COMPARATIVE STUDY ON DIELECTRIC PROPERTIES OF BARIUM TITANATE SYNTHESIZED BY SOLID STATE AND AUTO COMBUSTION METHOD

A

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
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CERTIFICATE

This is to certify that the project entitled "**Comparative study of properties of Barium Titanate synthesized by Solid State and Auto-combustion Method**" submitted by **Amrit Abhishek Dhal** to the National Institute of Technology, Rourkela in partial fulfillment of the requirements for the award of the degree of Bachelor **of Technology in Ceramic Engineering** is a record of bonafide research work carried out by him under my supervision and guidance.

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.

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Date **108CR043**

Abstract

Barium titanate is a well-known ferroelectric and piezoelectric material with high permittivity (more than 1000) and one of the most widely used ceramic materials in the electric industry, especially in multilayer ceramic capacitors (MLCC). The current trend in MLCCs to increase the number of active layers to 200-400 and to lower the dielectric thickness below 2-3µm. To achieve this objective, ultrafine and non-agglomerate powders are required. Preparation methods significantly influence the purity, stoichiometry, particle size or microstructure of the $BaTiO_3$ powder, which in turn influences the dielectric property of the compound. So, present situation is in a need of such a synthesis route which can produce barium titanate of expected particle size with a high permittivity and depressed Curie peak. In the current work, two synthesis routes, solid state synthesis and auto-combustion synthesis has been discussed along with the comparative study of properties of the powder obtained from both the methods.

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Chapter 1

Introduction

Barium Titanate

$BaTiO_3$ is a well-known ferroelectric and piezoelectric material having excellent dielectric properties. Its main application is as a dielectric in MLCC (MultiLayered Ceramic Capacitor) due to its high dielectric constant and low losses. The dielectric properties are controlled by purity and microstructure which in turn is dependant on the method of preparation.

Crystal Structure and Polymorphism property of $BaTiO_3$

$BaTiO_3$ shows the property of polymorphism as it can assume five different crystal structures with changing temperature [1]. Its Curie point is around 130°C. And above this point the lattice structure of the unit cell is cubic. Below this Curie point the structure starts distorting. And it slightly changes from cubic to the tetragonal with the orientation of dipole moment along the c direction. Other transformations occur at temp. close to 0°C and -80°C, below 0°C the unit cell is

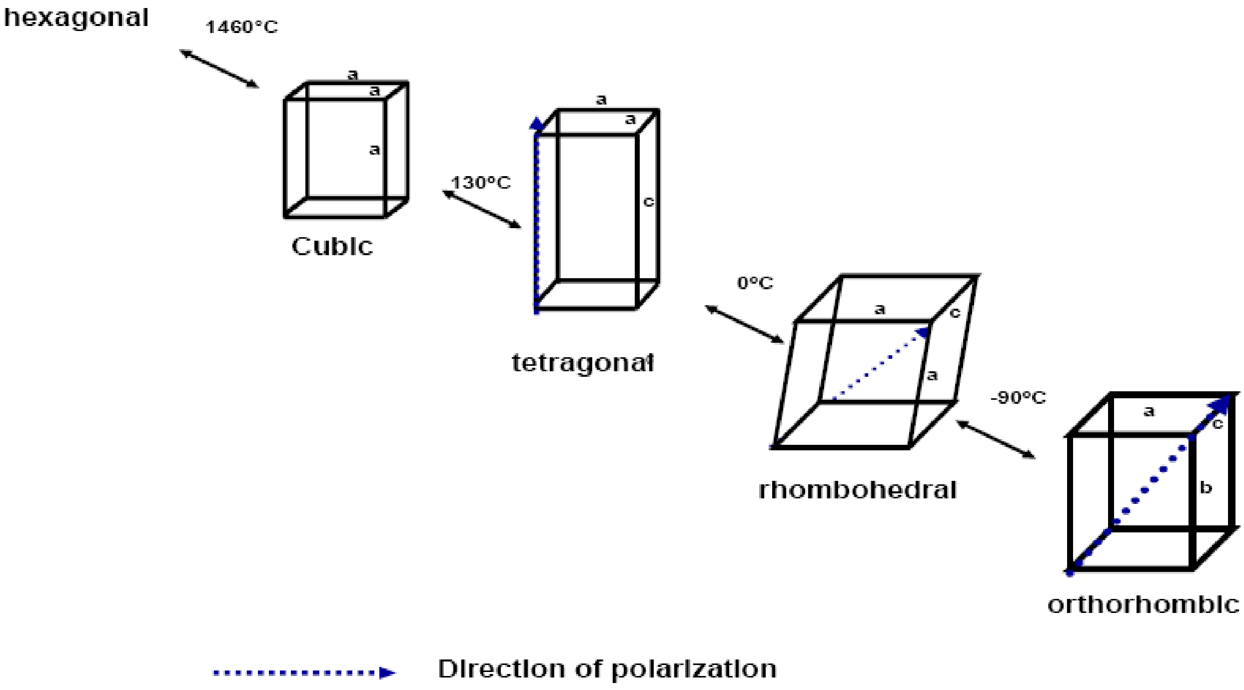


Fig.1.1 Phase changes in $BaTiO_3$

orthorhombic and below -80°C it is rhombohedral with polar axis along body diagonal.

Ferroelectric property of $BaTiO_3$

$BaTiO_3$ has a perovskite crystal structure and above curie temperature (approximately 130°C), it becomes cubic in shape with Ba^{2+} ions at the vertices, O^{2-} ion in the face center position and Ti^{4+} ion in a body-centered position as shown in fig 2. In this case, polarization happens as a result of the unit shift of axially elongated Ti^{4+} ion crystal. This polarization occurs without any application of external electric field or pressure. So,it is known as "spontaneous polarization”. A characteristic that has a spontaneous polarization and a property of changing orientation of spontaneous polarization by an external electric field to reverse is called "ferroelectricity." So, $BaTiO_3$ shows ferro electric property.

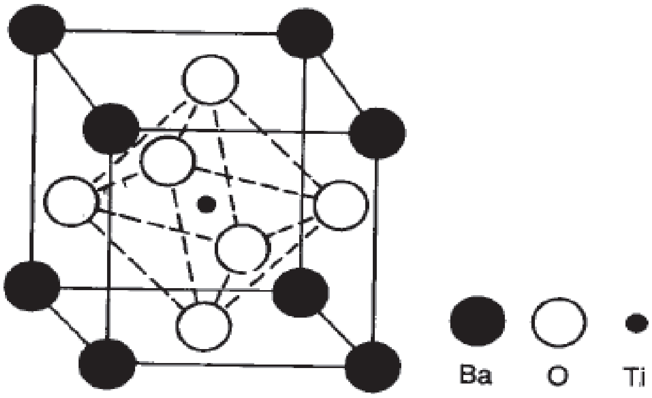


Fig.1.2 Unit Cell Structure of $BaTiO_3$

Dielectric Property of $BaTiO_3$

This is the most important property of $BaTiO_3$ for which it finds application in as a dielectric in MLCC (Multilayered Ceramic Capacitor). Generally $BaTiO_3$ has very high dielectric constant and very low losses. This dielectric constant can be increased further by doping with Nb or Co. The dielectric properties are controlled by purity and microstructure which in turn are dependent on the method of preparation. So, the dielectric constant is a function of temperature, frequency and dopants. Fig.3 shows the change of dielectric constant of $BaTiO_3$ with temperature variation.

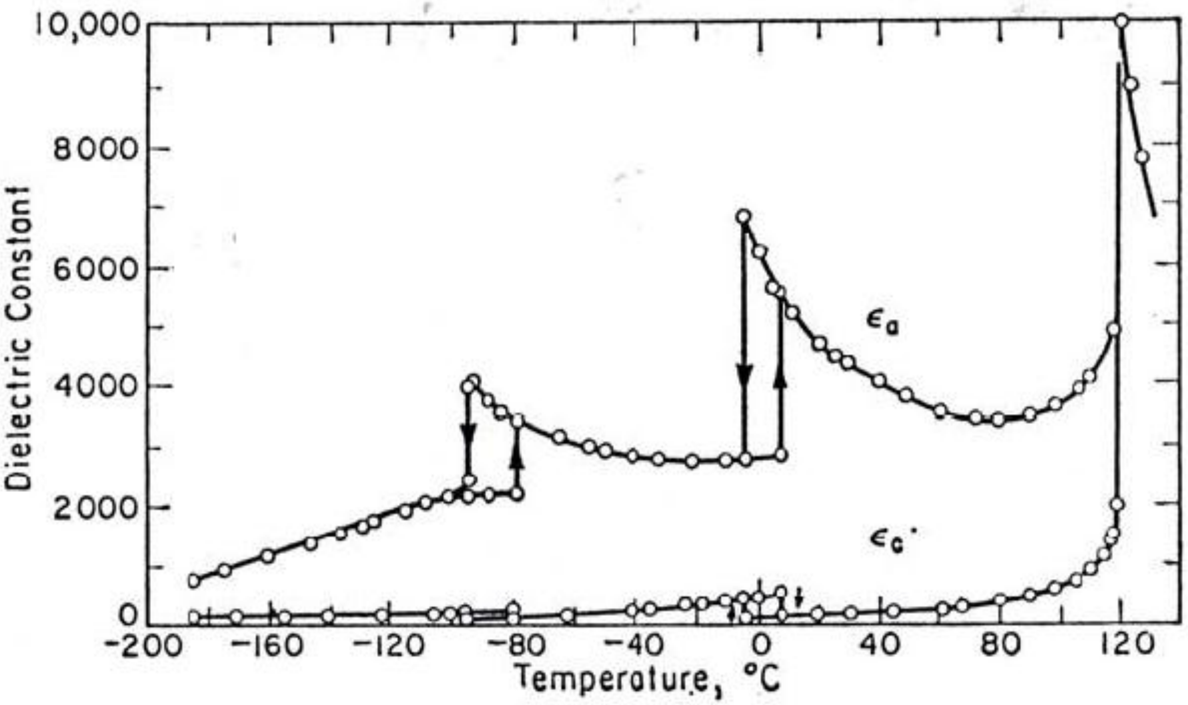


Fig.1.3 Variation of dielectric constant with temperature

Applications

As in case of barium titanate substitution can make Curie point temperature to shift towards higher or lower value, barium is substituted with some amount of strontium (BST) to have a better dielectric and ferroelectric property. And this BST films are used in Infrared sensor applications. Its main application in electric industry is as dielectric in MLCC (Multilayered Ceramic Capacitor). As $BaTiO_3$ has the property of positive temperature of co-efficient of resistivity, so, it finds application in thermistors e.g. in thermal switches [2]. The recent special and unusual application of barium titanate is in the Underwater Sound Hydro Engineering and Medical Fields [3].

Chapter 2

Literature review

Barium titanate synthesis methods

Barium titanate (BaTiO3) can be synthesized by various methods. There are many methods like sol-gel method, hydrothermal method, mechanochemical synthesis method, molten salt method etc. Which method is to be followed is completely depends upon the desired characteristics of barium titanate. Here in the present work two main methods of preparation, solid state method and auto-combustion method are discussed. As the present electronics industry is in the favor of Barium titanate with smaller particle size but desired dielectric value and further Dielectric constant of BaTiO3 varies with varying grain size (At first it increases with decrease in size upto some critical value then it starts falling with decrease in particle size). Grain size also affects the Curie temperature [4]. So, the synthesis route is very important as it will decide the purity and microstructure and thus the dielectric permittivity and Curie temperature of the $BaTiO_3$ powder.

Solid State Method

In this method of preparation, starting materials are $BaCO_3$ and TiO_2. First these two starting materials are ball milled with zirconia ball for proper mixing and then it is calcined and sintered with very high temperature for phase formation. The temperature needed is about 1000°C to 1300°C. In the course of this method some intermediates formed which are Ba_2TiO_4 and Ti-rich phases [5]. In this solid-solid reaction the mass transport mechanism takes place by grain boundary or bulk diffusion. The curie temperature of the final product depends on the mechanical stress introduced by milling and the ratio between barium to titanium. This method involves repeated grinding, milling and calcinations at high temperature. This high calcination temperature involved this process leads large particle size with a wide size distribution and high degree of particle agglomeration [6] and it also contains impure phases due to incomplete reaction [7].

But the particle size of the $BaTiO_3$ can be controlled by controlling some of the parameters. The first parameter is the size of TiO_2 (starting material). Smaller the size of TiO_2 small will be the end product powder and as the small particle can offer large surface area this small size TiO_2 can accelerate the reaction rate by availing large surface area. The second parameter is the milling conditions of $BaCO_3$. The proper milling conditions of $BaCO_3$ make it spherical and provide better surface area for better reaction [8]. Also this leads to lowering the temperature requirement for the reaction. Thus the particle size can be controlled by controlling starting material size, milling and calcinations conditions.

Auto-combustion Method

For the synthesis of high quality $BaTiO_3$ with improved properties auto-ignition process is one of the best processes. Here in this method a redox reaction takes place in precursor solution between the fuel (citric acid) and oxidant ($Ba(NO_3)_2$. EDTA makes complexes with the metal ions and a gel are formed with on heating self-ignites itself and give rise to a black residue along with the evolution of large amount of gases. This black residue on calcinations produces pure phase $BaTiO_3$, this is confirmed through XRD. Generally the barium titanate powder obtained from this method has cubic structure.

The characteristics of the powder are strongly influenced by initial oxidant to fuel molar ratio. Changing PH also influences the formation of barium titanate, its density, dielectric behavior and particle size. It is found that this method of producing barium titanate is better than the conventional solid state method as it provides high dielectric constant or relative permittivity, low dissipation factor or low loss and better relative density and finer particle. Due to having very fine particle, sometimes these particles get agglomerated. Another disadvantage is porosity. Due to evolution of large amount of gases it has relatively high porosity. But the barium titanate obtained from this method is pure in phase.

Other Chemical methods for barium titanate synthesis

There are many chemical routes for producing barium titanate. Some are discussed below:

Sol-Gel Process

Now a days this sol-gel method is considered as a better method for obtaining barium titanate powder of small particle size as it can produce pure and small sized barium titanate powder in relatively low temperature. Barium titanate film of nano scale (~16μm) can be fabricated by this method.

In this process first titanium isopropoxide and barium acetate were mixed in deionized water in molar ratio 1:1. Acetic acid, acetylacetone and glycerin were also added to it to prevent precipitation. All these things are done in room temperature. Then it is dried at 100°C for a day in an oven and gives rise to a gel. This gel is of $BaTiO_3$, which on annealing at different temperature give rise to barium titanate powder. Then the phase is conformed through XRD.

This method has a significant drawback that it contains large no of vacancy defects in the lattice [9]. This problem is due to presence of the hydroxyl ligand in the sol.

Hydrothermal Process

As the barium titanate is having perovskite structure, so, hydrothermal method of production is very suitable for it. It requires relatively low temperature to produce pure phase barium titanate. High pH(>12) value and high concentration of barium ion is favorable for this method of production. This higher conc. of Ba ion and higher value of pH (>12) along with added OH^{-} ion helps in uniformity of grain. And this uniform grain size leads to very good dielectric property [10].

The reaction mechanism can be represented as follows [11]:

$Ti + 2H_2O \rightarrow TiO_2 + 2H_2\uparrow$

$TiO_2 + 2H_2O \rightarrow Ti(OH)_2$ (aq)

$Ba^{2+}Ti(OH)_4$ (aq) $\rightarrow BaTiO_3(s) + 2H^{+} + H_2O$

Generally for higher concentration of Ba^{+} (around 4N conc) particle obtained is of uniform size of 18μm. Again for low concentration of the metal ion uniformity increases with increasing temperature. Grain size increases with increasing reaction time. In case of film, thickness increases with increasing grain size. In this method of preparation phase obtained is very pure, only phases of α-Ti and cubic $BaTiO_3$ are seen in the XRD pattern.

But this method has the drawback same as that of sol gel process. It also contains large no of vacancy effects in lattice structure due to the involvement of hydroxyl ligand.

Objective of the Project

Objective

In the present work synthesis of phase pure $BaTiO_3$ has been carried out by citrate-nitrate auto-combustion route and by solid state process. Both processes gives a comparative study of properties of Barium Tiatanate. The following works to be completed

- Obtaining phase pure $BaTiO_3$ at lower calcination and sintering temperature by auto combustion process and comparing it to the method of preparation of same in solid state method.
- Preparation of high dense material and study & comparison on density due to different sintering temperature.
- Effects of Powder morphology on the densification behavior of $BaTiO_3$ prepared by Solid State and Auto-combustion method.
- Investigating the role of powder morphology on dielectric properties of $BaTiO_3$ prepared by both methods.

Chapter 3

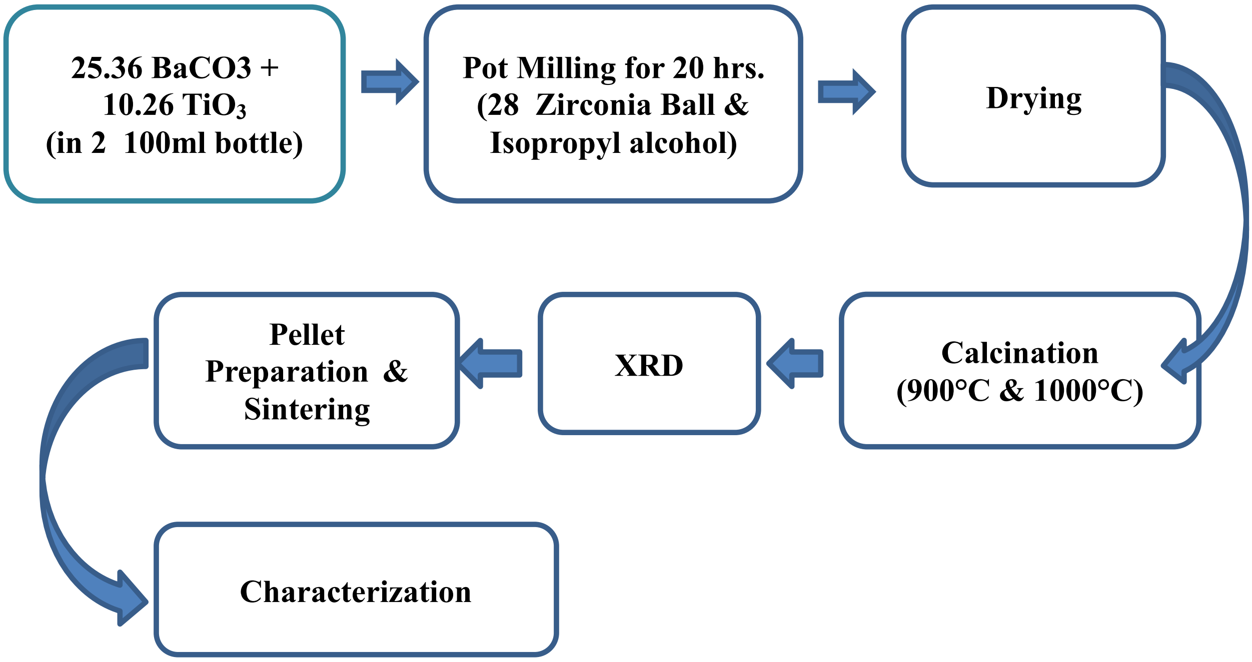
Experimental Procedure

Solid State Method

Powder Synthesis

Barium Titanate powder was prepared by solid state method as following. For the yield of 30g $BaTiO_3$ the calculated batch of 25.36 g of $BaCO_3$ and 10.26g of TiO_2 were taken. These powders were mixed together in two 100ml plastic bottles equally. These bottles were placed in a pot for pot milling. Pot milling was done for 20hr for proper mixing and milling of two powdery compounds. For one bottle 28 Zirconia ball is taken and iso-propyl alcohol was also taken as liquid medium. After proper milling of 20hr the material taken out to a or two petri dish (as size) plate and placed under IR lamp for drying. After drying the whole material was kept in drier.

Some amount of dried powder was calcined at 900^0 C for 2hr and 4hr to investigate whether desired phase appear or not was checked by XRD analysis. As pure barium titanate phase was not obtained on calcination at 900^0C so again it was calcined at a temperature of 1000^0C for 4hr raising hearth furnace. Upon XRD analysis it can be conformed that pure BaTiO3 phase is present. Maximum (80%) amount of powder was calcined at 1000^0C for 4hr.The calcined powder was undergone for the process of planetary milling. For planetary milling the material with iso-propyl alcohol was poured in Zirconia bowl, 27 zirconia ball is given to each bowl for proper milling. The duration was 3hr. After the milling the material taken out and dried.



Flow chart of preparation of powder and pellet by solid State method

Preparation of Bulk sample (Pellet)

The fully crushed fine powder is very considerable for pellet preparation. The powder which was calcined at 1000^0C for 4hr was mixed with 3 wt. % PVA (Poly Vinyl Alcohol) with the help of mortar and pestle. PVA act as binder and it helps to hold whole structure of the compacted desired shape. The binder mixed powder was pressed in Carver Press. 0.75g of powder was taken in a die of diameter of 12mm. The uniaxial pressing was done at 4 ton and a dwelling time of 90 sec was given for each sample. The die was regularly cleaned after pressing of each pellet with acetone and stearic acid. The pressed green pellets were sintered at 1100^0C, 1200^0C, 1250^0C, 1300^0C with a heating rate of 4^0C/min in electrical furnace with a holding time of 4hr and at 650^0C a holding time of 1hr was given for binder burn out.

Density measurement

Dry weight of all sintered sample was taken. All samples sintered at different temperature were taken in beakers respectively. All beakers were three fourth filled up with kerosene.

Beakers were placed in vacuum chamber for 30min. After treatment from vacuum chamber, suspended weight of each sample was measured and noted down for respective sample. And at last soaked weight was measured.

$$\text{Bulk density} = \frac{\text{Dry Weight}}{\text{Soaked Weight} - \text{Suspended Weight}} * \text{Density of Liquid}$$

The density of kerosene taken is 0.81g/cc.

Phase analysis of calcined powder and sintered pellet

The phase of calcined powder and sintered pellet that evolved was studied by X-ray diffraction method (Philips PAN) using Cu Kα radiation wavelength of 1.54Å. The voltage was 35 kV and current was 25 mA. The samples were scanned in the range of 15^0 to 80^0 and the scan rate was 0.02^0/sec. The phases that present can be identified by the software X’pert High Score and Origin by matching the peak. And this experiment is based on Bragg’s law

$n\lambda = 2d \sin\theta$

Where, n= order of diffraction

d=inter planer spacing

θ= angle between incident ray and planer surfece

Lattice parameter and Tetragonality (c/a ratio) was calculated by using same X’pert high score software and another software known as chekcell.

Microstructure Analysis

Microstructure of sintered pellets had been studied using Scanning Electron Microscope (JEOL-JSM 6480LV) at applied generator voltage of 15 KV. Pictures of all as fired samples sintered at different temperature were taken for microstructure analysis.

Dielectric measurement

For dielectric measurement samples were prepared by electroding with silver paste, this silver paste was applied upon both side of surface. This experiment was conducted by using Solatron S1 1260 Impedence/Gain phase analyser with Solatron 1296 dielectric interface. The frequency range was varied from 10Hz to 1MHz for this dielectric measurement. Also Dielectric behaviour with temperature (at 200^0C) have been studied keeping the pellet in a furnace attached with the electrode.

Auto-combustion Method

Powder Synthesis

By auto-combustion process Barium Titanate powder was prepared as by this method pure $BaTiO_3$ can be obtained. Here in this method, a redox reaction takes place in precursor solution between the fuel and oxidant. Fuels that can be used in this method are citric acid, urea, ethyl glycol etc. and oxidants that can be used are mainly the nitrates of different metals. Chelating agents like EDTA or acetic acid are also used to make complexes with the metal ion. In the course of this process a gel gets formed from the solution and on heating it, self-combustion occurs. This self-combustion associated with evolution of large amount of gases generally consisting of H_2O, NO_2 or basically NO, resulting in a black residue which on calcination produces BaTiO3.

Here for this experiment of producing $BaTiO_3$ by auto combustion method, citric acid is taken as fuel, precursor for producing metal ions are $TiO(NO_3)_2$, $Ba(NO_3)_2$ and EDTA is taken as the chelating agent. Another precursor needed is ammonium nitrate.

Preparation of $TiO(NO_3)_2$ solution and its estimation

200ml of H_2SO_4 was taken in 1Ltr. Beaker. 80gm of $(NH_4)_2SO_4$ was added slowly with continuous stirring when beaker was on heater. When smoke appeared TiO_2 of 10gm was poured slowly with continuous stirring. Stirring was done until a yellow (colour of olive oil) transparent solution was obtained. This solution was kept at rest for cooling of beaker for handling.

The above procedure can be represented as a reaction as follows:

$$TiO_2 + H_2SO_4 \rightarrow TiO(SO_4) + H_2O$$

This solution was mixed in 500ml of distilled H_2O and then it put in the ice bath and NH_3 was added up to PH 9 and 10.

At this point a white precipitation occurred due to formation of titanyl hydroxide ($TiO(OH)_2$).

The above procedure can be represented as a reaction as follows:

$$TiO(SO_4) + 2NH_3(aq.) \rightarrow TiO(OH)_2 \downarrow + (NH_4)_2SO_4$$

Then the precipitate was washed frequently for consecutive days to make it sulphate free and it was tested with Barium chloride whether it is sulphate free or not. And then this washed precipitate is dissolved in dilute nitric acid.

The above procedure can be represented as a reaction as follows:

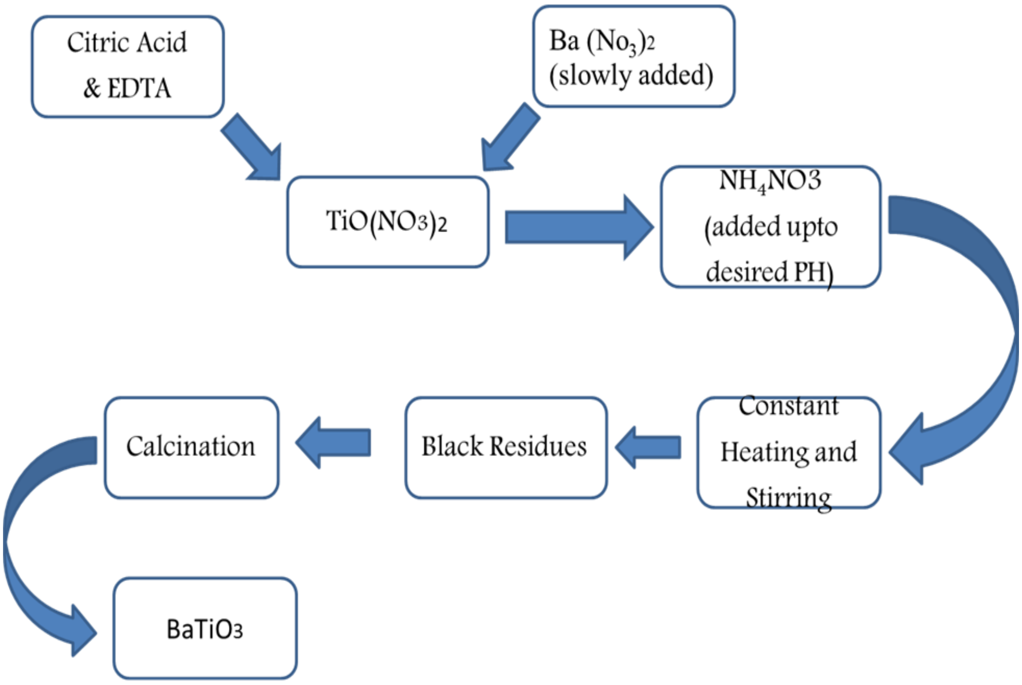
$$TiO(OH)_2 + 2HNO_3 \rightarrow TiO(NO_3)_2 + 2H_2O$$

So, $TiO(NO_3)_2$ is produced for further use as precursor.

For estimation of strength, 10 ml of $TiO(NO_3)_2$ was taken and filtered carefully. The filtered residue was taken in platinum crucibles. The residue was kept in platinum crucibles. Crucibles were kept in furnace for firing for 1000^0C for 2hr. When firing was over the crucibles were taken out and weight was recorded. Average of weight loss was taken and strength was measured. According to this strength weight of precursor and chelating agent that to be used was measured.

Combustion Synthesis to get $BaTiO_3$ Powder

During this work barium titanate powder was prepared by citrate-nitrate gel. Precursors like TiN, $Ba(NO_3)_2$, citric acid, ammonium nitrate and EDTA was taken according to calculated weight and the ratio was 1:1:1.5:12:0.1. Desired pH was controlled by addition of NH_4OH. The solution was placed on a hot plate and stirring was also done continuously and simultaneously. A viscous gel formed due to dehydration of homogeneously mixed solution and upon further heating this gel self-ignites followed by swelling of the gel and became floppy. This swelling can be handled by glass rod and maximum precaution should be taken during this. The ignition caused a product of ash which was voluminous. This powder was taken out and grinded by agate mortar. Then the ash like mass was calcined at the temperature 650^0C for 4hr and pellet sintered at 1200^0C for 4hr.



Flow chart of preparation $BaTiO_3$ by Auto combustion Process

Preparation of Bulk sample (Pellet)

The fully crushed fine powder is very considerable for pellet preparation. The powder which was calcined at 650^0C for 4hr was mixed with 3 wt. % PVA (Poly Vinyl Alcohol) with the help of mortar and pestle. PVA act as binder and it helps to hold whole structure of the compacted desired shape. The binder mixed powder was pressed in Carver Press. 0.75g of powder was taken in a die of diameter of 12mm. The uniaxial pressing was done at 4 ton and a dwelling time of 90 sec was given for each sample. The die was regularly cleaned after pressing of each pellet with acetone and stearic acid.

The pressed green pellets were sintered at 1200^0C, 1250^0C with a heating rate of 4^0C/min in electrical furnace with a holding time of 4hr and at 650^0C a holding time of 1hr was given for binder burn out.

All the characterization of XRD, density, microstructure and dielectric measurement were done successfully like previously mentioned.

Chapter 4

RESULTS AND DISCUSSION

Thermal decomposition behaviour of gel obtained by Auto combustion process

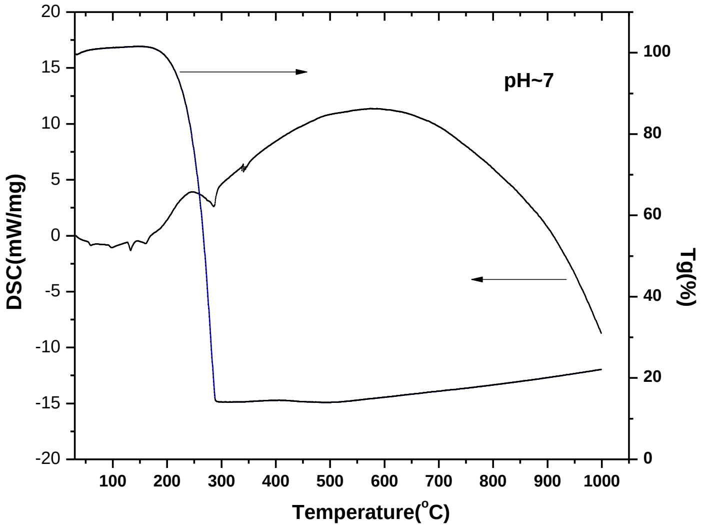


Fig 4.1 DSC/TG Curve for gel produced during Auto Combustion at pH 7

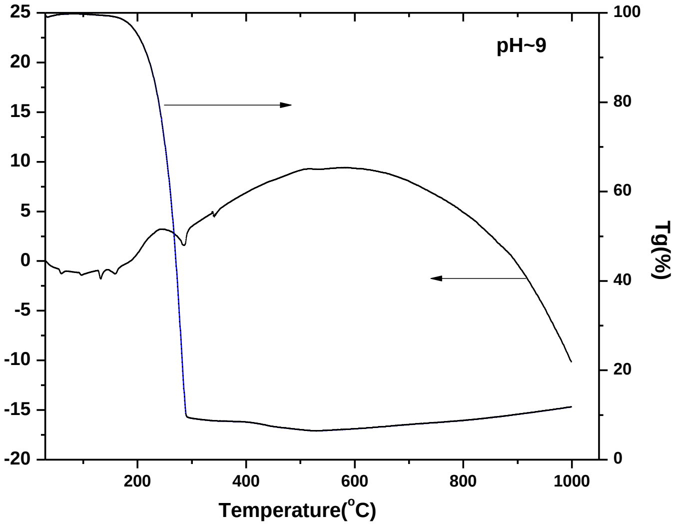


Fig 4.2 DSC/TG Curve for gel produced during Auto Combustion at pH 9

The DSC/TG curve of the gel is shown in fig 4.1 and fig 4.2. It was observed that from the DSC curve there are four endothermic peaks. The first endothermic peak is due to removal of physical adsorbed water present in gel. The next two peaks may be due to decomposition of excess citric acid. A broad exothermic peak is obtained at 600^0C that may be attributed with pyrolysis of organic compound and due to metal chelate complexes. The high weight loss may be due to decarboxylation of citric acid and EDTA. Near 300^{0}C there is a weight loss and an exothermic peak and this may be due to decomposition of carbonaceous material.

Phase analysis of $BaTiO_3$ powder and pellet prepared by solid state method

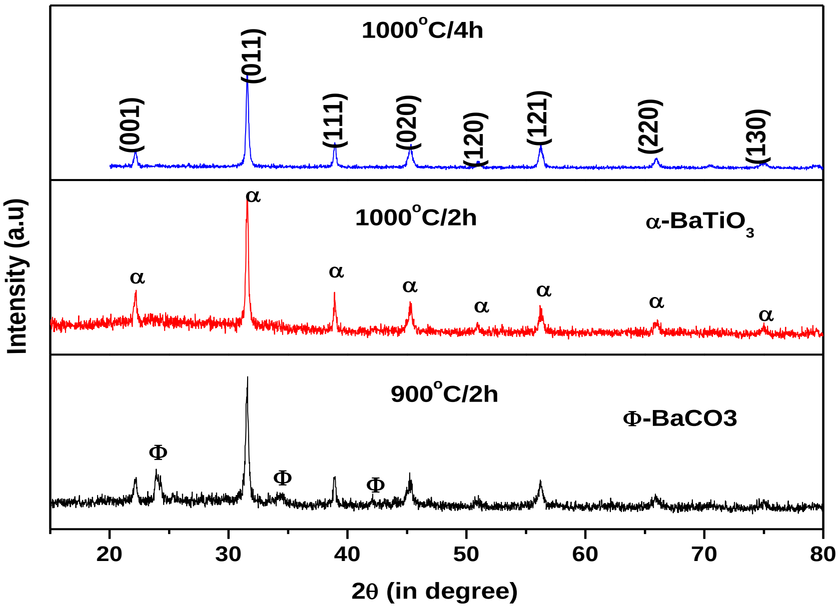


Fig 4.3 XRD plot of calcined powder (at different temperature) prepared by solid state method

At 900^{0}C the single phase was obtained. The cubic structure was obtained on calcination at a temperature of 900^{0}C for 4hr. Or it may call as pseudocubic structure. This cubic structure may be continuing but with greater crystal size when material calcined at 1000^{0}C/4hr. When the sample sintered at 1100^{0}C per 4hr tetragonality pattern was there. Upon increasing the sintering temperature the pure phase formation occur showing sharp peak. The c/a ratio for powder that is calcined 1t 1000^{0}C is 1.00169. And c/a ratio of pellet that is sintered at 1250^{0}C/4hr is 1.0071 and 1300^{0}C/4hr is 1.0033. Due to this new green pellet is again sintered at temperature at 1250^{0}C and 1300^{0}C. This anomaly may be due to improper sintering.

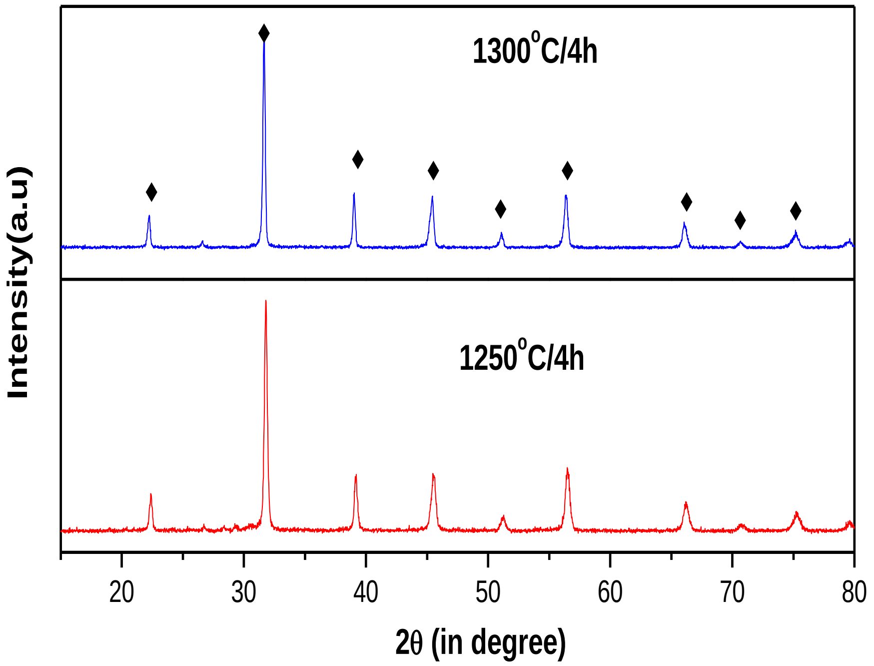


Fig 4.4 XRD plot of sintered pellet (at different temperature) prepared by solid state method

XRD Analysis of material prepared by Auto Combustion Process

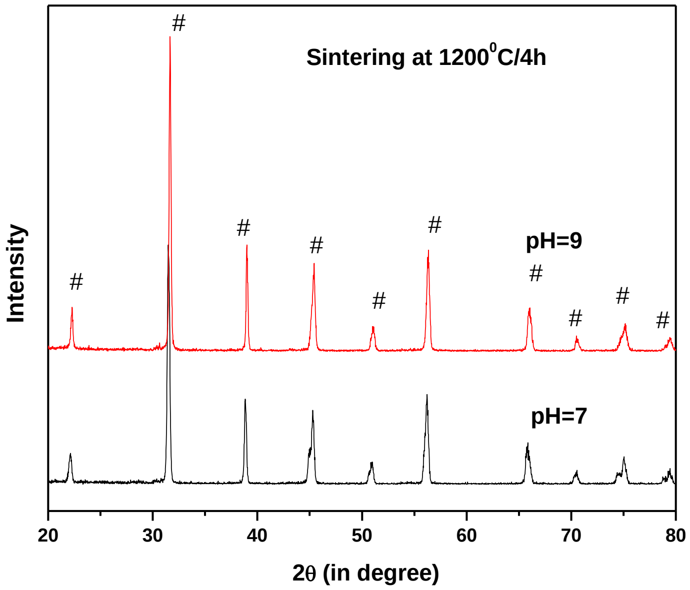


Fig 4.5 XRD plot of sintered pellet prepared by auto combustion method

X-Ray Diffraction Analysis of pellets prepared by auto-combustion process sintered at 1200^0C for 4hr is done. The graph shows pure phase of $BaTiO_3$ formation when sintering is held at 1200^{0}C for both pH 7 and pH9. But sharp peak is obtained by the material prepared at pH 9. The sharp and broadening of peak determines the crystal size and pure phase formation. The calculated c/a ratio is 1.0076 and 1.0083 for pH 7 and pH 9 respectively.

Table No: 4.1 Comparison of c/a ratio of samples of two processes

Process	Sample Name	c/a ratio
Solid State	BT 1300	1.0033
Solid State	BT 1250	1.0071
Auto Combustion	BT pH7	1.0076
Auto Combustion	BT pH9	1.0083

Relative density of samples

Bulk Density (BD) of sample sintered at1200^{0}C synthesized by Solid State (SS) process is 5.21g/cc and Relative Density is 86.68%. This sintering temperature is considered for reference and minute comparison. BD of sample sintered at 1250^{0}C is 5.474g/cc and relative Density is of about 91.08%. BD of pellet fired at 1300^{0}C is 5.4g/cc and Relative Density is 89.85%. This anomaly may be explained by SEM analysis of microstructure.

BD of sample prepared by Auto Combustion process at pH 1 is 5.45 and Relative Density is 90.68%. Sample of this pH is considered for reference and minute comparison. BD of sample of pH7 is 5.64g/cc and Relative Density is 93.84%. And BD of sample of pH 9 is 5.69g/cc and Relative Density of same sample is 94.67%.

Table No: 4.1 Comparison of Relative Density of samples of two processes

Process	Sample Name	Relative Density (in %)
Solid State	BT 1300	89.85
Solid State	BT 1250	91.08
Auto Combustion	BT pH7	93.84
Auto Combustion	BT pH9	94.67

SEM Analysis for study of Microstructure of samples prepared

Solid State Method

Pellet sintered at 1250^0C **Pellet sintered at 1300^0C**

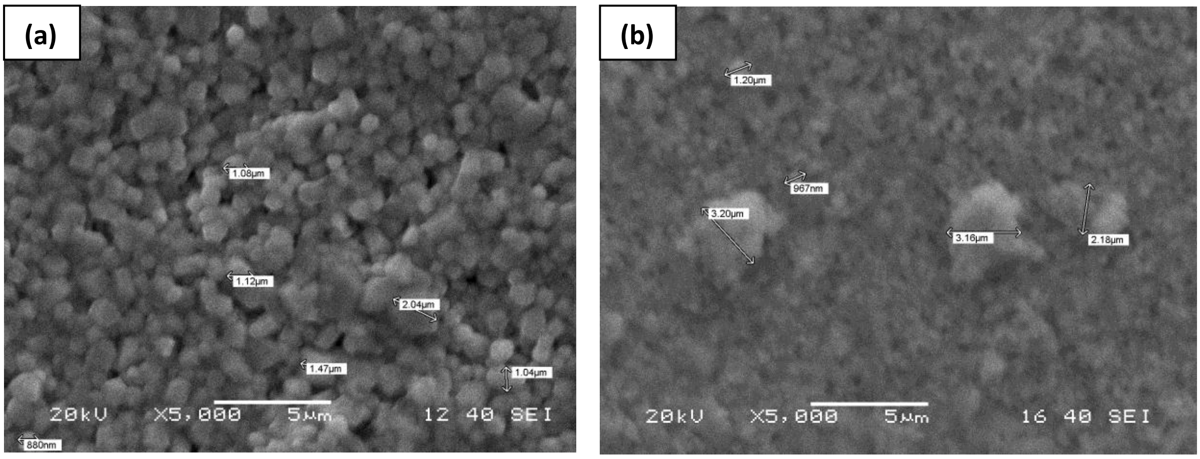


Fig4.6 Comparative study of SEM of pellet sintered at 1300^0C and 1200^0C

Auto-Combustion Method

Pellet of pH 7 **Pellet of pH 9**

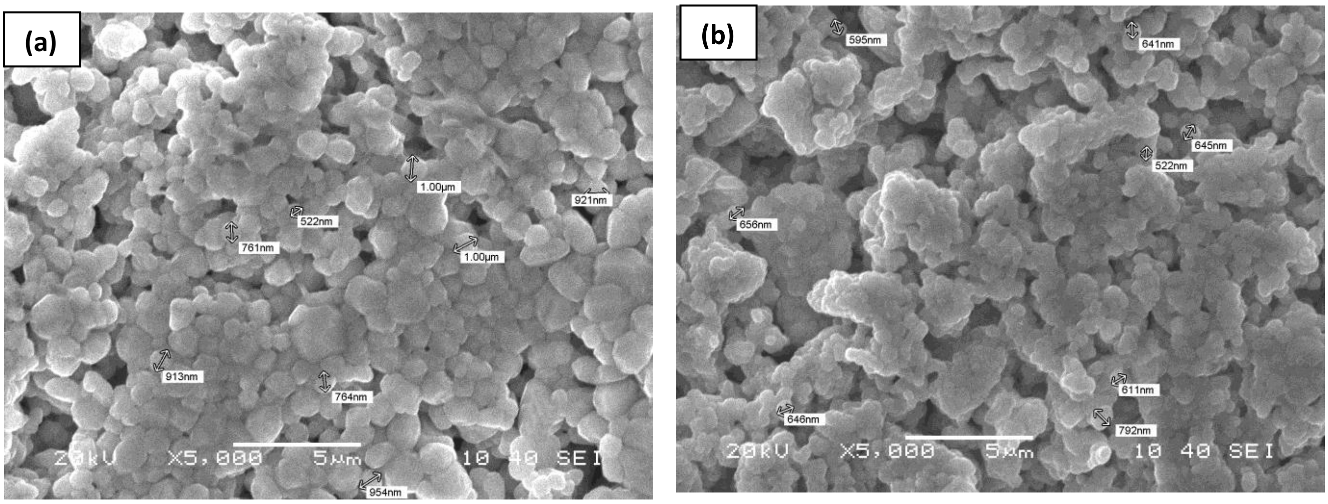


Fig 4.7 Comparative study of SEM of pellet of pH 7 and pH 9

The samples prepared by Solid State method have individual grain size bigger than 1.0µm. it can be observed no agglomeration is there (voids and pores are observable). More or less uniform grain size obtained. And this SEM report can be taken to explain the lower BD or relative density of pellet sintered at 1300^{0}C.

The samples prepared by Auto-combustion method as shown in Fig 4.7 (a) and (b) have individual grain size of sub-micron. Agglomeration takes place in each case i.e. for pH 7, pH 9. Grain size of sub-micron might be producing the dense sample. The particular behaviour of one grain can't be estimated as many grains got agglomerated. For easy study, all grain size marked figure is given in one place.

Dielectric Measurement (at Room Temperature)

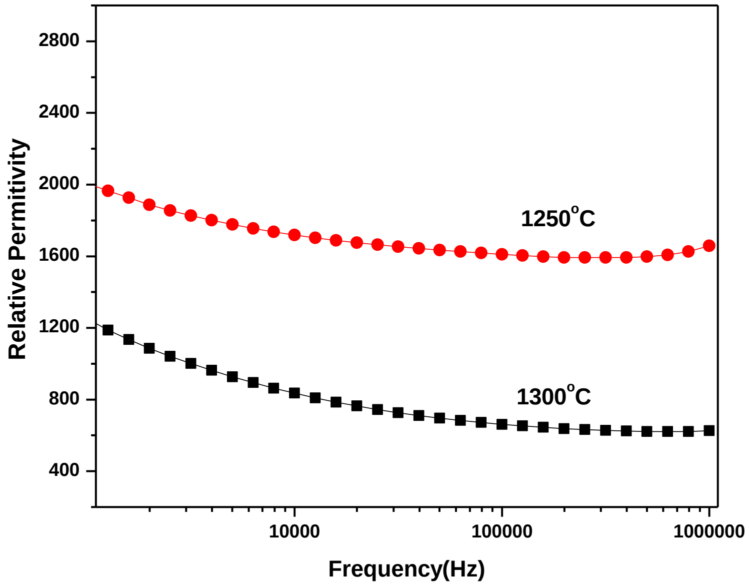


Fig 4.8 Graph of relative permittivity at room temperature of sintered pellet prepared by solid state method

In this Fig 4.8 Dielectric constant Vs. Frequency at room temperature is shown as a function of sintering temperature. The dielectric constant was found to be increased according to the temperature. The increase of dielectric constant may be due to decrease in porosity with increase in sintering temperature. From the microstructure it is found that sintered pellet at 1300^{0}C have less porosity.

In this figure, the frequency dependent dielectric los (tan δ) is shown as a function of sintering temperature at room temperature. The dielectric loss of sample sintered at 1300^0 C is less in the entire frequency range studied. It is also observed that the loss factor or tan δ value decreases with increase in frequency. This high dielectric loss may be compiled due to porosity present in sample of low sintered sample.

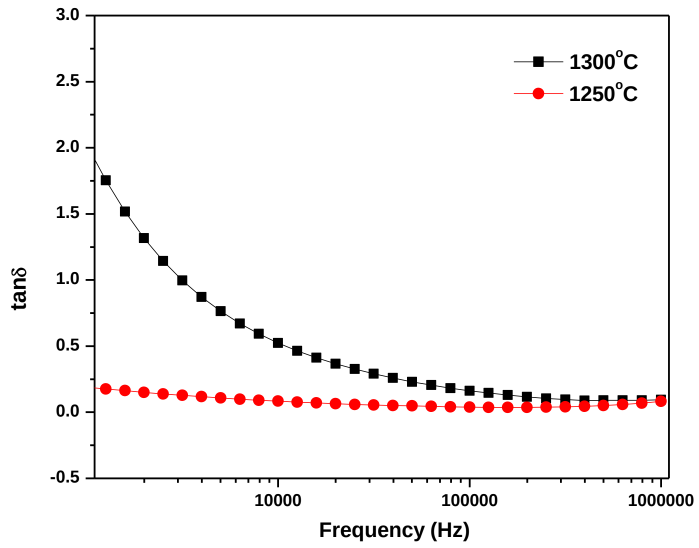


Fig 4.9 Graph of loss factor at room temperature of sintered pellet prepared by solid state method

Dielectric Measurement (at temp. of 200^0C)

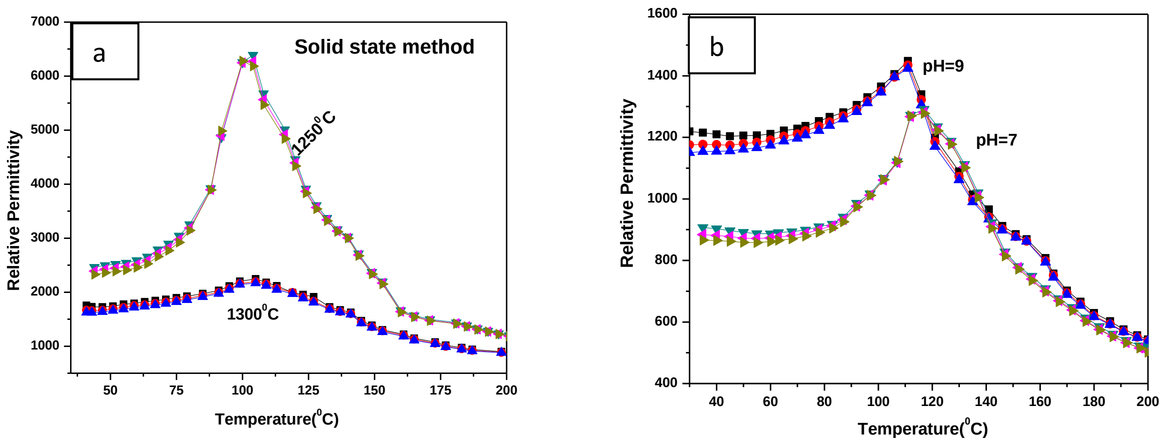


Fig 4.10 Comparative study of relative permittivity at a temperature of 200^0C of pellet (a) sintered at 1250^0C & 1300^0C prepared by Solid state method and (b) pH 7 and 9 by Auto-combustion method

The temperature dependent dielectric constant barium titanate sample sintered at 1250^0C and 1300^0C is studied and given in above figures. Fig 4.10 (a) shows dielectric constant against frequency of sample sintered at 1250^0C. The Observed Curie Temperature from this graph is nearly 107^0C. This indicates that the ferroelectric transition occur will at 107^0C. From fig it is observed that the Curie temperature is at 106^0C. So ferroelectric transition will occur at 106^0C.

Fig 4.10 (b) represents the dielectric constant of sample prepared by auto combustion process at pH of 7 and 9. From this graph it is observed that the Curie temperature is at nearly 119 for samples of pH 9 and 118 for samples of pH 7. The observed increasing order of dielectric constant of pH 9 may be due to the increase in grain size and more relative density than pH 7. Hence the ferroelectric transition is at 118 for samples prepared at pH9 and 117 for samples prepared at pH 7.

Loss Factor

Solid State Method

Fig 4.11 shows the loss factor against temperature with dependency of frequency. The comparative high loss factor of sample sintered 1300^0C may be due to density and microstructure of material. It is the comparative study of loss factor of samples sintered at 1250^0C and 1300^0C

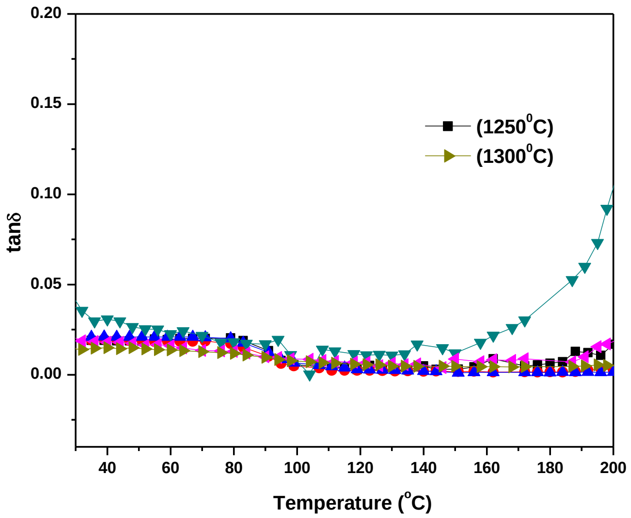


Fig 4.11 Graph of loss factor at a temperature of 200^0 C ofsintered pellet prepared by solid state method

Auto-combustion Method

The fig and fig portraits the loss factor of samples prepared by auto combustion at pH 7 and pH 9. From the figures it is observed that loss factor is low in case of pH 9. And it can be attributed to the microstructure and high dandified body of pH 9.

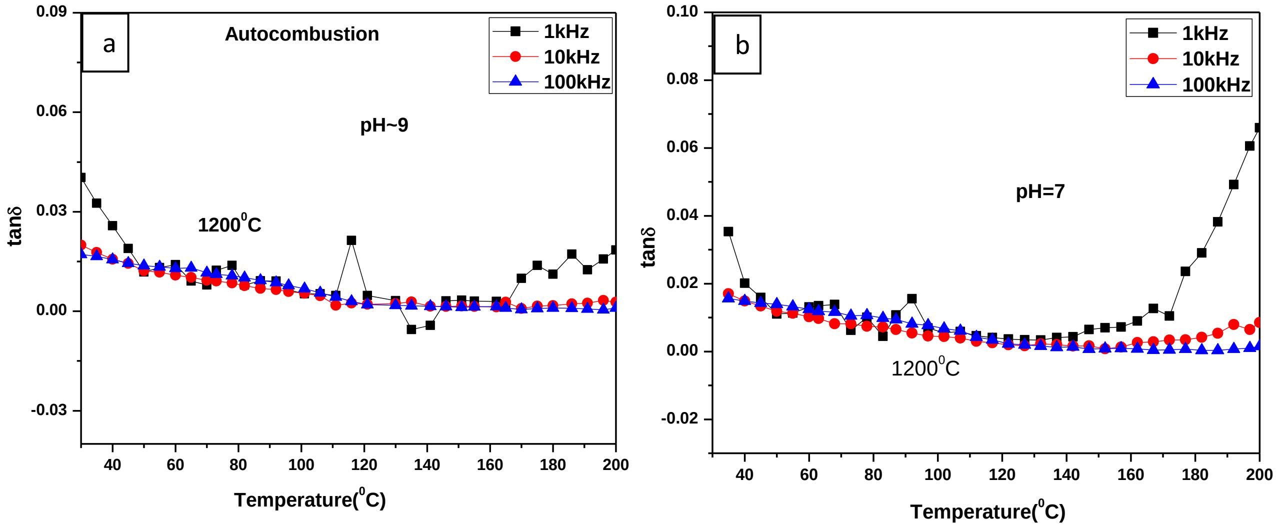


Fig 4.12 Graph of loss factor at a temperature of 200^0 C of sintered pellet prepared by auto combustion method (a) at pH 9 and (b) at pH 7

Chapter 5

Conclusion

Conclusions

Barium titanate powder prepared by Solid State method has pure phase when it is calcined at 1000^0C for 4hr. From the XRD study it can be concluded after a soaking period of 4hr at a temperature 1000^0C there is sharp peak and high c/a ratio tan other samples calcined at low temperature and less soaking time period.

All characterization like XRD, Bulk Density, SEM, and Dielectric Property Measurement at room temperature and at high temperature is done. From these experiments it can be concluded that sintering process should be done carefully as due to this all properties degraded although it is sintered at high temperature. In each case dielectric property is measured.

Pure phase of tetragonal Barium Titanate is obtained by Auto Combustion process. Application area which includes non-hysteretic tenability with relative permittivity value below 1000 these ferroelectrics (reduced grain size) could serve the technical purpose.

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