Frequency And Temperature Dependence Of The Dielectric Constant In $Ba_{1-x}Sr_xTiO_3$ Pellets

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Abstract- In this paper we illustrate results concerning measurements of the real and imaginary part of the dielectric constant of $BaTiO_3$ pellets doped with Sr, as a function of temperature and frequency. Substitution of Ba with Sr was up to 40% (x=0.1, 0.2, 0.3, 0.4, 0.5). It is shown that the Curie temperature of the ferroelectric to paraelectric transition is a monotonic dependence of Sr% and has an influence in the dielectric constant. Furthermore, frequency dependence also illustrates that oscillation ability of the electric dipoles is not monotonic, being dependent on the ferroelectric dipole interaction.

1. Introduction

Dielectric materials have concentrated the interest of many research groups because of their technologic interest that mainly concerns their property of electric polarisation which modifies their dielectric functions. Dielectric materials are also used in the construction of radio-frequency transmission lines. In practice, most dielectric materials are solid. Examples include porcelain (ceramic), mica, glass, plastics, and the oxides of various metals. Dry air and vacuum are excellent dielectrics and are used in various capacitors and some types of transmission lines.

There are some dielectric crystals illustrating a spontaneous electric polarization in which the direction of polarization can be reoriented between crystallographically defined states by an external electric field. Materials which show these properties are called ferroelectrics [1]. High dielectric coefficients over a wide temperature and frequency range are used as dielectrics in integrated capacitors. Among the different ferroelectrics, oxides showing a perovskite structure or a related structure are of particular importance. In alternating electric fields, moving charges cause a frequency-dependent phase shift between applied field and charge displacement. To express this mathematically, the relative dielectric permittivity is written as a complex function:

$$\varepsilon_r = \varepsilon'_r + i\,\varepsilon''_r \qquad\qquad (1)$$

The real part ε'_r characterizes the displacement of the charges, and the imaginary part ε''_r the dielectric losses [2]. The crystal structure of barium titanate is often regarded as the archetypical structure of a ferroelectric [3]. In the cubic high temperature phase this material does not display any spontaneous polarization and the system is paraelectric. Upon cooling, a phase transition occurs during which the positive and negative metal ions displace with respect to each other, leading to a tetragonal deformation. Due to the asymmetry in this displacement a spontaneous polarization in the direction of the tetragonal axis appears. Additional distortions are also possible with this structure like rhombohedral and ortborhombic. In this work, the permittivity of $Ba_xSr_{1-x}TiO_3$ pellets was measured as a function of temperature and frequency. First we describe the experimental settings in order to take those measurements. Furthermore the effects of Sr content and dielectric and ferroelectric properties of $Ba_xSr_{1-x}TiO_3$ pellets are presented and discussed.

II. Experimental set-up

Measurements have been realised by using oscillation circuits. Copper plates were used to cover the $Ba_xSr_{1-x}TiO_3$ pellets, while nitrogen and heating furnaces have been used to arrange cryogenic and high temperatures respectively. These materials have important applications in the science and the technology of material because of their high dielectric permittivity and low dielectric losses [1]. The samples were prepared by sintering. The used raw materials were: $BaCO_3$ with molecular weight (M.W.) = 197 gr, $SrCO_3$ with M.W. = 147,5 gr, and TiO_2 with M.W.= 80 gr, all in form of powder. The powders were mixed stoichiometrically according to the following reaction:

$$x\,BaCO_3 + (1-x)\,SrCO_3 + TiO_2 \;\rightarrow\; Ba_x\,Sr_{1-x}\,TiO_3 + CO_2\,,$$

and then pressed into pellets. Sintering took place at 1350^oC resulting in the following pellet samples: $BaTiO_3$, $Ba_{0,8}Sr_{0,2}TiO_3$, $Ba_{0,7}Sr_{0,3}TiO_3$, $Ba_{0,6}Sr_{0,4}TiO_3$ and $Ba_{0,5}Sr_{0,5}TiO_3$.

Results have been obtained measuring the real and imaginary part of the dielectric constant in various temperatures from 100K to 500K and in a frequency range from 10 Hz to 1 MHz increasing logarithmically. These results clearly indicate the Curie points of these pellets. From these results it can be seen that these pellets can be used as the precursor material for thermistor applications with transition points at various frequencies dependent on the Sr concentration. The oscillation circuit we used in order to take these measurements is illustrated in figure 1.
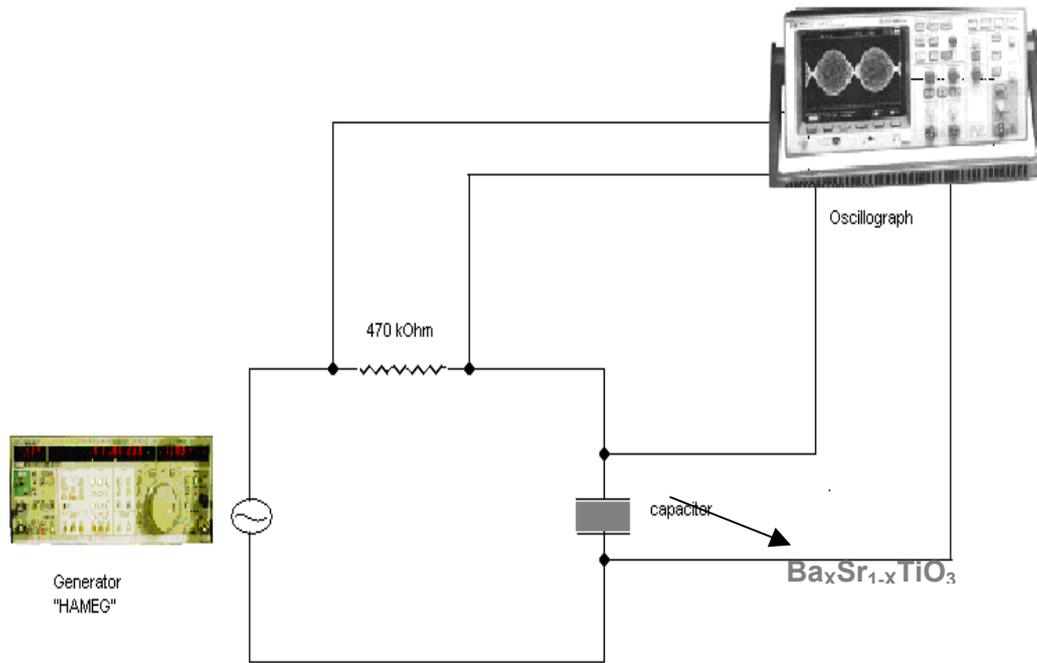
Figure 1. Oscillation circuit.

Two conducting copper disks of 1 inch diameter were used as the capacitance plates including $Ba_xSr_{1-x}TiO_3$ pellets. An AC current generator with adjustable excitation frequency was connected in series with a 1% precision resistor 470 kOhm and the above-mentioned capacitance. The voltage output of the capacitor and the precision resistor were the two input of the used digital oscilloscope. The output of the digital oscilloscope was driven to a PC using an IEEE 488 card. After having the experimental data the real and imaginary parts of ε (ε′, ε″) were obtained by a software code developed at the laboratory, calculating

$$\varepsilon = \sqrt{\left(\varepsilon'^{\,2} + \varepsilon''^{\,2}\right)} \text{ and } \delta = \tan^{-1}\left(\frac{\varepsilon''}{\varepsilon'}\right). \tag{3}$$

where δ is the phase difference between real and imaginary part of the dielectric constant. No lock-in amplifier was needed due to the high signal to noise ratio which was of the order of 90 db.

The capacitance bridge was inserted into a purpose – made cryogenic device allowing temperature changes from 100K to 300K. The cryogenic furnace is illustrated in figure 2. Copper was chosen as furnace material because of its high thermal conductivity, thus allowing better distribution of heat to the capacitance bridge. Liquid nitrogen was inserted into a dewar flask. Consequently the cryogenic furnace was inserted into the dewar. The temperature of the capacitance bridge was adjusted by displacing it up and down the cryogenic furnace. Before of each experiment a refrigerator was filled with enough quantity of nitrogen, in which the device was sinking. Capacitance's bridge temperature was measured by a thermocouple, the output of which was driven to the above mentioned PC.

III. Experiment results and discussion

The structural characterization of pellets was obtained using an X-Ray diffractometer (Siemens 5000). Indicatively an XRD analysis for the fifth sample is given in figure 3. All samples had very similar XRD response, thus indicating a solid solution of Sr into $BaTiO_3$. A representative selection of experimental data, concerning the dependence of ε′ and ε″ of the various $Ba_xSr_{1-x}TiO_3$ pellets on frequency at given temperatures is given in figures 4,5,6,7 and 8.

The relaxation phenomena that are observed to the diagrams above are a result of inactivity of charges due to electric dipole inertia. In many cases, a restoring force is also developed, which affects the charges and opposes the force of the electric field. In charge systems like dielectric substances the

combination of inactivity and restoring forces results in resonance phenomena like in mechanical systems [4]. Those phenomena cause minimum and maximum peaks as shown in figures 4, 6 and 7. The resonance phenomena cause an increase of the charges displacement and as a result of this the polarisation and dielectric constant are regularly increased. As soon as the frequency is increased a little bit more, the system presents reverse behavior that leads to relaxation phenomena where the polarisation and permittivity are constant and not influenced by the frequency any more.
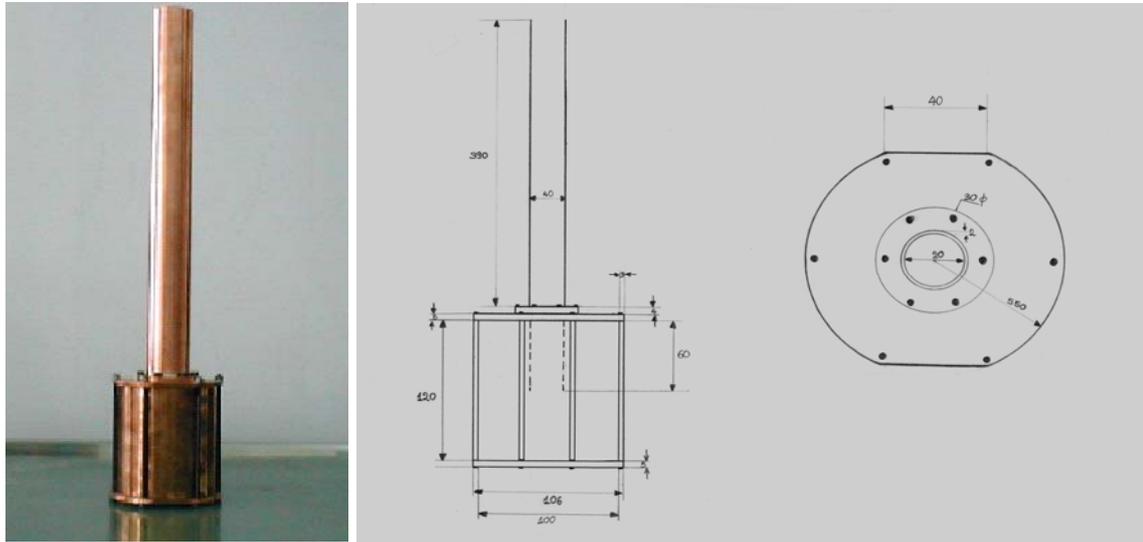
Figure 2. Cryogenic device and its mechanical drawing.
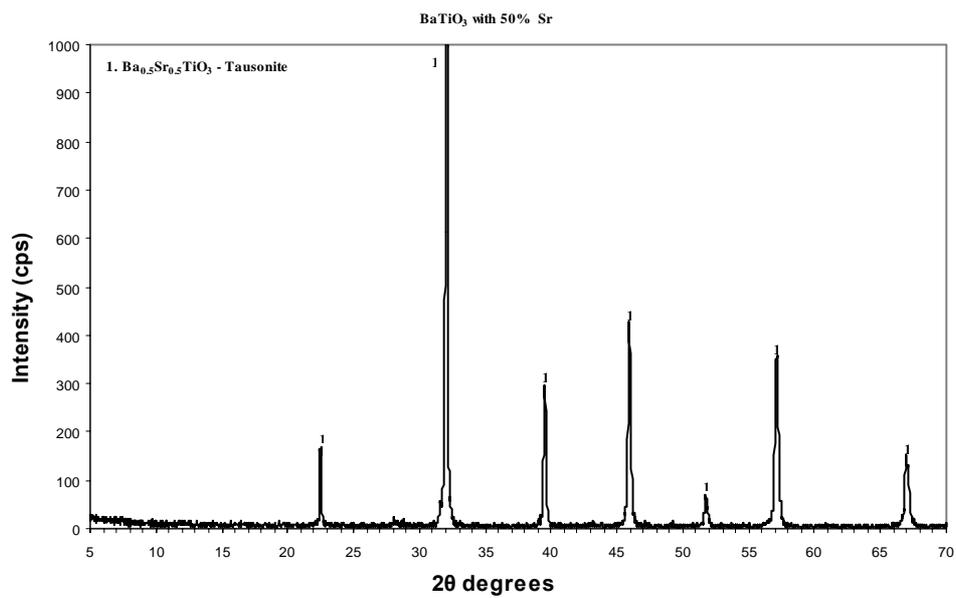
Figure 3. XRD analysis for Ba $_{0.5}$Sr $_{0.5}$TiO$_3$.

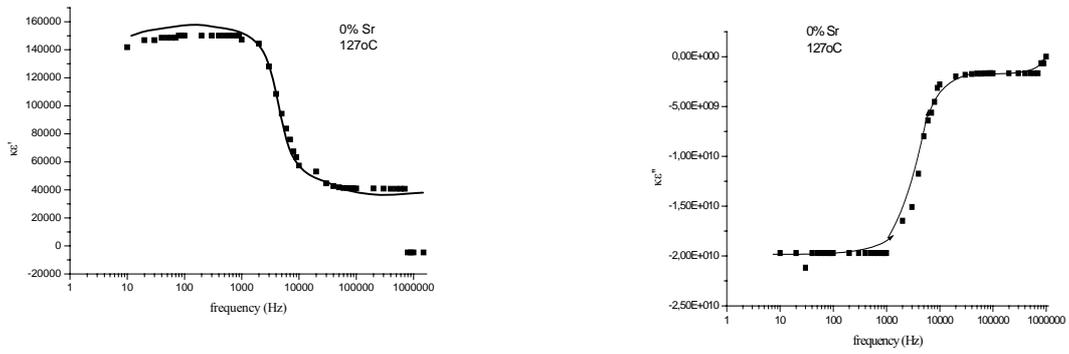Figure 4. Frequency dependence of the real and imaginary parts of ε in 0% Sr at -170C.

Figure 5. Frequency dependence of the real and imaginary parts of ε in 0% Sr at 127C. The paraelectric phase transition can be observed.
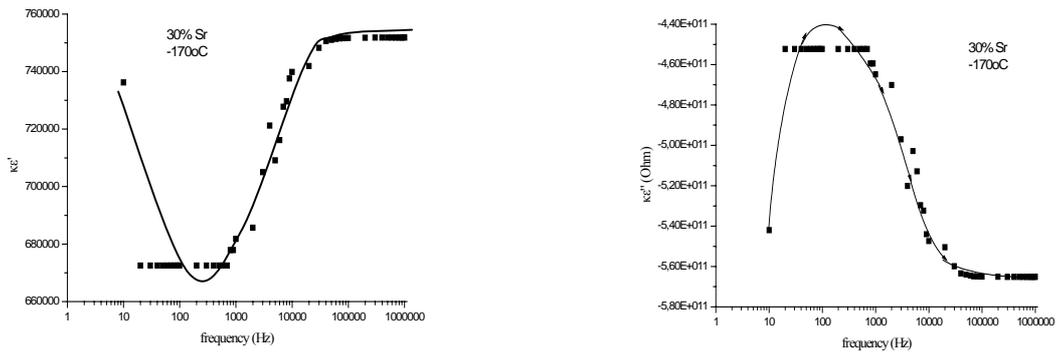

Figure 6. Frequency dependence of the real and imaginary parts of ε in 30% Sr at -170C.
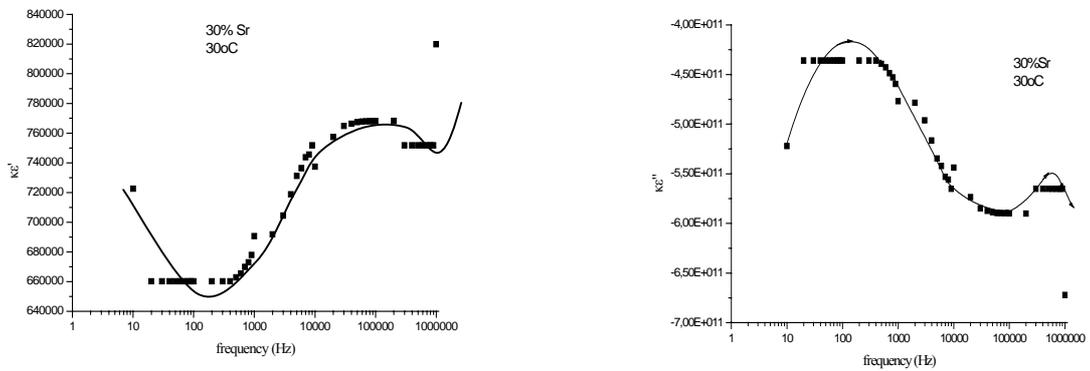

Figure 7. Frequency dependence of the real and imaginary parts of ε in 30% Sr at 30C. The starting of the phase transition can be observed at a lower temperature than in 0% Sr.
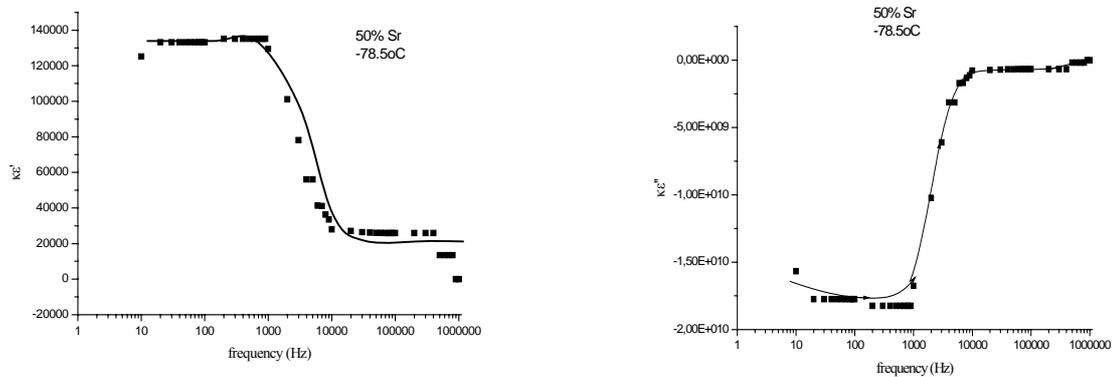

Figure 8. Frequency dependence of the real and imaginary parts of ε in 50% Sr at -78.5C. It can be seen that phase transition starts in even lower temperature.

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The uncertainty of measurements of the real and imaginary parts of the permittivity is mainly due to the air gaps at the copper disk interface layer. Any other random geometrical changes were eliminated using a fixed non-metallic mechanical head.

As known, the Curie temperature of $SrTiO_3$ is roughly -200°C and that of BaTiO3 is between 110-150 ^{o}C. As $BaTiO_3$ is doped with Sr its Curie temperature changes and it can be stabilised at a temperature plateau. The dependence of the real part of ε on temperature is illustrated in figure 9. It can be seen that the ferro -to- paraelectric phase transformation occurs in the same temperature region for 0% up to 40% Sr , indicating that Sr is a solid solution into the $BaTiO_3$, thus following the same rules of such transformation like $BaTiO_3$. For larger concentration of Sr into the $BaTiO_3$, the Curie temperature drops indicating a phase change, probably a Ba solid phase solution into $SrTiO_3$.
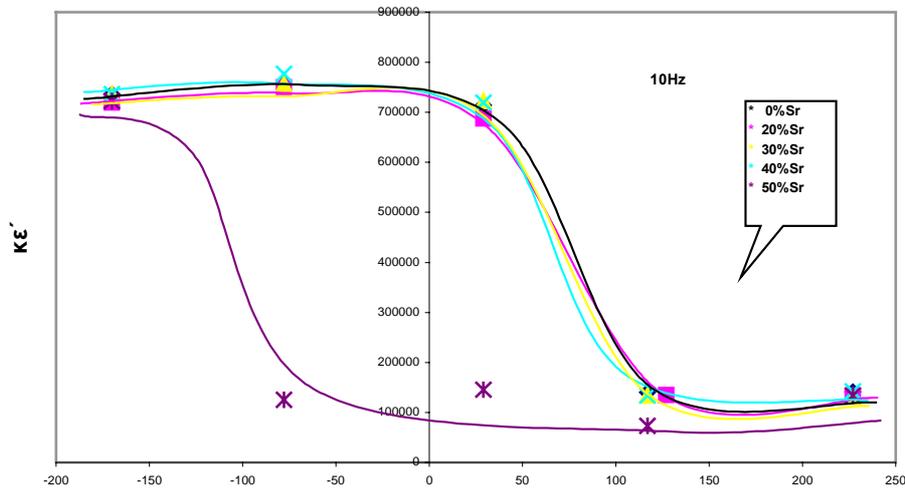
Figure 9. Temperature dependence of the real part of ε for the fifth samples at the frequency of 10 Hz.

References

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