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Synthesis of calcium phosphate bioceramics by citrate gel pyrolysis method

H.K. Varma*, S. Suresh Babu

Bioceramic Laboratory, Biomedical Technology Wing, Sree Chitra Tirunal Institute for Medical Sciences and Technology, Poojappura, Thiruvananthapuram 695012, India

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Abstract

Hydroxyapatite granules have been prepared by the pyrolysis of an amorphous polymeric precursor compound containing calcium–phosphate–nitrate–citrate species. The precursor phase on heating at around 550–650 °C turned into crystalline phase. The thermogravimetrical analysis (TGA/DTA) study revealed that the decomposition and crystallization is completed below 650 °C. Fourier transform infrared spectroscopy (FTIR) studies conducted on the precursor phase heated at various temperatures showed that the carbonate substitution occurred in the phosphate moieties at lower temperatures of heating. The X-ray diffractometry (XRD) revealed that the hydroxyapatite formation is highly uniform with respect to apatite phase. The scanning electron microscopy (SEM) showed that the product is highly porous.

Keywords: Citrate precursor; Hydroxyapatite; Synthesis; Bioceramic

1. Introduction

Synthetic calcium hydoxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) HAP is a well-known bioceramic material used in medical field as bone substitute material. This is mainly due to its excellent biocompatibility and bone bonding ability and due to its structural and compositional similarity to that of the mineral phase of hard tissue in human beings [1–3]. It is used in the form of porous granules, sintered and porous blocks, powders for different surgical applications. A number of papers have been published on the preparation and processing of apatite bioceramics during the last decade. These are mainly produced by the precipitation method by adding phosphate solution into a calcium salt solution, under specific pH and temperature. Generally, the precipitation method is a time consuming route as the precipitates are usually kept in the mother liquor overnight in order to attain the desired Ca/P ratio to the final HAP precipitate [4]. Citrate based polymer precursor route is a well-known processing technique for the rapid preparation of a variety of oxidic ceramics [5,6]. Here, an amorphous citrate precursor containing cations and anions are heated to get compounds having peculiar morphological and sintering characteristics. A polymeric precursor route has been reported earlier for the preparation of calcium phosphate ceramics derived from calcium nitrate and ethyl phosphate [7]. Now we report on a preparation method for calcium hydroxyapatite by citrate combustion synthesis and the low temperature decomposed precursor shows carbonate substitution at the phosphate sites. The product derived by this technique consists of large number of pores originated as a result of the evolution of gases produced during the decomposition of the amorphous precursor material.

2. Experimental

10.5 g of citric acid (AR, Emerck) was dissolved in 20 ml of distilled water in a 500 ml beaker. To the above solution, 5.92 g of calcium nitrate tetra hydrate (LR, Ranbaxy) and 1.73 g of ammonium dihydrogen orthophosphate was added and stirred till all the components were completely dissolved. The solution was then heated over a hot plate till the contents turned into a homogenous paste which on continued heating turned in to a charred black mass. The material was then heated at temperatures of 450, 550, 650, 900, and 1150 °C for 1 h in a muffle furnace.

* Corresponding author. Tel.: +91-471-340801; fax: +91-471-341814.
E-mail address: varma@sctimst.ac.in (H.K. Varma).

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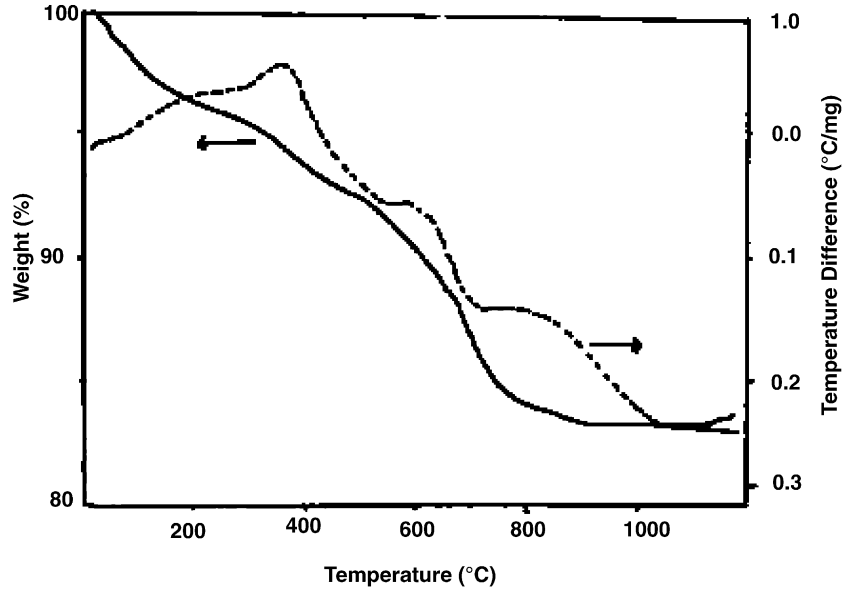

Fig. 1. TGA/DTA scan of citrate precursor heated upto 1200 °C.

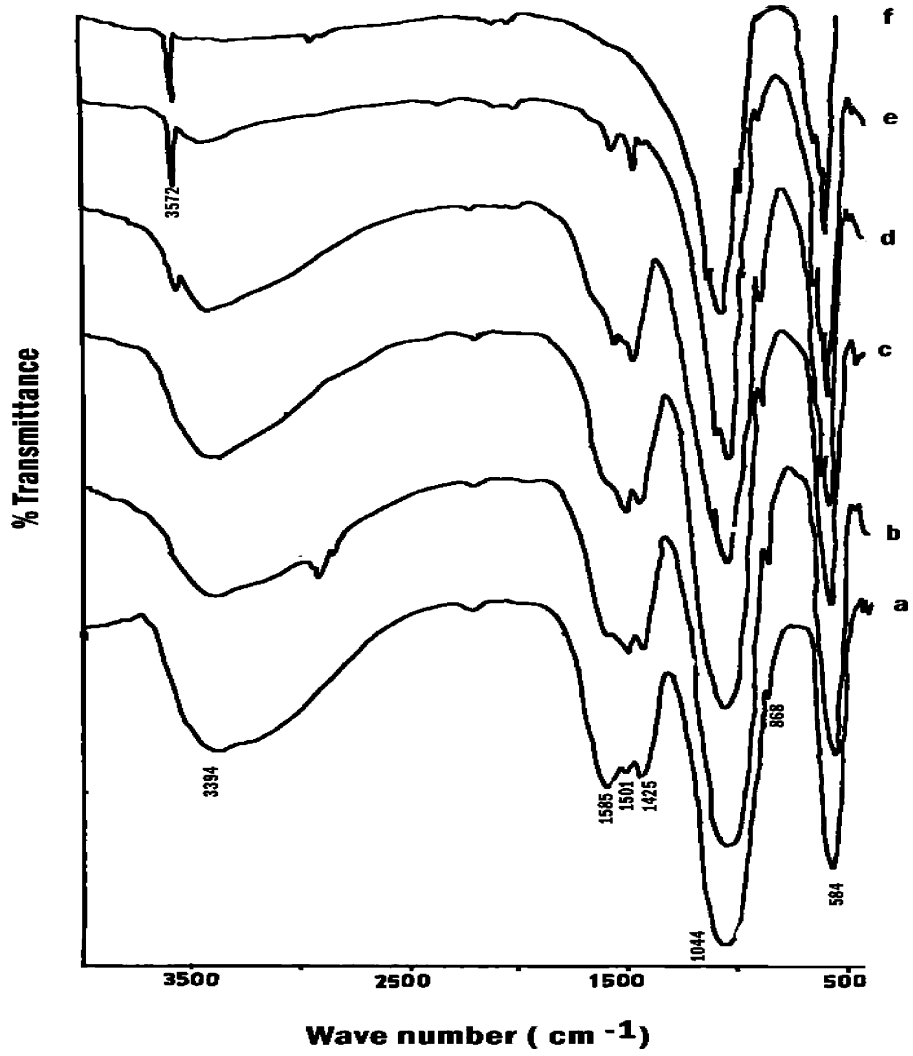

Fig. 2. FTIR spectra of: (a) citrate precursor, and the same heated at: (b) 450 °C, (c) 550 °C, (d) 650 °C, (e) 900 °C, and (f) 1150 °C, respectively.

The thermogravimetric analysis of the charred gel was performed in Universal V1.12E TGA/DTA machine of TA Instruments, USA. The Fourier transform infrared spectroscopy (FTIR) spectra was recorded using Nicole and the X-ray diffractometry (XRD) spectra were recorded in Siemens D 5005 X-ray diffractometer using Cu Kα radiation. The Surface morphology of the precursor as well as the heat treated sample were observed in a Hitachi S2400 scanning electron microscope.

3. Results

The citrate–calcium–phosphate solution on heating turned into a uniform gel which later charred into a black powdery precursor mass with evolution of large amount of gases on continued heating. The yellow fumes appearing during the charring stage indicated the decomposition of nitrate from the gel. Most of the nitrate species from the calcium nitrate turned into oxides along with citrate ions leaving a non hygroscopic, amorphous precursor material. When the charring was not allowed to complete, the resultant product was a hygroscopic one due to incomplete decomposition of nitrate species.

Fig. 1 shows the thermogravimetrical analysis (TGA/DTA) chart of the citrate precursor heated up to 1200 °C. As seen in the TGA, the total weight loss is about 15%. The decomposition was completed at around 700 °C and above that temperature, there was no weight loss. The DTA shows oxidation exotherm of the citrate–calcium–phosphate amorphous gel followed by broad endotherm in the range 400–600 °C during which crystallization of a hydroxyapatite phase has taken place.

Fig. 2 shows the FTIR spectra of the precursor and the same heated at various temperatures up to 1150 °C. The spectra show the characteristic peaks of absorbed water, hydroxyl, phosphate, and carbonate species. The broad peaks at around 300–3800 cm^{-1} are due to absorbed water. The strong stretching mode, υ's, peak at 3572 cm^{-1} is attributed to hydroxyl group [8] which is present in samples heated at 900 and 1150 °C as prominent peak. The major absorption peaks in all the figures are of phosphate at around 1050 and 565 cm^{-1}. The $\upsilon 4$ phosphate absorption around 660–520 is present as a broad peak in sample heated up to 650 °C and on further heating the peaks got resolved to three at 570, 601, and 632 cm^{-1}. The $\upsilon 3$ phosphate absorption band, the most prominent peak of the phosphate in apatite appears as a broad band for samples heated up to 650 °C. Here also it has been split in to peaks at 960, 1049, and 1091 cm^{-1}. In addition to the above peaks, the $\upsilon 3$ carbonate absorption peaks appeared around 1400–1600 cm^{-1} in all samples except the one heated at 1150 °C [9]. The $\upsilon 2$

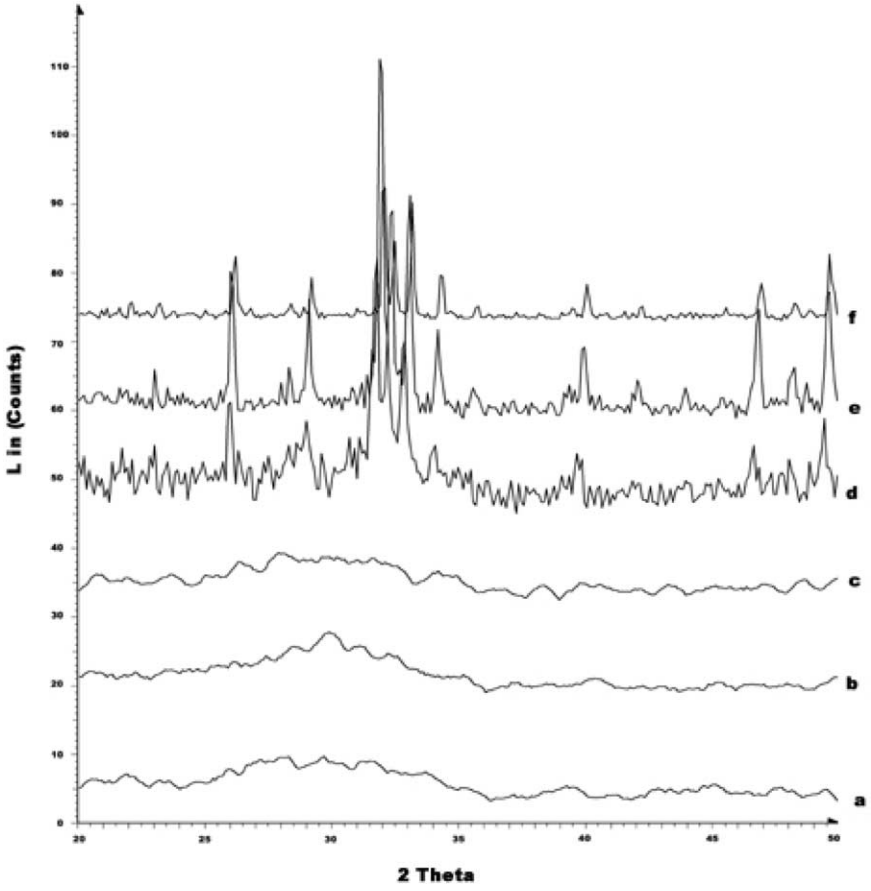

Fig. 3. XRD patterns of: (a) citrate precursor, and the same heated at: (b) 450 °C, (c) 550 °C, (d) 650 °C, (e) 900 °C, and (f) 1150 °C, respectively.

vibrational mode absorption of carbonate at 870 cm^{-1} is also present.

Fig. 3 shows the XRD patterns of precursor and the heat treated samples. The precursor as well as the sample heated up to 550 °C are amorphous while the samples heated above 650 °C are of calcium hydroxyl apatite. The amorphous to crystalline transformation occurs in between 550 and 650 °C. The sample heated above 650 °C show characteristic hydroxyapatite peaks (JCPDF 9-432) without any secondary phases. No calcium carbonate peak is present.

The morphological features of the precursor as well as the heated samples are given in the scanning electron microscopy (SEM) pictures of Fig. 4a–e. The precursor as well as the heat treated samples were in the form of porous granules. Fig. 4a shows the surface morphology of the precursor compounds. The surface of the gel is highly uniform and

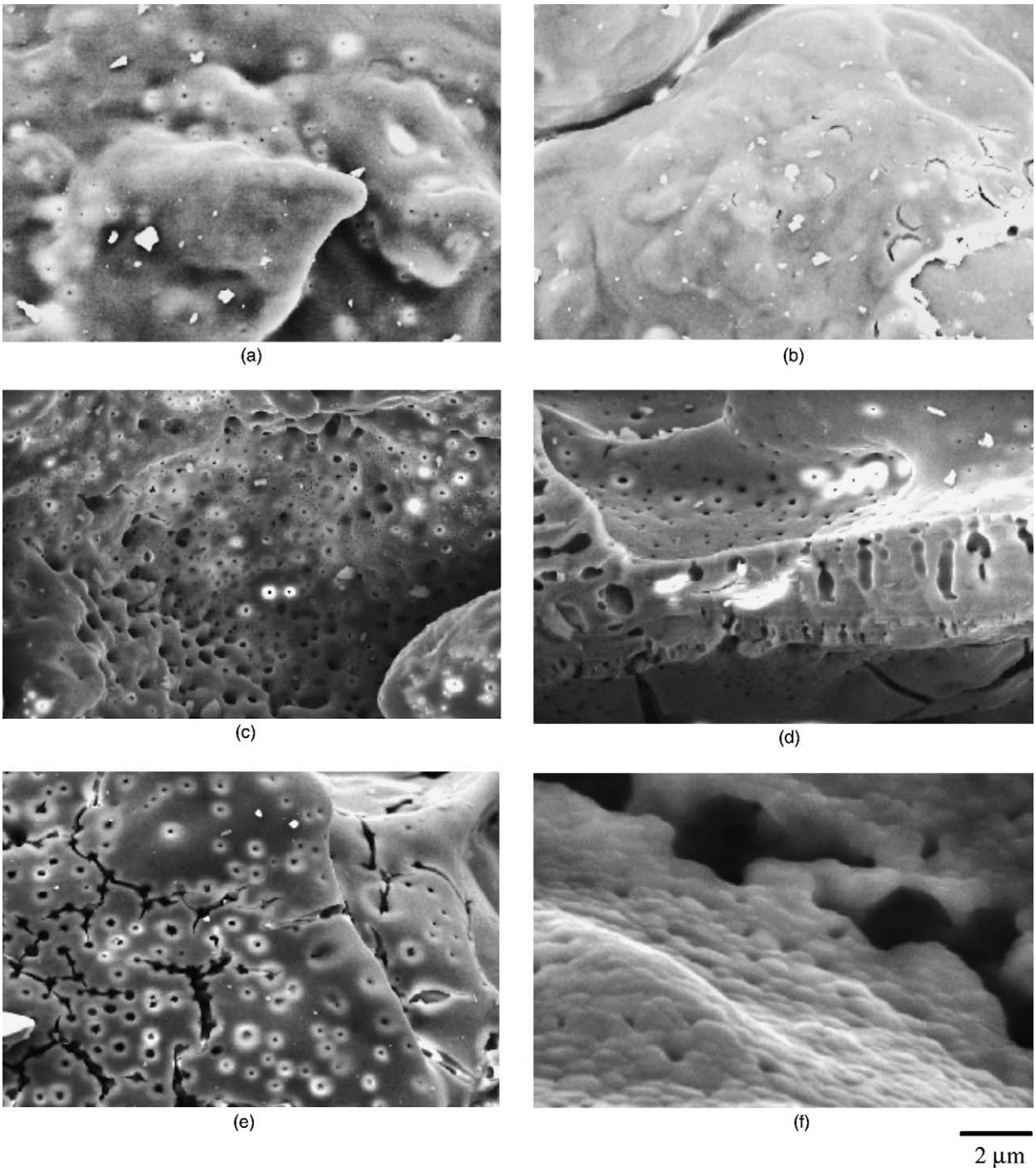

Fig. 4. Surface morphology of granules of: (a) citrate precursor, and the same heated at: (b) 450 °C, (c) 550 °C, (d) 650 °C, (e) 900 °C, and (f) 1150 °C, respectively.

polymeric. In order to observe the morphological changes as a function of heat treatment, the granules heated at different temperature were also observed under SEM. Fig. 4b–e shows the surface texture of the samples heated at 450–1150 °C. When the heat treatment temperature reaches 550 °C, more porosity is generated due to the decomposition and crystallization of matrix even though most of the porosities are generated during the initial decomposition of the citrate precursor gel. Fig. 4e shows the morphology of the sample heated at 1150 °C. Sintered grains of 2 μm size are visible.

4. Discussion

The preparation of hydroxyl apatite bioceramics through different chemical methods other than precipitation route has been published with a view to reduce the preparation time. The precipitated calcium phosphates are kept in the mother liquor overnight to increase the Ca/P ratio to close to 1.67. The present work is a simple precursor combustion method to generate hydroxyapatite in short time. The thermogravimetric analysis shows that the decomposition of the nitrates and citrates was over during the charring stage of the citrate gel. The charred gel is an amorphous calcium phosphate which undergoes crystallization around 550–650 °C.

Carbonate substitution of calcium hydroxyapatite has been extensively studied and FTIR has been used to distinguish between substituted and pure hydroxyapatite by comparing the carbonate and phosphate bands [3]. In the carbonated derivative, $\upsilon 3$ band of phosphate at around 1050 cm^{-1} appear as a single intense band whereas in hydroxyapatite it appears as three distinct bands at 1100, 1085, and 1050 cm^{-1}. In the present set of spectra given in Fig. 2, the samples heated above 900 °C show splitting of band and at 1150 °C, the bands around the above regions appear similar to that of pure hydroxyapatite. Another distinct phosphate band of $\upsilon 4$ bending mode appears around 660–520 cm^{-1}. Here also the carbonate apatite gives a single band while hydroxyapatite has three bands as the temperature of heating the precursor increased. The splitting appearing in the case of 1150 °C heated sample again shows the decomposition of carbonate at high temperature and also shows that the carbonate is substituting at the phosphate sites rather than the hydroxyl sites.

The carbonate ions can substitute at the hydroxyl or phosphate sites in the hydroxyapatite crystal lattice. The 1650–1300 cm^{-1} bands are due to $\upsilon 3$ vibration mode and 878 cm^{-1} band is due to the $\upsilon 2$ vibrational mode of carbonate ion. In all the samples, except that of 1150 °C compound, the above bands are quite strong indicating the carbonate hydroxyl apatite formation. There is no considerable variation in the intensity of hydroxyl peaks at 3572 cm^{-1} in the case of samples heated at 900 and 1150 °C but the intensity of carbonate peaks are considerably reduced accompanied by degenerate splitting of phosphate bands in the range 1050 and 600 cm^{-1} due to decomposition of carbonate species at elevated temperatures. Hence it is believed that the carbonate is substituted predominantly at phosphate sites rather than hydroxyl sites [3] in the present hydroxyl apatite compound.

The XRD patterns clearly shows the amorphous to crystalline hydroxyaptite transformation at the temperature around 550–650 °C without the formation of major secondary phases. The combustion synthesis through polymer precursor pyrolysis is generally used for the preparation of oxides. The scanning electron microstructure of the heated gels showed the porous nature of the apatite and the submicron grain structure due to the fact that only in the 1150 °C compound, the microstructure show the 2 μm grains while in all the other sample, grain structure could not be resolved due to the smaller crystallite size.

5. Conclusions

An amorphous polymeric precursor compound containing calcium–phosphate–nitrate–citrate species has been synthesized. The precursor phase on heating at around 650 °C converted to calcium apatite. The product is highly porous in nature and further work is in progress to estimate the nature of porosity and to develop porous granules for infra bony defect filling application. The low temperature sintered granules show the carbonate substitution, which is expected to increase the bioactivity. Further work is needed to understand the status of carbonate species in the hydroxyapatite lattice.

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References

[1] L.L. Hench, J. Wilson, Introduction to Bioceramics, Advanced Series in Ceramics, World Scientific, Singapore, 1993.
[2] C.P.A.T. Klein, A.A. Driessen, K. De Groot, van der Hooff, Biodegradation behaviour of various calcium phosphate materials in bone tissue, J. Biomed. Mater. Res. 17 (1983) 769–784.
[3] I.R. Gibson, W. Bonfield, Novel synthesis and characterization of an AB type carbonate substituted hydroxyapatite, J. Biomed. Mater. Res. 25 (2001) 687–708.
[4] K. De Groot, Ceramics of calcium phosphates: preparation and properties, in: K. De Groot (Ed.), Bioceramics of Calcium Phosphates, CRC Press, Boca Raton, FL, 1983, pp. 100–114.
[5] H.K. Varma, K.P. Kumar, K.G.K. Warrier, A.D. Damodaran, Thermal decomposition of citrate precursor for 1-2-3 high Tc superconductor, J. Mater. Sci. Lett. 8 (1990) 1313–1316.

[6] N. Balagopal, H.K. Varma, K.G.K. Warrier, A.D. Damodaran, Citrate precursor derived alumina–ceria powders, Ceram. Int. 18 (1992) 107–111.
[7] H.K. Varma, S.N. Kalkura, R. Sivakumar, Polymeric precursor route for the preparation of calcium phosphate compounds, Ceram. Int. 24 (1998) 467–470.
[8] S. Koutsopoulos, Synthesis and characterization of hydroxyapatite crystals: a review study on the analysis methods, J. Biomed. Mater. Res. 26 (2002) 600–612.
[9] Y. Doi, Sintered carbonate apatite as bone substitutes, Cells Mater. 7 (1997) 111–122.