Journal of Ceramic Processing Research. Vol. 16, No. 3, pp. 308~312 (2015)

J O U R N A L O F
Ceramic Processing Research

Synthesis nano bio-ceramic powder β-$Ca_2P_2O_7$

Behzad Mehdikhani[a,*] and Gholam Hossein Borhani[b]
[a,b]*Malek ashtar industrial university, Material department*
[a]*Standard Research Institute, Building and construction department*

Nano-size beta calcium pyrophosphate(β-$Ca_2P_2O_7$) powders with average grain size of 80 nm were prepared by sol gel method with calcium nitrate 4-hydrate$Ca(NO_3)_2 \cdot 4H_2O$ and different amount of diammonium hydrogen phosphate $(NH_4)_2HPO_4$(0.4 and 0.6 molar) as calcium and phosphorus precursors. The pH of the system was maintained up to (pH = 10) by the adding of sodium hydroxide. The white precipitate stirred for 2 hour and washed with distilled water and filtered. Filtered cake was dried at 80 ºC and calcined at 600 ºC. The dried and calcined powders were characterized for phase composition using X-ray diffractrometry (XRD) and Fourier transform-infrared spectroscopy (FTIR). The particle size and morphology was studied using scanning electron microscopy (SEM).

Key words: biomaterial,nano powder, β-pyro calcium phosphate, Sol gel, FTIR spectroscopy.

Introduction

Calcium phosphates are in the limelight owing to their biomedical applications and the absence of toxicity of their constituents. Many Ca-P materials such as resorbable and nonresorbable ceramics, cements, drug carriers, prosthetic coatings, and composite materials show numerous applications: bone reconstruction and replacement, bone defect-filling drug carrier, and coatings of metal prostheses [1-4]. The application of calcium phosphates as bone substitute began by Albee [5] who reported the use of a tricalcium phosphate compound in a bony defect promoted osteogenesis. Many years later, Levitt et al [6] and Monroe *et al.* [7] were the first to propose the use of calcium phosphate ceramics for dental and medical implant materials. Variations in Ca-P composition can lead to different dissolution/precipitation behavior and may therefore also affect the bone response [8]. Materials such as Hydroxyapatite, β-tricalcium phosphate, β-calcium pyrophosphate and fluoroapatite are amongst the few that have attracted a lot of interest. Calcium phosphate compounds are suitable for implantation, compounds with a Ca/P ratio less than 1.0 are not suitable for biological implantation due to their high solubility [9]. Pyrophosphate based biomaterials are attractive for bone replacement since $P_2O_7^{4-}$ ions are thought to participate in the bone mineralisation process [10-11]. One of the first reports of sintered dicalcium pyrophosphate as a biomaterial was that of Kitsugi *et al*. [12] who showed that after 10 weeks of implantation the sintered dicalcium pyrophosphate had formed a bond with bone. Other studies have shown that sintered dicalcium pyrophosphate is more rapidly resorbed in vivo than sintered hydroxyapatite [8]. One of the key factors identified in the failure of orthopedic implants was insufficient tissue regeneration around the biomaterial immediately after implantation, mainly because of poor surface interaction of biomaterials with the host tissue [13]. Several literature reports suggest that decrease in ceramic grain size results in enhanced bone cell function. Specifically, compared to conventional micron grained ceramic, nanostructured alumina, titania, and hydroxyapatite show enhanced in vitro adhesion of osteoblasts. Osteoblast functions were also found to be increased at ceramic spherical grain sizes below 60 nm [14]. A number of synthesis techniques have been used for the preparation of Ca-P powders, that can be divided into two broad categories, such as, solid-state process [15-18] and wet-chemical method [19-23]. Powder synthesized by solid-state process suffers from stoichiometrical inhomogeneity, wide particle size distribution and hard agglomeration which motivated [24]. Ca-P nano powders can be synthesized using different wet chemical synthesis routes which include wet precipitation, sol gel, hydrothermal, microemulsion and surfactant based template system [25]. The sol-gel processing of calcium phosphate has been studied for some years. However, there is lack of report on the convenient synthesis of different calcium phosphate powders through only changing the ratio of calcic and phosphorous sources. The simple operation process, few used machines, and low cost can supply large amount of different calcium phosphate powders for further applications, such as bone cements, tissue engineering scaffolds and other bioactivity increasing uses etc [26].

*Corresponding author:
Tel : +00989126417516
Fax: +00982413230496
E-mail: mehdikhani@standard.ac.ir

Synthesis of nano crystalline Ca-P powders using different surfactants and template system have been reported [27-28]. However, the composition, physic chemical properties, crystal size and morphology of synthetic Ca-P is extremely sensitive to preparative conditions and sometimes it resulted into non stoichiometric calcium phosphate powders [29]. The mentioned factors play an important role in the biological behavior of calcium phosphates [30-32]. In the present research work, a wet chemical reaction such as the sol gel method was carried out to prepare β-$Ca_2P_2O_7$. The most conventional is the precipitation in aqueous medium starting from $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ as raw materials. However, the synthesis of a pure pyrophosphate calcium phase ($Ca_2P_2O_7$ or CPP) by this method requires a close control of many parameters such as, reaction pH, ripening time, temperature, stoichiometry of the raw materials. A light variation of these experimental parameters can generate drastic variations in composition of the final product and reveal the hydroxyapatite phase ($Ca_{10}(PO_4)6(OH)_2$ or HA) or β-tricalcium phosphate (β-TCP). Also powder particle size and morphology were controlled by varying different synthesis parameters such as pH of the reaction mixture and calcination temperature. Powders were characterized using X-ray diffraction (XRD), Fourier transformation infrared (FTIR) spectroscopy and scanning electron microscopy (SEM).

Experimental Procedure

The nanoβ-$Ca_2P_2O_7$ powders are synthesized by the reaction of calcium nitrate 4-hydrate ($Ca(NO_3)_2 \cdot 4H_2O$, 98%, Merck) with diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, 99%, Merck). Fig. 1 shows the flow chart of the sol-gel preparation of β-$Ca_2P_2O_7$.About 1 M calcium nitrate 4-hydrate and (sample A = 0.4 M, sample B = 0.6 M) diammonium hydrogen phosphate solutions were prepared by dissolving the crystals in double distilled water. Calcium nitrate 4-hydrate solution was added drop wise to the diammonium hydrogen phosphate solution while stirring. Ammonia (NH_3) was added drop wise to the above mixture resulting in white precipitation. The NH_3 was added till the precipitation complete and final pH = 10 was obtained.

This precipitated solution was stirred for 2 h and aged at room temperature for 24 h. The white precipitate washed with distilled water, and then washed with 100% ethanol to remove NH_4^+ and NO_3^-ions then it was filtered in a filter glass with application of mild suction. After filtration the compact, sticky filter cake was dried at 80 ºC for 24 h. As dried powders were crushed by using mortar and pestle and calcined in alumina crucible at 600 ºC for 2 h using an electrical furnace and employing a heating rate of 10 ºC/min. The Ca/P ratio of the dried powder was measured by inductively coupled plasma atomic emission spectroscopy (model Varian). No differences were observed in the Ca/P values between the as-dried and calcined powders. For evaluation of crystalline phases which were developed by chemical method, X-ray diffractometer (Siemens, model D-500). With CuKα radiation was used. Silicon powder was used as the standard material for semi-quantitative measurements of precipitated phases. For infrared spectroscopy, samples were pulverized and were mixed by a given amount of potassium bromide (KBr) and pressed as very thin tablet and their infrared spectra has been performed by FTIR Bomem(Quebec, Canada) MB100 model in 400-4000 cm^{-1} wavenumber region. Spectroscopy was used for phase analysis and scanning electron microscopy (SEM) was used to observe the morphology. Fig 2 shows SEM micrographs of sample A and B powders, respectively, both before calcination.

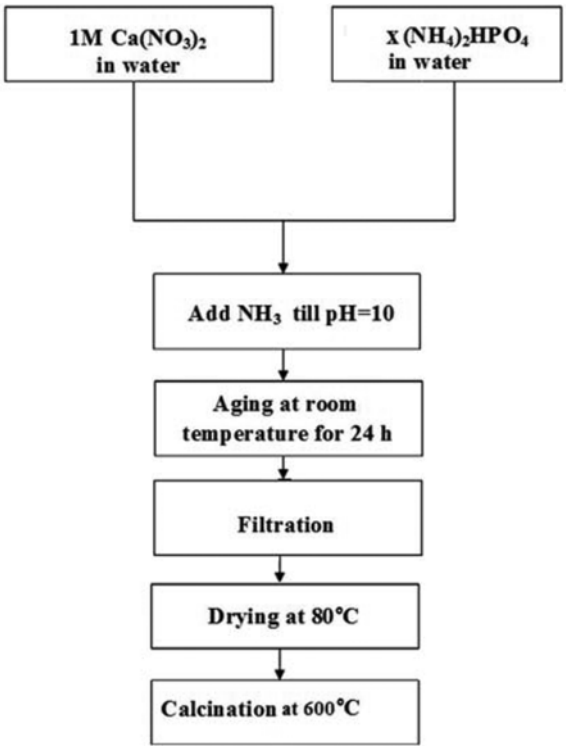

Fig. 1. Chemical precipitation flowchart used in the synthesis of β-$Ca_2P_2O_7$bioceramic powders. X = 0.4, 0.6 M.

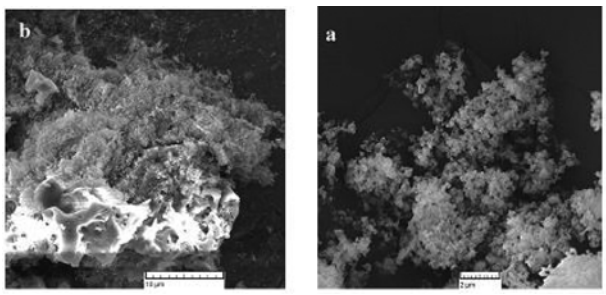

Fig. 2. SEM micrograph of samples before calcination, a) sample A, b) sample B.

Table 1. The ICP analysis of the prepared β-$Ca_2P_2O_7$ powders.

Sample NO.	$(NH_4)_2HPO_4$	Ca	P	Ca/P ratio
A	0.4	39.87	19.43	1.59
B	0.6	39.40	22.01	1.30

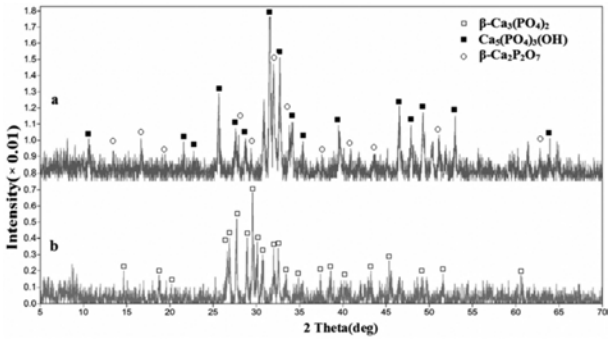

Fig. 3. XRD patterns of powders: a) hydroxyapatite/β-TCP powder, b) β-$Ca_2P_2O_7$.

Results and Discussion

The effects of the initial Ca/P molar ratio on the composition of the precipitates were given in table 1.

The ICP analysis was performed on the precipitates after drying at 80 ºC for 24 h. Ratio of the Ca/P for sample A and B are 1.59 and 1.30 respectively. The unreacted precursors are believed to be washed out during filtering process.

X-ray analysis

The XRD analysis was performed using the X-ray diffractometer. The XRD patterns of the powders sintered at 600 ºC are shown in Fig. 2. The straight base line and sharp peaks of the diffractogram in Fig. 3 confirmed that the product was well crystallized. It can be seen that the main component of sample A is hydroxyapatite/β-TCP powder phases consisting of β-TCP and HAP (Fig. 3a).

It is observed that the characteristic bands of HAP are much more obvious than those of β-TCP. This indicates that the ratio of the HAP is higher than that of β-TCP in sample A. The sample B is pure β-$Ca_2P_2O_7$ that shown in Fig. 3b. Increasing $(NH_4)_2HPO_4$ up to 0.6 M reduced Ca/P ratio to 1.30 that confirmed by XRD results. In sample B, β-$Ca_2P_2O_7$ formed. There are mono-, di-, tri-, and tetra-calcium phosphates, in addition to hydroxyapatite/β-TCP powder and β-$Ca_2P_2O_7$, which have ratios of 5/3, 3/2 and 1 for calcium and phosphorus (Ca/P), respectively. Different phases are used in different applications depending upon whether a degradable or a bioactive material is desired [33].

FTIR spectroscopy

FTIR was carried out to study the chemical structure of the samples. Fig. 4 shows the characteristic peaks of hydroxyapatite/β-TCP powder. FTIR spectrum shows the

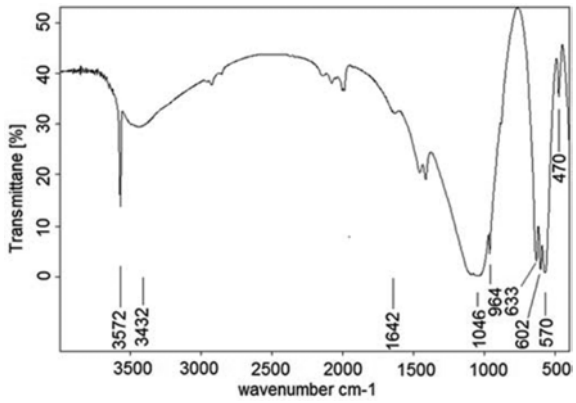

Fig. 4. FTIR spectrum of hydroxyapatite/β-TCP powder. Sample A.

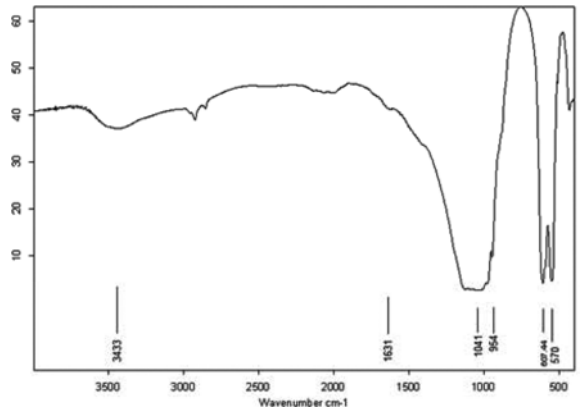

Fig. 5. FTIR spectrum of β-$Ca_2P_2O_7$ powder. Sample B.

characteristic absorption peaks of sample A. The broad bands at 3433 cm^{-1} and 1642 cm^{-1} were attributable to adsorbed water, while sharp peak at 3572 cm^{-1} was attributable to the stretching vibration of the lattice OH^- ions and the medium sharp peak at 633 cm^{-1} was assigned to the O-H deformation mode. The characteristic PO_4^{3-} appeared at 470, 570, 964 and 1046 cm^{-1} [34-35]. The observation of the asymmetric P-O stretching vibration of the PO_4^{3-} bands at 964 cm^{-1} as a distinguishable peak, together with the sharp peaks at 633, 602, 570 cm^{-1} correspond to the triply degenerate bending vibrations of PO_4^3 in hydroxyapatite. Our FTIR results were similar to the references [34-36].

The FTIR spectra for nano powders β-$Ca_2P_2O_7$ contained various bands from the respective phosphate groups of β-$Ca_2P_2O_7$ as indicated in Fig 5, which were in agreement with other reported results [37-38]. The bands at 1041 cm^{-1} was assigned to the components of the triply degenerate antisymmetric P-O stretching mode. P-O symmetric stretching mode was detected at 954 cm^{-1}.

The bands at 607 and 570 cm^{-1} were attributed to components of the triply degenerate O-P-O bending mode and the doubly degenerate O-P-O bending mode was evident at 475 cm^{-1}. The absence of any characteristic bands at 631 and 3572 cm^{-1} corresponding to the hydroxyl group denies the presence of any hydroxyapatite phase at

Table 2. The crystallite size of synthesized powderobtained from Scherrer equation XRD.

sample	Crystallite size (nm)
A	50
B	80

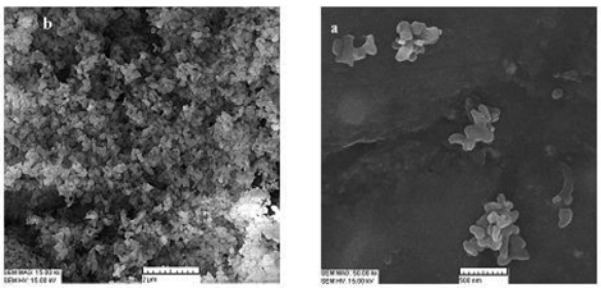

Fig. 6. SEM image of hydroxyapatite/β-TCP powder, ($(NH_4)_2HPO_4$ = 0.4) at two different magnifications. a = 50000, b = 15000.

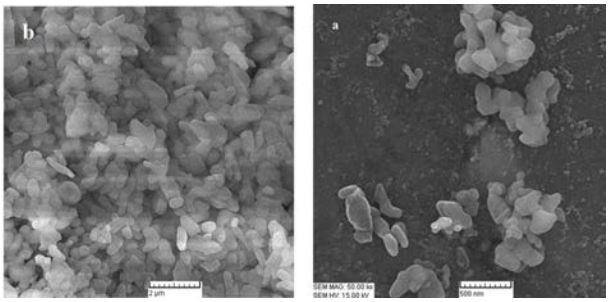

Fig. 7. SEM image of β-$Ca_2P_2O_7$, ($(NH_4)_2HPO_4$ = 0.6) at two different magnifications. a = 50000, b = 20000.

600 ºC in powder after calcination [38-39]. The mean crystallite size (D) was calculated from the XRD line broadening measurement from the Scherrer equation [40]:

$$D = 0.89\lambda/\beta\cos\theta$$

Where λ is the wavelength (Cu Kα), β is the full width at the half maximum of the β-$Ca_2P_2O_7$ line and θ is the diffraction angle. The determined crystallite size (determined by Scherrer equation) from XRD (Fig. 2) of sample A and B powders are given in table 2. The morphologies of sample A and B after calcination were shown in Fig. 6 at two different magnifications.

The as-dried hydroxyapatite/β-TCP powder precursor was almost spherical and highly agglomerated, and the observed crystallite size was about 50 nm. The necking among the particles was apparent due to localized sintering at 600 ºC. Fig 7 shows aggregates of β-$Ca_2P_2O_7$ at two different magnifications. Crystallite size of precipitated sample B was about 80-150 nm that confirmed XRD results. During calcination of β-$Ca_2P_2O_7$ at 600 ºC, the crystallinity has increased which seems to be predominating factor in forming well defined sharp XRD peaks rather than particle size, hence no overlaps are seen. Similar phenomena has also reported during synthesis of other phases of calcium phosphates like hydroxyapatite, where XRD study of the chemically pure hydroxyapatite revealed that the crystallites of 40-60 nm size gave rise to diffraction peak broaden but those of 75, 100, and, especially, 130 nm size had very sharp diffraction peaks [41-42]. Certain agglomeration (Fig. 7a) of β-$Ca_2P_2O_7$ particles was observed, due to the large surface area and energy associated to these nano particles [43].

Conclusions

In this study, the synthesis of a nanosized β-$Ca_2P_2O_7$ powder via sol gel method is reported using calcium and phosphorous precursors. This process showed that high purity product of nano β-$Ca_2P_2O_7$powder and hydroxyapatite/β-TCP composite could be obtained by this simple process. Sample prepared by 0.4 M $(NH_4)_2HPO_4$ formed hydroxyapatite/β-TCP powder and Ca/P ratio was 1.50. Sample prepared by 0.6 M $(NH_4)_2HPO_4$ formed β-$Ca_2P_2O_7$and Ca/P ratio was 1.30.SEM images showed agglomerated particles with particle size of 80 nm for β-$Ca_2P_2O_7$ powder. Next work will consider about mechanical properties of pyrocalcium phosphate.

Acknowledgments

The authors are indebted to ceramic laboratory in institute of standard and industrial research of Iran, that supplied the raw materials for the development of this research and to ceramic department (International University of Iran) for its financial support.

References

1. Z Amjad, 'Calcium phosphates in biological and industrial systems,' Boston: Kluwer Academic, 1998. p. 145-369.
2. R. Z LeGeros, Calcium phosphates in oral biology and medicine. In: Myers HM. Monographs in oral science, vol. 15. San Francisco: Karger, 1991.
3. B. D Ratner, A. S. Hoffman, F. J. Schoen, J. E. Lemons, Biomaterials science: An introduction to materials in medicine. San Diego: Academic Press, 1996. p. 81-83.
4. J. C. Elliott, Recent studies of apatites and other calcium orthophosphates In: Bres E, Hardouin P, editors. Montpellier: Sauramps Medical, 1998. p. 25-66.
5. F. Albee, Studies in bone growth-Triple calcium phosphate as a stimulusosteogenesis. Annals of surgery, 71 (1920) 32-39.
6. G. W. Levitt, 'Forming Methods for Apatite Prosthesis, 'J. Biomedical Materials Research., [3] (1969) 683-685.
7. W. Votava, D. Bass, J. McMullen, 'New calcium phosphate ceramic material for bone and tooth implants, 'J. Dental Research., 50 [4] (1971) 860.
8. U. Gbureck, .T Holzel, I. Biermann, J. Barralet, L. M. Grover, 'Preparation of tricalcium phosphate/calcium pyrophosphate structures via rapid prototyping, 'J. Mater Sci: Mater Med., [19] (2008) 1559-1563.
9. S. Dasgupta, 'Nanostructure hydroxyapatite and tricalcium phosphate based ceramics for bovine serum albumin

protein delivery and bone implants using microwave sintering', Washington state university, materials science program., 2008.
10. R. I. Martin, P. W. Brown, 'Formation of Hydroxyapatite in Serum, 'J. Materials Science-Materials in Medicine., 5 [96] (1994) 102. 121.
11. A. F. Lemos, A. H. S. Rebelo, J. H. G. Rocha, J. M. F. Ferreira, 'A Method for Simultaneously Precipitating and Dispersing nano-sized Calcium Phosphate Suspensions, 'J. Key Engineering Materials, (2005) 284-286.
12. T. Kitsugi, T.Yamamuro, T. Nakamura, S. Kotani, T. Kokubo and H. Takeuchi, 'Four calcium phosphate ceramics as bone substitutes for non- weight-bearing, 'J. Biomater., 14 [3] (1993) 216-224.
13. J.O. Hollinger and K. Leong, 'Poly (a-hydroxy acids): carriers for bone morphogenetic proteins, 'J. Biomaterials., [17] (1996) 187-194.
14. T. J. Webster, C. Ergun, R. H. Doremus, 'Enhanced functions of osteoclast-like cells on nanophase ceramics, 'J. Biomaterials., [22] (2001) 1327-1333.
15. A. Bigi, E. Foresti, M. Gandolfi, M. Gazzano, N. Roveri, 'Isomorphous substitutions in tricalcium phosphate: the different effects of zinc and strontium', J. Inorg. Biochem., [66] (1997) 259-265.
16. Y. Yokogawa, Y. Kawamoto, M. Toriyama, T. Suzuki, S. Kawamura, 'Tricalcium phosphate coating on zirconia using calcium metaphosphate and tetracalcium phosphate', J. Ceram. Soc. Jpn., [99] (1991) 28-31.
17. R. Famery, N. Richard, P. Boch, 'Preparation of and tricalcium phosphate ceramics, with and without magnesium addition', J. Ceram. Int., 178 [20] (1994). 327-336.
18. Y. Pan, J.L. Huang, C.Y. Shao, 'Preparation of TCP with high thermal stability by solid reaction routes', J. Mater Sci., [38] (2003) 1049-1056.
19. S.C. Liou, S.Y Chen, 'Transformation mechanism of different chemically precipitated apatitic precursors into tricalcium phosphate upon calcinations', J. Biomaterials., [23] (2002) 4541-4547.
20. M. Jarcho, R.L. Salsbury, M.B. Thomas, R.H. Doremus, 'Synthesis and fabrication of tricalcium phosphate (whitlockite) ceramics for potential prosthetic applications', J. Mater. Sci., [14] (1979) 142-150.
21. M. Akao, H. Aoki, K. Kato, A. Sato, 'Dense Polycrystalline tricalcium phosphate for prosthetic applications', J. Mater Sci., [17] (1982) 343-346.
22. K. Itatani, T. Nishioka, S. Seike, F.S. Howell, A. Kishioka, M. Kinoshita, 'Sinterability of calcium orthophosphate powder prepared by spray-pyrolysis', J. Am Ceram Soc., 77 [3] (1994) 801-805.
23. A.C Tas, F. Korkusus, M. Timucin, N. Akkas, 'An investigation of the chemical synthesis and high-temperature sintering behavior of calcium hydroxyapatite (HA) and tricalcium phosphate (TCP) bioceramics', J. Mater Sci. Mater. Med., [8] (1997) 91-96.
24. E. Palin, H. Liu, T. J Webster, 'Mimicking the nanofeatures of bone increases bone-forming cell adhesion and proliferation', J. Nanotechnology., [16] (2005) 1828-1835.
25. A. Deptula, W. Lada, T. Olzczak, A. Borello, C. Alvani, A. Dibartolomeo, 'Preparation of spherical powders of hydroxyapatite by sol-gel process', J. Non. Cryst. Solids., [147] (1992) 537-541.
26. F. Zhao, W. L. Grayson, Ma T,B. Bunnell, Lu WW, 'Effects of hydroxyapatite in 3-D chitosan-gelatin polymer network on human mesenchymal stem cell construct development, 'J. Biomaterials., [27] (2006) 1859-67.
27. M. Uota, H. Arakawa, N. Kitamura, T. Yoshimura, J. Tanaka, T. Kijima, 'Synthesis of High Surface Area Hydroxyapatite Nanoparticles by Mixed Surfactant-Mediated Approach', J. Langmuir, 180 [21] (2005) 4724-4728.
28. D. Rautaray, S. Mandal, M. Sastry, 'Synthesis of Hydroxyapatite Crystals Using Amino Acid-Capped Gold Nanoparticles as a Scaffold', J. Langmuir., [21] (2005) 5185-5191.
29. K. Deepak, Pattanayak, R. C. Rajalaxmi Dash, B. T. Prasad,T.R. Rama Mohan, 'Synthesis and sintered properties evaluation of calcium phosphate ceramics, 'J. Materials Science and Engineering: C., [27] (2007) 684-690.
30. S. R. Radin, P. Ducheyne, 'Effect of bioactive ceramic composition and structure of in vitro behavior. III. Porous versus dense ceramics, 'J. Biomed Mater Res., [28] (1994) 1303-1309.
31. K. De Groot, 'Effect of porosity and physiochemical properties on the stability, resorption and strength of calcium phosphate ceramics. In Bioceramics: Material characteristics versus in vivo behaviour. Ducheyne P, Lemmons J, ed. New York: Academy of Sciences, 1988. pp. 227-233.
32. R. Li, A. E. Clark, L. L. Hench, 'An investigation of bioactive glass powders by sol-gel processing, 'J. ApplBiomater., [2] (1991) 231-239.
33. B. Mehdikhani, B. Mirhadi and N. Askari, Sintering effects on the hardness of β-tricalcium phosphate, J. Ceramic Processing Research. [13] (2012) 486-490.
34. R. Murugan and S. Ramakrishna, Bioresorbable composite bone paste using polysaccharide based nano hydroxyapatite, 'J. Biomaterials., [25] (2004) 3829-3835.
35. W. Li, L. Yue, L. Chunzhong, 'In situ processing and properties of nanostructured hydroxyapatite/alginate composite', J. Nanopart Res., [11] (2009) 691-699.
36. W. Aili, L. Dong, Y. Hengbo, W. Huixiong, W. Yuji, R. Min, J. Tingshun, C. Xiaonong, and X. Yiqing, 'Size-controlled synthesis of Hydroxyapatite nanorods by chemical precipitation in the presence of organic modifier, 'J. Mat. Sc. Eng., [27] (2007) 865-869.
37. R.Z. Legeros, In Calcium Phosphates in Oral Biology and Medicine; Edited by Myers, H.M., Karger, Switzerland, 1991, 85.
38. J.C. Elliott, In Structure and chemistry of the apatites and other calcium orthophosphates, Studies in Inorganic Chemistry, Elsevier, Netherlands, 1994, l8, p. 112.
39. M. Vallet-Regý, J. Pena, I.Izquierdo-Barba, 'Synthesis of β-tricalcium phosphate in layered or powdered forms for biomedical application', J. Solid State Ionics., [172] (2004) 445-449.
40. L.A. Azaroff, Elements of X-ray Crystallography, McGraw-Hill, New York, 1968. pp. 38-42.
41. Z. Zyman, J. Weng, X. Liu, X. Li, X. Zhang, 'Phase and structure changes in hydroxyapatite coatings under heat treatment', J. Biomaterials., [15] (1994) 151-155.
42. Z. Zyman, I. Ivanov, D. Rochmistrov, V. Glushko, N. Tkachenko, S. Kijko, 'Sintering peculiarities for hydroxyapatite with different degrees of crystallinity', J. Biomed. Mater. Res., [54] (2001) 256-263.
43. C.L. Martin, G. Delette, D. Bouvard, 'Discrete element simulations of the compaction of aggregated ceramic powders', J. Am. Ceram. Soc., [89] (2006) 3379-3387.