

# Microwave Synthesis Of Lanthanum Doped Nano Hydroxyapatite Prepared From Duck Egg Shell.

G. Nedunchezian, C. Vijayaraj, D. Benny Anburaj

**Abstract:** The current study, Lanthanum doped hydroxyapatite [  $\text{La-Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  ] was synthesized from low expenses duck eggshell as calcium source with di-ammonium hydrogen phosphate  $(\text{NH}_4)_2\text{HPO}_4$  as a phosphate source, the pH was sustain at 10 using ammonium hydroxide  $(\text{NH}_4\text{OH})$ , followed by microwave irradiation for 30 min. Then the deposit was washed with de-ionized water and the sample was collected and calcined at  $900^\circ\text{C}$  for 2hr, the achievable hydroxyapatite was afford as nano rod of  $\approx 20$  nm range along with quantitative yield. Synthetically this approach has contained lot of priority than other events. Since it is too simple and proper way on the subject of, such a biological devastate materials of remaining duck egg shell. The functional groups, structural, morphological studies and the elemental analysis of the entire yield were characterized by different systematic techniques.

**Keywords:** Lanthanum; Hydroxyapatite; Microwave irradiation; Calcium phosphate; Bone substitute.

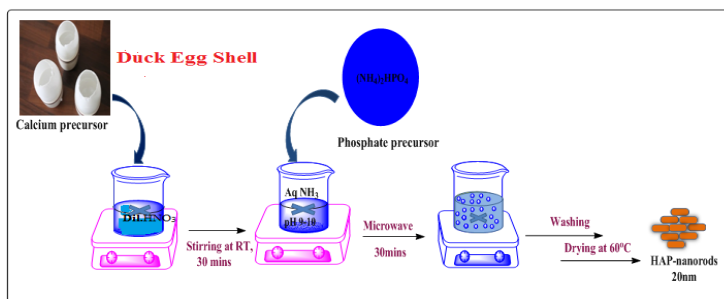
## 1. INTRODUCTION

Hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) is one of the major essential part which has been broadly used for substituting the injured part of the human body, primarily for bones, tooth and fractured or damaged parts, form a variety of hard tissues etc [1,2]. To be sure, the major part of apatite calcium phosphate of bone mineral is made up of calcium carbonate. Due to this connection, the synthesised pure and lanthanum doped nano HAp originates to have better bio-activity and bio-compatibility to the relevant as expected occurring calcium phosphate. In addition, the frequent applicability of synthesised nano HAp is rewarded to their agreeable chemical relations all over the hard and host tissues. Due to these reasons, HAp has been required to be extensively used in medical field as implants or as bone filling material. HAp synthesis including precipitation, sol-gel, combustion synthesis etc.,[4]. However, most of the predictable methods such as hydrothermal, micro emulsion and mechanochemical process respectively [5] are in use to synthesis HAp nano particles. The fabrication of nano sized HAp with acceptable size, shape and clarity is relatively complicated [6]. For convenient applications in the field of medicine, the better densification of HAp is significant [7-9]. The overall recompense after the nano sized HAp offers a enormous deal of substance to investigate a novel synthesis method for carry out engineered nano-HAp. The technique connected with microwave-irradiation is one of the finest methods to synthesise nano size HAp, which covers shorter reaction time and lesser-energy utilization and etc. However, most of the techniques absorb the mixture of both predictable and microwave irradiation method for a period of time [10-12]. In the earlier time, there have been established several reports which deal the fabrication of nano sized HAp through microwave-irradiation. Recently, Nedunchezian et.al., has been reported the microwave technique elsewhere [16]. In addition, the effectiveness of biological material for the fabrication of HAp is also a fortunate route for the reason that of its precious impact on biological and reasonable profit.

Though, this method requires being more optimistic in order to utilize the biological waste and manage over the contamination. Additionally, to the best our knowledge, the microwave –assisted synthesis of nano sized HAp from duck egg shell has been less explored. Relating this analysis, we are involved to focus on the microwave –assisted synthesis of nano sized HAp from duck eggshell, while it is extremely enriched with  $\text{CaCO}_3$  and also it is easily obtainable sources. Thus, the duck egg- shell, a waste material after use of egg white and yolk, has been used as calcium source to synthesise highly pure and low-cost hydroxyapatite using di-ammonium hydrogen phosphate under microwave irradiation condition. The synthesised powder was characterized by XRD, FTIR, FE- SEM and EDAX analytical techniques.

## 2 EXPERIMENTAL MEASUREMENTS

### 2.1 Synthesis of HAp



The duck egg shells were collected and washed with tap water, followed by distilled water to relieve of surplus deposits. They were dried in direct sun light [17] for 24hr and crushed by pestle and mortar, 200 size mesh used to sieve to obtain fine powder [18]. The duck eggshell powder was dissolved in dilute nitric acid and the mixture was added to a solution of di-ammonium hydrogen phosphate and the pH was maintaining at 10 using ammonium hydroxide. Then stoichiometric amount of  $\text{LaCl}_3$  were added to the solution. The mixed solution was stirred for 1hr and quickly transferred to a domestic microwave oven (LG, India) and irradiated at 800W energy of frequency employing 2.45 GHZ for 30 min continuously. After the irradiation, the residue was washed with de-ionized water three times and then dried in a vacuum oven at  $60^\circ\text{C}$  for 12hr.

- PG & Research Department of Physics, Thiru.Vi.Ka. Govt. Arts College, Tiruvarur-610003, India
- PG & Research Department of Chemistry, Thiru.Vi.Ka. Govt. Arts College, Tiruvarur-610003, India
- PG & Research Department of Physics, D.G.Govt. Arts College, Mayiladuthurai-609001, India

\* Corresponding Author: gncphysics@gmail.com

## 2.2 CHARACTERIZATIONS

The phase analysis of the as-synthesized nano sized hydroxyapatite was analyzed by X-ray powder diffraction technique using Cu-K $\alpha$  radiation and the powder morphology was observed by FE- SEM (JEOL JSM 6701-F USA) fitted with EDAX (INCA, oxford instrument, UK) techniques. The FTIR spectroscopy (RXI Perkin Elmer) was used to identify the functional groups of as-synthesized hydroxyapatite.

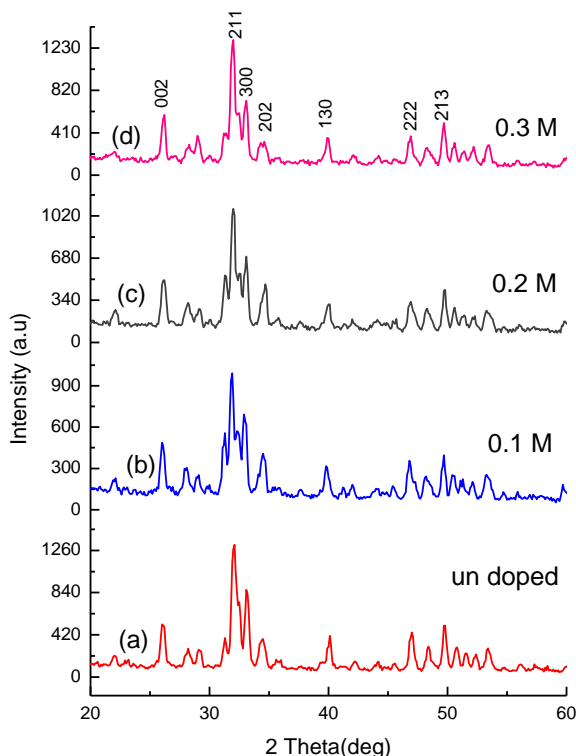
## 3 RESULTS AND DISCUSSION

### 3.1 Phase Analysis

The XRD diffraction patterns of the as-synthesized un doped HAp powder and lanthanum doped HAp powders calcined at 900° C were shown in Fig 1. The result shows that all the observed major peaks assign the presence of nanosized HAp in all the samples. The expansion of the peak in Fig. 1(a) designate that the as-synthesized un doped HAp powder were dried at 60° C, and Fig.1(b-d) indicate lanthanum doped HAp powder with 0.1M, 0.2M, 0.3M concentration with calcinations of 900° C. To check the effect of calcinations, and analyzed the phases [20]. As the temperature of 900° C, The sharpening of the peak at 25.9°, 31.8°, 32.9°, 34.0°, 39.8°, 46.7° and 49.6° occurs related to the planes (002), (211), (300), (202), (130), (222) and (213), which represents the high crystallinity of the calcined HAp. Clearly, these results were good in concurrence with standard JCPDS Card No-89-6437.

**Table.1** Crystallite size of Nano sized HAp powders

Sl.No.	Molarities	Sample	Crystallite Size (nm)
1	0.1M	Un doped HAp	12.21
2	0.1 M	La doped HAp	19.20
3	0.2 M	La doped HAp	18.20
4	0.3 M	La doped HAp	16.20



**Figure.1** XRD- Analysis of hydroxyapatite powder (a). Un doped HAp, (b). La doped HAp (0.1 M), (c). La doped HAp (0.2 M), (d). La doped HAp (0.3 M)

$$D = k \lambda / \beta \cos \theta. \text{ Where } \beta = \text{FWHM} \times \pi / 180$$

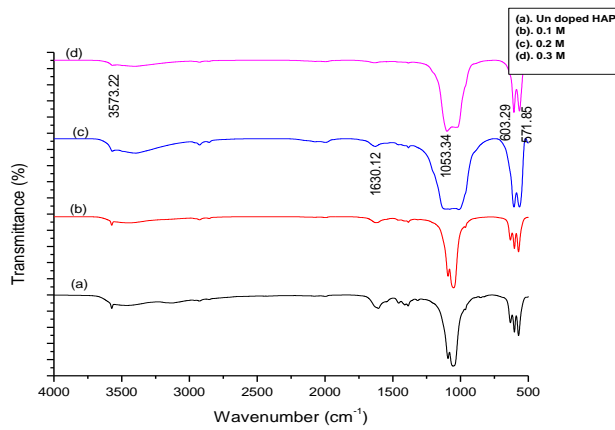
$$K=0.94$$

$$\lambda=1.5406 \text{ \AA}$$

Further, the crystallite size was calculated for as-synthesized and calcined powders from the XRD pattern by Debye-Scherrer formula[21], which discloses that the average crystallite size was apparently 12.21 nm for as-synthesized un doped nano sized HAp, 19.20 nm for the La (0.1 M) doped HAp, further the crystallite size 18.20 nm, 16.20 nm for 0.2 M and 0.3 M ratio of La doped HAp's consequently, the doping level were increased the crystallite sizes of La doped HAp's are decreased as recognized to the temperature 900°C as illustrate in the table 1 [22].

### 3.2 Chemical composition

The FTIR spectrum of as-synthesized un doped HAp, La doped HAp with various doping concentrations like 0.1 M, 0.2 M, 0.3 M HAp are shown in the Fig 2. The characteristic peaks at 1053.34 cm<sup>-1</sup>, and the peaks at 571.85cm<sup>-1</sup>, correspond to stretching vibration of PO<sub>4</sub><sup>3-</sup> ions and the deformation of PO<sub>4</sub><sup>3-</sup> ions respectively. The broad OH stretching band around 3573.22cm<sup>-1</sup>, proves the adsorption for H<sub>2</sub>O molecules. A region of peak at 1630.12 cm<sup>-1</sup>, designate the existence of carbonate in trace level. Further, the peaks are responsible for stretching mode of CO<sub>3</sub><sup>2-</sup>. The formation of apatite was confirmed by the appearance of doublet at around 603.29 cm<sup>-1</sup> - 571.85cm<sup>-1</sup>, which denotes the bending mode of P- O bonds in phosphate ions, in the present study [23-25].

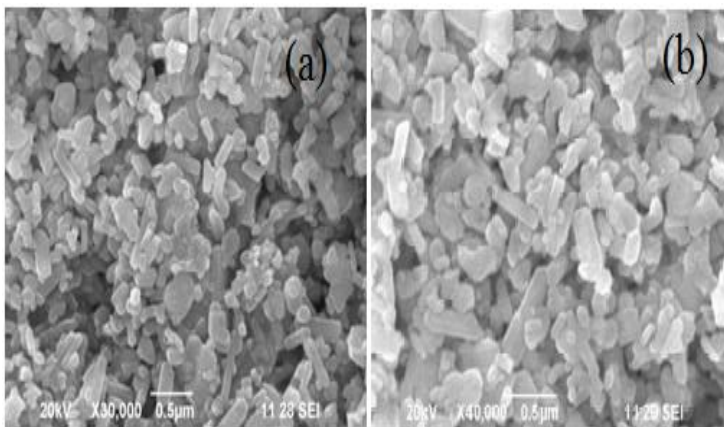


**Figure. 2** FTIR Spectrum of HAp powders.

(a) Un doped HAp, (b) La doped HAp (0.1 M), (c) La doped HAp (0.2 M), (d) La doped HAp (0.3 M).

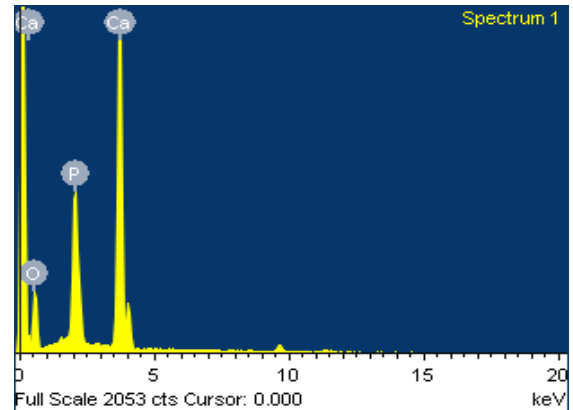
**3.3 Morphological studies**

Fig.3 (a-b) shows the powder morphology of as-synthesized (a) un doped HAp, (b) Lanthanum doped HAp. Reveals that the as synthesized un doped HAp has intense apatite with fine nano rod like shape morphology with less crystallite of highly agglomerated [20]. The changes in the morphology of the Lanthanum doped nano sized HAPs are due to the increase in the crystallinity of the powder included with the calcined temperatures at 900°C. The Lanthanum doped calcined HAP powder acquire the nano rod like morphology with homogenous microstructure, as the temperature increases, aggregation increases which results deformed spherical particle. This is due to the diminishing of the chance of relevant growths in grains and the development of densification of the particles [24]. The Fig.4 and Fig 5 shows the EDAX Spectrum of hydroxyapatite before and after doped with lanthanum. The presents of Ca, P, O, and La to be confirm the formation of lanthanum doped apatite [26, 27]. The presented elements with weight percentage and atomic percentage were tabulated in the table1 and table 2.



**Figure. 3** FE-SEM images of nano sized HAp powders:

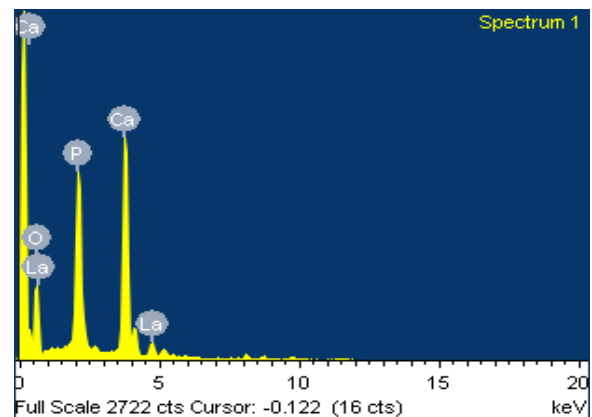
(a) Un doped HAp, (b) Lanthanum doped HAp



**Figure.4** EDAX Analysis of un doped HAp

**Table. 2** Elemental Analysis of un doped HAp

Sl.No.	Element	Weight %	Atomic %
1.	O K	50.95	70.23
2.	P K	17.24	12.28
3.	Ca K	31.80	17.50



**Figure.5** EDAX Analysis of Lanthanum doped HAp

**Table. 3** Elemental Analysis of Lanthanum doped HAp

Sl.No.	Element	Weight %	Atomic %
1.	O K	52.95	74.27
2.	P K	14.05	10.18
3.	Ca K	25.64	14.36

4.	La L	07.36	01.19
----	------	-------	-------

#### 4 CONCLUSIONS

In this study we bring to a close the undoped and lanthanum doped hydroxyapatite nano rods were successfully synthesized assisted by microwave irradiation using duck egg shell powder as calcium source with di-ammonium hydrogen phosphate as phosphate source. The synthesized HAp powder was characterized by a variety of systematic techniques to validate the progress of apatite. We suggested that the HAp novel material suitable for bio medical applications.

#### REFERENCES

- [1]. M. Dasgupta Adak, K. M. Prohit , Trends Biomater. Artif.organs. 25(3) (2011) 101-106.
- [2]. F. Abu Osman, W.A.B. Ibrahim, H.S .Wan Abas, H.N Abd Rahman, Biomed Proceedings 21 (2008) 333–336.
- [3]. K. Prabakaran, A. Balamurugan, S .Rajeshwari, Bull.mater.Sci. 28(2) (2005) 115-119.
- [4]. G. Gergely, F. Weber, I. Lukacs, A. L. Toth, Z.E. horvath, J.mihaly, C. Balazsi, J. Ceramic International, 36 (2010) 803-806.
- [5]. H. Khandelwal, Satya Prakash, Journal of Minerals and Materials Characterization and Engineering, 4 (2016) 119-126.
- [6]. Dong. Z, Li. Y, Zou. Q. Appl. Surf. Sci., 255 , (2009), 6087-6091.
- [7]. D.L .Goloshchapov, V.M .Kashkarov, N.A. Rummyantseva, P.V. Seredin, A.S. Lenshin, B.L. Agapov, E.P. Domashevskaya J.CeramicInternational,doi.10.1016/j.ceramint.2012.11.050
- [8]. S .Bose, S .Dasgupta, S .Tarafer, A. Bandyopadhyay, Acta. Biomater. 6 (2010) 3782-3790.
- [9]. A .Bianco, I .Caccitti, M .Lombardi, L .Montanaro, Mater. Res. Bull. 44 (2009) 345-354.
- [10]. P .Parhi, A .Ramanan, A.R .Ray, Mater. Lett. 58 (2004) 3610- 3622.
- [11]. Y .Park, Y .Ryu, S .Yoon, R .Stevens, H .Park, Mater. Chem. Phys. 109 ( 2008) 440-447.
- [12]. A .Jalot, C .Tas , S .B .Bhaduri, J. Mater. Res. 19 (2004) 1876-1881.
- [13]. D .Gopi, J. Indhira, S .Nithiya, S. L .Kavitha, U. Kamachi Mudali, K .Kanimozhi, J. Bull. Mater. Sci. 36 (2013) 799-805.
- [14]. M.Elkady, M. Mahmoud, Abd-El Rahman, J. Non. Cryst. Solids. 357 (2011) 1118- 1129.
- [15]. S . J .Kalita, S .Varma, Mater.Sci Eng.C. 30 (2010) 295 303.
- [16]. G .Nedunchezian, D. Benny Anburaj, J. Sembian Ruso, C .Vijayaraj, M .Mariappan, S. Johnson Jeyakumar, Indo Asian Journal of Multidisciplinary, 1(4) (2015) 345-354.
- [17]. A. Singh, Bull. Mater.Sci. 35(6) (2012) 1031-1038.
- [18]. D .Benny Anburaj, Ph.D., Thesis, Bharathidasan University, (2005).
- [19]. R. Murugan, K. Panduranga Rao, T. S .Sampathkumar, Key Engineering Materials, 242 (2003) 51-54.
- [20]. N. Iqbal, M. R .Abdul Kadir, N. H .Mahmood, N .Salim, G. R. A. Froemming, H. R .Balaji, T . Kamarul, Ceramic International, 40, (2014), 4507-4513.
- [21].V.Porkalai, D. BennyAnburaj,B. Sathya,G. Nedunchezian ,R.meenambika,J.Mater.Sci.Mater Electron, (2016) doi.10.10s7/s10854-016-5826-1.
- [22]. R. Murugan, S .Ramakrishnan, J. Cryst. Growth. 274 (2005) 209-213.
- [23]. M .Dasgupta Adak, A. K .Chottopadhyay, K. M .Prohit, J. Chemical and Analytical Science. 2(1) (2011) 7-9.
- [24]. S. S. Asghar Abidi, Q. Murtaz, J. Mater.Sci. Technol. 30 (2014) 307-309.
- [25]. K .A. Gross, Komarovska, and Viksna, Journal of Astralian Ceramic Society, 49(2) (2013) 129-135.
- [26]. S. Jadalannagari, K. Deshmukh, S. R. Ramanan, M. Kowshik, J. Appl.Nano Sci. 4 (2014) 133-141.
- [27]. G. Nedunchezian, D.BennyAnburaj, B.Gokulakumar, S. Johnson Jeyakumar, International Journal of Recent Scientific Research. 6(12) (2015) 7793-7797.