Dielectric studies of nano structured BaTi$_{1-x}$Sn$_x$O$_3$ solid solutions

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ABSTRACT

BaTi$_{1-x}$Sn$_x$O$_3$ (BTSx) ceramics had been prepared by temperature sintering technique. Initially, the samples were calcined at a temperature at 900 °C for 2 hours, after that ball milling was done and then the samples were sintered at a temperature of 1150 °C for 3 hours. X-ray diffractometry, Scanning Electron Microscopy, Energy Dispersive Spectroscopy and Dielectric measurements were carried out and structural, micro structural and elemental analyses were discussed in brief.

Keywords: BTSx; XRD; SEM; Dielectric Constant

1. INTRODUCTION

Ferroelectric materials have been harnessed in a number of applications such as thermally stable ceramic capacitors, positive temperature coefficient (PTC) devices, microwave applications, sensors and actuators. The suitability of the materials for devices is mainly governed by their physical properties such as dielectric constant, tangent loss, pyroelectric and piezoelectric properties that, in turn, depend on the type and class of materials and their route of synthesis or fabrication [1]. Titanate ceramic materials have been considered as interesting materials for room temperature applications, mainly due to their high dielectric properties and low tangent loss. Lead titanate (PbTiO$_3$) ferroelectric material has the highest Curie temperature among all perovskite ferroelectrics. Many other ferroelectric ceramics including lead zirconate titanate (PZT), lead lanthanum zirconate titanate (PLZT) and relaxor ferroelectrics like lead magnesium niobate (PMN) have been developed and utilized for a variety of applications.

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 octahedra are slightly distorted. The

anion need not be oxygen. This structure may be described as a simple cubic unit cell with a large cation (A) on the corners, a smaller cation (B) in the body center and oxygens (O) in the centers of the faces as

A wide variety of cations can be substituted in the perovskite structure. The relationship $t = (R_A+R_0)/\sqrt{2} (R_B+R_0)$, which describes the ideal cubic perovskite structure where t = 1.0 and R_A, R_B and R_0 indicate the ionic radius of large cation, small cation, and anion respectively. Those structures whose tolerance factor t is about 0.95-1.0 are cubic, those with lower values are slightly distorted but non-ferroelectric and those slightly over 1.0 tend to be ferroelectric.

Many piezoelectric (including ferroelectric) ceramics such as barium titanate ($BaTiO_3$) lead lanthanum zirconate titanate (PLZT), lead magnesium niobate (PMN), potassium niobate ($KNbO_3$), potassium sodium niobate ($K_xNa_{1-x}NbO_3$) and potassium tantalite niobate [$K(Ta_xNb_{1-x})O_3$] have a perovskite type structure. Practical applications of barium titanate include electronic devices, such as multilayer ceramic capacitors (MLCCs), communication filters and piezoelectric sensors [2].

Barium titanate (BaTiO3)-based ceramics caught attention since last few decades, owing to their remarkable dielectric properties and wide range of applications [1-3]. $BaTiO_3$ has been extensively investigated and several methods of preparation of high purity, homogeneous, reactive fine $BaTiO_3$ powders at low temperatures have been reported [3-5]. These methods include solid state sintering route, co-precipitation, sol-gel, hydrothermal and co-precipitation plus inverse micro-emulsion method. Impurities or additives doped into $BaTiO_3$ even in small proportions have been reported to change its dielectric properties appreciably for potential applications. Recently, solid solution $BaTi_{1-x}Sn_xO_3$ (BTSx) is attracting enormous attention due to the applications of capacitors, relaxors, sensor and the advantages of low internal stresses, low production costs and the possibility to design systems from lead-free materials [7-8]. Wei et al. reported the dielectric relaxation in paraelectric phase of Ba(Ti, Sn)O_3 ceramics [9]. Markovic et al reported BTSx materials have high values of dielectric permittivity, which depends on the Sn content. It has been reported in literature that substitution of tin (Sn) in the place of Ti in $BaTiO_3$ decreases T_c [10]. The present work is aimed at investigating the effect of substitution of Sn on dielectric properties and Curie temperature T_c on these materials prepared in Nano form.
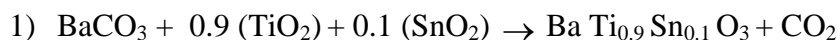
2. EXPERIMENTAL DETAILS

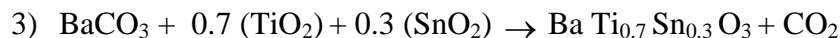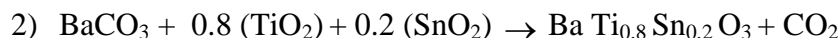### 2. 1. Preparation of Barium Tin Titanate System

The present series of Ferroelectric compositions were prepared by using a temperature sintering technique. AR grade chemicals of $BaCO_3$, TiO_2 and SnO_2 have been taken to prepare the compositions mentioned below. The required amounts of raw materials have been weighed according to molar ratio to yield the following compositions.

1. $BaTi_{0.9}Sn_{0.1}O_3$
2. $BaTi_{0.8}Sn_{0.2}O_3$
3. $BaTi_{0.7}Sn_{0.3}O_3$

and it can be indicated by the following equations also

1) $BaCO_3 + 0.9 (TiO_2) + 0.1 (SnO_2) \rightarrow Ba Ti_{0.9} Sn_{0.1} O_3 + CO_2$

2) $BaCO_3 + 0.8 (TiO_2) + 0.2 (SnO_2) \rightarrow Ba\, Ti_{0.8}\, Sn_{0.2}\, O_3 + CO_2$

3) $BaCO_3 + 0.7 (TiO_2) + 0.3 (SnO_2) \rightarrow Ba\, Ti_{0.7}\, Sn_{0.3}\, O_3 + CO_2$

For each composition the weighed raw materials have been ground in an agate mortar and pestle for more than 8 hours. To achieve homogeneity a small quantity of methanol is added to the mixture, and the resulting slurry has been well ground until all methanol evaporated. Calcination of the mixture was done at 900 °C for 3 hours in an Aluminum crucible covered with a lid. The rate of heating and cooling are 300 °C for 60 minutes. As the reaction is greatly facilitated by heating, cooling and grinding the sample periodically [11], the calcination procedure was repeated twice causing the reduction of the surface area of the mixture. The effect of grinding is to maintain a high surface area and to bring fresh surface in contact. Therefore, the homogeneous material with small particle size may be obtained. For further decrease in particle size the ball milling technique was applied. The applied RPM is 300 rotation/ min and applied for period of 10 hours. The calcined powder was again grounded for 1 hour and binder is added (5 % Polyvinyl Alcohol, PVA), to bring the particles closer. The powder obtained after grinding with PVA has been pelletized, using a steel die by applying a pressure of (2-3) tons/cm^2. The pellet has been placed on a platinum foil on which a small quantity of the calcined powder was sprinkled and the pellet has been closed with a platinum crucible. The binder has been expelled by keeping the pellet at a temperature at 600 °C for 2 hours, and then the temperature has been raised to the sintering temperature of the sample. In accordance with the literature, the value of the sintering temperature was kept at 1150 °C for 3 hours. The sintered pellets were polished to make the two surfaces parallel and dried over a hot plate. The two surfaces of the pellet have been made conductive by coating with silver paste and at heated to 300 °C for 10 minutes. The samples having dimensions of 10 mm diameter and nearly 2.2 mm thickness have been used in the present study.

2. 2. X-ray diffraction

Raigaku XRD machine was used to record X-Ray Diffraction pattern of all samples, operated using Cu Kα radiation of wavelength of 1.54059Å and parabolic filter is used.

2. 3. Dielectric measurements

The sample is placed in position and the capacitance at room temperature is measured. The sample is now heated by feeding power to the plate-heater. As the sample is thin, the temperature difference across the sample is negligible and the temperature given by the thermocouple D is taken as the sample temperature. The capacitance C is measured at different temperatures, as the sample is first heated and subsequently cooled.

The dielectric constant ε is calculated from the relations

$$\varepsilon = C/C_o$$
$$C_o = \varepsilon_o\, A/d$$

where, C is the capacitance with sample, A the area of the upper plate and d the thickness of the sample. ε_o is the permittivity of free space; C_o is the capacitance of a parallel plate air condenser having the same area and thickness as the sample.

2. 4. Density

For a homogeneous object, the mass divided by the volume gives the density. The mass is normally measured with an appropriate balance; the volume may be measured directly (from the geometry of the object) or by the displacement of a fluid. Hydrostatic weighing is a method that combines these two. If the body is not homogeneous, then the density is a function of the position:

$$\rho(\vec{r}) = dm/dv$$

where, **dv** is an elementary volume at position $\vec{r}$. The mass of the body then can be expressed as

$$m = \int_V \rho(\vec{r}) dV.$$

3. RESULTS AND DISCUSSION

3. 1. X ray Diffraction patterns

The XRD pattern of pure BaTiO$_3$ is also shown in Fig. 1. The x-ray diffraction patterns of the samples sintered at 1150 °C with x = 0.1, 0.2 & 0.3 in Fig. 2, 3 and 4. And the samples sintered at 1150 °C showed the characteristic peaks of barium titanate (JCPDS card#50626). The XRD patterns obtained in the samples sintered at 1150 °C are much similar to the XRD pattern observed in pure BaTiO$_3$ indicating the single phase perovskite structure is formed in all the samples. From the nature of peaks and by comparing with the standard spectrum it can be seen that there can be no drastic variation in the lattice parameters after the substitution of the tin in the place of titanium. However no attempt was made to estimate the lattice parameters in the Tin (Sn) substituted samples.
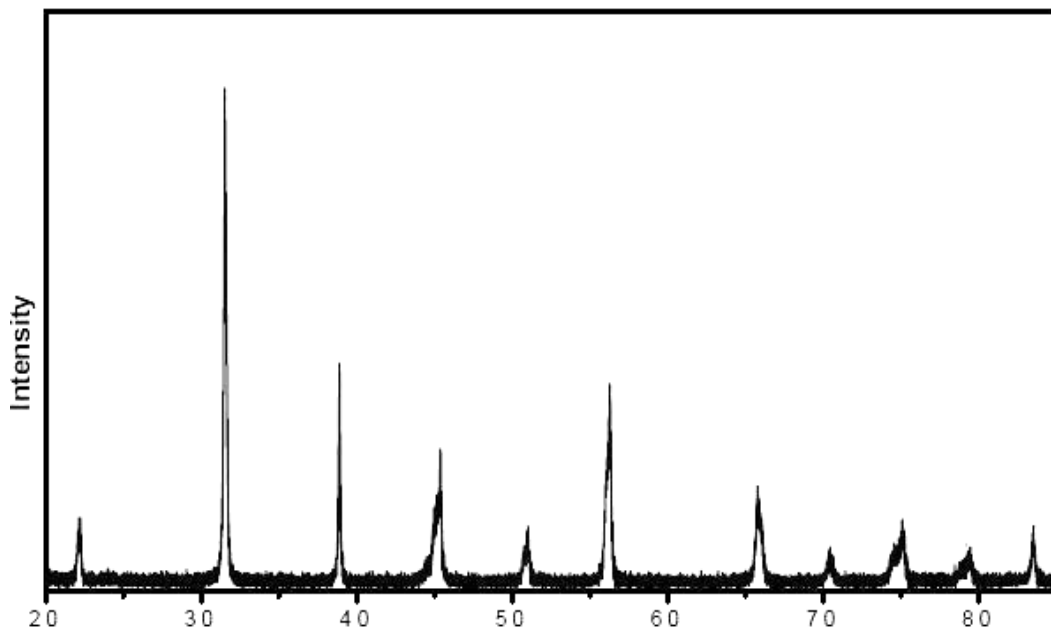

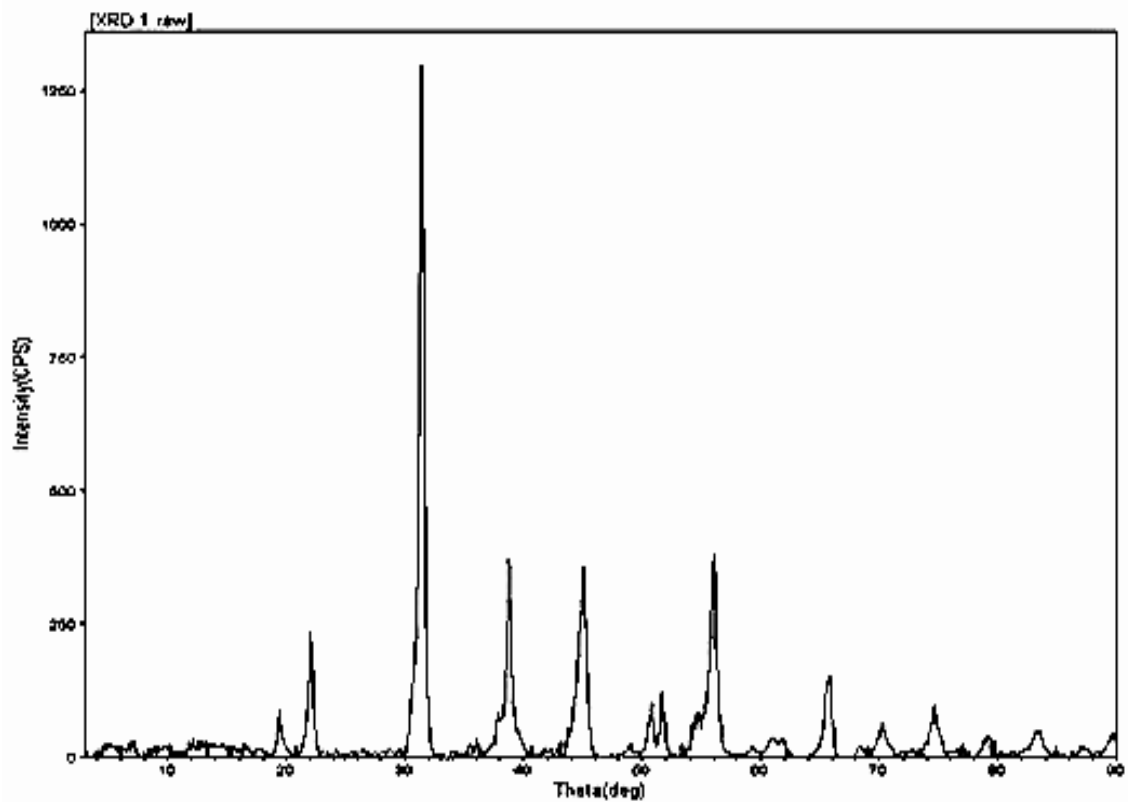**Fig. 1.** XRD image of BaTiO$_3$ sintered at 1150 °C.

Fig. 2. XRD image of Ba Ti $_{0.9}$Sn$_{0.1}$ O$_3$ sintered at 1150 °C.
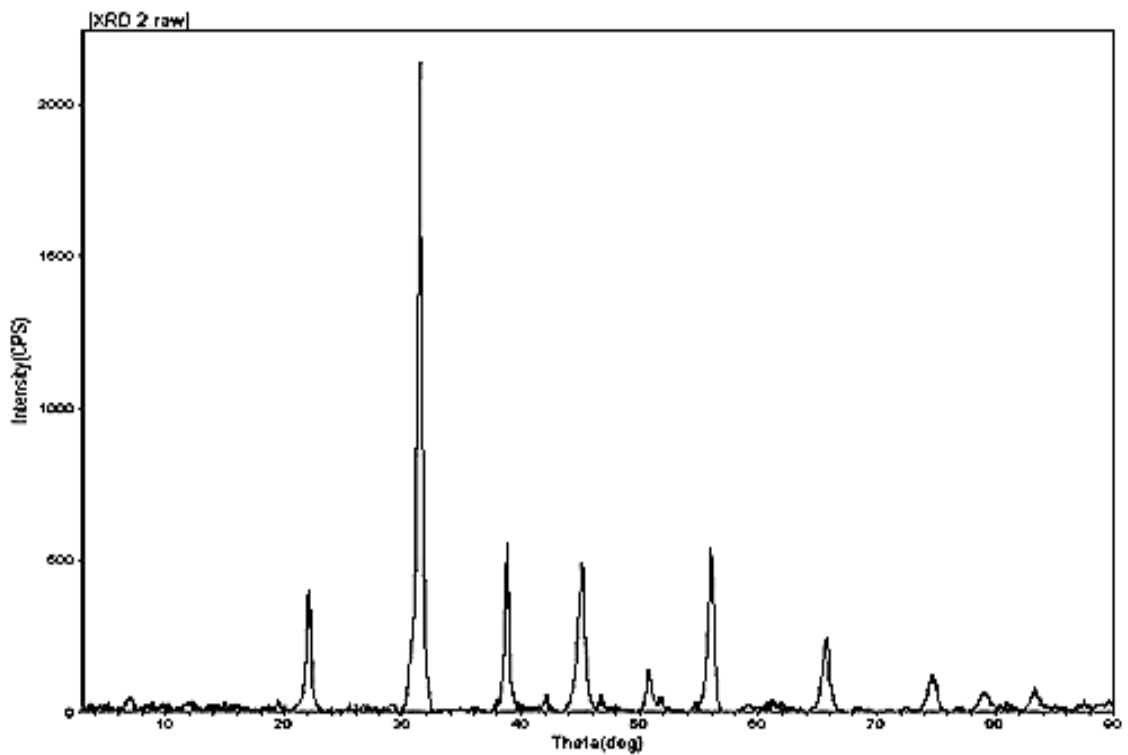
Fig. 3. XRD image of BaTi$_{0.8}$Sn$_{0.2}$O$_3$ sintered at 1150 °C.
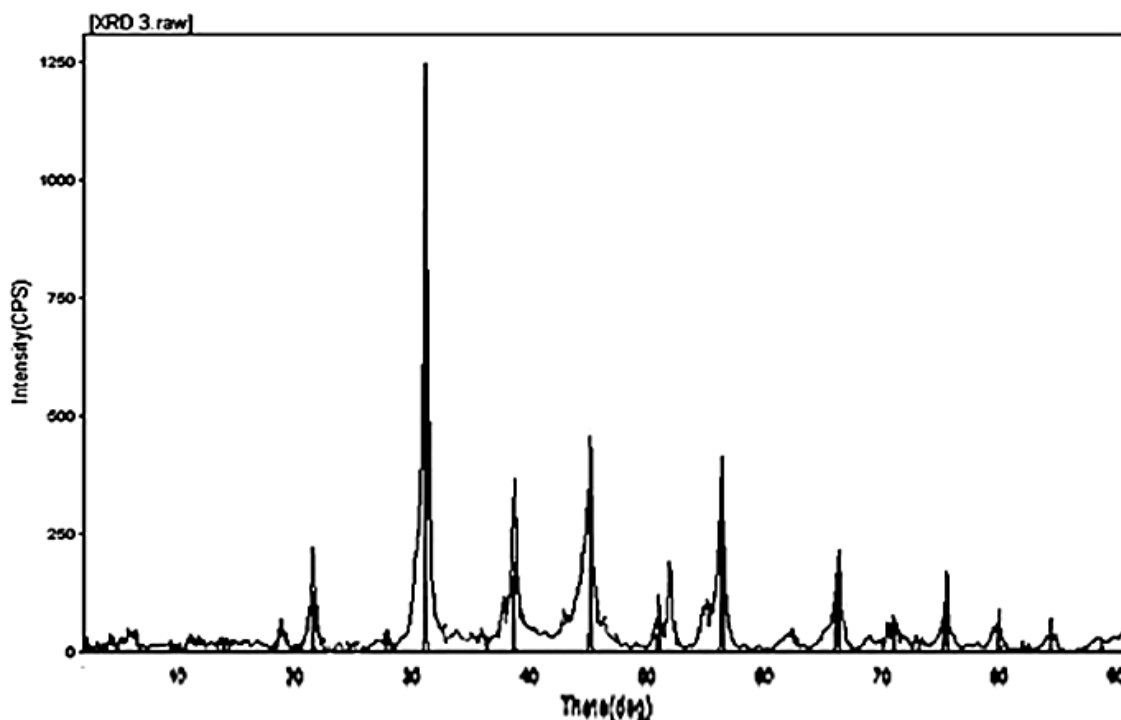
[XRD 3.raw]

Fig. 4. XRD image of $BaTi_{0.7}Sn_{0.3}O_3$ sintered at 1150 °C.

From the width of the (FWHM) XRD peak of the sintered samples, the particle size has been estimated using the formula,

$$\tau = K\lambda / \beta \cos \theta$$

The particle sizes obtained for the three samples are indicated in the Table 1.

Table 1

| S. No	Sample	Particle size (nm)
1	Ba Ti $_{0.9}$ Sn$_{0.1}$ O$_3$	27
2	Ba Ti $_{0.8}$ Sn $_{0.2}$ O$_3$	26
3	Ba Ti $_{0.7}$ Sn $_{0.3}$ O$_3$	25.5

3. 2. Morphology (SEM) & Elemental analysis (EDX)

The morphology of the samples was examined by Scanning Electron Microscopy. Figure 5 shows the SEM photographs of the surfaces of the $Ba_{1-x}Sn_xTiO_3$ specimens sintered at 1100 °C. There is no significant variation in grain size is observed in samples a & b. But some larger grains are clearly observed in samples b & c, which is may be attributed to the doping with Tin (II). The average grain size was determined by linear intercept method from the SEM micrograph of the surface and it was observed that the grain sizes are observed in the range of 30-55 nm.
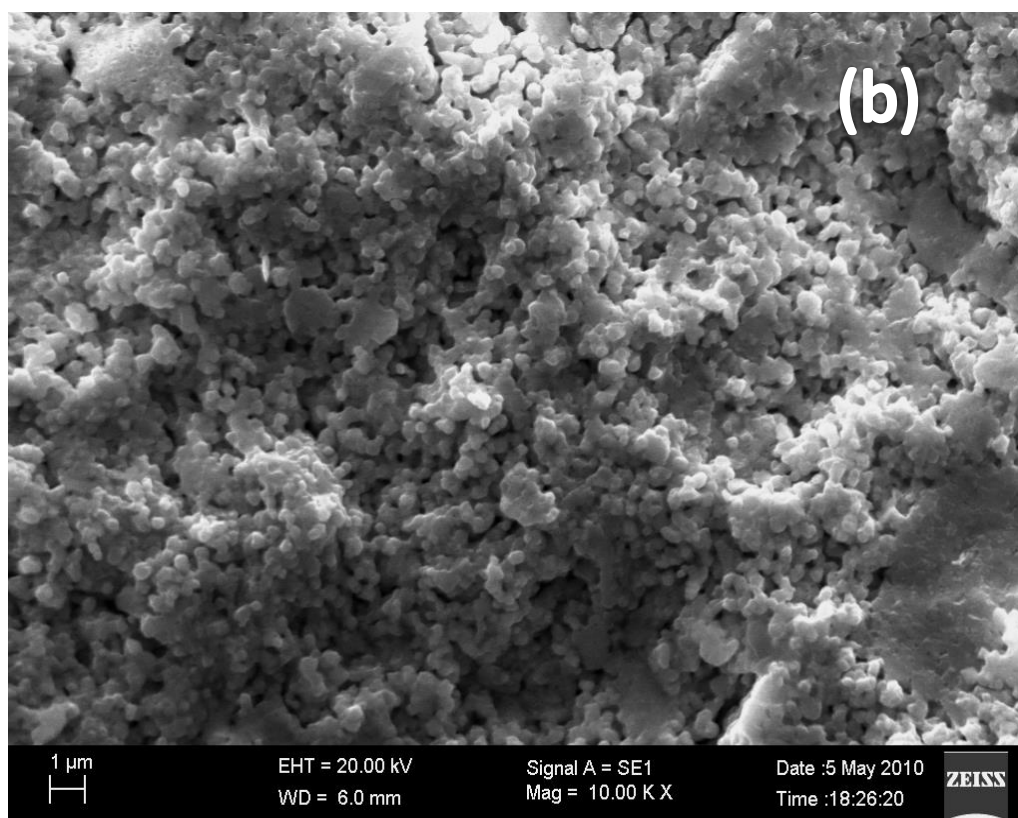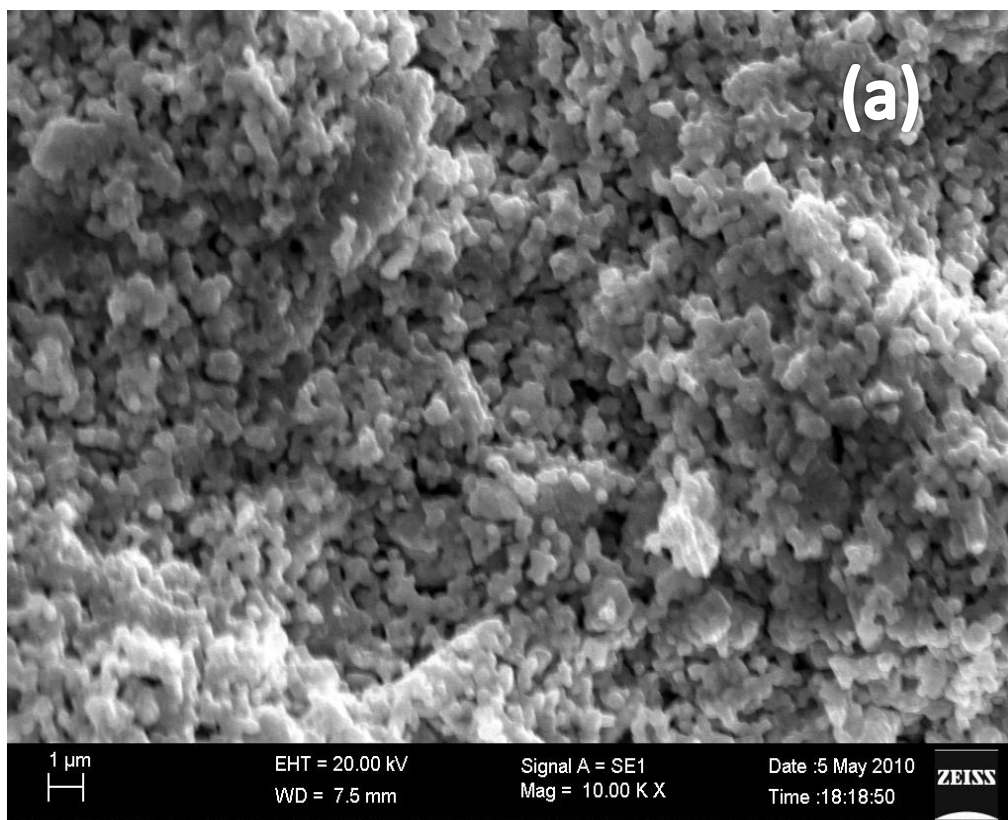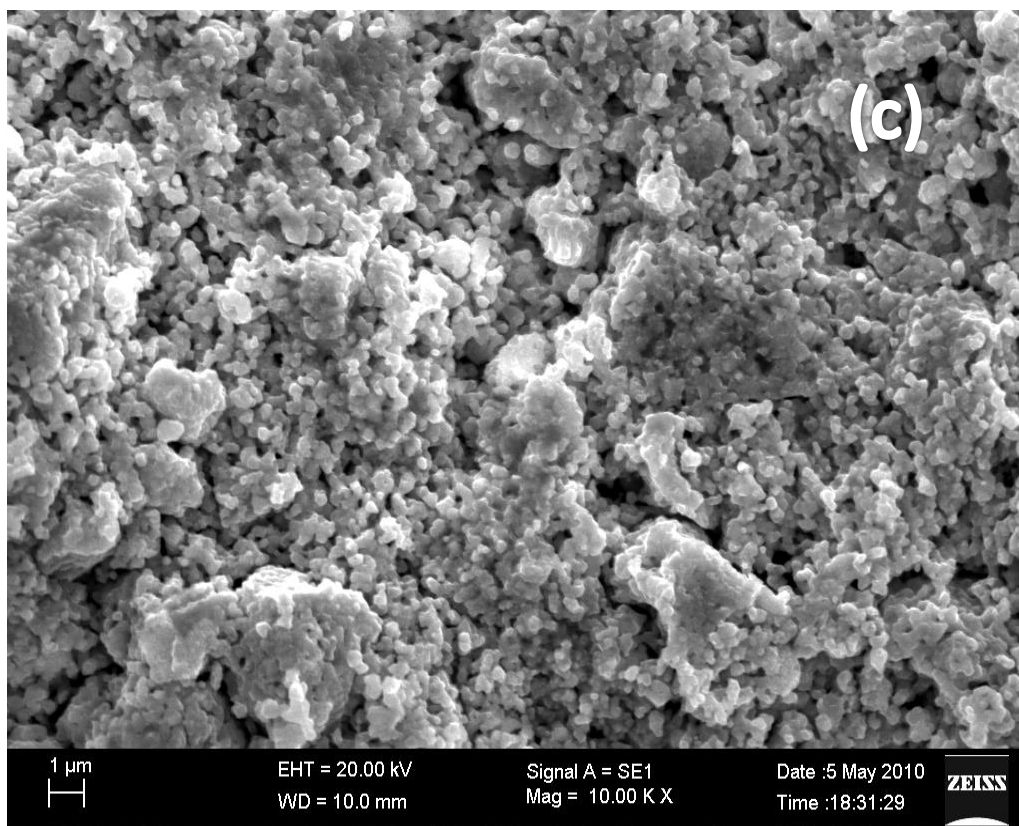
Fig. 5. SEM images of $Ba_{1-x}Sn_xTiO_3$ system,
(a) $BaTi_{0.9}Sn_{0.1}O_3$ (b) $BaTi_{0.8}Sn_{0.2}O_3$ (c) $BaTi_{0.7}Sn_{0.3}O_3$
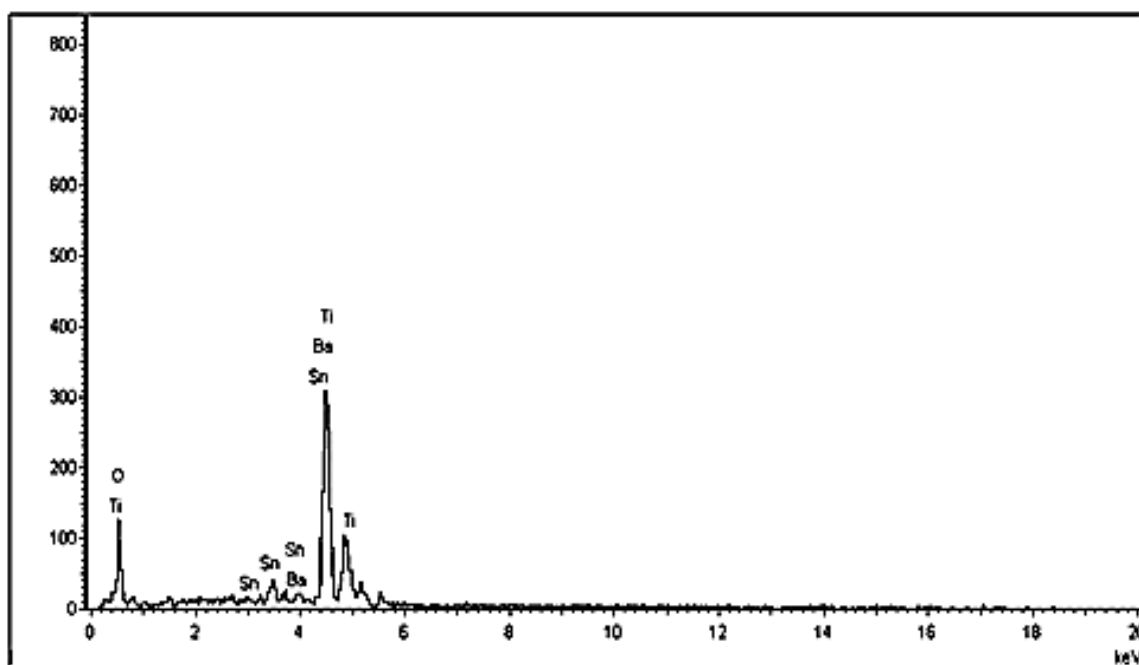
Fig. 6. EDX image of $BaTi_{0.9}Sn_{0.1}O_3$.

The Energy Dispersive spectrographs for $Ba_{1-x}Sn_xTiO_3$ system with x = 0.1, 0.2 and 0.3 are shown below Fig. 6-8. From the spectrographs, it was apparent that all elements were detected and confirmed the stoichiometry of the samples.
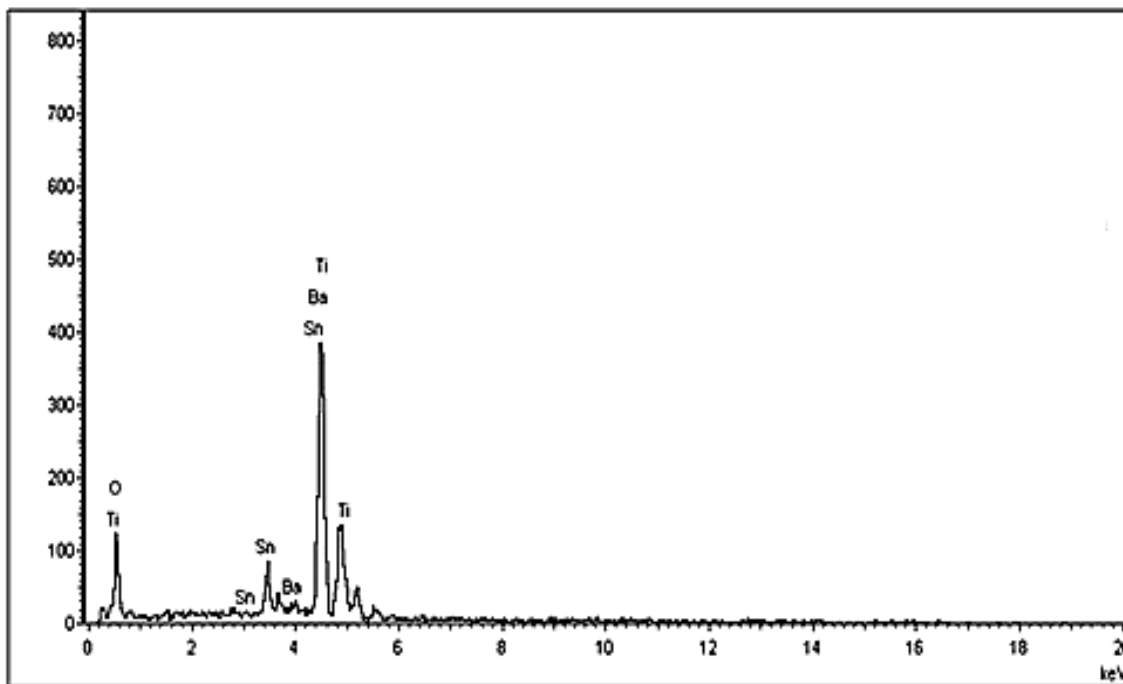

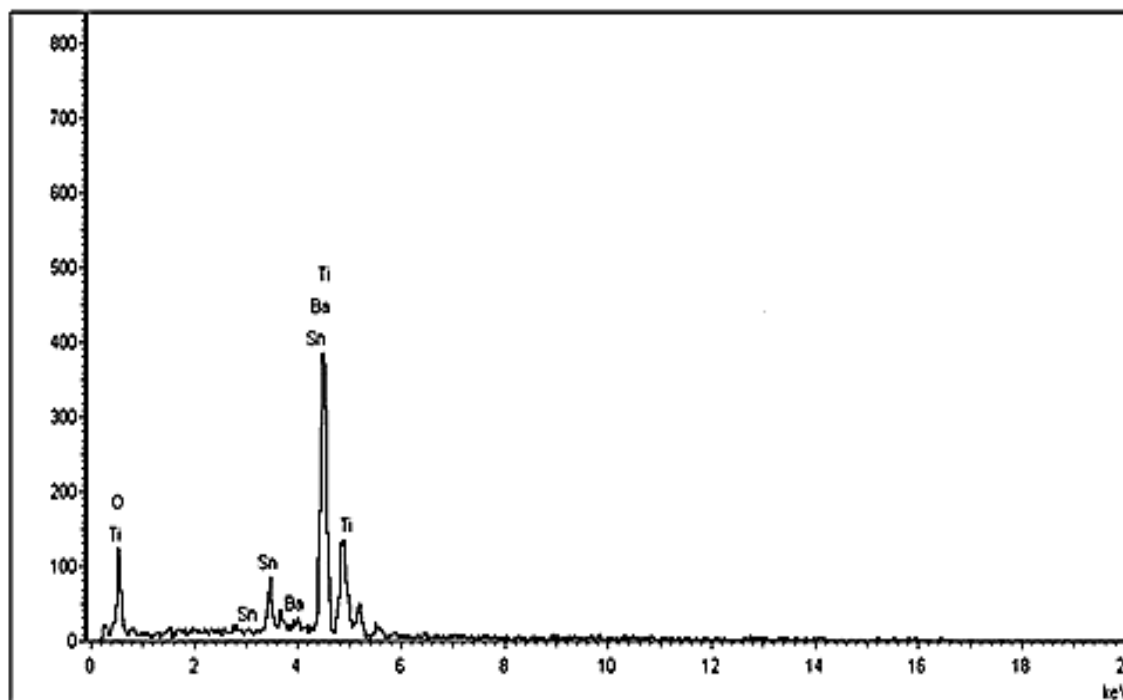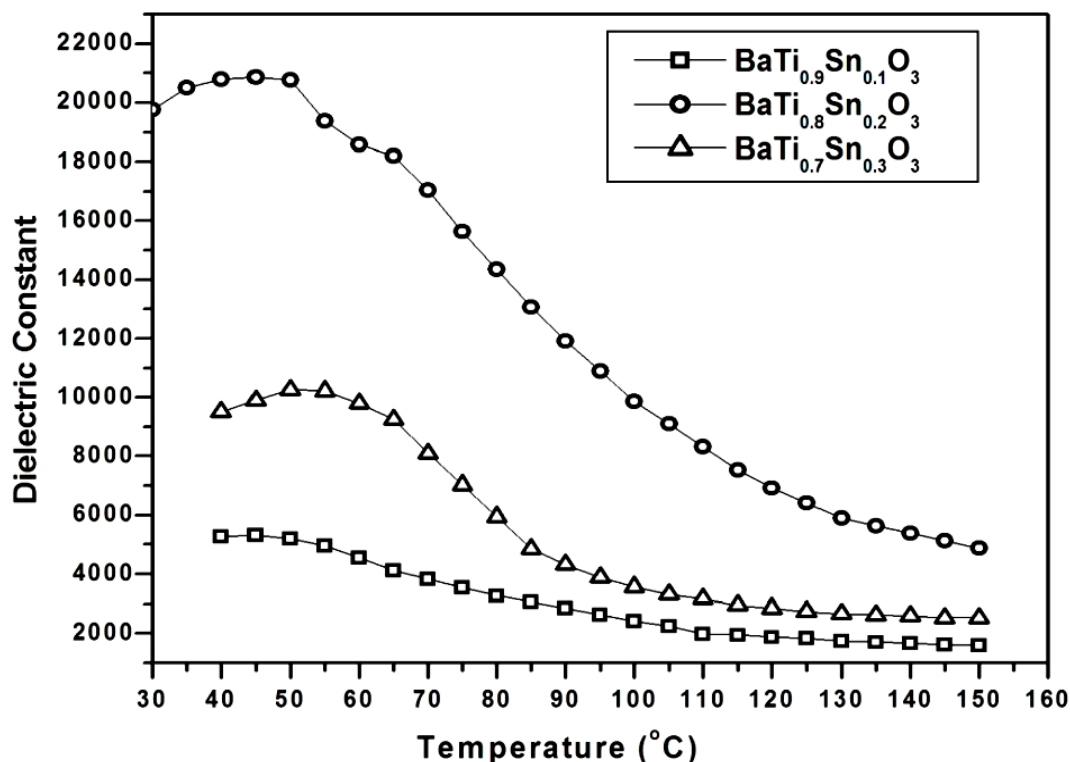**Fig. 7.** EDX image of $BaTi_{0.8}Sn_{0.2}O_3$.

Fig. 8. EDX image of $BaTi_{0.7}Sn_{0.3}O_3$.

3. 3. Dielectric Constant

The variation of DC dielectric constant as a function of temperature is shown in Fig. 9.

Fig. 9. Variation of Dielectric Constant with temperature for $Ba_{1-x}Sn_xTiO_3$ (x = 0.1, 0.2 and 0.3).

It can be seen from the variation of the dielectric constant as a function of temperature that the temperature at which the dielectric constant becomes maximum increases as tin substitution increases from 0.1 to 0.2 then decreases to 0.3. It has been reported in literature [12] that with increasing Sn concentration, the temperature with maximum dielectric constant (T_m) decreases almost linearly [12].

However, in the present studies the temperature T_m was found to increase up to x = 0.2 and decreased in the last sample x = 0.3 and this trend was exactly opposite to the variation in grain size. The densities of the samples were found to decrease with increase of tin concentration as can see from the Table 2.

The samples are characterized by large dielectric constants and the maximum dielectric constant seems to occur for the sample with 20 % tin concentration. The dielectric peaks for all the samples are characteristic of a diffused phase transition. The average grain sizes estimated for these samples are also indicated in the Table 2.

It can be seen for the sample showing maximum dielectric constant having minimum grain size. It has been observed in literature [13] that addition of Tin leads to grain size that is higher than that of pure barium titante.

Table 2

S. No.	Sample	ε_m	T_m (°C)	Density	Grain size (nm)
1	Ba Ti $_{0.9}$ Sn $_{.0.1}$ O$_3$	5324	49	5.04	40
2	Ba Ti $_{0.8}$ Sn $_{.0.2}$ O$_3$	20759	54	5.02	30
3	Ba Ti $_{0.7}$ Sn $_{.0.3}$ O$_3$	10400	44	4.98	55

4. CONCLUSION

$Ba_{1-x}Sn_xTiO_3$ system with x = 0.1, 0.2 and 0.3 was prepared by temperature sintering technique. Structural characterization was done by X-ray Diffractometry. From SEM micrographs of all samples showed that grain size was increased from x = 0.1 to 0.2 then decreased thereafter, so as the temperature with highest dielectric constant. Highest dielectric constant was recorded for x = 0.2.

References

[1] Shrabanee Sen, R. N. P. Choudhary, *J. Appl. Phys.* 99 (2006) 124114/1.

[2] M. T. Buscaglia, M. Bassoli, V. Buscaglia, *J Am Ceram Soc*. 88 (9)(2005) 2374-2379.

[3] Z. C. Li, B. Bergman, *J Euro Ceram Soc*. 25 (2005) 441- 445.

[4] J. H. Adair, J. Crampo, M. M. Mandanas, E. Suvaci, *J Am Ceram Soc.* 89(6) (2006) 1853-1860.

[5] K. Y. Chen, Y. W. Chen, *Powder Tech.* 141 (2004) 69-74.

[6] K.H. Felgner, T Muller, H. T. Langhammer, H. P. Abicht, *Material Letters* 58 (2004) 1943-1947.

[7] M. T. Benlhrache, N. Benhamla, S. Achour, *J. Euro. Ceram. Soc*. 24 (2004) 1493-1496.

[8] X. Chen, W. Lu, S. C. Shen, *Solid State Communications* 130 (2004) 641-645.

[9] J. Zhao, X. Wang, R. Chen, L. Li, *Ceram. Int.* 33 (2007) 207-212.

[10] Ramesh Babu, A. V. Prasad Rao, *J. Mater. Sci. Lett.* 16 (1997) 313.

[11] Anthony R. West, "*Solid state chemistry and its applications",* John Wiley & Sons, 1987.

[12] T. Wang, X. M. Chen, X. H. Zheng, *J. Elec. Ceramics.* 11 (2003) 173.

[13] Ramesh Babu, A. V. Prasad Rao, *J. Mater. Sci. Lett.* 16 (1997) 313.