Phys. Status Solidi B **253**, No. 10, 2073–2078 (2016) / **DOI** 10.1002/pssb.201600339

physica status solidi b
www.pss-b.com
basic solid state physics

Intensive electrocaloric effect in triglycine sulfate under nonequilibrium thermal conditions and periodic electric field

V. S. Bondarev*[,1,2], E. A. Mikhaleva[1], M. V. Gorev[1,2], and I. N. Flerov[1,2]

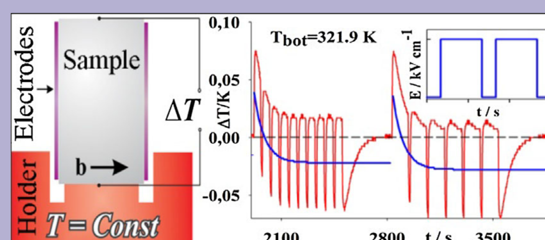
[1] Kirensky Institute of Physics, Siberian Branch RAS, 660036 Krasnoyarsk, Russia
[2] Institute of Engineering Physics and Radioelectronics, Siberian Federal University, 660074 Krasnoyarsk, Russia

Received 17 May 2016, revised 3 August 2016, accepted 3 August 2016
Published online 19 August 2016

Keywords electrocaloric effect, ferroelectrics, nonequilibrium processes, phase transitions

* Corresponding author: e-mail vbondarev@yandex.ru, Phone: +7 391 249 45 07, Fax: +7 391 243 89 23

We present the results of both direct measurements and modeling of the intensive electrocaloric effect ΔT_{AD} in ferroelectric triglycine sulfate under nonequilibrium thermal conditions and periodically varying electric field. In the narrow region around the phase transition temperature T_C, a visible difference was observed between the electrocaloric responses at applying ΔT^{ON} and removal ΔT^{OFF} of the constant electric field: $|\Delta T^{ON}| < |\Delta T^{OFF}|$ and $|\Delta T^{ON}| > |\Delta T^{OFF}|$ at $T < T_C$ and $T > T_C$, respectively. The variation of the frequency and profile of the periodic electric field at $T < T_C$ allowed one to obtain the gradual decrease in the average temperature of the top of the sample compared to the bottom kept at the constant temperature. At low frequency electric field, qualitative agreement was found between the time dependences of the measured experimentally and calculated ΔT values.



Experimental and modeling studies of electrocaloric effect ΔT_{AD} in triglycine sulfate showed that the applying/removal of a periodic electric field to/from the bulk sample decreases the average value of the waiving temperature of the top T_{top} compared to $T = \text{const}$ of the bottom. Both frequency and duty cycle of the electric field impulses strongly affect T_{top}.

1 Introduction In the process of continuous development and improvement of refrigeration systems, a cooling method based upon the use of caloric effects (CE) in solids is considered in recent years as one of the most promising and topical one. The extensive ΔS_{CE} and intensive ΔT_{AD} CE are associated with the change in entropy (at $T = \text{const}$) and temperature (at $S = \text{const}$) of materials under variation of external field (electric, magnetic, uniaxial, or hydrostatic pressure).

Recently, a lot of investigations were devoted, first, to searching solids, particularly ferroics, showing large electro(ECE)-, magneto(MCE)-, and/or baro(BCE)-caloric effects, [1–5] second, to analysis of the ways to increase the efficiency of both solid refrigerants as well as some refrigeration cycles [6–11] and, third, to designing some model refrigerators [12–14].

On the one hand, solid refrigerants have a series of undoubted merits compared to gas working substances, one of which is associated with rather large volume cooling power and, as the result, with compactness of the solid cooling devices. But on the other hand, methods utilizing ECE, MCE, and BCE in classical manner have a serious demerit. Indeed, in order to realize the solid cooling cycle, it is necessary not only to switch on/off the field from time to time, but also to have an ability to remove/bring the heat from/to the solid working substance.

Different variants solving this problem were discussed for movable and motionless refrigerants. The models of refrigerators with magnetocaloric and electrocaloric elements periodically moving between a source of magnetic/electric field, heat source and heat sink, as well as with the moving magnets, were considered in reviews [12, 13, 15]. For the cycle with unmovable working body, heat switches or shifters (mechanical, liquid crystal, etc.) were suggested to provide its thermal contact in turn with cooled object and environment [16–18]. Another way was considered using an additional intermediate thermodynamic cycle generally with liquid or gas working substances, providing the periodical or constant heat exchange between load and solid refrigerant as well as refrigerant and reservoir [19, 20].

In order to avoid such a serious disadvantage, some solid state cooling methods using ECE excluding the necessity to use thermal switches and moving parts were discussed [21–24]. For example, recently, a theoretical consideration of the effect of the periodic electric field on the ECE in the bulk linear electrocaloric element under nonequilibrium thermal conditions was performed [22]. The bottom of the sample was kept at constant temperature T_{bot} and the top was thermally isolated. It was shown that in such a case, the temperature of the top T_{top} oscillates around some average value, which decreases step by step down to some limit value lying lower than T_{bot}. Thus, such a process is followed by the appearance of both the temperature gradient along the ECE element and the thermal flow from the top to the bottom, both of which depend on the thermal conductivity and size parameters of element, shape, and frequency of periodic electric field, etc. In spite of the fact that this cooling method seems to be simple and rather promising, as we know, attempts to its experimental realization are still missing.

The efficiency of considered attractive cooling was theoretically analyzed on solid solutions of ferroelectrics and ferroelectric-relaxors [22, 25], which are characterized by the smeared behavior of the dielectric properties and can be considered as heterogeneous materials.

In the present paper, the effect of both constant and periodic electric field on intensive ECE was examined in a single crystal of triglycine sulfate (TGS) under nonequilibrium thermal conditions. We performed also the numerical calculations in the manner suggested by Starkov et al. [22]. The choice of the object under investigation was connected with several reasons. First, TGS is a classical strong homogeneous ferroelectric medium. Second, this crystal is an uniaxial ferroelectric that allows one to apply simply the strongly directed electric field and observe nonsmeared ECE. Third, thermal, dielectric, and electrocaloric properties of TGS under equilibrium conditions in the region of the $P2_1/m-P2_1$ ferroelectric phase transition were carefully studied earlier [26, 27].

2 Experimental Scheme of the experimental setup for measuring intensive ECE is shown in Fig. 1. The TGS sample 1 was cut in the form of rectangular prism with the sizes of $5\times5\times7\,mm^3$ and installed on the copper holder 2. Silver electrodes 3 were put on the opposite faces athwart ferroelectric axis b. The holder with the sample was put into the measuring block, which was placed in a vacuum camera with the pressure of about 10^{-3} mm Hg. Using vacuum grease a reliable thermal contact between sample−holder and holder−block was provided. The temperature of the experimental block as well as holder and sample was measured and controlled using a platinum thermometer.

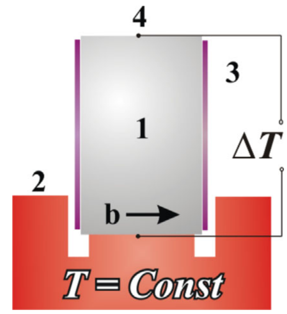


Figure 1 Schematic of the experimental installation: (1) sample, (2) holder, (3) silver electrodes, (4) thermocouple; b – ferroelectric axis.

The scheme of temperature measuring and controlling was placed into the thermostat at ambient conditions, which allowed one to increase both a long-term stability and sensitivity of the thermometer up to 10^{-4} K and 5×10^{-5} K, respectively, for about 7–8 h.

The temperature difference T_{top}–T_{bot} between top and bottom of the sample, which was appeared as the result of switch on/off of the electric field, was precisely detected by copper-constantan thermocouple 4. The stability of measurements was about 5×10^{-4} K and sensitivity to the temperature change has reached 10^{-4} K.

A dc power homemade supply was used to apply the electric field to the sample. In order to minimize the heat flows between the sample and the dc power as well as between the top and the bottom of the sample, contact wires with rather small diameters ~0.05 mm were used.

The X-ray powder diffraction has shown an absence of any impurities in the TGS single crystal. On the second stage of the sample characterization, both spontaneous polarization and permittivity were studied using above setup. The dielectric constant was measured with the immittance meter E7-20 at 1 kHz. The study of the pyroelectric current in the sample cooled previously under electric field 3 kV cm^{-1} (coercive field 0.3 kV cm^{-1} [28]) was carried out in zero field heating mode at the constant rate of ~0.5 K min^{-1} using a precise amplifier of current.

Figure 2 illustrates a rather good agreement between measured polarization and previous data [29]. The maximum value of $\varepsilon\approx3\times10^4$ as well as the temperature $T_C = 322.37$ K of the $P2_1/m-P2_1$ phase transition are also very close to those observed in Ref. [27]. All the facts above confirm the high quality of TGS under study.

3 Results and discussion Intensive ECE ΔT_{AD} in TGS was earlier studied in a classical manner in the

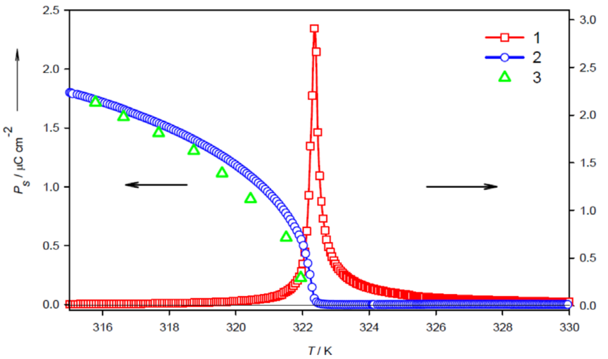


Figure 2 Experimental temperature dependences of dielectric constant and spontaneous polarization. (1, 2) present data, (3) data obtained in Ref. [29].

adiabatic process (S = const) of switching on/off the external electric field, i.e., in equilibrium thermal conditions [26]. It this paper, we performed the ΔT measurements keeping the bottom of the TGS sample at constant temperature (Fig. 1).

In order to avoid an additional heat load on the sample, the vacuum isolation was used only. Therefore, we use further the term “free” top. In such nonequilibrium conditions, the electric field variation has simultaneously led to ECE and, as the result, to the appearance of the temperature gradient along the sample with the maximum $|\Delta T| = |T_{top} - T_{bot}|$ value on the “free” top of the sample. Figure 3 illustrates the results of the experimental measurements in such a manner of the ΔT electrocaloric response at two temperatures of the bottom close to T_C in ferroelectric (321.9 K) and paraelectric (322.9 K) phases. The rising and falling field rates were kept equal.

It was found that the application of the electric field $E = 3\,\text{kV cm}^{-1}$ leads to a rapid increase in the temperature difference $\Delta T^{ON} = (T_{top}–T_{bot})^{ON}$ with a rate of $d\Delta T^{ON}/dt \approx 0.5\,\text{K min}^{-1}$ up to 0.0825 K at $T < T_C$ (Fig. 3a) and 0.045 K at $T > T_C$ (Fig. 3b). Keeping the electrocaloric element for several minutes at a constant electric field was always accompanied by gradual decrease of the T_{top} temperature up to T_{bot}. The removal of the field was followed by the appearance of the negative ΔT^{OFF}: −0.0875 K ($T < T_C$) (Fig. 3a) and −0.044 K ($T > T_C$) (Fig. 3b). The $T_{top}–T_{bot}$ difference was changed almost with the same rate of $d\Delta T^{OFF}/dt \approx 0.5\,\text{K min}^{-1}$. The data obtained show a visible inequality in the $|\Delta T^{ON}|$ and $|\Delta T^{OFF}|$ values with the opposite relation between them in both temperature regions: $T < T_C$ and $T > T_C$.

Thus, the electrocaloric response ΔT in TGS under nonequilibrium thermal conditions at $T_C - T = 0.47$ K and $E = 3\,\text{kV cm}^{-1}$ was found comparable with $\Delta T_{AD} = 0.09$ K determined in adiabatic process at the same $T_C–T$ and rather lower electric field $E = 1.7\,\text{kV cm}^{-1}$ [26]. The main reason of that is associated with the appearance of both the temperature gradient along the sample at applying electric field and as the result a heat exchange between the sample and holder kept at a constant temperature.

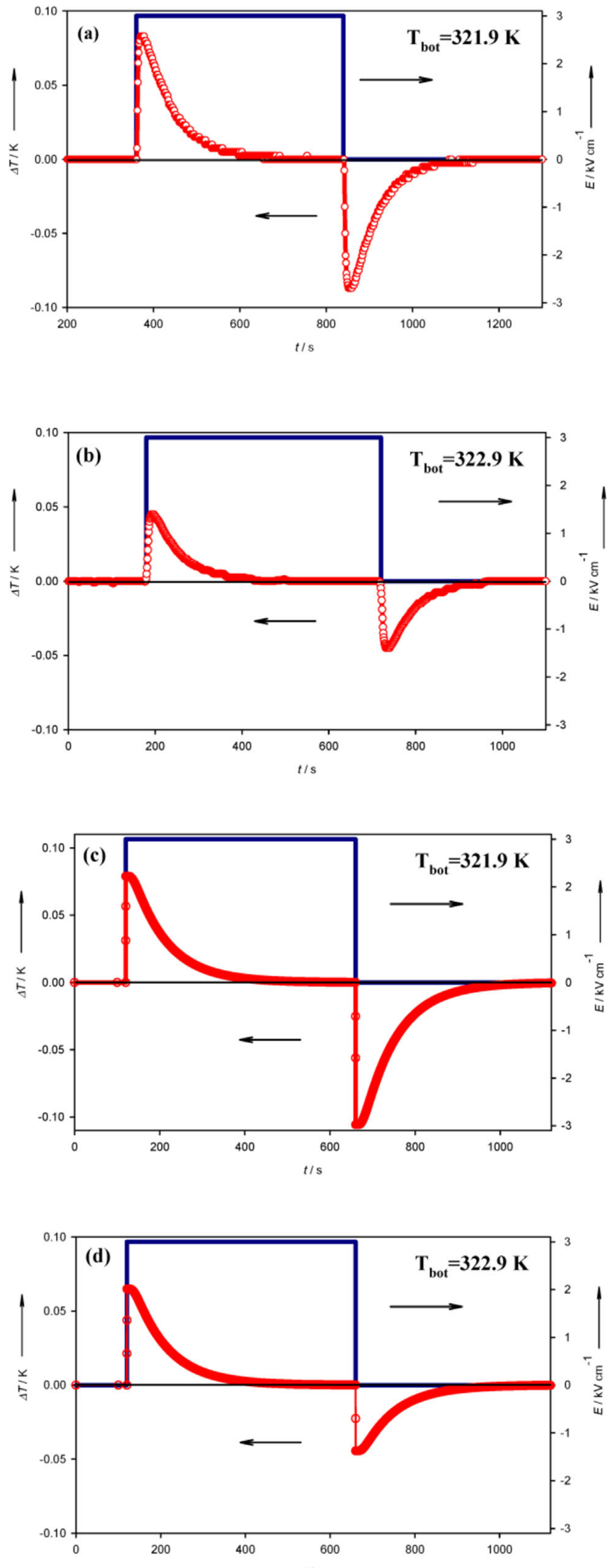


Figure 3 The profiles of electric field variation $\Delta E(t)$ and associated $\Delta T(t)$ response in ferroelectric (a, c) and paraelectric (b, d) phases of TGS. Experimental (a, b) and calculated (c, d) data.

A series of the measurements performed with a direct and inverse sign of the external electric field have shown high reproducibility of the results. The instrumental error of the ΔT value determination has not exceeded ± 0.0005 K.

Thus, the data obtained show that applying and removal of an electric field to/from the ferroelectric TGS sample with the stabilized temperature of the bottom are associated with the nonequivalent values of absorbed and released heat. One can think that such a phenomenon could originate from the kinetics of the electrocaloric response at second order phase transition in TGS under nonequilibrium thermal conditions.

Similar results were recently observed in the experimental studies of the electrocaloric processes in $BaTiO_3$ multilayer structure [21]. In the direct measurements of the heat flow in an isothermal process using differential scanning calorimeter, the kinetic processes were connected with the variation of the rising and falling rates of the electric field.

The ECE investigations in TGS under nonequilibrium thermal conditions were also performed in wide temperature range 300–323 K at $E = 3\,\mathrm{kV\,cm^{-1}}$. Figure 4 shows the temperature region where the difference $|\Delta T^{\mathrm{OFF}}| - |\Delta T^{\mathrm{ON}}|$ is mostly pronounced.

One can see that the temperatures of the maximum $|\Delta T^{\mathrm{ON}}|$ and $|\Delta T^{\mathrm{OFF}}|$ values are not coincided and lie lower than T_{C}. The temperature region with $|\Delta T^{\mathrm{ON}}| \neq |\Delta T^{\mathrm{OFF}}|$ is rather narrow. However, the maximum difference $|\Delta T^{\mathrm{OFF}}| - |\Delta T^{\mathrm{ON}}| = 0.0083$ K found at 321.6 K is rather large constituting almost 10% of the ΔT and shows the cooling of the "free" top of the sample when the bottom is kept at constant temperature.

On the next stage, the effect of nonequilibrium thermal conditions on the electrocaloric response in TGS was studied under periodic electric field of varying frequency. The inset in Fig. 5a shows one of the profiles of the electric field which were examined to observe the behavior of the temperature of the sample. Periodic E impulses with frequency varied in the range 0.1–5 Hz have led to periodical heating/cooling of the sample and the change of the temperature gradient along it. Step by step, the thermal regime was stabilized and the T_{top}–T_{bot} value was waiving around some average temperature.

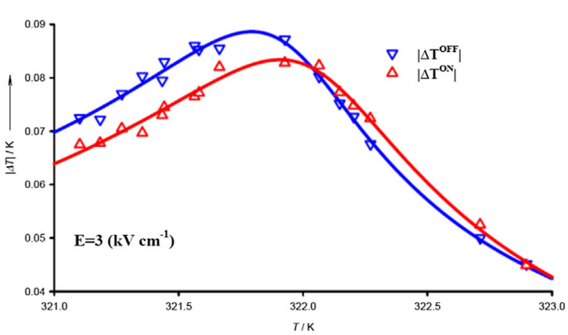


Figure 4 Temperature dependences of the intensive ECE in applying $|\Delta T^{\mathrm{ON}}|$ and removal $|\Delta T^{\mathrm{OFF}}|$ modes at $E = 3\,\mathrm{kV\,cm^{-1}}$.

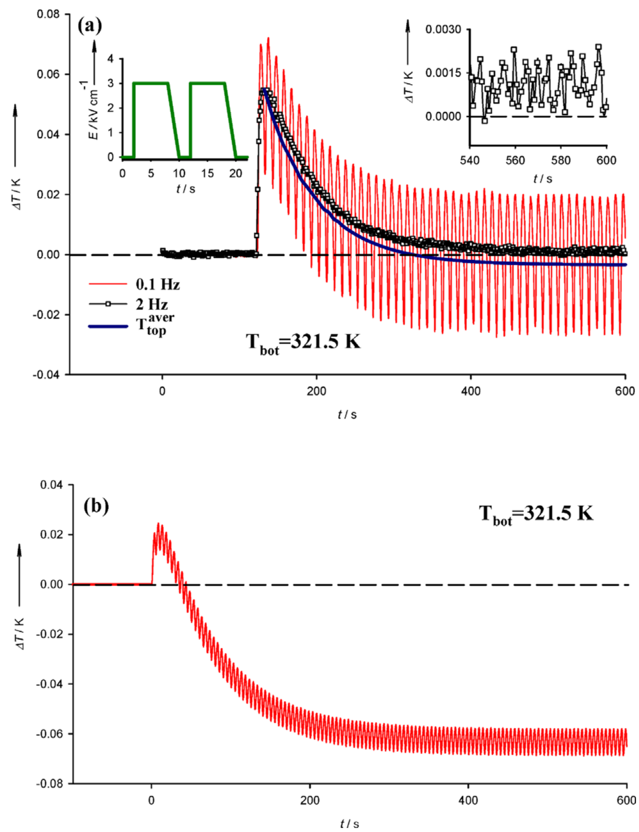


Figure 5 The experimental (a) and calculated (b) time dependences of the temperature difference ΔT between the top and bottom of the TGS sample under varying frequency of the electric field. Solid line is the average temperature of the top $T_{\mathrm{top}}^{\mathrm{aver}}$. Insets show the profile of the electric field and nonreversible increase of ΔT due to the Joule heat.

It was found that the behavior of the T_{top}–T_{bot} difference depends strongly on the frequency of the electric field variation (Fig. 5a). The increase of the frequency decreases the amplitude of the ΔT vibrations, which are almost completely suppressed at 2 Hz. In such a case, the time $\Delta T(t)$ dependence looks similar to the behavior of $\Delta T(t)$ observed in the $E = 3\,\mathrm{kV\,cm^{-1}} = \mathrm{const}$ process (Fig. 3). One more important point is that the initial ΔT^{ON} and ΔT^{OFF} values appeared at applying and removal E are lower compared to the values found in experiments with constant electric field. The observations above can be associated with such reasons as finite rate of the polarization switching, thermal resistance on the boundary between the sample and thermocouple, low thermal conductivity of the sample, etc.

The time dependence of the average temperature of the "free" top at the fixed T_{bot} in the process of periodical switching electric field can be presented as

$$T_{\mathrm{top}}^{\mathrm{aver}}(t) = T_{\mathrm{bot}} + \left(\Delta T^{\mathrm{ON}} + \Delta T^{\mathrm{OFF}}\right)/2. \qquad (1)$$

In accordance with Eq. (1), the time dependence $T_{top}^{aver}(t)$ is shown as solid line in Fig. 5a when T_{bot} is kept at the temperature $T = T_{max}^{OFF} - 0.25$ K at varying electric field of $E = 3$ kV cm^{-1} and 0.1 Hz. After several minutes of the E application, the average value $(\Delta T^{ON} + \Delta T^{OFF})/2$ became negative that means lowering of the average temperature T_{top}^{aver} of the "free" top compared to the constant T_{bot} temperature. In the case of parameters above, the difference $T_{top}^{aver} - T_{bot} = -4 \times 10^{-3}$ K was experimentally observed (Fig. 5a). In accordance with the amplitude of the $(\Delta T^{ON} + \Delta T^{OFF})/2$ waiving, the lowest temperature of the "free" top is $T_{top} \approx T_{top}^{aver} - 0.25$ K.

Thus, one can say about a cooling of the top of the sample under periodic electric field and nonequilibrium thermal conditions.

It was of interest to compare the experimental data obtained with the results of theoretical consideration of the ECE effect in TGS of the same geometry and in similar thermal conditions in the framework of the approach suggested in Ref. [22, 25]. The one-dimensional heat conductance equation was used

$$\rho C_E \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \lambda(x) \frac{\partial T}{\partial x} - T \left(\frac{\partial P}{\partial T}\right)_E \frac{\mathrm{d}E}{\mathrm{d}t}, \qquad (2)$$

where ρ is the density of TGS; C_E (=const) the heat capacity; λ (=const) the coefficient of the thermal conductivity.

We performed calculations of the temperature distribution along the sample depending on time. Using experimental data on $\varepsilon(T)$ and $P(T)$ obtained for the sample under investigation, we determined the coefficients of the thermodynamic potential $\Delta\Phi = A_T(T - T_c)P^2 + BP^4 + CP^6$.

Table 1 demonstrates a good coincidence between the values of coefficients calculated for different samples using different initial data. On the ground of analysis of the electric equation of the state, the $(\partial P/\partial T)_E$ derivatives were estimated.

On the ground of analysis of the electric equation of the state, the $(\partial P/\partial T)_E$ derivatives were estimated.

On the first stage, the calculations of the ΔT^{ON} and ΔT^{OFF} values were performed in the process $(E = 0) \rightarrow (E = 3$ kV cm$^{-1}) \rightarrow (E = 0)$ (Fig. 3c and d). It is seen that both values in ferroelectric and paraelectric phases are rather close to experimentally found and relations between them are similar: $|\Delta T^{ON}| < |\Delta T^{OFF}|$ at $T < T_C$ and $|\Delta T^{ON}| > |\Delta T^{OFF}|$ at $T > T_C$. At the same time, the differences $|\Delta T^{ON}| - |\Delta T^{OFF}|$ in both temperature regions are little bit greater than experimental found values.

Then the simulations of the $\Delta T(t)$ dependences were performed at periodic E impulses with a frequency of 0.1 Hz (Fig. 5b). One can see that the effect of cooling in such a case is more pronounced compared to experimental observations. On the other hand, it is necessary to point out that the greatest calculated difference T_{bot}–$T_{top} = 0.07$ K is only three times greater than the experimental value.

We have also carried out the experimental examinations of the effect of the duty cycle $D = BC/AC$ of the electric field impulse (inset in Fig. 6) on the $\Delta T(t)$ behavior. Figure 6 shows the results of measurements at three frequencies f: 0.025 Hz (curves 1 and 2 with the D values of 0.4 and 0.7, respectively), 0.016 Hz (curve 3, $D = 0.8$) and 0.008 Hz (curve 4, $D = 0.9$). One can see that the average value of the ΔT waiving temperature difference between the top and bottom of the sample decreases and becomes negative with the decrease and increase of the f and D parameters, respectively.

Thus, we have found that using ECE under periodic electric field in ferroelectrics under nonequilibrium thermal conditions one can obtain a thermal flow directed from the "free" top of the sample to its bottom kept at constant temperature. That is in principal one can realize the linear ferroelectric cooling set up.

Some discrepancies were found between the data of experimental measurements and modeling simulations with the periodic electric field. First, the $(\Delta T^{ON} + \Delta T^{OFF})/2$ empirical value is lower than expected one. Second, the increase of the electric field frequency is accompanied by

Table 1 Comparison of the coefficients of the thermodynamic potential.

A_T (10^3 K^{-1})	B (10^9 m^3 J^{-1})	C (10^{17} m^6 J^{-2})	initial data	Ref.
1.91	1.07	21	P_S, ε	this work
1.84	1.1	20	P_S, ε	[30]
1.84	1.1	5	C_E, ε	[30]

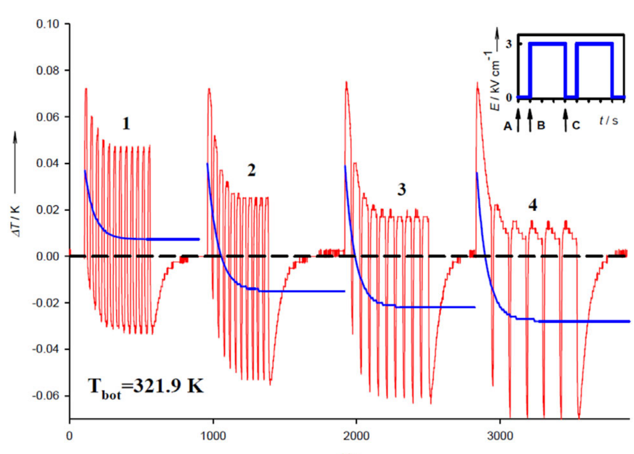


Figure 6 The time dependences of the temperature difference ΔT under varying frequency f and duty cycle D of the electric field: $f = 0.025$ Hz, D $(=BC/AC) = 0.4$ and 0.7, curves 1 and 2, respectively; 0.016 Hz, $D = 0.8$, curve 3; 0.008 Hz, $D = 0.9$, curve 4. Solid lines demonstrate the top $T_{top}^{aver} - T_{bot}$ behavior calculated using Eq. (1). Inset shows the profile of the electric field.

decrease and increase of the temperature $T_{top}^{aver}-T_{bot}$ difference in experiments and calculations, respectively.

The main reasons of the facts observed can be connected with the following points:

(i) Pure thermally isolated top of the sample. In such a case, there is a "free" heat exchange between the top and environment.

(ii) Pure thermal contact of the thermocouple with the top and bottom.

(iii) Joule heat. At low frequency (0.1 Hz), we have observed a good reverse of the ΔT value to zero during the processes of $E=$const and at removal of electric field. But beginning from $f \geq 1$ Hz at the same $E = 3$ kV cm^{-1}, the small irreversible part of the ΔT increase was detected, which could be associated with the heat release on the electric resistance of the sample (Fig. 5).

4 Conclusions

We have performed experimental and modeling studies of the intensive ECE ΔT in a classic ferroelectric crystal TGS under nonequilibrium thermal conditions. It was found that the applying/removal of the constant electric field to/from the bulk prismatic sample with thermally stabilized bottom are accompanied by:

(i) a shift relative to each other in the temperature scale of the temperature dependent differences $\Delta T^{ON}(T) - \Delta T^{OFF}(T)$ between the top and bottom with the maximum values at $T_{max}^{ON} > T_{max}^{OFF}$ lying below phase transition temperature T_C;

(ii) the negative and positive $|\Delta T^{ON}| - |\Delta T^{OFF}|$ values at $T < T_{max}^{OFF}$ and $T > T_{max}^{ON}$, respectively.

Experiments with periodic electric field under the same thermal conditions have shown:

(i) that the average value of the waiving temperature of the top can be obtained lower compared to constant temperature of the bottom;

(ii) a strong dependence of the average temperature on the frequency and duty cycle of the electric field impulses.

The results of analysis in the framework of the theoretical model suggested by Starkov [22, 25] allowed one to find:

(i) a rather good agreement between the directly measured and calculated values of ΔT^{ON} and ΔT^{OFF} at constant electric field with the same relations between them at $T < T_{max}^{OFF}$ and $T > T_{max}^{ON}$;

(ii) qualitative coincidence of the parameters above obtained in periodic electric field of the low frequency.

Summarizing the results obtained, one can suppose that in spite of rather low negative difference $\Delta T^{OFF} - \Delta T^{ON} < 0$ observed in the case of TGS, ECE in noneqilibrium thermal conditions at $T < T_{max}^{OFF}$ could be considered as promising to design the cooling line using ferroelectric elements with the more pronounced value of $d(\Delta T)/dE$.

Acknowledgements The reported study was funded by RFBR and Government of Krasnoyarsk Territory according to the research project no. 16-42-240428 p_a.

References

[1] M. Valant, Prog. Mater. Sci. **57**, 980 (2012).
[2] J. F. Scott, Annu. Rev. Mater. Res. **41**, 229 (2011).
[3] I. N. Flerov, M. V. Gorev, A. Tresso, and N. M. Laptash, Crystallogr. Rep. **56**, 9 (2011).
[4] A. Smith, C. R. H. Bahl, R. Bjørk, K. Engelbrecht, K. K. Nielsen, and N. Pryds, Adv. Energy Mater. **2**, 1288 (2012).
[5] S. Crossley, N. D. Mathur, and X. Moya, AIP Adv. **5**, 067153 (2015).
[6] X. Moya, S. Kar-Narayan, and N. D. Mathur, Nature Mater. **13**, 439 (2014).
[7] J. He, J. Chen, J. T. Wang, and B. Hua, Int. J. Thermal Sci. **42**, 169 (2003).
[8] I. N. Flerov, E. A. Mikhaleva, M. V. Gorev, and A. V. Kartashev, Phys. Solid State **57**, 429 (2015).
[9] A. Kitanovski, U. Plaznik, U. Tomc, and A. Poredoš, Int. J. Refrig. **57**, 288 (2015).
[10] U. Tomc, J. Tušek, A. Kitanovski, and A. Poredoš, Appl. Therm. Eng. **58**, 1 (2013).
[11] X. Moya, E. Defay, V. Heine, and N. D. Mathur, Nature Phys. **11**, 202 (2015).
[12] M. Tishin and Y. Spichkin, The Magnetocaloric Effect and its Application (IOP Publishing, Bristol, Philadelphia, 2003), p. 475.
[13] K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
[14] U. Plaznik, A. Kitanovski, B. Rožič, B. Malič, H. Uršič, S. Drnovšek, J. Cilenšek, M. Vrabelj, A. Poredoš, and Z. Kutnjak, Appl. Phys. Lett. **106**, 043903 (2015).
[15] H. Gu, X. Qian, X. Li, B. Craven, W. Zhu, A. Cheng, S. C. Yao, and Q. M. Zhang, Appl. Phys. Lett. **102**, 122904 (2013).
[16] R. I. Epstein and K. J. Malloy, J. Appl. Phys. **106**, 064509 (2009).
[17] Y. D. Wang, S. J. Smullin, M. J. Sheridan, Q. Wang, C. Eldershaw, and D. E. Schwartz, Appl. Phys. Lett. **107**, 134103 (2015).
[18] S. J. Smullin, Y. Wang, and D. E. Schwartz, Appl. Phys. Lett. **107**, 093903 (2015).
[19] M. P. Hehlen, A. H. Mueller, N. R. Weisse-Bernstein, and R. I. Epstein, Proc. SPIE **8638** (Laser Refrigeration of Solids VI, San Francisco, California, USA), 86380D (2013).
[20] Y. V. Sinyavskii, Chem. Pet. Eng. **31**, 501 (1995).
[21] Y. Bai, G.-P. Zheng, and S.-Q. Shi, J. Appl. Phys. **108**, 104102 (2010).
[22] A. S. Starkov, S. F. Karmanenko, O. V. Pakhomov, A. V. Es'kov, D. Semikin, and J. Hagberg, Phys. Solid State **51**, 1510 (2009).
[23] A. Khodayari and S. Mohammadi, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **58**, 503 (2011).
[24] I. Starkov and A. Starkov, Ferroelectrics **480**, 102 (2015).
[25] A. V. Es'kov, S. F. Karmanenko, O. V. Pakhomov, and A. S. Starkov, Phys. Solid State **51**, 1574 (2009).
[26] B. A. Strukov, Fiz. Tverd. Tela **11**, 892 (1969).
[27] S. A. Taraskin, B. A. Strukov, and V. A. Meleshina, Fiz. Tverd. Tela **12**, 1386 (1970).
[28] F. Iona and G. Shirane, Ferroelectric Crystals (Pergamon Press, Oxford, London, New York, Paris, 1962), p. 53.
[29] E. F. Dudnik, V. M. Duda, and A. I. Kushnerev, Phys. Solid State **42**, 139 (2000).
[30] I. E. Gordon and D. G. Boal, Ferroelectrics **17**, 411 (1977).