# Effect of heat treatment time on the dielectric properties of BST

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**Abstract**

Structural and microstructural properties of sol gel processed $BS_xT$ (x = 0.0, 0.05) ceramics have been investigated. Dielectric properties of these ceramics have also been studied as functions of frequency [1kHz-2MHz] at different measurement temperatures (30-200 ℃). Heat treatment duration effect on dielectric properties and structural ones has been investigated. The results show that heat treatment and its duration has significant effects on structural, dielectric properties and the average grain size of the samples. Scanning electron microscopy (SEM) analysis show quite regular morphology of the grains and an average grain size which decreases with introduction of Sr, in agreement with structural characterization. Raman analysis has given results which are in accordance of XRD and SEM characterizations. Moreover, the permittivity variations as functions of the frequency, show a decrease in the interval [1kHz-100kHz], followed by an anormal increase in the interval [100kHz-1MHz].

**Keywords:** Structural, XRD, Raman, Dielectric properties

## 1. Introduction

Among the large class of ferroelectric ceramics, barium titanate (BT), which has the $ABO_3$ perovskite-type structure remains the most studied from both experimental and theoretical points of view. Indeed, since its discovery BT has attracted much attention due to its potential of applications in a variety of domains (Jaouher Amami (2006), A.G.A. Darwish (2010), I.K. Battisha (2010), M. Kellati (2004) as it belongs to technical ceramics which are in particular known for their dielectric, ferroelectric, semiconductor and electro-optic properties. These can be modified by substitutions on A or B sites. The Curie point of BT is around 130 ℃ which value is too high for use as electronic components (ceramic capacitors, ceramic ultrasonic, memories and sensors ...). Introduction of Sr in BT matrix has been shown to lower the transition temperature in the range from 130 to -200 ℃ (Jaouher Amami 2006), to lower dielectric losses at low frequencies and to increase the permittivity. These mentioned effects depend on different parameters such as method of preparation of the samples, nature and percentage of dopants, heat treatment, etc.

In this work we study the effect of Sr doping on structural and dielectric properties of sol gel processed BT ceramics. These properties are investigated as functions of the two parameters temperature and frequency. The sol gel method has been adopted to elaborate the samples due its numerous advantages of low temperature processing, nonvacuum requirement, and low cost, excellent control of the stoichiometry and a good homogeneity of the powders in spite of crystallization at relatively low temperature (A.G.A. Darwish 2010, I.K. Battisha 2010 and M. Kellati, 2004).

## 2. Experimental

$BaTiO_3$ (BT) and $Ba_{0.95}Sr_{0.05}TiO_3$ (BST), powders were prepared by a modified sol–gel method (K. Bouayad, 2005, S. Komarneni 1999) through the destabilization of colloidal solution (DCS). For preparing the powders, we used as starting materials, barium acetate, $Ba(CH3COO)_2,3H_2O$ (99.9% purity), titanium alcoxide, $Ti[OCH(CH_3)_2]_4$ (97% purity) and strontium carbonat $SrCO_3$, (97.9% purity), lactic acid ($CH_3CH (OH) COOH$) and acetic acid $CH_3COOH$ were used respectively as a peptizing agent and solvent to dissolve strontium carbonate.All chemicals were purchased from Johnson Matthey GmbH Alfa, Karlsruhe. Tow solutions of BSxT (x= 0, 0.05) were prepared. The corresponding powders were calcined at 1000 ℃ during 4h. For Scanning Electronic Microscopy analysis, the samples in pellet shapes were prepared and obtained by pressure with a uniaxial pressure equal to 10 tons/cm$^2$. Then, the pellets were sintered according to the following sintering cycle: a first temperature level at 600 ℃ during 1h was performed for removing the PVA followed by a second level at 1100 ℃ with two durations: 4 h ($BST_{4h}$) and 8h (BT and $BST_{8h}$), with a heating rate of 3 ℃/min. The crystallinity

and phases of the powders were examined using X-ray diffraction (XRD). Dielectric measurements were carried out in the frequency range [1kHz–2MHz], at a temperature ranging between 30 and 200 ℃.

## 3. Results and discussion

### 3.1. XRD studies

X-ray diffraction characterization are shown in Figure.1.A. The two samples with x = 0 and x = 0.05, calcined at 1000 ℃ for 4h crystallize in the perovskite phase with the presence of a secondary micro-phase corresponding to $BaCO_3$ which may come from unwanted amount of unreacted $BaCO_3$ resulting from the reaction of BaO with atmospheric $CO_2$ and the burn-out of organic materials or as a result of incomplete heat treatment. Zooms of the peak (110) in the range *36 <2θ <39* (Figure.1.B) shows the displacement of the peak position (110) to higher angles, which indicates incorporation of Sr atoms in BT matrix in agreement of with the literature (A. Elbasset 2013, Bo Hou 2006,    Xiao Wei 2008, Shou-Yi Kuo 2001 and S. Kongtaweelert 2006) Figure.1.C.

shows the gradual change of the structure to pseudo cubic (C. Gervais, D. 2004, W. Li, Z. Xu, R 2010 and F. Lin 2010) confirmed in section 3.3 by Raman investigations. The structure of BST can be also observed through the lattice constants calculations. We have calculated by a least square fitting procedure, from the X-ray peaks intensities, the lattice parameters a and c. The c and a parameters of the unit cell for BST (x=0,05) are found equal to 4.0391 and 3.9995Å, respectively. Indeed the strontium decreases the parameter c /a from 1.0102 for BT to 1.0099 for $BS_{0.05}T$.This behaviour is attributed to the difference in the ionic radius of the $Ba^{2+}$, $Ti^{4+}$ and $Sr^{2+}$ ($Ba^{2+}$=1.35Å, $Ti^{4+}$= 0.61Å and $Sr^{2+}$=1.18Å) ions. The substitution of Ba and/or Ti ions by Sr, presenting smaller ionic radius, induces a shrinkage of the lattice that have for direct consequence a decrease of the c/a ratio. As BT crystallizes at room temperature in the quadratic phase, it can be concluded that under sintering at 1100 ℃ during 4H, BT doped with 5% of strontium may crystallize in the pseudo-cubic structure.

### 3.2. SEM analysis

Scanning Electron Microscopy (SEM) images of the synthesized BSxT pellets are shown in figure 2 for x equal 0.0 and 5%. The analysis of these pictures allows the study of the microstructure and the comparison of the size

of the nanocrystals. For all samples, we have observed that the fine particles aggregate into grains, which present a quite regular morphology in shape. Assuming particles to be spherical, the calculated average particle diameter changes from around 1700nm (x=0) to around 590nm (x=0.05, heat treated at 1000 ℃ during 4h). This decreasing of the grain size confirms the decreasing of the c/a ratio deduced from X-ray analysis. Moreover, we observed an increase in grain size with the duration of heat treatment time (590 nm for $BS_{0.05}T_{8h}$ and 390 nm for $BS_{0.05}T_{4h}$).

### 3.3. Raman investigations

Micro Raman spectroscopy is an excellent complimentary characterization tool to identify the phase evolution as a function of Sr substitution in BT lattice. $BaTiO_3$ has five atoms and fifteen degrees of freedom per unit cell. In cubic phase it has Oh symmetry, and the 15 degrees of freedom divided into the optical representations 3F1u +F2u, while another $F_{1u}$ symmetry mode corresponds to acoustical branch. At room temperature $BaTiO_3$ is tetragonal and has $C_{4v}$ symmetry. The frequency-covered range is from 200 to 1000cm$^{-1}$. Based on the crystallography, Raman-active modes for tetragonal $BaTiO_3$ ($P_{4mm}$) are 4E(TO + LO) + 3A$_1$(TO + LO) +B$_1$(TO + LO), while no Raman-active mode is predicted for the cubic phase ($P_{m3m}$) ( Jr .M. DiDomenic, 1968).The number of Raman peaks in experimentally obtained unpolarized spectrum of polycrystalline samples is commonly less than the number of theoretically derived modes, not only because of great overlapping of A$_1$ and E modes, as wel las B$_1$ and E modes,which frequencies are very close to one another, but also due to the existence of a coupled mode interaction and overdamped character of the lowest optical E mode (E(TO$_1$) soft mode) (V.P. Pavlovic 2011). In our investigations, the results of the X-ray analysis are in accordance with those obtained by Raman spectroscopy measurements.

Raman peaks have been recorded and assigned to more than one phonon mode of tetragonal $BaTiO_3$, as presented in Fig.3. This figure reveals the existence of the following modes: a dip around 204cm$^{-1}$ assigned to A$_1$(TO$_1$) phonon mode, a sharp peak at 307cm$^{-1}$ attributed to the B$_1$ and E(TO/LO) modes, a broad band centered around 231cm$^{-1}$ corresponding to A$_1$(TO$_2$) phonon mode, and the asymmetric broad band near 516cm$^{-1}$ corresponding to E(TO) and A$_1$(TO$_3$) modes. Finally, the highest frequency peak near 715cm$^{-1}$ is observed, in

which both $A_1$(LO) (the hardest LO mode)    and E(LO) character seem to be present. It must also be noted that the Raman peaks at 307 and 715cm$^{-1}$ are specific to the tetragonal phase of the $BaTiO_3$ as described in (R. Naik, 2000). The observed Raman peaks of the $BaTiO_3$ agree well with the powder Raman spectra reported by Osada et al (M. Osada, 1999). These results are in good agreement also with investigations which pointed out that two asymmetric broad $A_1$(TO) modes, at 231 and 516cm$^{-1}$, are sensitive to structure defects (Y. Liu, 2004). On the other hand the disappearance of $A_1$ ($TO_1$) mode and the decrease of the intensity of $A_1$($LO_3$) / E ($LO_4$) mode in BST points out that doping BT with Sr gives rise to an increase in symmetry.

### 3.4. Dielectric constant and loss tangent

The dielectric properties dependence on the frequency of the prepared samples are described in terms of the dielectric permittivity (ε'), loss tangent (tanδ) and other related physical properties. Fig.4 shows the thermal variation of the real part of the dielectric permittivity (ε' ) (Figs. (a), (c) and (d)) and the dielectric losses (Fig. (b)) of BT, ($BST_{4h}$) and ($BST_{8h}$) samples as a function of frequency, in the temperature range between 30 and 200 ℃. These variations of $ε_r$ obtained (Figure.4) show that the dielectric constant increases with increasing frequency up to a critical point (ε'$_{max}$) and then decreases. Moreover a relaxation process is observed as the temperature increases. When a material is subjected to an electric field, the displacement of positive and negative charges of dipoles causes the appearance. at sufficiently low frequencies, of a reorientation of these dipoles in the direction of the field, and all of the polarization mechanisms are involved. As the frequency increases, a phase shift can occur between the switching field and the reorientation of the dipoles; this phenomenon is responsible for the dissipation of a part of the field energy in the material around a so-called relaxation frequency fr. So, when the frequency increases, the number of mechanisms involved in the polarization decreases, which reflects the decrease in the permittivity.

Fig. 4 shows an increase of the permittivity and the shift of its maximum to lower frequencies with increasing temperature until 135 ℃ and then decreases for temperatures superior to 135 ℃. The same behavior is observed for the dielectric losses. The dielectric behavior of barium titanate in the tetragonal phase is in good agreement with that characterized by XRD and Raman (Fig.1.c and Fig.3) the increase in the dielectric permittivity (ε'$_{max}$) with increasing temperature is often expected due to the contribution of more than one type of polarization, For the barium strontium  titanate system $BST_{8h}$ and $BST_{4h}$, no significantly changes can be observed in the dielectric permittivity at temperatures lower than 122 and 126 ℃.

Temperature dependence of ε' and loss tangent for BT, $BST_{4h}$ and $BST_{8h}$ samples is shown in figure.5. The compositions investigated here displayed dielectric properties characteristic of normal ferroelectrics ( N. Setter 2001, N.W. Thomas 1990).The maximum of the permittivity occurred around the Curie temperature (T c), which was found to shift downwards for the sample $BST_{8h}$ with 5 mol% of strontium, i.e. from 135 ℃ for pure BT to 122 ℃ for $BST_8$. This could be attributed to the increase in the internal stress, which helped the materials to overcome the energy barrier of the transition. Such decrease in Curie temperature in $BST_{8h}$ may result from the substitution of strontium which causes a decrease in the crystallite size and affects the lattice parameter as obtained from XRD section shown in Table.1. The radius of the $Sr^{2+}$ ion (1.2 Å) is almost the same as $Ba^{2+}$ (1.4 Å), which explains that this decrease in the $T_c$ value may be related to the fact that strontium carbonate has different lattice constants that add a stress into the lattice (D.C.Kongtaweelert, S.Panichphant, 2006). On the other hand the increase of the heat treatment time causes a decrease of the transition temperature ($T_c$) ($T_c$ = 122 ℃ for $BS_5T_{8h}$ and $T_c$ = 126 ℃ for $BS_5T_{4h}$) and an increase of the dielectric constant (Fig.5).

The thermal evolution of the dielectric loss at various frequencies of pure BT Fig.5 shows that the dielectric losses remain almost constant up to 100 kHz and then increase with frequency and reach a maximum value in the vicinity of $T_c$. This increase is primarily due to the increased mobility of defects. However, the behavior of the maximum of the permittivity, $ε_{max}$, depending on the frequency (f), shows a decrease in the interval [1kHz-100 kHz], followed by an abnormal increase in the interval [100kHz-1MHz]; up to our knowledge, this behavior has not been observed, We can also conclude from this study that the paraelectric ferroelectric phase transition and the maximum of the permittivity, $ε_{max}$ strongly depend on the two factors that are heat treatment and chemical composition.

### 4. Conclusion

The sol-gel method was used to obtain $BS_xT$ powders, from which pellets were prepared and sintered at 1100 ℃ ($BS5T_{4h}$ for 4h and $BS5T_{8h}$ for 8h). The structural characterization showed that $BS_xT$ crystallized in the

pseudo-cubic phase and that strontium gave rise to an increase of symmetry of BT. Dielectric studies showed an increase in the dielectric permittivity and a lowering of the Curie temperature ($T_c$) for $BS_{0.05}T_{8h}$. Moreover, the paraelectric-to- ferroelectric phase transition and the maximum of the permittivity are strongly dependent on two factors that are heat treatment temperature and the chemical composition, and that the behavior of the maximum of the permittivity, εmax, as a function of the frequency (f), shows a decrease in the range [1kHz-100kHz], followed by an <u>anormal </u>increase in interval [100kHz-1MHz] which result has not been, up to our knowledge, reported in the literature.

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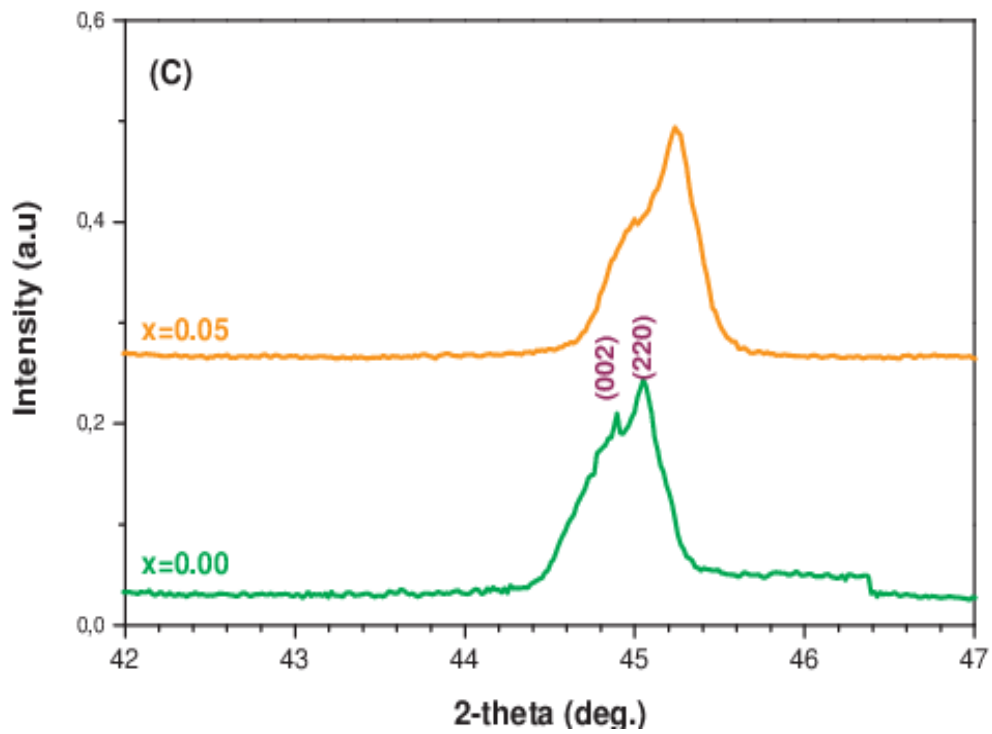D.C. Kongtaweelert, S. Panichphant, (2006),Curr. Appl. Phys. 6 (2006) 47.
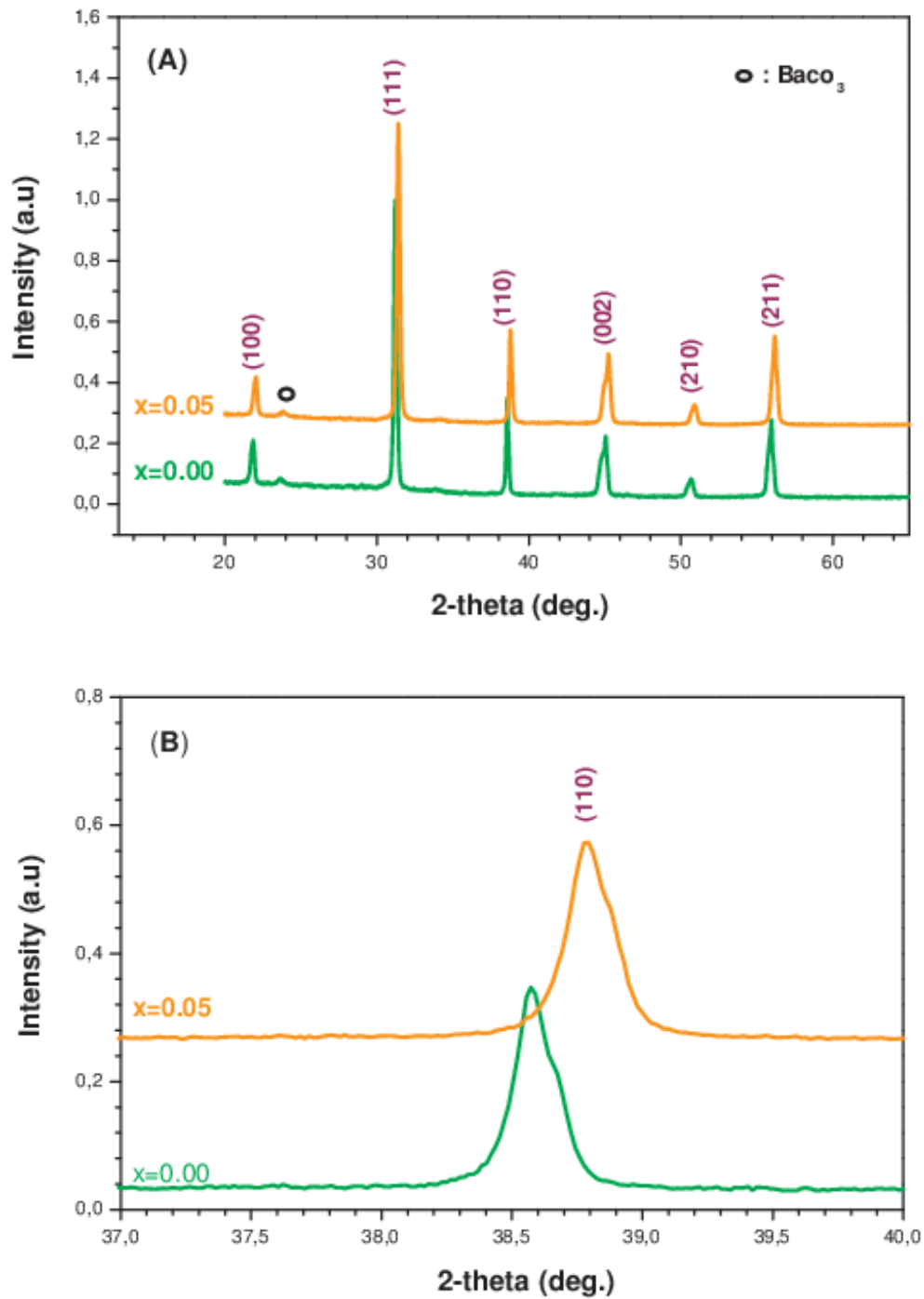
Fig.1.(A),(B) and (C) X-ray diffractograms of $Ba_{1-x}Sr_xTiO_3$ powders samples calcinated for at1000 ℃ (A),Expansion of the angles (2θ) located between 42° and 47° (B) and 37 ° and 40 °(C), respectively.
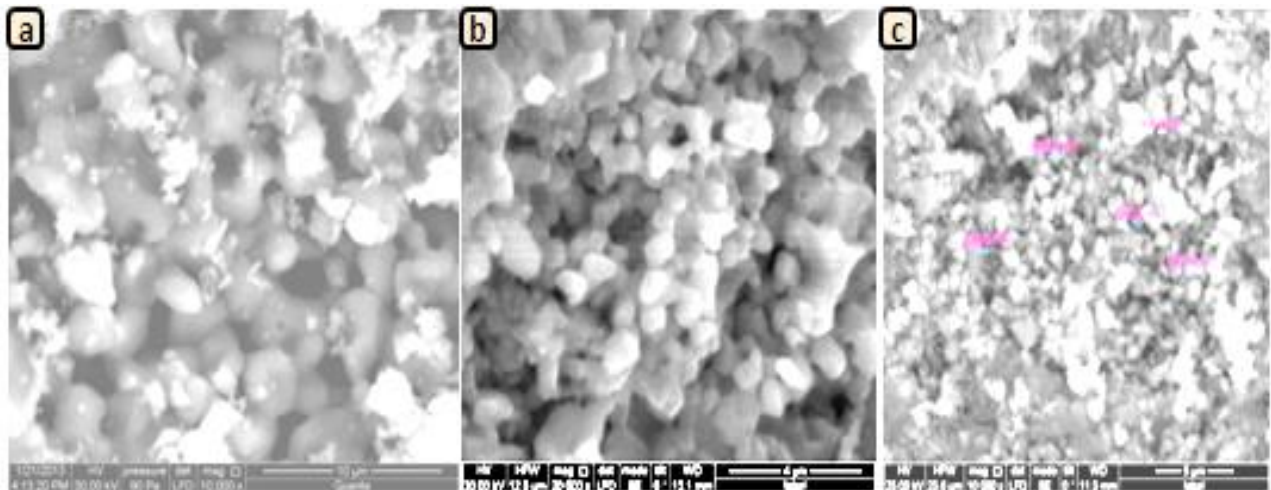


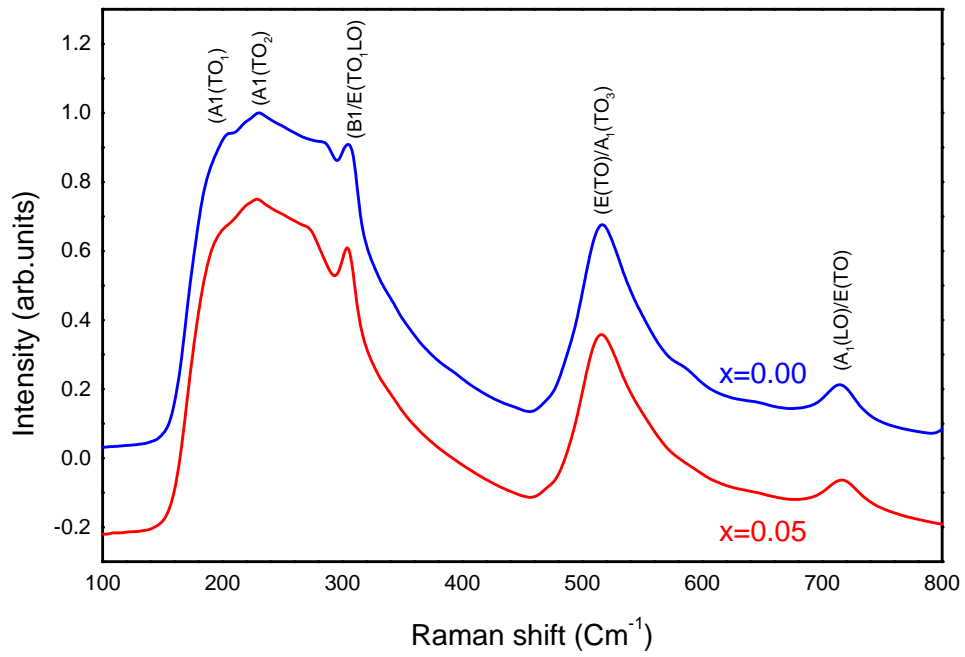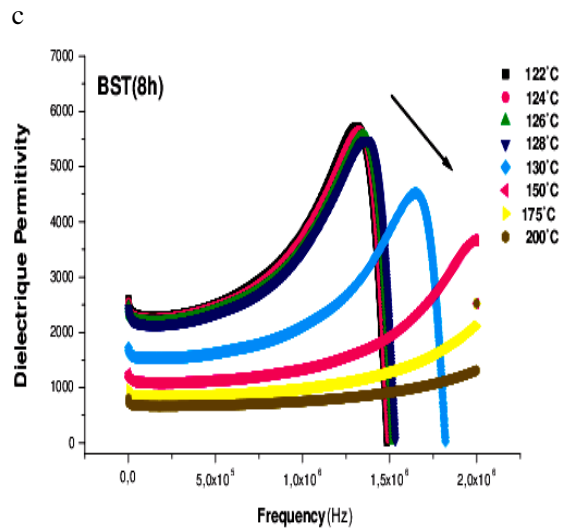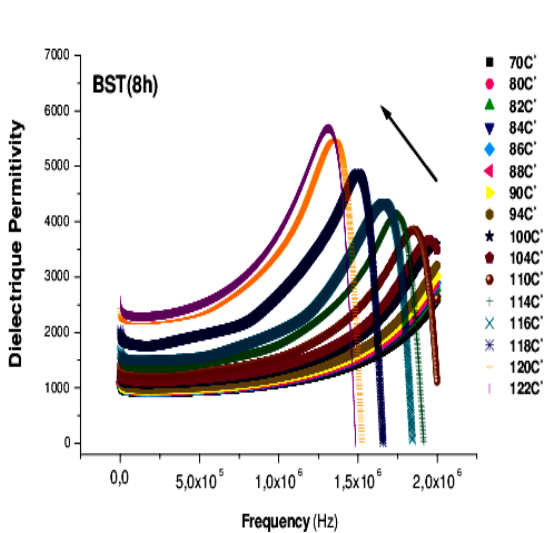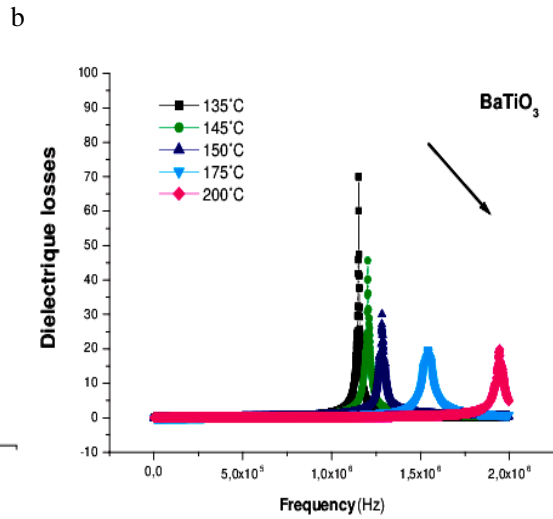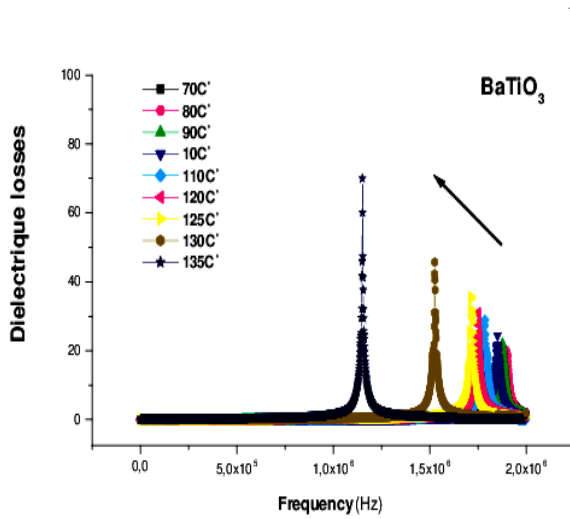Figure.2. SEM images of: a) BT b) $BST_{8h}$ and c) $BST_{4h}$.
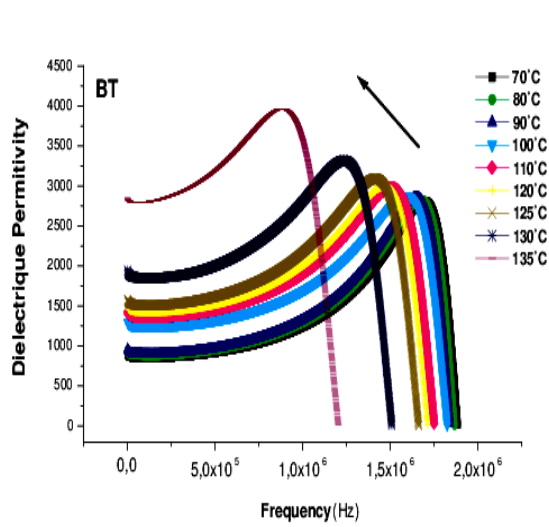
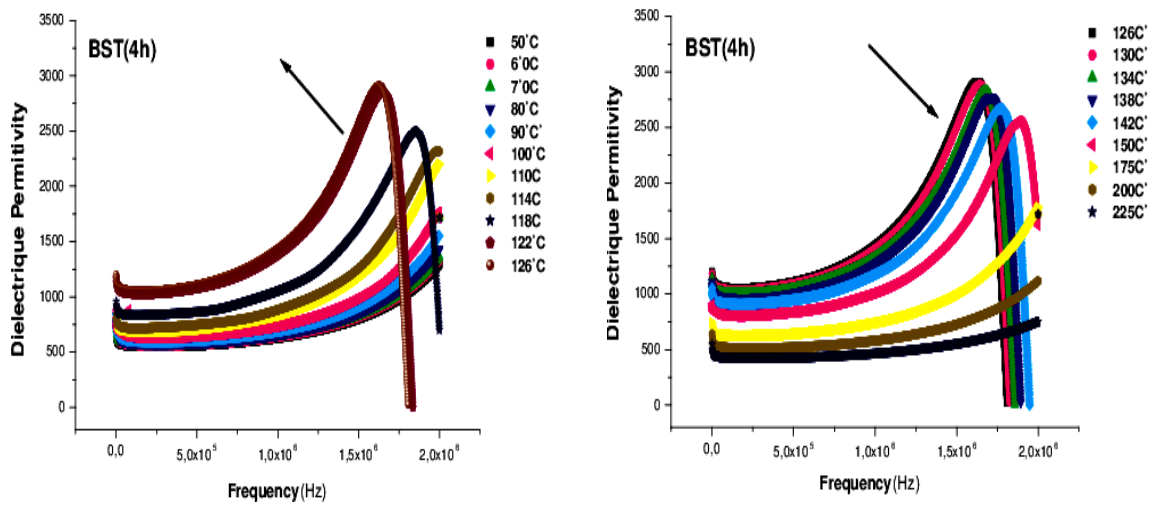Figure.3. Raman spectra of $Ba_{1-x}Sr_xTiO_3$
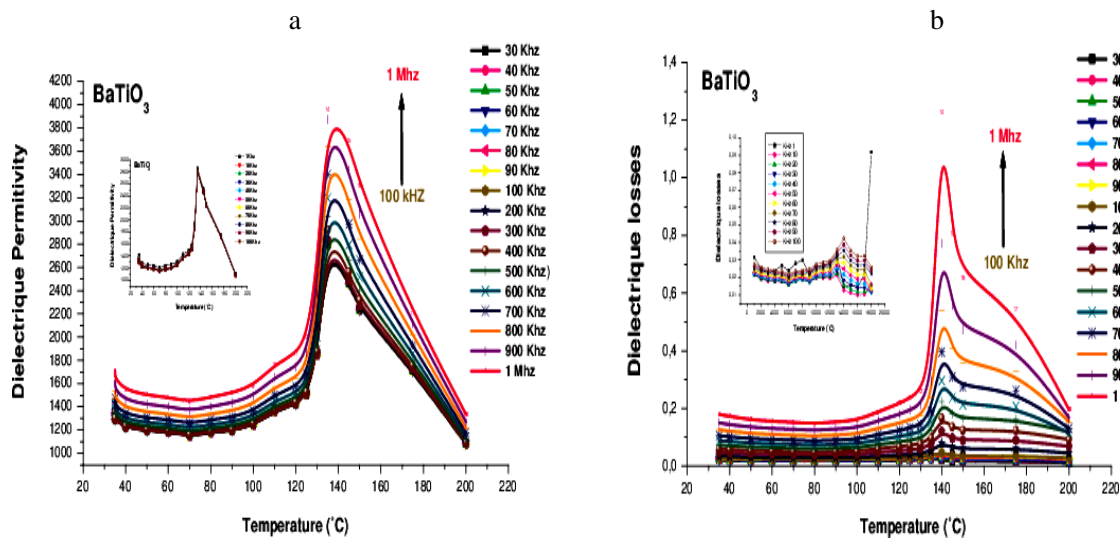
a



b



c
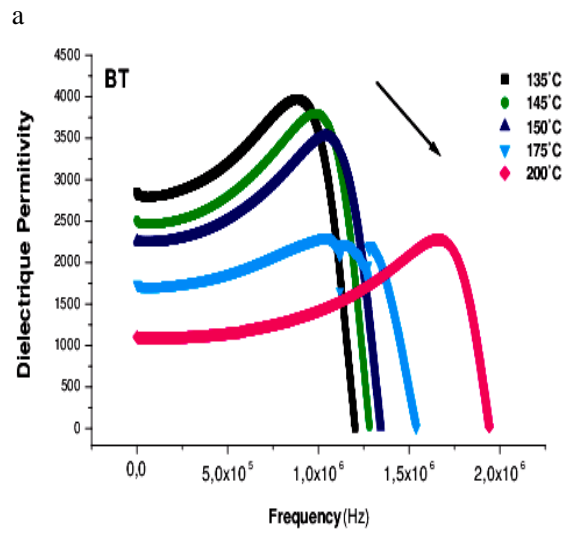


d

Fig.4.The frequency dependence of dielectric permittivity and the loss tangent of BT, $BST_{8h}$ and $BST_{4h}$ powder samples.
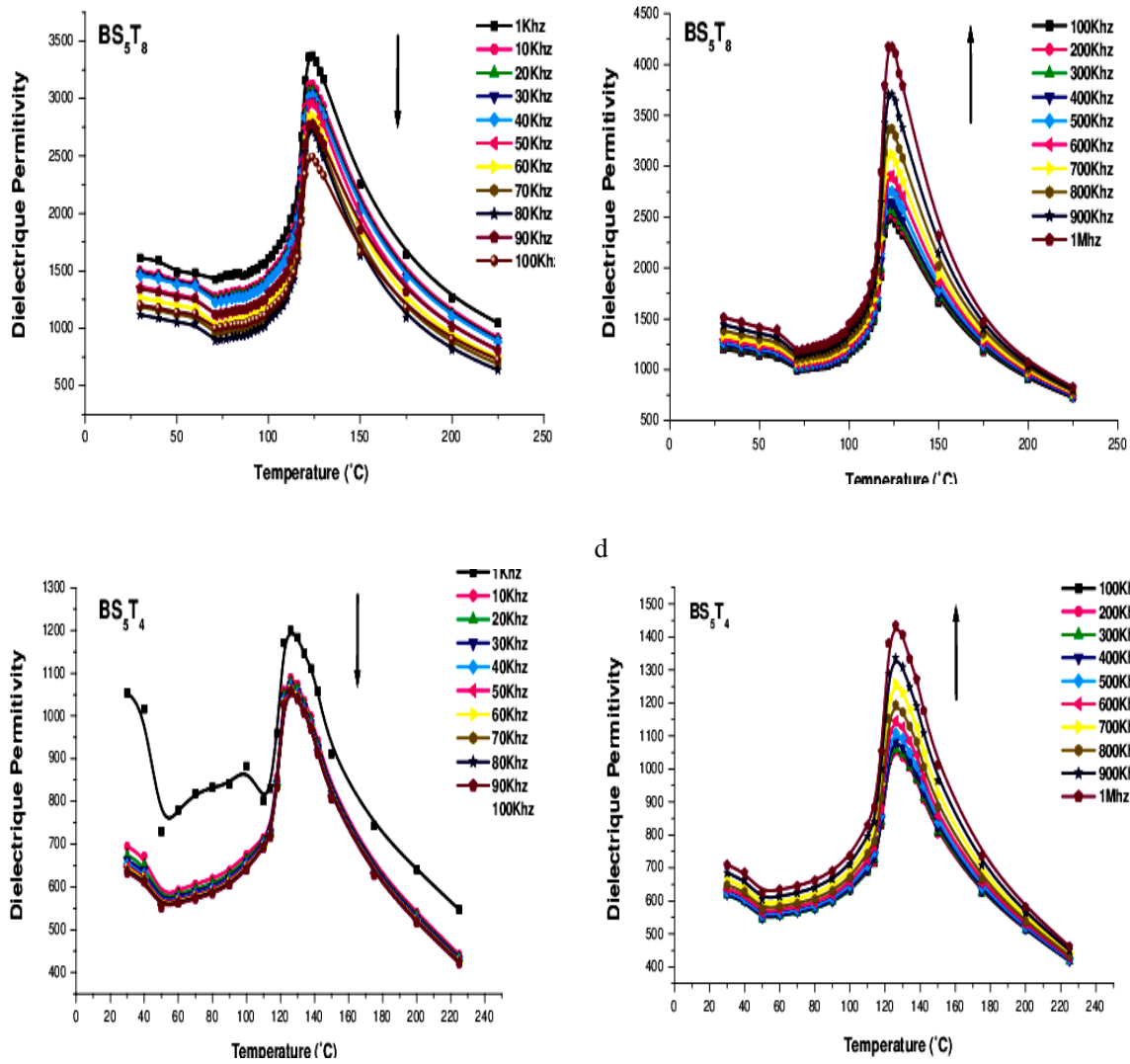
a

b



c

d

Fig.5.Temperature dependent dielectric constant and loss of different BT, $BST_{8h}$ and $BST_{4h}$, measured at different frequencies

Table1. Effects of Sr doping on the lattice parameters and the average crystallite size for $Ba_{1-x}Sr_xTiO_3$

| (x%) | c (Å) | a (Å) | c/a | c-a (Å) | Volume (Å$^3$) |
|------|-------|-------|-----|---------|----------------|
| 0.0 | 4.0421 | 4.0014 | 1.0102 | 0.0407 | 64.7189 |
| 5.0 | 4.0391 | 3.9995 | 1.0099 | 0.0396 | 64.6094 |

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