorg. Chem.* **13** (1974) 207.
5. A. DEPTULA, W. LADA, T. OLCZAK, A. BORELLO, C. ALVANI and A. DIBARTOLOMEO, *J. Non-Cryst Solids.* **147** (1992) 537.
6. M. VALLET-REGI, M. T. GUTIERREZ-RIOS, M. P. ALONSO, M. I. FRUTOS DE and S. NICOLOPOULOS, *J. Solid State Chem.* **112** (1994) 58.
7. H. HATTORI and Y. IWADATE, *J. Am. Ceram. Soc.* **73** (1990) 1803.
8. M. YOSHIMURA, I. I. SUDA, K. OKAMOTO and K. IOKU, *J. Mater. Sci.* **29** (1994) 3399.
9. M. G. S. MURRAY, J. WANG, C.B. PONTON and P. M. MARQUIS, *ibid.* **30** (1995) 3061.
10. G. K. LIM, J. WANG, S. C. NG and L. M. GAN, *Mater. Lett.* **30** (1996) 431.
11. M. YOSHIMURA, H. SUDA, K. OKAMOTO and K. IOKU, *J. Mater. Sci.* **29** (1994) 3299.
12. P. PARHI, A. RAMANAN and A. R. RAY, *Mater. Lett.* **58**(27–28) (2004) 3610.
13. *Idem. ibid.* (submitted).
14. M. OZAWA and S. SUZUKI, *J. Am. Ceram. Soc.* **85** (2002) 1315.
15. J. M. HUGHES, M. CAMERON and K. D. CROWLEY, *Am. Mineral.* **74** (1989) 870.
16. K. SUDARSANAN and R. A. YOUNG, *Acta Crystallogr. Sec. B.* **28** (1972) 3668.
17. O. S. BONDAREVA and Y. U. A. MALINKOVSKLL, *Kristallografiya.* **31** (1986) 233.
18. R. D. SHANON, *Acta Crystallogr.* **A32** (1976) 751.

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