The Influence "Heating-Cooling" Process Rate on Temperature Hysteresis of Ferroelectric Capasitor Structures

A.I .Dedyk[1], Yu.V. Pavlova[1], A.A. Semenov[1],
A. Es`kov[1], P.Yu. Beliavskiy[1] I.L. Mylnikov[1]
[1]St. Petersburg Electrotechnical University,
'LETI'
St. Petersburg, Russia
Email: dedyk_ai@mail.ru

O.V. Pakhomov[2], A.S. Starkov[2], I.A. Starkov[3]
[2] National Research University of Information
Technologies, Mechanics and Optics,
St. Petersburg, Russia
[3]Institute for Microelectronics, TU Wien
Wien, Austria

Abstract—**We have investigated the influence of the time mode of cooling, electric field and electroconductivity on the thermal hysteresis in capacitor structures based on ceramics $Ba_{0.55}Sr_{0.45}TiO_3$ with 12 wt.% magnesium-containing supplements. Different mechanisms of the appearance of thermal hysteresis are discussed.**

Keywords-componen; ferroelectric ceramics; thermal hysteresis; pyroelectric current.

I. INTRODUCTION

Ceramic based on barium strontium titanate (BST) is among the most widely used in engineering ferroelectrics with perovskite structure [1-3]. To reduce losses (tanδ) in BST structures commonly used maintenance of impurities of Mg and Mn [4,5]. The best results for reducing tanδ (~ 10^{-3}) while maintaining nonlinear dependence of the dielectric permittivity ε on the electric field strength (E) were obtained for Mg doping [6]. However, despite the reached results fails to reduce the losses caused by changes in temperature under the influence of an electric field (electrocaloric effect) [7]. Therefore, of special importance is research on the BST ceramics dielectric properties with the consistent impact of the electric field and temperature.

II. EXPERIMENTAL PROCEDURE

Specimen preparation $Ba_xSr_{1-x}TiO_3$ (x = 0.4 – 0.7), as well as specimen $Ba_{0.55}Sr_{0.45}TiO_3$ with 12wt.% (BSTM) magnesium-containing supplements was conducted on the developed ceramic technology [4]. Sintering temperature of ceramics was about 1350 – 1540^0C. The data of X-ray analysis demonstrated that the samples had the perovskite structure with cubic symmetry, but a second phase was observed in the form of Mg_2TiO_4. The gold electrodes were deposited by magnetron sputtering in an Ar atmosphere on the polished ceramic samples in form of disks with the thickness of 0.5mm and diameter of (5-6)mm.

Measurements of the temperature dependence of capacitance and dielectric losses were performed at a frequency of 1MHz using a digital bridge E7-12. The sample temperature was varied in the range of (400–78)K, the temperature change rate was varied in the range of (0.025 – 0.5)K/s.

Measurements of capacitance-voltage characteristics of the samples at 300K showed the presence of hysteresis at the level of a few percent for all values of voltage. Dielectric permittivity at 300K was ε(0) = 830, dielectric loss tangent at $U = 0$ was tgδ ~10^{-4}.

Thermal cycle of measurements of differential capacitance consisted in the cooling of the samples from 290K to 140K and in heated again to 290K. The dependencies of temperature differential capacitance $C(T)$ were measured for ten values of the bias voltage from 0 to 900V at the rate of change of temperature 0.025K/s. The maximum values of the dielectric permittivity for these samples were $\varepsilon_m(0)$ = 6700, $\varepsilon_m(300)$ = 4150, $\varepsilon_m(900)$ = 1900. The graph in Fig. 1 shows the dependence of $C(T)$ for BST sample in the absence of electric field and for two values of voltage from the specified range. Capacitance values decreased with increasing bias voltage (Fig.1a), and the temperature of maximum shifted to the right on the temperature axis. Thermal hysteresis is observed both in the ferrophase and paraphase.

By the temperature hysteresis we mean not only the temperature shift of the maximum capacity on cooling (T_{m1}) and on heating (T_{m2}) - ($\Delta T_m = |T_{m1} - T_{m2}|$), but also the relative decrease of the maximum capacity on cooling (C_{m1}) and on heating (C_{m2}) - ($\Delta C_m/C_{m1}) = (C_{m1} - C_{m2}$) / C_{m1} (see, Fig.2).

It should be noted that the temperature hysteresis is dependent on the rate of cooling and heating of the samples. Thus, in the absence of offset voltage at a rate of temperature change of 0.025K/s the temperature hysteresis was ΔT_m = 2K and the maximum of the temperature dependence of the capacity on heating of the samples shifted to higher temperatures. Moreover, the temperature hysteresis for the same sample at a rate of temperature change 0.5K/s increased to ΔT_m = 27K (Fig.1b), and the direction of displacement of the maximum temperature dependence T_{m2} changed to the opposite, temperature hysteresis of the capacitance $\Delta C_m/C_{m1}$ also increased.
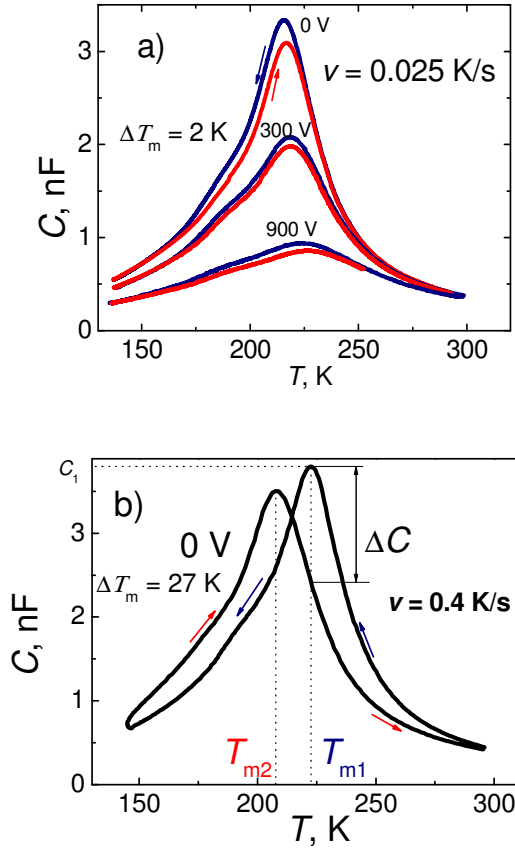
Fig. 1. Capacitance dependences of $Ba_{0.55}Sr_{0.45}TiO_3$ ceramics sample with 12wt.% of Mg for the several values of bias voltage for the temperature variation rate.

It was established that at the rate of the temperature changing of ~0.05K/s the temperature hysteresis ceases to depend on the cooling rate of samples. In experimental studies, it was found that the temperature hysteresis parameters obtained in the heating mode, were more sensitive to the rate of the temperature changing than the same hysteresis parameters obtained in the cooling mode. The experimental dependence of the ΔT_m on the rate of temperature changing in heating mode for samples of different composition is presented in Fig.2.

Studies of the BSM ceramics by scanning electronic microscope JSM-6460LV JEOL shows that ceramics has crystallites and granules of different sizes (from 1μm to 10μm) and contains at least two phases – the main perovskite phase and the intergranular layers. It is found that in the intergranular space also crystallites of different sizes (from 0.3μm to 5μm) and composition are contained. Composite BST ceramics with the addition of magnesium has a heterophase structure consisting of the main phases, a solid solution of BST and phases containing magnesium, which has a significant impact on reducing the dielectric losses.

For comparison, we present all the mentioned above characteristics of the homogeneous ceramic PMN-PT.
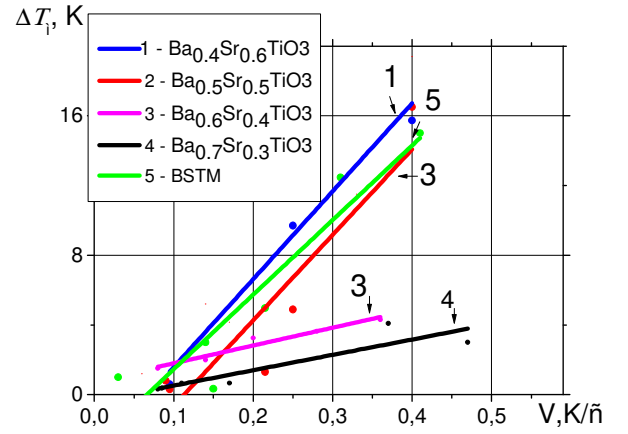

Fig.2. Experimental dependence of the ΔT_m on the rate of temperature changing for samples of different composition

III. RESULTS AND DISCUSSION

In our opinion the observed phenomenon of the temperature hysteresis in the structures based on the of BST ceramics with the addition of magnesium is associated with a high microinhomogeneities of samples in contrast to much more homogeneous and single-phase samples of PMN-PT ceramics. The presence of microinhomogeneities of this compound may leads to several causes for temperature hysteresis: (1) the formation of mechanical stress and relief from mechanical stress in successive cycles of heating and cooling of samples; (2) the appearance of internal electric fields of defects at the boundaries of the inhomogeneities that reduce the dielectric permittivity in the existence of fields.

For processing of the experimental results, we used a procedure which allows for the combination of temperature and field dependences of the capacity to calculate the temperature and field dependence of the polarization of the investigated material. We used the expansion of the Landau-Ginzburg theory for the electric field in powers of polarization. In the other hand, for the parallel-plate capacitor the surface density of free charges on the plates is equal to the vector of electric induction D inside the ferroelectric. Expression for the differential capacitance c_d can be written as

$$c_d = \left(\frac{\partial q}{\partial u}\right) = S\left(\frac{\partial D}{\partial u}\right)_T = \varepsilon_0 S\left(\frac{\partial E}{\partial u}\right)_T + S\left(\frac{\partial P}{\partial u}\right)_T. \quad (1)$$

Further, we obtain an equation for the polarization by integrating of the second term of the right side of the previous formula by the voltage (at constant temperature):

$$P = S\int c_d d\tilde{u} + \frac{\varepsilon_0}{d}u + \text{const}. \quad (2)$$

Thus, the total polarization P is the sum of the spontaneous polarization ($const = P_s = 0$ in the paraelectric phase), not depending on the voltage, and induced polarization, which is at zero voltage must be zero.
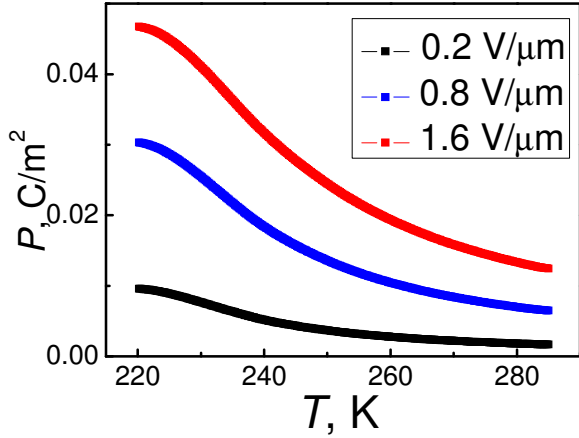
Fig. 3. Temperature dependence of the polarization.

Fig. 5. The current-voltage characteristic for BST sample with addition of magnesium.

After smoothing and regularization of the grid of experimental values $c_d(u, T)$ were calculated values of the $P_{ij}=P(u_i, T_j)$ by numerical integration of the last expression. Where u_i and T_j are the experimental values of voltage and temperature. The temperature dependence of the polarization for different constant field strength is shown in Fig.3.

The pyroelectric coefficient p for this sample in the paraelectric phase was calculated from the obtained dependences $P(T,E)$.

$$p = \left(\frac{dP}{dT}\right)_E, \qquad (3)$$

whose values were in the range $(2-8)\cdot 10^{-4} C/(m^2\ K)$. Pyroelectric current j_{pir} with a known rate of temperature changing $v= dT/dt$ can be calculated by the formula

$$j_{\text{pir}} = pv = p\left(\frac{dT}{dt}\right). \qquad (4)$$

The value of pyro current for different temperature was calculated for the rate of temperature changing equal to 0.4C/s. The obtained data are shown in Fig.4.
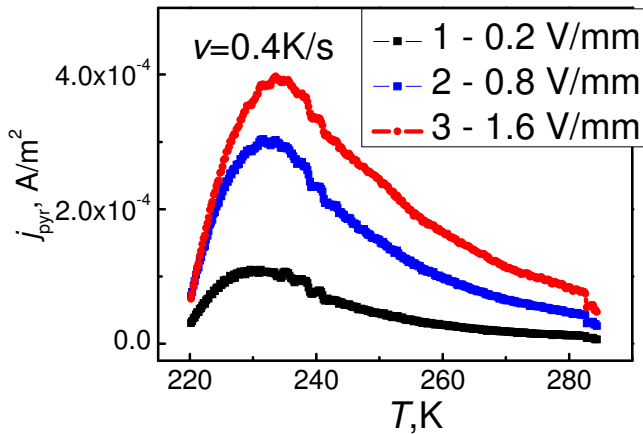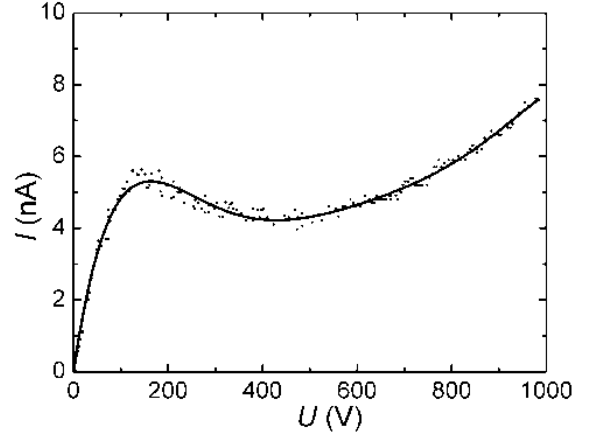

Fig. 4. Temperature dependence of the pyro current.

Evaluation of samples resistance carried out for ohmic section of current-voltage characteristic gives the value of resistance R ~ 6 10^{10} Ωm. , The conductivity of the samples was $(3.2 \pm 0.4)\ 10^{-10}$ $Ωm^{-1}m^{-1}$. We have previously shown [6] that the presence of negative differential resistance and the exponential increase of the current on characteristic always lead to larger values of the dielectric hysteresis.

Comparison of the dependences presented in Fig.4 and Fig.5 shows that pyroelectrical current and conduction current have the same order of magnitude. The experimental value of the samples conductivity allows to estimate the electric field, which created by pyro current on the ferroelectric structure electrodes $E_{\text{pyr}} = (10^5 - 2*10^6)$V/m. According to obtained data can be concluded that in the absence of an external electric field temperature hysteresis is caused by pyroelectric effect. Typical current-voltage characteristic of the BST sample with addition of magnesium is shown in Fig. 5.

IV. CONCLUSIONS

Research has shown that the capacity of the structures based on BST and BSTM ceramics depends on heating (cooling) rate. The effect is caused by the dependence of the temperature hysteresis from the rate of temperature changing. Moreover, with increasing rate of the temperature change the temperature hysteresis values increase as well. By reducing the cooling rate to a value of ~ 0.05K/s the temperature hysteresis ceases to depend on the cooling rate of the samples. In the absence of external electric field, presence of the temperature hysteresis is due to the pyroelectric effect.

From performed measurements it also follows that the phenomenon of temperature hysteresis is due to a high degree of microinhomogeneities of BST ceramic samples with magnesium additive. For substantially more homogeneous and single phase the samples PMN-PT ceramic temperature hysteresis phenomenon was not observed.

REFERENCES

[1] A. Smolenskiy, V.A. Bokov, V.A. Isupov, N.N. Krainik, R.E. Pasinkov, N.S. Shur, Ferroelectrics and antiferroelectrics. Nauka, L., 1971.

[2] M. Lines & A. Glass Principles and applications of ferroelectrics and related materials.. Clarendon Press, Oxford, 1979.

[3] Ferroelectrics at microwaves (Segnetoelektriki v tehnike SVCH in Rus), edited by O.G. Vendik, Sov. Radio, Moskov, 1979.

[4] E.A. Nenasheva, A.D. Kanareikin, A.I. Dedyk, Y.V. Pavlova "Electrically controlled BST-Mg ceramic components for applications in accelerator technology", Phys. of the.Sol. State (ФТТ), vol 51, № 8, pp. 1554—1560, 2009.

[5] S. F. Karmanenko, A. I. Dedyk, N. N. Isakov, A. S. Gordeichuk, A. A. Semenov, L. T. Ter-Martirosyan and J. Hagberg, "Study of the effect of manganese impurities on dielectric characteristics of BSTO films", Tech. Phys., vol.46, № 4, pp. 498-502, 2001.

[6] Dedyk A.I, Nenasheva E.A., Kanareykin A.D., Pavlova Ju.V.et all, " Journal of Electroceramics, , Vol. 17, № (2-4), pp. 433-437, 2006.

[7] Starkov, A.S., and Pakhomov, O.V. "Influence of the dynamic polarization of a ferroelectric material on the magnitude of its electrocaloric response", Tech. Phys. Lett., vol 36, № 3, pp. 1-3, 2010.