Complex impedance, dielectric relaxation and electrical conductivity studies of Ba$_{1-x}$Sr$_x$TiO$_3$ ceramics

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Abstract. In this work, we prepared series of Ba$_{1-x}$Sr$_x$TiO$_3$ (BSxT) powders, with different strontium concentrations ($x = 0, 0.025, 0.075, 0.10, 0.125$ and $0.15$), by the sol-gel method. The variation of structure in the Ba$1$-xSr$x$TiO$3$ system was analyzed using XRD and Raman techniques. The field dependence of dielectric relaxation and conductivity was measured over a wide frequency range from room temperature to 400 °C. The activation energy, calculated from the thermal variation of the conductivity for different frequencies, showed that the Sr has significant effects on the properties of BaTiO$_3$. Relaxation times extracted using the imaginary part of the complex impedance ($Z''(\omega)$) and the modulus ($M''(\omega)$) were also found to follow the Arrhenius law and showed an anomaly around the phase transition temperature.

Key words. BST, Conductivity, Activation energy, Complex impedance ($Z'(\omega)$ and $Z''(\omega)$), Relaxation times

1. Introduction

Ferroelectric materials of the ABO$_3$ perovskite type crystal structure have been widely used in microelectronic industries due to their high dielectric constant and low leakage current [1–6]. The most important examples of such ferroelectric materials are BaTiO$_3$ (BT) and SrTiO$_3$ (ST). BaTiO$_3$ is a ferroelectric for which the origin of ferroelectricity derives from the displacement of ions relative to each other. It is well known also that the temperature of transition from ferro-to-paraelectric state, T$_c$, and the dielectric properties of BaTiO$_3$ can be systematically changed by chemical substitution of barium and/or titanium by a wide variety of isovalent and aliovalent dopants [7–9] while SrTiO$_3$ is in paraelectric state of polarization. A well known solid solution of both BaTiO$_3$ and SrTiO$_3$ is barium strontium titanate (Ba$_{1-x}$Sr$_x$TiO$_3$ or BSxT), has been considered to be an important material for tunable microwave devices such as phase shifters, tunable filters, delay lines, tunable oscillators, induced piezoelectric transducer etc. This because of its high dielectric constant, large electric field tunabilities, relatively low dielectric loss, variable Curie temperature (from 243 to 127 °C) depending on the composition of strontium, large polarizations, large permittivity and large induced strains that are achievable [10–13].

On the other hand, it is known that all the above mentioned properties are basically influenced by the temperature and the frequency in perovskite structure-type materials. Therefore, the temperature dependence of the dielectric permittivity for some frequencies has been widely studied and reported as an important feature in order to determine the temperatures and character of the phase transition in
ferroelectric materials [14–16]. To the best of our knowledge, no works focusing on the study of the
dielectric properties in the BSxT system in a very wide frequency interval, and for different
temperatures of measure, have been reported in the literature, but only for few frequencies. Therefore
the objective of the present work is to investigate the phenomenon of relaxation of the BSxT
ferroelectric ceramics in a wide temperature and frequency ranges.

2. Preparation
Solutions of barium acetate, Strontium carbonate and the ground Ti are mixed in stoichiometric
proportions, depending on the chemical formulation Ba$_{1-x}$Sr$_x$TiO$_3$ under agitation for 5 min. The
destabilization of this solution is assured by evaporation of the solvent in an oven at the temperature of
80 °C for 96 h. The different steps in the preparation of the Ba$_{0.975}$Sr$_{0.025}$TiO$_3$ powders are similar to
those we have in our previous work [17]. Raw powder, after grinding, is calcined in air at 1000 °C for
4 h, in a programmable oven. Phase identification of the samples was performed using X-ray
diffraction (Cu K ray, $\lambda = 1.5418$ Å) and Raman spectrum. These compositions were then pressed into
pellets of 12 mm diameter and a thickness of 1 mm under a uniaxially pressure equal to 10 tons/cm$^2$.
The pelletized samples were finally sintered at 1100 °C for 8 h in a programmable furnace. Silver
paste was added to both faces of the disks, These compositions were then pressed into pellets of 12
mm diameter and a thickness of 1 mm under a uniaxially pressure equal to 10 tons/cm$^2$. The pelletized
samples were finally sintered at 1100 °C for 8 h in a programmable furnace. Silver paste was added to
both faces of the disks, which were then fired at 60 °C as electrodes.

3. Results and discussion

3.1. X-ray diffraction studies
Fig. 1 shows the X-ray diffraction patterns obtained on the powders of BSxT (x = 0, 0.025, 0.05,
0.075, 0.1, 0.125, and 0.15) calcined at 1000 °C for 4h. In this figure it is clear that all BSxT powders
crystallize in the perovskite phase without presence of secondary phases. Zoom in on the peak (111)
(Fig. 2) shows a shift in the position of the latter to larger angles, which highlights the incorporation
and effect of Sr on BT, these results are consistent with the literature [18-21]. On the other hand the
intensity of the (111) peak also diminishes with the mole fraction Ba/Sr, due to the difference of
atomic numbers between Ba and Sr [21]. In the Fig. 3, and for low Sr content (from 0 to 0.075), we
note the presence of (200) and (002) peaks around $2\theta = 44.58^\circ$, which are characteristic of the
quadratic phase [22]. With the increase in the rate of Sr, the two peaks tend to merge, and cannot
practically be distinguished for x = 10%. Which indicates a decrease in the tetragonality of the unit cell
and thus a gradual transition from tetragonal to pseudocubic phase.
Figure 1. Evolution of the XRD spectra of the Ba$_{1-x}$Sr$_x$TiO$_3$ powder, calcined at 1000°C.

Figure 2. The zoom peak (111) in the range 36° < 2θ < 39°
Fig. 3. Zoom peak (200) in the range 40° < 2θ < 48°

Fig. 4 shows the evolution of the Raman spectra at room temperature of the solid solution Ba$_{1-x}$Sr$_x$TiO$_3$ as a function of x, in the frequency range 100-1000 cm$^{-1}$. On the Raman spectrum of the pure sample (x = 0), we observe a strong and asymmetrical wide band due to the recovery of A(TO1), A(LO1) and A(TO2) modes between 200 cm$^{-1}$ and 280 cm$^{-1}$. It is also observed a narrow band around 305 cm$^{-1}$ associated with the modes B1 and E(TO3 + LO2), and a broad and asymmetric band at around 520 cm$^{-1}$ associated with A1(TO3) and E(TO4) modes, and another wide band (weak intensity) at around 720 cm$^{-1}$ associated with A1(LO3) and E(LO4) modes. Furthermore, the peak intensity at 305 cm$^{-1}$, assigned to B1+E(TO3 + LO2) modes, decreases as the temperature increases and disappears when the phase becomes cubic [23-25]. When Sr concentration increases (Fig. 4), the three peaks at around 200 cm$^{-1}$, 230 cm$^{-1}$ and 285 cm$^{-1}$ in BT tend to merge into a broad band located between 190 cm$^{-1}$ and 290 cm$^{-1}$ in BSxT. We also note the decrease in intensity of modes E(TO3 + LO2)/B1 and E(TO4)/A1 (TO3) and a widening of the band E(LO4)/A1(LO3). These are the result of shifting of Raman frequencies of the modes, but also of the presence of a local disorder of the phase which is due to the presence of Sr. The E(TO3) mode around 305 cm$^{-1}$ tends to expand and decrease in intensity indicating a tendency towards pseudo-cubic phase. These results are consistent with those found by Shou-Yi Kuo, Wen-Yi Liao, and Wen-Feng Hsieh [20].
3.2. Relaxation frequency fr for BSxT compositions

The thermal variation of the relaxation frequency, fr, for BSxT samples is shown in the curves of Fig.5. The results obtained show that BaTiO₃ relaxation frequency decreases with the temperature to reach its minimum value near Tc then increases. A possible mechanism responsible of this behaviour is based on the fact that the Ti⁴⁺ ion is displaced from the center of the oxygen octahedron and can occupy different potential wells (double potential well model). The relaxation process is then associated with Ti⁴⁺ ions cooperative jumps between the different wells. This movement would be consistent about a length Ic correspondent to that of a correlation chain [26-27]. The observed minimum can be explained by the growing Number of Ti⁴⁺ ions contributing to the cooperative movement along the correlation chains when the temperature approaches and tends towards Tc. Thus, the inertia of the chain increases (Ic increases) and the relaxation frequency decreases to a minimum value in the vicinity of the temperature of transition. On the other hand when the strontium content increases, the minimum of the curve fr = f (T) becomes more broad (diffuse). This study shows that the relaxation frequency value fr, at Tc (Fig.6) increases when x increases from 0 to 0.15, this can be explained by the substitution of Sr in BaTiO₃ which leads to a deformation of BO6 octahedra, probably involving shorter correlation chains and therefore leads to an increase of the relaxation frequency, which may be related to the nature of A-O bond (A: Ba, Sr) and / or to the polarisability of atoms.
3.3. Conductivity

To study the transport mechanism in BTSx, we plotted the thermal variation of the conductivity for different frequencies. The conductivity was calculated using the following relation:

$$\sigma = \omega \varepsilon_0 \varepsilon' = \omega \varepsilon_0 \varepsilon' \tan(\delta)$$  \hspace{1cm} (1)

Fig.7 shows that the conductivity of BS$_{2.5}$T passes through a maximum at the temperature $T_m$ of ferroelectric-to-paraelectric transition. In addition, it increases as a function of frequency from $3.95 \times 10^6$ for 0.1 kHz to $4.10 \times 10^6$ for 100 kHz in the vicinity of $T_m$. The increase becomes significant when the frequency exceeds $5.10^5$ Hz. This behaviour can be related directly to the relaxation phenomenon which results in a leakage current due to the energy dissipation. The shape of the curves recorded on the other BS$_x$T compounds ($x \neq 0.025$) are similar to that of BS$_{2.5}$T, and they differ from each other only by the position of the transition temperature $T_m$. In order to ensure the reproducibility of these results, the experiments have also been conducted in cooling mode. On the fig.8 we present...
the thermal evolution, on heating and cooling, of the conductivity of BSxT compounds recorded for the frequency 100 kHz. The results show that the temperature of ferroelectric-to-paraelectric transition in the cooling process is lower than that corresponding to the heating process.

![Graph showing conductivity vs. temperature for BSxT compounds at different frequencies.](image)

**Figure 7.** Conductivity of BS$_{0.025}$T as a function of temperature

![Graph showing conductivity vs. temperature for BSxT compounds, uphill and downhill.](image)

**Figure 8.** Evolution of the conductivity as a function of the temperature, uphill and down of BSxT

On the other hand, it is noted that maximum values are lower during the cooling process. When the temperature increases, and below $T_m$, the conductivity follows the Arrhenius law:

$$\sigma = \sigma_0 e^{-\frac{E_a}{k_B T}} \quad (3)$$
With the activation energy $E_a$, $T$ the absolute temperature in Kelvin and $k_B$ is Boltzmann's constant ($k_B = 1.3806.10^{-23}\ \text{J/K}$).

The fig.9 shows activation energy variation as a function of the frequency. The parameter $E_a$ shows an increase for low frequencies ($f < 100\ \text{kHz}$) followed by an almost linear increase with frequency above 100 kHz. The corresponding recorded values remain low confirming that the B $S_{0.025}T$ is a conventional ferroelectric material [28-29].

![Figure 9. Activation energy (Ea) as a function of frequency of BS$_{0.025}$T](image)

3.4. The Complex Impedance

The permittivity is not the only possible representation of the response of a material to an alternating current. Additional derived quantities can be used as: The admittance $Y(\omega)$: $Y(\omega) = 1 / Z(\omega)$, Modulo, $M(\omega)$: $M(\omega) = \omega C_0 Z(\omega) = i\omega C_0 / Y(\omega)$. Where $C_0$ is the capacity of the empty cell.

From these relations one can find the real part $Z'$ and $Z$ imaginary "impedance. $Z' = \varepsilon' / 2\pi f \varepsilon_0$ and $Z'' = \varepsilon'' / 2\pi f \varepsilon_0$ (where $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts of the permittivity).

The results of the complex impedance can be represented in different ways: Argand diagram ($Z' = f (Z')$, $Z''$ and $Z'$ as functions of the frequency. Argand diagrams of these samples showed a single semi semicircle in the frequency range considered (Fig.10), which means that the electric material interface and the domain walls are not contributing to the electrical response [30].
Figure 10. Argand diagram (Z" = f (Z')) of different samples BSxT at different temperatures.

However, it is possible in the case of a ceramic not to observe separately the second arc representing this mentioned contribution. It can either be masked by the existing semi-circle arc (deformed) or be completely absent from the diagram [31] which is the case of ZrO$_2$ (Y$_2$O$_3$ + MgO) and Bi$_2$O$_3$: Er$_2$O$_3$ compounds. Or, since we do not have enough frequency values, it was not possible to observe the second arc. It is well known that the ceramic microstructure also plays a key role in the electrical behaviour of BaTiO$_3$ doped with a donor [32].

Fig.11 shows the variation of the real part of the impedance (Z') as a function of the frequency at different temperatures and compositions. It shows a decrease as a function of the frequency in the low frequency region followed by a saturation region in the high frequency region. This indicates the presence of different type of polarizations in the material at low frequency.
The dielectric data were used to evaluate the relaxation time ($\tau$) of the electrical phenomena in the material using the relation:

$$\tau = \frac{1}{\omega_{\text{max}}} = \frac{1}{2\pi f_{\text{max}}} \quad (4)$$

Where $f_{\text{max}}$ is the relaxation frequency. The nature of the variation of $\tau$ with temperature of all the compounds is shown in Fig.12. The curves appear to follow the Arrhenious relation which is given by:

$$\tau = \tau_0 \exp \frac{E_{\tau}}{kT} \quad (5)$$

Where $\tau_0$ is a pre-exponential factor, $E_{\tau}$ is the activation energy, $k$ is the Boltzmann constant and $T$ is the absolute temperature. Activation energy values evaluated from the slope of log ($\tau$) vs. $10^3 T^{-1}$ curve are 3.18, 1.51, 1.14, 0.81 eV for $x = 0, 0.05, 0.10, 0.15$ respectively. It is clear that the value of activation energy decreases with an increase in Sr concentration. The small value of activation energy may be due to the ionized oxygen vacancies.
4. Conclusion
In this work, we have successfully prepared a series of Ba$_{1-x}$Sr$_x$TiO$_3$ samples. The phase formation of the samples was confirmed by XRD technique and spectroscopy Raman. The frequency dependent electrical data were used to study the conductivity and to estimate the activation energy (Ea). The results showed that the relaxation frequency value $f_r$, at $T_c$ increases when $x$ increases from 0 to 0.15, which behaviour may be explained by the fact that the substitution of Sr in BaTiO$_3$ leads to a deformation of the BO6 octahedron, which probably implies shorter correlation chains and can be linked, with the AO binding nature ($A$: Ba, Sr) and/or polarizability of atoms. Argand diagrams are represented by a single semi semicircle which means that the electro material interface and the domain walls are not contributing to the electrical response, however the behaviour of the conductivity may be directly related to the relaxation phenomenon which results in a leakage current due to the energy dissipation.

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