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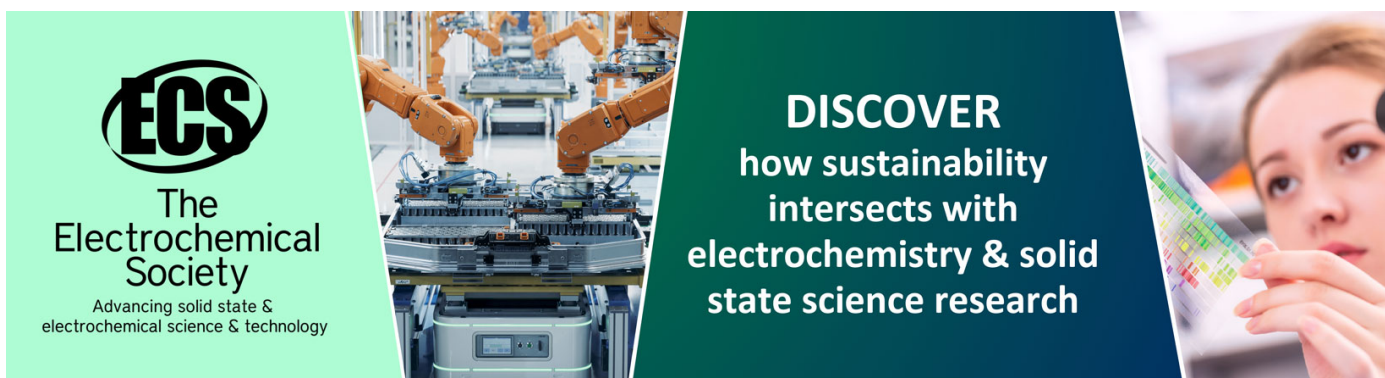
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Multicaloric effect in barium titanate nanotube

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Abstract. One of the characteristic features of multiferroic materials is the dimensional effect, when the physical properties of a sample depend on its size. To describe this effect, it is necessary to take into account not only the basic physical quantities: the electric field, polarization, strain tensor, stresses, temperature, but also their spatial derivatives (gradients). In this case, both the order of differential equations describing the behaviour of the sample and the number of boundary conditions increase. As a result, a surface layer appears near the boundary, in which the above-mentioned physical quantities change abruptly. The thickness of this layer is 1-5nm. The properties of a similar layer for a barium titanate nanotube and its effect on its thermal properties are investigated. It is shown that as the nanotube size decreases, the multicaloric effect (μ CE) increases. At a nanotube thickness of 5nm μ CE is 3 times greater than the effect for bulk materials.

1. Introduction

Caloric effects (CEs) consist in changing the temperature or entropy of the sample when the field is applied or removed. The main caloric effects are the magnetocaloric, electrocaloric (ECE), and elastocaloric ones which correspond to the influence of a magnetic, electric, and elastic field, respectively. The magnitude of CEs is determined by the temperature dependence of the magnetic, electric, or elastic constants. The greatest values are achieved near phase transitions, where the temperature dependence of the above coefficients is especially significant. If a change in thermal properties of a sample depends on several fields, then the presence of the multicaloric effect (μ CE) [1] is indicated. Interaction of fields of different nature can lead to a significant increase in magnitude of CEs (synergistic phenomena) and μ CE can exceed single components. Since this interaction increases with a decrease in the dimensions of the sample, a multiple increase in μ CE should be expected for nanometer-scale objects. One of the possibilities of this interaction is the flexoelectric effect (FEE). Direct FEE is the occurrence of polarization due to inhomogeneous strain. The inverse FEE is defined as the appearance of a strained bending of a thin plate when it is polarized. Experiments carried out on BaTiO₃ single crystals (size of the order of tens of micrometers) confirmed the existence of both direct and inverse FEE [2].

The dependence of the flexoelectric coefficients on temperature results in the appearance of a flexocaloric effect (FCE), as first predicted in [1]. According to the calculations for the PMN ceramics with a strain gradient of 1m^{-1} , the temperature change in the FCE depends on the ambient temperature



and varies from $5\mu\text{K}$ at $T=240\text{K}$ to $-6\mu\text{K}$ at $T=299\text{K}$. Calculations based on a first principles approach confirmed the existence of FCE in the barium strontium titanate (BST) ceramics [3]. The effect is 1.5K at $T = 289\text{K}$ under the application of a strain gradient of $1.5\mu\text{m}^{-1}$. The highest known value of FCE is 60K and it was obtained as a result of calculations for BST ceramics. However, it is reached in a layer of thickness on the order of 1nm [4]. In this case the magnitude of the FEE is determined by enormous values of the strain gradient (10^6 - 10^7m^{-1}) because of the presence of a misfit strain existing at the boundaries of two crystals with different atomic lattice constants. From the results reported in literature, it follows that the FCE increases with decreasing film thickness. For instance, the magnitude of flexocaloric effect is less than 1% of the electrocaloric effect for BST film of 100nm thickness. In turn, the values of FCE and ECE coincide for 16nm films, while FCE already exceeds ECE by 3 times for thin 5nm films.

When describing any physical phenomena in nanoscale multiferroic materials, one should take into account not only the basic physical quantities: the electric and magnetic field strengths, polarization and magnetization, the strain and strain tensor, temperature, but also their spatial derivatives (gradients). A theory that takes into account the gradients of deformation in elastic bodies was developed in the mid-sixties of the last century [5]. A general theory describing the joint action of electric, magnetic, elastic, and thermal phenomena with allowance for gradient terms near phase transitions has been developed in recent years by a number of authors (see, for example, [2,6,7]). The equations of state of these materials, as a rule, are derived on the basis of variational principles from the condition of minimality of the thermodynamic potential W . The boundary conditions, according to the calculus of variations, must also be determined by the same potential.

In the presence of four fields (electric, magnetic, elastic, and thermal) there are altogether 10 gradient effects. This makes it difficult to estimate them accurately. In view of this, in order to simplify the subsequent calculations, we exclude from consideration the magnetic field and the temperature gradients. The magnetic field can be taken into account just as an electric field. For nonlinear ferroelectrics, both the gradients of the electric field strength and the polarization or electric-displacement gradients can be considered. However, in the sequel we confine ourselves to the case of only the presence of the polarization gradient in W . Besides, it is natural to assume that the thermodynamic potential, which is a scalar quantity, does not include the polarization itself, but its square. As a result, there are 3 gradient effects. The contribution to W of these effects is given by the squares of the gradients of the components of the polarization vector and the strain tensor, as well as products of the gradients of these quantities. Since the 3 gradient effects depend on the temperature, they must contribute to the entropy or temperature of the sample. This means that there are 3 caloric effects associated with gradient phenomena, which we will call gradient-caloric. As an example of the application of the new model, μCE in a barium titanate nanotube is investigated.

2. The approach

Let us describe a sample occupying the volume V bounded by the surface S . For such a purpose, we use the energy density w and introduce displacement vectors $\mathbf{u}$ with components u_i , ($i = 1, 2, 3$), and the potential φ . In the usual way, we define the electric field $E = -\varphi_{,i}$, the strain tensor $u_{ij} = (u_{i,j} + u_{j,i})/2$, and the gradient of deformations $v_{ijk} = u_{k,ij}$. Hereinafter, the subscript after the comma means differentiation with respect to the corresponding variable in the Cartesian coordinate system x_1, x_2, x_3 . We believe that the energy density w , in addition to the electric field E_i , depends both on the strain tensor u_{ij} and on its gradient v_{ijk} . Moreover, it is assumed that w depends on the polarization components P_i and their derivatives $P_{i,j}$. Then the total energy W stored in the volume V has the form

$$W \equiv \int_V w(u_{ij}, v_{ijk}, E_i, P_i, P_{i,j}) dV. \quad (1)$$

The equation (1) means that the sample under consideration has both elastic and electrical properties that depend not only on the deformation and the electric field, but also on the gradients of deformation

and polarization. Such a medium for brevity will be called the gradient-electroelastic. Varying (1) leads to the relation

$$\delta W = \int_V (\sigma_{ij} \delta u_{ij} + \tau_{ijk} \delta v_{ijk} + D_i \delta E_i + \frac{\partial w}{\partial P_i} \delta P_i + J_{ij} \delta P_{i,j}) dV, \quad (2)$$

in which σ_{ij} , τ_{ijk} , D_i , J_{ij} are, respectively, the stress tensor, the higher-order strain tensor [5], the electric displacement, and the conjugate quantity

$$\sigma_{ij} = \frac{\partial w}{\partial u_{ij}}, \quad \tau_{ijk} = \frac{\partial w}{\partial v_{ijk}}, \quad D_i = \frac{\partial w}{\partial E_i}, \quad J_{ij} = \frac{\partial w}{\partial P_{i,j}}. \quad (3)$$

In (2),(3) we use the Einstein summation convention, whereby we agree to sum over repeated indices. Note that the variables σ_{ij} , τ_{ijk} , D_i , J_{ij} and u_{ij} , v_{ijk} , E_i , $P_{i,j}$ are generalized forces and coordinates conjugated to one another – the generalized forces are associated with the generalized coordinates. Using the Ostrogradskii-Gauss theorem allows one to transform the volume integrals in (2) to surface integrals

$$\begin{aligned} \delta W = \int_V & \left[(\sigma_{jk,j} - \tau_{ijk,ij}) \delta u_k + D_{i,i} \delta \varphi + \left(\frac{\partial w}{\partial P_i} - J_{ij,j} \right) \delta P_i \right] dV + \\ & + \int_S [(\sigma_{jk} - \tau_{ijk,i}) n_j \delta u_k + \tau_{ijk} n_i \delta u_{k,j} + D_j n_j \delta \varphi + J_{ij} n_j \delta P_i] dS, \end{aligned} \quad (4)$$

where n_j are the components of the normal vector to S . The extremality condition (1), according to (4), gives us the equations

$$\varsigma_{jk,j} = 0, \quad D_{i,i} = 0, \quad \frac{\partial w}{\partial P_i} = J_{ij,j}, \quad (5)$$

in which the generalized stress ζ_{jk} is defined by the equality $\zeta_{jk} = \sigma_{jk} - \tau_{ijk,i}$. To obtain the boundary conditions, we emphasize that the quantities $\delta u_{k,j}$ cannot be considered independent, since they are determined by the values δu_k on the surface S . In view of this, we represent $\delta u_{k,j}$ as

$$\delta u_{k,j} = d_j^\parallel \delta u_k + n_j d^\perp \delta u_k, \quad (6)$$

i.e. decompose the derivative into the normal and tangential components [5-6]

$$d^\perp \equiv n_k \frac{\partial}{\partial x_k}, \quad d_j^\parallel \equiv (\delta_{jk} - n_j n_k) \frac{\partial}{\partial x_k}, \quad (7)$$

where δ_{jk} is the Kronecker symbol. After substituting (6) in (4) and taking into account (5), the surface part of the total energy variation δW_{us} containing δu_{jk} can be written out from (4) as

$$\delta W_{us} = \int_S (T_k \delta u_k + R_k d^\perp \delta u_k) dS. \quad (8)$$

Here we use the notation

$$T_k \equiv n_i \varsigma_{ik} + n_i n_j \tau_{ijk} (d_i^\parallel n_l) - d_j^\parallel (n_i \tau_{ijk}), \quad R_k \equiv n_i n_j \tau_{ijk}. \quad (9)$$

From (8), it follows that the following 20 boundary conditions must be satisfied at the interfaces of the flexoelectrics:

$$[\varphi] = 0, \quad [u_k] = 0, \quad [P_k] = 0, \quad [d^\perp u_k] = 0, \quad [R_k] = 0, \quad [T_k] = 0, \quad [n_k D_k] = 0, \quad [n_k J_{ik}] = 0. \quad (10)$$

The symbol $[X]$ denotes the jump in the quantity X when passing through the interface. The first three conditions are the standard continuity of the potential, displacements, and polarization. Continuity of the normal component of the electric displacement $n_k D_k$ is also included in the ordinary boundary conditions of electrostatics. The continuity condition of T_k is a generalization of the continuity condition for $n_i \sigma_{ij}$ in the usual theory of elasticity. New are the conditions of continuity for $d^\perp u_k$ and R_k . Thus, the electroelastic field in a flexoelectric must satisfy 5 equations (5), 20 conditions on the internal interfaces of media (10) and 10 conditions on the outer boundaries, which can consist of the specification u_k , $d^\perp u_k$, φ , P_i or T_k , R_k , n_k , D_k , $n_k J_{ik}$, or a combination of the listed conditions. In particular, in accordance with (9), the following equalities must be satisfied on the external free boundaries

$$n_k D_k = 0, \quad T_k = 0, \quad R_k = 0, \quad n_k J_{ik} = 0. \quad (11)$$

We emphasize that the above derivation of equations and boundary conditions does not depend on the form of w . It is a generalization to the case of a flexoelectric of a similar derivation for an elastic body [5].

For the thermal properties description, we assume that the energy (1) depends also on the temperature T . Then the specific entropy $s = -\partial w / \partial T$ and the total entropy $S = -\partial W / \partial T$ are determined in a standard manner. Variation of entropy occurs by analogy with the variation of energy and gives us

$$\begin{aligned} \delta S = & \int_V \left[\left(\frac{\partial \sigma_{jk}}{\partial T} \right)_{,j} - \left(\frac{\partial \tau_{ijk}}{\partial T} \right)_{,ij} \right] \delta u_i - \left(\frac{\partial D_i}{\partial T} \right)_{,i} \delta \varphi - \left(\frac{\partial^2 w}{\partial P_i \partial T} - \frac{\partial J_{ij,j}}{\partial T} \right) \delta P_i \right] dV - \\ & - \int_S \left[\left(\frac{\partial \sigma_{jk}}{\partial T} - \frac{\partial \tau_{ijk,i} n_j}{\partial T} + \frac{\partial T_k}{\partial T} \right) \delta u_k + \frac{\partial R_k}{\partial T} d^\perp \delta u_k + \frac{\partial D_j n_j}{\partial T} \delta \varphi + \frac{\partial J_{ij} n_j}{\partial T} \delta P_i \right] dS. \end{aligned} \quad (12)$$

It is important to underline that the relation (12) is derived for the first time and allows determining all the thermal characteristics of the gradient-electroelastic medium. One may conclude that there are 2 types of caloric effects – volume and surface. Surface effects, if we neglect the temperature dependence of the normal vectors, do not give a contribution to the change in entropy for free boundaries (when (11) is fulfilled). Such a contribution exists for a fixed boundary. In addition to volume and surface caloric effects, dynamic effects due to the time dependence of the variables occurring in w must also exist by analogy with the FEE [2]. To take them into account, we should add time derivatives to (1). Nonetheless, we will not do this in this study since dynamic CE's deserve consideration in a separate article.

3. Multicaloric effect in barium titanate nanotube

As a simple example of using the equations derived above, let us consider the problem of calculating the electroelastic field in a nanotube from a gradient-electroelastic material – barium titanate. We denote the internal radius by R_1 , the outer radius by R_2 , and the height of the nanotube by H . We use a cylindrical coordinate system r, θ, z , whose origin is located in the center of the bottom base (see figure 1(a)). The electric potential is equal to 0 at the bottom base and to the given value V at the upper base (for $z = H$). On the outer boundary (at $r = R_2$) we will consider the given mechanical pressure p . The internal pressure is set to 0. The remaining boundary conditions are considered to be free (11). Because of the axial symmetry of the problem, only the components of the displacement vectors u_r, u_z and the polarizations P_r, P_z are different from 0. The energy density in the model under consideration can be written in the form

$$w = w_{\text{LGD}} + w_{\text{elast}} + w_{\text{str}} + w_{\text{grad}}, \quad (13)$$

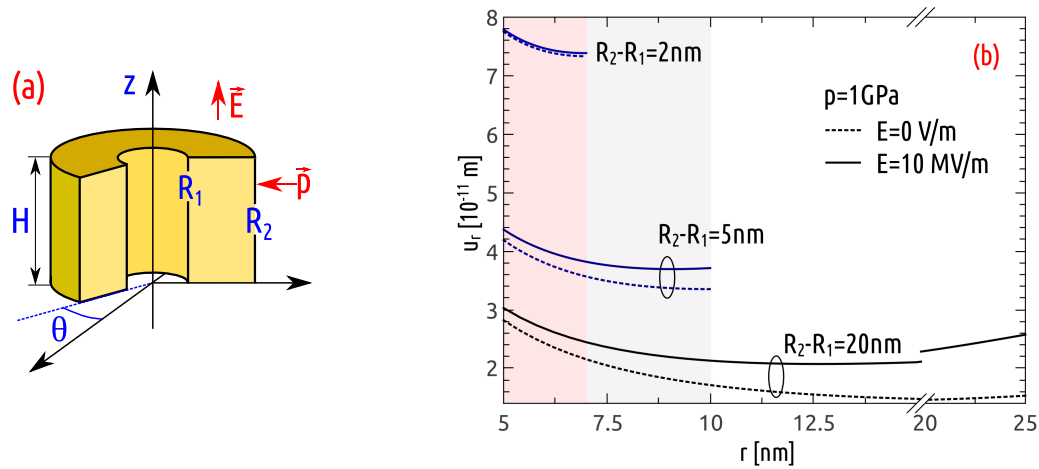


Figure 1. (a) The barium titanate nanotube under consideration. **(b)** The coordinate dependence of the displacement u_r for different values of nanotube thickness.

where

$$w_{\text{electr}} = a_1(P_1^2 + P_2^2 + P_3^2) + a_{11}(P_1^4 + P_2^4 + P_3^4) + a_{12}(P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) + a_{111}(P_1^6 + P_2^6 + P_3^6) + a_{112}[P_1^4(P_2^2 + P_3^2) + P_2^4(P_1^2 + P_3^2) + P_3^4(P_1^2 + P_2^2)] + a_{123}P_1^2 P_2^2 P_3^2, \quad (14)$$

$$w_{\text{elast}} = \frac{1}{2}c_{11}(u_{11}^2 + u_{22}^2 + \sigma_{33}^2) + c_{12}(u_{11}u_{22} + u_{11}u_{33} + u_{22}u_{33}) + \frac{1}{2}c_{44}(u_{32}^2 + u_{13}^2 + u_{12}^2), \quad (15)$$

$$w_{\text{str}} = q_{11}(u_{11}P_1^2 + u_{22}P_2^2 + u_{33}P_3^2) + q_{12}(u_{11}(P_2^2 + P_3^2) + u_{22}(P_1^2 + P_3^2) + u_{33}(P_2^2 + P_1^2)) + q_{44}(u_{23}P_2P_3 + u_{13}P_1P_3 + u_{12}P_1P_2). \quad (16)$$

$$w_{\text{grad}} = f_{ijkl}(u_{ij}P_{k,l} - u_{ij,l}P_k) + g_{ijkl}P_{k,l}P_{i,j} + h_{ijklmn}u_{ij,k}u_{lm,n}. \quad (17)$$

Here a are the Ginzburg-Landau coefficients, c_{ij} are the elastic constants/moduli of elasticity, q_{ij} are the coefficients of electrostriction, f_{ijkl} , g_{ijkl} , h_{ijklmn} are the gradient coefficients. Calculation results for solving the equations (5) with the above boundary conditions are presented in figures 1(b), 2.

4. Conclusion

The model outcome allows us to draw several important conclusions. Among them is the fact that the multicaloric effect in nanometer-sized samples can significantly (several times) exceed the effect in structures larger than 1mm. The latter finding can be used for creating a chip-size solid-state cooler as the obtained values of the temperature change for the multicaloric effect are sufficient for the operation of the device. The attention of the study has been directed toward the flexocaloric effect. As the nanotube size decreases, the FCE increases. Moreover, the flexocaloric effect can be either positive or negative and strongly dependent on the direction of the strain gradient. The difference can reach dozens of times. In this study we have considered only the strain gradient in the radial direction. The sign and magnitude of FCE may be different for other directions.

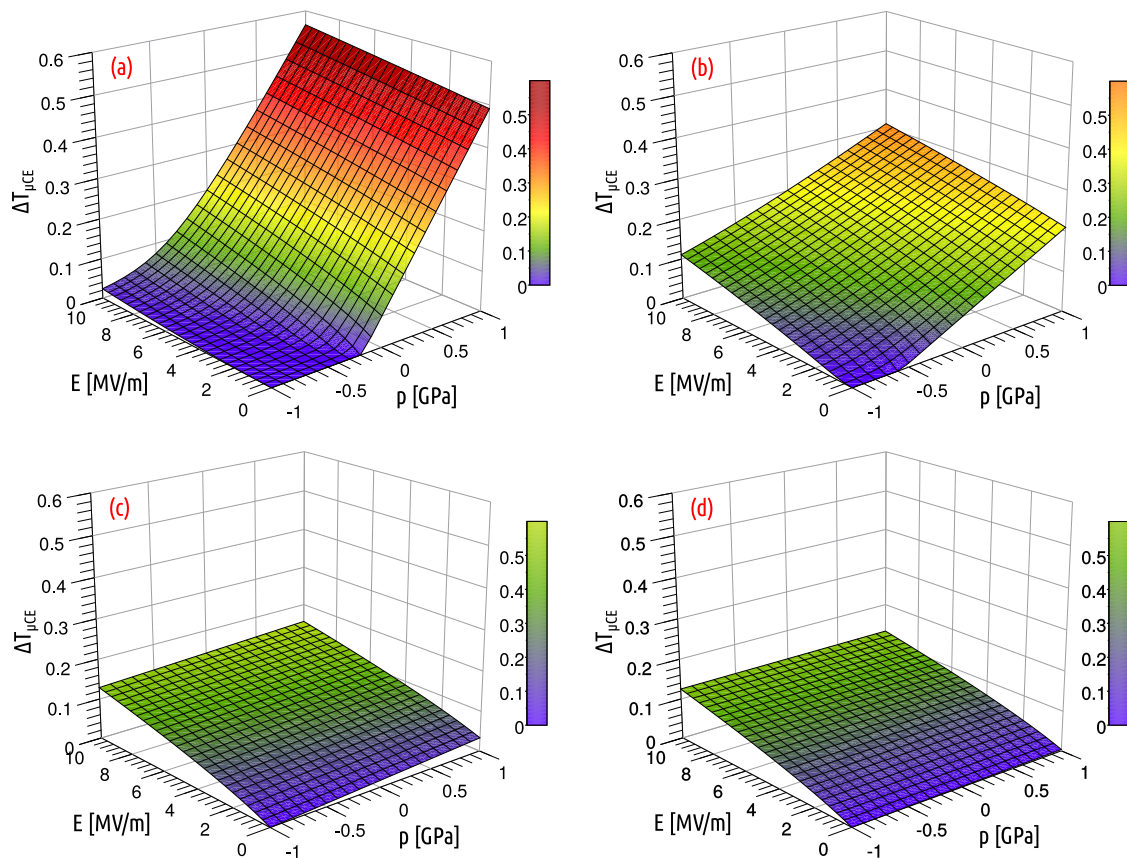


Figure 2. The temperature change in the multicaloric effect for a barium titanate nanotube **(a)** 2nm, **(b)** 5nm, **(c)** 20nm, and **(d)** 50nm thick.

Acknowledgments

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