Dielectric and Microstructural Properties of PbO Doped $BaTiO_3$

Shoumya Nandy Shuvo, Sujit Saha, Md. Miftaur Rahman

Abstract:-The Barium Titanate ($BaTiO_3$) based ceramics has potential technological applications in multilayer Ceramics Capacitors (MLCC), thermistors, self-regulating electric heating system, transducers etc. The aim of the research is to find out the structural modifications and corresponding change in properties of $BaTiO_3$ when small amount of glass was added. Lead oxide (PbO) was used as glass for the doping which was in the powder form. In this research the effects of different level of PbO doping, sintering parameters and dielectric properties of PbO doped $BaTiO_3$ were observed and studied. At first, PbO was mixed with pure $BaTiO_3$ nanopowder at two different compositions by ball milling. Mixed powder was dried and after the addition of binder, the powder was pressed into pellets with the 5 ton pressure. After that, the green pellets were again dried. Then sintering was done at 800^0C in a muffle furnace. After sintering, percentage theoretical density was measured. Then, using the 'Precision Impedance Analyzer', Dielectric constant, Dielectric loss and Capacitance were observed for the two different doping levels up to 10MHz frequency. Scanning electron microscopy (SEM) of the sample was then performed to observe the microstructural properties precisely. The result of the experiment was quite fascinating. It is found out that by modifying the sintering parameters and doping level of PbO with $BaTiO_3$, better dielectric properties can be attained. Scanning Electron Micrograph indicates that by increasing the doping level of PbO, grain refinement is possible within 100nm range with precise uniformity.

Keywords: Barium Titanate based ceramic, Nano-doping, Di-electric constant, Di-electric loss, Grain refinement

I. INTRODUCTION

Barium titanate is the harbinger of electronic ceramics which is obviously the first ferroelectric ceramics and a good candidate for a variety of applications due to its excellent dielectric, ferroelectric and piezoelectric properties [1]. In fact, the discovery of barium titanate led to a series of discoveries of many new ferroelectric substances, on which interesting studies, both experimental and theoretical, have been carried on. The discovery of barium titanate is most significant in that it is useful from the technological point of view [2,3] Barium titanate ($BaTiO_3$) is a very attractive material in the field of electroceramics and microelectronics due to its good characteristics.

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Its high dielectric constant and low loss characteristics make barium titanate an excellent choice for many applications, such as capacitors, multilayer capacitors (MLCs) and energy storage devices. Doped barium titanate has found wide application in semiconductors, positive temperature coefficient resistors, ultrasonic transducers, piezoelectric devices, and has become one of the most important ferroelectric ceramics [4,5]. Moreover the excellence of its piezoelectric properties is unsurpassed by any other piezoelectric material. Therefore, it is now beginning to be used for electro-mechanical transducers or electro-acoustic transducers and will surely gain very wide fields of application in future. The properties of $BaTiO_3$ have been the subject of study of many authors. It is well known that the properties of $BaTiO_3$ powders and ceramics strongly depend on the synthesis route and sintering regime. In this paper, the electric, dielectric and piezoelectric characteristics and applications of $BaTiO_3$ ceramics were studied. Despite the advantages offered by $BaTiO_3$ regarding small size capacitors their use is limited by number of operating variables [6]. The electric field strength and the operating temperature are strong determinants of dielectric constants. Dielectric properties also vary significantly up on the following factors:

a) Size of individual grain and grain boundaries
b) Presence and distribution of the impurity
c) Stress imposed by surrounding grains
d) Presence of second phase particle
e) Condition of the material at the start of manufacturing
f) Procedure of manufacturing and various processing variables [7,8]

The dependence on temperature along with other properties such as the dielectric constants can be modified by forming solid solutions or doping the base perovskite with a range of composition. Successful attempts are made to substitute the atoms of perovskite from different lattice positions. e.g. the corner atoms or atoms positioned at the octahedral holes. For example, in $BaTiO_3$,Ba^{2+} is replaced by Pb^{2+}, Sr^{2+} ions .Similarly the Ti^{2+} is replaced by Zr^{4+}, Hf^{4+} [9-11]. Such doping brings certain modification to the structure of the perovskite which lead to versatility in the dielectric properties. Therefore, a considerable effort has been given to the development of best composition along with associated forming characteristics to improve the dielectric characteristics [12].

II. METHODOLOGY

1. Raw Materials and their characterization

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Barium titanate in pure nano powdered form is the main raw material in this experiment and Lead(II) oxide or Lead Monoxide which is also in powder form is used as dopant to get a glassy phase.

$BaTiO_3$ powders belongs the white crystals and this powder is odourless. Melting point of $BaTiO_3$ is 1625^0C with a density of $6.02g/cm^3$ [13]. Compared to $BaTiO_3$, lead (II) oxide is yellowish powder and has a lower melting point of 888^0C with a density of $9.53g/cm^3$.[14]

2. Sample Preparation

For making the expected disc type samples, two types of compositions are taken into consideration. Table 1 and Table 2 shows two types of samples which are doped with the different percentage of PbO powder.

Table 1: Doping level of PbO in BaTiO3 in Sample 1

Raw materials	Weight of raw materials(gm)	Doping level
$BaTiO_3$	15 gm	20%
PbO	3gm	

Table 2: Doping level of PbO in BaTiO3 in Sample 2

Raw materials	Weight of raw materials(gm)	Doping level
$BaTiO_3$	25gm	16%
PbO	4gm	

2.1 Ball milling

The powders are taken to a laboratory type pot mill which contains yttria (Y_2O_3) stabilized zirconia balls. The balls are of two types based on their size. One size is 3 mm and other is 5 mm. The balls and pots must be cleaned ultrasonically to remove slightest of dust which may show up as impurity in the final structure with resultant harmful properties. The balls stay at the bottom and powders stay on balls. Then acetone is added in sufficient quantity which acts as the milling media. After that, the mouth of pot is closed tightly and then shaken to mix the ingredients. Then powders are milled for 16 to 20 hours so that all the zirconia can be mixed with barium titanate.

2.2 Drying

After milling, the powders containing acetone are separated from the balls very carefully. Then powders are dried; for quick drying powders are kept at 100^0C for 2 to 3 hours. It's very important to dry the powders completely otherwise they cannot be pressed.

2.3 Preparation of Binder

As binder, Poly vinyl alcohol (PVA) is the best choice for PbO doped $BaTiO_3$ powder. To get proper strength of binder, the composition is a great factor. At first, in a bicker 10gm of powders are taken along with 100cc of distilled water. Then the bicker containing that mixture is put onto the burner for heating. And the mixture is heated about to 70^0C temperatures. And the mixture is becoming viscous .The mixture is slowly stirred until the mixture became transparent .Stirring is done to remove the bubbles. After the heating period completed, the temperature of the binder is taken down to the room temperature.

2.4 Mixing binder with sample

After the preparation of the binder the, binder is mixed with the sample. 5 drops of binder is used for the sample-1, and 6 drops of binder is added to sample-2. During addition, the stirring is must which is needed to avoid agglomeration .Even after the addition the stirring is done for 20-25 minutes to avoid agglomeration and to get uniform and fine powders. The stirring is done by a stirrer.

2.5 Drying

To remove all the moisture and acetone the samples are kept in a oven at about to 100^0C for 1 hour .Drying is needed because moisture have a negative effect during pressing .

2.6 Compaction

After mixing with binder and drying, the powders are taken for compaction. Compaction is done by only pressing .The parts of the pressing die is cleaned carefully with acetone. Samples are uniaxially pressed into pellets .During pressing the pressure is about 5 ton . And the holding time is just 2 minutes.

2.7 Sintering

Sintering is a very important part of this experiment. A Muffle furnace is used to sinter the pellets. At first, alumina powders are kept in a crucible and then Pellets were kept into the crucible on the alumina powders. There is an alumina plate in the furnace and some alumina powders are being spread over the plate. This makes an alumina bed in the furnace which is necessary to protect the furnace from contamination. Then the crucible is placed on that alumina bed [21]. In sintering process, the heating and cooling cycle depends on the raw materials behavior during heating & cooling and their melting points and their properties. At first, the samples were heated to 450^0C at the rate of 3^0C per minute. And then hold the samples at that temperature (450^0C) for 2hr. Then again heating is done up to 800^0C at 5^0C per minute. And then second holding period is given for 2 hour .After the holding period the samples are cooled to the room temperature at rate of 4^0C per minute. Figure 1 shows the sintering cycle of the samples.

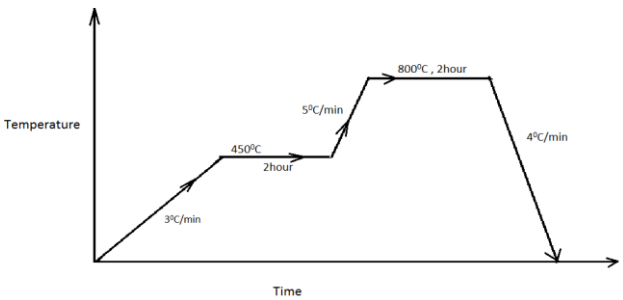

Fig. 1: Sintering cycle

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3. Property measurement

3.1 Percent theoretical density

After sintering stage, the weight is taken of different samples of two types of compositions. Then average weight is calculated .after that the dimensions of those samples are measured by using a digital slide calipers or called a micrometer .These measured resultant densities are then compared to theoretical densities .And then this will be expressed as percent theoretical density .

3.2 Dielectric properties

At first, the samples are coated with silver coating. Dielectric properties of samples were measured using an in precision impedance analyzer [WAYNE KERR 6500B series]. All the measurements were subjected to AC current only both room temperature and high temperature frequency dependency were measured. Dielectric constant was measured from the capacitance value obtained from the analyzer according to equation as below-

$$k' = \frac{C_p\, d}{\epsilon_0 A} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where k' is the dielectric constant, C_p is the capacitance value measured by the impedance analyzer, d is the thickness of the sample, ε_0 is the permittivity of vacuum, A is the area of the sample in contact with the conducting layer [19,20]. A tube furnace type oven and custom sample holder was used at the department of MME. This set up was used to heat the sample during high temperature property measurement.

3.3 Scanning Electron Microscopy (SEM)

At first, the samples are coated with 'Pt' by auto fine coater. This nano ranged coating is done for 20 second. The coating is given to the sample to increase the conductivity of the surface .and another reason is to reduce the emitted charge.
After the coating, the sample is taken into scanning electron microscope. Samples are placed into the microscope. At that time, the distance between the sample and lens column is taken down to 8mm from 32 mm. The voltage is given in the microscope 5kvolt .Then microstructure of the sample is seen through the monitor which is connected with the microscope.

3.4 Energy dispersive spectroscopy (EDS)

After the SEM test, the EDS is done with using the same machine .With EDS in an electron microscope, we can obtain elemental analysis while examination the microstructure of materials. In this operation voltage was kept 5kV.

III. RESULTS & DISCUSSIONS

Percentage of Theoretical density measurement

To measure the percentage of theoretical density of lead oxide doped Barium titanate , mass and volume of sintered samples are taken by calculation. Firstly, the samples were polished softly with clean cloth or paper. Density of $BaTiO_3$ = 6.02g/cm^{3}and Density of PbO= 9.53 g/cm^3.

For sample: 1

PbO= 20%, $BaTiO_3$=80%
Theoretical density = 6.722 g/cm^3
And , measured density can be found by the equation :

$$\text{Density} = \frac{m}{\pi\frac{d^2}{4}\times t}$$

where, Average mass (m) =0.948g
Average Diameter (d) =11.90mm.
Average thickness (t) = 1.91 mm
So, the density will be =4.462 g/cm^3
And the percent theoretical density

$$= \frac{measured\ density}{theoretical\ density}\times 100\%$$

$$= \frac{4.462 g/cm^3}{6.722 g/cm^3}\times 100\%$$

$$= 66.37905\%$$

For sample: 2

PbO = 16%, $BaTiO_3$=84%
Theoretical density = 6.6052 g/cm^3
And, measured density can be found by the equation:

$$\text{Density} = \frac{m}{\pi\frac{d^2}{4}\times t}$$

Where, Average mass (m)=0.9707g
Average Diameter (d)=11.49mm.
Average thickness (t)=1.88 mm
So, the density will be =4.9796 g/cm^3
And the percent theoretical density

$$= \frac{measured\ density}{theoretical\ density}\times 100\%$$

$$= \frac{4.9796 g/cm^3}{6.6052 g/cm^3}\times 100\%$$

$$= 75.39\ \%$$

Uniaxial press was needed for pressing the green samples (pellets) from the powder. Some parameters are very important for pellet preparation. The parameters are pressure, holding time and thickness of the sample. These parameters must be optimized to get good green samples, which may give the good results. Pressure was applied slowly to the samples to achieve uniform distribution of pressure throughout the sample. The holding time is another important parameter. The holding time for the load is 2 minutes. For both types of samples porosity is very large. In sample 1 where doping level is 20%, the porosity is 33.23% and at the sample no 2 where doping level is 16%, the porosity is 24.61%. The reason for this porosity may be due to lack of uniformity in the pressing or compaction. The porosity has decreased upon increasing the percentage of dopant, i.e, PbO.

Dielectric properties

Silver paste was painted on the samples. Samples were then connected with impedance analyzer and the dielectric properties were measured.

For sample 1:

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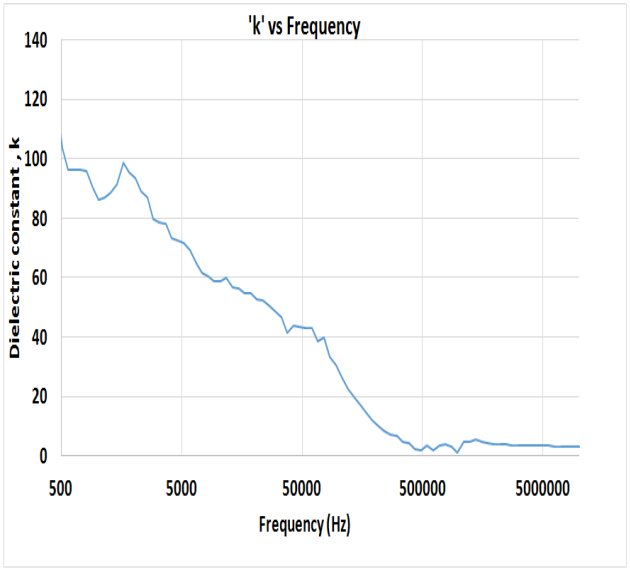


Fig. 2: Dielectric constant vs frequency of sample 20% Lead oxide doped Barium Titanate at room temperature

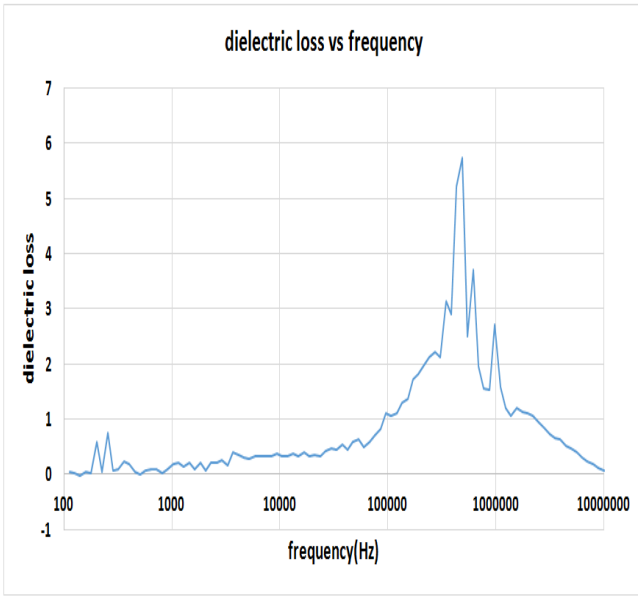


Fig. 3: Dielectric loss vs frequency of sample 20% Lead oxide doped Barium Titanate at room temperature.

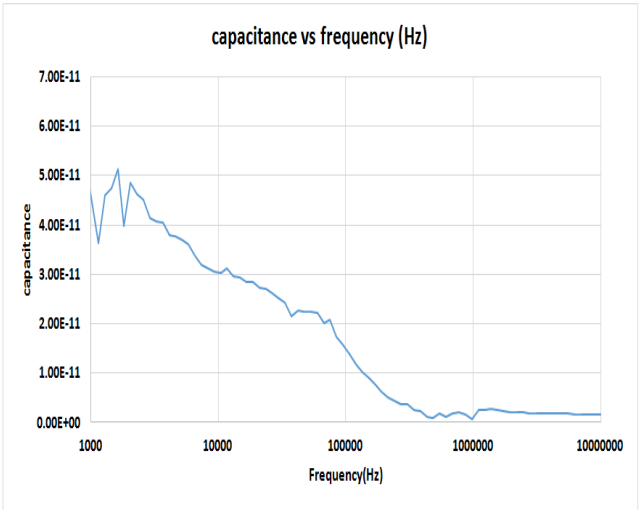


Fig. 4: Capacitance vs frequency of sample 20% Lead oxide doped Barium Titanate at room temperature.

For sample 2:

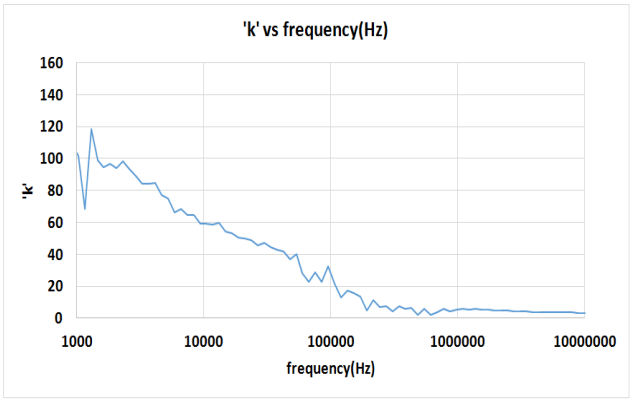


Fig. 5: Dielectric constant Vs Frequency of sample 16% Lead oxide doped Barium Titanate at room temperature.

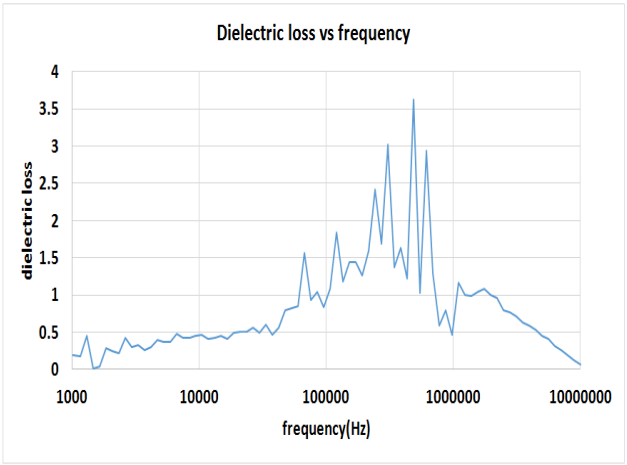


Fig. 6: Dielectric Loss Vs Frequency of sample 16% Lead oxide doped Barium Titanate at room temperature.

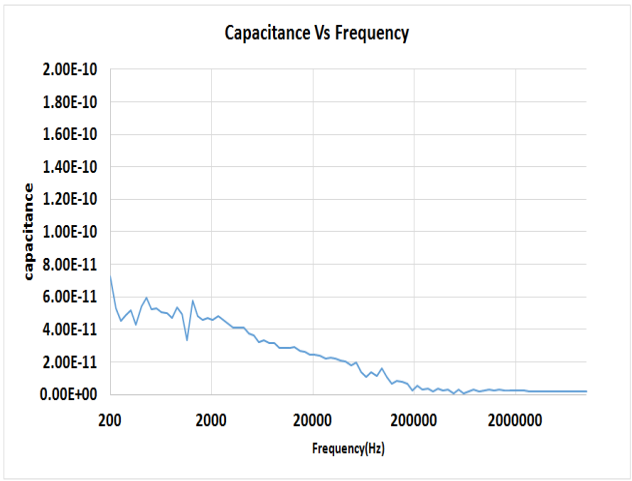


Fig. 7: Capacitance Vs Frequency of sample 16% Lead oxide doped Barium Titanate at room temperature.

The polarization requires time to respond to an applied field. As the frequency of applied field is increased, various mechanisms will be unable to follow the electric field and will drop off. Electronic polarization occurs very rapidly. So it stays even at high frequencies.

At very high frequencies, none of the mechanisms is capable of following the field, and the relative dielectric constant approaches 1.0 [15,16]. For doping level 20% (sample 1) the As dielectric constant is proportional to capacitance, so capacitance Vs frequency graph follow the same path like dielectric constant Vs frequency graph. But in dielectric loss Vs frequency graph for sample type 1, the dielectric loss start increasing at 100000Hz frequency and maximum dielectric loss is 5.79 at 486260 Hz. After reaching the maximum value, dielectric loss fall down gradually. And in dielectric loss Vs frequency graph for sample type 2, the dielectric loss start increasing at 42292 Hz frequency and maximum dielectric loss is 3.63 at 486260Hz. After reaching the maximum value, dielectric loss fall down gradually. But in the graph for this sample some another peaks are seen before and after the maximum value as the dielectric loss falls to some extent at some points. For both type of sample the dielectric loss became 1 at 10 MHz. Table 3 shows the comparison between two samples in terms of dielectric constants, dielectric losses and theoretical densities. It can be observed that at 100 kHz frequency, dielectric constant of Barium Titanate doped with 20% PbO is higher than that of Barium Titanate doped with 16% PbO. At 10MHz, the dielectric constants for both the samples are low and so are the dielectric losses.

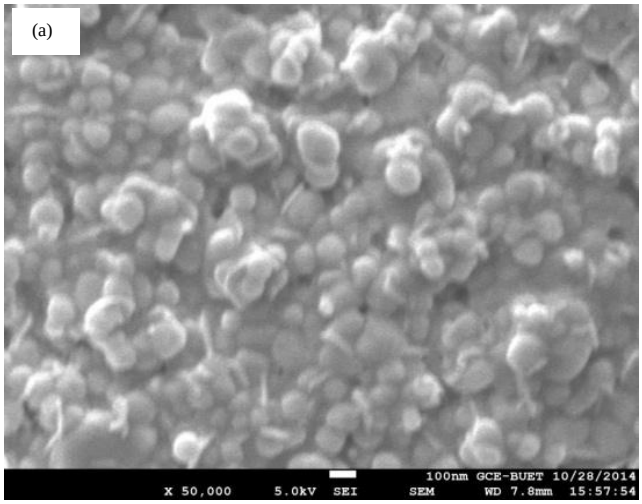
dropping of dielectric constant starts at 1629 Hz. But at sample 2 when doping level is 16% the dropping of dielectric constant starts at 1291 Hz.

Table 3: Room Temperature Dielectric Properties of PbO doped $BaTiO_3$ samples

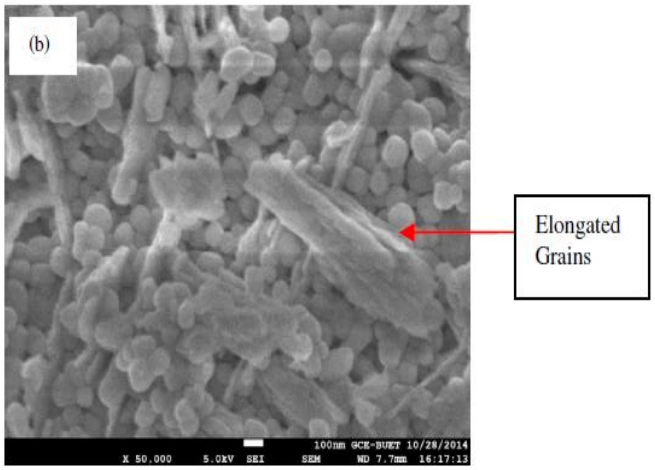
Doping level	Sintering Temperature	Holding Time	%TD	Dielectric Constant, k (100 kHz)	Dielectric Constant, k (10MHz)	Dielectric loss (100 kHz)	Dielectric loss (10MHz)
20% (Sample 1)	800^0C	2hour	66.38	28.58	3.06	1.08	0.068773
16% (Sample 2)	800^0C	2hour	75.39	27.10	3.43	0.9652	0.06381

Scanning Electron Microscopy (SEM)

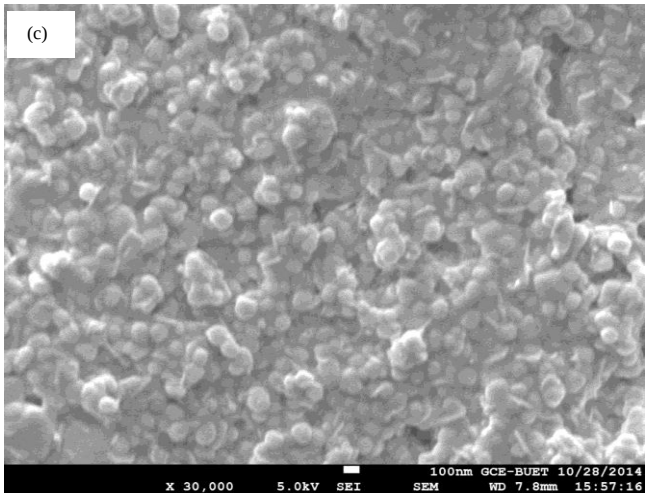
Microstructural features are needed to examine or to observe the most of the ferroelectric properties and dielectric properties. So, scanning electron micro study is needed to observe the microstructural features. Microstructure of small grains with less porosity is the ultimate goal of all commercial polycrystalline ceramics. Before the SEM test a nano ranged Platinum coating was given to the samples to make the samples conductive. Another reason for coating is to reduce the emitted charge which is mandatory to get the better results. Actually the microstructures reveal domains inside grains. So at different doping level, the micrographs are observed to see the effects of doping of PbO. In the conducted research, the maximum magnification was 50000 x at 5kV .And the grain size was taken up to **100nm**.



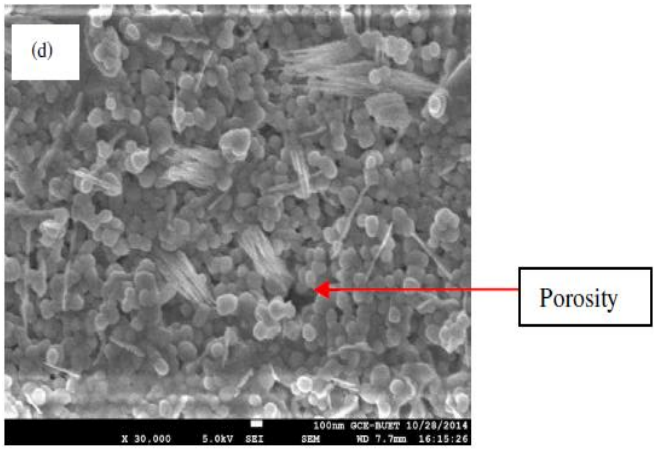
(a)Doping level 20% (at 50,000X magnification)



(b) Doping level 16% (at 50,000X magnification)



(c) Doping level 20% (at 30,000X magnification)



(d) Doping level 16% (at 30,000X magnification)

Fig. 8: Scanning electron micrograph of different type of samples at same magnification and at same voltage:
(a) Doping level 20% (at 50,000X magnification)
(b) Doping level 16% (at 50,000X magnification)
(c) Doping level 20% (at 30,000X magnification)
(d) Doping level 16% (at 30,000X magnification)

From the microstructures it can be seen that when pure Barium titanate is doped with 20% Lead Monoxide (PbO), most of the grain particles obtained were successfully in the 100 nm range which were also uniform and spherical. On the other hand, when doping level is 16%, most of grains are spherical but some 'needle' shaped grains are appeared through the spherical grains. The needle shaped or elongated grains are due to the inadequate inhibition of grain growth which was checked when 20% doping level was used. Some white lines are seen at the micrographs shown above. As the samples are non-conductive so they keep holding the electrons at those regions.

IV. CONCLUSION

Theoretically Pb^{2+} ion increases the curie temperature of $BaTiO_3$. Adding PbO to the industrial ceramics makes the materials more magnetically and electrically inert. So, PbO was doped with $BaTiO_3$ based ceramics using the powder metallurgy technique to study the change and modification of the different important properties of pure $BaTiO_3$ based ceramics. Two type of doping level was used for this study. One was 20% PbO doping level and another was 16% PbO doping level. Pressing was done very carefully by manual pressing machine. And samples were pressed at 5 ton pressure for 2 minutes. Here, sintering temperature to produce the dense sample was found to be 800^0 by a trial and error process. The heating rate was 5^0C/min and the holding period was 2hour at the sintering temperature. Percentage theoretical density was calculated to see the perfection of the process parameters. And the percentage of porosity was observed from that calculation. Dielectric constant, dielectric loss and capacitance were observed up to 10 MHz frequency. And the difference between the samples of those properties was studied for the different doping levels at room temperatures. It was observed that at certain standard frequency, i.e, 100kHz, the dielectric constant increases upon increasing doping level. Difference between the microstructure of two types of samples was studied by SEM and it was observed that upon doping of pure Barium titanate with 20% Lead Monoxide (PbO), grain particles with 100nm range were successfully obtained in major portions with proper uniformity and spherical shapes, whereas, upon doping of 16% PbO, some elongated grains were observed due to inadequate inhibition of grain growth which was overcome when 20% doping level was used. Therefore by modifying the sintering parameters and increasing doping level of PbO with $BaTiO_3$, better dielectric property and grain refinement can be obtained.

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