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Synthesis of apatite structure based $BiNaCa_3(PO_4)_3OH$ and its application for condensation reaction

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Abstract

Mono, di and trivalent ions containing hydroxyapatite of the formula $BiNaCa_3(PO_4)_3OH$ has been synthesized and the compound's catalytic activity in three component Biginelli condensation was studied. The compound was characterized by powder XRD, FT-IR, SEM and TGA/DTA techniques. The unit cell dimensions of the compound were determined to be $a = 9.412(2)$ Å, $C = 6.92(2)$ Å and the unit cell volume is 530.9 $Å^3$. The substituted hydroxyapatite phase showed enhanced reactivity in the one pot synthesis of 3,4-dihydropyrimidin-2(1H)-one by Biginelli reaction and resulted in an increased yield of the product.

Keywords: A. Powders: Chemical preparation; C. Chemical properties; D. Apatite; Powder X-ray diffraction

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1. Introduction

Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) is one of the major inorganic constituents of bone and teeth. The compound exhibits non-toxicity, biocompatibility, bioactivity, osteoconductivity and possesses non-inflammatory and non-immunogenic nature [1]. Hence, it has been recognized as a substitute material for defective bones and teeth [2,3].

Hydroxyapatite crystallizes in the hexagonal system with $P6_3/m$ space group. The structure was described by Beevers and McIntyre and confirmed by Young and co-workers [4]. In the crystal lattice formed by corner – connected Ca–O octahedra and P–O tetrahedra the divalent metal ions occupy two nonequivalent crystallographic sites (4f (Ca1), 6h (Ca2)). It is known that other divalent cations with a similar charge-to-size ratio to calcium can readily be substituted in the lattice of hydroxyapatite. Literature reports demonstrate the flexibility of the apatite structure upon substitution of other aliovalent cations in the 'Ca' sites, pentavalent and tetravalent ions such as V^{5+}, As^{5+}, and Si^{4+} in the 'P' site and halide, oxide ions in the 'OH' site [4]. In addition to understand the changes in crystal chemistry, such heteroionic substitutions are also significant due to the extensive biological and catalytic applications of HAP.

Application of HAP based catalysts has been reported for a variety of organic reactions such as hydration of nitriles [5], Knoevanagel reaction [6], Michael addition [7], Friedel-crafts alkylation [8], and Biginelli reaction [9,10]. Ion-exchanged HAP, where the metal ions are incorporated in the phosphate framework exhibit interesting reactivity [11–13]. A characteristic feature of ion-exchanged hydroxyapatites such as RuHAP is found to be their high stability during catalytic oxidation reactions.

Biginelli has reported a novel one pot, three component synthetic route for 3,4-dihydropyrimidin-2(1H)-one [DHPM] [14]. Articles are continuously reporting on the synthesis of this compound and its derivatives with different synthetic protocols mainly because of the remarkable pharmacological efficiency of the multifunctionalized DHPMs [15–23]. Current study investigates the catalytic activity of trivalent and monovalent ion substituted hydroxyapatite of the formula $BiNaCa_3(PO_4)_3OH$ as a heterogeneous catalyst in the synthesis of DHPM and selected derivatives.

2. Experimental procedures

2.1. Materials

Bismuth nitrate (98%), calcium nitrate (98%), sodium nitrate (98%) were obtained from SD Fine Chemicals, India and

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orthophosphoric acid (98%) from Qualigens Fine Chemicals, India.

2.2. Synthesis

The metal ion solutions were prepared as follows. Required quantities of bismuth nitrate, sodium nitrate and calcium nitrate salts were weighed accurately. The molar ratio of the metal ions Bi:Na:Ca was maintained as 1:1:3. A solution of bismuth nitrate was prepared by dissolving the required quantity of bismuth nitrate in 6 ml of 1:1 HNO_3 and 10 ml water. To the solution 20 ml of methanol was added. Sodium nitrate solution was prepared by dissolving the nitrate salt in 5 ml of water and made alcoholic by adding 20 ml of methanol. Calcium nitrate solution was prepared by dissolving the salt in 20 ml of methanol. Similarly, orthophosphoric acid solution (3 M) was prepared in 30 ml of methanol. To the calcium nitrate solution, sodium nitrate and bismuth nitrate solutions were added successively. The mixture was stirred for 5 min. To the homogenized mixture phosphoric acid solution was added in small quantities while stirring. Formation of white precipitate was noticed. The contents were stirred for 5 h at room temperature. The mixture was kept for digestion over water bath for 8 h. The solvent was evaporated and the white mass obtained was heated at 500 °C, 800 °C, 900 °C, 1000 °C, and 1100 °C for 10 min at each temperature with intermittent grinding. The furnace cooled products were analyzed to check the phase formation.

2.3. Catalytic activity

The catalytic activity of the title compound was studied by varying temperature, solvent and catalyst amount to optimize the condition. The scheme of the reaction is shown in Fig. 1.

2.3.1. Catalysis at room temperature and under reflux condition

A mixture of aldehyde (10 mmol), ethylacetoacetate (10 mmol), urea (10 mmol) and catalyst (0.5 g) were mixed by stirring over a period of time mentioned in Table 1. The catalyst amount was varied between 0.25 and 2.0 g. After the completion of the reaction (monitored by Thin Layer Chromatography, TLC) the catalyst was separated by filtration. The organic product mixture was poured into water. The solidified product was collected and dried. The product was recrystallized from ethanol. Similar procedure was followed for the reaction in the presence of various solvents such as acetonitrile, acetic acid, n-hexane, toluene, ethanol and chloroform. The experiment was carried out under reflux condition with and without solvents. The procedure involved all the steps mentioned above except the reflux condition.

Table 1
Effect of the amount of the catalyst and temperature.

Catalyst	Room temperature % yield (time)	Reflux % yield (time)
2 g	81 (45 min)	58 (15 min)
1 g	24 (60 min)	66 (15 min)
0.5 g	47 (60 min)	70 (15 min)
0.25 g	28 (90 min)	28 (15 min)

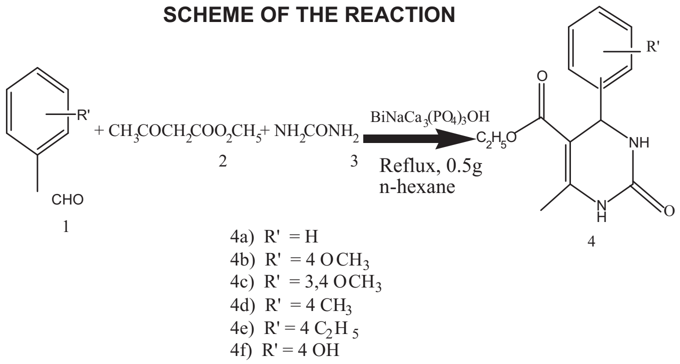

Fig. 1. Scheme of the Biginelli reaction.

2.3.2. Characterization

The inorganic product was characterized by powder X-ray diffraction (XRD) (D8 Advance, Bruker) with CuK_a radiation in the 2θ range 10–70° at room temperature. The lattice parameters were calculated by least square method (LSQ). Fourier Transform Infrared Spectra (FT-IR) was recorded in the range 4000–400 cm^{-1} using Thermonicolet Avator 330 USA model. Scanning electron micrograph (SEM) was obtained with scanning electron microscope Hitachi 3000H. Thermal behavior of the compound was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using SDT Q600 instrument in nitrogen atmosphere at a heating rate of 20 °C/min. The organic products obtained were analyzed by proton nuclear magnetic resonance (^1H NMR, Bruker – 500 MHz) and FT-IR spectroscopy. The melting points of the organic compounds were measured in open capillaries on a Sunbim Melting Point apparatus.

3. Results and discussion

3.1. Synthesis and characterization of $BiNaCa_3(PO_4)_3OH$

Powder X-ray diffraction analysis of the compound synthesized indicates single phase and good crystallinity. The X-ray diffraction pattern is shown in Fig. 2. The pattern is indexed based on Hydroxyapatite, $Ca_5(PO_4)_3OH$ (JCPDS file # 860740). The compound crystallizes in hexagonal crystal system. The lattice parameters of the compound are determined by least square fitting of high angle lines. The unit cell parameters are: $a = 9.412(2)$ Å, $C = 6.92(2)$ Å and the unit cell volume is 530.9 $Å^3$. Compared to the parent calcium hydroxyapatite ($a = 9.42$ Å, $C = 6.88$ Å), substitution of 'Na' and 'Bi' in calcium site results in slight increase in the 'c' lattice parameter and a negligible decrease in 'a' lattice parameter.

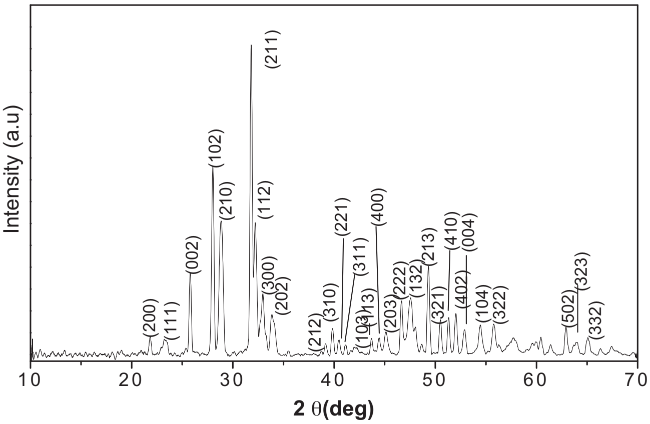

Fig. 2. Powder X-ray diffraction pattern of $BiNaCa_3(PO_4)_3OH$.

The infrared spectrum shown in Fig. 3 displays the characteristic vibrational modes corresponding to hydroxyapatite. The P–O bands in the range 948–1038 cm^{-1} indicates P–O symmetric (ν_s) and asymmetric stretching (ν_{as}) vibrations. The bands in the range 563–600 cm^{-1} indicate the P–O bending vibrations. The –OH stretching vibration is observed at 3559 cm^{-1} [24,25].

The scanning electron micrograph of the powder sample of $BiNaCa_3(PO_4)_3OH$ is shown in Fig. 4. The examination of the SEM picture indicates the formation of homogeneous product with a formation of diffused crystallites. It is noticed that the range of smaller to bigger crystallite size is obtained. The bigger size could be due to agglomeration of smaller crystallites during the process of sintering. Thermogravimetric analysis was carried out at a heating rate of 20°/min in nitrogen atmosphere in the temperature range RT-900 °C. The thermogram and differential thermogram are shown in Fig. 5. Negligible weight loss is noticed. Thus the compound is found to be thermally stable without undergoing decomposition.

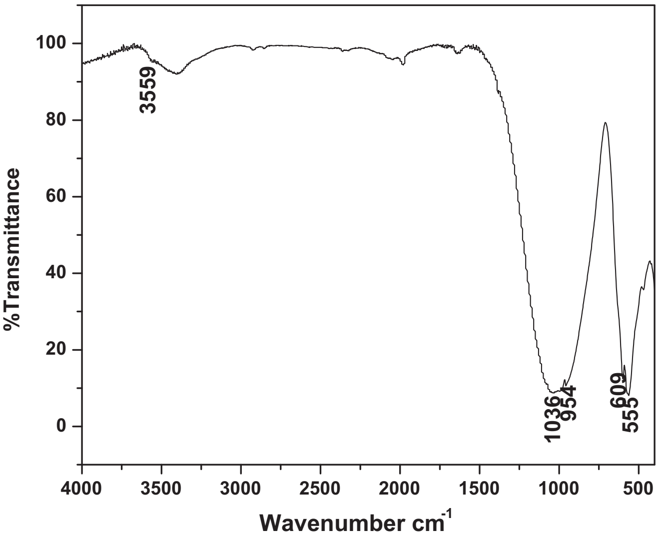

Fig. 3. FT-IR spectrum of $BiNaCa_3(PO_4)_3OH$.

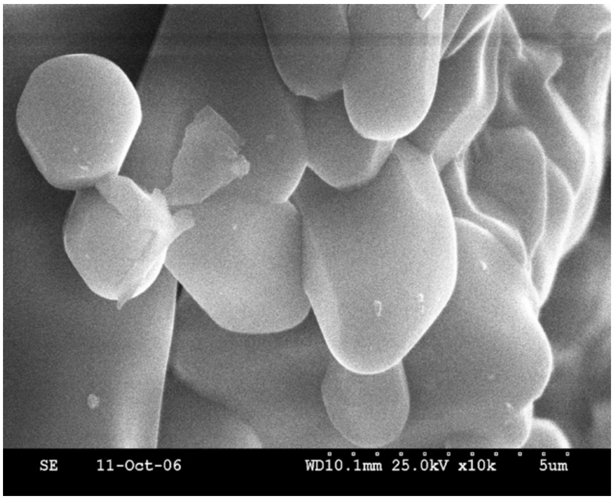

Fig. 4. SEM micrograph of $BiNaCa_3(PO_4)_3OH$.

3.2. Catalytic activity

The results obtained under different experimental conditions followed for the model reaction carried out using benzaldehyde, ethylacetoacetate and urea are summarized in Tables 1–3. It is noticed that at room temperature, maximum yield of the product is obtained with 2.0 g of the catalyst. Further reduction of the catalyst amount leads to reduced yield of the product and longer reaction time. Under reflux condition, no direct relation between the amount of the catalyst and the yield is derived. Maximum yield of the product is obtained by using relatively lesser amount of the catalyst (0.5 g). No change in the reaction time required for the completion of the reaction is noticed with respect to the catalyst amount.

The experiments carried out in the presence of various solvents such as acetonitrile, acetic acid, n-hexane, toluene, ethanol and chloroform demonstrate the influence of the solvent on the course of the reaction both at room temperature and reflux conditions. The amount of the catalyst is kept as 2.0 g for room temperature reaction and 0.5 g for reflux condition. At

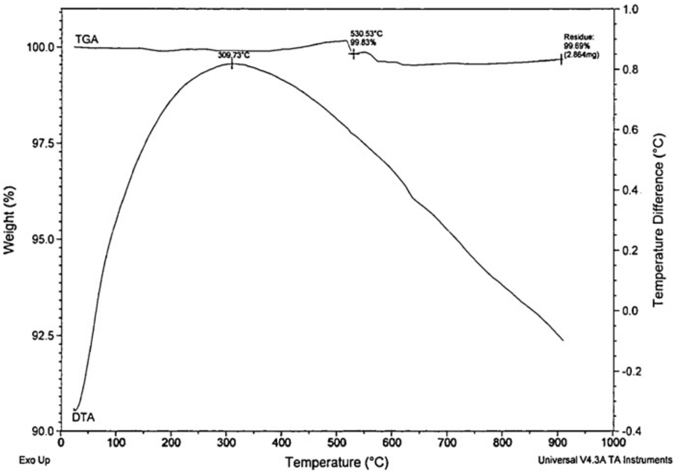

Fig. 5. TGA/DTA curve of $BiNaCa_3(PO_4)_3OH$.

Table 2
Optimization of the solvent at room temperature.

Solvent	Catalyst (g)	Time (h)	Yield (%)
Acetic acid	2	3	76
Acetonitrile	2	4	27
Ethanol	2	3	32
n-Hexane	2	3	20
Chloroform	2	3	0.1
Toluene	2	4	0.2
None	2	0.75	81

Table 4
BiNaCa$_3$(PO$_4$)$_3$OH catalyzed synthesis of different dihydropyrimidinones under reflux condition using n-hexane as solvent.

Products	R^1	Time (h)	Yield (%)	M.Pt (°C)
4a	H	3.5	76	200–202
4b	4-OCH$_3$	6	90	200–201
4c	3,4-OCH$_3$	7	53	178–180
4d	4-CH$_3$	3.5	44	217–219
4e	4-C$_2$H$_5$	12	14	174–176
4f	4-OH	13	80	236–238

room temperature, it is noted that the presence of acetic acid resulted in substantial yield (Table 2). Whereas, under reflux condition the presence of n-hexane and acetic acid show a considerable increase in the yield compared to that obtained in the absence of solvents (Table 3). The reusability of the catalyst has been examined using the phosphate recovered by filtration and washing. The yields of the products after second and third runs are given in Table 3.

The scope of the utilization of the catalyst is tested using substituted aromatic aldehydes possessing electron-donating and electron-withdrawing substituents such as methyl, ethyl, hydroxy and methoxy groups. The reactions have been performed under reflux condition mainly due to the lesser consumption (0.5 g) of the catalyst. Though relatively higher yield is obtained in the presence of acetic acid the catalyst recovery is found to be less in comparison with n-hexane as a solvent. Hence, n-hexane is chosen as the solvent for the reactions involving the derivatives. The substituted aromatic aldehydes resulted in the moderate-to-good yields of the desired products in the presence of the current catalyst. The results are summarized in Table 4. The ^{1}H NMR and FT-IR data of the derivatives are given in Table 5. From the results it is noted that under the current experimental condition, the nature of the substituent in the aromatic moiety affects the yield of the respective products. Presence of electron releasing groups leads to lower yield of the respective products.

Survey of the application of apatite compounds as catalysts for Biginelli reaction reveals that pure calcium hydroxyapatite, Ca$_5$(PO$_4$)$_3$OH is less active for the condensation [9]. Similarly, pure fluorapatite, Ca$_5$(PO$_4$)$_3$F shows negligible catalytic activity [10]. However, surface modified hydroxyapatites using metal halides exhibit promising catalytic activity. Metal chlorides such as ZnCl$_2$, CuCl$_2$, NiCl$_2$ and CoCl$_2$ doped hydroxyapatite are tested by El Badaoui et al. [9]. In the case of fluorapatite, doping with metal halides considerably enhanced the catalytic activity [10]. Such an enhanced catalytic effect is noticed in the present substituted apatite system BiNaCa$_3$(PO$_4$)$_3$OH. The advantages of the current apatite phase are: higher yield (~81%) of the product 3,4-dihydropyrimidin-2(1H)-one at room temperature, shorter reaction time (45 min) and solventless condition. It is noted that the cation or anion substitution or variation in the stoichiometry presents significant differences in surface and bulk properties of hydroxyapatite [26,27]. The composition BiNaCa$_3$(PO$_4$)$_3$OH is derived by replacing two divalent calcium ions by a trivalent bismuth ion and a monovalent sodium ion. Doping of lewis acidic metal chlorides in hydroxyl and fluoro apatites enhanced their catalytic activities with respect to the Biginelli condensation [9,10]. Hence, it is presumed that the random

Table 3
Optimization of the solvent under reflux condition.

Solvent	Catalyst (g)	Time (h)	Yield (%)
Acetic acid	0.5	3.5	80
Acetonitrile	0.5	1.5	25
Ethanol	0.5	9.5	49
n-Hexane	0.5	3	76, 66^a, 60^b
Chloroform	0.5	6	35
Toluene	0.5	4	32
None	0.5	0.5	70

Note:
(i) a, b – yield after 2nd and 3rd runs.
(ii) reduction in the yields could be due to the reduced amounts of the catalyst used in the 2nd and 3rd runs as 0.485 g and 0.401 g that were recovered after the prior run.

Table 5
Spectral data for the derivatives (^{1}H NMR and FT-IR).

4a	^{1}H NMR: 9.163 (S, 1H, NH), 7.711 (S, 1H, NH), 7.233 (m, 5H, Ar–H), 5.126 (S, 1H, CH), 3.961 (q, 2H, CH2), 2.234 (S, 3H, CH3), 1.063 (t, 3H, CH3) IR (KBr): 3245, 3114, 1725, 1700, 1648
4b	^{1}H NMR: 9.159 (S, 1H, NH), 7.676 (S, 1H, NH), 7.154–6.87 (m, 4H, C6H4), 5.095 and 5.089 (d, 1H, CH), 3.986 (q, 2H, OCH2CH3), 3.71 (S, 3H, OCH3), 2.24 (S, 3H, CH3), 1.089 (t, 3H, CH3) IR (KBr): 3246, 3112,1724, 1706, 1651
4c	^{1}H NMR: 9.17 (S, 1H, NH), 7.69 (S, 1H, NH), 6.9–6.7 (m, 3H), 5.11 (d, 1H, CH), 4.12 (q, 2H, OCH2CH3), 3.73 (S, 6H, OCH3), 2.28 (S, 3H, CH3), 1.15 (t, 3H, CH3) IR (KBr): 3248, 3111, 1722, 1708, 1654
4d	^{1}H NMR: 9.15 (S, 1H, NH), 7.689 (S, 1H, NH), 7.117 (S, 4H), 5.104 (d, 1H, CH), 4.00 (q, 2H, OCH2CH3), 2.261 (S, 3H, CH3), 2.236 (S, 3H, CH3), 1.104 (t, 3H, CH3) IR (KBr): 3243, 3113, 1704, 1649
4e	^{1}H NMR: 9.175 (S, 1H, NH), 7.709 (S, 1H, NH), 7.148 (S, 4H), 5.110 (d, 1H, CH), 4.00 (q, 2H, OCH2CH3), 2.551 (q, 2H, CH2), 2.241 (S, 3H, CH3), 1.133 (t, 6H, CH3) IR (KBr): 3245, 3118, 1704, 1650
4f	^{1}H NMR: 9.33 (S, 1H, OH), 9.118 (S, 1H, NH), 7.627 (S, 1H, NH), 7.035–6.68 (m, 4H), 5.044 (d, 1H, CH), 3.982 (q, 2H, OCH2CH3), 2.232 (S, 3H, CH3), 1.112 (t, 6H, CH3) IR (KBr): 3508, 3285, 3119, 1688, 1645

substitution of bismuth and sodium ions for two calcium ions in the hexagonal lattice of HAP leads to increased catalytically active sites. Bismuth compounds such as bismuth chloride, and bismuth nitrate have been reported as catalysts for the preparation of dihydropyrimidones [28,29]. Microwave synthesis in the presence of bismuth nitrate leads to good results. It is noted that the same catalyst does not work well at high temperature as well as at room temperature under normal experimental conditions. Bismuth (III) chloride catalyzed reaction under reflux condition results in good yield with longer reaction duration. In the current system, the substitution of both bismuth and sodium modifies the host apatite lattice in such as way that the surface becomes active and accelerates the reaction at room temperature with out the presence of solvent. Thus, the system demonstrates as one of the economical and environment friendly catalyst. The promotion of the catalytic activity of $Ca_5(PO_4)_3OH$ upon substituting Na^+ and Bi^{2+} for two Ca^{2+} could be viewed from possible change in the acidic character of the lattice. Considering the similar size of the three ions Na^+, Ca^{2+} and Bi^{3+} [30], replacement of Ca^{2+} by Bi^{3+} introduces a highly charged ion into the lattice thus enhancing the acidic character [31].

4. Conclusions

The present work reports the synthesis of an analogue of calcium hydroxyapatite of the formula $BiNaCa_3(PO_4)_3OH$ and demonstrates its catalytic activity for the one-pot synthesis of dihydropyrimidin-2-ones. The phosphate exhibits promising catalytic activity at room temperature under solvent free condition for the preparation of 3,4-dihydropyrimidin-2(1H)-one. Compared to pure hydroxyapatite, the substituted phase displays enhanced activity in shorter reaction duration.

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