

Parametric Enhancement of Electrocaloric Effect by Periodically Varying External Field

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Abstract—The mutual influence of an external electric field and mechanical stresses on the electrocaloric effect has been studied. Under certain conditions, the varying external field produces parametric enhancement of the electrocaloric effect. Using this phenomenon, it is possible to realize the Carnot cycle in ferroelectric energy converters and solid-state coolers.

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In view of the tendencies to miniaturization and increasing power of electronic devices, the problem of their cooling and thermostating is topical. Among various cooling and thermostating technologies, of special interest are those based on the use of magnetocaloric and electrocaloric (EC) effects [1–7]. The main advantage of the EC effect is the possibility of directly converting heat into electricity. The basic equation of the EC effect, which has been derived in 1878 by W. Thomson, can be written as follows [8]:

$$C_E dT = -T \partial P / \partial T dE, \quad dT = \gamma dE, \quad (1)$$

where T is the absolute temperature, P is the polarization, E is the electric field strength, C_E is the heat capacity at a constant field strength, and γ is the EC coefficient

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

It follows from Eq. (1) that the maximum change in the temperature takes place in a region of maximum pyroelectric coefficient $p = \partial P / \partial T$. For ferroelectrics, this is a region of temperatures close to the Curie point T_C , where the Landau–Ginzburg theory of second-order phase transitions is applicable. According to this theory, the polarization as a function of the field strength can be expressed as follows:

$$E = aP + bP^3, \quad (2)$$

where $a = a_0(T - T_C)$, a_0 is the Curie–Weiss constant, and b is the coefficient of nonlinearity. A maximum change in the temperature upon a single application or removal of the field, $\Delta T = 40$ K, was observed for a 450-nm-thick $\text{Pb}_{0.88}\text{La}_{0.08}\text{Az}_{0.65}\text{Ti}_{0.35}\text{O}_3$ film at a field strength of 1250 kW/cm. It should be noted that a comparison of the two sides in the Thomson formula (1) for the available experimental data shows

that the right side is 10–15% larger than the left side [5, 7]. This fact has been recently explained in [9].

Determination of polarization P is based on the measurement of a hysteresis curve during cyclic variation of the field strength. In this case, it is necessary to take into account the dynamic effects and replace relation (2) by the Landau–Khalatnikov equation:

$$r \frac{\partial P}{\partial T} = E - aP - bP^3, \quad (3)$$

where r is the effective “internal” resistance. For small r , the polarization can be expressed as follows [10]:

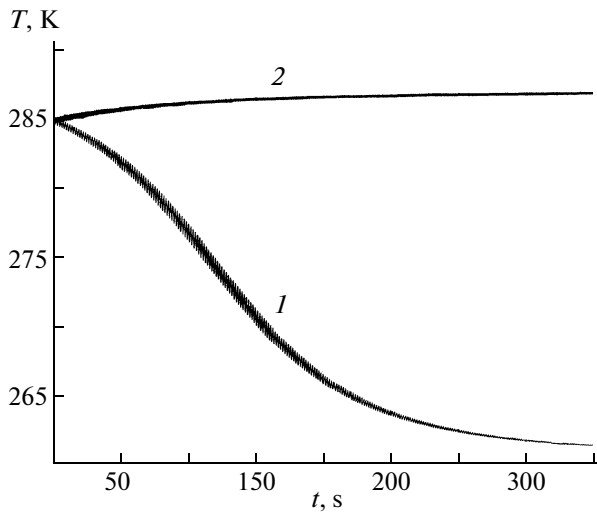
$$P = P_{\text{st}} + P_{\text{dyn}}, \quad P_{\text{dyn}} = -\frac{r}{a + 3bP_{\text{st}}^2} \frac{\partial P_{\text{st}}}{\partial t}, \quad (4)$$

where P_{st} is the quasi-static polarization determined from Eq. (2) and P_{dyn} is the dynamic correction that accounts for an increase in ΔT in the case of indirect measurements. The adiabatic equation in the Landau–Ginzburg theory is written as follows [3]:

$$T - T_0 = \frac{a_0}{\kappa} (P^2 - P_0^2), \quad (5)$$

where κ is a constant quantity and T_0 and P_0 are the initial temperature and polarization, respectively. The validity of Eq. (5) has been repeatedly confirmed (see, e.g., [3–7]). Thus, Eq. (2) is applicable to the description of quasi-static processes, while the dynamic processes should be described using Eq. (3). In the immediate vicinity of the Curie point, the left-hand side of this equation should be additionally refined by adding terms describing the pyroelectric and piezoelectric currents [10].

The problem encountered in creating coolers is the organization of a thermodynamic cycle. Under the adiabatic conditions, the overall change of the temperature upon the application and removal of electric



Temporal variation of the temperature of PMN-PT ceramics in response to periodic oscillations of the applied electric field and mechanical stress with a relative phase shift of (1) $\varphi = \pi$ and (2) $\varphi = 0$.

field is zero. Therefore, it is necessary to implement non-adiabatic processes (isothermal, or those with constant E or P). The adiabaticity can be violated, e.g., by using thermal switches or taking into account heat exchange with the environment and the inhomogeneity of the temperature field in a sample [1, 2, 11, 12]. For example, the results of numerical calculations for BaSrTiO₃ (BST) [11, 12] showed that, after 1000 switching cycles, the system attains a steady-state regime, in which the temperature oscillates about the average value that is 20 K below the initial temperature. The measurements of temperature during periodic variation of the electric field were performed by Wiseman [3]. In the first cycle, the application of the electric field led to an increase in the sample temperature by 0.043 K, while switching the field off led to a decrease in the temperature by 0.046 K, so that the total temperature change per cycle was $\delta T = 0.003$ K. This dependence has been qualitatively predicted by Lawless [4]. The EC effect can be increased by using multilayer structures. In particular, it was shown in [13] that, for a switching frequency of 1 Hz, the second layer of an EC material increases the EC effect in BST ceramics by 2.5 K.

In the present investigation, we have used the dependence of polarization P on an auxiliary parameter, which can be represented by a magnetic field (magnetoelectric effect) or a mechanical stress. Let us consider the free energy functional of the following type:

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

where $F_0(T)$ is a certain function of the temperature, η is the second (in addition to P) order parameter, σ is an

external field, and α and β are constant coefficients. In what follows, η implies deformation and σ denotes elastic stress, so that β is the elastic modulus and α is the piezoelectric modulus. Note that, for crystals, α , β , η , and σ are tensor quantities [14]. The free energy given by expression (6) describes a piezoelectric effect that is quadratic with respect to polarization P .

Writing the condition of minimum for the free energy according to Eq. (6) yields the following system of equations:

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

from which the order parameters P and η are determined as functions of the known variables E and σ . For $\alpha = 0$, the second equation of system (7) describes the usual Hooke's law. Excluding η from this equation, we obtain the following relation:

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

which determines the dependence of polarization P on E , η , and σ . The entropy and heat capacity of the system are determined as follows:

$$S = -\frac{\partial F}{\partial T}, \quad C_E = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_E.$$

Denoting $F_0''(T) = k$, we obtain the following expression for the EC coefficient:

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

According to the above formulas the EC coefficient γ depends on stress σ .

According to the results of calculations [15], the EC effect in compressed (clamped) BST ceramics is characterized by $\gamma_{cl} \approx 0.6\gamma_{free}$, where γ_{cl} and γ_{free} are the EC coefficients for the clamped and free ceramics. For BaTiO₃, the analogous relation is $\gamma_{cl} \approx 0.8\gamma_{free}$ [5]. It is important to note that the process of external field variation can be isothermal (with neglect of the barocaloric effect), which makes it possible to organize the most effective thermodynamic cycle, a four-stage Carnot cycle. First, the electric field is applied to a preliminarily clamped sample, and the sample is adiabatically heated. At the next stage, the external pressure is isothermally reduced to zero. At the third stage, the electric field is switched off. Finally, the sample is isothermally clamped. The resulting change δT in the sample temperature per cycle can be exactly calculated using formulas (1), (5), and (8). It can also be qualitatively estimated through ΔT . Adopting the ratio of $\gamma_{cl}/\gamma_{free} = 0.8$, we obtain $\delta T = 0.2\Delta T$, which significantly exceeds the corresponding value in the absence of a control mechanical stress. Indeed, $\delta T = (0.01 - 0.02)\Delta T$ according to numerical calculations [11–13] and $\delta T = 0.05\Delta T$ according to experimental data [3].

Since the organization of a Carnot cycle is technically difficult, let us consider a simpler case of period-

ically varying applied electric field and mechanical stresses:

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

where E_0 and σ_0 are the amplitudes, ω is the frequency, and φ is the phase shift. In this case, the EC coefficient can be expressed as follows:

$$\gamma \approx \gamma_0(1 + \gamma_1 \sin(\omega t + \varphi)), \quad (10)$$

where γ_0 , γ_1 , and ψ are constant (time-independent) parameters. The results of a numerical solution of Eqs. (1) and (10) for a lead magnesium niobate–lead titanate (PMN–PT) ceramics are presented in the figure. As can be seen, a difference between the initial and steady-state temperatures strongly depends on the phase shift, and both heating and cooling of the ceramic sample can take place.

Thus, by consistently varying the electric field and external pressure, it is possible to ensure a five- to tenfold increase in the EC effect. The same approach can be used to enhance the magnetocaloric effect. It was demonstrated [16] that a 1 GPa pressure applied to $\text{La}_{0.69}\text{Ca}_{0.31}\text{MnO}_3$ single crystals increases the phase transition temperature by 25 K, thus decreasing the magnetocaloric effect to less than half.

Finally, it should be noted that there are different variants in selecting the order parameter η and external force σ . In piezomagnetism, it is possible to develop pressure by applying a magnetic field. The pressure can also be produced using the second layer of a piezoelectric, to which voltage E_2 is applied consistently with E . Another possible variant employs the barocaloric effect controlled by the electric field. In addition, it is possible to use multiferroics, in which the caloric effect not only depends on the main parameters (temperature and field strength), but can also be modulated by some other parameter.

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