Temperature hysteresis of the capacitance dependence $C(T)$ for ferroelectric ceramics

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The influence of applied electric field, temperature variation rate, and free charge carrier density on the hysteresis of $C(T)$ dependence is investigated on ferroelectric ceramic capacitors. The measurements were performed on the ceramic capacitors of $Ba_{0.55}Sr_{0.45}TiO_3$ containing 12 wt % of Mg complex additive and the $0.87Pb(Mg_{1/3}Nb_{2/3})O_3-0.13PbTiO_3$ ceramics. The investigations were directed to study of electrocaloric response of ferroelectric ceramics. Various mechanisms of temperature hysteresis are discussed. © *2011 American Vacuum Society.* [DOI: 10.1116/1.3532944]

I. INTRODUCTION

Nowadays the interest to various ferroelectric ceramics is rather high because of a lot promising applications in digital and analog electronics, microwave devices, thermal conversion and energy harvesting systems, temperature, and control apparatus.

The ceramics based on $Ba_xSr_{1-x}TiO_3$ (BST) perovskite compound are the ferroelectric materials most widely applied for various applications and technologies.[1–3] However, the initial $Ba_xSr_{1-x}TiO_3$ solutions have rather high level of dielectric losses ($\tan\delta \sim 10^{-2}$) for applications both in the microwave electronics[3] and the electrocaloric elements in the cooling and energy harvesting systems.[4] The second lack of these materials is their unreliability of the properties after initial influence of electric field that is presented as dielectric hysteresis.[3,5,6] The introduction of Mg and Mn doping[7–10] allows controlling the dielectric characteristics of BST ferroelectric. The best results to decrease the dielectric loss factor are composed $\sim\tan\delta \sim 10^{-3}$ at nonlinear dependence of dielectric permittivity on bias voltage applied to BST ceramics containing Mg.[10–12] However, despite on the reached results[11,12] it is not possible to avoid completely the hysteresis phenomena that play a defining role that used by ceramic BST as the elements revealing electrocaloric effect.[4,13,14]

Therefore, the investigations of temperature and electrical field influence on dielectric characteristics of BST ceramics containing Mg additives present the special meaning and interest. Along with the investigations of BST ceramics the relaxor ferroelectric $[yPb(Mn_{1/3}Nb_{2/3})O_3-(1-y)PbTiO_3]$ (PMN-PT) ceramics are studied as well.

II. EXPERIMENTAL PROCEDURE

Temperature dependences of the capacitance and dielectric losses of ferroelectric ceramics were measured at frequency of 1 MHz. It is known that BST solid solutions have no dispersion of dielectric permittivity (ε) in a range of frequencies $f=10^2-10^{12}$ Hz. We carried out the frequency measurements of dielectric permittivity and quality factor[4] of BST:Mg investigated ceramic samples in a range of $10^3-5\times10^{10}$ Hz that have confirmed an absence of frequency dispersion ε and a little reduction in the quality factor (increase in dielectric losses) with frequency enhancement.

Temperature dependence measurements of the capacitance and dielectric losses were carried out at frequency of 1 MHz using automatic impedance digital bridge device E7-12.[4] The measurement error did not exceed 0.02 pF and the fractional error of dielectric permittivity definition was no more than 0.2%. The amplitude of a measuring field was stabilized at 2.5 V/cm. The leakage current measurements of sample conductivity were carried out by means of electrometer B7-30 in a range of $10^{-13}-10^{-5}$ A. The fractional error of current measurement did not exceed 10%.

Voltage-capacitance characteristics (VCCs), current-voltage characteristics (CVCs), and temperature dependencies $C(T)$ were measured at different values of bias voltage. The installation was capable of performing measurements for values of bias voltage in the range $U=\pm1000$ V. During the measurement process the temperature was automatically controlled. The absolute error of temperature measurements did not exceed 0.05 K in the temperature range of 78–400 K; temperature variation rate was changed in the range of 0.025–0.5 K/s. The temperature cycle of differential capacitance measurements consisted of the cooling process from 290 down to 140 K and further heating process back to 290

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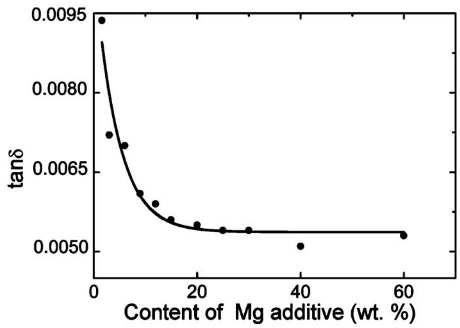

FIG. 1. Dependence of dielectric losses of BST ceramics on the content of Mg additives ($f=10$ GHz).

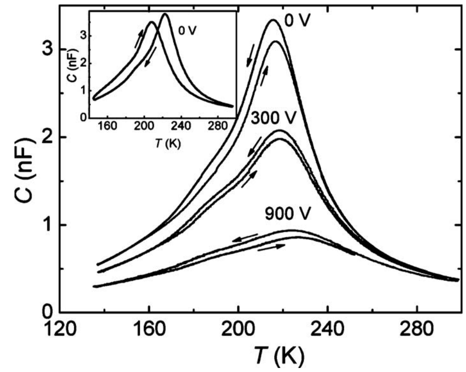

FIG. 2. Capacitance dependences of BST ceramic sample for the several values of bias voltage for the temperature variation rate of 0.025 K/s. The inset shows the same dependence for temperature variation rate of 0.5 K/s.

K. The dependencies of differential capacitance on temperature $C(T)$ were measured for ten values of bias voltage—from 0 to 900 V.

Applicability of the ferroelectric material for technical purposes is determined by the values of dielectric permittivity ε, dielectric losses tan δ, and tunability coefficient (k). The coefficient is the ratio of the brought dielectric permittivity at zero electrical field to ε value at maximal intensity of electrical field. The Mg additives to BST compound decrease dielectric losses, which is important for microwave applications. The investigated samples of $Ba_xSr_{1-x}TiO_3$ $(x=0.55)$ contained 12 wt % of Mg additive. Figure 1 shows the dependence of tan δ on Mg-containing additive. It is visible that the selected BST compound has dielectric loss parameter tan $\delta=(5.5-6.0)\times 10^{-3}$ that is much lower compared with original BST compound. Earlier[4] we have shown that the magnesium additive decrease dielectric permittivity, at Mg concentration of 10–25 wt % dielectric permittivity, is standing at the level $\varepsilon=500-600$ and the tunability coefficient is sufficiently high that is important for microwave tunable devices as well as for thermal conversion processes. Thus, the indicated Mg additive concentration corresponds to the required working parameters of the capacitor structures $\varepsilon \geq 500$; tan $\delta \leq 10^{-2}$ and in microwave region $k \geq 1.2$ at the fields $E_{max}=4-5$ V/μm.

The composition and weight content of Mg additives, the synthesis temperature (1350–1540 °C), have been chosen to provide a weak interaction between two main phases in ferroelectric ceramic. The porosity of the ceramic samples did not exceed 5%. The polished ceramic samples having disk shape with thickness of 0.5 mm and diameter of 5–6 mm were covered by gold electrodes using magnetron sputtering. The x-ray diffraction analysis has shown that the samples contained perovskite cubic phase and the second Mg_2TiO_4 spinel phase. It was found that basic BST perovskite phase contained magnesium atoms (up to 5 at. %) that change the parameter of a crystal lattice.

The $0.87Pb(Mg_{1/3}Nb_{1/3})O_3-0.13PbTiO_3$ (PMN-PT) ceramic samples were sintered using the technology described earlier[15] in the Laboratory of Microelectronics and Material Physics of the University of Oulu. The ceramics thickness was 1–1.4 mm and the electrode diameter was 7.6 mm. The x-ray diffraction analysis has showed a presence of single perovskite phase.

III. RESULTS AND DISCUSSION

Figure 2 shows the $C(T)$ dependencies for BST sample in the absence of electrical field and two values of bias voltage from the indicated region. The dielectric permittivity for the chosen samples had the following maximal values: $\varepsilon_m(0)=6700$, $\varepsilon_m(300\text{ V})=4150$, and $\varepsilon_m(900\text{ V})=1900$. An increase in bias voltage leads to capacitance value decrease; the temperature of C_m is displaced to the right on temperature axis. Such temperature displacement of $C(E,T)$ dependencies is usual for the ferroelectric materials with wide and spread phase transition of the second order.[1,2] However, on dependences of temperature hysteresis both in ferroelectric and paraelectric phase was observed.

As a temperature hysteresis we understand not only a displacement of temperature maximum of the sample capacitance at cooling (T_{m1}) and heating $(T_{m2})-(\Delta T_m=|T_{m1}-T_{m2}|)$ but also a relative reduction in the maximum values of capacitance at cooling (C_{m1}) and heating $(C_{m2})-(\Delta C_m/C_{m1})=(C_{m1}-C_{m2})/C_{m1}$.

The temperature of capacitance hysteresis of the investigated BST:Mg samples has showed unusual behavior of perovskite material with influence of external electric field. The nonlinearity reduction in most part of perovskite materials shows that hysteresis phenomena become less appreciable; i.e., the hysteresis is decreased at influence of electric field $E \sim 10^5$ V/m.[1,3] In our case in the beginning the temperature hysteresis of the ceramic capacitance was decreased at voltage influence, and, from the voltage of ~500 V that corresponds to $E \sim 10^5$ V/m, the hysteresis was increased (see Fig. 3).

It is necessary to note that the temperature hysteresis depends on a speed of cooling and heating of the samples. So the temperature hysteresis in the absence of voltage at speed of temperature change ~0.025 K/s has made $\Delta T_m=2$ K and the maximum of the capacitance temperature dependence at heating of the samples was displaced to higher tem-

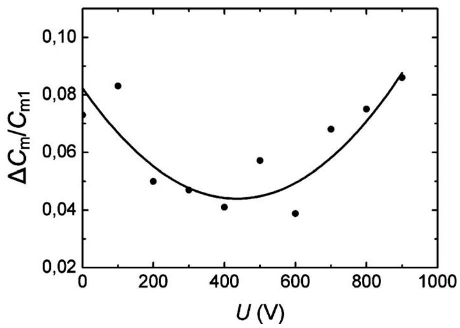

FIG. 3. Capacitance temperature hysteresis dependence on bias voltage for BST:Mg sample.

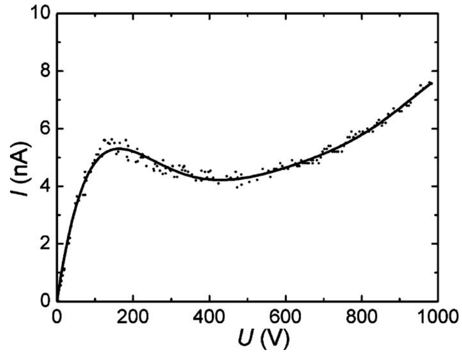

FIG. 5. Current-voltage characteristics of BST:Mg sample.

perature. The temperature hysteresis for the same sample at speed of temperature change ~ 0.5 K/s is increased to $\Delta T_m = 27$ K (inset of Fig. 2). Thus, a displacement direction to a maximum of temperature dependence T_{m2} is changed to opposite; the temperature hysteresis of the capacitance $\Delta C_m / C_{m1}$ is also increased. The heating mode has appeared more sensitive to a speed of temperature change than a cooling mode. It has been established that at speed of change in temperature $V \sim 0.05$ K/s the temperature hysteresis ceases to depend on a speed of cooling of the samples.[16]

More detailed research of temperature hysteresis in BST:Mg structures has also been measured and voltage-capacitance characteristics were obtained at 300 K (Fig. 4). The ambiguity of the capacitance on VCC characteristics was the units in percent and it was observed at every value of voltage. Such view VCC corresponds to the hysteresis loops of large width that is usual behavior for relaxor ferroelectrics. In ferroelectric phase the hysteresis reaches tens of percent. At $T=300$ K and zero bias voltage the permittivity value $\varepsilon(0)=830$; the loss tangent at $U=0$ was $\tan \delta \sim 10^{-4}$. An increase in $\tan \delta$ upon increasing in bias voltage was observed for most part of ferroelectric samples.

The conductivity of the samples and the existence of free charge carriers can render a significant influence on the hysteresis phenomenon;[13] therefore, the measurements of current-voltage characteristics are helpful. Typical current-voltage characteristics of BST ferroelectric ceramics with Mg additives are presented in Fig. 5. Three regions are clearly observed on the plot: at low voltage the dependence corresponds to Ohm's law. In the following region, where current decrease is observed, a voltage increase is revealed, so some kind of negative differential resistance is identified. At higher voltage (more than 500 V) exponential current growth is exhibited. Estimation of sample resistance for the Ohm-related region results with $R \sim 6 \times 10^{10}$ Ω; the specific sample resistivity was found to be $(3.2 \pm 0.4) \times 10^{-10}$ Ω^{-1} m^{-1}. Earlier we have showed in Ref. 12 that the presence of negative differential resistance and exponential growth on CVC is currently leading to high value of hysteresis value.

An observation of the same characteristics for PMN-PT ceramics gives the temperature dependencies of the capacitance at zero and two other values of bias voltage, as it is shown in Fig. 6. An increase in bias voltage leads to a lowering of $C(T)$ curves and temperature of the capacitance maximum is shifted insignificantly ($\Delta T_m = \pm 1$ K). Dielectric hysteresis on $C(U)$ dependences is not observed, as it is shown in Fig. 7. Ohm's law region and negative differential resistance regions are distinguished clearly, but exponential growth at higher voltages is not found (Fig. 8). The following values of dielectric characteristics for PMN-PT samples were calculated by the experimental results: $\varepsilon_m(0)=18\,000$, $\varepsilon_m(450)=16\,000$, and $\varepsilon_m(950)=12\,000$. At $T=300$ K the dielectric permittivity was 8200; $\tan \delta \sim 10^{-1}$ and $R=2 \times 10^{-10}$ Ω.

The investigations of voltage-capacitance and current-voltage characteristics and the dependencies $C(T)$ have shown that the phenomenon of temperature hysteresis exhib-

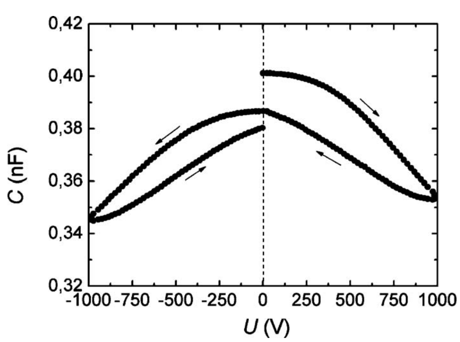

FIG. 4. Capacitance-voltage characteristics of BST:Mg sample.

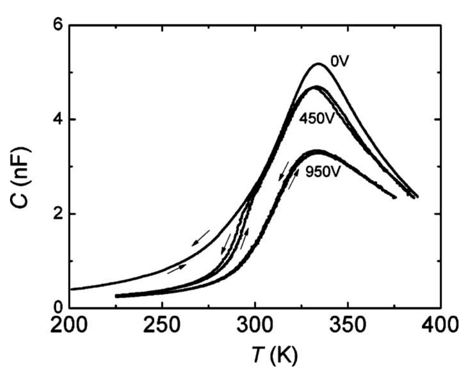

FIG. 6. Capacitance dependences of PMN-PT sample for the several values of bias voltage.

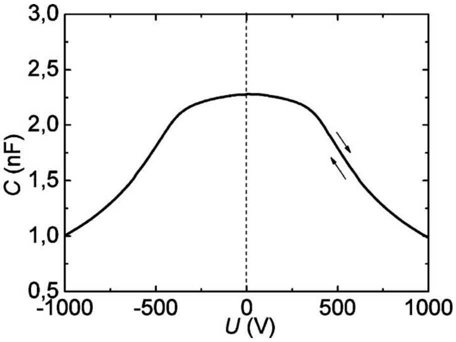

FIG. 7. Capacitance-voltage characteristics of PMN-PT ceramic sample.

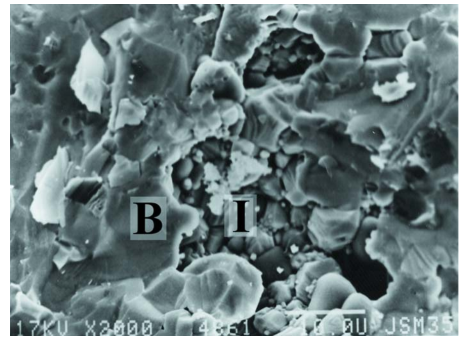

FIG. 9. (Color online) Microscopy pattern of ferroelectric BST:Mg ceramic sample.

ited in BST ceramic with Mg-content additives could be explained by means of high level of inhomogeneities, which are contained in the ceramic samples in comparison to significantly higher homogeneous single-phase PMN-PT ceramics. Scanning electron microscope images of BST ferroelectric ceramics containing Mg additives were obtained using the JSM-6460LV JEOL microscope. Some images are presented in Fig. 9. The BST ceramics contain the crystallite and noncrystalline inclusions of various dimensions $(1,\ldots,10\ \mu\text{m})$. Apparently, the ceramics contain at least two phases: main perovskite phase and intergranular contaminations (shown as B and I in Fig. 9). Intergranular medium also contains small crystallites of $0.3,\ldots,5\ \mu$m.

The x-ray microstructural analysis has shown that basic BST phase is composed of two perovskite phases with lattice parameters of 3.935–3.941 and 3.954–3.966 Å. Pure BST ceramic of the chosen composition has lattice parameter of 3.9513 Å. The first phase, which has lower than pure BST ceramic lattice parameter, is related to the phase with lower content of Ba ions. It is known[3,17] that in some solid solutions of BST the lattice parameter decreases linearly from 4.040 Å (at $x=1$) to 3.905 (at $x=0$). Slight increase in lattice parameter of the second phase can be associated with partial substitution of Ti (Ref. 4) in BST (Ref. 18) lattice with Mg (Ref. 2) or with increase in Ba content up to $x\sim0.6$ (reference value for $x=0.6$ equals to 3.965 Å). Thus, composite BST ceramics with magnesium additives have heterophase structure, composed of basic BST phase solid solution and phase with magnesium content. Some ceramic areas containing 1%–30% of the crystalline magnesium containing phase render considerable influence on highly defective phase of ferroelectric ceramics.

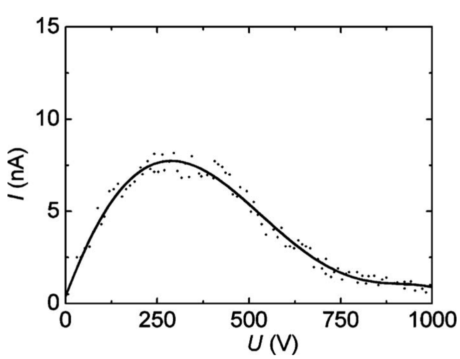

FIG. 8. Current-voltage characteristics of PMN-PT ceramic sample.

The shown microinhomogeneities lead to temperature hysteresis, and it could be connected with the following purposes:

(1) an enhancement of mechanical strains and deformations and following relaxation of the mechanical stress in the process of sequential cooling and heating cycles;
(2) an appearance of the defect internal electrical fields at the inhomogenity borders that decrease dielectric permittivity at the region of the field presence; and
(3) screening of the free carriers of the polarized regions of the crystals.

The appearance and relaxation of the mechanical strains, i.e., the existence of elastic hysteresis mechanism, are supported by the fact that temperature hysteresis value depends on sample cooling and heating rate.

The existence of internal electric fields of the defects in perovskite ferroelectrics is supported by the dependence of capacitance temperature hysteresis on applied field (Fig. 3), and it relates to the existence of dielectric hysteresis at all values of bias voltage (Fig. 4). Dielectric hysteresis of capacitance was discussed earlier,[7,19,20] and the estimation of internal electric field values was given, $E\sim5\times10^5-10^6$ V/m.

Apparent influence on dielectric[4] and consequently temperature hysteresis is exerted by conductivity of samples (Fig. 3). Temperature hysteresis of the ferroelectric capacitance is decreased (Fig. 5) in the range, where current decreases—the range of negative differential resistance—and it increases as voltage values, which corresponds to exponential growth of current ($E\sim2\times10^5$ V/m). Free charge carriers, screening polarized areas in the single crystals, do not take part in further processes of repolarization. This is the third cause of temperature hysteresis. This mechanism should have most influence in ferroelectric phase. The second and third causes of temperature hysteresis reveal the mutual influence to each other.

IV. CONCLUSIONS

We have obtained the temperature hysteresis of the capacitance based on the ceramics $Ba_{0.55}Sr_{0.45}TiO_3$ containing 12 wt % of Mg complex additive. The correlation is between temperature hysteresis and thermocycling regime of the measurement process.

The increase in thermocycling process leads to the growth of temperature hysteresis. The high limit rate of temperature variation was 0.05 K/s. Exponential growth of the current at voltage intensity of 2×10^5 V/m caused an essential influence on the temperature hysteresis.

The phenomenon of temperature hysteresis is connected with high level of the microinhomogeneities with Mg-containing doping.

Similar temperature hysteresis on single-phase PMN-PT ceramics was not observed. The dependence of temperature hysteresis on the rate of thermocycling was not established.

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