

# INFLUENCE OF SOME PROCESS PARAMETERS ON STRUCTURE AND MOLECULAR PROPERTIES OF CALCIUM PHOSPHATE NANOPOWDERS

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## ABSTRACT

Sol-gel route has been regarded as one of the versatile techniques to prepare calcium phosphate (CaP) nanoceramics. Extensive studies encapsulating sol-gel based synthesis procedures showing effects of various process parameters on physico-chemical, structural, thermal and biological properties of CaP based synthetic powders. Hence it is always a tedious task to choose a particular synthesis methodology in light of dearth of a single detailed literature incorporating the comparison and effects of different synthesis procedures. In the present study, authors comprehensively studied the effects of phosphorous reagents, and other processing parameters on chemical composition of synthetic CaP powder. XRD and FTIR techniques were used for systematic characterization. This manuscript has been expected to fulfill the need of opting for a particular route to synthesize CaP nanopowders.

**Keywords:** Calcium phosphate, hydroxyapatite; XRD, FTIR, sol-gel

## 1. Introduction

Over the past decades, demands of calcium phosphate (CaP) based bioceramics have been continuously increased consequently wide efforts have been devoted to develop its synthesis routes [1]. It is widely known that among the CaP salts, Hydroxyapatite (HAP) is the principal inorganic constituent of human bones and teeth [2] and have been extensively studied owing to its various biological characteristics viz. non-immunogenicity [2], non-inflammatory behavior [2], high osteoconductivity and/or osseointegrability [2] and good biocompatibility [3,5]. Over the last many years, diverse CaP synthesis methods have been suggested claiming control over its varied properties. With such a great variety of synthesis routes; choosing a specific route to synthesize a well defined powder for a specific application can be so laborious [1] and often leads to dilemma.

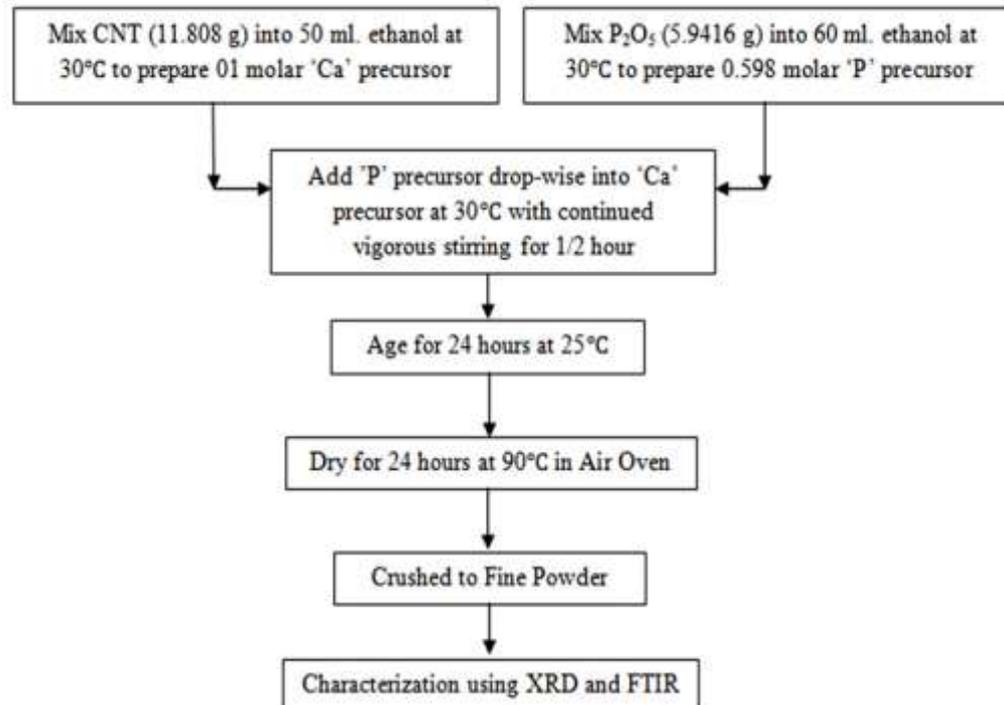
After an extensive literature review to synthesize CaP based powder including solid state synthesis [6-7], mechano-chemical synthesis [8,9,19], conventional chemical precipitation technique [10-11], hydrolysis [12], hydrothermal [13] and many more methods; only sol-gel route is among the wet chemical technique which has recently attracted much attention due to its many advantages including high product purity, homogeneous composition, low synthesis temperature [1,4], nano-dimensional structure size, narrow particle

size spread and stoichiometric Ca/P ratio (1.67) etc. Typical sol-gel process usually comprises of various steps viz. mixing of  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  reagents in aqueous and/or an organic solvents followed by aging at different temperatures and periods, gelation, centrifugation/drying and finally heating at higher temperatures, known as calcination/sintering. A little alteration in any of these process parameters causes a dominating change in varied properties of final product. Certain investigations have been reported, revealing the effects of different  $\text{Ca}^{2+}$  [14,18,33] and  $\text{PO}_4^{3-}$  precursors [14-18,20,21,22,34], water and/or ethanol as solvents [15,17], combination of stirring time [2,20-22], aging time and temperature [2,20-22], drying temperature and time [2,3,20,21] followed by different calcination temperatures and their respective timings [2,3,20,21] on physico-chemical constitution, crystallinity, crystal size and shape, thermal behavior [35] and finally biocompatibility aspects [36]. Many a times, it has been a common observation that such synthesis procedures are not elaborated in a meaningful manner which further shoots up the bewilderment of naïve researchers.

Keeping it in mind, authors synthesized nano-dimensional CaP based powders using phosphorous pentoxide (PP) and calcium nitrate tetrahydrate (CNT) as  $\text{Ca}^{2+}$  ion sources. Resultant nanopowders were analyzed for their structural constitution in a comprehensive manner.

## 2. Materials and method

CNT [ $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ; Merck, 98%) and PP [ $\text{P}_2\text{O}_5$ ; Merck, 97%] were used as  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  ion sources. DDH<sub>2</sub>O (lab made) and ethanol [ $\text{C}_2\text{H}_5\text{OH}$ ; Merck, 99.9%] were used as solvents. Synthesis protocol of CaP nanopowder has been shown in Figure 1.



**Figure 1. Synthesis methodology**

### 2.1. Powder Characterization

XRD (Philips X'Pert 1710) was performed using  $\text{CuK}\alpha$  radiations. Different structural parameters were determined using fundamental crystallographic formulae. Calcium to phosphorous (Ca/P) molar ratio was calculated using Eq. (1):

$$\frac{Ca}{P} = \frac{10-x}{6} \tag{Eq. (1)}$$

Chemical stability of HAP powder was represented in terms of chemical equation on the basis of calcium deficiency, (x) by using Eq. (2):

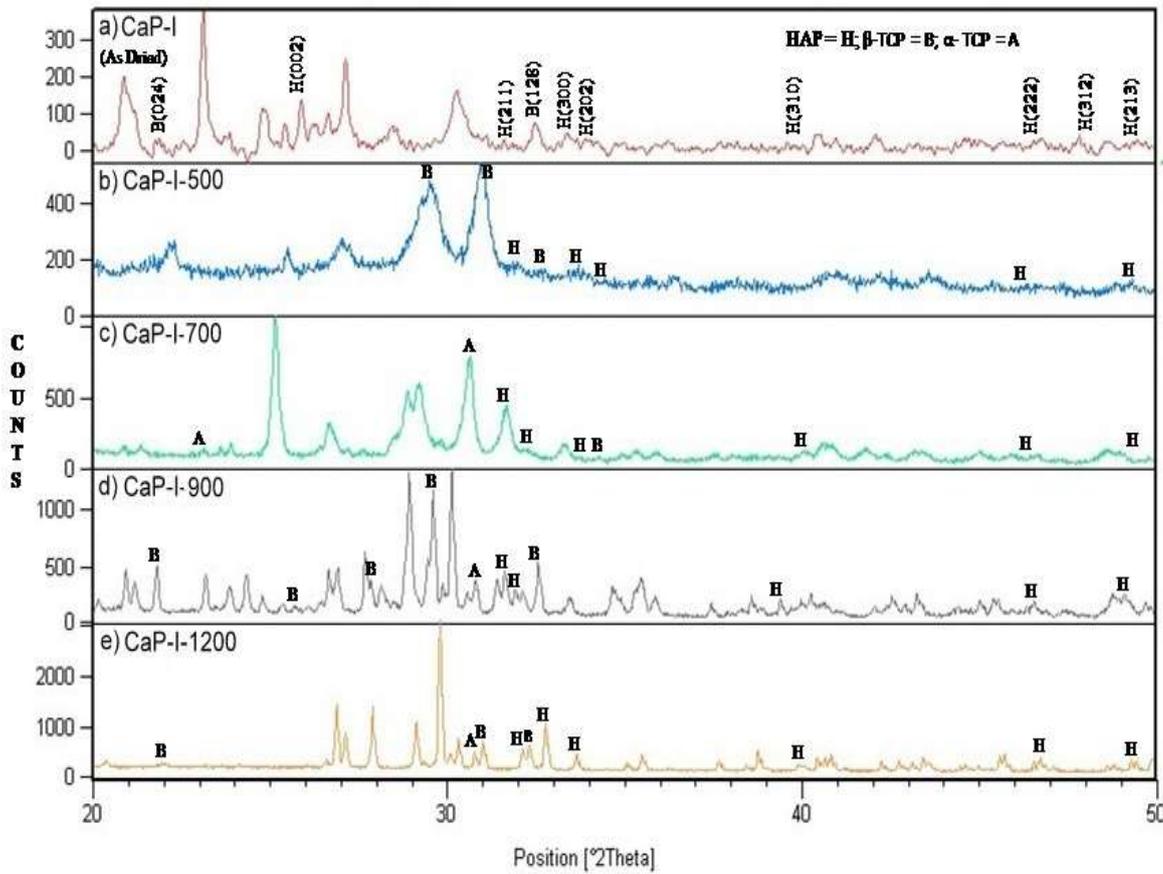


FTIR (Perkin Elmer) spectra were recorded from 500-4000 cm<sup>-1</sup> for each sample.

### 3. Results and discussion

#### 3.1. Qualitative and quantitative phase analysis

XRD patterns of CaP-I nanopowders sintered at different temperatures and corresponding results have been shown in Figure 2 and Table 1, respectively.



**Figure 2. XRD patterns of CaP-I nanopowders sintered at a) as dried, b) 500°C, c) 700°C, d) 900°C and e) 1200°C**

Chemical reactions to form apatite ionic structure as per the synthesis methodology of CaP-I have been proposed in Eq. 3-5.

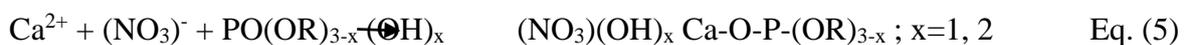
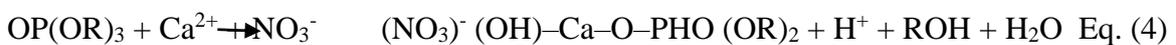
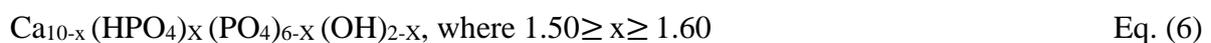


Table 1. Structural Properties of CaP-I nanopowders

Parameters	CaP-I-As Dried	CaP-I-500	CaP-I-700	CaP-I-900	CaP-I-1200
Major Phases	HAP; $\beta$ -TCP	HAP; $\beta$ -TCP	HAP; $\beta$ -TCP; $\alpha$ -TCP	HAP; $\beta$ -TCP; $\alpha$ -TCP	HAP; $\beta$ -TCP; $\alpha$ -TCP
HAP Lattice Parameters (nm)	a=9.380; c=6.887; c/a=0.734	a=9.498; c=6.921; c/a=0.728	a=9.376; c=7.267; c/a=0.774	a=9.443; c=8.103; c/a=0.857	a=9.396; c=6.849; c/a=0.728
Mean Crystallite Size (nm)	48.757	70.71	93.753	98.782	135.798
Weight Fractions	HAP=0.3451 $\beta$ -TCP=0.3451	HAP=0.0653 $\beta$ -TCP=1	HAP=0.3224 $\beta$ -TCP=0.6672	HAP=0.2752 $\beta$ -TCP=0.3373	HAP=0.307 $\beta$ -TCP=0.1754
Estimated Ca Deficiency, x	0.519	0.942	0.690	0.583	0.381
Ca/P Ratio	1.58	1.50	1.55	1.56	1.60

By adopting the synthesis methodology of CaP-I, multiphase calcium phosphate (MCP) nanopowder was derived consisting of  $\beta$ -TCP and HAP in major proportions along with certain peaks belonging to  $\alpha$ -TCP were also noticed. As dried gel Figure 2(a) indicates amorphous nature of powder [25] consisting of almost equal proportions of  $\beta$ -TCP and HAP characterized by weak intensity and broader peaks. Upon increasing the temperature to 500°C; biphasic structure converted into monophasic i.e.  $\beta$ -TCP only accompanied by a little amount of HAP. Crystallite size and crystallinity of all phases were observed to increase with the sintering temperature as indicated by reducing peak widths ascribed by various patterns shown and calculated in Figure 2 and Table 1, respectively [2,24,25]. HAP and  $\beta$ -TCP were observed to be the major phases present throughout along with traces of  $\alpha$ -TCP started appearing after 500°C showing its decomposition behavior [25]. In contrast to Costescu [2] which revealed the complete absence of  $\beta$ -TCP above sintering temperature of 1000°C, synthetic CaP-I powders still contained resorbable TCPs even up to 1200°C [35-36]. Lattice parameters of HAP crystals were also found to increase primarily 'c' axis dimension with the increase in sintering temperature in accordance with various researches [2,24,33-34]. Effect on Ca<sup>2+</sup> deficiency and Ca/P molar ratio with respect to sintering temperature has been enumerated in Table 1 confirmed the nature of synthesized nanopowder to be BCP having Ca/P ratio in between 1.5-1.67.

Crystallinity of CaP-I powders was observed to increase with the rise of sintering as indicated by decreasing peak width reflections of (002) and (310) planes as shown in Table 2 and complements with the various research findings [2,3,25]. Chemical stability of CaP-I powders can be proposed in terms of Eq. (6) based on Ca deficiency, x as

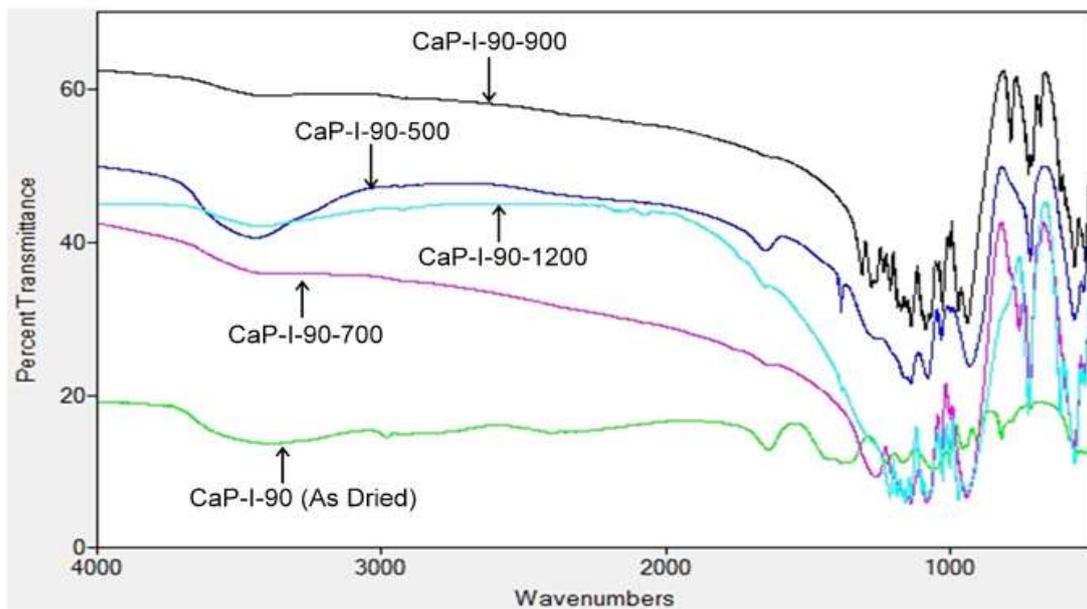


**Table 2. Peak width measurement of (002) and (310) reflections to represent crystalline behavior of CaP-I powders**

	Planes	CaP-I-As Dried	CaP-I-500	CaP-I-700	CaP-I-900	CaP-I-1200
Peak Width ( $2\theta$ )	(002)	0.1673	0.1171	0.1673	0.1004	0.1224
	(310)	0.0836	0.0612	0.1673	0.0816	0.1428

### 3.2. FTIR analysis

Ionic structure of synthesized CaP-I nanopowders have been shown in Figure 3.



**Figure 3. FTIR spectra of CaP-I powders**

Various constituent functional groups viz. water-adsorbed deformation ( $3441, 3431, 3423 \text{ cm}^{-1}$ ); OH- water adsorbed deformation ( $1647, 1639 \text{ cm}^{-1}$ ) [33]; carbonate stretching band ( $1384, 1383, 1382 \text{ cm}^{-1}$ ) [35-36];  $\delta\text{OH HPO}_4^{2-}$  ( $1211, 1210 \text{ cm}^{-1}$ );  $\nu_3 \text{ HPO}_4^{2-}$  ( $1139, 1138 \text{ cm}^{-1}$ ) along with  $\nu_3 \text{ PO}_4$  ( $1086, 1080, 1045, 1033 \text{ cm}^{-1}$ );  $\nu_1 \text{ PO}_4$  ( $1073, 973, 959 \text{ cm}^{-1}$ ) [33-34];  $\nu_4 \text{ PO}_4$  ( $613, 566, 565 \text{ cm}^{-1}$ ) [37],  $\nu_2 \text{ PO}_4$  ( $471 \text{ cm}^{-1}$ ) were detected in CaP-I nanodimensional powders as shown in Figure 3.

### 4. Conclusion

CaP nanopowders with biphasic structure were synthesized using different synthesis conditions. Ca/P ratio was found to lie between 1.5-1.67 which is an indication of their resorbable nature. Based on the results of present investigation; structural constitution of all synthesized powders was noticed to resemble having little variation in one or two parameters. Presence of HAP phase at the lower temperature in all the powders turned out to be a main achievement. Reduced decomposition temperature of apatite to  $\beta$ -TCP was also observed. Admittedly, other desirable properties viz. high thermal stability and powder crystals of nano-dimensional size recommend the synthesized powders suitable for biomaterial applications.

## References

- [1] Shojai M.S., Khorasani M.T., Khoshdargi E.D., Jamshidi A.: Synthesis methods for nanosized hydroxyapatite of diverse structures. *Acta Biomaterialia* (2013) doi: <http://dx.doi.org/10.1016/j.actbio.2013.01.012>.
- [2] Costescu A., Pasuk I., Ungureanu F., Dinischiotu A., Costache M., Huneau F., Galaup S., Coustumer P.L., Predoi D.: Physico-chemical properties of nano-sized hexagonal hydroxyapatite powder synthesized by sol-gel. *Digest Journal of Nanomaterials and Biostructures* 5 4 (2010) 989-1000.
- [3] Predoi D., Balcan R.A.V., Pasuk I., Trusca R., Costache M.: Calcium phosphate ceramics for biomedical applications. *Journal of Optoelectronics and Advanced Materials* 10 8 2008 2151-2155.
- [4] Fathi M.H., Hanifi A.: Evaluation and characterization of nanostructure hydroxyapatite powder prepared by simple sol-gel method. *Materials Letter* 61 2007 3978-3983.
- [5] Nathanael A.J., Mangalaraj D., Ponpandian N.: Controlled growth and investigations on the morphology and mechanical properties of hydroxyapatite/titania nanocomposite thin films. *Composites Science and Technology* 70 2010 1645-1651.
- [6] Pramanik S., Agarwal A.K, Rai K., Garg A.: Development of high strength hydroxyapatite by solid-state-sintering process. *Ceramics International* 33 2007 419-426.
- [7] Teshima K., Lee S.H., Sakurai M., Kameno Y., Yubuta K., Suzuki T.: Well-formed one-dimensional hydroxyapatite crystals grown by an environmentally friendly flux method. *Crystal Growth and Design* 9 2009 2937-2940.
- [8] Silva C., Graça M.P.F., Valente M., Sombra A.S.B.: Crystallite size study of nanocrystalline hydroxyapatite and ceramic system with titanium oxide obtained by dry ball milling. *Journal of Materials Science* 42 2007 3851-3855.
- [9] Fahami A., Ebrahimi K.R., Nasiri T.B.: Mechanochemical synthesis of hydroxyapatite/titanium nanocomposite. *Solid State Science* 13 2011 135-141.
- [10] Afshar A., Ghorbani M., Ehsani N., Saeri M., Sorrell C.: Some important factors in the wet precipitation process of hydroxyapatite. *Material Design* 24 2003 197-202.
- [11] Fomin A., Barinov S., Ievlev V., Smirnov V., Mikhailov B., Kutsev S.: Nanocrystalline hydroxyapatite ceramics. *Inorganic Materials* 45 2009 1193-1196.
- [12] Sakamoto K., Yamaguchi S., Nakahira A., Kaneno M., Okazaki M., Ichihara J.: Shape-controlled synthesis of hydroxyapatite from tricalcium bis (orthophosphate) in organic-aqueous binary systems. *Journal of Materials Science* 37 2002 1033-1041.
- [13] Zhu K., Yanagisawa K., Onda A., Kajiyoshi K., Qiu J.: Morphology variation of cadmium hydroxyapatite synthesized by high temperature mixing method under hydrothermal conditions. *Materials Chemistry and Physics* 113 2009 239-243.
- [14] Ioitescu A., Vlase G., Vlase T., Ilia G., Doca N.: Synthesis and characterization of hydroxyapatite obtained from different organic precursors by sol-gel method. *J. Therm. Anal. Calorim* 96 2009 937-942.

- [15] Chen J., Wang Y., Chen X., Ren L., Chen L., He W., Zhang Q.: A simple sol-gel technique for synthesis of nanostructured hydroxyapatite, tricalcium phosphate and biphasic powders. *Materials Letters* 65 2011 1923-1926.
- [16] Lee H.U., Jeong Y.S., Park S.Y., Jeong S.Y., Kim H.G., Cho C.R.: Surface properties and cell response of fluoridated hydroxyapatite/TiO<sub>2</sub> coated on Ti substrate. *Current Applied Physics* 9 2009 528-533.
- [17] Zhang W., Wang C., Liu W.: Characterization and tribological investigation of sol-gel ceramic films on Ti-6Al-4V. *Wear* 260 2006 379-386.
- [18] Simon V., Lazar D., Turcu R.V.F., Mocuta H., Magyari K., Prinz M., Neumann M., Simon, S.: Atomic environment in sol-gel derived nanocrystalline hydroxyapatite. *Materials Science and Engineering B* 165 2009 247-251.
- [19] Nakamura S., Isobe T., Senna M.: Hydroxyapatite nano sol prepared via a mechanochemical route. *Journal of Nanoparticle Research* 3 2001 57-61.
- [20] Agrawal K., Singh G., Puri D., Prakash S.: Synthesis and characterization of hydroxyapatite powder by sol-gel method for biomedical application. *Journal of Minerals and Materials Characterization & Engineering* 10 8 2011 727-734.
- [21] Agrawal K., Singh, G., Prakash, S., Puri D.: Synthesis of HA by various sol-gel techniques and their comparison: a review. *Proc. National Conference on Advancements and Futuristic Trends in Mechanical and Materials Engineering, Punjab Technical University, Punjab, India* 1998.
- [22] Vijayalakshmi U., Rajeswari S.: Influence of process parameters on the sol-gel synthesis of nano hydroxyapatite using various phosphorous precursors. *Journal of Sol-Gel Technology* 63 2012 45-55.
- [23] Landi E., Tampieri A., Celotti G., Sprio S.: Densification behavior and mechanisms of synthetic hydroxyapatite. *Journal of European Ceramic Society* 20 2000 2377-2387.
- [24] Meza D., Figueroa I.A., Morales C.F., Barba M.C.P.: Nano hydroxyapatite crystals obtained by colloidal solution. *Revista Mexicana De Fisica* 57 2011 471-474.
- [25] Fathi M.H., Hanifi A.: Evaluation and characterization of nanostructure hydroxyapatite powder prepared by simple sol-gel method. *Materials Letter* 61 2007 3978-3983.
- [26] Kalita S.J, Bhatt H.A.: Nanocrystalline hydroxyapatite doped with magnesium and zinc: synthesis and characterization. *Materials Science and Engineering C* 27 2007 837-848.
- [27] Gozalian A., Behnamghader A., Daliri M., Moshkforoush: Synthesis and thermal behaviour of mg-doped calcium phosphate nanopowders via the sol-gel method. *Scientia Iranica* 18 6 2011 1614-1622.
- [28] Liu D.M., Troczynski T., Tseng W.J.: Water based sol-gel synthesis of hydroxyapatite: process development. *Biomaterials* 22 2001 1721-1730.
- [29] Manishaben Jaiswal, "COMPUTER VIRUSES: PRINCIPLES OF EXERTION, OCCURRENCE AND AWARENESS ", *International Journal of Creative Research Thoughts (IJCRT)*, ISSN:2320-2882, Volume.5, Issue 4, pp.648-651, December 2017, <http://doi.one/10.1729/Journal.23273> Available at [http://www.ijcrt.org/viewfull.php?&p\\_id=IJCRT1133396](http://www.ijcrt.org/viewfull.php?&p_id=IJCRT1133396)

- [30] Shirkhanzadeh M.: Calcium phosphate coatings prepared by electrocrystallization from aqueous electrolytes. *Journal of Materials Science: Materials in Medicine* 60 1995 90-93.
- [31] Daculsi G.: Biphasic calcium phosphate concept applied to artificial bone implant coating and injectable bone substitute. *Biomaterials* 19 1998 1473-1478.
- [32] Masuda Y., Matubara K., Sakka S.: Synthesis of hydroxyapatite from metal alkoxides through sol-gel technique. *Journal of Ceramic Society* 98 1990 1266-1277.
- [33] Westheimer F.H., Huang S., Coritz S.: Rates and mechanisms of hydrolysis of esters of phosphorous acids. *Journal of American Chemical Society* 110 1988 181-185.
- [34] Singh A.: Hydroxyapatite, a biomaterial: its chemical synthesis, characterization and study of biocompatibility prepared from shell of garden snail, *Helix aspersa*. *Bulletin of Materials Science* 35 2012 1031-1038.
- [35] Manishaben Jaiswal "Big Data concept and imposts in business" *International Journal of Advanced and Innovative Research (IJAIR)* ISSN: 2278-7844, volume-7, Issue- 4, April 2018 available at: [http://ijairjournal.in/Ijair\\_T18.pdf](http://ijairjournal.in/Ijair_T18.pdf)
- [36] Singh A.: Novel attempt to develop porous hydroxyapatite synthesized from snail shell (*helix aspersa*) by using naphthalene as porogen. *Trends in Biomaterials & Artificial Organs* 29 2015.
- [37] Mehta D., George S., Singh A.: Assessment of different synthesis route of hydroxyapatite and study of its biocompatibility in synthetic body fluids. *International Journal of ChemTech Research* 9 2016 267-276.
- [38] Rasool I., Singh A.: In vitro studies of biomaterial device "hydroxyapatite" prepared from different routes for biomedical applications. *In Vitro*, 11 2018.
- [39] Trukhanov, S.V., Trukhanov, A.V., Salem, M.M., Trukhanova, E.L., Panina, L.V., Kostishyn, V.G., Darwish, M.A., Trukhanov, A.V., Zubar, T.I., Tishkevich, D.I. and Sivakov, V.: Preparation and investigation of structure, magnetic and dielectric properties of  $(\text{BaFe}_{11.9}\text{Al}_{10.1}\text{O}_{19})_{1-x}(\text{BaTiO}_3)_x$  bicomponent ceramics. *Ceramics International* 44 2018 21295-21302.