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Influence of Synthesis Method and the Precursor on the Preparation of Barium Titanate Nano Particles

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Research Article

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ABSTRACT

Different synthesis routes and different starting precursors can have different effects upon the properties of materials. In this paper, two different methods: solid state method, sol-gel method has been used to prepare $BaTiO_3$ powders. $BaCO_3$, $Ba(OH)_2.8H_2O$ and $[CH_3COO]_2Ba$ were used as barium precursor and TiO_2, $Ti[OCH[CH_3]_2]_4]$ as titanium precursor. With the help of thermal gravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscope (SEM), the powder characterization has been compared. The results show that sol-gel derived powders are having larger grain growth compared to solid state powders irrespective of starting precursors. It is also evident that dielectric constant value is a function of grain size. Another important findings are starting precursor also plays a major role especially for the grain size and dielectric constant value. The barium hydroxide octahydrate precursor was showing better result than barium acetate precursor.

INTRODUCTION

Barium titanate is the first ferroelectric ceramic, which exhibit ferroelectric properties at and above room temperature, i.e. up to Curie temperature. Since it has high dielectric constant and low dielectric loss, it is used as capacitors and multilayer ceramic capacitors [1-4]. Barium titanate is a chemically and mechanically stable perovskite, and generally perovskites exhibit primitive cubic crystal structure. But $BaTiO_3$ can exist in five phases in different temperature, listing from higher temperature to lower temperature: hexagonal, cubic, tetragonal, orthorhombic, rhombohedral crystal structure. Even though $BaTiO_3$ can be synthesised using various methods, these methods have a great influence on the structure and properties of the final $BaTiO_3$ powder. The frequently used methods for the synthesis of $BaTiO_3$ are: solid state reaction method, mechanochemical synthesis, wet chemical methods, Low Temperature Aqueous Synthesis (LTAS), Low Temperature Direct Synthesis (LTDS), combustion synthesis, solvothermal synthesis, oxalate route, microwave heating, micro emulsion process and different chemical routes. Wet chemical methods include sol-gel process, hydrothermal process, coprecipitation method and polymetric precursor method [5-10]. Each method has its own advantages and disadvantages.

Here we used two methods for the synthesis of $BaTiO_3$ and they are solid state reaction method and sol-gel process. Solid state reaction method is a simple method for the preparation of $BaTiO_3$ and it has higher productivity and lower cost. In Sol-gel method chemical precursors first converts into a sol and then to a gel which on drying and sintering gives amorphous oxides. Sol-gel also needs high temperature for sintering like solid state method otherwise there is a chance for the presence of hydroxides. The reaction parameters such as reaction time and reaction temperature can be varied to optimize reaction in order to get highest value of dielectric [11]. Not only the synthesis method and reaction parameters but also the starting precursors have great role in the quality of the product [12]. Therefore we tried to synthesis $BaTiO_3$ from different starting reagents. The samples are then characterised using XRD, SEM, TGA-DTA, dielectric studies and frequency dependence to optimize the starting material and the method of preparation.

EXPERIMENTAL WORK

Barium titanate was synthesized using three different barium sources and two titanium sources. Two methods were used for the synthesis of Barium titanate: solid state reaction method and sol-gel process.

Solid State Process (Ssbc@900)

The Barium titanate powder is synthesized from barium carbonate (99% Purity) and titanium dioxide (99.9% Purity). The $BaCO_3$ and TiO_2 are mixed in 1:1 ratio. The equimolar dried $BaCO_3$ and TiO_2 powders are weighed accurately and mixed in an agate mortar and pestle for 2 h in acetone medium. The powder mixture is dried and kept at 60 °C. The sample is calcined at 900 °C for 3 h with heating and cooling rates of 3 °C/min. The calcined powder is grinded in a mortar pestle to obtain fine powder. The chemical reaction for the $BaTiO_3$ formation by heating $BaCO_3$ and TiO_2 powder mixture is: $BaCO_3+TiO_2 \rightarrow BaTiO_3+CO_2$. The flow chart for the preparation of $BaTiO_3$ using solid state method is given in **Figure 1**.

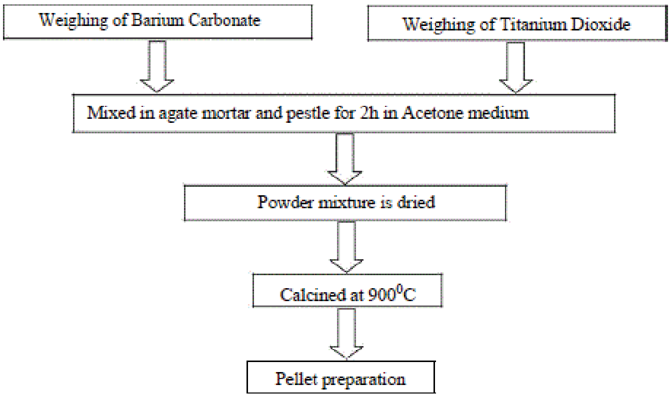

Figure 1. Flow diagram of Solid State Method for the preparation of $BaTiO_3$ (SSBC@900).

Sol-Gel Process (SGBA@900)

$BaTiO_3$ powder is synthesized by using barium acetate (chemical formula: $[CH_3COO]_2Ba$), TITP (chemical formula: $[Ti[OCH[CH_3]_2]_4]]$) as precursors. Acetic acid (CH_3COOH) is used as solvent and 2-methoxy ethanol is used to stabilize titanium (1 V) iso-propoxide. Barium acetate (8.5 g) is dissolved in acetic acid (35 ml) by continuous magnetic stirring at 60 °C for half an hour. The solution is then refluxed at 110 °C for 2 h. Titanium (IV) iso-propoxide (0.11 mol) is dissolved in ethanol (C_2H_6O) and 2-methoxy ethanol is added to it to form a separate solution at room temperature. Ba solution is added drop by drop, into Ti solution and pH of the solution is maintained in the range of 8- 9 by adding buffering agents as KOH. The barium acetate and TITP are added in 1:1 ratio. Refluxing the mixture again resulted in the formation of a thick white gel.

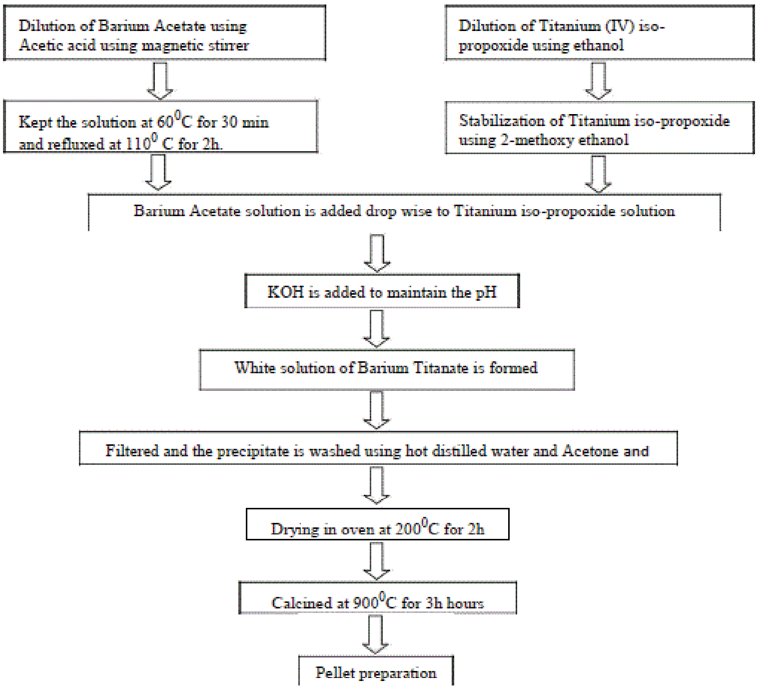

Figure 2. Flow diagram of Sol-Gel Method for the preparation of $BaTiO_3$ using Barium Acetate and TITP (SSBA@900).

Distilled water is added to the gel and the solutions are mixed by stirring on a hot plate with a magnetic stirrer. The solution is then filtered and washed using hot distilled water and acetone. It is kept in the oven and heated to 200 °C for 2 h. The powder is then calcined at 900 °C in a muffle furnace with heating and cooling rates of 3 °C/min. The calcined powder is grinded in a mortar pestle to obtain fine powder. The flow chart for the preparation of BT by sol-gel method using barium acetate and TITP is given in **Figure 2**. The chemical reaction for the $BaTiO_3$ formation is as follows:

$BaCO_3+TiO_2 \rightarrow BaTiO_3+CO_2.$

$2Ba(CH_3COO)_2=2BaO+4CO_2+6H_2O$

$BaO+CO_2=BaCO_3$

$(C_3H_7O)_4Ti \rightarrow TiO+2C_3H_6+2C_3H7OH$

$xBaCO_3+TiO_2 \rightarrow BaTiO_3+CO_2.$

Sol-Gel Process (SGBH@900)

The $BaTiO_3$ powder is synthesised using barium hydroxide octahydrate ($Ba(OH)_2.8H_2O$) and TITP ($[Ti[OCH[CH_3]_2]_4]]$) as precursors. During synthesis, the aqueous solution of $Ba(OH)_2.8H_2O$ is prepared by dissolving 6.891 g of $Ba(OH)_2.8H_2O$ in water (64 ml). Simultaneously TITP (5.9373 ml) is taken in a conical flask. Then 14 ml ethanol (C_2H_6O) is used as the reactive solvent. 2-Methoxy Ethanol (2 drops) is added to stabilize TITP. The aqueous barium solution is added drop wise in the Titanium solution under continuous stirring. The weighed amount of NaOH (48 g) is dissolved in 100 ml of distilled water to prepare 12 N alkaline solution. The 12 N NaOH solution is added to maintain the pH of the reaction as pH=8-9. During the reaction the mixture is stirred continuously with high speed to avoid any agglomeration and for preparing the homogeneous solution. After complete addition of reagents in the required amount the temperature of the reaction is increased from 40°C to 100°C. The reaction is carried out for 80 minutes. After 12 h of aging $BaTiO_3$ suspension is filtered and washed using hot distilled water and acetone to remove barium carbonate and kept for 48 h. It is then calcined at 900°C in a muffle furnace with heating and cooling rates of 3°C/min. The calcined powder is ground in a mortar pestle to obtain fine powder. The flow chart for the preparation of BT by sol-gel method using barium hydroxide octahydrate and TITP is given in **Figure 3**. The chemical equation for the reaction is:

$$15Ba(OH)_2+Ti(OCH(CH_3)_2)_4+C_2H_6O+21O_2 \rightarrow BaTiO_3+14BaCO_3+32H_2O$$

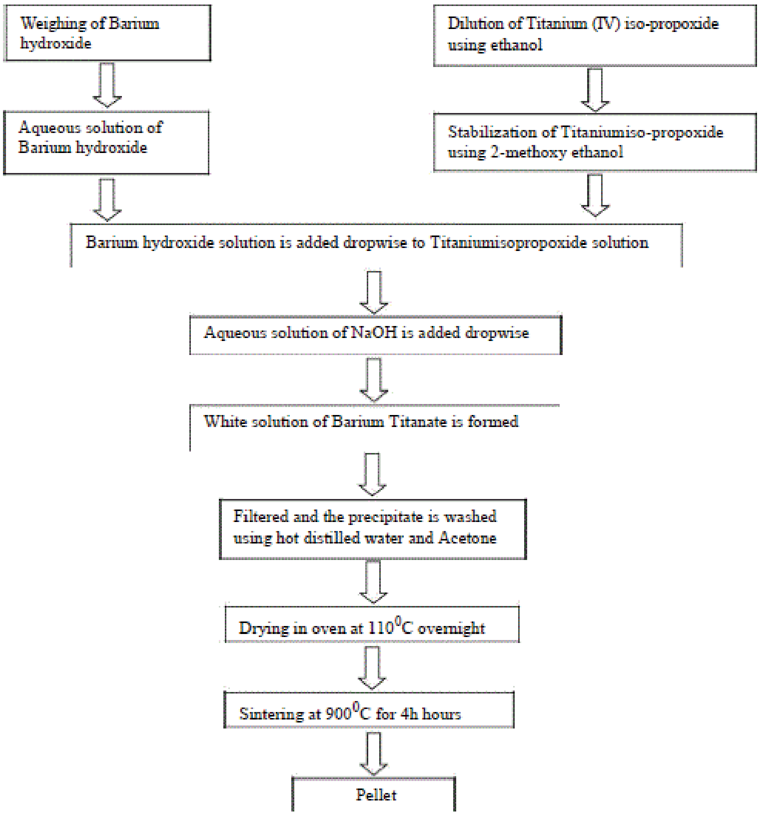

Figure 3. Flow diagram of Sol-Gel Method for the preparation of $BaTiO_3$ using Barium Hydroxide Octahydrate and TIT (SSBH@900).

Characterization

The crystalline structure of the calcined powder is investigated by X-ray powder diffractometer using CuKα (λ=1.5406 Å) radiation in a wide range of Bragg angle 2θ ($15° \leq 2\theta \leq 70°$) with a scanning step of 0.0198691. The crystalline size is measured from X-Ray diffraction pattern using Scherer Equation $\tau=K\lambda/\beta \cos(\theta)$ where, τ is the mean size of the particle, K is a dimensionless shape factor with a typical value of about 0.9, λ is the wavelength of the CuKα radiation (λ=0.15406 nm), β is the line broadening at half the maximum intensity and θ is the Bragg angle in degrees. Pellets of powdered samples of $BaTiO_3$ were prepared by adding Poly Vinyl Alcohol (PVA) as a binder. Binder (PVA) is prepared by dissolving 1.2 g of PVA in 100 ml water and makes it into 10 ml by boiling. After adding the binder into the prepared powder sample is uniaxially pressed into cylindrical pellet of diameter 12.96 mm and thickness 3.323 mm using a hydraulic press at a constant pressure of 3.5 tons. The pellets are heated to 900°C for 1 h in a silica crucible to remove the binder. Thermal behaviour of the samples was observed using the thermo gravimetric analysis system. The microstructure and morphology of the sintered Barium titanate are characterized by Scanning Electron Microscopy. Curie temperature and the dielectric constant of the sample in temperature range 27°C to 161°C were measured. The dielectic constant, dissipation factor and resistivity are measured at room temperature for varying frequency using LCR meter. The spontaneous polarization (Ps), coercive field (Ec) and the breakdown voltage (Eb) were obtained from the ferroelectric hysteresis loop observed at 1 to 10 Hz using a ferroelectric tester system (Radiant Technologies, Inc., RT66A) (**Table 1**).

Table 1. Method and Precursors.

Sample	Method	Precursors
SSBC@900	Solid State Method	Barium Carbonate and Titanium dioxide
SGBA@900	Sol-Gel process	Barium Acetate and Titanium tetra isopropoxide
SGBH@900	Sol-Gel process	Barium Hydroxide and Titanium (IV) isopropoxide

RESULTS AND DISCUSSION

X-Ray Diffraction

Figure 4 shows the X-Ray diffraction pattern of SSBC@900, SGBA@900 and SGBH@900. It is evident that the prepared $BaTiO_3$ samples are in simple cubic phase because the observed peaks are at 22.25°, 31.52°, 38.97°, 45.31°, 50.95°, 56.61°, 66.31°, and 70.61°, respectively. Corresponding Miller indices are (001), (110), (111), (200), (210), (211), (202), (212), and (311), respectively. It shows sharp peaks for all three samples. When comparing the three XRD graphs $BaTiO_3$ prepared by sol-gel method using Barium hydroxide and TITP show high intense peaks. The peaks observed in XRD pattern of sol gel samples were appears slightly shifted towards lower 2θ angles compared to solid state sample. This may be due to the change in lattice parameter and that is evident from the particle size measurement. **Table 2** gives the particle size of the samples calculated from the famous Scherrer equation. It is found that particle size for all samples prepared using different methods is almost same.

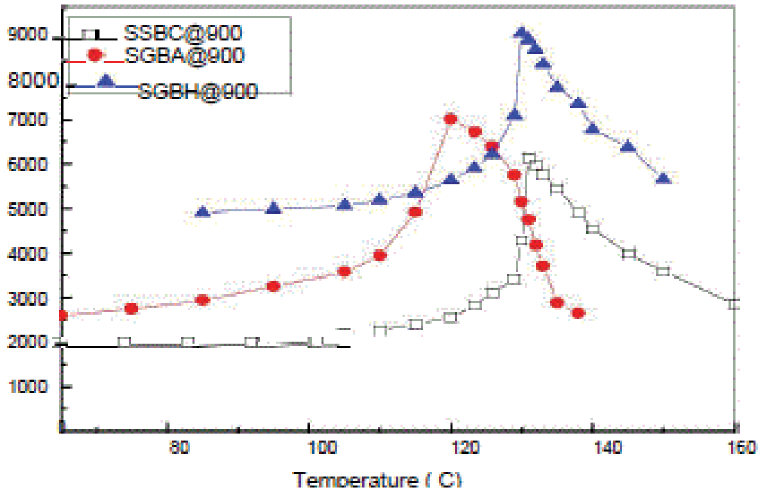

Figure 4. XRD pattern of $BaTiO_3$ prepared using different starting materials by Solid State and Sol Gel Process.

Table 2. Particle size in Nanometre.

Sample	Particle size (nm)
SSBC@900	39.07
SGBA@900	35.0319
SGBH@900	35.0731

Dielectric Behaviour of the Samples

Figure 5 shows the variation of dielectric constant as a function of temperature. All the samples have curves similar to the standard dielectric curve of $BaTiO_3$ i.e., dielectric constant value gradually increases with temperature, and then suddenly reaches a peak value at Curie temperature and then decreases. The Curie temperature and corresponding dielectric constants are tabulated below **Table 3**.

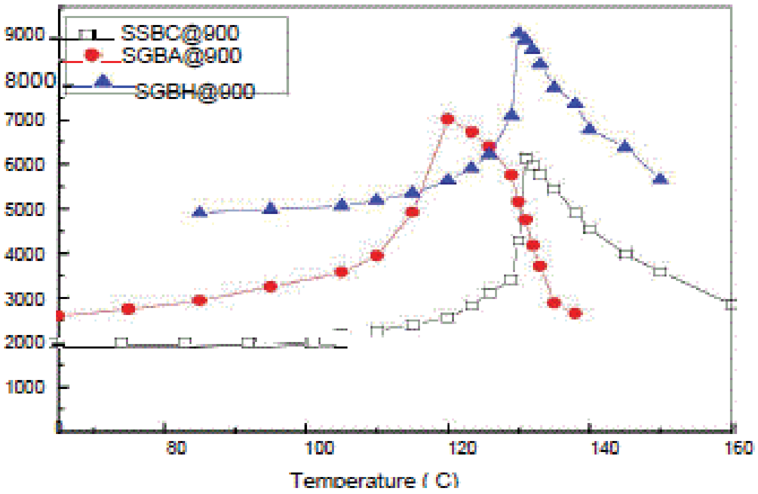

Figure 5. Variation of dielectric constant with temperature

Table 3. Curie temperature and dielectric value of different samples of $BaTiO_3$.

Sample	Curie temperature (°C)	Dielectric constant
SSBC@900	131	6140
SGBA@900	120	7007.40
SGBH@900	130	8943.20

From the table it is evident that SGBH@900, prepared from Barium hydroxide octahydrate and TI TP, shows high dielectric constant compared to the remaining three samples. The dielectric constant of SGBH@900 is 8943.2117 at 130°C (Curie temperature).

Microstructure of the Samples

Scanning Electron Micrograph showing the morphology of Barium titanate pellets prepared by different precursors under same magnifications in **Figure 6a-6c**. It is seen that Barium titanate particles are well dispersed. The sizes of the crystals vary in a relatively wide range between 1 and 5 µm and some of them form micro aggregates with different shapes. A small amount of pores with dimensions corresponding to the crystalline phase size is uniformly distributed in the sample volume. The sol-gel powders are of high reactivity, but very often agglomeration-aggregation phenomena favours the presence of large pores which leads to grain coarsening and difficult sintering [13,14]. The density of Sol Gel prepared samples is higher as compared to the Solid State preparation. It is clear that the grain growth found to be enhanced which helps in densification. This is expected to happen due to the sol-gel procedure involves molecular level mixing and results in the homogeneous material formation. Sol-gel is process which avoids contamination of the material and yields better stoichiometric control. It provides a better grain size and grain shape control. It controls the crystallinity and dispersibility of synthesised $BaTiO_3$ nanoparticles [15]. The results also suggested that optimising the size and starting precursor could control the final grain size. Mechanical grinding of precursor changes the morphology from large rode like grains to small spherical shape **(Figure 6)**.

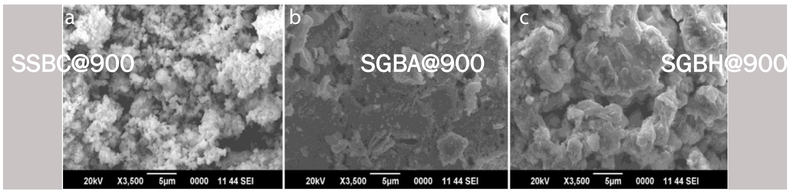

Figure 6: (a-c) SEM Micrographs of sintered $BaTiO_3$ Prepared by (a) Solid-State process; (b and c) Sol-gel Process.

Thermal analyses (TGA, DTA,) of the $BaTiO_3$ powder precursor prepared by solid state process and sol gel are shown **Figure 7a-7c**. The TG and DTG of the gel were carried out at a heating rate of 20°C/min up to 900°C, in air. The DTA curve of two sol gel samples (SGBA@ and SGBH@900) shows one sharp endothermic peaks at 95 to 100°C and corresponding to the volatilisation of absorbed water on the grain surface, isopropanol and acetic acid and, to the evaporation of methoxy ethanol respectively. The second major weight loss that occurs in the temperature range 225 to 280°C is due to the pyrolysis of the organic groups (exothermic peak). A further exothermic peak at 620°C probably due to the crystallization of the perovskite phase. The last exothermic peak observed in the temperature domain 732-760°C is associated with the decomposition of small amounts of barium carbonate formed by decomposition of acetyl groups. But in the case of solid state precursor the starting exothermic peak at 130.9°C was absent because the amount of water content is minimum that sample.

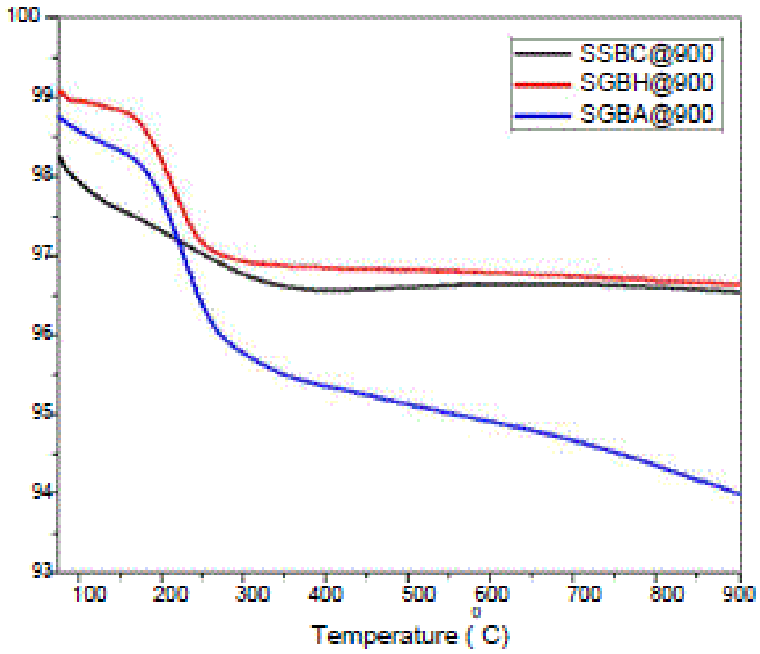

Figure 7. TG image of SSBC@900, SGBA@900 and SGBH@900.

Frequency Dependence of the Optimized Sample

Frequency studies on the optimized sample were conducted using LCR meter. Various factors such as dielectric constant, resistivity and dissipation factor were studied. The dissipation factor, D, of any material describes quantitative dissipation of the electric energy due to different physical processes such as electrical conduction, dielectric relaxation, dielectric resonance and losses from nonlinear processes such as hysteresis (Burfoot 1967). When we measure the dielectric loss at a single frequency, we cannot, in general, distinguish between them. They all give rise to just one measurable quantity, namely, the total measured D. The variation of D against frequency is shown in **Figure 8a**. It is observed that D increases with increasing frequency and attains highest value at around 10 kHz. Electrical resistivity is an intrinsic property that quantifies how strongly a given material opposes the flow of electric current. The dissipation factor (D) is a measure of loss-rate of energy.

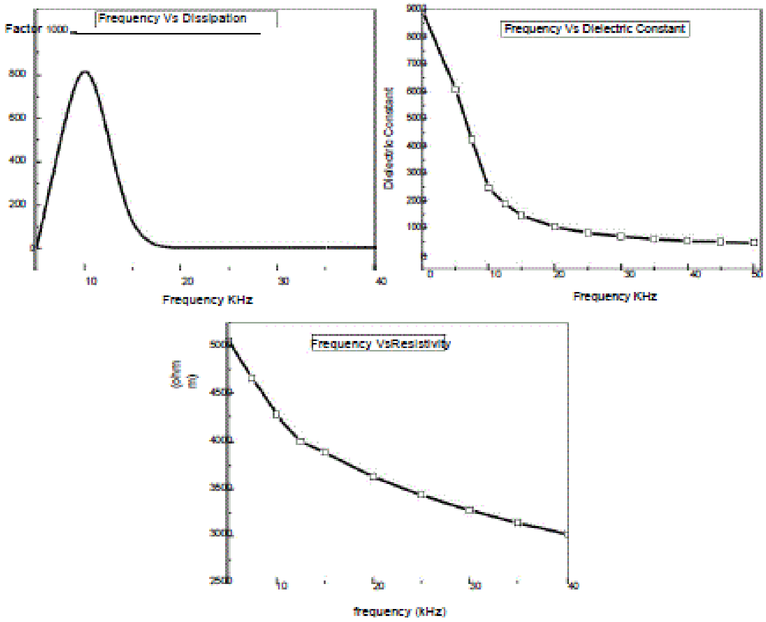

Figure 8. Frequency vs. Dielectric Properties of SGBH@900

Figure 8 shows the dependence of frequency with dielectric constant. As frequency increases dielectric constant decreases. At zero frequency it coincides with the dielectric constant measured at room temperature in the temperature vs. dielectric constant studies (**Figure 5**). Resistivity also shows similar behaviour as that of dielectric constant. Since the dielectric constant is the study of capacitance, the ability of a body to store an electric charge. It same as the ability of a material to oppose the flow of electric charge (resistivity). **Figure 9** shows the polarization versus electric field (P-E) curves at RT for the samples prepared by sol-gel route using the precursor Barium Hydroxide and Titanium (IV) isopropoxide for different frequencies. Since the stability of the ferroelectric phase can be determined by structural transition with additional factors like incorporation of foreign atoms [16]. It is evident that persistence of ferroelectricity results from the long-range polar orders of dipoles [17]. Any disruption in the polar order would affect the ferroelectricity. Generally, reduction of polarization occurs due to reduction in grain size [16], the presence of structural imperfections such as oxygen vacancies and dislocations [16]. It is also observed that the value of coercive field (Ec) remains high and the maximum polarization value reduces sharply (P-max) as the frequency increases.

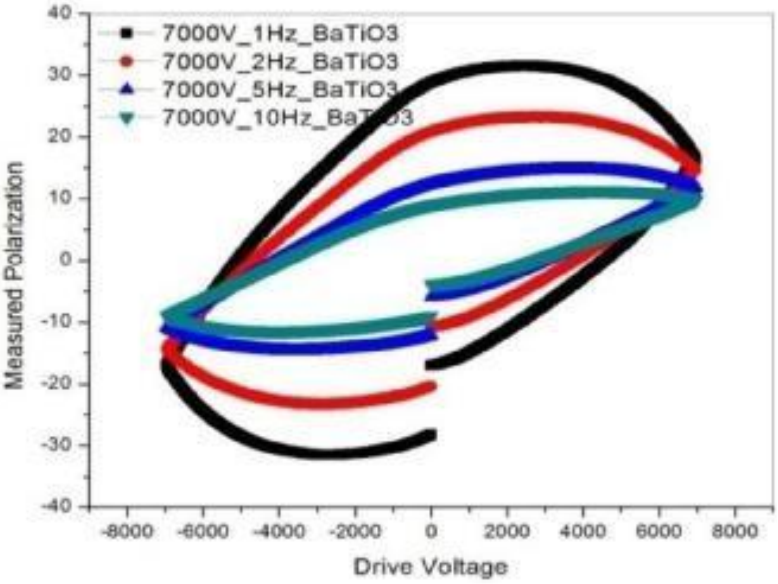

Figure 9. The room temperature P-E loops of $BaTiO_3$.

CONCLUSIONS

Based on XRD, dielectric study and SEM results it has seen that though SSBC@900, prepared using solid state reaction method, shows better dielectric properties, it has pores in the structure arises due to some defects in the morphology. SGBA@900, prepared from Barium Acetate and TITP has weak crystallisation occurred and very low dielectric constant. Therefore it can be concluded that the $BaTiO_3$ powder produced by sol-gel process using Barium hydroxide octahydrate and TITP, is the best method of preparation. It has intense and sharp peaks formed during crystallisation and shows high dielectric constant at Curie temperature 130°C.

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