PREPARATION AND CHARACTERIZATION OF HYDROXYAPATITE- BARIUM TITANATE COMPOSITE.

A THESIS SUBMITTED IN PARTIAL FULLFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF TECHNOLOGY

BY

ALOK KUMAR PANDA

Roll No- 107CR009

Department of Ceramic Engineering

National Institute of Technology

Rourkela

2010-2011

Preparation and characterization Of Hydroxyapatite- Barium Titanate Composite.

A THESIS SUBMITTED IN PARTIAL FULLFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF TECHNOLOGY

BY

ALOK KUMAR PANDA

Roll No.- 107CR009

Under the Guidance of:

Prof. Swadesh Kumar Pratihar

Department of Ceramic Engineering

National Institute of Technology

Rourkela

2010-2011

CERTIFICATE

This is to certify that the project entitled, **“Preparation and Characterization of Hydroxyapatite-Barium Titanate composite”** submitted by **Alok Kumar Panda** is an authentic work carried out by him under my supervision and guidance for the partial fulfillment of the requirements for the award of **Bachelor of Technology Degree** in **Ceramic Engineering** at **National Institute of Technology, Rourkela.**

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

Date- 16/05/2011 **(Prof. Swadesh Kumar Pratihar)**

Rourkela **Dept. of Ceramic Engineering**
NIT Rourkela

ACKNOWLEDGEMENT

I would like to express my heartfelt thanks and gratitude to Professor Swadesh k. Pratihar Department of Ceramic Engineering, NIT Rourkela, my guide and my mentor , who was with me during every stage of the work; and whose guidance and valuable suggestions has made this work possible.

Further, I would also like to thank all the faculty members and staff of Department of Ceramic Engineering, NIT Rourkela for their invaluable support and help during the entire project work.

I would further like to thank all the research scholars, especially Mr. Bhabani Shankar sahu, Mr. Abhisek Choudhury, Mr. Ganesh kumar sahoo and last but not the least Miss Geetanjali parida, for their round the clock help and support during the entire project work.

I would also like to thank Mr. S Paria, Department of Chemical Engineering, NIT Rourkela and Professor Pawan kumar, Department of Physics, NIT Rourkela, for providing the support in doing particle size analysis and silver coating of the pellets respectively.

Last but not the least I want to thank almighty lord for the successful completion of the project work.

Alok kumar panda

Roll No- 107CR009

ABSTRACT

The present work deals with the synthesis and characterization of hydroxyapatite- barium titanate composite. The composites have been prepared varying the barium titanate amount in the range of 10- 40 weight% in the hydroxyapatite matrix. The barium titanate powders used in this study has been prepared following solid state synthesis technique, followed by the grinding in a pot mill. The synthesized barium titanate powders have been characterized using X-ray diffraction, particle size analysis and isoelectric point measurements. A stabilized barium titanate suspension has been prepared using Darvan-C polyelectrolyte at basic pH.

Calcium nitrate tetrahydrate ($Ca(NO_3)_2 . 4H_2O$) and di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) have been used as precursors for calcium ($Ca^{2+)}$ and phosphate ($((PO_4)^{3-)}$ ions respectively, which were then precipitated over the stabilized barium titanate suspension. The suspension has been allowed to settle, washed with cold water and calcined to obtain the composite powders. The synthesized hydroxyapatite-barium titanate composites have been characterized using X-ray diffraction and dilatometry. The synthesized composite powders have been pelletized and sintered at three different temperatures. The sintered pellets have been characterized using bulk density, shrinkage and X-ray diffraction measurements. The pellets are coated with silver paste and have been characterized for their dielectric behavior using a dielectric interface.

List of Figures:

List of Tables:

CONTENTS Page No.

CHAPTER 1

INTRODUCTION

Hydroxyapatite which is given by the formula ($Ca_{10}(PO_4)_6(OH)_2$) is a well-known bio-material which belongs to the calcium phosphate group [1]. Hydroxyapatite is also an important component of human body parts which are hard such as bone and teeth etc.[2] Hydroxyapatite is a well-studied bioactive material. It can form biological and chemical bonds with the surrounding body tissues after implantation [3]. Further hydroxyapatite is entirely non-toxic and exhibits good biocompatibility with several tissues such as skin, muscle tissues and also hard tissues such as bone [4]. All these properties make hydroxyapatite as one of the most useful biomaterial. The exchange of phosphate (PO_4^{3-}) and calcium (Ca^{2+}) ions to precipitate more apatite on the hydroxyapatite surface is recognized as the mechanism of interaction between bone and hydroxyapatite. This process helps in bonding of the implant with the bone of the host and also promote bone formation [5,6]. Therefore the usefulness of hydroxyapatite as a biomaterial is undoubtable. However there may be certain ways or techniques to further improve the bone integration property of hydroxyapatite, which may lead to improved cell proliferation and growth. This would further improve the integration of the implant with the body and enhance bone healing [7].

The polarization of hydroxyapatite seems to be a good choice in this regard. It has been found that there is much better bone growth and osteobonding due to the generation of charge on the surface of polarised hydroxyapatite [8-11]. The polarization of the hydroxyapatite surface does not occur by the same mechanism of polarization as in ferroelectrics i.e. dipole rotation. Rather it was assumed to develop under an applied electric field by the migration of protons in the hydroxyl (OH-) columns of the hydroxyapatite [12]. Further, it was observed that the negatively charged surface of the polarized hydroxyapatite showed an enhanced growth of apatite crystals

[12]. Polarization of hydroxyapatite has been achieved at high temperatures by using an electric field [13]. Similarly polarization of barium titanate ceramic which is done after poling treatment at high temperature (above the Curie temperature) exhibits an increased growth of calcium phosphate crystals in the negative surface [14].

In this context the synthesis of hydroxyapatite-barium titanate composite assumes an important position. This composite material showed enhanced osteogenesis compared to pure hydroxyapatite [15].

Thus the present work aims to prepare the composite of hydroxyapatite-barium titanate through the coating of barium titanate with hydroxyapatite. Therefore the objective of the study is underlined as follows:

1.1 Objective of the present study:

- To prepare barium titanate powder sample.
- To stabilize the barium titanate powder sample using polyelectrolyte.
- To prepare hydroxyapatite-barium titanate composite powder sample by the proposed coating mechanism as shown in Fig 1.1.
- To characterize the hydroxyapatite-barium titanate composite sample.

Proposed mechanism for the hydroxyapatite-barium titanate composite preparation

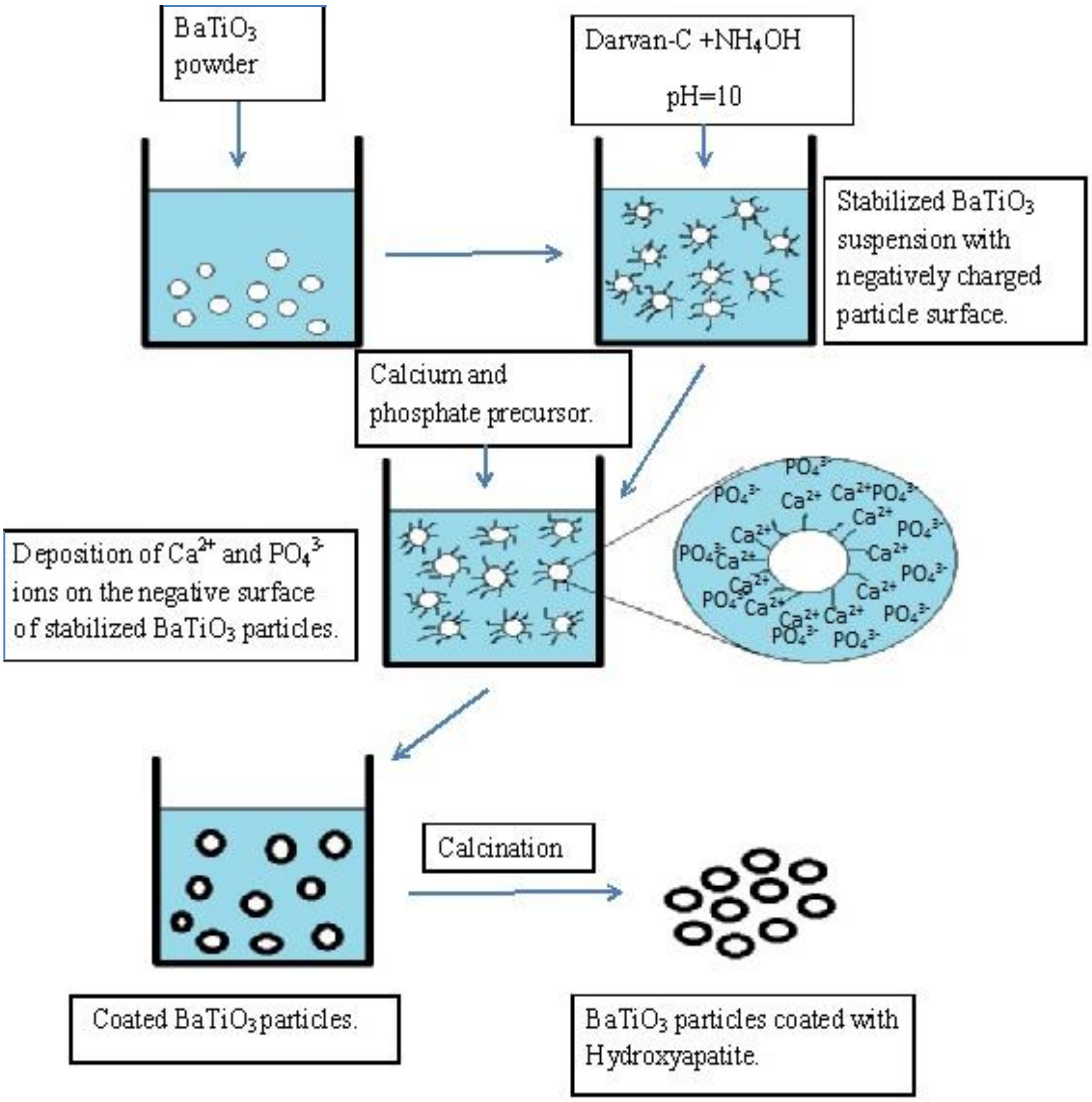


Fig 1.1 The proposed coating mechanism for hydroxyapatite-barium titanate composite preparation.

CHAPTER 2

LITERATURE REVIEW

2.1 Preparation of barium titanate

Xia et. al. [16] have studied the effect of different precursors on the properties of the barium titanate powders produced from hydrothermal method. The various precursors combination used were $Ba(OH)_2.8H_2O$ and TiO_2 in aqueous media ; barium acetate and TiO_2 in aqueous media; and $Ba(OH)_2.8H_2O$ and tetrabutyl titanate in either aqueous or alcohol solution as the reaction media. It has been reported that the amount of barium titanate formation depends on the reaction temperature, alkalinity of the precursor solution and the Ba/Ti ratio. It has also been reported that the yield of $BaTiO_3$ increases with increase in reaction temperature, alkalinity of the precursor solution and the Ba/Ti ratio. Further powders synthesized using tetrabutyl titanate are smaller as compared to the powders synthesized using TiO_2.

Buscaglia et. al. [17] have studied the effect of different particle sizes of the barium carbonate precursor on the calcination temperature and the properties of barium titanate prepared by solid state synthesis method. The barium carbonate precursor had a combination of three different particle sizes (650, 140, and 50 nm), while the TiO_2 used was nanocrystalline having a particle size of 70 nm. It has been reported that the calcination temperature influences the yield of barium titanate powder by solid state synthesis. Barium titanate powder characteristics depend on the size of barium carbonate used for the synthesis. It has also been reported that the calcination temperature for the formation of pure barium titanate increased on using coarse fraction of barium carbonate. Further the powder of barium titanate synthesized using coarse fraction of barium carbonate was large in size as compared to powders synthesized from the fine fraction of $BaCO_3$.

Yane’z et. al. [18] studied the effect of mechanical activation i.e. milling on the barium titanate powder produced from barium carbonate and titanium oxide precursor. The milling was carried out using stoichiometric solid powder precursors. It has been reported that the formation temperature and rate of the formation of the barium titanate depend on the milling process. It has also been reported that milling increases the rate of formation of barium titanate while it reduces the formation temperature.

Chen et. al.[19] have studied the properties of barium titanate powder synthesized through two different routes- conventional batch stirred tank reactor(BSTR) method and high gravity reactive preparation(HGRP). The precursors used in both the cases were $BaCl_2.H_2O$ and $TiCl_4$. It has been reported that the powders synthesized in the conventional technique have a larger average particle size as compared to the powder prepared using HGRP. It has been further reported that the dielectric and sintering properties are similar for both the techniques.

2.2 Preparation of hydroxyapatite:

I. Bogdanoviciene et. al. [20] studied the effect of different complexing agents on the hydroxyapatite synthesized through sol-gel technique. The complexing agents used in the study were ethylene diammine tetra-acetic acid (EDTA) and tartaric acid (TA). The precursors used for the synthesis were ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) and calcium acetate monohydrate. It has been reported that the characteristics of the obtained hydroxyapatite depends upon the type of complexing agent used for the synthesis. It has been further reported that the hydroxyapatite powder obtained from the EDTA route showed agglomerated structure, the powders obtained from TA route gives powders having rod like structure.

I. Mobasherpour et. al [4] have studied the effect of calcination temperature on the hydroxyapatite prepared through the precipitation technique. The precursors used were calcium nitrate tetrahydrate which acts as the source of calcium and di- ammonium hydrogen phosphate as the source of phosphate. It has been reported that the characteristics of the hydroxyapatite powder depends upon the calcination temperature. It has been further reported that the presence of hexagonal hydroxyapatite was confirmed with increase in calcination temperature and further the size of the powder increases with the increase in calcination temperature.

Yang et.al. [21] have studied the thermal stability of the hydroxyapatite prepared through precipitation and microwave irradiation technique. The precursors used in both the synthesis technique were same: calcium nitrate tetrahydrate as a source of calcium, phosphoric acid as the source of phosphate, ammonia solution and glucose. It has been reported that the thermal stability of the hydroxyapatite depends upon the aging time in precipitation technique; and also upon the microwave power and time of irradiation. It has been further reported that the thermal stability of hydroxyapatite powder increased with the increase in aging time, as well as an increase in microwave power and irradiation time.

Saeri et. al. [22] have studied the effect of aging time and heating of the precipitate on the hydroxyapatite prepared through wet precipitation process. The precursors used in the preparation of hydroxyapatite were calcium hydroxide as the source of calcium and phosphoric acid as the source of phosphate. It has been reported that the characteristics of the prepared hydroxyapatite depends upon the aging time and the post-heating temperature of the precipitate. It has been further reported that there is growth of hydroxyapatite particles with increase in aging time and the crystallinity of the powder increases with increase in temperature upto 1200°C.

Tas [23] has studied the synthesis of hydroxyapatite powder through the biomimetic synthesis technique. The precursors used were calcium nitrate tetrahydrate as the source of calcium and diammonium hydrogen phosphate as the source of phosphate. The synthesis is done in the presence of synthetic body fluid (SBF) at 37°C and pH 7.4. It has been reported that the hydroxyapatite prepared through this technique showed excellent thermal stability, without decomposition even at 1600°C.

2.3 Stabilization of barium titanate:

M.C. Blanco Lopez et al. [24] has studied the effect of pH on the stabilization of barium titanate dispersed in an aqueous media using both an anionic and cationic polyelectrolyte. Quaternary alkyl ammonium polymers of molecular weight 150,000 and 7,600 were used as cationic polyelectrolyte while ammonium salt of polyacrylic acid having a molecular weight of 4000 was used as the anionic polyelectrolyte. It has been reported that the anionic polyelectrolyte was effective in stabilization of the suspension at alkaline pH (>8), while the cationic polyelectrolytes with a high molecular weight tend to bridge the particles; and do not help in stabilizing the suspension.

M.C. Blanco Lopez et al. [25] have studied the effect of polyelectrolyte concentration on the stabilization of barium titanate dispersed in an aqueous media using both an anionic and cationic polyelectrolyte. The polyelectrolytes used were Quaternary alkyl ammonium polymers of molecular weight 150,000 and 7,600 as the cationic polyelectrolyte while ammonium salt of polyacrylic acid having a molecular weight of 4000 as the anionic polyelectrolyte. It has been reported that the cationic polyelectrolytes are not good for stabilization of barium titanate suspension at any pH. It has been further reported that the anionic polyelectrolytes are suitable for stabilization at very low concentration of polyelectrolyte at higher pH (>9), while the concentration of polyelectrolyte required for stabilization increases with decreasing pH (6-8). However flocculation occurred with 0.5% concentration of the anionic polyelectrolyte at pH 4.

2.4 Hydroxyapatite-barium titanate composite:

Gittings et. al. [13] have studied the effect of incorporation of barium titanate in hydroxyapatite and also tried to polarize a pure hydroxyapatite sample. The precursors for hydroxyapatite-barium titanate composite were hydroxyapatite and barium titanate powders. Both the pure sample as well as the composite was poled, although the poling of composite was done at high temperature. It has been reported that 80% of barium titanate was required in the composition for the composite to show piezoelectric behavior. It has been further reported that the pure hydroxyapatite sample can be polarized at high temperature.

Feng et. al.[15] have studied the effect of incorporation of barium titanate in hydroxyapatite on the osteogenesis behavior of hydroxyapatite. The hydroxyapatite-barium titanate composite were prepared by solid mixing and poled. The osteogenesis behavior has been studied by the implantation of the composite as well as pure hydroxyapatite sample in the jawbones of dog. It has been reported that after poling the composite showed piezoelectric behavior (d_{33} = 6pC/N). It has been further reported that the hydroxyapatite-barium titanate sample showed greater osteogenesis as compared to the pure hydroxyapatite sample.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Preparation of barium titanate powder:

Barium titanate required in the study was prepared using the solid state synthesis technique. The raw materials used were barium carbonate (Merck, 99%) and titanium (IV) oxide (Merck, 99%).

The solid state reaction between the ingredients can be summarized by equation 1:

$$BaCO_3 + TiO_2 \longrightarrow BaTiO_3. \quad - (1)$$

A 1:1 stoichiometric amount of barium carbonate and titanium (IV) oxide were taken for the synthesis of barium titanate. The raw materials were mixed thoroughly in an agate mortar. The dry mixing of the mixture was followed by wet mixing with iso-propyl alcohol, in order to obtain an uniform mixture. The process of mixing was repeated several times. This was followed by the calcination of the mixture in a raising hearth furnace, at a temperature of 1000°C for 2 hours. The Batch composition in Table 3.1:

Precursors	Weight (%)
$BaCO_3$	71.19
TiO_2	28.81

Table 3.1: Batch composition for synthesis of barium titanate powder.

3.2 Stabilization of barium titanate powder:

The synthesized barium titanate powders were stabilized using Darvan-C polyelectrolyte. A small amount of powder was dispersed in distilled water, followed by the addition of Darvan-C polyelectrolyte. The suspension was then set for ultrasonication using an ultrasonic vibratometer. The ultrasonication was done for 10 minutes until all the agglomerates are broken down. A 1:1 ammonia solution was added to the suspension after ultrasonication to maintain a pH of 10. The suspension was kept in constant stirring to form a stable suspension.

3.3 Preparation of hydroxyapatite- barium titanate composite powders:

The Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) required in the study was prepared using calcium nitrate tetrahydrate ($Ca(NO_3)_2 . 4H_2O$) and di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) as the precursors. The overall reaction for the formation of hydroxyapatite can be summarized by equation 2 :

$$10\ Ca(NO_3)_2 + 6\ (NH_4)_2HPO_4 + 8\ NH_4OH \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 20\ NH_4NO_3 + 20\ H_2O. \qquad - (2)$$

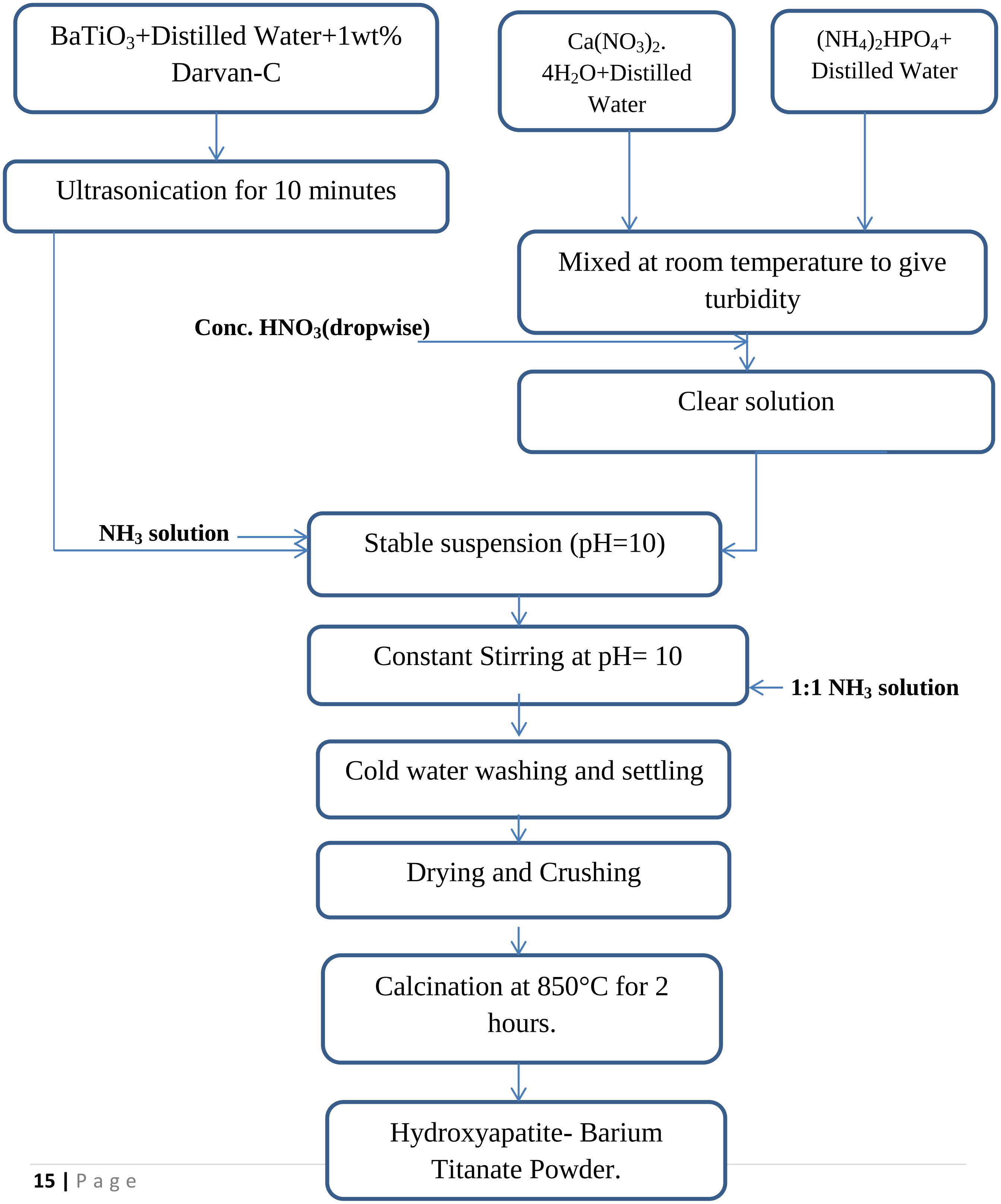
Solutions of 1M strength of calcium nitrate tetrahydrate and di-ammonium hydrogen phosphate were prepared. These were mixed to give turbidity at room temperature, which turns into a clear solution upon dropwise addition of concentrated nitric acid. The clear solution was transferred dropwise to the stabilized barium titanate suspension through a burrete. The pH of the system was maintained at 10 with constant stirring of the suspension. The resulting suspension was allowed to settle for 24 hours, followed by cold water washings to remove ammonia. The washed precipitate was dried at 80°C in an oven and crushed to form a powder. The powder was calcined in a raising hearth furnace at 850°C for 2 hours to give the hydroxyapatite- barium titanate powders. Four different compositions of the composite were prepared containing 10-40 weight

% of barium titanate and a total of 10 g powder was synthesized for each composition. The batch composition of the composites was given in Table 3.2.

COMPOSITION (BT- Barium Titanate HA- Hydroxyapatite)	Weight of Hydroxyapatite(HA) in the composition.(g)	Weight of ($Ca(NO_3)_2 \cdot 4H_2O$) required.(in g)	Weight of ($(NH_4)_2HPO_4$) required. (in g)
10 BT – 90 HA	9	21.156	7.09
20 BT – 80 HA	8	18.805	6.31
30 BT – 70 HA	7	16.454	5.52
40 BT – 60 HA	6	14.103	4.73

Table 3.2: Batch composition of the different compositions of the composite.

Fig 3.Flow chart for the composite powder preparation:



3.4 Pelletization & firing

0.7g of powder was weighed for preparing pellets of each composition. The powders were mixed with few drops of poly-vinyl alcohol (PVA 2%) in an agate mortar. The powders were then pressed in a circular die of diameter 12mm at 3 ton pressure with a dwell time of 120 seconds. The pellets were then fired at 1100°C, 1050°C and 1000°C with a soaking time of 2 hours.

3.5 Characterization

X-ray diffraction (XRD): The XRD of the barium titanate powder, synthesized hydroxyapatite-barium titanate composite powder and the sintered hydroxyapatite-barium titanate pellets were done using Philips X-Ray diffractometer (PW 1730, Holland) with nickel filtered Cu Kα radiation (λ = 1.5406 A°) at 40 kV and 30mA having a scan range(°2 θ) of 15-80° at a scan speed (°2 θ/sec) of 0.04.

Particle size analysis: The particle size distribution of the synthesized barium titanate powder was done in an aqueous media using Malvern particle size analyzer.

Dilatometry: The dilatometry of the hydroxyapatite-barium titanate composite sample (containing 40 wt% of barium titanate) was done using a single push rod dilatometer (NETZSCH) from 30°C to 1200°C in air.

Shrinkage: The shrinkage of the sintered pellets were calculated using the following formula:

Shrinkage (%) = (Initial Volume – Final Volume)* 100 / Initial Volume

Bulk Density: The bulk density measurement of the sintered pellets of the composite was done by calculating the dry, soaked and suspended weight after putting the pellets in vacuum for 1 hour. The bulk density is calculated by Archimedes principles and is given by the following formula:

Bulk Density = ((Dry Weight) / (Soaked Weight – Suspended Weight))*density of the liquid.

Dielectric measurements: the sintered pellets were first coated with a silver paste and cured at 200°C for 30 minutes to provide the electric contacts. The dielectric measurement was done using a 1296 Solartron dielectric interface at room temperature.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 X-Ray Diffraction pattern of barium titanate powder:

The X -Ray Diffraction pattern of the barium titanate powder prepared through solid state route calcined at 1000°C is shown in Fig. 4.1.

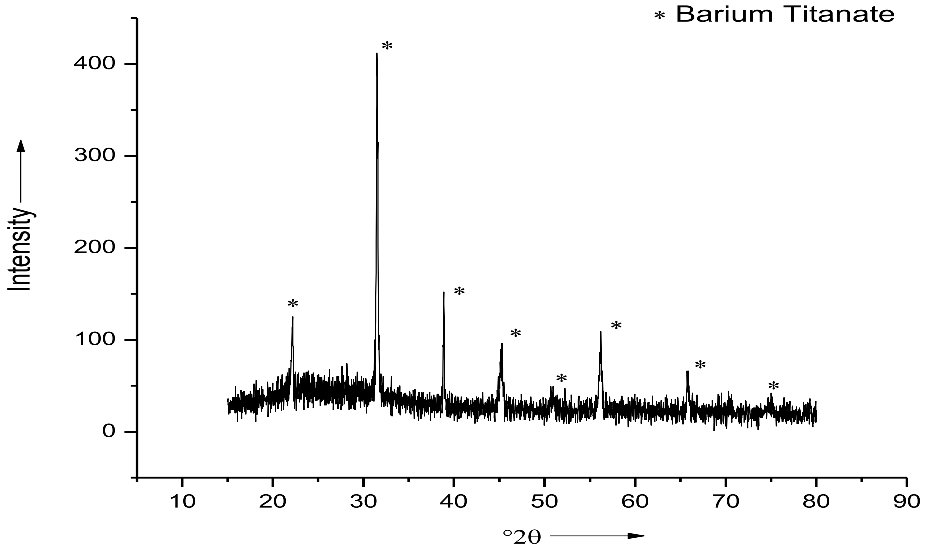


Fig 4. 1. X-Ray Diffraction Pattern for the prepared $BaTiO_3$ using solid state synthesis.

The X-ray diffraction pattern shows that the barium titanate synthesized through solid state synthesis technique. The powder shows all the peaks of barium titanate and is completely pure in phase with no associated impurity. The sample is cubic with lattice parameters a = 4.0060 Å, The sample corresponds to JCPDS card no. 79-2263.

4.2 Particle size analysis:

The particle size distribution of the barium titanate powder sample was shown in Fig 4.2. The particle size distribution of the barium titanate powder after synthesis showed a bimodal behavior with much larger particle dimensions. The average particle size d_{50} was found to be 11.139 µm. Smaller particle size was desired for the suspension to be more stable. Therefore the powder was milled in a pot mill for 8 hours with a zirconia medium.

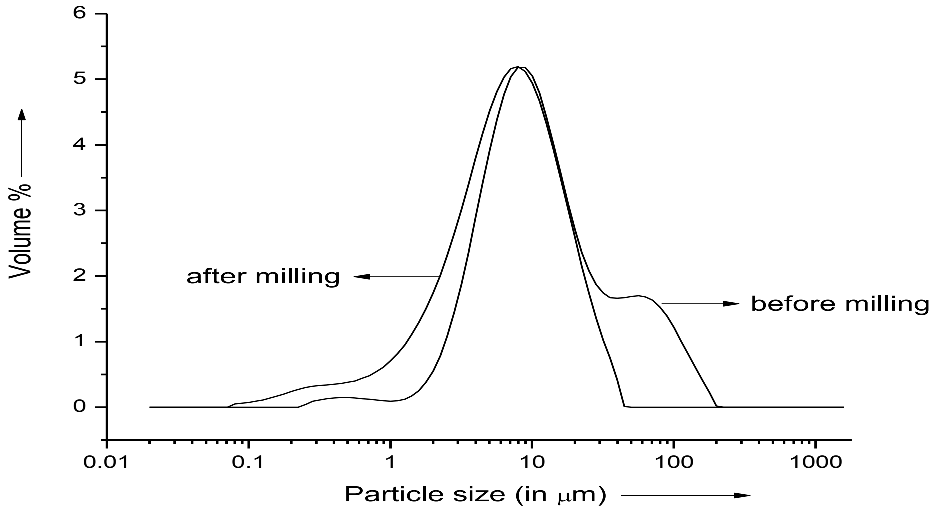


Fig 4.2: Particle Size Distribution of $BaTiO_3$ powder sample.

The powders obtained after milling showed a monomodal distribution of particles with relatively smaller particle dimensions. The average particle size d_{50} was found to be 7.08 µm. There is a shift in the distribution towards the lower dimension from the larger dimensions after milling and the particles can be used for suspension purpose.

4.3 Zeta potential analysis:

The zeta potential of the suspended powders in aqueous media at different pH is shown in Fig4.3. The zeta potential of the suspension was found to vary between +21 mV to – 35mV in the studied pH range of 2 to 10. Zeta potential is the measure of the stability of the suspension and the system having potential values greater than +30mV or less than -30 mV are stable due to electrostatic repulsion. Therefore the suspension is unstable between pH 2-6 owing to zeta potential lying in the unstable zone. While, the suspension at pH 8-10 might show stability.

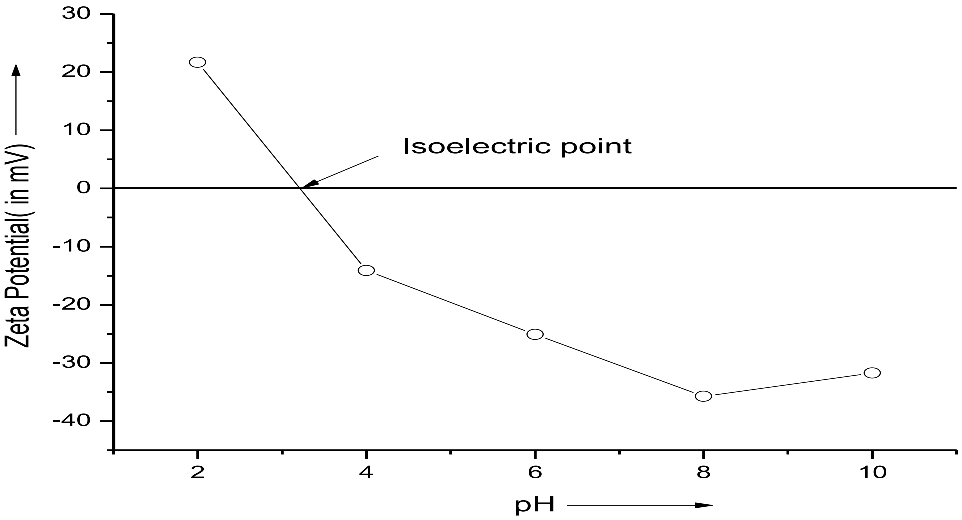


Fig 4.3 Zeta potential vs. pH curve for $BaTiO_3$ suspension containing no Polyelectrolyte

The **Iso-Electric point** i.e. the pH at which the Zeta potential is zero and the system is least stable, is found to be at **3.2**. The suspension showed a maximum zeta potential of -35 mV at pH 8. This value of zeta potential is assumed to be low for the precipitation of Ca^{2+} and PO_4^{3-} ions to form the surface calcium phosphate layer.

4.4 Stabilization of the barium titanate powder:

The zeta potential of the barium titanate suspension as a function of Darvan-C polyelectrolyte concentration is shown in Fig4.4. The Zeta potential of the system was measured at two different basic pH (9 and 10) as the function of polyelectrolyte concentration. Since hydroxyapatite is to be precipitated at pH 9 or 10, the zeta potential of the barium titanate suspension was analyzed at these pH to determine the optimum amount of polyelectrolyte.

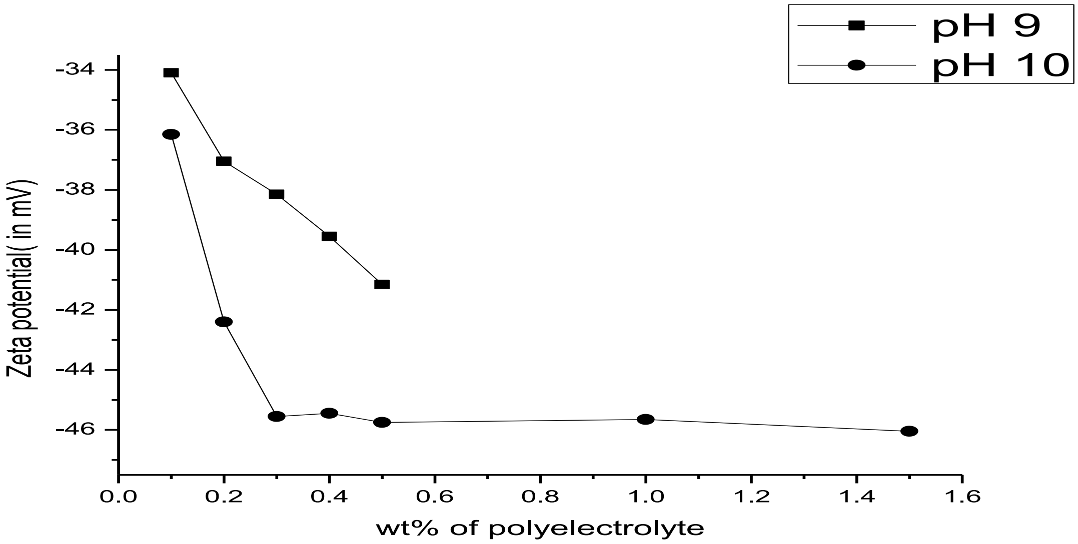


Fig 4.4: Zeta Potential vs. wt% of polyelectrolyte at two different pH

Addition of polyelectrolyte drastically improves the zeta potential to a value of nearly -45mV . Further the zeta potential value peaks around -45 mV for higher wt% of Darvan-C at pH 10. It is also noted that the zeta potential value is always better for pH 10 compared to pH 9 for the same polyelectrolyte concentration. The much lower Zeta potential value indicates a much stable suspension of barium titanate. Therefore, 1 wt% of Darvan-C at pH 10 was used for stabilization of barium titanate.

4.5 X-Ray Diffraction analysis of the prepared composite:

X-ray diffraction pattern of the calcined hydroxyapatite- barium titanate powder is shown in Fig. 4.5. The composite powder has been calcined at 850°C for 2 h. The X-ray diffraction pattern showed the presence of both hydroxyapatite and barium titanate phases. The samples are completely phase pure and the patterns further reveal the increase in the amount of barium titanate by the intensification of the peaks corresponding to barium titanate. The hydroxyapatite in the sample is hexagonal and corresponds to JCPDS card no.72-1243 with lattice parameters a = b =9.4320 Å and c = 6.8810Å.

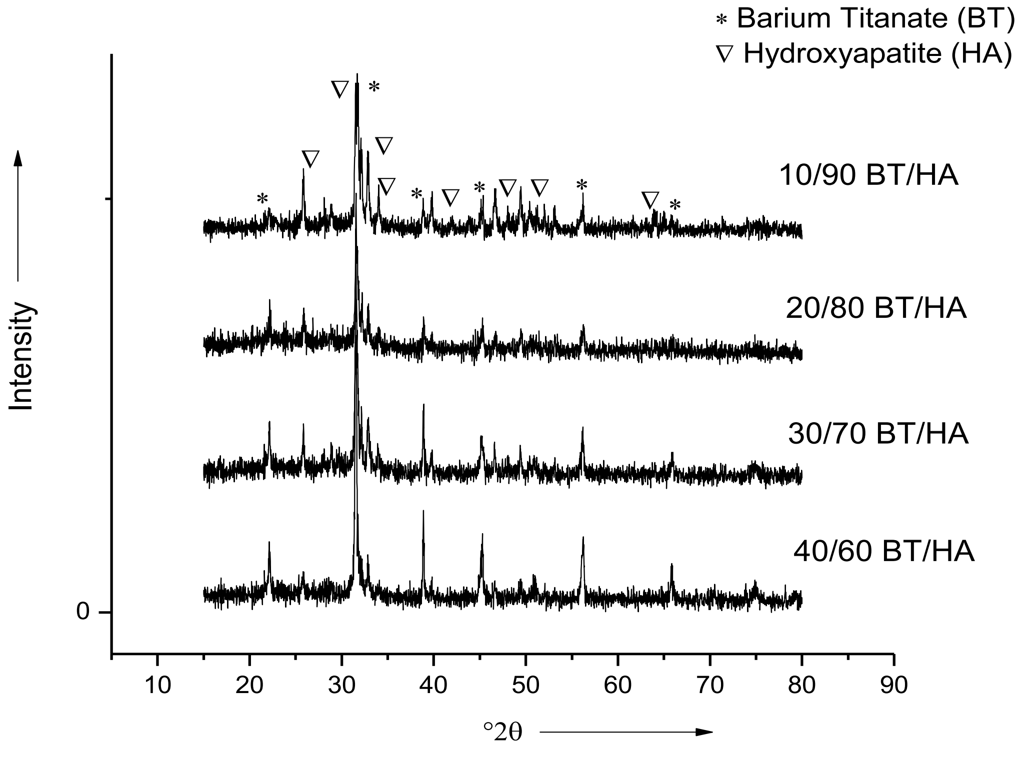


Fig 4.5: X-Ray Diffraction Pattern of Calcined Hydroxyapatite-Barium Titanate Composite.

The barium titanate in the sample is cubic and corresponds to JCPDS card no.75-0211 with lattice parameters a = 4.0057 Å. Thus a phase pure composite was obtained.

4.6 Dilatometery of the sample-:

The linear shrinkage behavior of the composite sample (containing 40 wt% barium titanate) with respect to temperature is studied by the dilatometer. Fig 4.6 shows the change in length with respect to original length of the sample as a function of temperature. The dL/Lo was found to increase linearly in the temperature below 950^{o}C. This corresponds to the thermal expansion of the composite. The onset of densification was found at 950°C. This indicates that practically no densification occurs below 950^{o}C in this system. The maximum shrinkage was found to be 10% at 1200^{o}C. The rate of densification was also plotted in the figure. It shows a peak around 1000°C. This indicates the maximum densification in this temperature zone.

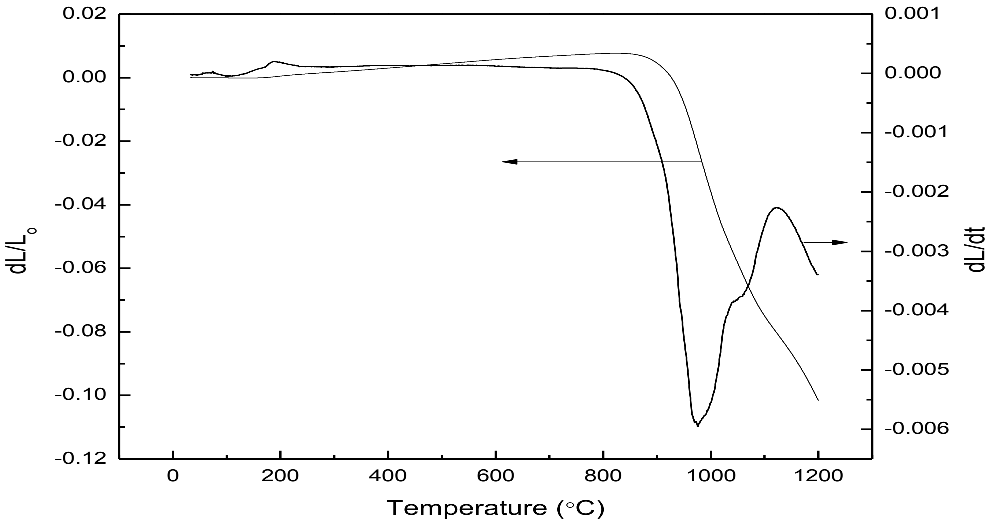


Fig 4.6. Change of length of the sample with respect to initial length and time with change in temperature.

4.7 Bulk density of the samples at sintering temperatures:

The bulk density of the pellets sintered at different temperature as function of composition temperature is shown in Fig 4.7. It could be seen from the figure that the bulk density of all the compositions increases with increase in sintering temperature. This is due to the increase in densification of all samples with increase in temperature, which is quite obvious. In general the bulk density rises with increase in amount of barium titanate in the composite. This may be due to the higher density of barium titanate, thereby causing the rise in the density of the composite with increased amount of barium titanate.

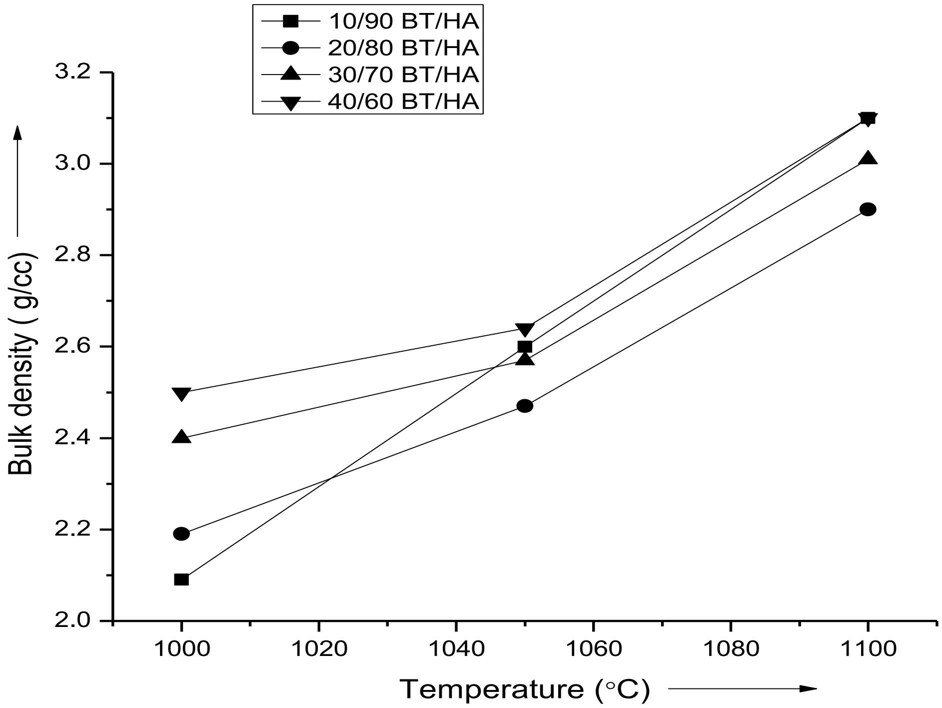


Fig 4.7 Bulk density of the different compositions as a function of temperature.

4.8 Shrinkage of the samples at sintering temperatures

The shrinkage of the pellets of various compositions as a function of sintering temperature is shown in Fig 4.8. It could be seen from Fig 4.8 that the shrinkage of all the compositions increases with the increase in the sintering temperature. This is due to the increase in densification with temperature. Further shrinkage of the composition decreases with increase in the barium titanate amount. This may be due to the densification of hydroxyapatite in the given temperature range, therefore the shrinkage increases with increasing hydroxyapatite amount, or decreasing barium titanate amount in the composite.

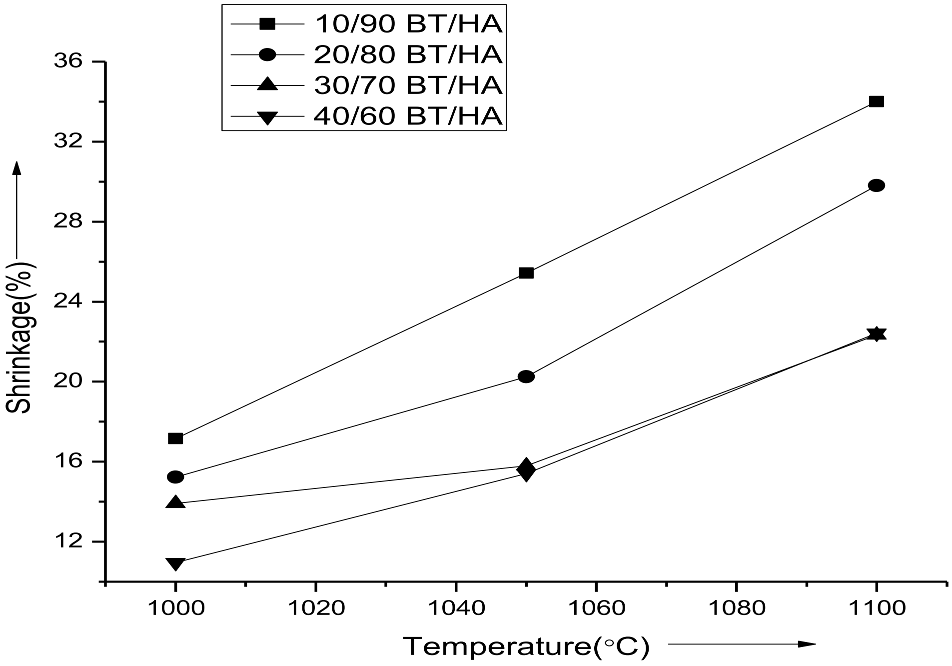


Fig 4.8 Shrinkage of various compositions as a function of temperature.

4.9 X-Ray Diffraction of sintered pellet:

The X-Ray Diffraction pattern of the sintered pellet is shown in Fig 4.9. It could be seen from the figure that the sintered composite mostly contains hydroxyapatite and barium titanate phase. However, a trace amount of impurity phases could also be detected from the XRD pattern. The impurity phases may be formed due to the reactions between hydroxyapatite and $BaTiO_3$.

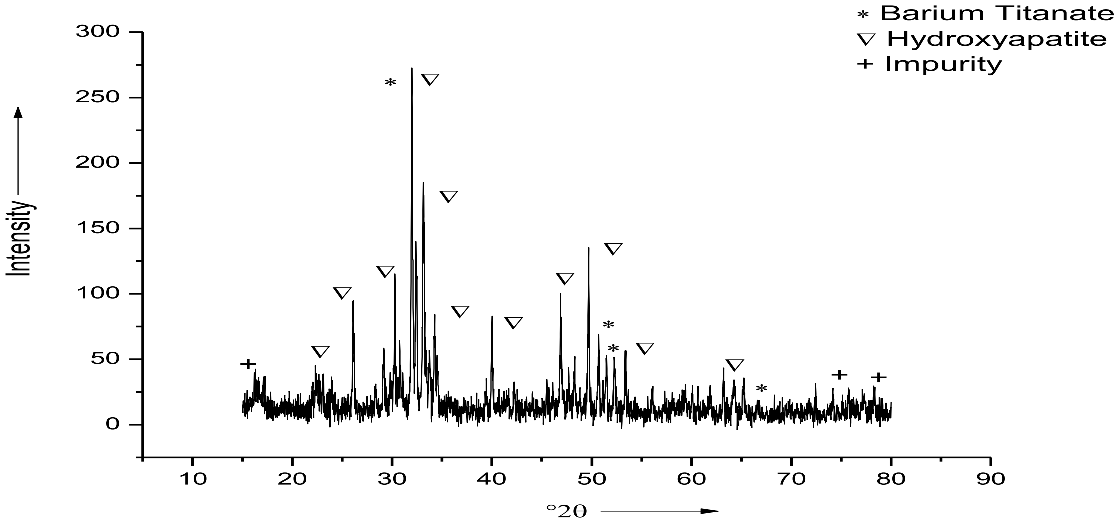


Fig 4.9. X-Ray Diffraction Pattern of the sintered pellet.

4.10 Dielectric measurement:

The Dielectric measurements of the various samples were taken at room temperature after providing ohmic contacts to the sintered pellets by application of silver electrode. The relative permittivity and dielectric dissipation factor has been shown in Fig. 4.10 (a) and (b) respectively.

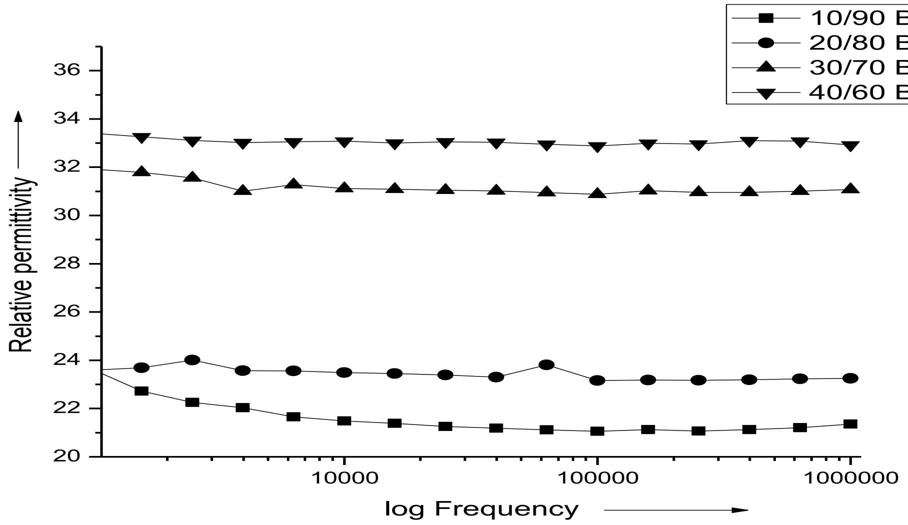


Fig 4.10(a): The relative permittivity as a function of frequency for different composition of hydroxyapatite (HA)- barium titanate (BT) Composite at Room Temperature.

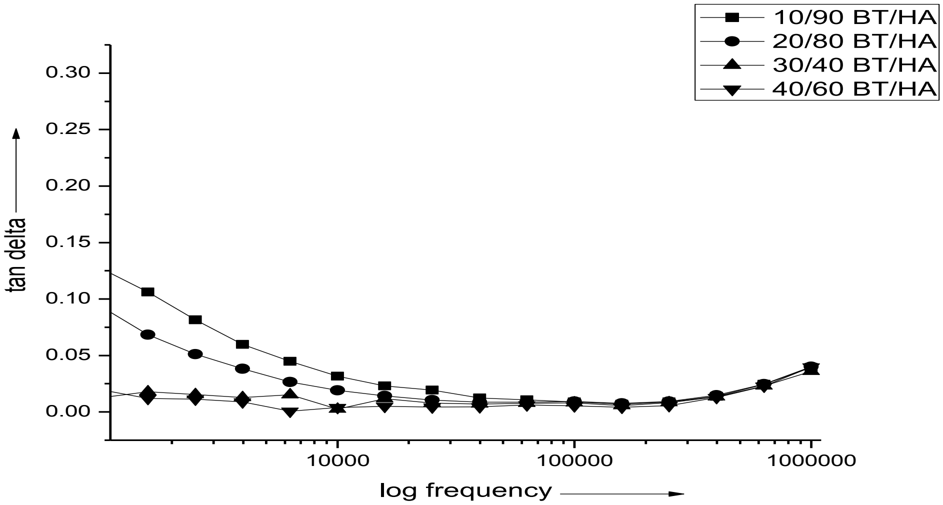


Fig 4.10(b): The dielectric dissipation as a function of frequency for different composition of hydroxyapatite (HA)- barium titanate(BT) composite at room temperature.

As indicated in Fig 4.10(a), the Relative permittivity (ε_r) increases with the increase in the amount of barium titanate in the composition, although the increase is very small. This may be due to the ferroelectric nature of barium titanate and it's associated high permittivity (1500-2000). The presence of barium titanate therefore can be said to improve the permittivity of hydroxyapatite composite. However the low permittivity values may be due to the porosity in the sintered samples.

Similarly, Fig 4.10(b), shows that the Dielectric dissipation (tan delta) decreases with the increase in frequency for all compositions. Further the dielectric loss also decreases with increase in barium titanate amount. This may be due to the low dielectric dissipation associated with barium titanate. However the dissipation value is comparatively high due to the associated porosity in the sintered sample.

CHAPTER 5

CONCLUSIONS & SCOPE OF FURTHER WORK

It can be concluded from the present study that:

1) The various compositions of hydroxyapatite - barium titanate composites were prepared by the possible coating of stabilized barium titanate particles by hydroxyapatite.
2) For the various compositions, while the bulk density showed a rising trend with increased barium titanate, the reverse is true for the shrinkage of the samples.
3) Further the measurement of dielectric properties of barium titanate indicates an increase in the relative permittivity values and a decrease in the dielectric dissipation values with increase in the barium titanate amount in the composite. Therefore increased amount of barium titanate may be useful in producing Polarised hydroxyapatite sample owing to rising permittivity and reduced dissipation values.

The further work that can be done in this study are:

1) The composites containing larger amount of barium titanate should be prepared and characterized.
2) The piezoelectric behavior of all the composite compositions should be tested.
3) The bioactivity of the composites should be tested in stimulated body fluid (SBF) at 37°C and pH 7.4.

REFERENCES

1. Afshar. A., Ghorbani M., Ehsani N., Saeri M.R., Sorrell C.C., Some important factors in the wet precipitation process of hydroxyapatite ,Materials and Design 24 (2003) 197–202

2. Hench LL. Biomaterials: a forecast for the future. Biomaterials 1998;19(16):1419 –1423.

3. Basu B., Nath S, fundamentals of biomaterials and biocompatibility, Indian Institute of Technology Kanpur, Chapter 1, page 8.

4. Mobasherpour I.,Soulati Heshajin M., Kazemzadeh A., Zakeri M., Synthesis of nanocrystalline hydroxyapatite by using precipitation method, Journal of Alloys and Compounds 430 (2007) 330–333.

5. Jarcho, M., Calcium phosphate ceramics as hard tissue prosthetics. *Clin. Orthop. Relat. Res.*, 1981, **157**, 259–278.

6. Hench, L. L., Bioceramics. *Joint American Ceramic Society.*, 1998, **81**, 1705–1728.

7. Kumar D., Gittings J.P., Turner I.G., Bowen C.R., Bastida-Hidalgo A., Cartmell S.H. Polarization of hydroxyapatite: Influence on osteoblast cell proliferation, Acta Biomaterialia 6 (2010) 1549–1554.

8. Takeda, H., Nakamura, S., Yamada, K., Tsuchiya, T. and Yamashita, K., Dielectric properties of poled hydroxyapatite ceramics. *Key Eng. Mater.*, 2000, **181–182**, 35–38.

9. Yamashita, K., Oikawa, N. and Umeqaki, T., Acceleration and deceleration of bone-like crystal growth on ceramic hydroxyapatite by electric poling ,*Chem. Mater.*, 1996, **8**, 2697–2700.

10. .Nagai, M., Shibuya, Y., Nishino, T., Saeki, T., Owada, H., Yamashita, K. and Umegaki, T, ., Electrical conductivity of calcium phosphate ceramics with various Ca/P ratios. *J. Mater. Sci.*, 1991, **26**, 2949–2953.

11. Yamashita, K., Enhanced bioactivity of electrically poled hydroxyapatite ceramics and coatings. *Mater. Sci. Forum*, 2003, **426–4**, 3237–3242.

.

12. Nakamura, S., Kobayashi, T. and Yamashita, K., Enhanced osteobonding by negative surface charges of electrically polarized hydroxyapatite *J. Biomed. Mater. Res.*, 2001, **57**, 477–484.

13. Gittings J.P., Bowen C.R., Turner I.G., Baxter F., Chaudhuri J., Characterisation of ferroelectric-calcium phosphate composites and ceramics, Journal of the European Ceramic Society 27 (2007) 4187–4190.

14. Park Y.J., Hwang K.S., Song J.E., Ong J.L., Rawls H.R., Growth of calcium phosphate on poling treated ferroelectric $BaTiO_3$ ceramics, Biomaterials 23 (2002) 3859–3864.

15. Feng J., Yuan H., Zhang X., Promotion of osteogenesis by a piezoelectric biological ceramic, Biomaterials 18 (1997) 1531-1534.

16. Xia C.T., Er- Shi W., Zhong W.Z., Guo J.K., Preparation of $BaTiO_3$, by the Hydrothermal Method, Journal of the European Ceramic *Society* 15 (1995) 1171-1176

17. Buscaglia M.T., Bassoli M., Buscaglia V. Solid-State Synthesis of Ultrafine $BaTiO_3$ Powders from Nanocrystalline $BaCO_3$ and TiO_2, J. Am. Ceram. Soc., 88 [9] 2374–2379 (2005).

18. Yanez C.G., Benitez C., Ramirez H.B., Mechanical activation of the synthesis reaction of $BaTiO_3$ from a mixture of $BaCO_3$ and TiO_2 powders, Ceramics International 26 (2000) 271-277

19. Chen J.F., Shen Z.G., Liu F.T., Liu X.L., Yun J., Preparation and properties of barium titanate nanopowder by conventional and high-gravity reactive precipitation methods, Scripta Materialia 49 (2003) 509–514

20. Bogdanoviciene I., Beganskiene A., To˜nsuaadu K., Glaser J., Meyer H..J., Kareiva A., Calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ ceramics prepared by aqueous sol–gel processing, Materials Research Bulletin 41 (2006) 1754–1762.

21. Yang Z., Jiang Y., Wang Y., Ma L., Li F., Preparation and thermal stability analysis of hydroxyapatite derived from the precipitation process and microwave irradiation method, Materials Letters 58 (2004) 3586– 3590

22. Saeri M.R., Afshar A., Ghorbani M., Ehsani N., Sorrell C.C., The wet precipitation process of hydroxyapatite, Materials Letters 57 (2003) 4064–4069

23. Tas A.C., Synthesis of biomimetic Ca-hydroxyapatite powders at 37°C in synthetic body fluids, Biomaterials 21 (2000) 1429-1438

24. Blanco Lopez M.C., Rand B., Riley F.L., Polymeric stabilisation of aqueous suspensions of barium titanate. Part I: Effect of pH. Journal of the European Ceramic Society 20 (2000) 1579-1586

25. Blanco Lopez M.C., Rand B., Riley F.L., Polymeric stabilisation of aqueous suspensions of barium titanate, Part II: Effect of polyelectrolyte concentration, Journal of the European Ceramic Society 20 (2000) 1587-1594