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Study of polar relaxation processes in $Sr_{(1-1.5x)}La_xTiO_3$ ceramics by using field-induced thermally stimulated currents

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Abstract

Polar relaxation processes in Lanthanum doped $SrTiO_3$ (STO) ceramics, with general formulae $Sr_{(1-1.5x)}La_xTiO_3$, were studied by undertaking field-induced thermally stimulated currents measurements below room temperature.

The experimental results obtained for doped ceramic ($x = 0.0133$) were analysed by using dipolar and space-charge relaxation thermally stimulated depolarization currents (TSDC) models in order to determine the nature of the relaxation processes involved.

Our results reveal the existence of different relaxation processes in the temperature range 60–300 K. Whereas at low temperature, a relaxation mechanism of a dipolar type was disclosed within the temperature interval centred around 100 K, a space-charge relaxation process could be identified in the temperature range 120–300 K. The temperature dependence of the relaxation parameters will be also discussed in detail.

Keywords: Electrical properties; Perovskites; Insulators; Impurities; Lanthanum

1. Introduction

Strontium titanate $SrTiO_3$ (STO) undergoes at $T \sim 100$K a structural phase transition from a paraelectric phase with cubic perovskite symmetry to a tetragonal antiferrodistortive state.[1] $SrTiO_3$ exhibits at low temperatures quantum behaviour, being one of the best known examples of a quantum paraelectric material. Owing to its significant polarisable crystalline structure, high dielectric permittivity that increases on cooling, and low microwave losses, $SrTiO_3$ is one of the most attractive materials for many high frequency and microwave applications, particularly at low temperatures.[1]

Great attention has been paid lately to the study of $SrTiO_3$ ceramics, although the permittivity values at low temperatures are several times smaller in ceramics than in single crystals, and the microwave losses in ceramics are higher and grain size dependent.[1,2] The lower permittivity, which implies a smaller softening of the soft mode, is established to be mainly related to the existence of micro-polar regions in undoped STO ceramics, apparently due to frozen dipole moments at the grain boundaries.

Recently detailed pyroelectric thermal cycles and dielectric measurements carried out in La doped STO ceramics, with general formulae $Sr_{(1-1.5x)}La_xTiO_3$ [3] reveal a complex non-ergodic behaviour related to the existence of different relaxations processes related to bulk and grain boundary dipoles and surface charge release.

In order to get a better knowledge of the relaxation behaviour in Lanthanum doped STO ceramics, we have carried out a field-induced thermally stimulated current study in the temperature range between 12 K and room temperature, for $x = 0.0133$. A detail discussion addressed to the nature of the relaxation processes associated with thermally activated polarization, and to the temperature dependence of their characteristic parameters is presented.

2. Experimental and modelling

The lanthanum doped STO ceramics were prepared by solid-state reaction. Chemical reagents of $SrCO_3$, TiO_2, and La_2O_3 were used. The weighed batches were mixed and wet milled with alcohol in agate pots on a ball mill of a planetary type for 5 h and dried in an oven at 70–80 °C for about 12 h. The samples were then calcined in a furnace between 950 and 1200 °C for 2 h at a rate of 5 °C/min. After calcinations, the powders were wet-milled again in agate pots with a planetary mill for 5 h. The

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milled and dried calcined powders were mixed with binder to improve the forming process. Then, they were uniaxially pressed into disks of $\Phi = (10–15)$ mm × (1–2) mm at 50 MPa and then isostatically pressed at 300 MPa. The pressed disks were sintered between 1240 °C and 1400 °C for 2 h in air and then furnace-cooled.[4]

The study of thermally stimulated depolarization currents was carried out in sequential thermal cycles as follows: (i) field cooling – cooling down from room temperature while a polarizing electric field E_p is applied; (ii) zero field heating – heating to room temperature under zero electrical field. The current was measured as a function of temperature, with a standard short circuit method,[5] while keeping a temperature rate of about 1 K/min. The temperature dependence of the corresponding polarisation was obtained by time integration of the electrical current. The sample temperature was measured with accuracy better than 0.1 K.

TSDC data were analysed by using the theoretical model presented in Ref. 6–8. According to this model the temperature dependence of the current density (J_D) during a TSDC experiment can be expressed as

$$J_D(T) = \left(\frac{P_e(T)}{\tau_0}\right) \exp\left(\frac{-E_a}{kT}\right) \times \exp\left[-\left(\frac{1}{q}\tau_0\right)\int_{T_0}^{T} \exp\left(\frac{-E_a}{kT}\right) dT'\right], \quad (1)$$

where P_e is the equilibrium polarisation, T_0 the polarizing temperature, τ_0 the relaxation time at infinite temperatures, E_a the activation energy, q the temperature rate, and k is the Boltzmann constant. The temperature dependence of the relaxation parameters was found by fitting a straightforward expression for $J_D(T)$ presented in Ref. 9, to the experimental data.

The dipole density (N_d) of the sample was obtained by using Langevin equation:

$$P_e = \frac{sN_d p_\mu^2 \kappa F_p}{kT_0} \quad (2)$$

where s is a geometrical factor, which depends on the possible dipolar orientation, p_μ their electric moment (κF_p) the local electric field operating on the dipoles.

3. Results and discussion

Fig. 1 shows the temperature dependence of TSDC and corresponding polarisation P in a $x = 0.0133$ doped STO ceramic, for different fixed magnitudes of the polarising electric field E_p.

The results presented in Fig. 1 give clear evidence for two well detached anomalies: the anomaly (I) that occurs around $T_{m1} \sim 80$ K, and the other one (II), which is observed around $T_{m2} \sim 200$ K. The band structure observed below 50 K reflects most probably the effect of a complex low-temperature, elastic and electrical domain configuration, which was previously put in evidence in pure STO. In the following we shall address our attention just to the results concerning anomaly I and anomaly II.

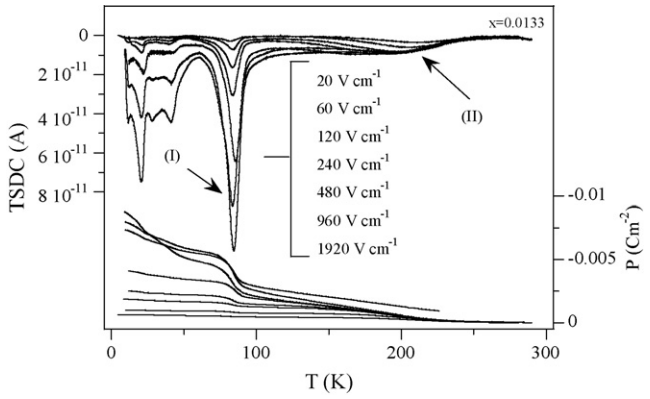

Fig. 1. TSDC and polarization as a function of the temperature at different fixed polarizing field E_p.

By observing Fig. 1, we conclude that anomaly I amplitude increases with increasing electric field E_p, while keeping fixed the temperature corresponding to its maximum amplitude. As can be seen in Fig. 1, anomaly II has completely different characteristics as compared to those of anomaly I. Anomaly II is much wider, and we observe that its amplitude starts to increase with increasing applied field, but then remains constant as the field is further increased. As it is still seen from Fig. 1, the temperature of its maximum amplitude is strongly field-dependent.

The field dependence of some peak characteristics can provide relevant information relatively to the nature of their own relaxation processes. One of the arguments advocated by Vanderschueren and Gasiot,[7] for distinguishing relaxation processes like dipolar relaxation and space-charge relaxation, is based on the field dependence of thermally stimulated depolarization currents. TSDC peaks corresponding to dipole relaxation mechanisms are characterized by field-independent maximum amplitude temperatures, and by maximum amplitudes that are strictly proportional to the field strength. A different pattern is obtained from processes involving space-charge polarization, since generally the build-up, release and equilibrium spatial distribution of the charge are strongly dependent on the applied field.

Fig. 2 shows the field dependence of the maximum amplitude (2a) and of the maximum amplitude temperature (2b) concerning anomaly I and anomaly II.

Accordingly to the theoretical predictions referred to above,[7] we can state that anomaly I is most probably associated with a dipolar type relaxation process, as the linear behaviour of the maximum amplitude (Fig. 2a) and the invariance of the maximum amplitude temperature (Fig. 2b) versus the applied field, clearly confirm.

The corresponding parameters for anomaly II have a marked different field-dependent behaviour, which reveals that anomaly II is most probably due to a space-charge relaxation process. This assumption is strongly supported by results previously reported (see Fig. 5 of Ref. 3), where we can observe just above ~100 K that the field-heating current becomes increasingly larger by increasing the temperature. This behaviour is commonly associated with space charge depolarisation mechanisms, where bulk and surface charge displacements play a major role.

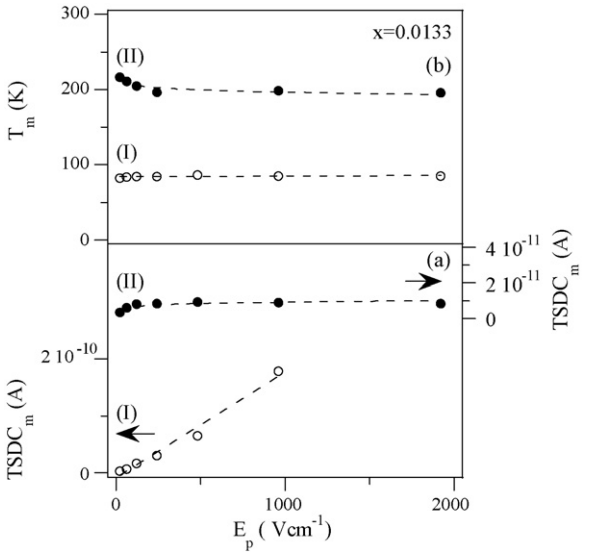

Fig. 2. Field dependence of the maximum amplitude (a) and of maximum amplitude temperature (b) of anomaly I and anomaly II.

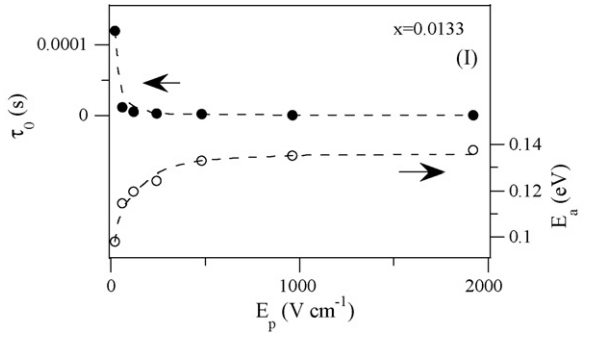

Fig. 3. Field-dependence of the activation energy (E_a) and relaxation time at infinite temperature (τ_0) of anomaly I.

We have used the model of Bucci et al.[6] to calculate the characteristic parameters of the dipolar relaxation process associated with anomaly I. The results are summarized in Fig. 3, where we can observe the activation energy (E_a) and the relaxation time at infinite temperatures (τ_0) concerning anomaly I, as a function of the polarizing electric field E_p.

E_a increases by increasing the field magnitude, and then reaches a constant value of ∼0.14 eV for $E_p > 240\ \mathrm{V\,cm^{-1}}$. For field intensities less than $240\ \mathrm{V\,cm^{-1}}$, the relaxation time at infinite temperature is field-dependent, but as the field increases, a nearly constant value of $\sim 4.7 \times 10^{-7}$ s is attained.

In order to estimate the relaxation time τ at room temperature, we have used the expression of Arrhenius law[7]: $\tau(T)=\tau_0\, e^{Ea/kT}$, and the constant values of E_a and τ_0 referred to above. The calculated value of the relaxation time at room temperature is ∼300 s. This too low value of τ clearly excludes the application of our system to the processing of electret-devices, at room temperature.

By using the Langevin Eq. (2) and high-field values of the relaxation parameters concerning anomaly I, we have estimated the average value of the dipole density (N_d), where typical values for the electric moment (2×10^{-29} cm) and s (1/3) were assumed. A dipole density of $\sim 1 \times 10^{17}$ dipoles/cm^3 was obtained.

In order to get a better knowledge about the type and origin of such dipoles, further experimental work is still needed.

Acknowledgements

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