Investigation of time and frequency characteristics of the electrocaloric response in ferroelectric materials

A S Anokhin¹,², A V Es’kov¹, O V Pakhomov¹, A A Semenov², E Lähderanta³, A Tselv¹ and A L Kholkin¹

¹International Laboratory: "Materials and Structures for Electro- and Magnetocaloric Energy Conversion", ITMO University, St. Petersburg 197101, Russia
²Department of Physical Electronics and Technology, St. Petersburg Electrotechnical University, St. Petersburg 197376, Russia
³Department of Mathematics and Physics, Lappeenranta University of Technology, Lappeenranta 53850, Finland

E-mail: asanokhin@itmo.ru

Abstract. Recently, much attention has been paid to the development of new microminiature solid-state cooling devices and heat energy converters based on the electrocaloric effect. But researchers pay little attention to aspects of the electrocaloric effect associated with its time and frequency characteristics. These phenomena must be taken into account when developing highly efficient thermodynamic cycles for solid-state cooling devices. In this work, we conducted an experimental study of the dependence of the electrocaloric response of a ferroelectric sample on the period and duty cycle of the control signal.

It was demonstrated that the value of the electrocaloric response in studied ceramics may vary by more than 15% depending on period and duty cycle of electric pulses.

One of the most promising technologies for solid-state heat conversion is use of electrocaloric effect in solid-state ferroelectric structures. Many laboratories in the world are conducting researches aimed at design of electrocaloric coolers and converters, searching of new materials with high electrocaloric performance and developing of novel thermodynamic cycles for thermal electrocaloric converters [1, 2]. Electrocaloric effect (ECE), as an inverse of pyroelectric effect, is induced by the change of polarization states when the external electric field is applied or removed to a polar material under the adiabatic conditions. This effect reaches highest values in ferroelectric materials because of their sharp nonlinear temperature and field dependences of electric polarization. To date, the electrocaloric effect has been fairly well studied in a wide range of different ferroelectric materials, such as single crystals, thin films, ceramics and layered structures, polymer ferroelectrics. But researchers mainly pay attention to the electrocaloric response of a ferroelectric material after a single change of electric field. While developing solid-state heat energy converters, it is necessary to take into account the change in electrocaloric response when applying a periodic electric field with different time characteristics. Only a few publications provide information about influence of pulse front delay or pulse number on electrocaloric response [3, 4]. Such characteristics usually aren’t considered in thermal and electrophysical modeling of solid-state coolers and their components. The influence of the frequency and duty cycle of the applied electric field on the magnitude of the electrocaloric response of a ferroelectric sample in non-adiabatic thermal conditions are investigated in this paper.
Ferroelectric samples for our study were selected from two well-studied ferroelectric ceramic materials, namely barium titanate and a solid solution of barium titanate - strontium titanate. Since pure barium titanate at high temperatures has high leakage currents and thus it is not very suitable for electrocaloric applications, barium titanate samples were doped with manganese ions in an amount of 1 wt. % (BaTi$_{0.99}$M$_{0.01}$O$_3$). Barium titanate, doped manganese, (BTMO) and solid solution of Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ (BSTO) ceramics were fabricated by the solid-state reaction method. The raw materials BaCO$_3$, TiO$_2$, MnO$_2$ for BTMO, and BaCO$_3$, SrCO$_3$, TiO$_2$ for BSTO, were ground by planetary micro-mill Fritsch “PULVERISETTE 7 premium line” for 30 min in distillated water using zirconia balls of 3 mm diameter as milling medium. The resultant mixtures were calcined at 1200 °C for 2 hours in air and the resultant BTMO and BSTO powders were milled again. After grinding granulation using 11 wt. % aqueous solution of methylcellulose binder-lubricant, the powders were dry-pressed into a disc with a diameter of 10 mm and a thickness of 1 mm under a pressure of 5 MPa. The green samples were sintered at 1350°C for BTMO and 1450°C for BSTO in air atmosphere for 2 hours and then cooled in furnace. The sintered samples were gradually double-side polished to thicknesses of 0.5 mm. Then the electrodes were made using silver-palladium paste. The paste was fired at temperature of 850°C for 30 min in air. Temperature dependences of dielectric constant and loss tangent were measured at frequencies of 1-100 kHz and voltage of 1 V using precision LCR meter Agilent E4980A. Figure 1 shows temperature dependence of dielectric constant for BTMO and BSTO.

Figure 1. The temperature dependence of dielectric constant for sintered BTMO and BSTO ceramic samples.

Figure 2 shows loss tangent (a) and current-voltage characteristic (b) for ceramic samples. Leakage currents was measured at constant temperatures using precision electrometer Keysight B2987A. Measurement procedure considered high relaxation time of studied samples, so static leakage current was measured 10 minutes after charging. Temperatures for leakage current measurements were determined by phase transition temperatures.

Both materials demonstrate relatively sharp peak of dielectric constant and insignificant dispersion of dielectric constant in considered frequency range. It should be noted, that BSTO exhibits much lower leakage currents near phase transition in compare to BTMO, resistivity of BSTO sample reaches value of 4.3·10$^{11}$ Ohm·m, at the same field resistivity of BTMO reaches 8.9·10$^8$ Ohm·m, this distinction explained by significant temperature dependence of resistivity in perovskites. For example, at temperature of 5 °C BTMO sample demonstrates resistivity of 2.4·10$^{12}$ Ohm·m, which is sufficiently high value for ferroelectrics. Although leakage currents in BTMO were high enough, they were not that high to impact on electrocaloric response. Further it will be demonstrated, that in both materials electrocaloric response during depolarization was comparable with electrocaloric response during
polarization, thus Joule heating does not significantly affect the electrocaloric effect. Raw estimation gives EC energy for polarization of BMTO near 120 °C $E_{EC} \approx 50-60$ mJ, while Joule heating under the same conditions reaches $E_{JH} \approx 0.07$ µJ.

**Figure 2.** The temperature dependence of loss tangent (a) and leakage currents (b) for sintered BSTO and BTMO ceramic samples.

The electrocaloric effect in ferroelectric samples was studied over a wide temperature range. The control of the initial temperature during measurements was carried out using a precision liquid thermostat Julabo FP32-ME. The control voltage on the sample was formed using a high-voltage amplifier Trek 609E-6 and an arbitrary pulse generator Agilent 33522A. The change in temperature due to the electrocaloric effect was measured by the contact method using a miniature platinum thermistor connected to a nanovoltmeter Agilent 34420A. Rectangular voltage pulses with a duty cycle of 50% were applied to the sample. The duration of the pulse period was twice as long as the thermal relaxation time of the sample and was 120 seconds. The magnitude of the electrocaloric response during polarization and depolarization was measured separately. The measurement procedure is described in more detail in [5]. Figure 3 shows the temperature dependences of the electrocaloric response for BSTO (a) and BTMO (b) samples respectively for different electric fields.

**Figure 3.** Temperature dependences of electrocaloric response due to polarization and depolarization for BSTO (a) and BTMO (b) ceramic samples at different electric fields.

BSTO and BTMO samples exhibits relatively high electrocaloric response for bulk ceramic. Also, BTMO sample shows high difference between polarization and depolarization responses at low electric
fields, it is connected with high nonlinearity of polarization and its temperature derivative in low electric field range, in BSTO ceramics this effect is much less pronounced.

An experimental study of the electrocaloric response magnitude for different periods of the control signal was made. The period of the electric field square pulses was ranged from 2 to 40 seconds. Figure 4 shows an example of the experimental temperature diagrams for BSTO sample under periodic electric field pulses with different periods and demonstrates the procedure for measuring the magnitude of the electrocaloric response during polarization and depolarization of a ferroelectric sample. The measurements showed the dependence of the magnitude of the electrocaloric response both during polarization and during depolarization of a ferroelectric sample. The temperature jump is slightly more sharp when the period of the electric field pulse is less than 10 seconds. It was observed, that at short periods an increase of electrocaloric response occurs. It was not possible to investigate the electrocaloric response for periods of less than 2 seconds in used measurement cell due to inertia of the temperature sensor and the high heat capacity of the bulk ferroelectric sample.

![Figure 4](image)

**Figure 4.** The experimental dependence of the temperature change on the sample on time for different period of control signal, $\Delta E = 4$ MV/m.

Figure 5 shows obtained dependences of the magnitude of the electrocaloric response on the period for a BSTO (a) and BTMO (b) samples at various temperatures and with an electric field strength of 3 MV/m and 2 MV/m respectively.

![Figure 5](image)

**Figure 5.** The dependence of the electrocaloric response on the period for a BSTO (a) and BTMO (b) samples at various temperatures near phase transition.

Given dependencies indicate that electrocaloric response increases with decrease of pulse period. There are several reasons for this effect. In particular, it could be explained be relaxation of
polarization, that possibility was assumed in [6]. Also it could be connected with evolution of polarization due to point defects, such as oxide vacancies [7] which could impact on domain structure and polarization values under high electric field.

The dependence of electrocaloric response on duty cycle of electric pulses for the same samples was studied. Measurements were made for a signal with a period of 10 seconds. The signal duty cycle was varied from 10% to 90%. The electrocaloric response was measured during polarization and depolarization of a ferroelectric sample at different temperatures. Both measured samples showed a similar characteristic with small difference between the values of ferroelectric response during polarization and depolarization in duty cycle of 50%, but this difference increases at high and low duty cycle values. Moreover, at low duty cycle values electrocaloric response during depolarization greatly exceeds the electrocaloric response during polarization. With high duty cycle values, the opposite effect was observed. The figure 6 (a) shows the dependence of the magnitude of the electrocaloric response on the duty cycle of the control signal at various temperatures for the BSTO sample. The same dependence for BTMO sample is presented at figure 6 (b).

![Figure 6](image_url)

Figure 6. The dependence of the magnitude of the electrocaloric response on the duty cycle of the control signal at various temperatures for BSTO (a) and BTMO (b) samples.

That dependencies are agreed with dependencies of electrocaloric response on period of pulses, and also they provides a new method to control cooling processes in electrocaloric coolers. Using of low duty cycle may allow to increase a useful depolarization electrocaloric and to minimize time under field, which lowers losses due to Joule heating.

In conclusion it can be noted, that the experimental detection and investigation of some aspects of the electrocaloric effect could have a great practical importance for developers of solid-state thermal energy converters based on the electrocaloric effect. Particular interest is the effect of the signal duty cycle on the electrocaloric response. This effect can be directly used in the development of effective thermodynamic cycles for solid state coolers.

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