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Microwave sintering time optimization to boost structural and electrical properties in $BaTiO_3$ ceramics

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ABSTRACT

$BaTiO_3$ ceramics with fine grain distribution were successfully fabricated by solid state reaction using microwave processing. The role of microwave sintering time for producing a controlled microstructure with optimized dielectric and ferroelectric properties in $BaTiO_3$ ceramics is discussed. X-ray diffraction data were refined with Fullprof program using Rietveld method, which showed perovskite-type tetragonal structure with space group P4mm for all prepared samples. The scanning electron microscope (SEM) revealed that the grain size found to increase with increasing microwave sintering time. Dielectric constant (ε_r) measured in frequency range 0.1 Hz to 10^5 Hz at different temperatures showed depressive behaviour in the higher frequency region which decreases with increasing frequency. The $BaTiO_3$ sample sintered at 1200 °C for 60 minutes exhibited best properties as high dielectric constant ($\varepsilon_r \approx 1.5 \times 10^4$) with lowest degree of diffuseness ($\gamma \approx 1.0741$). The ferroelectric properties were investigated using P-E hysteresis loop. The remnant polarization (P_r) increased while the coercive field (E_c) decreased with increasing microwave sintering time applying these are micro structural dependent. Optimum sintering time has been found resulting in high values of relative permittivity and remnant polarization.

Keywords: Barium Titanate, P-E Loops, phase transition, grain size, Curie Weiss law

INTRODUCTION

Barium Titnate ($BaTiO_3$) is extensively important ferroelectric material because of its better ferroelectric properties with high dielectric constant. Due to many advantages viz. High dielectric constant, high activity and suitable for nano sized device miniaturization, it finds many applications in microelectronic devices such as dielectric amplifier, multilayer capacitors, ferroelectric memories, transducers and Thermistors etc.[1-5] It is reported earlier that dielectric properties are sensitive to processing conditions.[1, 6] Focusing on calcination and sintering parameters to mold same material with different micro-structural properties (such as grain size and dielectric constant) will open up new fields for a promising future. For the improved ferroelectric and dielectric properties it is necessary to control the particle size and surface morphology. Various synthesis techniques leading different particle size and surface morphology are used to prepare $BaTiO_3$. These techniques are sol-gel,[7] hydrothermal,[8] sol-precipitation,[9] organic polymeric,[10] conventional and microwave assisted methods have been found successful for synthesis of nano-sized $BaTiO_3$. Microwave synthesis of materials is finding widespread applications due to its rapid and uniform heating mechanism in contrast with conventional synthesis where high temperature and long duration heat treatment is required. Microwave sintering is basically different because of its heating mechanism where sample gets heated by electromagnetic waves through suspector and leads to advantage of high product yield, energy saving, low temperature and reduced soaking time.[11,12] Microwave synthesis of barium titanate with different processing conditions such as soaking time, sintering atmosphere and heating rate are still subjects of research.

In the present work, barium titanate ceramics were synthesized using the solid-state reaction route with different sintering duration using microwave. The effect of microwave sintering time on structural, dielectric and ferroelectric properties has been investigated using XRD, SEM, impedance analyzer and P-E loop tracer.

EXPERIMENTAL DETAILS

Barium Titanate (BT) ceramics were synthesized with high purity $BaCO_3$ (99%, Aldrich), and TiO_2 (99%, Aldrich)

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as the starting materials. Stoichiometries mixture of the starting materials was ball milled for 6 hours using zirconium balls in distilled water at 500 ball's RPM. DTA and TG analysis carried out to determine adequate reaction temperature and decomposition of ball milled BT powder. These measurements were performed using a Q-600 SDT-TA instrument from room temperature to 1150°C with a heating rate of 5ºC/min, in air. The ball milled powder was calcined at 1050 °C for 90 minutes in the air atmosphere using a microwave furnace to obtain single-phase BT. The single phase formation of the calcined powder was identified as pure BT by X-ray diffraction analysis. The calcined powder was milled again for 30 minutes and mixed with 3 wt. % polyvinyl alcohol (PVA) as a binder. As prepared BT powder was pressed into disks of diameter ~ 12 mm and thickness ~ 1.5 mm under pressure of 15 MP for 5 minutes. The disks were sintered for different time duration 30, 60 and 90 minutes at 1200°C with heating rate 25°C/min., and then cooled to room temperature in closed furnace. Thus prepared samples were abbreviated as BTMS30, BTMS60 and BTMS90 respectively. The bulk densities of disks were measured using the Archimedes Principle. The crystalline phases of sintered samples were identified by X-ray diffraction on a diffraction-meter (XRD; MiniFlex2 Rigaku Japan) with Cu K_α radiation in a wide range of 2θ ($10° \leq 2\theta \geq 80°$) at a scanning rate 2 degree/minute, operated at 30 kV and 15 mA. The Rietveld refinement of X-ray data was carried out using Fullprof program. The microstructure of fractured pellets was investigated using a scanning electron microscope. The dielectric properties as a function of temperature (25°C -250 °C) in the frequency range (0.1Hz-10^5Hz) were analyzed by an impedance /gain-phase analyzer (Alpha-A high frequency analyzer, Nova-control Tech.). Polarization vs. electric field (P-E) hysteresis loops were sketched at room temperature using automatic P-E loop tracer (Marine India) with samples immersed in silicone oil to prevent electrical breakdown.

Results and Discussion

Microstructure, density and phase purity.

Figure 1 illustrates DSC/TGA curve of un-calcined ball milled $BaTiO_3$ powder from room temperature to 1150°C. It was observed from the curve that around 21 % weight loss occur from room temperature (RT) to 900°C. The curve displayed the process of weight loss in two steps, from 27 °C to 730 °C and 730 °C to 900 °C due to release of water, CO and CO_2 respectively.[13] Above 900°C, no considerable weight loss was observed. Therefore, DSC/TGA analysis hints to form a single phase $BaTiO_3$ around 900°C. In the present work, therefore the calcine temperature was selected at 1050°C for 90 minutes for all BT samples.

Figure 2 shows the X-ray diffraction patterns of microwave sintered BT ceramic samples. The crystal structure of these samples was identified as the tetragonal phase (t-$BaTiO_3$) and all peaks were indexed with JCPDS Card No.: 891428. Minor traces of $Ba_6Ti_{17}O_{40}$ were also detected around 28 degree, confirmed by JCPDS No.: 771566.

For more detailed structural information X-ray diffraction data were simulated by Fullprof program using Rietveld

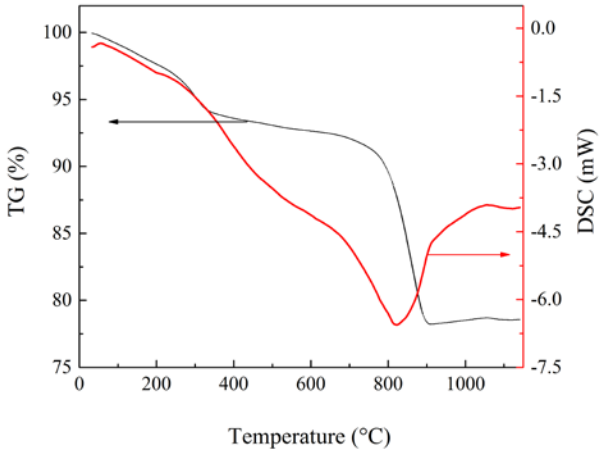

Figure 1. DSC/TGA curves for the ball milled $BaTiO_3$ powder.

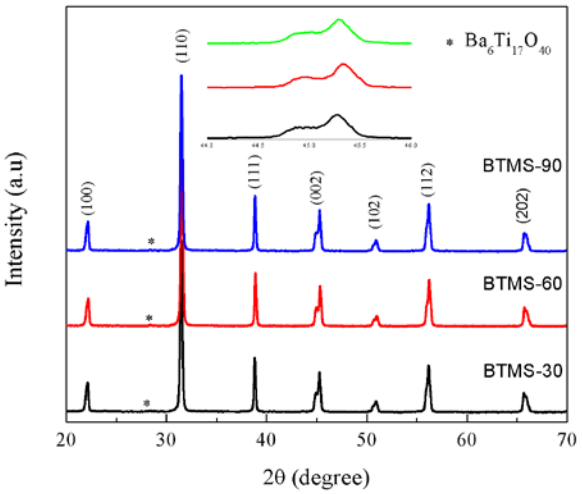

Figure 2. X-ray diffraction patterns of $BaTiO_3$ ceramics, sintered by microwave at 1200°C for 30 min, 60 min, and 90 min. Inset shows the enlarged view of peak splitting around 45 degree.

method.[14] The Rietveld method is used to simulate theoretical line profile until it matches with the experimentally measured profile based on least square approach also small R-values of refinements (Rp and Rwp) determine the quality of Rietveld fit.[15,16] Figure 3 shows the difference between experimental and simulated XRD patterns for all prepared ceramics samples. Crystal structure parameters and profile R-factors calculated from the Rietveld refinement listed in Table 1. It can be observed from the Table that both lattice parameters a and c found to be increases with increasing microwave sintering time. The axial ratio c/a for sample BTMS-60 found to be 1.0079 which is highest among all prepared BT samples. It indicates higher degree of tetragonality in BTMS-60 ceramic.

The tetragonal phase was also verified by the splitting of peak (002) around 45º- 46° into two peaks corresponding to (002+200) plane respectively,[17] as inset Figure 2. The sample BTMS60 displayed strong indication tetragonality as well. It was reported earlier that tetragonality is strongly influenced by the effect of internal stress on crystal structure. More the uncompensated internal stress through the grains lesser is the tetragonal distortion.[18] The crystallite size of sintered $BaTiO_3$ powder was calculated by the Debye

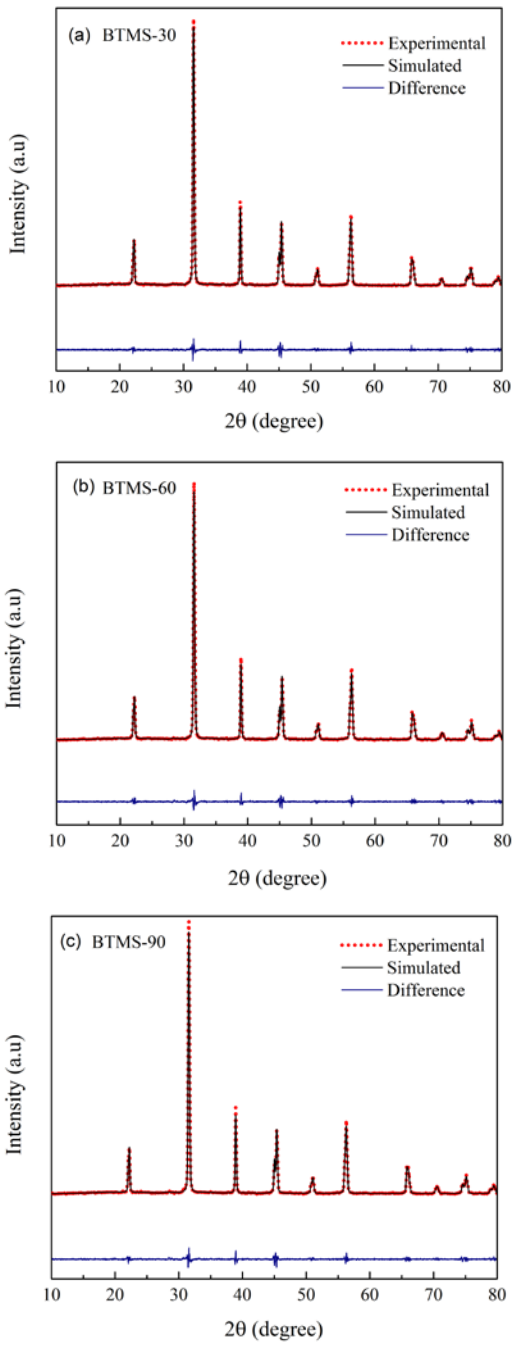

Figure 3. Rietveld refined X-ray diffraction patterns of all prepared $BaTiO_3$ ceramics samples.

Table1. Structural and lattice parameters a, b and c obtained from Rietveld refinement of prepared $BaTiO_3$ samples. χ^2, R_p and R_{wp} determine the quality of Rietveld fit.

Parameters	Sample		
	BTMS-30	BTMS-60	BTMS-90
Space group	P4mm	P4mm	P4mm
a=b (Å)	3.9947	3.9948	3.9952
c (Å)	4.0251	4.0265	4.0251
c/a	1.0076	1.0079	1.0075
Volume ($Å^3$)	64.23	64.26	64.25
Density (gm/cm^3)	6.058	6.066	6.068
χ^2 (chi^2)	2.79	2.77	2.97
R_p	6.37	6.48	6.58
R_{wp}	8.42	8.45	8.68

Scherer formula using line broadening of high intensity peak[19]:

$$D = \frac{0.9\lambda}{\beta Cos\theta} \qquad \text{(i)}$$

Where λ is the wavelength of X-ray, θ is the diffraction angle and β is full width at half maxima (FWHM). Thus calculated crystallite size was found 32, 30 and 33 nm for samples BTMS-30, BTMS-60 and BTMS-90 respectively. Density of prepared $BaTiO_3$ pellets was measured by the Archimedes principle using xylene. The density of pellets was measured 5.5, 5.6 and 5.7 g/cm^3 for samples BTMS30, BTMS60 and BTMS90 respectively, which corresponding to relative density of 90.7%, 92.3% and 93.9%, of the calculated theoretical density (Table 1) of BT at room temperature, which are in line with earlier reported values by O. P. Thakur et al.[20] Surface microstructure was investigated by SEM micrographs of fractured pellets, as shown in Fig. 4(a-c). It was observed from these figures that all prepared samples exhibited a uniform and dense microstructure. The average grain size of samples was calculated by linear intercept method. The BT samples sintered for 30, 60 and 90 minutes have an average grain size 290 nm, 375 nm and 360 nm respectively. The average grain size observed to increase with increasing time up to 60 minutes. Sample sintered for 90 minutes; show some abnormal grain growth with decreased average grain size 360 nm. The grain size measured by SEM exceeds that calculated from XRD data may be attributed to high calcine temperature (1050°C). It was reported earlier by H. Hsing et al that the deviation between XRD and TEM/SEM measurement becomes more significant due to occurrence of hard agglomeration and domains when calcine temperature exceed from 1000°C.[17]

Dielectric Analysis Investigation of dielectric properties as a function of frequency and sintering time have been carried out in frequency range from 0.1 Hz to 10^5 Hz (Fig. 5(a & b)) at different temperatures (Fig. 6 (a & b)). All the prepared samples shows higher values of dielectric constant (ε_r) at lower frequency which is usual behaviour of ferroelectric materials and may be attributed to collective contribution of all polarization mechanism, Figure 5(a). But at higher frequencies dielectric constant decreases and shows depressive behaviour due to filtration of different polarization mechanism such as interfacial, atomic, dipolar and ionic. Dielectric constant remains independent in the high frequency region because at higher frequencies electric dipoles unable to follow such highly alternating applied electric field which indicate the phenomenon of dielectric dispersion and can explain on the basis of change in space charge polarization and valence states of cations.[21,22] Dielectric constant increases with increasing sintering time may be attributed to increase in grain size with decreasing thickness and number of insulating grain boundary, causes an enhancement of local displacement for electrons, thus increased polarization resulting in high dielectric constant.[23] The room temperature highest value of dielectric constant (ε_r) =17765 (at 0.1 Hz) was obtained for BTMS-60 ceramic sample. The high dielectric loss (> 0.4) observed in Figure 5 (b) may occur due to contribution of high DC conductivity caused by accumulation of oxygen vacancies at the grain boundary during microwave sintering process.

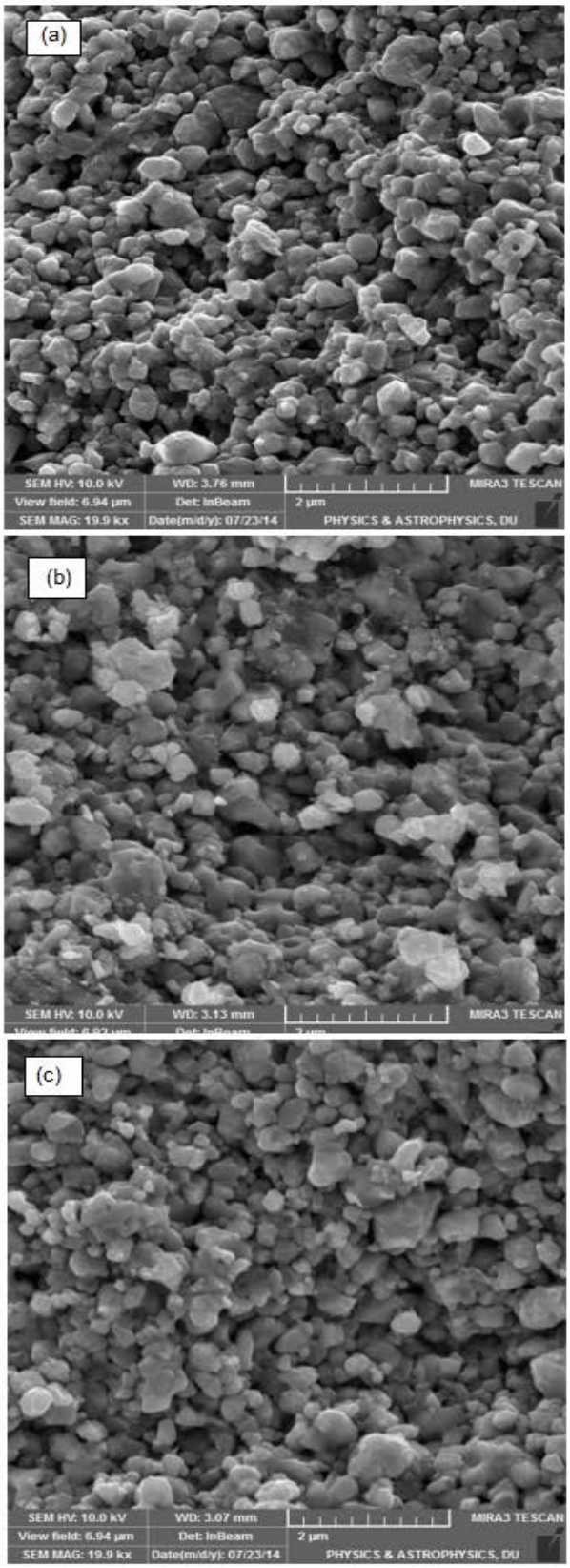

Figure 4. SEM micrograph of $BaTiO_3$ ceramics sintered by microwave for (a) 30 Min. (b) 60 min and (c) 90 min.

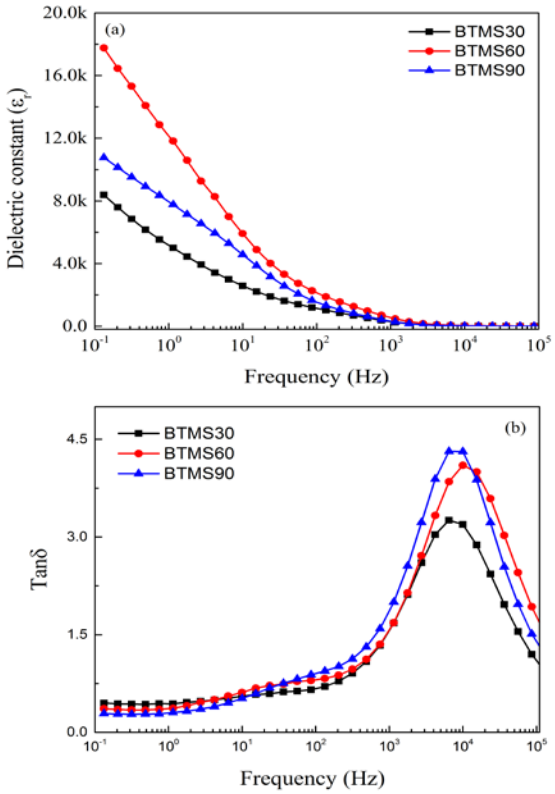

Figure 5. Frequency dependence of (a) dielectric constant (ε_r) and (b) dielectric loss (tanδ) of all $BaTiO_3$ microwave sintered samples with different time duration.

As the frequency of applied electric field increases and approaches to hopping frequency, resonance dominates over relaxation and dielectric loss increases with loss peak at resonance frequency.[24,18] It was observed that all BT samples show high dielectric loss at higher frequency due to their more conductive nature which is familiar behaviour of the Internal Barrier Layer Capacitor (IBLC) ceramics.[25]

Fig. 6(a-b) shows temperature dependence of dielectric constant (ε_r) and dielectric loss (tanδ) for all prepared BT samples. It was observed from Fig. 6(a) dielectric constant increases with temperature in the ferroelectric region, as dielectric polarization increases with increasing temperature due to charge hopping which consecutively increases the dielectric constant.[24] It can be seen from Table 2, that value of ε_r at 1 kHz for sample BTMS-60 is higher than BTMS-30 and BTMS-90 ceramics. The dielectric properties have remarkable differences at Curie temperature (T_C) for all BT samples. Same value of Curie temperature (T_C = 130°C) observed for all BT samples may be attributed to similar kind of stress related changes in these samples.

It was observed from the Fig. 6(b) that dielectric loss decreases with increasing temperature and minimum loss observed around Curie temperature. The same behaviour of dielectric loss versus temperature was reported by Han et al[26] for microwave sintered BT with high dielectric loss (tanδ ≈ 6.901). Figure 7 shows the plot of inverse dielectric permittivity versus temperature. In the vicinity of paraelectric region the dielectric constant follows Curie-Weiss law

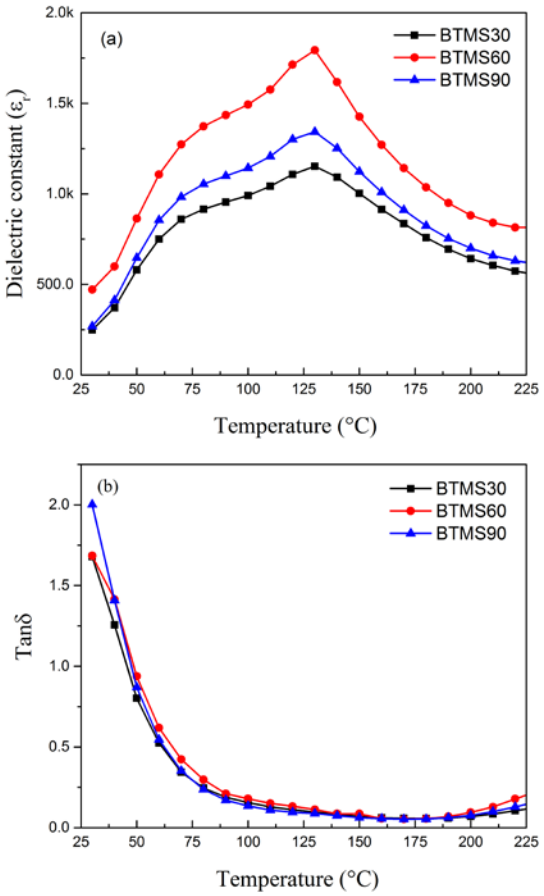

Figure 6. Temperature dependence of (a) dielectric constant (ε_r) and (b) dielectric loss (tanδ) of all $BaTiO_3$ microwave sintered samples with different time duration.

$$\epsilon_r = \frac{C}{T - To} \qquad (T > T_C) \qquad \text{(ii)}$$

Where C is Curie Weiss constant and T_o is Curie Weiss temperature.[27] The deviation of the dielectric behavior from Curie Weiss law can be defined by equation (iii)

$$\Delta T_m = T_{cw} - T_m \qquad \text{(iii)}$$

Where T_{cw} denotes the temperature at which dielectric constant just starts to deviate from the Curie Weiss law while T_m denotes the temperature corresponding to maximum dielectric constant.[28] A Modified Curie Weiss law proposed by Uchino and Nomura has been employed to explain the diffuseness,

$$\frac{1}{\epsilon_r} - \frac{1}{\epsilon_m} = \frac{(T - T_m)^\gamma}{C} \qquad \text{(iv)}$$

Where ε_r dielectric constant, ε_m dielectric constant at the Curie temperature (T_c) and γ is the degree of diffuseness ($1 < \gamma < 2$) and C is Curie constant. The diffuseness parameter determines the nature of the phase transition, with $\gamma = 1$ for normal ferroelectric and $\gamma = 2$ relaxor ferroelectric.[29] The plots of Log ($1/\varepsilon_r - 1/\varepsilon_m$) as a function of Log ($T-T_m$) at 1 kHz linearly fitted with equation (iv) are shown in Fig.8 (a-c) for all BT samples. The slope of these linearly fitted plots gives the value of diffuseness (γ).

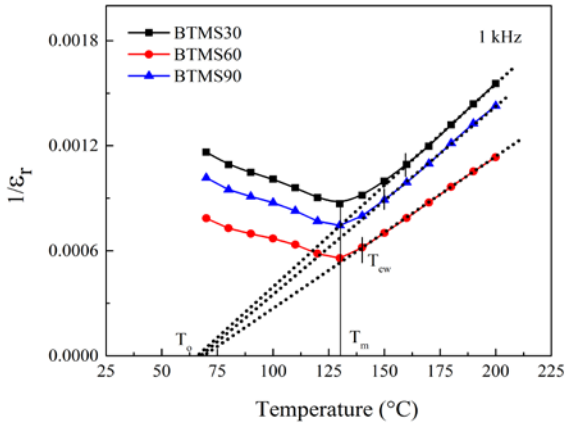

Figure 7. Temperature dependence inverse dielectric constant ($1/\varepsilon_r$) of $BaTiO_3$ samples at 1 kHz.

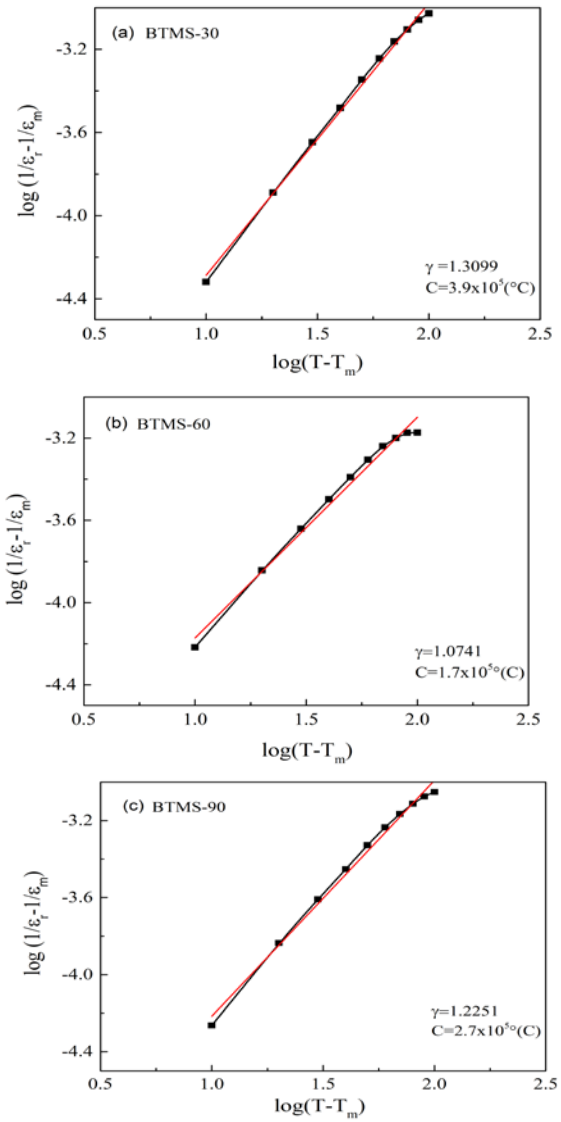

Figure 8. Linearly fitted Log ($T-T_m$) versus Log ($1/\varepsilon_r - 1/\varepsilon_m$) plots of $BaTiO_3$ samples sintered for (a) 30 min. (b) 60 min and (c) 90 min, at 1 kHz.

Table 2. Curie-Weiss Temperature T_o (°C), Curie Constant C (°C), Diffuseness parameter (γ), T_m, T_{CW}, ΔT_m, Dielectric constant (ε_r) and Dielectric losses (tanδ) for microwave processed $BaTiO_3$ ceramic samples.

Sample code	T_o(°C)	C(°C)	γ	T_m(°C)	T_{cw}(°C)	$\Delta T_m = T_{cw}-T_m$	ε_r (1kHz)	tanδ 1kHz (RT)
BTMS30	66	$3.9x10^5$	1.3099	130	160	30	1152	1.2564
BTMS60	70	$1.7x10^5$	1.0741	130	140	10	1793	1.4142
BTMS90	68	$2.7x10^5$	1.2251	130	150	20	1343	1.4082

The value of all above calculated parameters are listed in Table 2. The value of $\gamma > 1$ for all BT samples indicate gradual deviation from Curie-Weiss law and sintering time induced diffuse phase transition.

It was also observed that value of γ decreases as grain size increases. The most promising $\gamma = 1.07$ obtained for samples sintered for 60 minutes (BTMS60) which show a sharp phase transition at Curie Temperature (T_C).

PE Analysis

The ferroelectric hysteresis loop recorded at room temperature for all sintered samples of $BaTiO_3$ is shown in Fig. 9 (a-c). The formation of well saturated PE Loops in all prepared BT samples indicate ferroelectric nature of these ceramics. The remnant polarization (P_r) increased while the coercive field (E_c) decreased with increasing microwave sintering time may be attributed to micro structural changes. The values of remnant polarization, coercive field and maximum polarization (P_{max}) are summarized in Table 3.

Table.3. Remnant Polarizations (P_r), Coercive Field (E_c), and Maximum Polarization (P_{max}) for microwave processed $BaTiO_3$ ceramic samples.

Sample code	P_r(μC/cm^2)	E_c(kV/cm)	P_{max}(μC/cm^2)
BTMS30	1.538	6.756	5.624
BTMS60	2.403	4.411	8.781
BTMS90	2.346	5.619	7.436

The maximum values of remnant polarization $P_r = 2.403$ μC/cm^2 with reduced coercive field $E_c = 4.411$ kV/cm, were obtained for sample BTMS60, may be attributed to increase in domain wall motion and switching behaviour. In the ceramics, clamping effect and number of grain boundary decreases with increasing grain size. Bigger grains having surplus crystalline phase leads to increased ferroelectricity by minimizing the fraction of grain boundary.[30] In present work, ceramic BTMS-60 has bigger grain size resulting in fast domain switching and improved remnant polarization with low coercive field.

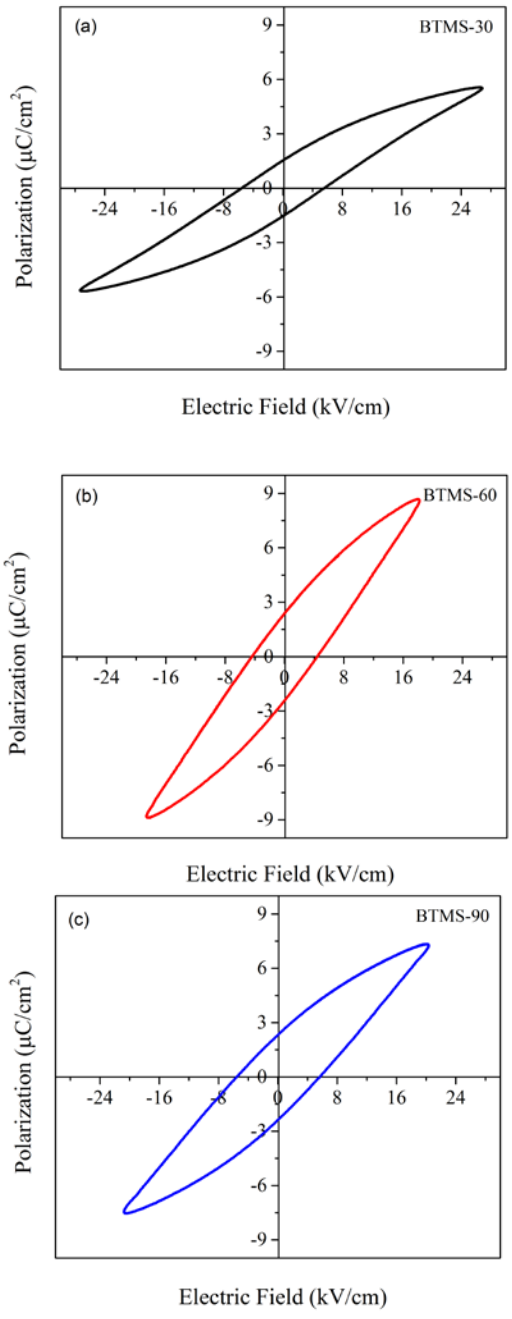

Figure 9. P.E hysteresis loop of $BaTiO_3$ samples sintered by microwave at 1200°C for (a) 30 min. (b) 60 min and (c) 90 min. (Test temperature and frequency is 25°C, 50 Hz respectively).

CONCLUSIONS

In the present work, microcrystalline barium titanate powder was synthesized by solid state reaction technique using microwave processing. X-ray diffraction patterns and Rietveld refinement data confirmed the perovskite-type tetragonal structure with space group P4mm for all BT ceramics, while the higher degree of tetragonality (with c/a =1.0079) was observed in BT ceramic sintered for 60 minutes at 1200 °C. The grain size of all samples were estimated by SEM images was found to increase with increasing microwave sintering time. The dielectric constant (ε_r) is depressive in the higher frequency region which decreases with increasing frequency. The lowest degree of diffuseness (γ = 1.07) obtained for sample BTMS-60 which show a sharp phase transition at Curie temperature (T_C = 130°C), also Curie temperature was found independent of microwave sintering time. The remnant polarization (P_r) increased while the coercive field (E_c) decreased with increasing microwave sintering time may be attributed to micro-structural changes. The optimal dielectric and ferroelectric properties (ε_r = 17765 (at 0.1 Hz), tanδ = 0.4 (0.1 Hz), C = 1.75x10^5 °C, γ = 1.07, E_c = 4.4 kV/cm, P_r = 2.4 $\mu C/cm^2$) were achieved for BTMS-60 ceramic.

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