Ferroelectrics

Solid-State Cooler: New Opportunities

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The main physical ideas behind the development of the novel solid-state cooling system have been summarized. The basic strategy relies on strengthening of the electrocaloric effect. We show that for this purpose additional piezoelectric layers or new multiferroic materials can be used as a practical realization. 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 [1, 2]. 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 [2, 3]. 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 [3–8]. The first experimental observations of the ECE were held in 1930 at the Rochelle salt [9]. The further studies of various materials have led to the temperature change due to the ECE only by $\Delta T = 2.3$ K [3]. 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 kV/cm, ΔT of 12 K was achieved [4]. 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 kV/cm [5].

2. Features of the Electrocaloric Effect Theoretical Description

The basic formula describing the ECE is derived by Thompson [10]

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

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 [11]. In this case the polarization dependence on the electric field is given by

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

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 [12]. Experimentally observed polarization hysteresis (obtained at a periodic variation of the electric field) [4] suggests that dynamic effects have to be taken into account. In other words, the Eq. (2) should be replaced by the Landau-Khalatnikov equation [12]

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

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

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

where P_{st} is the quasi-static part of the polarization defined by the Eq. (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 [4, 8].

The adiabatic equation for the Landau-Ginzburg model is [13]

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

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 [3, 8]. As a consequence, the Eq. (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 [12].

3. Electrocaloric Effect Reinforcement 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 magneto-electric effect) or the mechanical stress (with piezoelectric or piezomagnetic effects as the driving force) can play role of this parameter. The free energy is [11]

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

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 $a, b, \alpha, \beta, \sigma, \eta$ 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 Eq .(7) describes the usual Hooke's law. Eliminating η from the second Eq. (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 [14] 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 [15].

Quite similarly, the pressure can be used as an effective control parameter for the MCE. As shown in [16], for single La$_{0.69}$Ca$_{0.31}$MnO$_3$ crystals, an 1GPa 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 [17], taking into account non-uniformities in
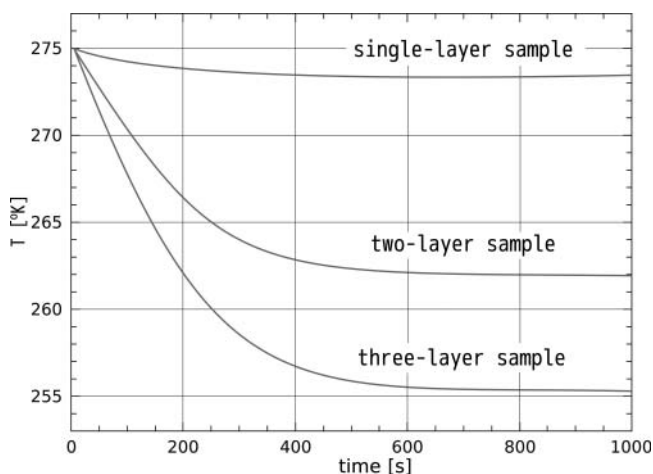
Figure 1. The simulation of the temperature dependence on number of involved cycles for a layered ferroelectric structure. The increase in the layers number results in a better refrigeration.

the temperature distribution and the surface effect of layer boundaries, confirm this idea. Thus, according to [17], 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 [2, 3], and switches based on micro-electromechanical systems (MEMS) and the Peltier elements [18, 19] 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 [20] or using of schemes without thermal key [17, 21, 22] 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 [21, 22]. 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 [6] 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 $\Delta T = 0.046$ K. As a result, the total change in temperature per cycle is 0.003 K. This tendency was qualitatively predicted in [7].

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.
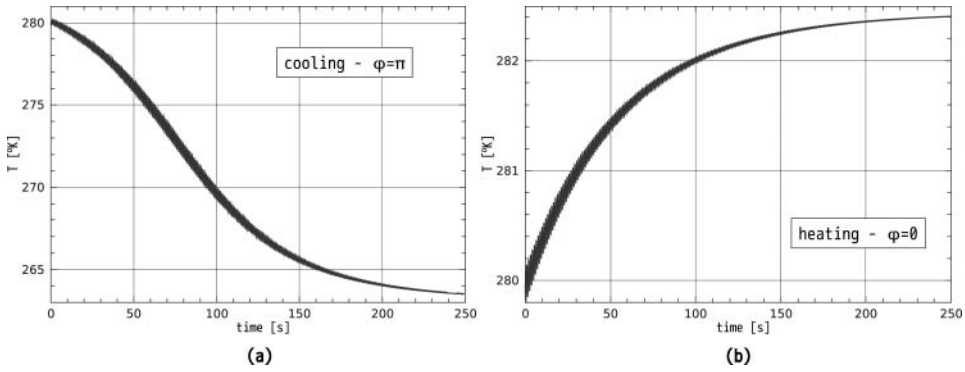
Figure 2. The time dependence of the sample temperature for (a) cooling (the phase shift $\varphi = \pi$) and (b) heating (the phase shift $\varphi = 0$).

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 ($\delta T = 0.01\Delta T$–$0.02\Delta T$ for numerical calculations [21], while experimentally δT is $0.05\Delta T$ [6]). 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:

$$E = E_0 \sin \omega t, \quad \sigma = \sigma_0 \sin(\omega t + \varphi), \tag{9}$$

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.

3. 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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