Chapter 3 Pure BaTiO₃

3.1 Introduction
The barium titanate: BaTiO₃ (BT) is the well known electroceramic material used mainly for the capacitor applications because of its high dielectric constant. Several methods have been reported during the last five decades for the synthesis of BT powders [art. 1.10]. However, the prior art routes suffer from the several considerable drawbacks. In view of this, the attempt are still being made in the direction of synthesis to overcome the problems associated with prior reports and provide thereby the new simple route for the generation of such powders. Further, there is considerable interest in evaluating new methods for the synthesis of BT powders in view of achieving better control over the physical and chemical characteristics in such way that it will give the better performance on measurements of dielectric-ferroelectric properties of the dense compacts after sintering.

3.2 Results and analysis
The BT powders were prepared by three different methods: (1) controlled acid-base reaction between the oxalotitanic acid and barium hydroxide at room temperature, (2) the exchange reaction between the ammonium titanyl oxalate and modified barium hydroxide at room temperature and (3) the microwave-hydrothermal (MH) reaction. The experimental results obtained are analyzed and presented in following section and sub-sections.

3.2.1 Acid-base reaction
The flowchart for the synthesis of barium titanyl oxalate (BTO) precursor leading to BT powders is given in fig 2.1. Initially, the titanium tetrabutoxide: (C₄H₉O₁₄)₂Ti (17ml, 0.05M) was dissolved in isopropanol (IPA) (180ml). The solution of oxalic acid (12.607 gm, 0.1M) was made in IPA (350ml). The titanium tetrabutoxide solution was added to oxalic acid solution with continuous stirring when white precipitate initially obtained is re-dissolved to obtain a clear solution of oxalotitanic acid: H₂TiO(C₂O₄)₂ (HTO) (0.05M) [1] through the following reaction (1).
The barium hydroxide: Ba(OH)$_2$ was added directly (or suspended in IPA) in solid form to the HTO solution. It was observed that the precipitation reaction did not start initially probably because of the unavailability of free Ba$^{2+}$ ions in the solution. For this purpose, sufficient amount of distilled water was added dropwise in the above mentioned solution when precipitation reaction started and resulting mixture was kept overnight for the reaction to go its completion. The neutralization reaction is proceeded only when necessary amount of water (350ml) is added dropwise to the solution. It was found that the addition of water helps to initiate acid-base reaction because the partial solubility of Ba(OH)$_2$ in semi-aqueous media is achieved, which allows the formation of free Ba$^{2+}$ ions required for the neutralization reaction. The Ba(OH)$_2$ gets dissolved to produce Ba$^{2+}$ ions as given below by reaction (2).

\[
\text{IPA + Water} \quad \text{Ba(OH)}_2 \rightarrow \text{IPA + Water} \quad \text{Ba}^{2+} + 2\text{OH}^- \quad (2)
\]

Similarly, HTO gets dissociated through the following reaction (3) to form H$^+$ and TiO(C$_2$O$_4$)$_2$$^{2-}$ species.

\[
\text{IPA + Water} \quad H_2\text{TiO(C}_2\text{O}_4\text{)}_2 \rightarrow \text{IPA + Water} \quad 2\text{H}^+ + \text{TiO(C}_2\text{O}_4\text{)}_2$$^{2-}$ \quad (3)
\]

When ionic product of Ba$^{2+}$ and TiO(C$_2$O$_4$)$_2$$^{2-}$ exceeds the solubility product of BTO, the neutralization reaction (4) occurs to precipitate BTO.

\[
\text{IPA + Water} \quad H_2\text{TiO(C}_2\text{O}_4\text{)}_2 + \text{Ba(OH)}_2 \rightarrow \text{IPA + Water} \quad \text{BaTiO(C}_2\text{O}_4\text{)}_2\cdot4\text{H}_2\text{O} + 2\text{H}_2\text{O} \quad (4)
\]

As soon as Ba$^{2+}$ ions are consumed to precipitate BTO more and more Ba(OH)$_2$ solid gets dissolved to maintain equilibrium concentration of Ba$^{2+}$ ions depending on its solubility at ambient conditions. This overall reaction is represented by equation (5) as given below.

\[
\text{Ba}^{2+} + 2\text{OH}^- + 2\text{H}^+ + \text{TiO(C}_2\text{O}_4\text{)}_2$$^{2-} \rightarrow \text{BaTiO(C}_2\text{O}_4\text{)}_2\cdot4\text{H}_2\text{O} + 2\text{H}_2\text{O} \quad (5)
\]
Thus the reactions (2) and (3) occur simultaneously till all Ba(OH)\textsubscript{2} and HTO are consumed. In this way, the main reaction (4) is driven to its completion and controlled kinetically. The pH of the final solution was ~3.1. This is same as that of the pH at which the BTO precipitates. The BTO precursor is calcined to obtain the BT powders.

3.2.1.1 Physico-chemical characterization of as-dried and calcined powders

The as-dried BTO and calcined BT powders are characterized by various physico-chemical techniques viz. micro- & chemical analysis, DTA/TGA, XRD, FTIR, XRF and SEM. Further for characterization purpose, the water of crystallization in BTO was considered to be 4H\textsubscript{2}O.

(a) Chemical characterization (micro- & chemical analysis)

The micro-determination of carbon and hydrogen in BTO was done by carrying out the combustion of BTO at 900\textdegree C in O\textsubscript{2} atmosphere using Hosli’s CH apparatus, whereas the standard quantitative chemical analysis methods [2] were employed to estimate the percentages of various elements/groups in BTO. The Table 3.1 and Table 3.2 give the micro- & chemical analysis data for BTO precursor respectively.

Table 3.1 Microanalysis data for BTO

<table>
<thead>
<tr>
<th>Element</th>
<th>Theoretical (%)</th>
<th>Experimental (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>10.66</td>
<td>9.83</td>
</tr>
<tr>
<td>H</td>
<td>1.78</td>
<td>1.70</td>
</tr>
</tbody>
</table>

Table 3.2 Chemical analysis data for BTO

<table>
<thead>
<tr>
<th>Element/Group</th>
<th>Theoretical (%)</th>
<th>Experimental (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>10.66</td>
<td>10.88</td>
</tr>
<tr>
<td>Ba</td>
<td>30.57</td>
<td>32.00</td>
</tr>
<tr>
<td>C\textsubscript{2}O\textsubscript{4}</td>
<td>39.17</td>
<td>37.84</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>16.02</td>
<td>15.30*</td>
</tr>
</tbody>
</table>

* Water content determined from the microanalysis data

From the Table 3.1 and Table 3.2 it is clear that the experimentally observed values are in good agreement with the theoretically calculated values, which indicates the composition of the BTO as BaTiO(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}.4H\textsubscript{2}O.
The experimentally observed and theoretically calculated weight losses are given in Table 3.3. It is clear from Table 3.3 that the weight losses are consistent. The water content obtained independently from microanalysis data (Table 3.1 & 3.2) agrees well with that measured from DTA/TGA studies. The total loss observed in BTO is 45.64% which is less by 2.4% as compared to the theoretical value, as CO₂ liberated in the 3rd stage may be trapped/adsorbed within the material. The experimental weight loss in step 1 matches with the theoretical weight loss corresponding to the 4H₂O. From this it is clear that the water of crystallization in the BTO formed in present work is equal to 4H₂O as considered for the theoretical calculation.

Table 3.3 DTA/TGA data for BTO

<table>
<thead>
<tr>
<th>Decomposition step</th>
<th>Theoretical weight loss (%)</th>
<th>Experimental weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. RT-225°C -(4H₂O)</td>
<td>16.03</td>
<td>16.01</td>
</tr>
<tr>
<td>2. 225-600°C -(4CO+3CO₂)</td>
<td>27.16</td>
<td>27.12</td>
</tr>
<tr>
<td>3. 600-750°C -(CO₂)</td>
<td>4.90</td>
<td>2.51</td>
</tr>
<tr>
<td>Total</td>
<td>48.09</td>
<td>45.64</td>
</tr>
</tbody>
</table>

From all these characterization studies, we infer that self-assisted acid-base reaction scheme given by equation (4) produces only pure BTO. Further, the temperature required to obtain the single-phase pure BT powders from the pyrolysis of BTO precursor is ~750°C.

**X-ray diffraction analysis**: The samples: BTO and the BTO calcined at 750°C in air are analyzed by the X-ray diffraction to understand the phase evolved and formation of the impurity phases, if any. The X-ray diffraction pattern of barium oxalate (BaC₂O₄, AR grade) is also given for the comparison. Fig. 3.2 (a) and (b) shows the XRD patterns of BTO precursor and BaC₂O₄ respectively. The careful analysis of XRD pattern [fig. 3.2 (a)] showed the presence of all reflections corresponding to the reported barium titanyl oxalate tetrahydrate (BTO) having monoclinic symmetry [4]. No lines corresponding to BaC₂O₄ and BaCO₃ [5] were detected in the as-dried precursor BTO. This confirms the formation of the single phase BTO precursor which is consistent with
3.2.3 Microwave-hydrothermal reaction

The flowchart for the synthesis of BaTiO₃ (BT) powders by the using the microwave-hydrothermal (MH) route is given in the fig. 2.3 of the experimental chapter. The 1.2M KOH solution is prepared in the distilled water. The 0.04M solution of the titanium is used for the synthesis. For this purpose, initially the required quantity of the potassium titanyl oxalate (KTO) was dissolved in distilled water. The sufficient amount of KOH solution (1.2M) was added to KTO solution (resulting pH >10). This gives the precipitate of hydrated titania. This precipitate of hydrated titania was filtered, dried and then dissolved in the dilute HNO₃ to obtain the solution of titanium. It is reported in the literature [36] that in the synthesis of the BT powders by the MH route, the BaCO₃ forms as an impurity phase. Hence, in order to maintain the Ba:Ti ratio ≥ 1.00 in the solution for getting the stoichiometric BT powders with ~100 % yield the excess concentration of Ba²⁺ ions was used. For this purpose, the 0.12 M solution of the Ba(NO₃)₂ was used for the present work. The same amount of the each precursor solution was added to sufficient amount of KOH solution (pH >10). This gives rise to the mixture of hydroxide of each precursor. The resultant solution was treated microwave-hydrothermally. The formation of the BaTiO₃ takes place under MH conditions by the dissolution-recrystallization reaction mechanism [37]. The final as-prepared powders were filtered, washed with dilute acetic acid to remove the BaCO₃ impurity and finally washed with distilled water several times.

3.2.3.1 Characterization of as-prepared powders

The as-prepared and the dilute acetic acid washed powders are characterized by the various physical techniques viz. XRD, FTIR, XRF and SEM.

Yield: The experimentally observed yield for the synthesis of BaTiO₃ by MH route is around 86 %. The yield is low. For each digestion experiment only 45ml solution of each precursor [0.04M Ti and 0.12M Ba] is used. This leads very small amount BaTiO₃ powder per synthesis experiment. Further, the operations like filtering, washing, drying as well as transferring of such low amount of powder may lead to the incorrect calculation of the yield. Furthermore, the formation of the BaCO₃ impurity [36] under
all MH conditions also decreases the yield. All these factors as mentioned above may be affecting in the getting the higher low yield.

The temperature, pressure vs. time profile: The variation of the temperature and pressure with the time during the MH synthesis of the BT powders is shown in the fig. 3.25. The MH conditions are 200°C, 200 psi and 30min. The ramp time (time required to reach the set conditions) is found to be ~ 7.5 min. Thus heating to the given temperature during MH synthesis is very fast. During the ramp time initially the temperature rises very fast as compared to the pressure upto ~ 100°C due to the dielectric heating of water.

Fig. 3.25 Temperature and pressure versus time profile for MH synthesis of BaTiO$_3$ powders under the conditions of 200°C, 200psi, 30min.

Above 100°C the temperature increases slowly while the pressure reaches very fast to the set value. It is clear from the fig. 3.25 that both the temperature and corresponding pressure remain constant during the hold time of 30min. The hold time is found to be exactly same as that of the set hold time. The variation in the temperature during the hold time is only ± 1°C whereas the pressure depends upon the corresponding temperature and the rate of dissolution-recrystallization reaction at that moment. The constant pressure during the hold time is the indication of the constant rate of the
kinetics of the dissolution-recrystallization reaction towards the formation of the stable particles of the target material.

**XRD analysis:** The phases formed in the MH synthesis of the BT powders are analyzed by the XRD diffraction. Fig. 3.26 (a) and (b) give the XRD patterns of the as-prepared powder obtained by the MH route under the conditions of the 200°C, 200psi, 30min and the as-prepared powder washed by the dilute acetic acid respectively. The fig. 3.26 (a) shows the mixed phase. All the major intense peaks are the reflections due to the cubic BaTiO₃ [5-7] while small peaks at 2θ = 23.9, 24.16, 34.08, 34.60 and 41.99⁰ are due to the orthorhombic phase of BaCO₃ phase [5].

![XRD patterns of BT powders](image)

The peaks due to the BaCO₃ are marked by the asterisk as shown in the fig. 3.26(a). This implies that the MH route generates the BT powders successfully under the condition of 200°C, 200psi, 30min. However, during the synthesis of BT powders in an air ambient and by using the distilled water as polar solvent, the BaCO₃ is always
forming as impurity phase due to the reaction of the Ba^{2+} ions with the dissolved CO_{2} (CO_{3}^{2-} ions) in water. The amount of BaCO_{3} formation may depend upon the percentage solubility of the CO_{2} at ambient conditions. The fig. 3.26 (b) is XRD pattern for acetic acid washed powder. It shows the reflections corresponding to the only cubic BaTiO_{3} phase [5-7]. Further, the all reflections are broad and perfectly symmetric. This implies that the BT particles formed in the MH synthesis are fine. Furthermore, the lattice parameter calculated from the slow scan of the (200) peak is found to be 4.029 Å and it matches with the reported value of 4.03 Å [7].

**FTIR analysis:** The FTIR spectrum of a dilute acetic acid washed powder prepared by using the MH conditions of 200°C, 200psi, 30min is shown in the fig. 3.27.

![FTIR Spectrum](image)

Fig. 3.27 FTIR spectrum of dilute acetic acid washed powder, prepared under the MH conditions of 200°C, 200psi, 30min.

This FTIR spectrum matches very well with the reported FTIR spectrum for the BaTiO_{3} [12-14]. The intense bands (marked by star) at 2923, 2854, 1463 and 1377 cm\(^{-1}\) are due to nujol used for recording the spectrum of the sample by using the mull technique. The broad band in the lower frequency range with center at 550 cm\(^{-1}\) corresponds to the stretching vibrations in the TiO_{6} octahedra [15] while peak at ~ 418 cm\(^{-1}\) is due to Ti-O bending vibrations [16]. Further, a very important observation is that the sharp bands at 2451, 1749, 1058, 856 and 694 cm\(^{-1}\) due to BaCO_{3} species are completely absent in the
above spectrum. This implies that the dilute acetic acid washed material contains only
the pure BaTiO$_3$ powder.

XRF analysis: The XRF analysis was followed to calculate the Ba:Ti ratio
(stoichiometry) in the resultant BT powders prepared by the MH route. The pure BT
powder obtained by the dilute acetic acid washing and the BT material supplied by the
Cabot company were taken for the analysis. The dry pellets of equal weight of above
two powders pressed the under the identical conditions were given for the XRF
analysis. The Ba:Ti ratio for the Cabot sample is 1.003. The XRF spectra for both are
shown in the fig. 3.28. Fig. 3.28 (a) and (b) give the XRF spectra for Cabot sample and
BT powder prepared by the present MH route respectively. The intensities for the Ba
and Ti for MH derived BT powder are found to be comparable with those obtained for
the standard Cabot sample.

Fig. 3.28 XRF data on (a) standard Cabot sample and (b) BT powders prepared by MH
route under conditions of the 200$^\circ$C, 200psi, 30min.

The Ba:Ti ratio for the MH derived BT powder is found to be 1.0025. Further, no peaks
corresponding to the other impurity ions like K$^+$ are observed in the XRF spectrum of
the standard Cabot sample. The XRF spectrum of the MH derived powder [fig. 3.28 (b)]
shows the presence of the impurity corresponding to the potassium (K). However, the
intensity of the potassium peak is very very small. This implies that the percentage of the potassium in the bulk powder is very small.

**SEM analysis:** The morphology, particle size & shape, its distribution and nature of agglomerates in the resultant MH derived BT powders are studied by using the scanning electron microscopy. The fig. 3.29 (a) gives the SEM photograph of the as-prepared BT powder generated under the MH conditions of 200°C, 200psi, 30min. It clearly shows the mixed phase which is the consistent with the XRD observations [fig.3.26 (a)]. The rod or the needle shaped structures are nothing but the BaCO₃ particles [14, 38]. The commercial BaCO₃ powder particles also show the needle shape morphology [38]. The nearly spherical agglomerates spread in between the needle shaped structures in the fig. 3.29(a) are the BaTiO₃ particles formed in the MH synthesis. The fig. 3.29 (b) shows the SEM photograph of the as-prepared powder washed by the dilute acetic acid.

![SEM photographs](image)

Fig. 3.29 SEM photographs of (a) as-prepared powder under the MH conditions of 200°C, 200psi, 30min and (b) as-prepared powder washed by dilute acetic acid

The needle shaped BaCO₃ particles are disappeared since the BaCO₃ is soluble in the acetic acid. The SEM photograph clearly shows the presence of only BaTiO₃ particles. In both pictures the primary BaTiO₃ particles are found to be spherical in nature. These primary spherical particles form the nearly spherical agglomerates as clearly seen from the fig. 3.29 (a) and (b). Each agglomerate contains around 5-6 primary particles of BT.
The primary particle size is found to \(-100\)nm. The average agglomerate size is \(~0.3\mu m\). This is consistent with the XRD observation, where all the reflections corresponding to BT phase are broad. The size and shape distribution of the agglomerate is found to be nearly uniform. Further, the spherical shape of the agglomerates is due to the spherical nature of the primary BT particles.

3.2.3.2 Characterization of sintered products

It is reported in the literature that (i) the sintering rate is high and (ii) more densification takes place even at the lower sintering temperature, for the BT pellets of MH derived powders compared to the materials obtained by the any other conventional routes [35]. However, for comparison purpose, the same sintering temperatures of oxalate powders are used for BT pellets obtained during the present work (for MH powders). The density calculation, XRD and SEM are used to characterize the pellets sintered at the different temperatures.

**Density:** The density of a pellet is calculated from the dimensions and weight of the pellet. The average green density for BT pellets is found to be 58-60%. The densities of the BT pellets sintered at the different temperatures are given in the Table 3.16. The % relative density is calculated from the theoretical density of BT (6.039 gm/cc) [17].

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Density (gm/cc)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250</td>
<td>4.94</td>
<td>81.80</td>
</tr>
<tr>
<td>1300</td>
<td>5.07</td>
<td>83.95</td>
</tr>
<tr>
<td>1325</td>
<td>5.26</td>
<td>87.10</td>
</tr>
<tr>
<td>1350</td>
<td>5.50</td>
<td>91.07</td>
</tr>
</tbody>
</table>

The density of the sintered pellets increases with increasing the sintering temperature. The pellets sintered at the 1250° C have very poor density of 81.8%. As the sintering temperature is further increased the density is also enhanced, reaching the values of \(~84\)% and \(~87\)% for the sintering temperature of 1300 and 1325° C respectively. The maximum density of \(~91\)% is attained on increasing the sintering temperature further to
the 1350°C. This implies that the higher sintering temperature (>1350°C) is necessary for the good densification. This lower densification even at the higher sintering temperature may be due to the presence of little excess Ba and slight potassium in the final BT powders (XRF analysis).

**XRD analysis:** The phases evolved in the sintered pellets are studied by X-ray diffraction. The fig. 3.30 (a), (b), (c) and (d) show the XRD patterns of the powders of the MH derived BT pellets sintered at the temperatures 1250, 1300, 1325 and 1350°C respectively. The XRD pattern of the pellet sintered at 1250°C [fig. 3.30 (a)] shows all the reflections matching with the cubic BaTiO₃ [5-7]. However, local symmetry may be the tetragonal because the peak (200) is not perfectly symmetric and it shows the small hump corresponding to the (002) reflection of the tetragonal BaTiO₃ [18]. Further, a very weak reflection at 2θ = 29.3° is also observed.

![XRD patterns](image)

Fig. 3.30 XRD patterns of the powder samples of the MH derived BT pellets sintered at (a) 1250, (b) 1300, (c) 1325 and (d) 1350°C

This single impurity peak corresponds to the Ba₂TiO₄ phase [19] and it is marked by asterisk. The XRD patterns of the powders of the pellets sintered at the 1300, 1325 and
1350°C [fig. 3.30 (b), (c) and (d)] show the presence of all the reflections of the tetragonal BaTiO$_3$ [18] only [Table 3.17]. The splitting of the cubic peaks into the tetragonal reflections increases/becomes more clear with increasing the sintering temperature from the 1300 to 1350°C. Further, no peaks of the phase like Ba$_2$TiO$_4$, BaTi$_3$O$_7$, and BaTi$_4$O$_9$ are observed in all the XRD patterns shown in fig 3.30 (b)-(d). Furthermore, the BaCO$_3$ impurity lines are also not observed in the XRD patterns of lower sintering temperature [fig. 3.30 (a)] which is consistent with earlier FTIR observation [fig. 3.27]. The $c_0/a_0$ ratio is calculated from the (002) and (200) reflections for all the above samples and their values are given in the Table 3.17. The ratio is found to be lower as compared to the reported data [19, 22].

**SEM analysis:** The microstructure analysis of the sintered pellets was done by SEM. The fig.3.31 (a)-(d) gives the SEM photomicrographs of the pellets sintered at 1250, 1300, 1325 and 1350°C respectively. The voids are clearly seen in all the sintered samples. This expected since the densities obtained during the sintering are of lower values [Table 3.16]. The maximum density obtained at the highest sintering temperature is only ~ 91%. In all the samples grain shape is nearly spherical/rounded with almost uniform distribution. For the sample sintered at the 1250°C the size of the grain is in the range 1-1.87 μm. The average grain size for this sample ~ 1.43 μm. From fig.3.31 (b)-(d) it is clear that the grain size increases with sintering temperature. The grains of the sample sintered at 1300°C are of almost same sizes. The average grain size for this sample is ~ 1.62μm. For the sample sintered at 1325°C, the larger grains are also seen. The grain boundary is not very clear. The grain size for same sample is found to be ~ 2.12 μm. In the sample sintered at 1350°C the smaller (~ 1μm) as well as bigger (~ 3.5 μm) grains are observed. The average grain size for this is noted be ~2.25 μm. More importantly the range for the grain sizes in all the samples is narrow with almost same shape. The data for the same is given in Table 3.17.
Table 3.17 Sintering data (phase, axial ratio: C & average grain size)

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Axial ratio (C)</th>
<th>Phase</th>
<th>Average grain size (µm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250</td>
<td>1.0032</td>
<td>Cubic + tetragonal</td>
<td>1.43</td>
</tr>
<tr>
<td>1300</td>
<td>1.0059</td>
<td>Tetragonal</td>
<td>1.62</td>
</tr>
<tr>
<td>1325</td>
<td>1.0076</td>
<td>Tetragonal</td>
<td>2.12</td>
</tr>
<tr>
<td>1350</td>
<td>1.0080</td>
<td>Tetragonal</td>
<td>2.25</td>
</tr>
</tbody>
</table>

Fig. 3.31 Scanning electron photomicrographs of BT pellets sintered at (a) 1250, (b) 1300, (c) 1325 and (d) 1350°C

3.2.3.3 Dielectric & ferroelectric properties

The variation of the dielectric constant and dielectric loss with temperature obtained from the capacitance measurements for the BT pellets of the MH derived powder sintered at different temperatures of 1250, 1300, 1325 and 1350°C are given in the fig.3.32 and fig. 3.33 respectively.
Fig. 3.32 Temperature dependence of dielectric constant (ε) for the pellets of the MH derived BT powders, sintered at the different temperatures of 1250, 1300, 1325 & 1350°C

Fig. 3.33 Temperature dependence of dielectric loss (dissipation factor: tanδ) for the BT pellets sintered at the different temperatures of 1150, 1200, 1250 & 1300°C
The dielectric constants at room and Curie temperature, dielectric loss at RT and the Curie temperature for the different dense compacts are given in the Table 3.18. The values of the dielectric constant for the pellet sintered at $1250^\circ C$, at RT and $T_c$ are very low. It shows the broad ferroelectric-paraelectric transition with the Curie temperature $\sim 121^\circ C$. With increasing the sintering temperature to $1300^\circ C$ the dielectric constant at both, RT as well as $T_c$ is increased but not very much. It also shows the broad transition at $T_c \sim 121$ similar to the pellets sintered at $1250^\circ C$. For the pellet sintered at $1325^\circ C$ the value of the dielectric constant at RT is increased suddenly to 1710 which is the comparable with the reported data [19, 22] [Table 3.18]. However, its value at $T_c$ is not increased considerably. The $T_c$ is found to be $122^\circ C$. For the pellets sintered at the $1350^\circ C$ the dielectric constant at RT is quite comparable with the reported data for the polycrystalline BT [Table 3.18]. Further, the dielectric constant at $T_c$ for the same sample is observed to be very close to the standard data [Table 3.18]. The transition is sharp and $T_c$ is shifted slightly to the higher temperature ($123^\circ C$). The very poor dielectric performance of the dense compacts obtained by sintering the BT pellets at $1250$, $1300$ and $1325^\circ C$ is due to the poor densification of the same materials.
broad transition at the lower sintering temperature may be due to the smaller grain size. The shift in $T_c$ for pellets sintered at 1325 and 1350°C is due to the increase in the grain size on firing at high temperature. The temperature dependence of the dielectric loss shows slow fall in its value from RT to $T_c$, small hump at $T_c$ and again slow fall with increase in temperature up to 200°C. The similar trend is observed for all the pellets sintered at the different temperatures. However, dielectric loss in the neighborhood of the RT is large and it is found that with increasing the sintering temperature from 1250 to 1350°C the loss decreases. The similar observation is found at all the temperatures in the range of RT-$T_c$. The high dielectric loss at RT for pellets sintered at lower temperature is due to the low magnitude of densification. This increases the porosity of the material and hence the concentration of the adsorbed H$_2$O in porous volume. This increases the loss for sample sintered at the lower sintering temperatures. The well defined hysteresis loops are observed for all the pellets sintered at different temperatures. The hysteresis loop parameters are obtained for all the pellets at the highest applied voltage without electrical breakdown. The results are summarized in the Table 3.18. The spontaneous polarization is low for all the pellets and reached to a maximum value of $\sim$5.6 for sample sintered at 1350°C. This may be due to lower densification at all the sintering temperatures. The coercivity is large and found to be comparable to the standard data [Table 3.18] for the sample sintered at 1300°C. This is due to the hysteresis loop of large width. Similarly, the breakdown voltage: $E_b$ is also low for sample sintered at lower temperature. This is because the maximum applied voltage which pellet can withstand is found to be very low due to the high porosity. However, for the pellet sintered at higher temperature the $E_b$ is quite comparable with the standard value [Table 3.18]. This is due to the increase in the density.

3.3 Discussion and conclusion
The BaTiO$_3$ (BT) powders are synthesized by (1) two newly investigated wet-chemical routes and (2) the time and energy saver microwave-hydrothermal method. These newly investigated wet-chemical routes involve the synthesis of the crystalline oxalate precursor powders: barium titanyl oxalate (BTO) at the room temperature (RT). The BT powders can be produced by the pyrolysis of the oxalate precursor in the air.
microwave-hydrothermal (MH) route is used to prepare the BT powders under the proper MH conditions/parameters with the controlled morphology of the resultant particles.

All the three methods are found to be very simple & easy and each of them involves only two steps in their operations: (1) preparation of the precursor solutions, either in the distilled water or in isopropanol (IPA) of appropriate morality and (2) synthesis of the oxalate molecular precursor /BaTiO₃ powders by carrying out actual chemical reaction. Further, it is also observed that the number of the things like glass ware, chemicals, space etc. required to carry out the actual chemical reaction for the synthesis of the active BT powders by using above mentioned routes are less in the number. Furthermore, all the three methods are found to be economically of low cost since the very cheaper chemicals like barium nitrate, potassium titanyl oxalate (KTO), potassium hydroxide, oxalic acid, titanium tetrabutoxide (BTM), barium hydroxide, ammonium oxalate etc are used during the synthesis of the BT powders directly or via precipitation of the oxalate precursor.

The two methods namely (I) Clabough's synthesis and (2) exchange reaction have been reported to precipitate the molecular precursor BTO [39, 13]. The Clabough's synthesis of the BTO precursor involves the following reaction (14).

\[
\text{TiCl}_4 + 2\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} \rightarrow \text{BaTiO(C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O} \xrightarrow{\text{Calcination} \ 750^\circ \text{C}} \text{BaTiO}_3
\]

The (1) use of the excess oxalic acid, (2) the precipitation of the BTO at the higher temperature (80°C) and (3) use of TiCl₄ (Ti precursor) which has vapor pressure at the RT and needs the Ti estimation from the batch to batch are some of the major problems associated with Clabough's synthesis of BTO [39] via reaction (14).

\[
\text{K}_2\text{TiO(C}_2\text{O}_4)_2 + \text{Ba(NO}_3)_2 \rightarrow \text{BaTiO(C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O} \xrightarrow{\text{calcination} \ 750^\circ \text{C}} \text{BaTiO}_3
\]

During the exchange reaction (15) the rate of addition of the Ba precursor in the potassium titanyl oxalate (KTO) solution is very important. The Ba(NO₃)₂ is the salt of the weak base and the strong acid and produces pH in the range of 2-2.5 [40] after the
dissolution. The variation of the local pH occurs during the slow addition of the Ba-precursor because of the higher pH of the KTO solution [pH \sim 3.5]. This leads the destabilization of the anionic Ti species: TiO(C$_2$O$_4$)$_2$\(^{2-}\) which further gives rise to the mixture of Ba and Ti oxalate to some extent along with the main BTO during the chemical reaction (15). There is introduction of the K\(^+\) ion impurity in the BTO during the reaction (15), which affects the dielectric properties to the great extent. It is reported that the thermal decomposition of BTO at T > 750\(^\circ\)C produces BT powders with good homogeneity and stoichiometry [41]. Although the chemistry occurring during the reactions (14) and (15) looks to be simple, many side reactions also occur causing the difficulties in the precipitation of a single phase BTO with higher yield. Also different parameters /factors like pH of precursors, mixing order during the reaction, oxalate solution, temperature of the precipitation etc. affects the preparation of the BTO and it has been shown that the mixture of the oxalate would form rather than BTO depending on the various above parameters [42]. The minor changes in the reaction conditions lead to completely different products [43-45]. The pH and hence the choice of the Ba precursor decides the stability of the TiO(C$_2$O$_4$)$_2$\(^{2-}\) species and the extent of the destabilization during generation of the BTO [13, 45] i.e. the destabilization will take place in the use of Ba(OH)$_2$ instead of the Ba(NO$_3$)$_2$ during the chemical reaction (15). In the case of the simple acid-base reaction the oxalotitanic acid (HTO) (pH \sim 1.5) is generated by the reaction (1) between the titanium tetrabutoxide (in isopropanol) and the oxalic acid at the RT (in isopropanol). It gives rise to the water and alcohol, which do not affect the pH of the HTO to the great extent. The HTO gets dissociated into the H\(^+\) and the TiO(C$_2$O$_4$)$_2$\(^{2-}\) through the reaction (3). The Ba(OH)$_2$ was added directly to the HTO solution. However, the neutralization reaction (5) didn't occur because of the unavailability of the Ba\(^{2+}\) since the Ba(OH)$_2$ is not soluble in the HTO or alcohol. The precipitation reaction (5) proceeded only when the necessary amount of the water is added to the above-mentioned mixed solution drop wise. The drop wise addition of water shifts the non-aqueous condition to the aqueous which allows the required solubility of the Ba(OH)$_2$ and makes the Ba\(^{2+}\) ions available for the neutralization reaction (5). The solubility of the Ba(OH)$_2$ and its dissociation governs the kinetics of the reaction leading to the precipitation of the BTO with the higher yield. This depends
upon the rate of drop wise addition of the water. When ionic product of Ba$^{2+}$ and the
TiO(C$_2$O$_4$)$_2$$^{2-}$ [reaction 5] exceeds the solubility product of BTO, the neutralization
reaction (5) occurs to precipitate BTO. The HTO is neutralized completely by the
controlled release of the Ba$^{2+}$ ions depending on the solubility of the Ba(OH)$_2$ and its
dissociation at ambient conditions. The reaction (5) is driven to its completion to form
BTO as Ba$^{2+}$ ions are regenerated to maintain the equilibrium. As Ba$^{2+}$ ions are
consumed to form BTO by reaction (5), more and more Ba(OH)$_2$ gets dissolved and
makes Ba$^{2+}$ ions available for the precipitation reaction. In this way reaction (5) is
kinetically controlled and driven to its completion till all Ba(OH)$_2$ and HTO are
consumed. Further, the addition of the water in the form of the droplets leads instant
precipitation of the BTO particles without varying the pH. Furthermore, the local pH is
also nearly constant since the precipitation occurs much faster as compared time span
required for the variation of pH due to the controlled solubility of highly basic Ba(OH)$_2$
at the ambient conditions. Also the water formed during the neutralization reaction (5)
does not affect the local pH to great extent. The controlled addition of water (in the
form of drops) leads to the controlled generation of the BTO particles which may give
rise to nearly equi-axed, isolated and less agglomerated nature for the resultant
agglomerates. The important point is that since the processing is carried out in the
acidic medium, there is no chance of forming BaCO$_3$ due to the reaction with
atmospheric CO$_2$. Secondly, the use of isopropanol-water system having lower
dielectric constant [40] as compared to water is effective in lowering the solubility of
BTO. All above discussion implies that the newly investigated acid-base reaction
between HTO and Ba(OH)$_2$ at room temperature solved the different problems like
excess use of oxalic acid, precipitation at higher temperature, estimation of Ti from
batch to batch, destabilization of anionic species resulting in the formation of mixture of
oxalates, contamination of BTO with K$^+$ etc. associated with Clabough's synthesis and
the exchange reaction [39, 13].

It is reported [45] that for a system Ti-H$_2$C$_2$O$_4$-H$_2$O, the stable anionic species
TiO(C$_2$O$_4$)$_2$$^{2-}$ are formed in the pH range of 2.5-3.1 if the titanium to oxalate ratio is
maintained as 1:2. Further, the working pH range for the Clabough's synthesis method
[39] is 2.5-3.1. This creates the problems like incomplete exchange, non-stoichiometry.
lower yield etc. On the other hand, for pH $> 5$ the stability of the anionic species TiO(C$_2$O$_4$)$_2$$^{2-}$ is affected drastically leading to the precipitation of the titanium hydroxide rather than the formation of the clear solution with soluble Ti species [24]. Further, the use of the Ti precursors like potassium titanyl oxalate (KTO), sodium titanyl oxalate (NaTO) etc. contaminates the final BTO precursor with K$^+$, Na$^+$ ions which are harmful to the dielectric properties. On the other hand, it is necessary to find the appropriate Ba precursor which will give the complete exchange to form the oxalate (BTO) with nearly equal to the theoretical yield. The halide/nitrates of Ba which are the salts of the strong acid and weak base produce pH in the range 2-2.5 [40] after their dissolution/dissociation. The fast exchange precipitation of the BTO by using the above Ba-salts with KTO/NaTO generates the free HNO$_3$/HCl, which decreases the pH leading to the incomplete exchange and non-stoichiometry in the resultant BTO powders. On the other hand, precursor like Ba-acetate (pH = 6.5-6.9) shifts the pH towards higher side $> 4.5$. This causes the destabilization of Ti species [TiO(C$_2$O$_4$)$_2$]$^{2-}$ producing thereby the mixture of oxalates [9]. In this case the temperature of pyrolysis of mixed oxalate precursor to obtain the BT is much higher ($> 900^\circ$C) than the normal decomposition temperature required to produce BT from BTO (650-750$^\circ$C) [9].

In the present newly developed exchange reaction initially the titanyl oxalate [23] is precipitated by using the reactions (6) and (7) between Ti-tetra butoxide and the oxalic acid which is further converted into the soluble ammonium titanyl oxalate (ATO) via reaction (8) by the addition of the ammonium oxalate. The clear solution of ATO is obtained by adding the sufficient amount of the water. This gives the dissociation of ATO into NH$_4$$^{+}$ and TiO(C$_2$O$_4$)$_2$$^{2-}$ through reaction (9) with the pH $\sim$4.25. The modified Ba-precursor solution having the pH $\sim$ equal to pH of ATO is prepared by partial neutralization reaction (10) between Ba(OH)$_2$ solution in distilled water and dilute HNO$_3$. The addition of the modified Ba-precursor solution into the ATO solution gives the instantaneous precipitation of BTO via reaction (11). The ATO is soluble in the water as the titanium has tendency to form anionic species: TiO(C$_2$O$_4$)$_2$$^{2-}$ by expanding its co-ordination [24]. Further since the ATO is salt of the strong acid and weak base the working pH is shifted to the higher side $\sim$ 4.25. The use of lower dielectric constant system: isopropanol-water lowers the solubility of BTO.
Furthermore, the NH$_3$OH and NH$_4$NO$_3$ are forming as byproduct during the exchange reaction (11) which keep the pH much away from the highly acidic conditions effective in lowering the solubility of BTO and can be easily removed during washing treatment. All these eliminated the problems like incomplete exchange, solubility of oxalate resulting in the lower yield, contamination of BTO with K$^+$/Na$^+$ non-stoichiometry etc. in the utility of the ATO during the cation exchange reaction (11). The pH of the modified Ba-precursor is equal to the pH of ATO. This use of modified Ba-precursor further also solved the problems like incomplete exchange, non-stoichiometry, and mainly the destabilization of the Ti species etc. associated with utility of the Ba-halide/nitrates/acetates. In microwave-hydrothermal (MH) synthesis the precursor (Ba and Ti) solutions are made in the water. It is reported [36] that during the microwave-hydrothermal synthesis under all the MH conditions the BaCO$_3$ always forms as an impurity phase. The excess Ba precursor is used in present work to increase the yield limited by the formation BaCO$_3$ impurity and control the morphology/size of the resultant BT particles [36]. The addition of the KOH mineralizer to the mixture of the precursor solution leads the hydroxide precipitation, which is further treated microwave-hydrothermally. The phase formation results due to the dissolution-recrystallization reaction mechanism.

The chemical characterization (micro- and chemical analysis) results [Table 3.1, 3.2, 3.7 & 3.8] suggest that the stoichiometric molecular precursor powders of BTO are formed in both the oxalate routes: simple acid-base reaction and exchange reaction via precipitation reactions (5) and (11) respectively. Further, the water of crystallization in barium titanyl oxalate (BTO) is found to be equal to 4H$_2$O from the microanalysis data [Table 3.1] in case of the acid-base reaction derived BTO rather than the 4.5H$_2$O [46]. In case of exchange reaction derived BTO, presence of adsorbed water is confirmed by thermal analysis results and then experimental data are compared with theoretical values [Table 3.9 & 3.10]. All these confirm the formation of the pure, stoichiometric BTO by the both the methods.

Experimentally, the yield of the BTO powder generated by the two oxalate routes is found to be > 99%. The small deviation (< 1%) from the theoretical value can be understood by considering the loss of the powders during the various physical processes.
(handling) like filtration, washing, drying, transferring etc. This implies that the destabilization has not occurred in both cases and this supports further the chemical characterization results. The destabilization will give the weight of the as-dried precipitate completely different from that of the theoretical yield of the BTO. However, in the case of the microwave-hydrothermal route yield is found to be very less. This lower value of the yield, may be due to the formation of the BaCO₃ impurity during all the MH reactions. The maximum 50ml reaction mixture of low molar concentration can be treated microwave-hydrothermally in one MH vessel. This gives very small amount of the active powder per MH synthesis experiment containing maximum 12 vessels. Thus, the lower yield in present case may be attributed to the loss during the washing, filtration of such very low amount of as-prepared powder, which may lead the incorrect value to the experimental observation. This may be the major reason of getting lower yield since its percentage limited by the BaCO₃ formation is effectively increased by the excess use of the Ba-precursor. Further, as far as the mass production is concerned the oxalate route is found to be more effective than the MH method. During a single 0.1M molar synthesis experiment by using the oxalate route maximum ~ 45 gm of precursor powder can be easily produced which will give ~ 12 gm of BT powder on pyrolysis of BTO. However, to generate the BT powder in the large scale by using the MH route, several experiments are required to perform.

The nature of the DTA/TGA plots in the temperature range of RT-1000°C for the BTO precursor generated by the above two oxalate routes matches very well with the reported thermal curves [3]. Each of them shows the three steps of decomposition [3]. Hence the decomposition scheme reported in the literature [3] is followed to calculate the weight losses during different stages for both cases. For the acid-base reaction derived BTO, the experimental values agree well with theoretical losses [Table 3.3]. The small deviation of experimental results from the theoretical values in step 3 and hence in total weight loss is due to the trapping of CO₂ within the material. This implies that the longer heating is required at the 3rd stage i.e at 750°C. The weight loss during the 1st step indicates the presence of the 4 moles of water in as-dried acid-base reaction derived BTO which agrees with the microanalysis results [Table 3.1 & 3.2]. However, for the exchange reaction derived BTO the total weight loss is higher than the
theoretical value which indicates the presence of the adsorbed water along with the 4H₂O. Hence after calculating the correct molecular weight of BTO by using the procedure described in the literature [4] and then adopting the same decomposition scheme [3] it is found that the experimental values of the weight losses during three stages are very close to the theoretical data [Table 3.11]. Further, it is also clear that the temperature required to obtain BT powders from the pyrolysis of BTO is only 750°C in both cases. This means that destabilization has not occurred in the both synthesis experiments [9]. The DTA/TGA data implies that the stoichiometric oxalate precursor is formed in both the cases. In the case of the exchange reaction the ATO is generated as the intermediate precursor which acts as a Ti precursor in the synthesis chemistry of BTO. The DTA/TGA curves [fig. 3.12] obtained for the presently synthesized ATO are observed to be quite similar to the reported plots of thermal analysis [27]. The three different major steps of the decomposition and four different stages during the first step itself are clearly seen in the thermal plots. Further, various peaks observed in the DTA curve of the presently synthesized ATO match very well with reported data [27]. The higher value of total experimental weight loss compared to the theoretical value for ATO to give TiO₂ indicates the presence adsorbed water+alcohol in as-dried ATO. Above observations further confirm that the stoichiometric ATO is formed in present synthesis route.

The XRD analysis of the as-dried precursor indicates again the formation of the single phase barium titanyl oxalate with monoclinic symmetry [4] for the both methods [fig. 3.2, and 3.15]. This confirms the water of crystallization to be equal to 4H₂O in case of exchange reaction derived BTO which was confirmed in micro-, chemical & thermal analysis. Further, in the case of the exchange reaction the XRD studies on the intermediate precursor ATO [fig. 3.14] suggest the generation of the single phase ATO with monoclinic symmetry [27] during the chemical reaction (8) since all the observed 'd' values are found to be very close to the corresponding reported d values [Table 3.12]. The XRD patterns of the powders obtained by heating BTO precursors generated by the two methods at 750°C show clearly the pure cubic BT phase [5-7] without any BaCO₃ [5] impurity [fig. 3.3 and 3.16]. This rules out the presence of BaCO₃ in as-dried BTO powders and confirms further the purity of the oxalate precursors. In case of the MH
route, the XRD pattern [fig. 3.26] of the dilute acetic acid washed powder also shows the pure cubic BT phase [5-7]. Further, the lattice parameter calculated for the all BT powders generated by the three different methods are in good agreement with reported data [7]. All above XRD observations are consistent with the chemical characterization and thermal analysis results in the case oxalate routes.

The FTIR spectra for the as-dried precursors [fig. 3.4 and 3.18] derived from the two oxalate routes match very well with the reported spectrum for single phase BTO [11]. All the vibrations and their intensities of different species in standard BTO [11] are observed in the as-dried precursor derived from the two methods. No vibrational bands corresponding to BaCO₃ and/or BaC₂O₄ are observed. In the case of exchange reaction, the FTIR spectrum for the intermediate precursor [fig. 3.17] is also found to be quite similar to that of the standard ATO [27] since all the standard vibrations of ATO along with their intensities are clearly observed in the spectrum of the presently prepared ammonium titanyl oxalate. Further, the FTIR spectra [fig. 3.5 and 3.27] for the BT powders obtained from the BTO and MH route show all the vibrations of the pure BT [15]. The FTIR results are also consistent with chemical, thermal and XRD data.

The XRF studies indicate the Ba/Ti ratio ~ 1.00 for the BT powders obtained from the two oxalate routes [fig. 3.6 and 3.19] without incorporation of any impurity like K⁺, Na⁺, Cl⁻. However, in the MH derived BT powder [fig. 3.28] ratio is found to be slightly excess [Ba/Ti = 1.0025]. This is due to the excess use of the Ba-precursor during the synthesis. Further, small impurity peak [fig. 3.28] corresponding to K⁺ in the case of MH derived BT is due to the KOH used for the hydroxide precipitation. This implies that sufficient number of washing should be done for MH derived powder. Further, the concentration of the Ba-precursor should not be large excess.

The SEM studies [fig. 3.7 and 3.20] are pointing mainly the agglomerated nature of the BTO particles irrespective of the method of synthesis. It is also noticeable that the both size and shape distribution is not very uniform. However, the primary particles are observed to be more or less spherical. This may be due to the non-uniform solubility among the primary particles [20, 34, 35]. The BT particles for the same are also nearly spherical plus agglomerated but distribution is wide in case of exchange reaction. This indicates that the further experimentation is needed to obtain uniformly distributed (size
& shape) and un-agglomerated particles of BTO. However, for MH derived BT [fig. 3.29] the particle size and shape distribution is uniform. It also shows the agglomeration but less. Both primary and less agglomerated particles are spherical in shape. The excess use of Ba-precursor plays an important role. The excess Ba ions (not used for the BaCO$_3$ and BaTiO$_3$ formation) may form positively charged atmosphere around a neutral BaTiO$_3$ particle with minimum surface to volume ratio. It avoids the interaction between such assemblies which are present nearby due to the electrostatic force of repulsion and controls the growth of the BT particle/agglomerate. Further, the particle/agglomerate size and the extent of the agglomeration depends upon the excess Ba$^{2+}$ ions concentration. Thus excess Ba-precursor might have helped in controlling the morphology of BT in present MH synthesis.

The densities of the sintered compacts [Table 3.4 & 3.13] for the BT powders generated by above two oxalate routes are comparable with the reported [19, 22] data but not very high. In all the three cases it increases with increasing the sintering temperature as reported in the literature [47, 47]. The maximum density equal to 96% is found. This may be due to the (1) oxygen non-stoichiometry in the sintered compacts and (2) wide distributed and agglomerated nature of particles in the as-dried and calcined powders.

The densities of the [Table 3.16] of BT compacts for MH route are low (max. = 91 %). This may be due to the presence of slightly excess Ba, and K$^+$ impurity ions in the BT powders. It is reported in the literature that for the BT powders with slight excess Ba requires the higher sintering temperature (> 1400°C) for the good densification [49]. Hence the density is lower in the present case. Further, density can be increased by using the sintering aids, heating in O$_2$ atmosphere etc. For this more study on the processing is needed.

The XRD studies on the sintered products [fig. 3.8, 3.21 & 3.30] clearly show the single phase BaTiO$_3$ having tetragonal symmetry with c/a ratio nearly equal to standard value in all three cases [19, 22] at all the sintering temperatures [Table 3.5, 3.14, 3.17]. The reflection corresponding to the Ba$_2$TiO$_4$ impurity at lower sintering temperature in case of MH route is due to the excess use of the Ba precursor.

The SEM studies on the sintered compacts show the increase in the grain size with increase in sintering temperature as reported in the literature [48] in all the three cases.
The smaller as well as bigger grains of very odd shapes are also observed in samples of the oxalate routes. This is because of the varied sizes of the BT particles in calcined powders. However for MH samples the grains are nearly uniform in sizes and shapes. This is due to the nearly uniform distribution of size & shape and less agglomeration nature of MH derived BT powders. This indicates the importance of controlling the particle size during the synthesis itself [41].

The dielectric properties are found to be comparable with the reported data [19, 22] in all the three cases. The dielectric constant at RT and \( T_c \) increases with increase in the sintering temperature in all the three cases as reported in the literature [48]. This is due to the increase in the density and grain size with increase in sintering temperature [48, 50, 51]. Further, there is increase in \( T_c \) with the sintering temperature [47, 48], which is again due to the increase in grain size with temperature [48, 50, 51]. However, at the lower sintering temperature, the dielectric constant at \( T_c \) for MH sample is very low with broad transition. This is because of the (1) fine nature of the grains [52] (2) incorporation of the \( K^+ \) impurity in the as-prepared powder and (3) slightly higher Ba/Ti ratio (1.0025) in as-prepared powder [53] and (4) lower densification. The dielectric loss in case of oxalate samples is observed to be comparable with the reported data [19, 22]. However, loss is high in case of MH samples. This is due to the lower densification in the case of the MH samples as compared to the oxalate samples [48]. In all the three cases the loss between the RT-\( T_c \) increases with decreasing the sintering temperature. This is because the density decreases with decreasing the sintering temperature i.e porosity increases. This results, in increase in percentage of adsorbed water in the pores [48]. This causes the increase in the loss [48]. With increasing the sintering temperature porosity decreases and hence the percentage of adsorbed water also decreases which in turn reduces the loss [48]. Further, for a given sample the loss decreases with increasing the temperature towards \( T_c \). This is due to evaporation of the water molecules. The hysteresis loop parameters are found to be very close to the reported values [19, 22] in case of oxalate samples only for the higher temperature of sintering. The data at the lower sintering temperatures indicate the poor densification. This is clearly found in the case of MH samples. The more experimentation is required to find control over
morphology in the as-dried precursor powders. The particle size can be controlled by using little modification like use of surfactants, aging etc. in the main route [50, 54].

**Conclusion:** The BT powders are synthesized successfully by the (1) two newly investigated oxalate routes via synthesis of the well known molecular precursor: barium titanyl oxalate (BTO) at room temperature and (2) energy and time saver microwave-hydrothermal route.

The oxalate routes have the various advantages: (a) methods are simple, fast and give the reproducible results (b) methods produced the single phase, stoichiometric barium titanyl oxalate (BTO) powders with ~100% yield (c) contamination of the unwanted impurity ions like Na\(^+\), K\(^+\), Cl\(^-\) which are harmful to the dielectric properties is avoided and (d) various problems like excess use of oxalic acid, precipitation at higher temperature, estimation of Ti from batch to batch, destabilization of anionic species resulting in formation of mixture of oxalates, incomplete exchange, solubility of oxalate resulting in the lower yield, non-stoichiometry etc. associated with the prior art methods are solved.

The microwave-hydrothermal route is also found to be very simple, fast and energy & time saver. The reaction kinetics and dissolution-recrystallization mechanism is very fast. Method gives highly reproducible results and morphology of powders can be controlled.

The further experimentation/modifications are required to obtain the uniformly distributed (in size and shape) un-agglomerated, BTO particles having higher sinterability property. Furthermore, more study is required to process such powders to obtain dense compacts of high dielectric-ferroelectric properties.
References

5. ASTM card No.: BaCO$_3$ [5-0378], BaC$_2$O$_4$ [1-0740] and JCPDS file No.: BaTiO$_3$ [27582].
18. ASTM card No.: tetragonal BaTiO$_3$ [5-0626].
29. (a) ASTM card No. 1-0809, (b) ASTM card No. 1-0858.