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Temperature response features of ferroelectric ceramics in electrocaloric effect study

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Temperature response of a material to an external electric field is the main method for electrocaloric effect study in ferroelectrics. In this work, for $0.65PbFe_{2/3}W_{1/3}O_3-0.35PbTiO_3$ solid solution as a model object, it is shown that with an increase in the electric field strength, current filamentation effect can occur. It leads to formation of local regions of increased conductivity in the sample. The associated thermal effect have short characteristic times, due to the small volume of the filament. They are comparable to the times of the electrocaloric response of the material, and can lead to significant errors in the detection of the electrocaloric effect.

Keywords: electrocaloric effect, temperature response, ferroelectric ceramics, current filamentation effect.

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Recent years have been marked by a growing interest in the study of the electrocaloric effect (ECE) in ferroelectrics, which is considered as one of the new approaches for the development of efficient energy storage and solid-state cooling devices [1–4]. The analysis of the dynamics of the electrocaloric response of a sample in a wide range of changes in amplitudes, shapes and durations of the electric field is of significant fundamental and applied interest, as it allows us to obtain new information about polarization processes in various materials and assess the prospects for their practical use. Increasing the metrological reliability of measuring the quantitative characteristics of the ECE, namely the electrocaloric temperature difference (δT) and the coefficient $e = \delta T/\Delta E$ (here ΔE — range of electric field variation), remains an urgent experimental task along with the determination of the breakdown voltage of the electric field E_{bd}. The value of the really achievable value of ΔE, which does not lead to a breakdown, may become the main factor limiting the possibility of practical application of the ECE due to the ratio $\delta T \sim \Delta E \leqslant E_{bd}$. However, in the published works on the study of the ECE, the issues of changing the conductivity of materials when a strong external electric field is applied and the associated thermal effects that limits the actual achievable value of δT are given undeservedly little attention. This problem is inextricably linked with the general task of studying materials under the influence of electric fields, the solution of which largely determines the prospects for the creation and development of an electronic components based on semiconductor and dielectric materials [5–10]. In addition to the development of the theory of irreversible „volumetric" thermal breakdown caused by the need to predict the behavior of insulating materials in strong electric fields [5], the study of „local" phenomena associated with the presence of various types of defects on the surface and in the volume of semiconductors, leading to local current density increasing and, accordingly, the local heating of the samples when exposed to an electric field microplasma breakdown [6], the effect of „current lacing" [7,8]. These studies, which peaked in the 60−80-ies of the last century and was associated with the rapid development of the semiconductor element base, have not lost their relevance. Currently, the increased interest in these studies is associated with the active search for new efficient materials for solar energy [9], for electromechanical transducers based on ferroelectric polymers, single crystals and ceramics of various compositions, the advantages of which are ease of manufacture, strength, stability, the possibility of obtaining complex configurations [10].

A phenomenon similar to microplasma breakdown in semiconductors is described by us in the work [11], where by the example of studying a batch of samples of multilayer ceramic samples (relaxor) $0.55Pb-Mg_{1/3}Nb_{2/3}O_3-0.45PbSc_{1/2}Nb_{1/2}O_3$ it was shown that for values of $E \sim (1/2)E_{bd}$ (E_{bd} — the expected value breakdown field) against the background of the electrocaloric response of samples, sudden temperature spikes occure. The resulting effect is well described in the framework of the partial discharge model in dielectrics [12], distorts the dynamics of the temperature response of the sample and can lead to an overestimation of experimental values δT.

In this paper we present the results of the study of a model object — ferroelectric solid solution $0.65PbFe_{2/3}W_{1/3}O_3-0.35\ PbTiO_3$ (PFW−PT) located near the morphotropic phase boundary (MPhB) [13]. The presence of MPhB in solid solutions is a characteristic feature, as well as an essential requirement for obtaining high electromechanical and dielectric characteristics and, as experimental data show, promising electrocaloric properties of [14].

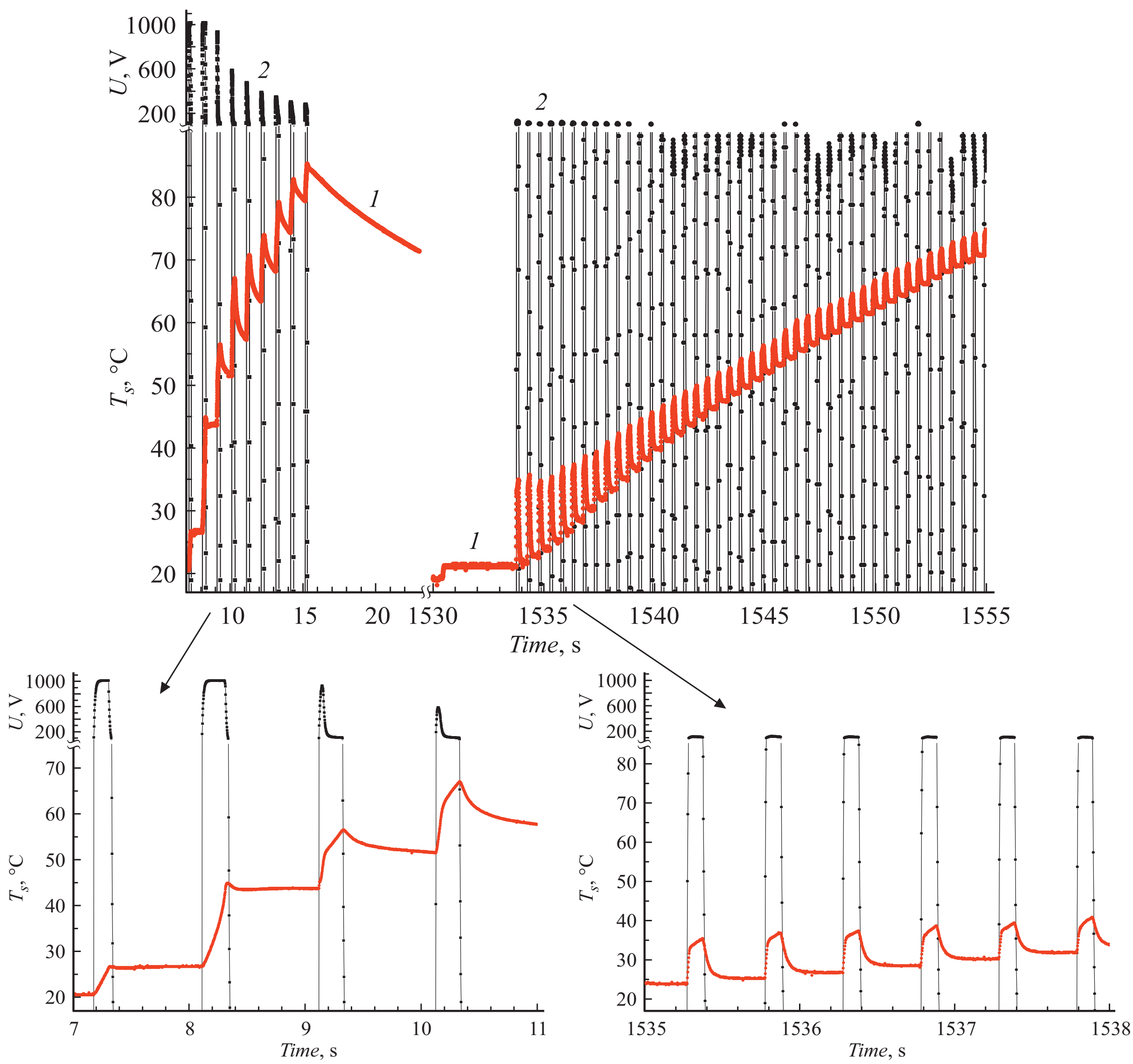

Figure 1. Experimental plots of synchronous monitoring of temperature response T_s (curve *1*) and voltage U (curve *2*) on a sample of ferroelectric ceramics of $0.65PbFe_{2/3}W_{1/3}O_3-0.35PbTiO_3$ solid solution (diameter 10 mm, thickness 0.92 mm) when a sequence of rectangular voltage pulses with an amplitude of $U = 1000$ V is applied to it. In the lower part of the figure, plots are shown reflecting the thermal effects of different nature in the sample caused by the volumetric conductivity of the sample and the effect of current lacing.

In these experiments, samples of ferroelectric ceramics PFW–PT were used in the form of tablets with a thickness of $d \sim 0.3-1$ mm, with a diameter of $D \sim 10$ mm with burnt silver electrodes. The study of the temperature response of the sample to the application of an electric field (direct measurement method in the study of the ECE) was carried out using a multichannel experimental setup, methods and algorithms for direct measurements of pyro- and electrocaloric effects published in [15].

Fig. 1 shows the results of monitoring the temperature response of a sample with a thickness of $d = 0.92$ mm when a sequence of rectangular voltage pulses with a period of 400 ms and a duration of 100–200 ms is applied to it with an amplitude of $U = 1000$ V ($E \sim 10$ kV/cm), installed at the output of the TREK609E-6 high-voltage voltage source. The value of $E \ll E_{bd} \approx 30$ kV/cm, where E_{bd} — the expected value of the breakdown strength for this sample (permittivity $\varepsilon \sim 10\,000$ in the room temperature range [13]) calculated according to [16]. Simultaneously with non-contact control of the sample surface temperature (curve *1* in Fig. 1), voltage control (curve *2* in Fig. 1) was carried out directly on the sample with a time resolution of 2 ms. It can be seen from Fig. 1 that during the first pulses of the field (up to 9 s), linear heating of the sample is observed, typical for Joule heating „by a volumetric“ conduction current inherent in this sample with known values of density (ρ), heat capacity (c) and specific conductivity ($\sigma(T)$). Note that in the temperature range of 20–110°C, the dependence of $\sigma(T)$ is exponential [17]. After the 9th second of the experiment, a change the temperature response is observed, accompanied by a voltage drop on the sample due to the limiting value of the current of the source used. The section of the temperature response after switching off the field pulses (after the 15th second of the experiment, Fig. 1) allows us to determine the thermal relaxation time constant of the sample $\tau_0 = 2H/\rho c d \approx 30\,\mathrm{s}$ taking into account the actual heat exchange conditions determined by the heat exchange coefficient (H) under the conditions of a specific experiment (see methodology in [15]). With the subsequent supply of high voltage pulses ($t > 1530\,\mathrm{s}$, Fig. 1), the temperature response of the sample has the form of reversible thermal effects with relaxation times τ_{on} (on), τ_{off} (off) $\ll \tau_0$, while the amplitude of the voltage pulses does not correspond to the set value of $U = 1000\,\mathrm{V}$ (Fig. 1), but is limited to the level of $U = 200\,\mathrm{V}$. Such dynamics of the temperature response of the PFW$-$PT sample is in good agreement with the model of reversible electron-thermal breakdown developed earlier for semiconductor materials and caused by the effect of current lacing [7,8]. As follows from [8], the characteristic times of such thermal processes are $\tau_{on} \sim 10^{-6}-10^{-10}\,\mathrm{s}$ for semiconductor structures with a thickness of $d \sim 1\,\mu\mathrm{m}$ are associated with the small volume of the cord, and the slight tightening of $\tau_{off} > \tau_{on}$ is due to the overlap of two thermal processes: fast switching off of the current cord and slow cooling of the heated sample volume as a whole.

The results presented in Fig. 2 allow us to calculate the quantitative parameters of the recorded thermal effect in the sample under study: time constants $\tau_{on} = 15\,\mathrm{ms}$, $\tau_{off} = 40\,\mathrm{ms}$ and amplitude $dT = 10^\circ\mathrm{C}$ at a sample temperature near room temperature. The value of $\tau_{on} = 15\,\mathrm{ms}$ agrees well with the characteristic electrocaloric response times of samples of similar size of ferroelectric ceramics of various compositions obtained experimentally in [15]. At the same time, the recorded amplitude of the temperature response $dT = 10^\circ\mathrm{C}$ significantly exceeds the typical values of the electrocaloric temperature difference $\delta T \sim 1-2^\circ\mathrm{C}$, achieved at the moment in bulk ceramic samples of various compositions [1–4].

In this paper, for the first time, the reversible thermal effect observed and experimentally registered for a ferroelectric solid solution of was $0.65\mathrm{PbFe_{2/3}W_{1/3}O_3}-0.35\mathrm{PbTiO_3}$, located on the MPhD. It can be explained within the framework of the model of reversible electron-thermal breakdown associated with the effect of current lacing. The obtained values of the heating and cooling time constants are comparable to the characteristic times of the electrocaloric response of ceramic materials.

The revealed features of the temperature response of the material in external electric fields are of particular importance in the ECE studies requiring the application of an alternating electric field with the maximum possible amplitude that does not lead to sample breakdowns. The uncontrolled occurrence of „anomalies“ of the temperature response of a sample of ferroelectric ceramics under of an external electric field associated with local changes in its conductivity can lead to significant errors when registering the ECE in new materials and an overestimation of δT in numerical simulation of the ECE without taking into account the actual value of the permissible change in the operating voltage. Such errors can be avoided only by simultaneously monitoring the dynamics of temperature and voltage changes on the test sample with high time resolution, as well as heat exchange conditions that determine the true value of the thermal relaxation time constant of the sample as a whole.

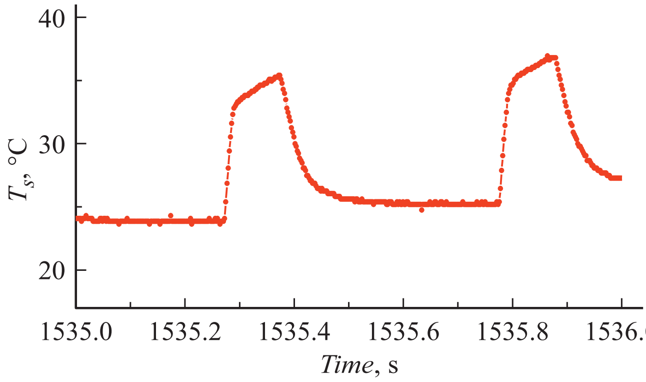

Figure 2. Temperature response of a sample of ferroelectric ceramics of a $0.65\mathrm{PbFe_{2/3}W_{1/3}O_3}-0.35\mathrm{PbTiO_3}$ solid solution, demonstrating a reversible electron-thermal effect in the current lacing mode.

This paper demonstrates the relevance of a comprehensive study of the fundamentals and mechanisms of volumetric and local changes in the conductivity of ferroelectric materials, which is of significant fundamental and practical interest, that stimulates further research.

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Conflict of interest

The authors declare that they have no conflict of interest.

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