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Microwave dielectric relaxation process in doped-incipient ferroelectrics

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Abstract

The electrical permittivity properties in the microwave frequency range were investigated in incipient and relaxor compositions of $Sr_{1-x}Ca_xTiO_3$ ceramics from 60 to 440 K. The results revealed that the origin of microwave dielectric relaxation process lies in the appearance of nanometric polar regions rather than any other ferroelectric or piezoelectric mechanism. The experimental data also showed that the relaxation frequency is reasonably independent of the correlation length. The occurrence of more stable polar phase into the grain bulk induced by dipole moment related to the grain boundaries was also verified.

Keywords: Dielectric properties; Capacitors; Microwave dielectric properties

1. Introduction

Over the last decades, the investigation of microwave dielectric properties of ferroelectric materials has been one of the most challenging tasks of ferroelectricity. Rather, microwave dielectric relaxations have been observed in the so-called "normal" ferroelectrics and relaxor ferroelectrics (relaxors). The occurrence of such relaxation process in so different kinds of ferroelectric materials has encouraged the development of several models to explain this physical phenomenon.[1–7] For instance, the relaxation phenomenon for "normal" ferroelectrics has been modeled in terms of a simple harmonic oscillator, in which the relaxation frequency (f_R) is dictated by the ratio between the force constant and effective mass of domain walls.[8,9] However, studies in the current literature reporting microwave dielectric properties in incipient-ferroelectric systems are scarcely found.

Strontium titanate ($SrTiO_3$) has been revealed a suitable material to investigate the microwave dielectric properties in ferroelectric systems. It is a well-known incipient-ferroelectric, in which some ferroelectric order can be induced by chemical substitution into its highly polarizable host lattice.[10–12] Indeed, it is reported that the substitution of Sr^{2+} by Ca^{2+} produces random electric fields that induce dipoles in a region with a correlation length r_c and, within this correlation length, polar nanodomains embedded in a non-polar matrix are formed.[13,14] Moreover, the continuous addition of Ca^{2+} induces a gradual formation of polar nanoregions and the appearance of a progressive interaction with a glass-like relaxor state.[13,14] Thus, Ca-modified strontium titanate, $Sr_{1-x}Ca_xTiO_3$, permits much flexibility to investigate the relationship between the microwave dielectric relaxation process and the dynamics properties of nanometer polar regions in incipient and relaxor ferroelectric materials.

The objective of this work is to investigate the microwave dielectric properties of $Sr_{1-x}Ca_xTiO_3$ ceramics with $x = 0.01$ and 0.10 in a wide range of temperature. The dependence of microwave dielectric relaxation process on the formation and growing of polar nanodomains via Ca^{2+} chemical substitution is discussed.

2. Experimental procedure

The solid state reaction method was used to prepare $Sr_{0,99}Ca_{0,01}TiO_3$ and $Sr_{0,90}Ca_{0,10}TiO_3$ ceramics, hereafter

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labeled as SCT-0.01 and SCT-0.1, respectively. According to the proposed $Sr_{1-x}Ca_xTiO_3$ phase diagram these compositions are incipient and relaxor ferroelectrics, respectively.[14] Briefly, $SrCO_3$, $CaCO_3$ and TiO_2 powders were mixed for 96 h by ball milling in isopropyl alcohol. The powders were calcined at 1000 °C for 2 h and X-ray diffraction analysis revealed only the perovskite phase. After calcination, the powders were uniaxially pressed at 20 MPa and sintered at 1300 °C for 8 h. Scanning electron micrographs analysis of polished samples revealed that the average grain size for both compositions was around 1.5 μm.

In addition, laser heated pedestal growth technique was utilized to prepare single crystals with the same nominal compositions. The pulling rate was 0.30 mm/min. Aiming to avoid the presence of cracks, the diameter of the fiber was controlled to be smaller than 0.5 mm. The samples were cut and polished and after that heat-treated at 600 °C for 20 min. Gold electrodes were sputtered on the ceramic samples in form of discs with 2.0 and 0.45 mm in diameter and thickness, respectively. For the single crystals the electrodes were sputtered on disc-shaped samples with 0.45 mm in diameter and 0.50 in thickness.

High frequencies dielectric measurements were performed on cooling using a Network Analyzer HP-8719C in a frequency and temperature range from 60 MHz to 2 GHz and from 440 to 90 K, respectively. Details of the experimental apparatus were described in details elsewhere.[15,16] During the cooling process, it was waited 5 min between each desired temperature to guarantee the thermal stability of the sample. Dielectric characterizations performed at 1 kHz were made on cooling from 300 to 15 K with a continuous rate of 1 K/min employing an Impedance Analyzer HP 4194A and a cryogenic refrigeration system (APD Cryogenics Inc.).

3. Results and discussion

Fig. 1(a)–(d) show representative curves of the frequency dependence of the real (ε') and imaginary (ε'') components of the relative dielectric permittivity measured at different temperatures for the SCT-0.01 and SCT-0.1 ceramics. In addition, it is also shown the dielectric spectrum of the respective single crystals measured at room temperature. The results reveal strong temperature dependent dielectric relaxations for both ceramic compositions in the entire temperature range investigated. However, for the single crystals, no relaxation is observed for the SCT-0.01, while a very subtle one is notice for the SCT-0.1.

Fig. 2(a) and (b) show the temperature dependence of the relaxation frequency (f_R) and the relaxation strength ($\Delta\varepsilon$) for both ceramic samples. The data reveal that at low temperatures $\Delta\varepsilon$ is higher for SCT-0.1 than for SCT-0.01, while f_R is quite similar for both compositions. It is also verified that the microwave dielectric relaxation persists at higher temperatures for the SCT-0.1. A quick inspection in the relaxation frequencies for both compositions curiously reveals that they are remarkably comparable to those found for other relaxors and "normal" ferroelectrics,[2,4,5,17] although the size of respective polar regions as well their correlation length differ significantly.

Fig. 3 shows the double-logarithmic plots of $1/\varepsilon'$ versus $T - T_m$ for SCT-99:1 and SCT-90:10 ceramics. The results

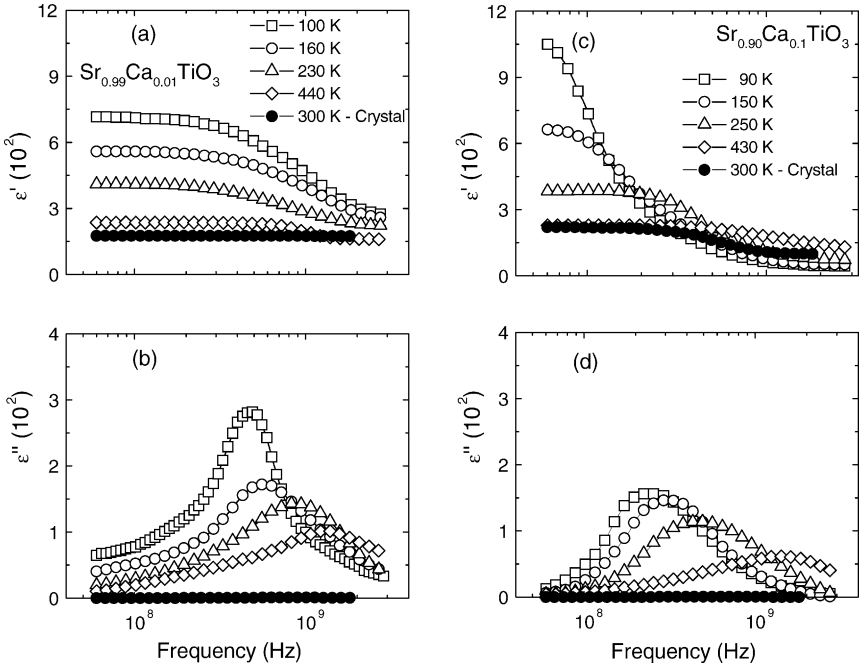

Fig. 1. Real (ε') and imaginary (ε'') parts of the relative dielectric permittivity as a function of the frequency and temperature for $Sr_{0.01}Ca_{0.99}TiO_3$ and $Sr_{0.1}Ca_{0.90}TiO_3$ ceramics (opened symbols) and single crystals (solid symbols).

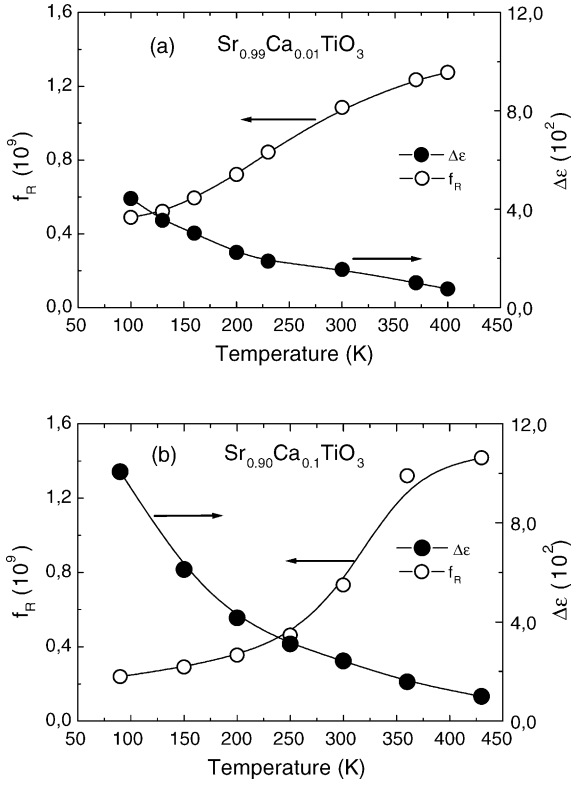

Fig. 2. Temperature dependence of the relaxation frequency (f_R) and the relaxation strength ($\Delta\varepsilon$) for: (a) $Sr_{0.01}Ca_{0.99}TiO_3$; and (b) $Sr_{0.1}Ca_{0.90}TiO_3$ ceramics.

show that SCT-99:1 and SCT-90:10 present a discernible deviation from the Curie–Weiss law at ≈80 and ≈110 K, respectively. Hysteresis loop measurements (not shown here) at room temperature revealed a characteristic slim loop, which means no measurable remanent polarization ($\langle P_r \rangle = 0$).

It is verified that the dielectric properties of $SrTiO_3$ are strongly dependent of the Ca-content, which induces gradually in the host lattice nanometric polar regions. Thus, the concept of appearance, growing and correlation length

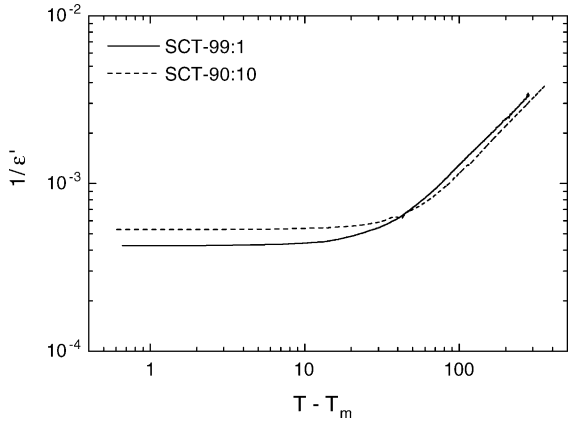

Fig. 3. Log–log plot of the temperature dependence of the electrical permittivity (ε') of $Sr_{0.01}Ca_{0.99}TiO_3$ (SCT-99:1) and $Sr_{0.1}Ca_{0.90}TiO_3$ (SCT-90:10) ceramics.

of polar nanoregions seems to be central to understand the microwave dielectric relaxation process. Then, based on the experimental results, the following scenario can be drawn to explain the microwave dielectric relaxation process of Ca^{2+}-doped-strontium titanate. In the very dilute case, which means low concentration of dipolar impurities and defects (SCT-0.01), there is a small amount of weakly correlated polar nanoregions embedded in a relative large paraelectric matrix. Thus, it may be assumed that their contribution to the dielectric response is small, being responsible for the low relaxation strength observed in the entire temperature range investigated. On other the hand, for higher amount of Ca^{2+} (SCT-0.1), higher is the concentration of dipolar impurities and defects in relation to the host paraelectric matrix, thus increasing the amount of polar nanoregions. Consequently, it may be assumed that their contribution for the dielectric response is higher and, consequently, the relaxation strength is higher.

Our data also reveal that the relaxation strength is much lower and persists up to lower temperatures for the single crystals than for the respective bulk ceramic samples. This effect suggest the existence of defects connected with the grain boundaries, which induce a polar phase in the grain bulk, as recently suggested by Petzelt and co-authors through infrared and Raman characterizations.[18] This process would be analogous to the Ca^{2+} doping. However, our data show clearly that whereas the polar phase induced by Ca^{2+} off-center positions disappears due to the high thermal fluctuations, the polar phase induced by defects connected the grain boundary is able to persist up to higher temperatures, inducing a more stable polar phase in the SCT ceramics. Therefore, these data provide supportive evidence that the microwave dielectric response and, consequently, the relaxation process can be directly related to the existence of polar nanoregions.

Concerning the correlation length of the polar regions, it is experimentally noticed that decreasing the temperature $\Delta\varepsilon$ increases for both SCT compositions. Rather, for a specific amount of doping, it is reported in the literature that with decreasing the temperature, the rapidly increasing of r_c increases the size of nanodomains, thus coupling them into growing polar domains and increasing their Coulombic interactions.[12,13] Consequently, it may be supposed that the increase of $\Delta\varepsilon$ with decreasing the temperature can also be associated with a major participation of more interacting-polar nanodomains in the dielectric response. On other hand, it is observed that $\Delta\varepsilon$ tends to zero at much higher temperatures for the SCT-0.1. This result can be explained assuming that the correlation length of polar regions for highly Ca^{2+} doped samples is stronger, thus being able to persist up to higher temperatures. In addition, our data also show that the dielectric relaxations persist up to temperatures much higher than T_m. It has been reported that polar nanoregions persists up to the Burns temperature (T_B), where deviation from the Curie–Weiss law is noticed,[19] as observed in Fig. 3. Therefore, these results corroborate the concept that although there is no measurable remanent polarization at high temperatures

($\langle P_r \rangle = 0$), the dielectric relaxation can be related with the condensation of polar nanodomains at T_B.

Curiously while the relaxation strength was significantly higher for the samples with higher amount on Ca^{2+} doping, the relaxation frequency (f_R) is almost independent of the composition (Fig. 2). Moreover, the relaxation frequencies observed in the incipient and relaxor ferroelectrics are very similar to those reported in the literature for "normal" ferroelectrics[2,17] in which micro sized domains with ferroelectric long-range order prevail. Therefore, it seems that the relaxation frequency is reasonably independent of the size of polar regions as well as their correlation length. Nevertheless, it has been suggested that f_R depends on the degree of order[20,21] and, consequently, on the range order. Undoubtedly, these preliminary results reveal interesting features about f_R and demand further investigations.

4. Conclusion

In summary, it was shown that the key questions concerning the microwave dielectric relaxation process in incipient and relaxor ferroelectrics lie in the appearance, growing and correlation length of polar nanoregions. The experimental results suggest that the occurrence of such relaxation process depend only on the presence of polar nanoregions. The clue to the origin of such process was provided by dielectric measurements in $Sr_{1-x}Ca_xTiO_3$ in the reasonable absence of defects (grain boundary), in the very diluted case and above T_B, which corroborated such concept. This picture will be checked and extended in further works. In particular, the influence of domain size and, consequently, the short and long-range order on the structure of the dielectric spectrum of "normal" and relaxor ferroelectrics will be compared.

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