CHAPTER 6

EFFECT OF MICROWAVE SINTERING ON THE STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF BaTiO$_3$ NANOPARTICLES

6.1 INTRODUCTION

Barium titanate (BaTiO$_3$) is a potential ferroelectric material with high dielectric constant and widely used in electronic components such as multilayer capacitors (MLCs), PTC thermistors, piezoelectric transducers, and a variety of electro-optic devices (Dan et al 2002, Yoon et al 2006, Vijatović et al 2008, Singh et al 2011). However, the dielectric, ferroelectric and piezoelectric properties of bulk BaTiO$_3$ depends on the crystalline structure, grain size, particle distribution, sintering density, sintering temperature, purity, etc., (Chu et al 2007, Fang et al 2011, Xie et al 2011). In order to improve the properties and application potential, recent focus is on the nanostructure BaTiO$_3$ material (Buscaglia et al 2004, Mao et al 2010, Pavlovic et al 2011).

The ferroelectricity is fundamentally associated with the domain structure and domain motion. The domain structure is formed during the cubic (paraelectric phase) to tetragonal phase (ferroelectric phase) transformation at Curie temperature. The configuration and type of domains depend on the presence of additives and on the microstructure obtained during the sintering process. The homogeneous and small grained microstructure with a single domain structure enables the stable and uniform ferroelectric behavior of
BaTiO$_3$ ceramics (Silveira et al 2013). Besides the crystallographic modification and external strain also has a great influence on the domain structure, where the grain size (microstructure) is very important parameter which influences on the domain width and domain energy.

The perovskite structure has the capability to host ions of different size, so large number of different dopants can be accommodated in the BaTiO$_3$ lattice. As shown in Figure 6.1, the coordination number of A (Ba$^{+2}$ - Barium) is 12, while the coordination number of B (Ti$^{+4}$ - Titanium) is 6. Any structure consisting of the corner-linked oxygen octahedra with a small cation filling the octahedral hole and a large cation (if present) filling the dodecahedral hole is usually regarded as a perovskite, even if the oxygen octahedral is slightly distorted. The perovskite structure has a wide range of substitution of cations A and B as well as the anions. However the principles of substitution must maintain charge balance and control the size within the range for particular coordination number. Because the variation of ionic size

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**Figure 6.1 Perovskite structure of BaTiO$_3$**

- O$^{2-}$ Oxygen
- A (Ba$^{+2}$ Barium)
- B (Ti$^{+4}$ Titanium)
and small displacements of atoms, that lead to the distortion of the structure and reduction of symmetry have profound effect on physical properties (Jaffe et al 1971, Hench et al 1990).

Microwave heating has been touted as a means of sintering variety of ceramic materials. The perceived advantages of microwave sintering over conventional sintering include more-uniform heating, better properties of the product, greater throughput with resulting smaller particle size, and greater energy efficiency. BaTiO$_3$ nanoparticles sintered by conventional resistive heating technique possess severe lattice strain. In the conventional heating process, the heat energy is absorbed by the surface of the sample and diffused through the bulk, introducing severe strain for the lattice.

The microwave sintering technique, due to its rapid and uniform volumetric heating with reduced grain growth at a given density, controls the particle size distribution and minimizes the thermal strain with consequently better mechanical properties (Oghbaei et al 2010, Vasudevan et al 2013). Hence for the preparation of strain free nanostructures, microwave sintering has been effectively used for pure and doped BaTiO$_3$ nanoparticles (Takahashi et al 2006, Sadhana et al 2008, Sharma et al 2011, Chen et al 2012, Sharma et al 2012). The structural properties of BaTiO$_3$ prepared by conventional and microwave sintering has been studied extensively. However there is no report on the comparison of optical properties of BaTiO$_3$ prepared by different sintering methods and also there is no report on the measurement of lattice strain co-efficient ($\varepsilon$) of the BaTiO$_3$ nanoparticles.

Many methods have been reported for the synthesis of BaTiO$_3$ nanoparticles such as oxalate precipitation, high energy ball milling, hydrothermal, sol-gel method (Ghosh et al 2007, Pavlovic et al 2011). Among these methods, high energy ball milling is effectively used for the preparation
of nanoparticles with controlled microstructure. In this work, the effect of microwave sintering on the structural, optical and electrical properties of BaTiO$_3$ nanoparticles has been systematically studied. Significant improvements in the structural and electrical properties have been observed for BaTiO$_3$ nanoparticles sintered by microwave technique compared to the conventional sintering.

6.2 EXPERIMENTAL PROCEDURE

6.2.1 Synthesis of BaTiO$_3$ Nanopowders

BaTiO$_3$ nanopowders were prepared from high purity (99.98%) precursors of BaCO$_3$ and TiO$_2$. Initially stoichiometric ratio of BaCO$_3$ and TiO$_2$ precursors were taken into the tungsten carbide (WC) vial (200ml capacity) containing WC balls (10 mm dia) as a milling media. The powder to ball ratio was taken as 1:10. Toluene was used as a lubricant for wet milling process to get a suitable viscosity and the milling was performed for 20 h at a speed of 300 rpm, to get a proper impact of WC balls with the powders. The viscosity of the mixture was controlled by the addition of toluene for every 2 h intervals. Finally the milled mixture was dried in hot air oven at 110$^\circ$C for 12 h.

6.2.2 Sintering

The milled powders were pre-calcined at 500$^\circ$C to remove the organic residues in the material and then ground into fine mixing. The pre-calcined samples were then sintered at 1000$^\circ$C for 2 h in air atmosphere by using conventional heating method at a heating rate of 5$^\circ$C/min and then cooled down to room temperature at the same rate after soaking for 120 min. Second batch of samples were sintered in a microwave furnace at 1000$^\circ$C at a heating rate of 50$^\circ$C/min and soaked for 30 min. followed by fast cooling to
room temperature at a rate of 20°C/min. Typical heating profile for conventional and microwave sintering at 1000°C is shown in Figure 6.2.

![Heating profile for conventional and microwave sintering of BaTiO$_3$ nanoparticles at 1000°C](image)

Figure 6.2 Heating profile for conventional and microwave sintering of BaTiO$_3$ nanoparticles at 1000°C

6.2.3 Characterization Studies

Powder X-ray diffraction analysis was performed using a Bruker D8 XRD with CuKα radiation (λ=1.5409Å) to confirm the crystal structure and phases present in the BaTiO$_3$ nanoparticles sintered at 1000°C by conventional and microwave sintering techniques. The mean magnitude of the local strain in the nanocrystalline samples was estimated from the X-ray diffraction pattern using Williamson-Hall pitch analysis (Yu et al 2000). High resolution scanning electron microscopy (HR-SEM) was performed to study the particle distribution and surface morphology of BaTiO$_3$. 

nanoparticles sintered at 1000°C by conventional and microwave sintering using a Hitachi S-3400 SEM. High resolution transmission electron microscopy (HR-TEM) study was performed using JEOL JEM 3010 HRTEM with an applied voltage of 200 kV to determine the exact particle size and crystalline nature of BaTiO$_3$ nanoparticles sintered at 1000°C by microwave heating technique.

UV-Vis spectroscopy was employed to determine the optical band gap of BaTiO$_3$ nanoparticles using Perkin Elmer Lambda 35 spectrometer. The optical band gap energy is related to the absorbance and photon energy by Wood and Tauc relation

\[ \alpha h \nu \propto (h \nu - E_{g\text{ opt}})^2 \]  \hspace{1cm} (6.1)

where $\alpha$ is the absorbance, $h$ is the Planck constant, $\nu$ is the frequency, and $E_{g\text{ opt}}$ is the optical band gap energy. The plot obtained between $(\alpha h \nu)^2$ vs. Photon energy (eV) determines the optical band gap ($E_g$) by linear fitting method. Fourier transform infra red (FT-IR) spectroscopy was carried out to reveal the vibrational states of the BaTiO$_3$ crystal lattice using a Perkin Elmer spectrum one model spectrophotometer.

The dielectric constant at room temperature was measured by using a high precision LCR meter with frequency ranging from 50 Hz to 5 MHz. To measure the ferroelectric hysteresis of BaTiO$_3$ nanoparticles, the pre-calcined powders at 500°C were compacted using uniaxial press. The pellets were subjected to both conventional and microwave sintering at 1000°C. Further the samples were polished and electroded with silver paste. After electroding the ferroelectric measurements were performed by using an automatic PE loop tracer.
6.3  RESULTS AND DISCUSSION

6.3.1  Powder XRD Analysis

Powder X-ray diffraction patterns shown in Figure 6.3 reveal that both the conventional and microwave sintered BaTiO$_3$ nanoparticles possess a high crystalline nature without any secondary and impurity phases.

![Figure 6.3 Powder X-ray diffraction patterns of conventional and microwave sintered BaTiO$_3$ nanoparticles at 1000°C](image)

The strongest peak was observed at 31.5° for the (101) plane and the tetragonal splitting was clearly observed at the (002) plane for the conventional sintered sample. The full width at half maximum (FWHM) for the (002) plane of microwave sintered sample is higher than the conventional sintering, which confirms the reduced particle size of microwave sintered
sample. From the peak broadening, the BaTiO$_3$ crystallites were found to be in the range 20 nm and 30 nm for the microwave and conventional sintered samples. The lattice parameters were determined to be $a = b = 3.97957$ and $c = 4.00483$, confirming the tetragonal structure with a $c/a$ ratio of 1.0063 for microwave sintered BaTiO$_3$ nanoparticles. For the conventional sintered nanoparticles the lattice parameters were estimated as $a = b = 3.97498$ and $c = 4.01683$, with a $c/a$ ratio of 1.0105.

6.3.1.1 Lattice Strain ($\varepsilon$)

From the XRD data, values of $\beta_{hkl} \cos \theta_{hkl}$ as a function of $4\varepsilon \sin \theta_{hkl}$ were plotted and the lattice strain co-efficient ($\varepsilon$) was estimated from the slope as shown in Figures 6.4 and 6.5.

Figure 6.4 Lattice strain curve ($\varepsilon$) of conventional sintered BaTiO$_3$ nanoparticles
The lattice strain co-efficient for the conventional sintered BaTiO$_3$ nanoparticles was estimated as $1.37 \times 10^{-3}$ (Figure 6.4). For the microwave sintered samples it was found to be $0.229 \times 10^{-3}$ (Figure 6.5). The reduced lattice strain observed for the microwave sintered sample might be due to the rapid heating and cooling cycle employed during sintering, which reduces the thermal stress accumulated in the material.

6.3.2 HR-SEM Analysis

HR-SEM studies show the formation of tetragonal shaped nanocrystals grown along the c-axis. The conventional sintered BaTiO$_3$ crystals were found to have wide distortions with random orientation as shown in Figure 6.6 (a), (b) and (c). The particles were packed with large pores in some places. Microwave sintered BaTiO$_3$ nanoparticles were found to have smaller particle size and uniform distribution compared to conventional sintered sample. Due to the rapid heating and lower sintering
temperature, growth of particles was restricted leading to the smaller particle size. The particles were densely packed and the porosity was found to be less for the microwave sintered samples as shown in Figure 6.6 (d), (e) and (f).

Figure 6.6  SEM images of (a), (b) and (c) conventional sintered and (d), (e) and (f) microwave sintered BaTiO$_3$ nanoparticles

For the conventional sintering, the particle size distribution ranges from 80 nm to 180 nm, with a Gaussian average particle size of 145 nm as shown in Figure 6.7. In the microwave sintering, the particle size distribution was in the range 60 nm to 160 nm, and the average particle size determined from the Gaussian fit was about 105 nm. Hence a reduction in the particle size of about 50 nm was observed microwave sintered samples (Figure 6.8).
Figure 6.7  Size distribution histogram of conventional sintered BaTiO$_3$ nanoparticles

Figure 6.8  Size distribution histogram of microwave sintered BaTiO$_3$ nanoparticles
Energy dispersive X-ray analysis (EDAX) was carried out to confirm the purity of the BaTiO$_3$ nanoparticles prepared by high energy ball milling, since high energy ball milling can introduce some impurities due to the impact of tungsten carbide balls through interaction with each other and also along the walls of the vial. From the EDAX analysis it was observed that barium titanate does not have any impurities even after milling for about 20 h. Figure 6.9 shows the EDAX spectrum of BaTiO$_3$ nanoparticles with high intense barium and titanium peaks.

![EDAX spectrum of BaTiO$_3$ nanoparticles](image)

**Figure 6.9  EDAX spectra of BaTiO$_3$ nanoparticles**

6.3.3 TEM Analysis

BaTiO$_3$ particles were found to be in the nanoscale range even after high temperature microwave sintering at 1000°C as shown in Figure 6.10 (a) and (b). The tetragonallity of the nanoparticles was clearly observed with the size of 85 nm as shown in Figure 6.10 (b). The (112) plane orientation was determined by measuring the distance between the two adjacent planes over a wide area and the average d-spacing value of 1.6344Å matches well with the
tetragonal d-spacing of the BaTiO$_3$ given in the JCPDS as shown in Figure 6.10 (c). This further confirms the tetragonal nature of BaTiO$_3$ nanoparticles. The selected area electron diffraction pattern (SAED), reveals the high crystallinity of BaTiO$_3$ nanoparticles. The bright spots were spaced crystallographically with perfect plane orientation as shown in Figure 6.10 (d).

Figure 6.10  (a) and (b) TEM images, (c) HRTEM image of (112) plane orientation and (d) SAED pattern of microwave sintered BaTiO$_3$ nanoparticles
6.3.4  UV-VIS Spectral Analysis

Figures 6.11 and 6.12 show the absorbance spectra of conventional and microwave sintered BaTiO$_3$ nanoparticles at two different sintering temperature. The spectra show a minor change in the absorption edge for conventional and microwave sintering, and also for different sintering temperatures.

![UV-Vis absorbance Vs wavelength of conventional sintered BaTiO$_3$ nanoparticles](image)

**Figure 6.11**  UV-Vis absorbance Vs wavelength of conventional sintered BaTiO$_3$ nanoparticles
Figure 6.12 UV-Vis absorbance Vs wavelength of microwave sintered BaTiO$_3$ nanoparticles

For conventional sintered BaTiO$_3$ nanoparticles, the band gap value was estimated to be 4.092 eV at 1000°C and 4.014 eV at 1100°C and for the microwave sintered BaTiO$_3$ nanoparticles the energy gap was 4.157 eV at 1000°C and 4.105 eV at 1100°C as shown in Figures 6.13 and 6.14.

Microwave sintered BaTiO$_3$ nanoparticles exhibited a higher band gap values compared to conventional sintering due to the effect of particle size reduction and the degree of structural ordering. As the sintering temperature was increased to 1100°C the band gap energy decreases. This indicates that the increase in sintering temperature increases the particle size leading to a reduction in energy gap values.
Figure 6.13  Absorption co-efficient Vs band gap of conventional sintered BaTiO$_3$ nanoparticles

Figure 6.14  Absorption co-efficient Vs band gap of microwave sintered BaTiO$_3$ nanoparticles
6.3.5 FT-IR Spectroscopy Analysis

FT-IR spectra of both conventional and microwave sintered samples are shown in Figure 6.15. In the FT-IR spectra, two dominant absorption peaks appear in the range 500 to 1000 cm$^{-1}$. Beyond 1000 cm$^{-1}$ no dominant absorption peaks were observed indicating the purity of the material. However, some minor peaks were observed in the range 1400 to 1700 cm$^{-1}$ and from 2800 to 3000 cm$^{-1}$. For both conventional and microwave sintered samples, peaks due to C-H vibrational stretching were observed at around 2860 and 2930 cm$^{-1}$. This C-H stretching vibration may be due to toluene used during milling. During the high temperature sintering, the carbon residues from toluene may react with moisture to form the C-H bond. However, there was not much difference in the C-H stretching frequency between the conventional and microwave sintering. But there was a marginal increase in the intensity of transmittance for microwave sintered samples.

![FT-IR spectra conventional and microwave sintered BaTiO$_3$ nanoparticles at 1000$^\circ$C](image)

Figure 6.15 FT-IR spectra conventional and microwave sintered BaTiO$_3$ nanoparticles at 1000$^\circ$C
Figure 6.16 shows the fingerprint region of BaTiO$_3$ nanoparticles sintered at 1000°C by conventional and microwave sintering technique. Two major absorption peaks were observed around 860 and 650 cm$^{-1}$. The stretching at around 460 and 510 cm$^{-1}$ corresponds to BaTiO$_3$ surface mode vibrations. The stretching around 560 cm$^{-1}$ corresponds to TiO$_6$ octahedral normal vibration mode. A broad stretching observed between 600 and 750 cm$^{-1}$ corresponds to Ti-O stretching vibration. A sharp peak observed at 860 cm$^{-1}$ corresponds to CO$_3^{2-}$ stretching, which originates due to the formation of δ-BaCO$_3$. The strong stretching vibrations of Ti-O, Ti-O$_6$, Ti-O$_2$ confirmed the BaTiO$_3$ nanocrystal formation, when sintered at 1000°C by both conventional and microwave sintering.

![FT-IR fingerprint region of conventional and microwave sintered BaTiO$_3$ nanoparticles at 1000°C](image)

**Figure 6.16** FT-IR fingerprint region of conventional and microwave sintered BaTiO$_3$ nanoparticles at 1000°C
6.3.6 Dielectric Measurements

Room temperature dielectric constant and dielectric loss measured for the conventional and microwave sintered BaTiO$_3$ nanoparticles are shown in Figures 6.17 to 6.20. With the increase of frequency, the dielectric constant and loss decreases exponentially. From the measurements, it was observed that the conventional sintered samples at 1000°C exhibit a low dielectric constant of $\varepsilon_r = 3440$ with a dielectric loss $\tan\delta = 0.1246$ at a lower frequency of 50 Hz. The microwave sintered samples exhibit high dielectric constant of $\varepsilon_r = 4445$ with low dielectric loss of $\tan\delta = 0.0961$ at lower frequency. The higher dielectric constant value observed for microwave sintered sample was attributed to the finer particles size distribution in the nanoscale range, which resembles dense microstructure without any significant porosity. When the particle size decreases grain surface contributes more than the grain structure for attaining high dielectric constant.

![Figure 6.17 Room temperature dielectric constant Vs frequency for conventional sintered sample](image)
Figure 6.18 Room temperature dielectric constant Vs frequency for microwave sintered sample

Figure 6.19 Dielectric loss vs. frequency for conventional sintered sample
6.3.7 Ferroelectric Measurements

The hysteresis loops for conventional and microwave sintered BaTiO$_3$ nanoparticles showed variation in polarization, coercivity and remanence values (Figures 6.21 and 6.22). The conventional sintered samples showed a polarization maximum ($P_{\text{max}}$) of 53.62 µC/mm$^2$, remanence ($P_r$) of 18.55 µC/mm$^2$ and a coercivity of 0.437 kV/mm at an applied voltage of 10 kV, and a frequency of 50 Hz. For the microwave sintered samples the $P_{\text{max}}$ was increased to 73.79 µC/mm$^2$ and the remanence and coercivity values were decreased ($P_r = 16.81$ µC/mm$^2$ and $E_C = 0.293$ kV/mm). Further increase in the voltage leads to a decrease in the ferroelectric behavior, which may due to the leakage of current through the samples. The reason for decrease in coercivity values for microwave sintered BaTiO$_3$ nanoparticles was due to the smaller particle size and their distribution compared to the conventional sintered samples.
Figure 6.21 P-E Hysteresis loops for conventional sintered BaTiO$_3$ nanoparticles

Figure 6.22 P-E Hysteresis loops for microwave sintered BaTiO$_3$ nanoparticles
BaTiO$_3$ nanoparticles were prepared by high energy ball milling and the effect of microwave sintering on the crystal structure, particle size, microstructures, optical and electrical properties has been investigated. In the microwave sintering, the tetragonal crystal structure is retained even at a lower sintering temperature of 1000°C compared to 1300°C for BaTiO$_3$ bulk material. The microwave sintered samples show low strain ($\varepsilon$) co-efficient with reduced particle size. The measured band gap ($E_g$) of about 4.157 eV for the microwave sintered sample is higher than the conventional sintering ($E_g = 4.092$ eV). The microwave sintered samples possess higher dielectric constant value of $\varepsilon_r = 4445$ with low dielectric loss of $\tan\delta = 0.0961$ compared to conventional sintered sample. The ferroelectric studies reveal a higher $P_{\text{max}}$ value of about 73 $\mu$C/mm$^2$ with reduced coercivity of 0.293 kV/mm and low hysteresis loss for the microwave sintered samples. In conclusion, the microwave sintered BaTiO$_3$ nanoparticles prepared by high energy ball milling can be effectively used for various applications such as MLCCs, sensors, transducers, thermistors, etc., owing to their promising structural, optical and electrical properties.