PRINCIPLES OF SOLID-STATE COOLER ON LAYERED MULTIFERROICS

A. STARKOV[a], O. PAKHOMOV[a], I. STARKOV[b], A. ZAITSEV[a], I. BARANOV[a]

[a] St. Petersburg National Research University of Information Technologies, Mechanics and Optics,
Institute of Refrigeration and Biotechnologies
9, Lomonosov Str., St. Petersburg, 191002, Russia
Fax: +7 812 3147865, e-mail: oleg.cryogenics@gmail.com
[b] Institute for Microelectronics, Vienna University of Technology,
A1040 Vienna, Austria
Fax: +43 1 58801 36099, e-mail: secretary@iue.tuwien.ac.at

ABSTRACT

We summarize the main physical ideas behind the development of the novel solid-state cooling system. The main strategy relies on strengthening of the electrocaloric effect. We show that for practical realization additional piezoelectric layers or new multiferroic materials can be used. Moreover, a combination of the electrocaloric effect and an external force is very promising. This force can be either the magnetic field or the mechanical stress. The proposed concept is supported by experimental data and theoretical calculations.

1. INTRODUCTION

Due to the decreasing size and increasing power of electronic components the problem of cooling and temperature control is one of the hottest in the modern electronics and electrical engineering. Among the various realizations of the traditional heat converters, the possibility of using magneto- and electrocaloric effects (MCE and ECE) in the solid state structures is of special interest (Tishin and Spichkin, 2003; Sinyavsky and Brodyansky, 1992). These effects are similar in nature, i.e. the impact of magnetic (in the case of MCE) or electric field (ECE) in the solid causes a change in the lattice temperature. The main drawbacks of the magnetocaloric systems are related to high costs and large sizes of magnetic field sources, the application of mechanics, and the large currents consumed by the Peltier elements (Sinyavsky and Brodyansky, 1992; Shebanovs et al., 2002). At the same time, the attractiveness of employment of the ECE is the ability to directly convert heat into electricity. Therefore, many laboratories are trying to develop a cooler that is based on the ECE. For this purpose search of new materials with high dielectric permittivity as well as strong dependence on the temperature is being performed (Shebanovs et al., 2002; Mischenko et al., 2006; Lu et al., 2010; Wiseman, 1969; Lawless, 1977; Neese et al., 2009). The first experimental observations of the ECE were held in 1930 at the Rochelle salt (Kobeko and Kurtschatov, 1930). The further studies of various materials have led to the temperature change due to the ECE only by $\Delta T = 2,3$ K (Shebanovs et al., 2002). The situation was substantially changed in 2006 when for a $PbZr_{0.95}Ti_{0.05}O_3$ film with a thickness of 350 nm at a field of 480 kW/cm, ΔT of 12 K was achieved (Mischenko et al., 2006). To date, the highest reported value is $\Delta T = 40$ K and is achieved employing a 450 nm thick $Pb_{0.88}La_{0.08}Zr_{0.65}Ti_{0.35}O_3$ film and applying a field of 1250 kW/cm (Lu et al., 2010).

2. FEATURES OF THE ELECTROCALORIC EFFECT THEORETICAL DESCRIPTION

The basic formula describing the ECE is derived by Thompson (Thomson, 1978).

$$C_E dT = -T \frac{\partial P}{\partial T} dE, \qquad dT = \gamma dE. \tag{1}$$

Here T is the temperature, P the polarization, E the electric field, C_E the heat capacity at a constant field, and γ the electrocaloric coefficient (ECC)

$$\gamma = -\frac{T}{C_E}\frac{\partial P}{\partial T}.$$

It can be seen from (1) that the greatest change in the temperature will be in the region where pyroelectric coefficient $p=\partial P/\partial T$ demonstrates a maximum. For ferroelectrics this is realized in the vicinity of the Curie temperature T_c, just in the area where the Landau-Ginzburg theory of phase transitions is applicable (Strukov B.A. , et al., 1998). In this case the polarization dependence on the electric field is given by:

$$E = aP + bP^3, \quad a = a_0\left(T - T_c\right), \tag{2}$$

where a_0 is the Curie-Weiss constant and b the nonlinearity coefficient.

At the beginning it is worth to discuss the accuracy of the above formulas (1) and (2). Applying the Thompson formula (1) to the experimental data one obtains that the right-hand side is exceeded by 10–15 %. The explanation of this fact is given in (Starkov et al., 2010-1). Experimentally observed polarization hysteresis (obtained at a periodic variation of the electric field) (Mischenko et al., 2006) suggests that dynamic effects have to be taken into account. In other words, the equation (2) should be replaced by the Landau-Khalatnikov equation (Starkov et al., 2010-1)

$$\alpha\frac{P}{T} = E - aP - bP^3. \tag{3}$$

Here α is the effective "internal" resistance. For small α the polarization can be represented as

$$P = P_{st} + P_{dyn}, \qquad P_{dyn} = -\frac{a}{a + 3bP_{st}^2}\frac{\partial P_{st}}{\partial t}, \tag{4}$$

where P_{st} is the quasi-static part of the polarization defined by the equation (2) and P_{dyn} the dynamic addition to the polarization. We assume that just appearance of this term explains the overestimation of ΔT obtained within the indirect approaches (Mischenko et al., 2006, Neese et al., 2009).

The adiabatic equation for the Landau-Ginzburg model is (Starkov et al., 2010)

$$T - T_0 = \frac{a_0}{k}\left(P^2 - P_0^2\right), \tag{5}$$

where k is a constant, which cannot be determined by the Landau theory, T_0 and P_0 are the initial temperature and polarization, respectively. The experimental dependence (5) was confirmed by various authors (Shebanovs et al., 2002; Neese et al., 2009). As a consequence, the equation (2) is suitable to describe only quasistatic processes, and for the dynamic processes (3) should be used. In the vicinity of the Curie point it is necessary to consider the pyroelectric current and the piezocurrent (Starkov et al., 2010-1).

3. ELECTROCALORIC EFFECT REINFORSMENT POSSIBILITIES

3.1. Additional External Force

The main idea of this work is to use the dependence of the polarization on an auxiliary parameter. The magnetic field (in this situation the ECE being reinforced by the magnetoelectric effect) or the mechanical stress (with piezoelectric or piezomagnetic effects as the driving force) can play role of this parameter. The free energy is (Strukov et al., 1998).

$$F = F_0(T) + \frac{aP^2}{2} + \frac{bP^4}{4} - EP + \alpha\eta P^2 + \frac{\beta\eta^2}{2} - \eta\sigma. \tag{6}$$

Here $F_0(T)$ is a function of T (explicit form in the Landau theory is not postulated), η the second (after P) order parameter, E the external field, while α and β are constants. Further under η we mean a deformation and under σ – elastic tension. Then α and β are elastic and piezoelectric modules, respectively. For the crystals a, b, α, β, σ, η are tensor quantities. The free energy (6) describes the quadratic piezoelectric effect. The extremality condition for (6) allows us to write the system of equations

$$(2\alpha\eta + a)P + bP^3 = E, \quad \alpha P^2 + \beta\eta = \sigma, \tag{7}$$

for determination of parameters P and η on known quantities E and σ. For $\alpha = 0$ the second equation (7) describes the usual Hooke's law. Eliminating η from the second equation (7) we come to the following relation

$$\left(2\frac{\alpha}{\beta}\sigma + a\right)P + \left(b - \frac{2\alpha^2}{\beta}\right)P^3 = E, \tag{8}$$

which defines the polarization as a function of E, η, and σ. The entropy and the heat capacity are

$$S \equiv -\frac{\partial F}{\partial T} = -F_0'(T) - \frac{a_0 P^2}{2}, \quad C_E \equiv -T\left(\frac{\partial^2 F}{\partial T^2}\right)_E = -TF_0'' - Ta_0 pP,$$

and, denoting $F_0''(T) = k$, find the ECC

$$\gamma(T,\sigma) = \frac{pP(T,\sigma)}{k + a_0 pP(T,\sigma)}. \tag{9}$$

The dependence of the electrocaloric coefficient γ on σ follows from these formulas. The theoretical calculations performed in (Prosandeev et al., 2008) lead to $\gamma_{cl} \approx 0.6\gamma_{free}$, where γ_{cl} and γ_{free} are ECC for a clamped and free ceramics. Experimental data gives the relation of $\gamma_{cl} \approx 0.8\gamma_{free}$ for BaTiO$_3$ ceramics (Akcay et al., 2007).

Quite similarly, the pressure can be used as an effective control parameter for the MCE. As shown in (Sun et al., 2006), for single La$_{0.69}$Ca$_{0.31}$MnO$_3$ crystals, an 1 GPa pressure increases the temperature of the phase transition by 25 K, which leads to a decrease in MCE by more than two times.

3.2. Multilayered Structures

Second, use of multilayer systems can significantly increase the value of ECE. Calculations performed on the basis of our model (Es'kov et al., 2009) taking into account non-uniformities in the temperature distribution and the surface effect of layer boundaries, confirm this idea. Thus, according to (Es'kov et al., 2009), at a frequency of 1Hz the second layer of electrocaloric material increases the ECE for BaSrTiO$_3$ (BST) ceramics by 12 K (see Fig. 1). In addition, for multilayer systems it is possible to use higher values of the electric field and they have a higher heat capacity. Moreover, the crucial factor in the organization of the thermodynamic cycle is use of heat keys. Both the classical scheme (Sinyavsky and Brodyansky, 1992; Shebanovs et al., 2002), and switches based on microelectromechanical systems (MEMS) and the Peltier elements (Mishenko, 2004), (Lawless, 2004) lead to a substantial increase in the size of the cooling element, and hence to loss of some benefits of the ECE. We suppose that employment of liquid crystals (Epstein et al., 2009) or using of schemes without thermal key (Es'kov et al., 2009), (Karmanenko et al., 2007), (Khodayari et al., 2011) is more promising.

3.3. Periodical Cycle Application

The following issues are crucial in the context of ECE-based cooling system development. The main problem is the organization of the thermodynamic cycle. At the adiabatic conditions, the change in the resulting temperature induced by the application/removal of the electric field is zero. Therefore, we need to

employ reversible nonadiabatic processes such as isothermal, constant field or constant polarization processes. The adiabaticity is violated when, for example, heat keys are used or a heat exchange with the environment and the heterogeneity of temperature distribution in the sample occurs (Karmanenko et al., 2007; Khodayari et al., 2011). For BST ceramics the calculations have shown that after 1000 cycles of switching the system relaxes to the steady temperature. Thus, the amplitude of temperature fluctuations around this value is less than the original one by 20 K. Such a behavior was reported in the work by Wiseman (1969) where the temperature variation induced by the periodic electric field was registered. Within the first cycle when the electric field is switching-on the sample temperature was increased by 0.043 K followed by the decrease with ΔT=0.046 K. As a result, the total change in temperature per cycle is 0.003 K. This tendency was qualitatively predicted in (Lawless, 1977).
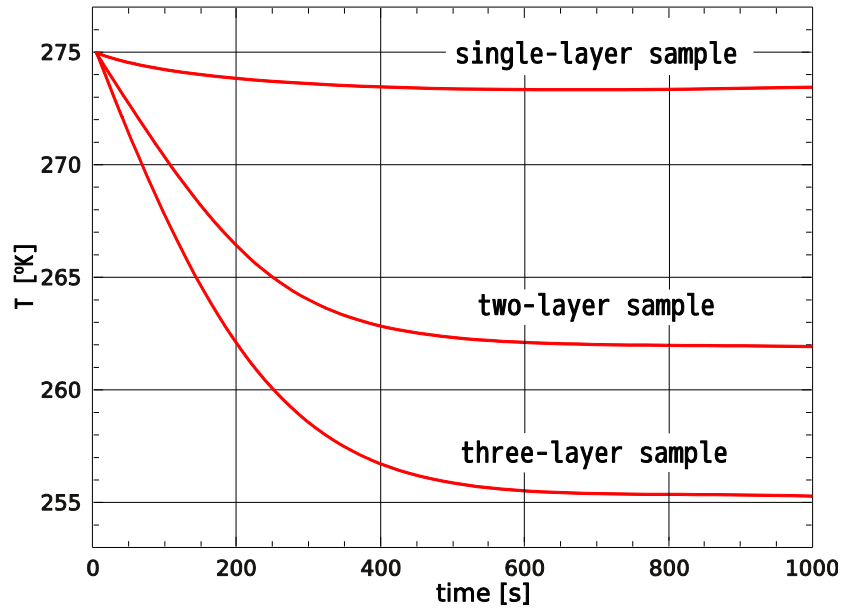

Figure 1. The simulation of the temperature dependence on number of involved cycles for a layered ferroelectric structure. The increase in the layers number results in a better refrigeration.

It is important that the process of changing of the external field described above can occur isothermally, which allows us to organize the most efficient thermodynamic cycle, i.e. the Carnot cycle. At the first stage the electric field is applied to the pre-compressed sample, which is warmed adiabatically. Within the second stage the external pressure is reduced to zero isothermally. The third stage presumes removal of the electric field, while during the fourth one the sample is compressed isothermally. The change of the sample temperature per cycle δT can be accurately calculated with the formulas (1), (5), (8). By choosing $\gamma_{cl} \approx 0.8 \gamma_{free}$ we find that $\delta T = 0.2 \, \Delta T$. This coefficient substantially exceeds the corresponding value at the absence of the periodical mechanical stress ($\delta T = 0.01$–$0.02 \, \Delta T$ for numerical calculations (Karmanenko et al., 2007), while experimentally δT is $0.05 \, \Delta T$ (Wiseman, 1969)). Thus, a consistent change of the electric field and external pressure can increase the ECE in 5–10 times. This fact provides an opportunity for practical realization of a high-performance solid-state cooling system.

Due to technological difficulties in the organization of the Carnot cycle, a simple case of periodic changes in the electric field and external force have to be considered:

$$E = E_0 \sin \omega t, \quad \sigma = \sigma_0 \sin(\omega t + \varphi) \text{,}$$

where E_0, σ_0 are the amplitudes, ω the frequency, φ the phase shift. Then one finds that $\gamma \approx \gamma_0 (1 + \gamma_1 \sin(\omega t + \psi))$ with the constants γ_0, γ_1, ψ. The time dependence of the sample temperature calculated for PMN-PT ceramics is shown in Fig. 2. One can see that the difference between initial and steady-state temperatures depends strongly on the phase shift. This difference is greater than the change of the sample temperature after a single application and removal of the field in 15–20 times.
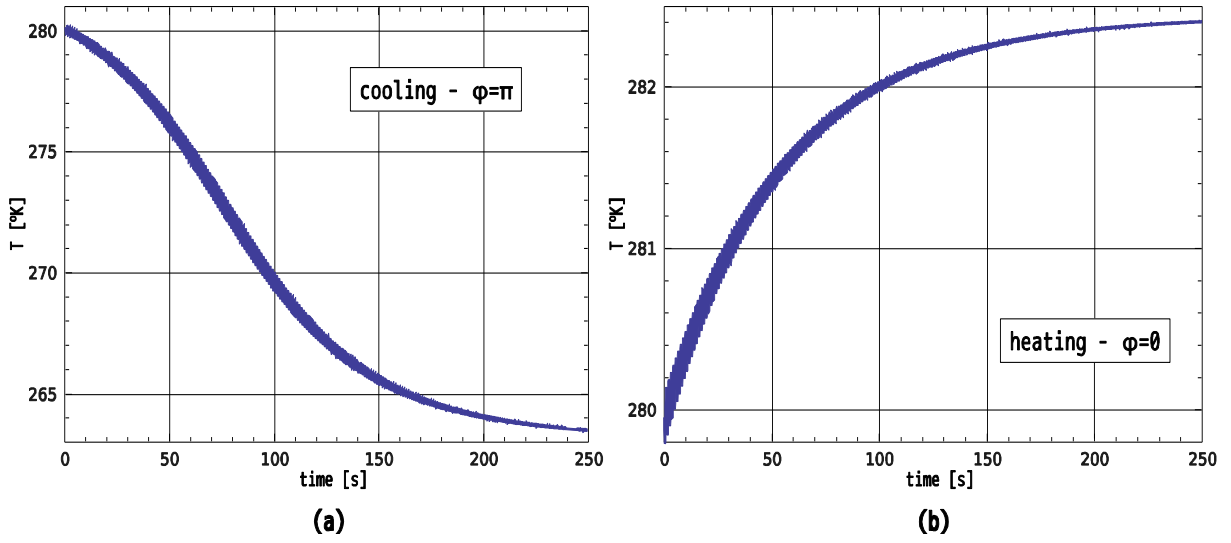
Figure 2. The time dependence of the sample temperature for (a) cooling
(the phase shift $\varphi = \pi$) and (b) heating (the phase shift $\varphi = 0$).

4. MULTICALORIC EFFECT

Describing possible types of interaction in a multiferroic, we'll neglect both flexoelectric effect and three other effects connecting one of the fields and the gradient of the other field. We'll issue from the following expression for free Gibbs energy of multiferroic (Kobeko and Kurtschatov, 1930; Strukov et al., 1998):

$$F = F_0(T) + \frac{a_I P^2}{2} + \frac{a_{II} P^4}{4} + \frac{a_{III} P^6}{6} + \frac{b_I M^2}{2} + \frac{b_{II} M^4}{4} + \frac{\overline{\overline{S}} U^2}{2} + \gamma \frac{M^2 P^2}{2} - \tag{10}$$
$$-U(\delta_P P^2 + \delta_M M^2) + \varepsilon U P - E P - H M - \sigma U.$$

Here are: $F_0(T)$ – the part of the free energy independing on the field; a_I, a_{II}, a_{III}, b_I, b_{II} – coefficients of Landau–Ginzburg; $\overline{\overline{S}}$ – coefficient of elasticity; γ – magnetoelectric coefficient; δ_p and δ_M – electro- and magnetostriction constants; ε – piezoelectric coefficient. When initiating polarization (magnetization), the sample is assumed to expand in the direction of polarization (magnetization); if it is so, δ_p, $\delta_M \geq 0$ (Kobeko and Kurtschatov, 1930). We neglect piezomagnetic and linear magnetoelectric effect following (Kobeko and Kurtschatov, 1930; Strukov et al., 1998), though it is enough to add some extra summands to (10) for their accounting, namely:

$$a_I = a_0(T - T_c), \ \overline{\overline{S}} = \overline{\overline{S}}_0 + \overline{\overline{S}}_1(T - T_c), \tag{11}$$

Here are: a_0 – Curie–Weiss constant; T_c – Curie temperature. The second equation in (11) is the ordinary linearization of temperature dependence of the coefficient of elasticity according to the law of Duhamel–Neumann which allows describing the effects of thermoelasticity.

As the temperature area close to the temperature of ferroelectric phase transfer is investigated we limit ourselves only by the first terms of the free energy development by M^2 and U. The availability of the summand with P^6 in (10) allows describing the phase transfers both of the first and the second type. While investigating multiferroic in the region of ferromagnetic or ferroelastic phase transfer, the free energy should be complemented with the higher orders of corresponding variables and the temperature dependence b_I should be taken into consideration.

First let's calculate some magnitudes needed for the further calculation:
entropy

$$S = -\frac{\partial F}{\partial T} = -F_0'(T) - \frac{a_0 P^2}{2} - \frac{S_1 U^2}{2}$$

and heat capacity with constants E, H, σ

$$C = -T\frac{\partial S}{\partial T} = -T(F_0''(T) + a_0 P\frac{\partial P}{\partial T} + \bar{\bar{S}}_1 U\frac{\partial U}{\partial T} \, .$$

According to Landau theory $F_0''(T)$ can be substituted for $F_0''(T_c) = -C_0$. Then the equation of adiabatic curve for multiferroic takes on form:

$$C_0 T - \frac{a_0 p^2}{2} - \frac{S_1 U^2}{2} = S_0 \, .$$

Here is S_0 – a certain constant.

For the ease of notation, let's work in new symbols. Intensive parameters or integrated forces E, H, σ we'll identify y_1, y_2, y_3 correspondingly. And extensive parameters or integrated coordinates we'll identify with x_1, x_2, x_3. For the description of nonequilibrium stage of the process we have the equation system:

$$\frac{\delta x_i}{\delta t} = -L_i \frac{\partial F}{\partial x_i} \, , \quad i = 1,2,3... \tag{12}$$

Here is L_i – kinetic coefficients. Since characteristic cycle time transcends the maximum relaxation time of three processes by some orders ($\approx 10^{-7} c$) we can substitute system (12) by the system of steady-state equations $\frac{\partial F}{\partial x_i} = 0$ which is written in the previous symbols as:

$$\begin{cases} E = (a_I + \gamma M^2 - \delta_P U)P + a_{II} P^3 + a_{III} P^5 + \varepsilon U; \\ H = (b_I + \gamma P^2 - \delta_M U)M + a_{II} M^3; \\ \sigma = sU - \delta_P P^2 - -\delta_M M^2 + \varepsilon P. \end{cases} \tag{13}$$

Now let's pass on to the equation derivation for temperature. For this purpose we'll consider the element exchanging with the environment according to the law or Newton: thermal current is proportional to temperature difference of the element and the environment:

$$T\frac{\partial S}{\partial t} = -k(T - T_r) \, . \tag{14}$$

Here k is the coefficient of heat-transfer; T_r – the environment temperature. System (13) is universal and equation (14) is characterized by the experimental conditions. Let's transform this equation having expressed all the magnitudes being part of it through extensive and intensive parameters. Taking into consideration the total differential formula

$$dS = \frac{\partial S}{\partial T}dT + \sum_{i=1}^{3}\frac{\partial S}{\partial y_i}dy_i \, ,$$

IIF-IIR Commission B2, A1 with E2

the equality $T\dfrac{\partial S}{\partial T}=C$ and Maxwell ratio $\dfrac{\partial S}{\partial y_i}=\dfrac{\partial x_i}{\partial T}$, we can rewrite equation (14) as:

$$C\frac{\partial T}{\partial t}+T\sum_{i=1}^{3}\frac{\partial x_i}{\partial T}\frac{\partial y_i}{\partial t}=-k(T-T_r).\tag{15}$$

For the unique definition of parameters equation system (13) should be supplemented with entry conditions:

$$T\big|_{t=0}=T_0,\ P\big|_{t=0}=P_0,\ M\big|_{t=0}=M_0,\ U\big|_{t=0}=U_0.\tag{16}$$

Initial data for temperature – T_0, for polarization – P_0, for magnetization – M_0 and for deformation – U_0 should be considered with each other, they should obey equation system (16): $E,H,\sigma=0$. When agreement is absent the system dynamics will be described with equations (12), (15).

Thus, dynamics of the cooling element is described with the system of three ordinary equations (13) and differential equation (15), where C – heat capacity (12). System (13), (15) should be solved jointly with the entry conditions (16) and given dependence of integrated forces on time $E=E(T)$, $H=H(t)$, $\sigma=\sigma(t)$.

Figure 3 shows numerical solution results of the given problem with the initial temperature of 280 K and the influence frequency of electric and magnetic field – 1 Hz. This results from the figure that the change of the phase shift size between the influence of the electric and magnetic field influences significantly on the temperature change dynamics. As a result, let's enumerate the main characteristics of multiferroic, needed for the construction of the solid cooler:

1. The phase transfer temperature is close to the room temperature or below it.
2. The evident thermal effect (not less than 1 K).
3. Not very small values of interaction coefficient (the contribution of the summands describing the interaction of different fields should exceed 1 %).
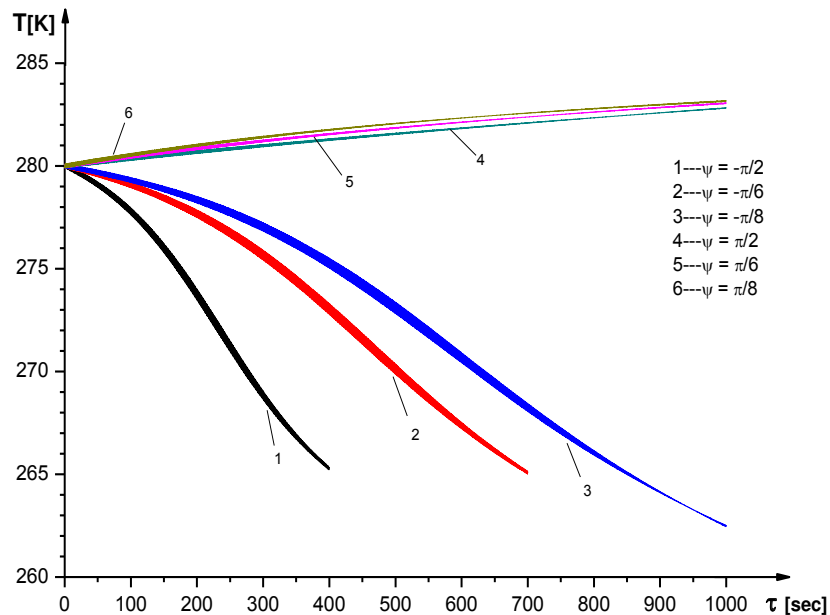

Figure 3. The temperature change results calculated when taking into account
the combined influence both of electric and magnetic fields with different phase shifts

When carrying out the enumerated conditions the problem of the solid cooler construction becomes solvable.

Unfortunately, at a point of time when the article was written in literature there was no description of multiferroics possessing all the enumerated characteristics though the certain characteristics were in existence which allows to hope to create such multiferroics in the nearest future.

5. CONCLUSION

We have suggested an approach for reinforcement of the electrocaloric effect in order to refine the cooling parameters of refrigerator, which is designed on multiferroics. This work has presented basic physical ideas how to improve the solid-state cooler parameters. These ideas are supported by calculations, thereby making them vital. One of the advantages of the presented approach is its generality, i.e. (6) in this form may be applied to piezomagnetics where the external force σ is pressure induced by the external magnetic field. Also (6) can be adopted for the case of the barocaloric effect where σ is the electric field. Another thinkable measure how to make the ECE more prominent is employment of the second piezoelectric layer. Further progress in the development and use of solid-state coolers operating on the basis of the caloric effect depends largely on the creation of novel (e.g. multiferroic) materials for which the caloric effect depends not only on the basic physical quantities (temperature and electric field for the ECE), but also on any other additional parameter (magnetic field, mechanical stress, and etc).

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