

SYNTHESIS AND CHARACTERIZATION OF $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ SYSTEM USING BARIUM CARBONATE

3.1 INTRODUCTION

Barium titanate (BaTiO_3) is well known and a widely investigate dielectric material, because of its interesting properties such as a high dielectric constant, low dielectric loss and piezo-electric behavior [98]. To improve the properties of BaTiO_3 , it can be modified by the partial substitution of Pb, Sr and Sn [99-101]. Barium titanate stannate [$\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$] is a binary solid solution system composed of ferroelectric barium titanate and non-ferroelectric barium stannate. Curie temperature and dielectric constant of [$\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$] can be widely shifted by changing the tin content. Furthermore, the permittivity is very high and the temperature is biased field sensitive, allowed these materials to be used in various applications like capacitors, bolometers, actuators and microwave phase shifters. A survey of the literature has revealed that the BTS has been successfully prepared via solid state reaction method [102-104] and it suggested that this solid solution system is a mutual soluble and the lattice constant increased by increasing the Sn content. The dielectric relaxation behavior was observed in BTS with $0.20 \leq x \leq 0.30$ [105]. Wei et al. reported that the BTS with $x = 0.10$ showed abnormal dielectric properties and strong electric non-linearity [106]. These make BTS interesting for dielectric amplifiers and switching circuit snubbers [107].

In the present chapter five compositions $x=0.00, 0.05, 0.15, 0.30$ and 0.40 of system [$\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$] have been synthesized by the solid state reaction method. The synthesis and characterization of these compositions have already been done by other workers [108-111]. It is

noticed that in these studies powders of $[\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3]$ were calcined at temperature 1200°C and x-ray diffraction patterns of the calcined powders was not recorded. In this present chapter calcination of $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$, powders have been carried out at 1000°C and 1100°C to understand how the formation of single phase tin doped barium titanate stannate samples proceeds.

3.2 RESULTS AND DISCUSSION

Samples with compositions $x = 0.00, 0.05, 0.15, 0.30$ and 0.40 in the tin doped barium titanate system, $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ have been synthesized by solid state reaction method. These compositions have been referred throughout this chapter by abbreviated nomenclature BTS0 (for $x = 0.00$), BTS5 (for $x = 0.05$), BTS15 (for $x = 0.15$), BTS30 ($x=0.30$) and BTS40 ($x=0.40$).

3.2.1 Thermal Analysis of the Mixture of BaCO_3 and TiO_2

The TG-DSC simultaneous analysis in an N_2 atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$ of mixed powders was carried out. The TG-DSC curves obtained for the stoichiometric mixture of BaCO_3 and TiO_2 for sample BTS0 are displayed in Figure 3.1. The thermo-gravimetric (TG) curve shows a weight loss of 16.57% in the measured temperature range $30\text{--}1000^\circ\text{C}$. A weight loss of approximately 0.7% in the temperature range $30 - 800^\circ\text{C}$ may be due to the release of absorbed water from the BaCO_3 or TiO_2 powders. Thereafter, a sharp weight loss from $800 - 1000^\circ\text{C}$ is observed on the TG curve. The weight loss in this temperature range is 15.86% which is attributed to the formation of one mole BaTiO_3 as a result of the reaction of one mole BaCO_3 and one mole TiO_2 according to the reaction shown below



The weight loss of 15.86% observed experimentally is in agreement with the theoretical weight loss calculated according to the reaction (3.1). Therefore, it is assumed that the weight loss

corresponds to the formation of one mole BaTiO_3 as a result of the reaction of one mole BaCO_3 and one mole TiO_2 . These results are in agreement with the results reported in the literature [112]. Due to the limitation of the furnace used in TG-DSC setup, data could not be recorded above 1000°C . The TG analysis data were used to fix the 1000°C as the lowest calcination temperature for all the samples synthesized in this chapter.

The DSC curve shows a strong endothermic peak around 828.5°C , corresponds to the chemical reaction between BaCO_3 and TiO_2 for the formation of BaTiO_3 . The small endothermic peaks from 900 - 1000°C may be due to the formation and decomposition of the small amount of intermediate phase Ba_2SnO_4 .

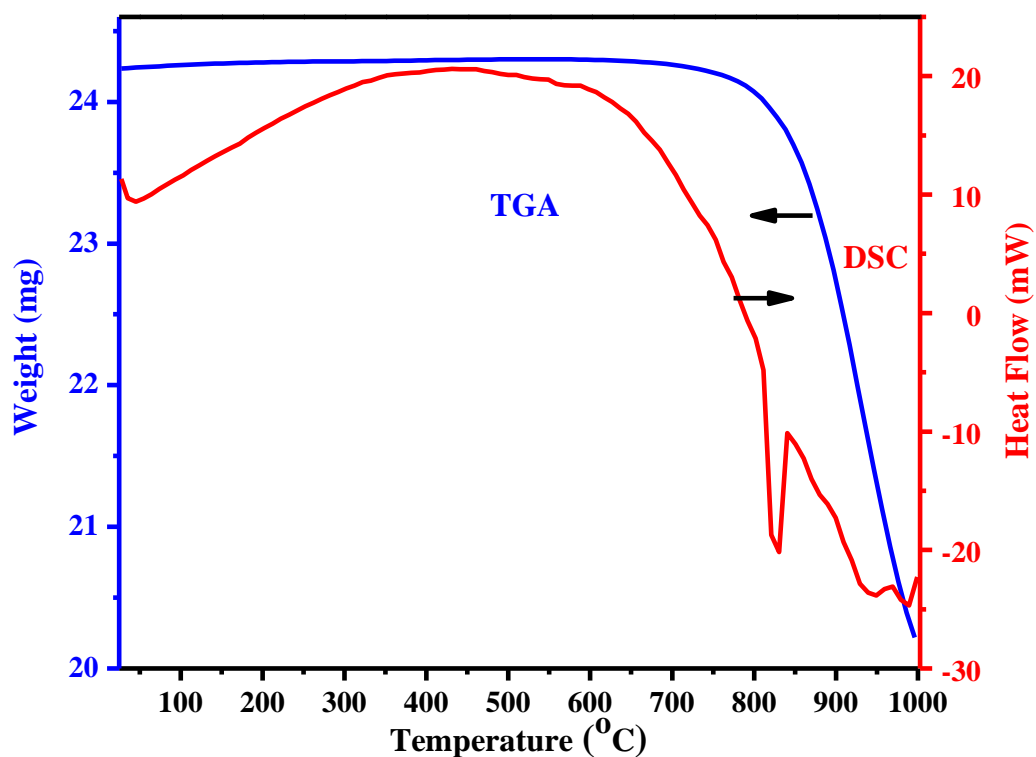


Figure 3.1 TGA and DSC curves of mixture of BaCO_3 and TiO_2

3.2.2 Phase Analysis and Crystal Structure

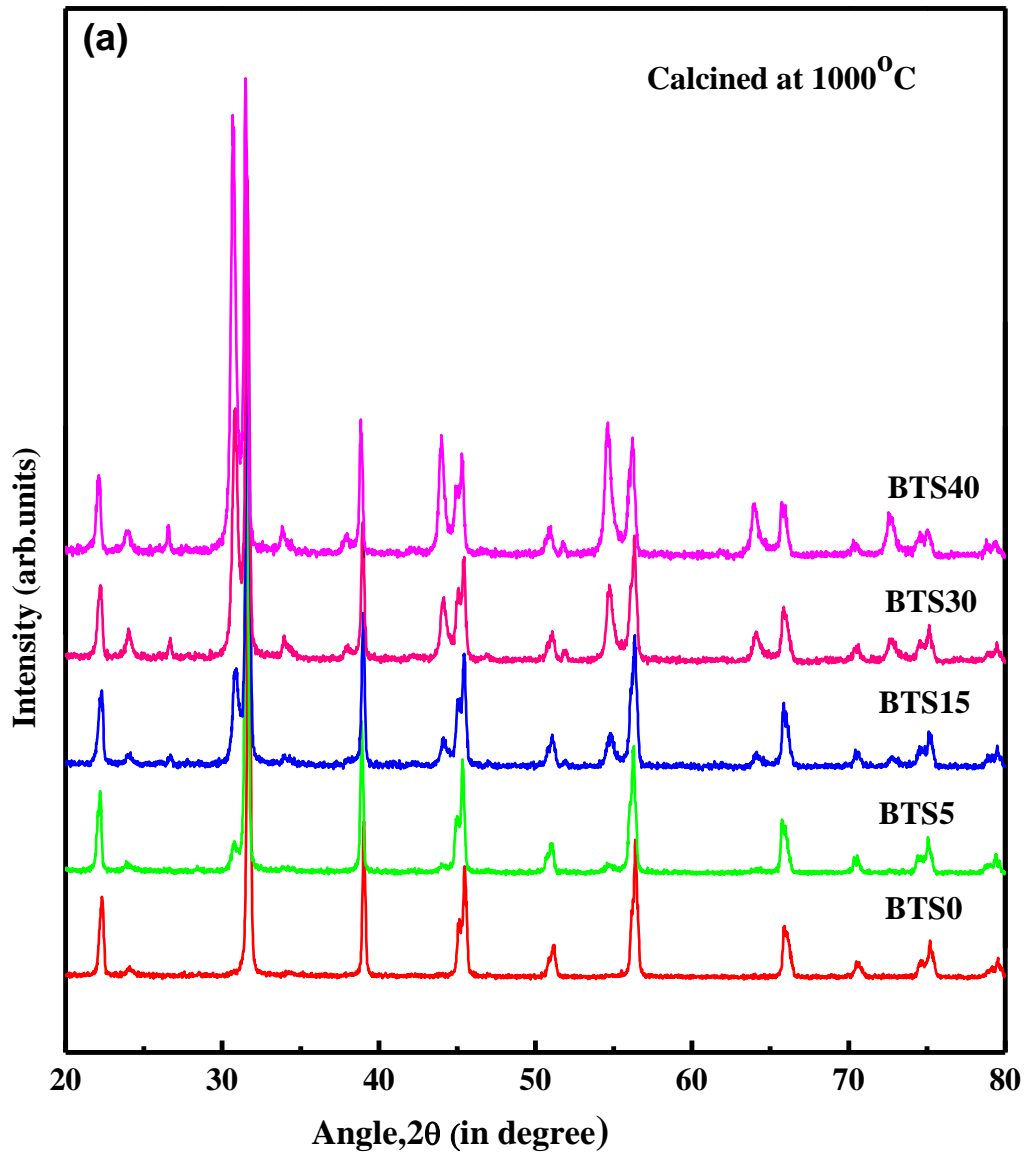
Figure 3.2(a), (b) and (c) show the room temperature XRD patterns of powders of the samples obtained after calcination at temperatures 1000 °C and 1100 °C for 12 h and sintering at 1350°C for 4 h, respectively. From the XRD pattern of the sample BTS0, it is clear that the formation of BaTiO₃ phase has completed after calcination at 1000°C, but a small amount of impurity phase BaCO₃ is present. As the calcination temperature increases, the peaks become sharper and the phase pure BaTiO₃ is found to form at 1100°C, which is completely devoid of any impurity phases. The crystal structure of BaTiO₃ powder at all the three temperatures (1000, 1100 and 1350 °C) is tetragonal (JCPDS No. 05-0626) because both (200) and (002) peaks (around $2\theta = 45^\circ$) are present in the XRD patterns. But it is noticeable that tetragonality increases with increasing heat treatment temperature, which is according to the literature [113]. XRD patterns of the calcined powder (at 1000°C) of the samples BST5 and BTS15 show peaks of impurity phases of BaCO₃, SnO₂, BaSnO₃ and BaTiO₃. As calcination temperature increases from 1000°C to 1100°C, the peaks of BaCO₃ and SnO₂ phases disappeared and peaks of BaSnO₃ and BaTiO₃ phases start overlapping. To further increase of temperature up to 1350 °C, overlapping peaks merge into one peak, which predicts that the two phases diffuse into each other to form a single phase solid solution BaTi_{1-x}Sn_xO₃ with chemical homogeneity. The crystal structure of BTS0 and BTS5 is tetragonal whereas of BTS15, BTS30 and BTS40 are cubic as it is obvious from the inset of the Figure 3.2(c). The phase transition from tetragonal to the cubic structure when the % Sn content increase is reported in the literature [114]. The lattice parameters of all the samples (from the XRD data of 1350°C) were obtained using software ‘Cell’ and given in the Table 3.1. Tetragonality (axial ratio c/a) decreases with the increasing of Sn content and approaches 1.0 of the cubic phase for samples BTS15, BTS30 and BTS40. An

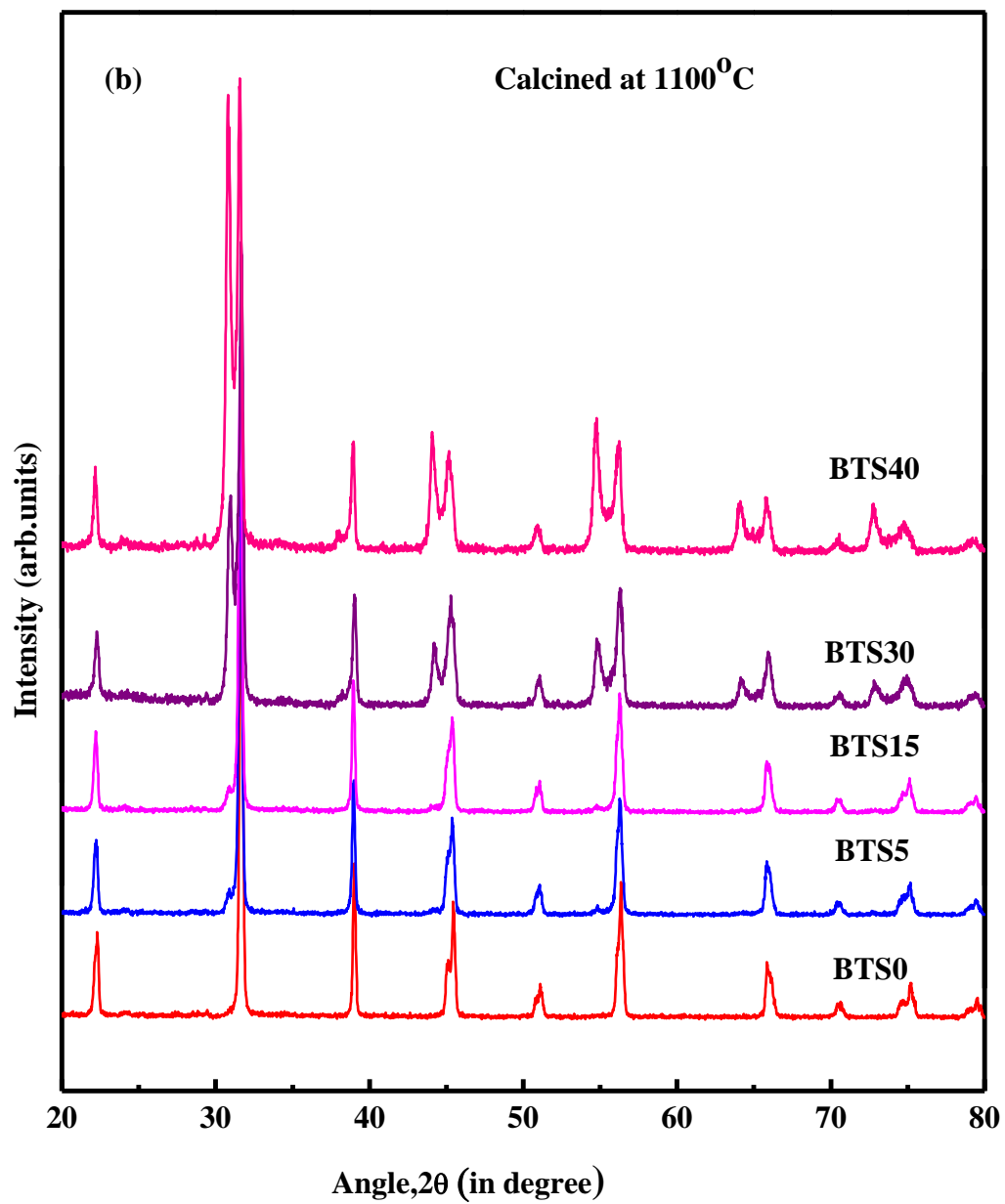
increase in the value of lattice parameter and transition of tetragonal crystal structure in a cubic crystal structure are clear indication that Sn^{4+} is systematically dissolved in the undoped and doped BaTiO_3 lattices.

The average crystallite size (D) of the sintered samples of BTS0, BST5, BTS15, BTS30 and BTS40 was calculated from the Equation 2.2. These values are given in Table 3.1. The bulk density (d_b) of the samples was obtained using Archimede's principal. Theoretical density (d_{th}) of the samples was calculated from the molecular weight of the samples and lattice parameters. The % porosity was calculated using Equation 2.3. The bulk density, theoretical density and % porosity of all the samples are presented in Table 3.1.

Table 3.1 Lattice parameter, tetragonality, theoretical density, bulk density, % porosity and crystallite size of the samples after sintering at temperature 1350°C

Sample $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$	Lattice Parameter (Å)		Tetrag- onality	Theoretical density (d_{th})	Bulk density (d_b)	% Porosity	Crystallite size (nm)	Grain Size (μm)
	a	c	c/a					
0.00(BTS0)	3.9954	4.0350	1.0099	6.01	5.75	4	36	3.4
0.05(BTS5)	4.0011	4.0156	1.0036	6.10	5.95	3	45	16.0
0.15(BTS15)	4.0206	4.0206	1.0000	6.21	5.35	11	57	4.5
0.30(BTS30)	4.0338	4.0338	1.0000	6.56	5.90	10	58	2.7
0.40(BTS40)	4.0453	4.0453	1.0000	6.63	6.03	9	66	2.5





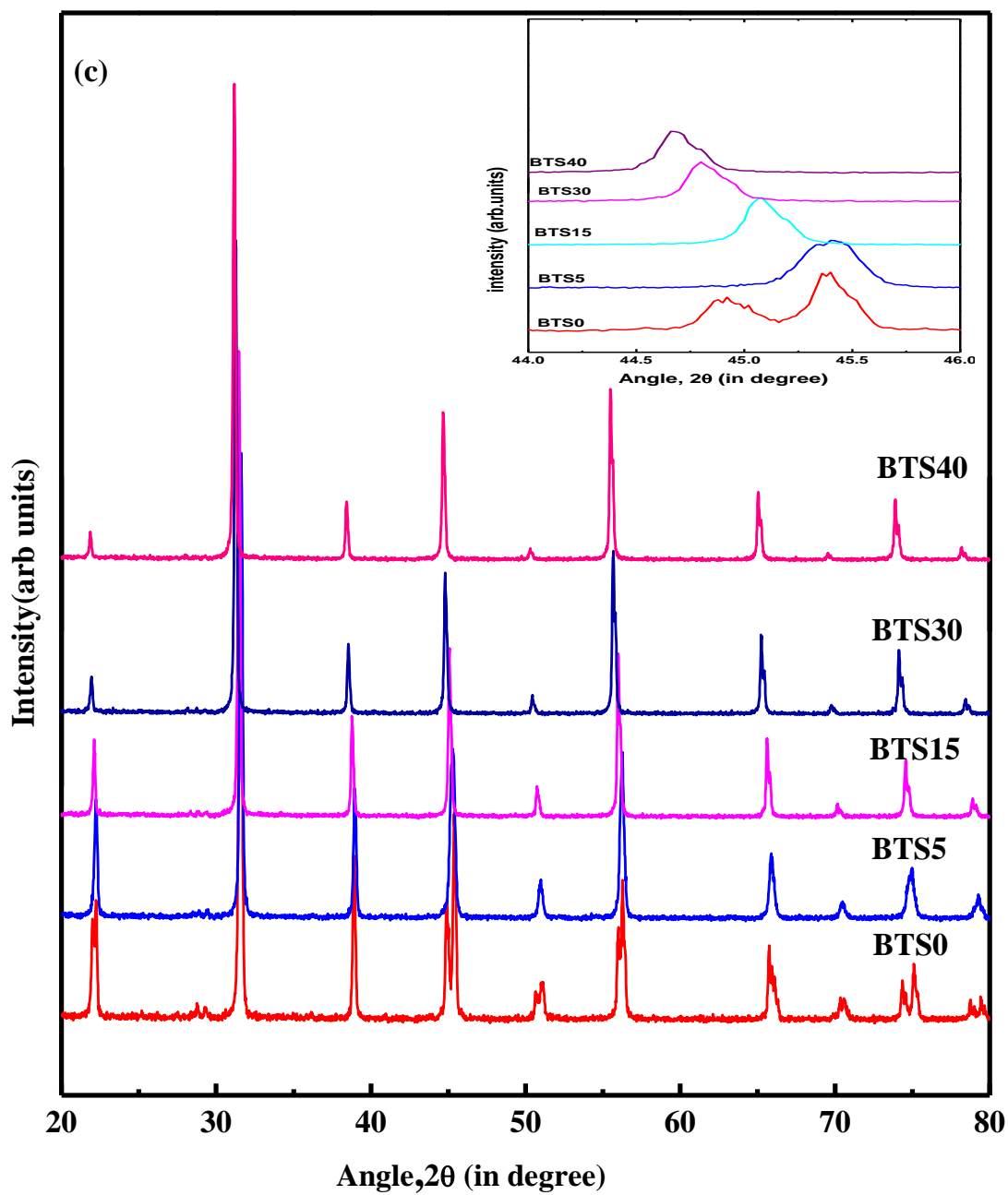


Figure 3.2 X-ray diffraction pattern of the samples obtained after calcination (a) at 1000°C, (b) at 1100°C and sintering (c) at 1350°C.

3.2.3 Fourier Transmission Infra-red (FTIR) Spectrum

According to the reported literature, BaCO₃ is the most common impurity of the BaTiO₃ based powders prepared by any methods. FTIR was found to be the most sensitive technique for the detection of BaCO₃. On the basis of FTIR analysis, BaCO₃ concentration down to 0.6% has been estimated [115]. In order to check the purity and incorporation of Sn⁴⁺ ion in the lattice of BaTiO₃, FTIR spectra of the samples BTS5 and BTS15 have been recorded and shown in Figure 3.3. The FTIR spectra of these samples were compared with the FTIR spectra of the end members BaTiO₃ and BaSnO₃. From the literature, it is noted down that in the FTIR spectrum of BaTiO₃ and BaSnO₃ strong peak around 540 cm⁻¹ and 640 cm⁻¹, respectively appears which is assigned to TiO₆ and SnO₆ stretching vibration that connected to the barium ion [116-120]. The FTIR spectrum of the synthesized samples BTS5 and BTS15 are similar to their end members except that the position of the strongest peak. The position of the strongest peak of samples BTS5 and BTS15 is 557.54 cm⁻¹ and 563.24 cm⁻¹, respectively. It is noticed that the position of strongest peak shifts systematically towards a higher wave number, i.e., towards higher energy with increasing concentration of dopant Sn. Since Sn is heavier (atomic mass 118.71 u) than Ti (atomic mass 47.867u), therefore, the energy required to set stretching vibration of TiO₆ is less than SnO₆. The shift in the peak from sample BTS0 to BTS15 is an indication of the incorporation of Sn⁴⁺ at Ti⁴⁺ site of BaTiO₃. Similar results have been reported for La-doped BaTiO₃ samples [121].

The very small absorption peak observed at approximately 1430 cm⁻¹ in both the samples can be interpreted as C–O vibration due to extremely small traces of BaCO₃. This result is contradictory to the result obtained by XRD [Figure 3.2 (c)] in which no peak of BaCO₃ is observed. Another weak peak appearance around 2362 cm⁻¹ indicates the presence of CO₂ gas in

the chamber of FTIR setup. Therefore, it seems that the formation of BaCO₃ takes place during the FTIR measurement due to adsorption of CO₂ gas either by the samples or by KBr.

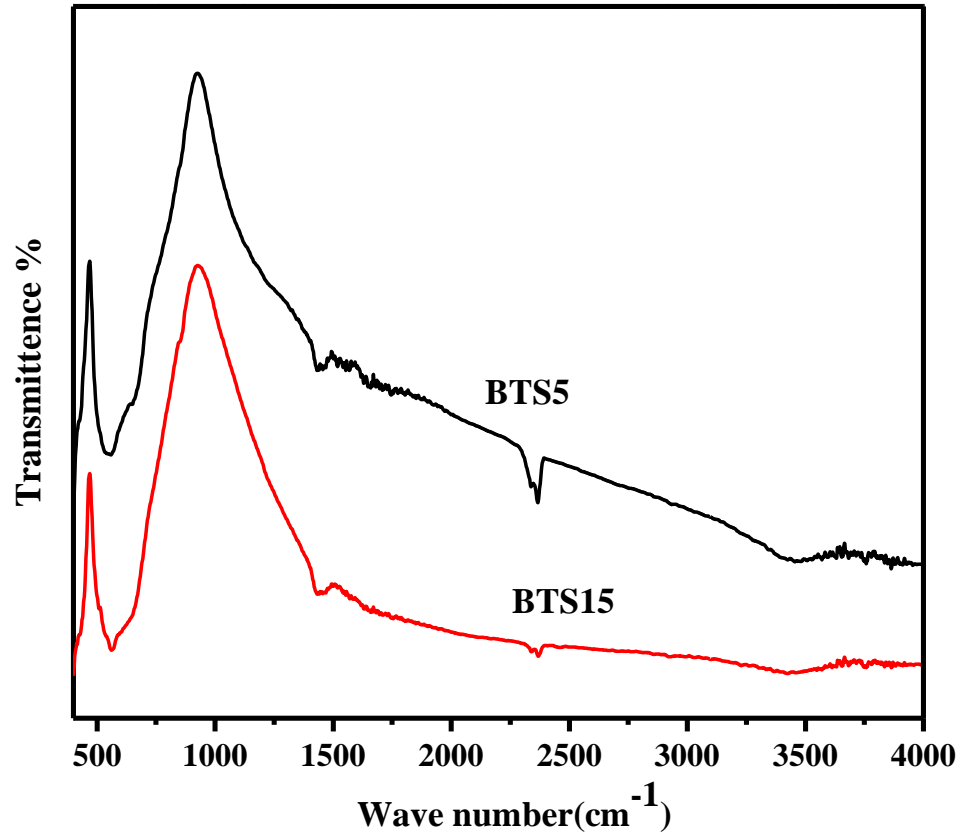


Figure 3.3 FTIR spectrum of the samples BTS5 and BTS15.

3.2.4 Micro-Structural Analysis

Scanning electron micrographs (SEM) were obtained to collect information about grain size, shape and the degree of powder agglomeration. The SEM images of the fractured surfaces of samples BTS0, BTS5, BTS15, BTS30 and BTS40 ceramics sintered at 1350 °C for 5h are shown in Figure 3.4. The average grain size (shown in Table 3.1) of the samples was determined using software ‘ImageJ.’ Morphology of the grains of the samples BTS0 and BTS5 are different

than that of the sample BTS15. Further, the microstructure of the samples BTS0 and BTS5 is dense, whereas of the sample BTS15, BTS30 and BTS40 are porous.

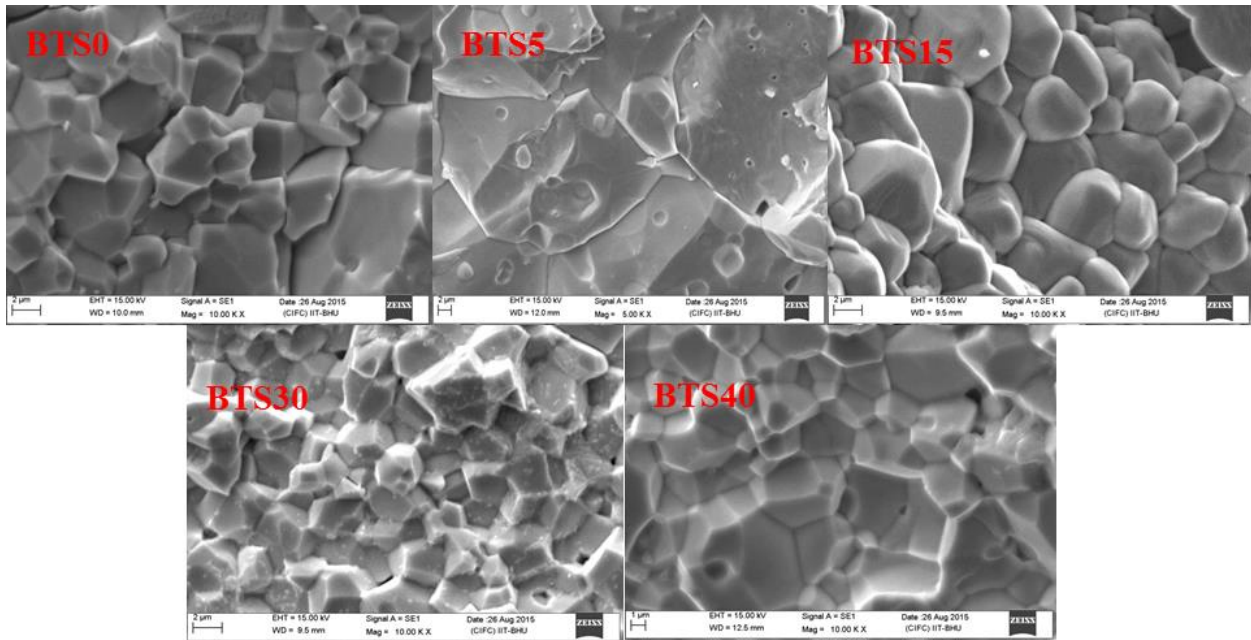


Figure 3.4 Scanning Electron Micrographs (SEM) of fractured surface of sintered samples

3.2.5 Energy Dispersive X-ray (EDX) Analysis

In order to check the compositional homogeneity of the synthesized powders, the compositional variation (in terms of the concentration profile of the elements) has been probed by recording EDXA spectra of different points randomly selected grain core and grain boundary regions. Typical EDXA spectra of the samples along with atomic % and wt% data of the elements are shown in Figure 3.5. The positions of all the peaks observed in the Figure 3.5 are in agreement with EDXA spectra reported for BTS ceramics [109]. It is noted that only the peaks of Ba, Ti, Sn and O are present in the EDXA spectra of the samples. For sample BTS0 atomic and weight % ratios of Ba/Ti are almost the same for all the regions, which supports the homogenous nature of the sample. For the samples BTS5, BTS15, BTS30 and BTS40 also it was found that

Sn ions are distributed uniformly throughout the sample without being segregated at the grain boundaries or volatilization of Sn during sintering.

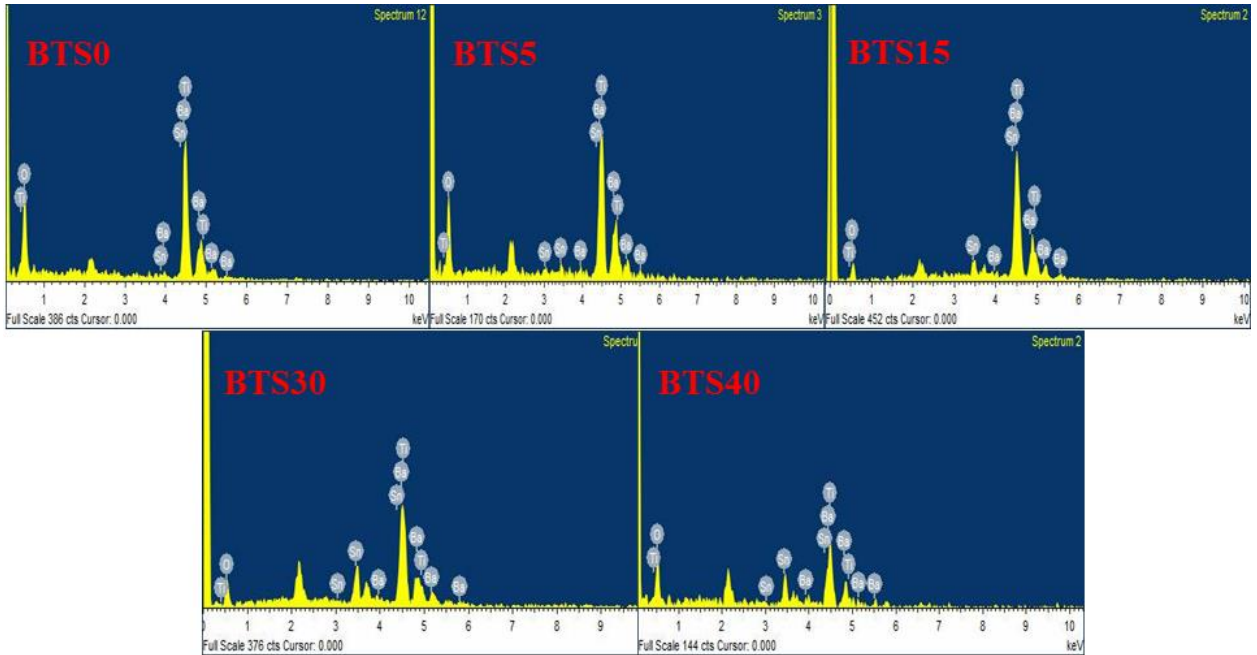


Figure 3.5 Energy dispersive x-ray analysis (EDXA) spectra of sintered samples

3.2.6 Dielectric Analysis

Variation of dielectric constant with temperature for samples BTS5 and BTS15 at three different frequencies 1, 10 and 100 kHz are shown in Figure 3.6 (a) and (b), respectively. The dielectric constant of the sample BTS5 and BTS15 shows the phase transition around 95°C and 10°C, respectively. These values are close to the values reported in the literature [110]. The phase transition temperature for sample BTS0 synthesized in this work is 123°C; therefore, it is clear that the phase transition temperature (T_m) shifts towards a lower temperature side with increasing concentration of Sn. The grain size of the samples BTS0, BTS5 and BTS15 does not vary significantly [grain size is in the range of (3–16) μm], the shift in the transition temperature can be explained by the structural change from tetragonal towards cubic modifications with

increasing the Sn addition, as demonstrated by the XRD analysis [Figure 3.2 (c)]. Similar results have been reported by other authors [122]. The result is that the phase transition temperature at which the crystalline symmetry of BTS samples change from cubic to tetragonal structure shifts progressively towards a lower temperature when the concentration of Sn increases. For the sample BTS15, the temperature corresponding to the maximum permittivity is below room temperature, which means that BTS15 ceramic should exhibit a cubic structure at room temperature which is again in good agreement with the XRD data [Figure 3.2 (c)] which indicated a fully cubic structure. As it is mentioned above that sample BTS05 and BTS15 exhibit diffused phase transition (DPT), in the literature the following empirical relation for the temperature variation of dielectric constant, ϵ for DPT ;

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_m} + \frac{(T-T_m)^\gamma}{C} \quad (3.2)$$

Where γ is the critical exponent and C is the Curie-Weiss like a constant. It is believed that the power factor γ close to 1 suggests normal ferroelectric; while close to 2 suggest relaxor ferroelectric. The experimental dielectric constant data were fitted to Equation (3.2) [Figure 3.7(a) and (b)] very well and the obtained γ values for both the samples BTS5 and BTS15 are given in Table 3.2.

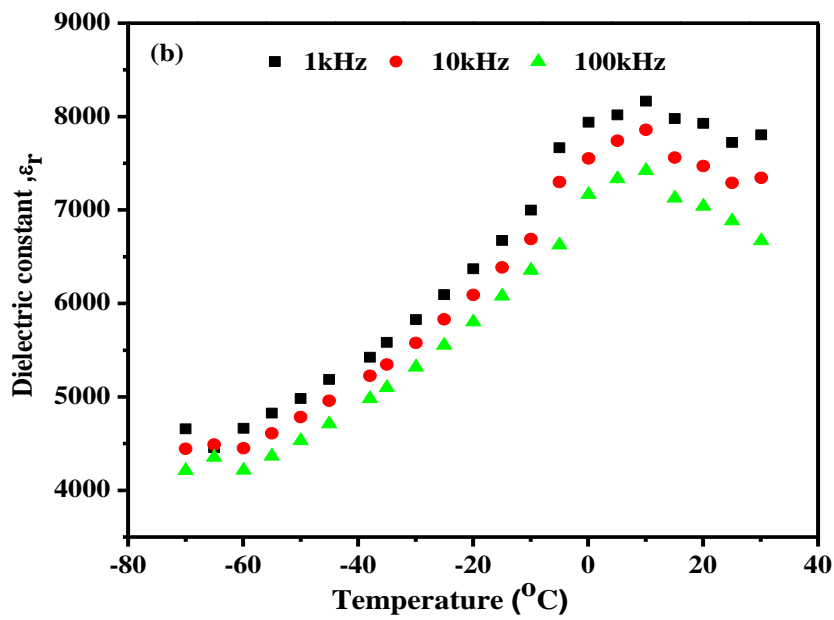
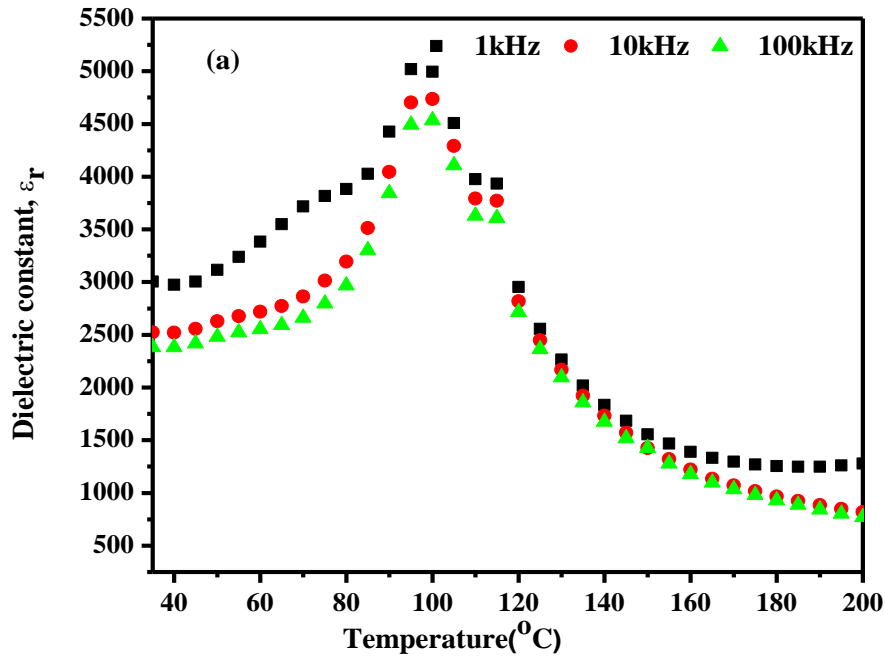


Figure 3.6 Variation of Dielectric constant with temperature of samples

(a) BTS5 and (b) BTS15 at 1350°C

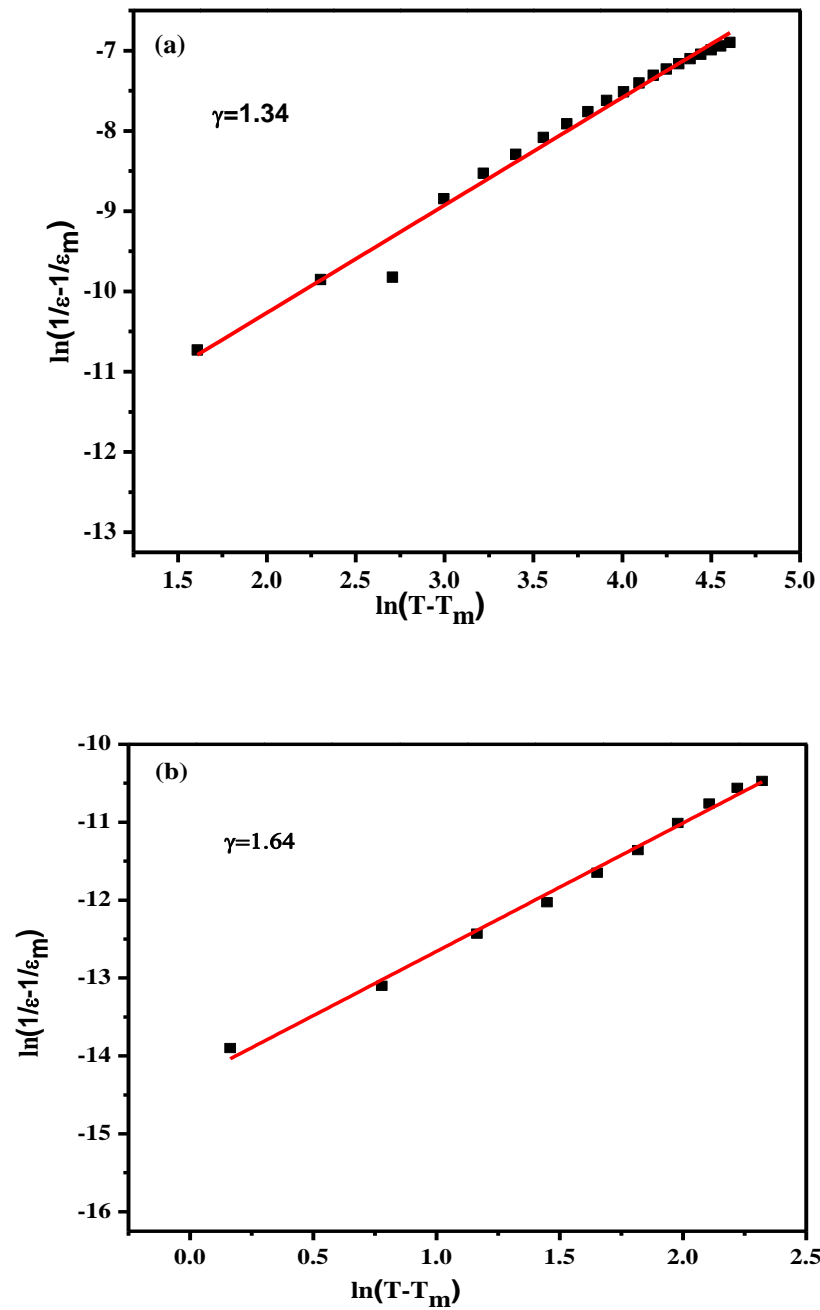
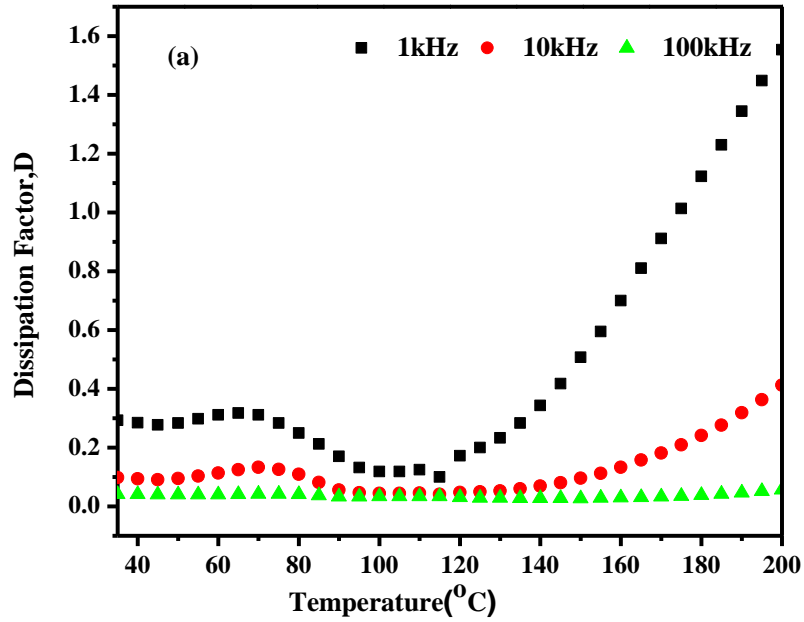


Figure 3.7 Plot of $\ln(1/\epsilon - 1/\epsilon_m)$ as a function of $\ln(T - T_m)$ of samples (a) BTS5 and (b) BTS15 at 10 kHz

Variation of dissipation factor for samples BTS5 and BTS15 at three frequencies 1, 10 and 100 kHz are shown in Figure 3.8 (a) and b. It is observed that dissipation factor of sample BTS15 is higher than that of BTS5 at room temperature 100°C. Room temperature value of dissipation factor at 10 kHz frequency of both the samples is presented in Table 3.2.



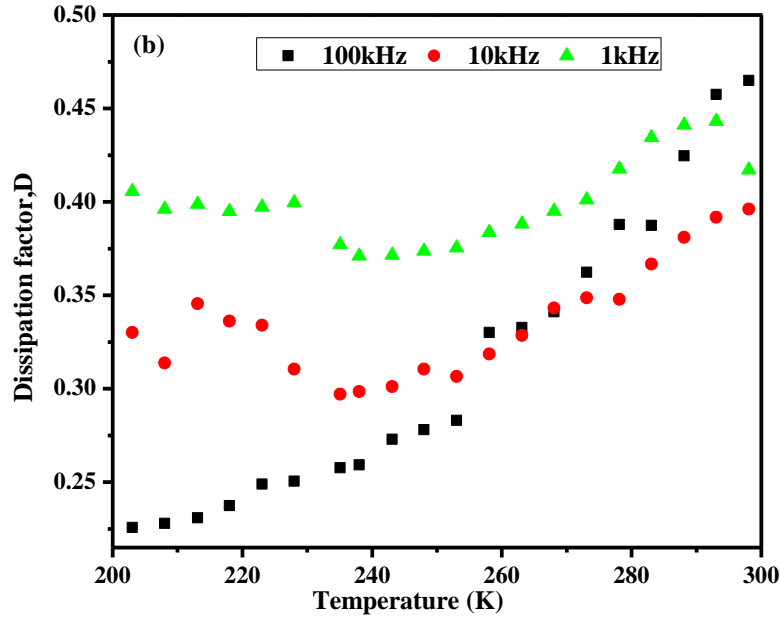


Figure 3.8 Variation of dissipation factor with temperature of samples (a) BTS5 and (b) BTS15

Table 3.2 The room temperature dielectric constant ϵ_{RT} , maximum dielectric constant ϵ_m , temperature (T_m) of dielectric constant maxima, diffusivity parameter (γ) and dissipation factor at room temperature (D_{RT}) at 10 k Hz frequency.

Sample $BaTi_{1-x}Sn_xO_3$	ϵ_m	ϵ_{RT}	D_{RT}	$T_m(^{\circ}C)$	γ
0.05(BTS5)	3792	2531	0.15	95	1.34
0.15(BTS15)	7858	7091	0.40	10	1.64

3.3 CONCLUSIONS

Simultaneous thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis up to 1000 °C and in a nitrogen atmosphere of a mixture of BaCO₃ and TiO₂ confirmed that formation of BaTiO₃ proceeds through a direct reaction between BaCO₃ and TiO₂. The single phase tetragonal BaTiO₃ was obtained at 1100°C and tetragonality is a function of temperature.

Analysis of the X-ray diffraction studies of calcined powder of BTS5 and BTS15 confirmed that formation of single phase solid solution $\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$ and $\text{BaTi}_{0.85}\text{Sn}_{0.15}\text{O}_3$ proceeds through the formation of BaTiO_3 and BaSnO_3 phases and reaction between them at temperatures > 1100 °C. The solubility of Sn in the BaTiO_3 lattice is a function of heat treatment temperature. The percent of the single phase solid solution and the lattice parameter were increased with increasing calcination temperatures. At room temperature samples BTS0, BTS5 have tetragonal crystal structure whereas sample BTS15 has a cubic crystal structure. Dissolution of Sn ion in the lattice of BaTiO_3 has further confirmed by Fourier transform infrared spectroscopy (FTIR) technique. Scanning electron micrographs of these samples clearly exhibited well-crystalized microstructure and grain size is more than $3 \mu\text{m}$. Energy dispersive x-ray analysis (EDXA) studies confirmed the presence of elements Ba, Ti, Sn and O. The value of dielectric constant and phase transition temperature is Sn concentration dependent. At room temperature dissipation factor of the sample, BTS5 is greater than sample BTS15.