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Caloric and Multicaloric Effects in Oxygen Ferroics and Multiferroics

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Abstract—The main problems of the current state-of-the-art research into the caloric effects observed in oxygen ferroics, multiferroics, and composites, as well as the influence of different factors (anisotropy, dimensional parameters, direct and indirect interferroic interactions) on these effects, have been considered. Possible ways to increase the caloric efficiency of materials have been analyzed.

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1. INTRODUCTION

Among the wonderful properties exhibited by ferroic materials (ferroelectrics, ferromagnets, ferroelastics), a special place is occupied by caloric effects (CE) associated with a reversible change in the entropy and temperature of the system in response to external fields (electric field E , magnetic field H , mechanical stress σ , or hydrostatic pressure p) under isothermal and adiabatic conditions, respectively. In accordance with the physical nature, the caloric effects are divided into the electrocaloric effect (ECE), magnetocaloric effect (MCE), and barocaloric effect (BCE). The changes in the extensive caloric effect ΔS_{CE} and in the intensive caloric effect ΔT_{AD} are determined by the external field strength Y and the temperature derivative of the conjugate order parameter X (polarization P , magnetization M , and linear r or volumetric deformation $\Delta V/V$) [1]:

$$\Delta S_{\text{CE}} = \int \left(\frac{\partial X}{\partial T} \right)_Y dY, \quad (1)$$

$$\Delta T_{\text{AD}} = - \int \frac{T}{C_Y} \left(\frac{\partial X}{\partial T} \right)_Y dY. \quad (2)$$

Here, C_Y is the heat capacity of the ferroics in a constant external field.

Interest expressed by researchers in specific features of the manifestation of caloric effects with a different physical nature is associated, first, with the possibility of revealing deeper relationships between the macro- and microscopic properties of ferroics and the external influences and, second, with the prospects for the use of ferroic materials as solid refrigerants in

refrigerators on the basis of actively developing alternative cooling methods [1–4].

From equations (1) and (2), it follows that the highest values of caloric effects in ferroics can be achieved in the region of a first-order phase transition, where the order parameter changes most rapidly with a variation in the temperature. However, hysteresis phenomena that accompany such transformations complicate the study of caloric effects and the use of appropriate ferroics [5]. In this respect, the most optimum are materials that undergo either diffuse first-order phase transitions, in which the latent heat is gradually absorbed/released in a wide temperature range, or second-order phase transitions close to the tricritical point.

The activity of studies of caloric effects, as well as many other specific properties of solids (for example, superconductivity, multiferroicity, etc.), is characterized by periodic recessions and spikes. One of the reasons for this phenomenon, in our opinion, is connected with the exhaustion of potential possibilities for the optimization of the required properties of one class of materials as well as with the discovery of a new chemical class, a different structural type, and/or a new design of materials, which make it possible to increase their caloric efficiency.

The results of intensive investigations of the electrocaloric and magnetocaloric effects in materials of various chemical compositions are generalized in a number of reviews [6–11]. Much less attention is paid to an equally interesting and certainly promising barocaloric effect [12–14]. One of the main advantages of the barocaloric effect is the universality associated with the direct relationship between this effect and the thermal expansion of the material, which is character-

Caloric parameters of some ferroics (T_{PT} is the phase transition temperature; ΔH and ΔE are the magnetic and electric field strengths, respectively; Δp is the hydrostatic pressure; *sc* is the single crystal; *cer* is the ceramics; and *f* is the film)

	T_{PT} , K	ΔT_{AD} , K	ΔH , kOe	ΔE , kV/cm	Δp , kbar	References
$\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (<i>sc</i>)	227	6.5	70			[15]
$\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (<i>cer</i>)	265	3.5	50			[16]
$\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (<i>f</i> —150 nm)	225	1.2	50			[16]
$\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (<i>sc</i>)	339	5.6	70			[15]
$\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (<i>cer</i>)	349	4.9	70			[15]
PMN–PT 85/15 (<i>cer</i>)	290	1.7		16		[17]
PMN–PT 72/28 (<i>sc</i>)	400	0.5		9		[18]
PMN–PT 70/30 (<i>f</i> —100 μm)	430	2.8		90		[19]
PMN–PT 67/33 (<i>f</i> —200 nm)	420	14.5		600		[20]
$\text{Ba}_{0.73}\text{Sr}_{0.27}\text{TiO}_3$ (<i>cer</i>)	300	1.0		24		[21]
Pb_2CoWO_6 (<i>cer</i>)	256	–4.8			0.5	*
NH_4HSO_4 (<i>sc</i>)	160	18			0.3	[22]
$\text{Rb}_2\text{KTiOF}_5$ (<i>cer</i>)	216	7			1.0	[23]

* Data of this work.

ized by an anomalous behavior upon phase transitions of any nature.

Oxygen ferroics, as compared with other materials, are of particular interest for several reasons. First, in oxygen ferroics, depending on the chemical composition and symmetry of the crystal lattice, there can exist one of three types of ordering (ferroelectric, ferromagnetic, or ferroelastic), thus inducing the electrocaloric, magnetocaloric, or barocaloric effect, respectively. Second, based on many of these compounds, it is easy to obtain solid solutions, which makes it possible to vary the temperature and degree of closeness of phase transitions to the tricritical point. Third, oxygen ferroics exhibit a wide variety of forms, because they can be prepared in the form of bulk crystals, micro- and nanoceramics, and film materials.

Surprisingly, until recently, there was almost no information about an experimental study of caloric effects with a different physical nature in the same ferroic material. Although it is clear that the caloric efficiency of a solid refrigerant can be increased if there is an opportunity to produce an effect on the system by several external fields simultaneously. As a rule, ferromagnetic and ferroelectric phase transitions are accompanied by changes in the unit cell parameters and unit cell volume due to the magnetoelastic or electroelastic interaction. In this case, the deformation is a secondary effect. According to expressions (1) and (2), in response to a magnetic (or electric) field and under a pressure, monoferroic materials can exhibit paired caloric effects, including the magnetocaloric (or electrocaloric) effect and the barocaloric effect, which is caused by a significant change in the derivative $(\partial V/\partial T)_p$ in the phase transition region.

In the case of multiferroic materials, in which there is a direct or indirect relationship between different parameters of the ferro-ordering, an external field of one nature can affect the parameter and, hence, the caloric properties of another nature. The caloric effect induced in this case can be considered as a multicaloric effect. According to this classification approach, only ferroelastics can be assigned to actually monoferroic–monocaloric materials.

In this study, we have analyzed the most important and interesting research results and the prospects for further investigation of individual, paired, and multicaloric effects in ferroic oxides of different structural types.

2. INDIVIDUAL CALORIC EFFECTS

An analysis of numerous publications dealing with caloric effects has demonstrated that the most attention has been paid to the electrocaloric and magnetocaloric effects, and the main directions of research are primarily associated with the search for new effective materials and/or possibilities of using increasingly high electric and magnetic fields. Only recently, attention has been drawn to the study of other possibilities to increase the caloric efficiency, in particular, of oxygen ferroelectrics and ferromagnets, the assortments of which are comparable to each other and consist predominantly of perovskite-like compounds and related solid solutions.

The table presents the experimentally determined values of ΔT_{AD} , which correspond to the intensive electrocaloric, magnetocaloric, and barocaloric effects for a number of ferroic materials in the form of crystals, ceramics, and thin films [15–23].

It can be seen from the table that, for bulk materials, the values of ΔT_{AD}^{MCE} observed in rather strong magnetic fields are several times higher than the values of ΔT_{AD}^{ECE} observed in electric fields not exceeding 25 kV/cm. However, when comparing the electrocaloric and magnetocaloric effects, it should be taken into account that measurements of each effect have their own specific features. At present, the use of magnetic fields with a high strength up to 100 kOe has no significant problems and test samples are not subject to special requirements. However, the corresponding magnets either are superconducting or have large dimensions. These features of the magnets make difficult the development of refrigerators based on the use of the magnetocaloric effect.

The use of an electric field is much more easily implemented by applying a voltage to electrodes deposited on opposite faces of the operating electrocaloric element in the form of a crystalline or ceramic plate. At the same time, serious disadvantages of bulk ferroelectrics are often a high conductivity and a limited dielectric strength. The first disadvantage is eliminated by growing more perfect single crystals and synthesizing compact ceramics. The second disadvantage is eliminated, in particular, by inducing significant electrocaloric effects at low voltages in film structures (see table). However, despite the high values of ΔT_{AD}^{ECE} , such elements with a small mass have very low values of the extensive parameter ΔS_{ECE} .

Obvious advances in the improvement of bulk dielectric ceramics are clearly demonstrated by the example of $BaTiO_3$ [24]. It was found that, as the size of grains in bulk samples decreases from 41 to 1.3 μm , the dielectric strength of the material increases by a factor of two, from 90 to 180 kV/cm.

Even more impressive results on the improvement of the dielectric strength were obtained for bulk transparent ceramics $Ba_{1-x}Sr_xTiO_3$ [25]. An increase in the strontium concentration leads to a significant increase in the maximum permissible strength of the electric field: $E = 300$ kV/cm for $x = 0.2$; $E = 500$ kV/cm for $x = 0.3$; and $E = 800$ kV/cm for $x = 0.5$.

The results of measurements of the electrocaloric effect in the ceramic $Ba_{0.73}Sr_{0.27}TiO_3$ solid solution (see table) [21] seem to be encouraging in the sense that the study of lead-free ferroelectrics is very promising not only from the environmental point of view. Expectations are confirmed by the recently performed ab initio calculations of the electrocaloric effect in the $Ba_{0.5}Sr_{0.5}TiO_3$ solid solution [26]. First, it turned out that, in the electric field $E = 60$ kV/cm, the value of $\Delta T_{AD}^{ECE} \approx 3$ K agrees satisfactory with the experimental data for $Ba_{0.73}Sr_{0.27}TiO_3$ [21]. Second, in the electric field $E = 800$ kV/cm, which, as shown in [25], is withdrawn by the $Ba_{0.5}Sr_{0.5}TiO_3$ solid solution, the calcu-

lated value of the intensive electrocaloric effect reaches a very high value of ~ 12 K [26].

A significant influence exerted by dimensional parameters of the sample on the electrocaloric effect can be judged from the comparison of the results obtained in the study of the PMN–PT solid solutions, which had the composition close to the concentration ratio of 70/30 and were prepared in the form of a bulk crystal, a thick film, and a thin film (see table). A decrease in the thickness of the sample resulted in a many-fold increase of the electric field strength, which led to a huge increase in the intensive electrocaloric effect up to 14.5 K [18–20]. Such high values of ΔT_{AD}^{ECE} and their nonlinear dependence on the electric field raise the question as to maximum permissible limits to which the external field strength can be increased. The answer to this question was proposed by Pirc et al. [27], who derived the equation for calculating the intensive electrocaloric effect in the saturation ΔT_{SAT} :

$$\Delta T_{SAT} = \frac{T \ln \Omega}{3 \epsilon_0 \Theta C_E} P_{SAT}^2 \quad (3)$$

Here, Θ is the Curie constant, Ω is the ratio of the numbers of possible orientations of dipoles in the paraelectric and ferroelectric phases.

Taking into account the relationship between the entropy of the phase transition ΔS and the polarization P , expression (3) can be represented as follows: $\Delta T_{SAT} = (T/C_E)\Delta S$. It can be seen that the larger is the entropy ΔS , the higher is the limiting value of the intensive (and extensive) electrocaloric effect.

A comparison of the calculated and experimental data shows that, for some ferroelectrics, for example, a 200-nm-thick PMN–PT 70/30 film, the experimental value of ΔT_{AD}^{ECE} (see table) is almost twice the calculated value of $\Delta T_{AD}^{ECE} = 8.5$ K [27]. Even a more significant difference is observed for the intensive electrocaloric effect measured experimentally in a thin film of the composition $(Pb_{0.92}La_{0.08})(Zr_{0.65}Ti_{0.35})O_3$: the experimental value is $\Delta T_{AD}^{ECE} = 40$ K for $\Delta E = 1250$ kV/cm [28], whereas the calculated value is $\Delta T_{AD}^{ECE} = 7.1$ K [27].

If the observed large difference between the experimental and calculated values of ΔT_{AD}^{ECE} is not related to the known difficulties encountered in measuring the temperature of film materials, the question arises as to whether there are any external factors, for example, mechanical coupling between the film and the substrate, which could induce an additional change in the temperature, apart from the change associated with the electrocaloric effect.

In contrast to ferroelectrics, dimensional parameters of magnetic materials do not limit the magnetic

field strength, but, according to the results of a series of experimental studies, can affect the behavior and value of the magnetocaloric effect in oxide magnetic materials [16, 29, 30]. Investigations of the temperature dependences of the magnetization of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ compound in the form of a bulk polycrystal, nanocrystalline powders (with grain sizes of 33 and 15 nm), and a thin film (with a thickness of ~ 150 nm) demonstrated that, upon changing over from the crystal to the polycrystal and with a decrease in the grain size, the first-order ferromagnetic phase transition passing through the tricritical point becomes a second-order phase transition and its temperature significantly decreases (see table) [16]. This leads to a decrease in the absolute value of the temperature derivative of the magnetization and, in accordance with expression (1), to an almost threefold decrease in the maximum absolute value of the intensive magnetocaloric effect (see table). However, the results of comparing the values of the relative cooling power $\text{RCP}(S)$, which is determined by integrating the function $\Delta S_{\text{MCE}}(T)$ in the temperature range corresponding to the full width at half-maximum (FWHM) of the curve $\Delta S_{\text{MCE}}(T)$ [31], are not so unambiguous. With an increase in the magnetic field strength, the maximum value of $\text{RCP}(S)$ for the film sample systematically exceeds the value for the bulk polycrystal, and, at a field strength of 50 kOe, the difference becomes more than 5%. It is interesting to note that the influence of size effects on the magnetocaloric effect in manganites manifests itself even upon changing over from the $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ single crystal to the related ceramic sample (with a grain size of less than 10 μm): the absolute value of $\Delta T_{\text{AD}}^{\text{MCE}}$ decreases, while the integral parameter $\text{RCP}(T)$ increases by 10% [32].

The magnetocaloric effect in the $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ manganite, which, being uniform from the crystallographic point of view, is a two-phase system with ferromagnetic and antiferromagnetic orderings, has been repeatedly investigated. The main result obtained in the investigation of the influence of the grain size on the magnetocaloric effect is the inhibition of the formation of an antiferromagnetic phase in manganite samples with grain sizes of less than 100 nm, which is indicated by the absence of the inverse magnetocaloric effect in these materials [29].

Noteworthy are the data obtained in the investigation of nanocomposites based on $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ embedded in gold [30]. It was found that the smaller are the grains and the more uniform are the grain sizes in the magnetite, the larger is the magnetocaloric effect. For particle sizes ranging from 4.6 to 7.4 nm, the extensive magnetocaloric effect is several times larger than the value of ΔS_{MCE} in the samples with a wider range of the grain size distribution (10–30 nm).

The barocaloric effect in ferroics has been investigated to a much lesser extent. One of the reasons is

that, in contrast to the relatively simple techniques for studying the electrocaloric and magnetocaloric effects, the direct measurement of the reversible change in temperature under hydrostatic pressure is a very complex problem [33]. Therefore, a method was proposed for determining the differences in entropies ΔS_{BCE} and temperatures $\Delta T_{\text{AD}}^{\text{BCE}}$ by analyzing the entropy–temperature–pressure diagram [12, 13]. In order to construct this diagram, it is sufficient to have information about the temperature dependence of the heat capacity of the material and the susceptibility of the phase transition temperature to pressure. Figure 1 presents the results obtained from the analysis of the dependence of the total entropy on the temperature and pressure for the oxygen ferroics Pb_2CoWO_6 , which undergoes two successive phase transitions at temperatures $T_1 = 303$ K and $T_2 = 256$ K [34]. In accordance with the positive and negative signs of the pressure coefficient ($dT_1/dp = 2$ K/kbar, $dT_2/dp = -40$ K/kbar), the anomalous part of the entropy associated with phase transitions is shifted with respect to the lattice entropy up and down in temperature, respectively (Figs. 1a, 1c). For a constant temperature or a constant entropy, we determined the differences in entropies $\Delta S_{\text{BCE}}(T, p) = S(T, p \neq 0) - S(T, p = 0)$ and temperatures $\Delta T_{\text{AD}}^{\text{BCE}} = T_{p>0} - T_{p=0}$, which corresponded to the extensive and intensive barocaloric effects. Different signs of dT_i/dp , which are caused by the increase and decrease in the unit cell volume at temperatures T_1 and T_2 , are responsible for the heating and cooling of Pb_2CoWO_6 in the region of these temperatures under pressure (Figs. 1b, 1d).

The table presents the values of $\Delta T_{\text{AD}}^{\text{BCE}}$ for some bulk, oxygen-containing, and fluorine–oxygen ferroics. It can be seen that, at close pressures, the barocaloric effect in Pb_2CoWO_6 is less than that in the NH_4HSO_4 ferroelectric [22] but is comparable to the value of $\Delta T_{\text{AD}}^{\text{BCE}}$ in the Rb_2KTiO_5 ferroelastics [23]. The main reason for the large barocaloric effect in NH_4HSO_4 is associated with a combination of the high value of the entropy $\Delta S = R \ln 4$ and the anomalously large pressure coefficient $dT/dp = 75$ K/kbar. Owing to the high values of $\Delta T_{\text{AD}}^{\text{BCE}}$ achieved at relatively low pressures, the aforementioned materials are considered to be competitive with respect to the generally recognized solid coolants based on the use of the magnetocaloric and electrocaloric effects [6, 8]. An advantage of this type of barocaloric materials is a high rate of change in $\Delta T_{\text{AD}}^{\text{BCE}}$ and ΔS_{BCE} with an increase in the pressure, which leads to a rapid achievement of the saturation (Fig. 2) [22, 23]. The latter circumstance ensures significant values of the integral caloric characteristics, such as the relative cooling power [31].

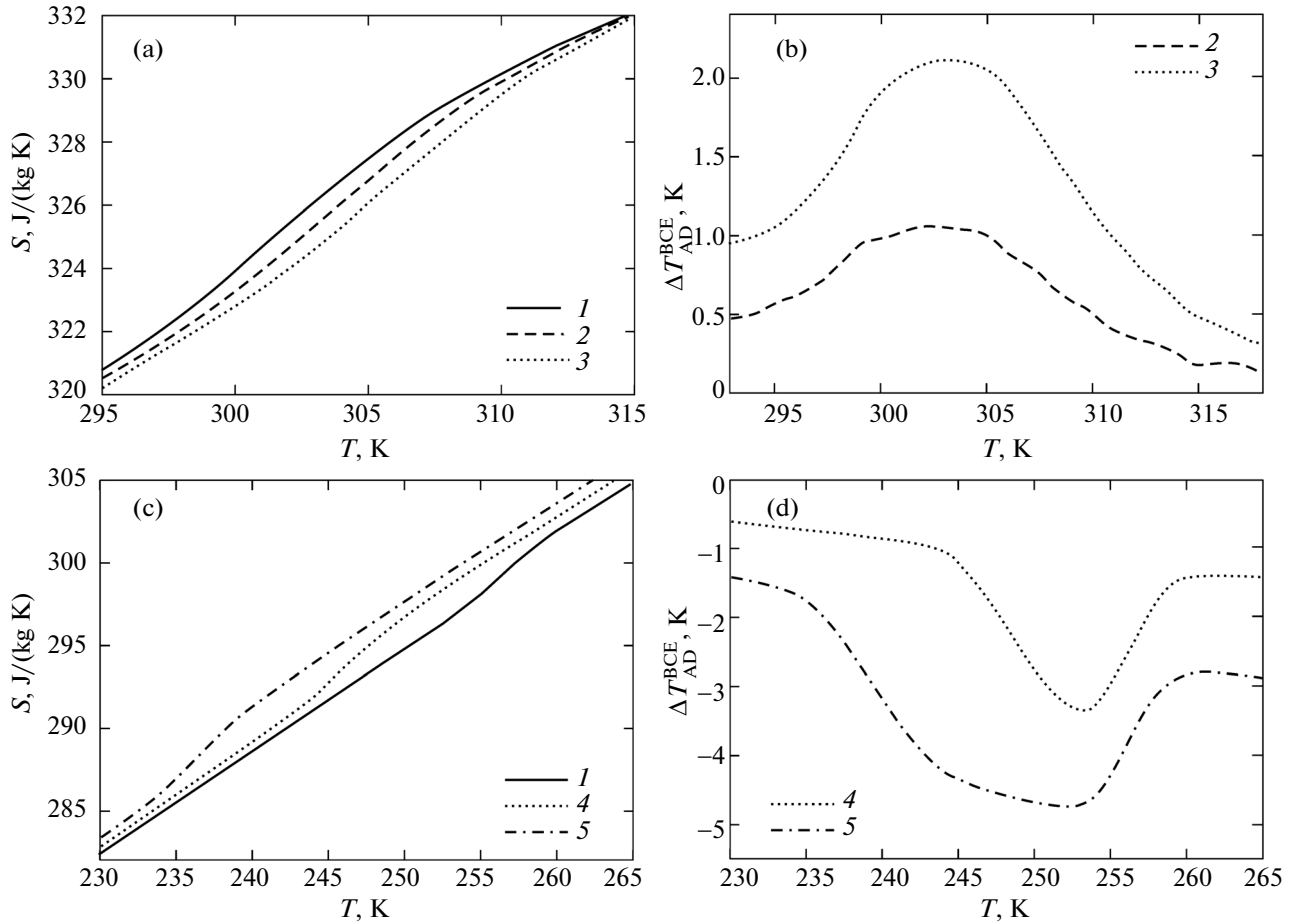


Fig. 1. Temperature dependences of the entropy S and the intensive barocaloric effect ΔT_{AD}^{BCE} in the region of phase transitions in Pb_2CoWO_6 at temperatures (a, b) T_1 and (c, d) T_2 under different pressures $p = (1) 0, (2) 1.0, (3) 2.0, (4) 0.25, (5) 0.5$ kbar.

The minimum pressure, at which the maximum value of the intensive barocaloric effect is achieved in a particular material, can be determined a priori if there is information about the temperature dependence of the heat capacity and the susceptibility to hydrostatic pressure [23]:

$$p \geq \frac{T\Delta S}{C_L(dT/dp)}. \quad (4)$$

Here, C_L is the lattice heat capacity and ΔS is the entropy of the phase transition.

So far, we did not focus attention on the anisotropy of the crystal and magnetic sublattices, which, certainly, can have an influence on the behavior and value of caloric effects. It is obvious that, for example, in single crystals of uniaxial ferroelectrics, the maximum change in the polarization and, hence, in the electrocaloric effect takes place when an electric field is applied along the ferroelectric direction. In the case of ceramic materials, we are dealing with some average caloric effects, the value of which is determined by the preferred orientation of the crystallites. Most likely,

this is the reason why often there is no agreement between the results of investigations of caloric effects in ceramic samples that had the same chemical composition but were prepared using different technological methods. For example, the values of the intensive electrocaloric effect measured for ceramic samples of the 0.9PMN–0.1PT composition by different but seemingly reliable methods proved to be significantly different: $\Delta T_{AD}^{ECE} = 0.55$ K at $E = 29$ kV/cm [35] and $\Delta T_{AD}^{ECE} = 1.25$ K at $E = 15$ kV/cm [36].

Information about a systematic experimental study of the anisotropy of the electrocaloric effect in multi-axial ferroelectric single crystals is not available. Moreover, as follows from the data presented above for ceramics, it is necessary to take a cautious approach to the comparison of the results obtained by different authors and different methods. Although it is obvious that, for example, in BaTiO_3 and related solid solutions, when the electric field is applied along the [100] axis, the normal electrocaloric effect ($\Delta T_{AD}^{ECE} > 0$ for

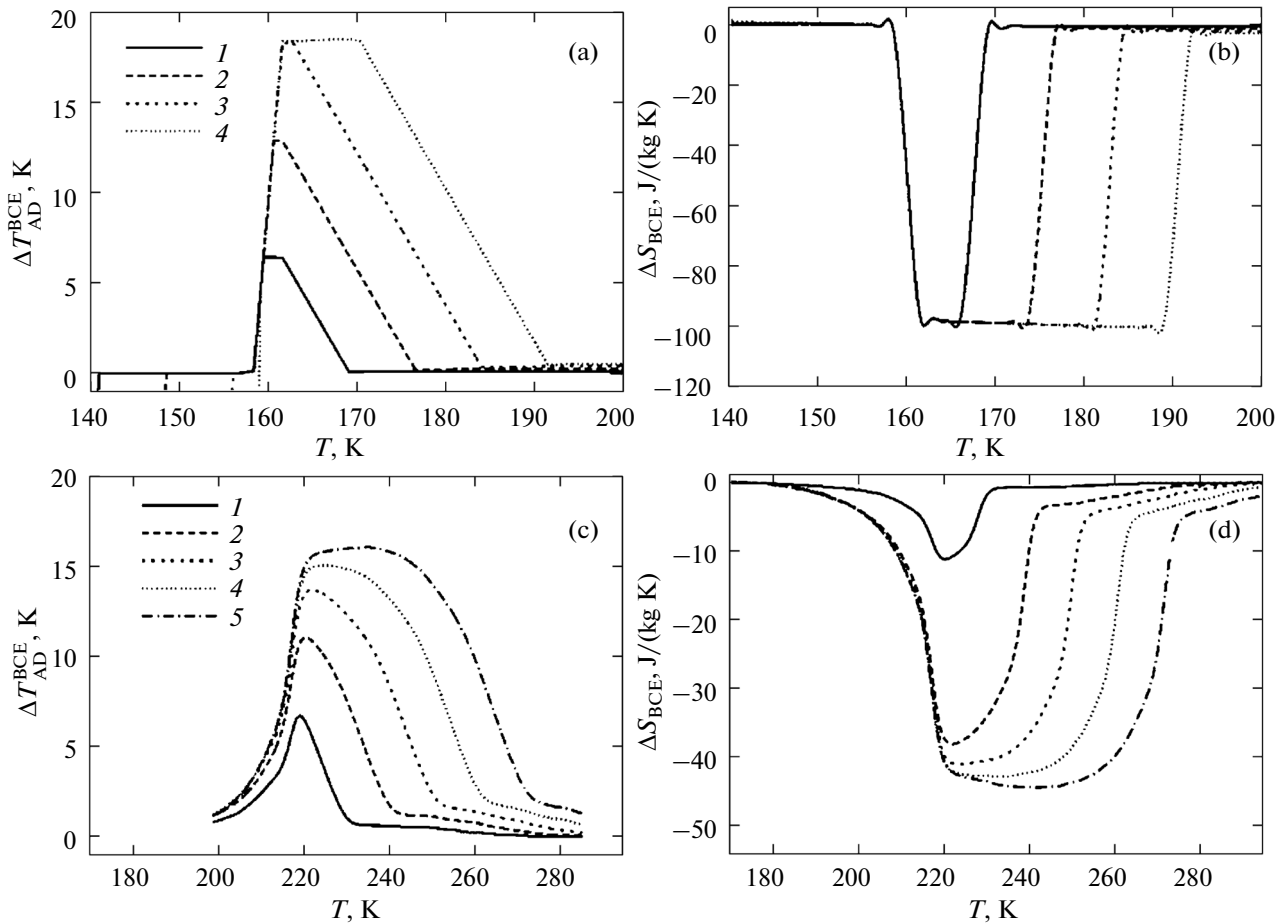


Fig. 2. Intensive ΔT_{AD}^{BCE} and extensive ΔS_{BCE} barocaloric effects: (a, b) in NH_4HSO_4 at pressures $p = (1) 0.1, (2) 0.2, (3) 0.3,$ and $(4) 0.4$ kbar and (c, d) in $\text{Rb}_2\text{KTiOF}_5$ at pressures $p = (1) 1, (2) 2, (3) 3, (4) 4,$ and $(5) 5$ kbar.

$\Delta E > 0$) can be realized upon the transition from the cubic phase to the tetragonal phase ($\partial P/\partial T < 0$), whereas the inverse electrocaloric effect ($\Delta T_{AD}^{ECE} < 0$ for $\Delta E > 0$) can occur upon the transition to the orthorhombic phase ($\partial P/\partial T > 0$). This circumstance is clearly demonstrated by the first-principles calculations of the electrocaloric effect in three phases of the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ crystal [26]. It was found that the sign of ΔT_{AD}^{ECE} can be controlled by varying the electric field. For example, when the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ sample in the tetragonal phase is thermostated near the transition to the orthorhombic phase, the variation in the initially noncollinear electric field over a wide range of strengths leads to a change in the intensive electrocaloric effect from -1.4 K for $\Delta E = 200$ kV/cm to $+0.4$ K for $\Delta E = 1000$ kV/cm. The change in the sign of ΔT_{AD}^{ECE} from negative to positive was explained in [26] by the observed significant shift of the temperature of the field-driven transition between the aforemen-

tioned phases, as a result of which the field and polarization vectors become collinear.

One of the first experimental studies of the anisotropy of the magnetocaloric effect was performed in the first half of the last century [37]. The rotation of a chromium ferromagnetic single crystal through 360° in a magnetic field led to a twofold change in the positive magnetocaloric effect ΔT_{AD}^{MCE} from the maximum to zero. Only in 1991, the attention was drawn to this phenomenon as promising in terms of the development of new principles of the solid state cooling [38].

Since rapid switching on and off of the magnetic field with a high strength presents certain difficulties, the magnetic refrigerant used in refrigerators based on the magnetocaloric effect is mechanically displaced into the magnetic field and back from it. The effect of the anisotropy applied in this case makes it possible to use a simpler process of rotation of the sample and/or the magnet with respect to each other.

There have been a number of recent studies of the influence of the relative orientation of a magnetic field

and a sample on the magnitude and sign of the magnetocaloric effect in ferroics that undergo magnetic phase transitions at low temperatures [39–41].

The orthorhombic perovskite TbMnO_3 below the Néel temperature $T_N = 9$ K undergoes an antiferromagnetic ordering of Tb^{3+} and Mn^{3+} ions. As a result, the application of an external magnetic field leads to an increase in the entropy and to a positive extensive magnetocaloric effect ($\Delta S_{\text{MCE}} > 0$) [39]. However, already in a magnetic field $H > 20$ kOe, the crystal transforms into the ferromagnetic phase, which is accompanied by a change in the sign of the magnetocaloric effect ($\Delta S_{\text{MCE}} < 0$). The anisotropy of the magnetocaloric effect appeared to be very significant—when the sample is rotated in the ab plane through an angle of 90° in a magnetic field of 50 kOe, the value of ΔS_{MCE} varies from 9 J/(kg K) to 0.

Similar results were obtained in the study of a hexagonal single crystal of the TmMnO_3 compound [40]. However, in this case, the anisotropy of the magnetocaloric effect was more pronounced: the maximum magnetocaloric effect $\Delta S_{\text{MCE}} \approx 9$ J/(kg K) along the c axis was almost 20 times greater than the extensive magnetocaloric effect along the a axis.

In the case when the orthorhombic single crystal of HoMn_2O_5 was rotated in the bc plane through an angle of 90° in a magnetic field of 70 kOe, the maximum extensive magnetocaloric effect reached the value of $\Delta S_{\text{MCE}} \approx 12.5$ J/(kg K) [41], which significantly exceeded the magnetocaloric effect in the aforementioned magnets. In the authors' opinion, this difference in the values of the magnetocaloric effect is explained by the giant magnetocrystalline anisotropy. The calculations in terms of formula (2) showed that the intensive magnetocaloric effect also has sufficiently high values: $\Delta T_{\text{AD}}^{\text{MCE}} = 6.7$ K at $H = 70$ kOe. An important aspect of the investigations is the lack of saturation of the extensive magnetocaloric effect ΔS_{MCE} in HoMn_2O_5 in the range of measured magnetic fields. This indicates that there is a possibility to obtain higher values of the magnetocaloric effect with a further increase of the magnetic field strength.

The results of investigations into the influence of the anisotropy of the crystal lattice on the barocaloric effect in related oxyfluorides $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ and $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ are no less interesting and impressive [42]. At room temperature, these crystals have the orthorhombic symmetry $Cmcm$, but upon cooling, they undergo phase transitions of different natures: the tungstate at $T_1 = 201$ K becomes a ferroelastic (space group $P\bar{1}$), while the molybdate at $T_1 = 271$ K transforms into an antiferroelectric (space group $Pnma$). The values of $\Delta T_{\text{AD}}^{\text{BCE}}$ determined at the pressure $p = 5$ kbar along the axes a , b , and c of the initial orthorhombic unit cell are found to be very large in magni-

tude and opposite in sign: 4 K along the a axis, -4 K along the b axis, and 7 K along the c axis in $(\text{NH}_4)_2\text{WO}_2\text{F}_4$; and 9 K along the a axis, 12 K along the b axis, and -8 K along the c axis in $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$. Owing to the strong anisotropy of the barocaloric effect, the studied oxyfluorides can be considered as promising materials for the use in the design and fabrication of cooling devices operating according to the principle of sequential application/removal of mechanical stresses along the crystallographic axes characterized by different signs of $\Delta T_{\text{AD}}^{\text{BCE}}$.

3. PAIRED CALORIC EFFECTS

Paired caloric effects, i.e., effects with a different physical nature, which can be induced in the same material under simultaneous or sequential application of the corresponding fields, are of obvious interest and can be defined as follows:

$$dS = \left(\frac{\partial S}{\partial T} \right)_{p, E, H} dT + \left(\frac{\partial S}{\partial p} \right)_{T, E, H} dp + \left(\frac{\partial S}{\partial E} \right)_{T, p, H} dE + \left(\frac{\partial S}{\partial H} \right)_{T, p, E} dH, \quad (5)$$

$$dS = -\frac{T}{C_{p, E, H}} \left[-\left(\frac{\partial V}{\partial T} \right)_{p, E, H} dp + \left(\frac{\partial P}{\partial T} \right)_{E, p, H} dE + \left(\frac{\partial M}{\partial T} \right)_{E, p, H} dH \right]. \quad (6)$$

Taking into account that ferroelectric and magnetic transformations are almost always accompanied by an anomalous behavior of thermal expansion of the material, the barocaloric effect can be considered as a phenomenon that accompanies the electrocaloric effect or magnetocaloric effect.

As far as we know, simultaneous investigations of the barocaloric and magnetocaloric effects, until recently, were carried out for only a few magnetic materials, in particular, for Ni–Mn–In alloys, which undergo ferromagnetic and martensitic phase transitions in a narrow temperature range [14, 43]. For oxygen ferroics, the electrocaloric and barocaloric effects were compared for the first time by using the example of NH_4HSO_4 and TGS ferroelectrics, which undergo second-order phase transitions [22]. On the one hand, it turned out that, at the same small electric field strength $E \approx 1.5$ kV/cm, the intensive electrocaloric effect in TGS $\Delta T_{\text{AD}}^{\text{ECE}} = 0.120$ K is almost five times greater than that in the ammonium hydrosulfate $\Delta T_{\text{AD}}^{\text{ECE}} = 0.025$ K. On the other hand, at the same relatively low pressure $p = 0.4$ kbar, the intensive barocaloric effect in NH_4HSO_4 ($\Delta T_{\text{AD}}^{\text{BCE}} = 0.45$ K) is substan-

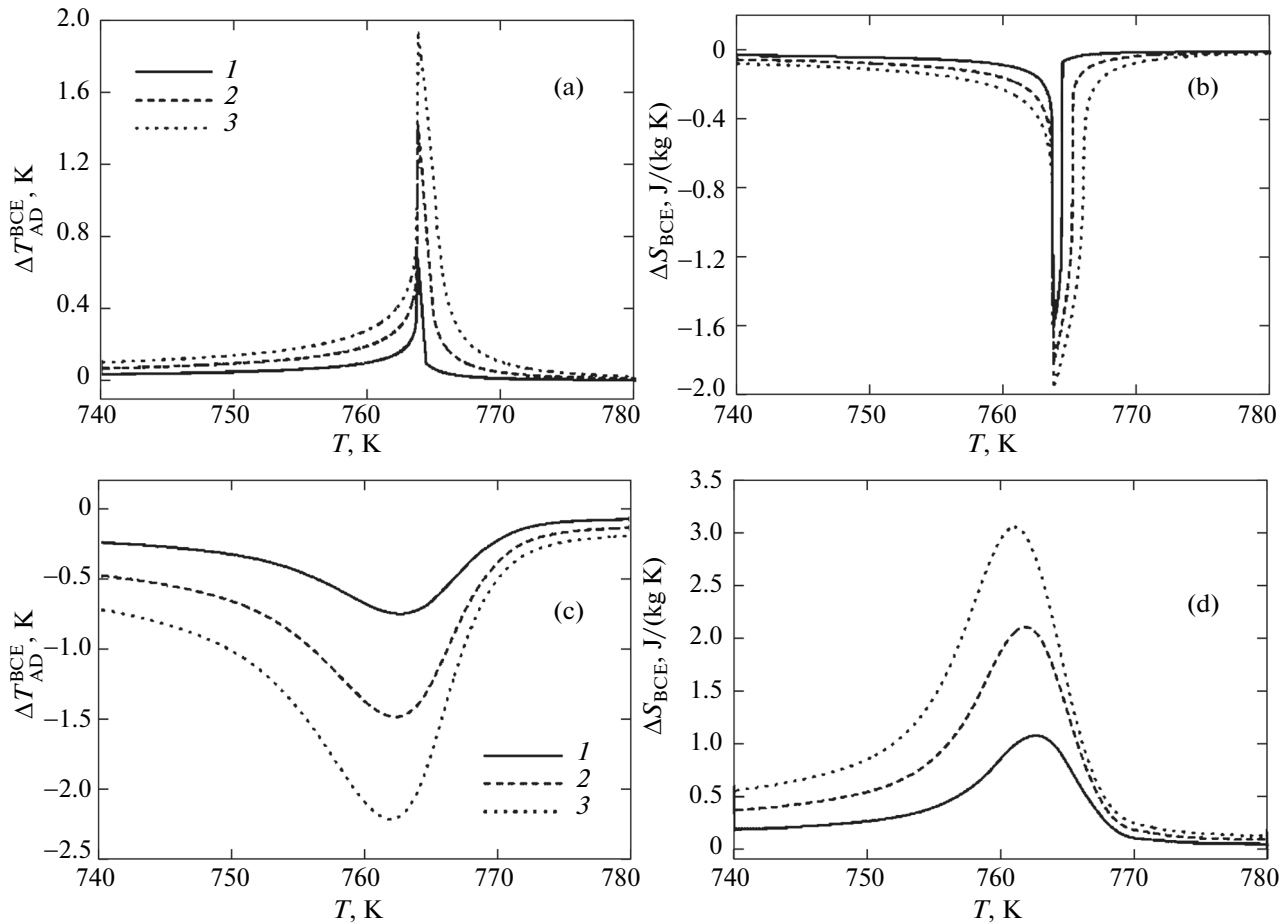


Fig. 3. (a, b) Intensive and extensive electrocaloric effect in electric fields $E = (1)$ 1, (2) 2, and (3) 3 kV/cm and (c, d) intensive and extensive barocaloric effect at pressures $p = (1)$ 0.1, (2) 0.2, and (3) 0.3 kbar in PbTiO_3 .

tially greater than that in TGS ($\Delta T_{\text{AD}}^{\text{BCE}} = 0.14$ K). This example shows that the caloric efficiency of ferroelectrics can be significantly improved by the inclusion of the barocaloric effect.

Equally interesting results were obtained in the investigation of paired caloric effects in PbTiO_3 [44]. The observed changes in the electrocaloric and the barocaloric effects with variations in the temperature at different electric field strengths and different pressures differ significantly from each other (Fig. 3). First, owing to the negative pressure coefficient caused by a decrease in the unit cell volume with increasing temperature, the barocaloric effect in lead titanate, unlike the electrocaloric effect, is inverse; i.e., under pressure, the temperature decreases and the entropy increases. Second, a sharp narrow peak is characteristic of the dependences $\Delta T_{\text{AD}}^{\text{ECE}}(T)$ and $\Delta S_{\text{ECE}}(T)$, in contrast to the smooth rise and decay in the quantities $\Delta T_{\text{AD}}^{\text{BCE}}(T)$ and $\Delta S_{\text{BCE}}(T)$. As a result, noticeable barocaloric changes in the temperature and entropy are retained in a much wider range of temperatures. The

latter circumstance suggests that the relative cooling power RCP will also be sufficiently large at low pressures [31]. It should be specially noted that the absolute intensive electrocaloric and barocaloric efficiencies of PbTiO_3 are rather significant: in order to change the temperature by +2.2 and −2.2 K, it is necessary to use a weak electric field with a strength of 2 kV/cm and a very low pressure of 0.3 kbar.

A quite satisfactory agreement between the experimental data [44] and the results of first-principles calculations of the electrocaloric and barocaloric effects upon the ferroelectric–ferroelastic transition in PbTiO_3 was achieved in the case of the separate application of an electric field and pressure [45]. At the same time, it was shown that the total intensive effect observed with the simultaneous use of these fields is not equal to the sum of the individual electrocaloric and barocaloric effects: $\Sigma \Delta T_{\text{AD}} \neq \Delta T_{\text{AD}}^{\text{BCE}} + \Delta T_{\text{AD}}^{\text{ECE}}$ [45]. This is understandable because the validity of the simple summation of caloric effects in equations (5) and (6) is very conditional. The point is that, when applying a single field, the temperature behavior of the

conjugate order parameter changes as the tricritical point is approached or removed. Then, the temperature dependences of the non-conjugated order parameters can become diffuse, which leads to a decrease in their temperature derivatives and to a decrease in the corresponding caloric effect. In any case, the total entropy change in response to several fields cannot exceed the value corresponding to the entropy of the phase transition.

Paired caloric effects typical of magnetic oxygen ferroics were investigated only in the $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ manganite, which undergoes a second-order ferromagnetic phase transition at a temperature of approximately 340 K [15]. Although this transition does not lead to a change in the symmetry of the crystal lattice, the anomalous behavior of thermal expansion has a pronounced character. Therefore, $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ can exhibit both the magnetocaloric and barocaloric effects. However, owing to the relatively small entropy of the phase transition ($\Delta S = 3.8 \text{ J}/(\text{mol K})$) and low susceptibility of the transformation temperature to hydrostatic pressure ($dT/dp = 1.7 \text{ K}/\text{kbar}$), the intensive and extensive magnetocaloric effect and barocaloric effect have normal values. As was shown in [15], in order to change the temperature of $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ by $\sim 0.5 \text{ K}$, it is necessary to use a pressure of 2 kbar and a magnetic field of 5 kOe.

A comparison with the ferroelectrics considered above demonstrates that the paired MCE + BCE effect in the manganite is comparable to the ECE + BCE effect in TGS and, to some extent, in NH_4HSO_4 , which also undergoes second-order phase transitions with a rather small entropy, but it is significantly exceeded by the effect observed in PbTiO_3 , which is characterized by a typical order–disorder transformation with a high pressure coefficient.

4. MULTICALORIC EFFECTS

Considerable interest in multiferroic materials is associated with the possibility of controlling their properties with a different physical nature (ferroelectric, ferroelastic, ferromagnetic) by varying a single or a few external fields [46–49]. As a rule, most attention is paid to the search for and study of materials with a significant magnetoelectric effect due to the wide possibilities of its application in microelectronics and spintronics [47]. However, there is another promising way to use unique properties of multiferroics, according to which the caloric effects associated with different order parameters can be induced by a single external field. Therefore, in this case, we are dealing with the multicaloric effect. For example, the external magnetic field can cause the magnetocaloric effect and induce an internal electric field, which, in turn, leads to a change in the polarization and to the appearance of the electrocaloric effect. These fields are related by the expression [50]

$$dE = \alpha_m (\varepsilon_0 \chi^e)^{-1} dH. \quad (7)$$

Here, α_m is the coefficient of direct magnetoelectric interaction $dP = \alpha_m dH$, ε_0 is the permittivity of free space, and χ^e is the electric susceptibility.

Let us assume that the pressure and entropy are constant. Then, using (6) and (7), we obtain the following expression for the intensive multicaloric effect:

$$dT = -\frac{T}{C_{p, E, H}} \left[\frac{\alpha_m}{\varepsilon_0 \chi^e} \left(\frac{\partial P}{\partial T} \right)_{E, p, H} + \left(\frac{\partial M}{\partial T} \right)_{E, p, H} \right] dH. \quad (8)$$

The expression for ΔT in the case of a multiferroic material in an electric field has a similar form.

We have no information about direct measurements of changes in the temperature of a multiferroic material in any of the fields. However, in the recent work [51], the multicaloric effect was calculated using expression (8) for single-phase polycrystalline multiferroic NdCrTiO_5 , which undergoes phase transitions to the ferroelectric and ferromagnetic states in a narrow temperature range near 21 K [51]. It was found that, in a magnetic field of 50 kOe, the total change in the temperature is 6.9 K, which consists of the magnetocaloric effect $\Delta T_{\text{AD}}^{\text{MCE}} = 6.3 \text{ K}$ and an additional contribution of 0.6 K due to the multicaloric interaction $(\alpha_m/\varepsilon_0 \chi^e) dP/dT$. The relatively small additional change in the temperature, apart from the temperature change associated with the magnetocaloric effect, which amounts to $\sim 10\%$ of the total intensive caloric effect ΔT_{AD} , most likely, is explained by the fact that, in single-phase multiferroics, the magnetoelectric interaction is relatively weak [51]. At the same time, the interaction between two ferroic phases can be enhanced, for example, in a composite. In such material, the electric and magnetic order parameters arise/change in separate but closely related phases. In this case, the magnetoelectric and multicaloric effects are determined by piezoelectric, piezomagnetic, electrostrictive, and magnetostrictive properties of the components [48].

The above statement is strongly confirmed by the results of the analysis within the framework of the approach similar to that using expression (8) for the experimental data on the magnetization in an electric field of a two-phase composite in the form of a 20-nm-thick $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ manganite film deposited onto a relaxor–ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 substrate [52]. The significant inverse piezoelectric effect, which is induced in the substrate after applying an electric field, gives rise to strains in the manganite film, which lead to a significant increase both in the ferromagnetic phase transition temperature (by $\sim 15 \text{ K}$) and in the magnetization (by $\sim 20\%$). The latter circumstance indicates that the electric field has an indirect influence on the degree of magnetic order in the manganite and, hence, on the magnitude of the

magnetic entropy. The change in the entropy of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ film was estimated in [52] based on the equation

$$\Delta S = \int_0^E \frac{\alpha_e}{\chi_m(T, T_C)} \left(\frac{\partial M}{\partial T} \right)_H dE, \quad (9)$$

where α_e is the coefficient of the inverse magnetoelectric interaction $dM = \alpha_e dE$ and χ_m is the magnetic susceptibility.

It was found that, in the electric field $E = 7$ kV/cm, the sufficiently large magnetocaloric effect $\Delta S_{\text{MCE}} = -1.4$ J/(kg K) is comparable to the value of $\Delta S_{\text{MCE}} = -2.1$ J/(kg K) obtained in a magnetic field of 10 kOe for bulk manganite [53]. In this case, it should be taken into account that the total caloric effect, i.e., the multicaloric effect, in the composite will be larger due to the direct electrocaloric effect induced in the PMN–PT substrate, which undergoes a ferroelectric phase transition near the temperature of the ferromagnetic phase transition in the manganite film. In [52], it was rightly pointed out that the use of the indirect method for controlling the magnetic properties of the composite by varying an external electric field will encourage the development of miniature refrigerators based on the magnetocaloric effect.

Another impressive and promising example of the possibility of using piezoelectric and electrostrictive effects to increase the caloric efficiency of materials is provided by the results of the study of a $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ composite film deposited on a BaTiO_3 substrate [48]. These materials have close values of the ferromagnetic and ferroelectric phase transition temperatures. The distortions observed in the crystal structure due to the transition between the tetragonal and orthorhombic phases give rise to mechanical stresses in the BaTiO_3 substrate, which lead to an increase in the magnetization of the film by a factor of approximately 4. Thus, it is clear that magnetoelastic interactions in the composite can induce a significant magnetocaloric effect in the magnetic component at a temperature 30°C below the ferromagnetic phase transition temperature, where the temperature derivative of the magnetization in the absence of mechanical stresses is far from the maximum.

Above, we considered examples of multicaloric effects in layered film composites. However, as was already noted, the extensive parameter of these materials ΔS_{CE} (J/K) is not very large because of the very small weight of the film. From this point of view, bulk composites are more promising. Recently, we investigated the electrocaloric, magnetocaloric, and barocaloric effects in the mixed two-phase multiferroics $x\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3-(1-x)\text{PbTiO}_3$ ($x = 0.85, 0.18$) [32]. The temperatures of the ferromagnetic and ferroelectric phase transitions in lead manganite and lead titanate differ significantly from each other (340 and 760 K,

respectively). Therefore, it might be expected that each of the components will play the role of a passive matrix with respect to the other component. However, direct measurements and the analysis of the entropy–electric field–temperature diagram showed a significant difference in the concentrations of components in composite materials leads to an increase in the caloric effect. In the composite with $x = 0.85$, the magnetocaloric effect $\Delta T_{\text{AD}}^{\text{MCE}}$ is larger than that in the initial compound $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$, and this difference increases with an increase in the magnetic field (Fig. 4a).

The observed phenomenon can be explained by assuming that the application of a magnetic field not only causes a magnetocaloric effect but also simultaneously leads to the appearance of mechanical stresses (internal pressure) in the composite due to the elastic interaction between the magnetostrictive $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ and piezoelectric PbTiO_3 phases. Since the ferromagnetic transition is accompanied by a significant barocaloric effect (Fig. 4b), the intensive caloric effect observed in the composite in the case of direct measurements performed in a magnetic field, most likely, can be considered as a sum of the true magnetocaloric effect and the barocaloric effect induced by the internal pressure. The ratio between the magnetocaloric and barocaloric effect in the magnetic field $H = 5.3$ kOe is approximately equal to 5 : 1. According to the estimates, the pressure generated at the interface between the $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ and PbTiO_3 grains in this magnetic field is approximately 0.2 kbar.

The electrocaloric effect observed upon the ferroelectric phase transition in composite materials is also greater than that in pure PbTiO_3 , but in weak electric fields: $E < 3$ kV/cm for $x = 0.18$ and $E < 1$ kV/cm for $x = 0.85$ (Fig. 4c) [32]. In these ranges of electric fields, the derivative $(\partial P/\partial T)_E$ for composites is larger than that for lead titanate. It can be assumed that, here, also, a significant role is played by the piezoelectric and electrostrictive properties of PbTiO_3 , as well as by the large difference between the thermal expansion coefficients of the components, which caused a displacement of the phase transition to the tricritical point.

It should be noted that, in the ranges of variations in H , E , and p studied in [32], the behavior of the intensive barocaloric effect is consistent with the magnetocaloric and electrocaloric effects upon the ferromagnetic (Figs. 4a, 4b) and ferroelectric (Figs. 4c, 4d) phase transitions, respectively. According to expression (2), the pronounced trend of $\Delta T_{\text{AD}}^{\text{ECE}}$ and $\Delta T_{\text{AD}}^{\text{BCE}}$ to saturation indicates that, upon the phase transition in the PbTiO_3 component, the increase in E and p does not compensate the decrease in the derivatives $(\partial P/\partial T)$ and $(\partial V/\partial T)$. Therefore, the ferroelectric phase transition in composites is much more prone to a smearing under the action of E and p than the ferro-

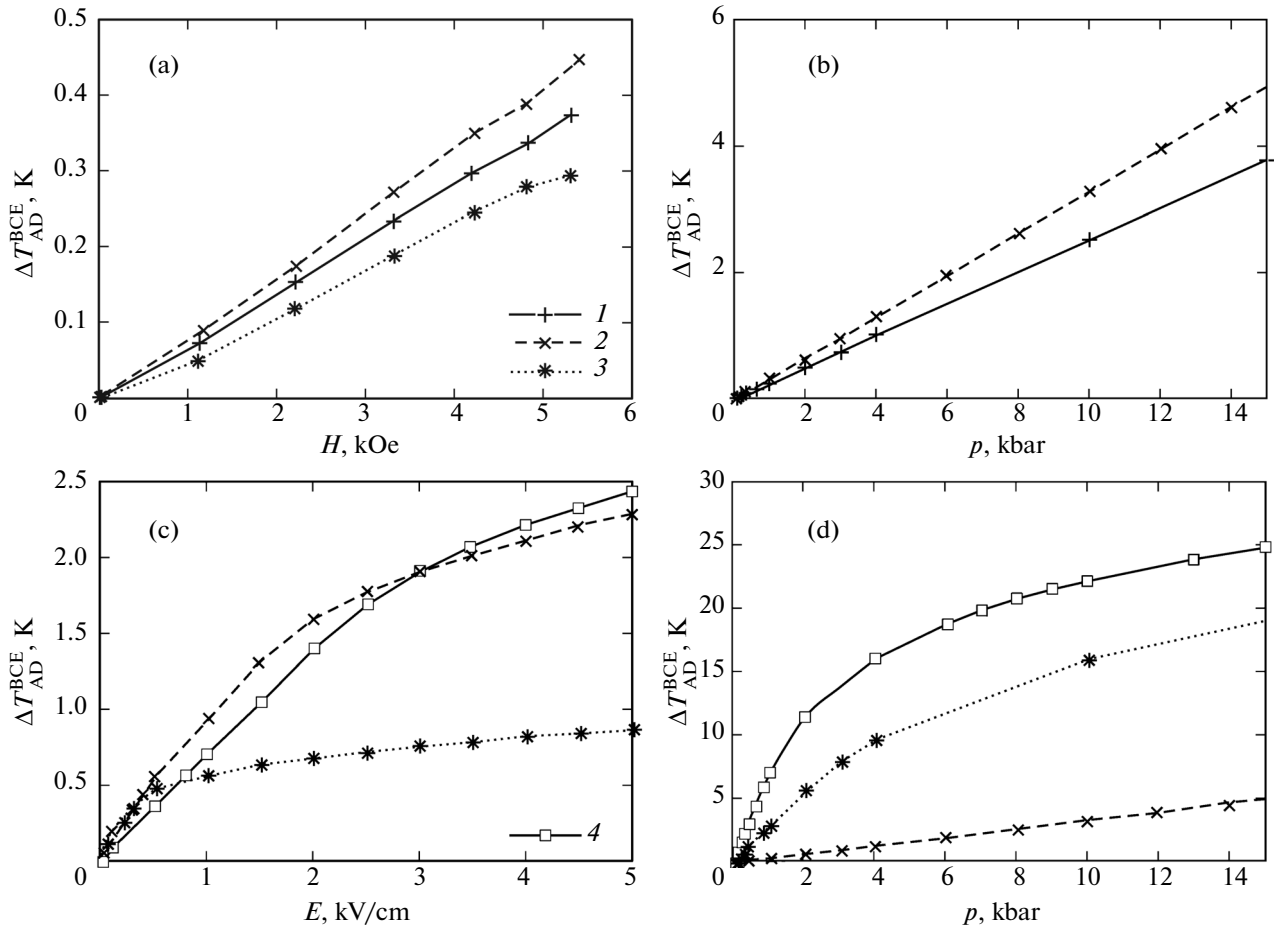


Fig. 4. Dependences of the intensive magnetocaloric (ΔT_{AD}^{MCE}), electrocaloric (ΔT_{AD}^{ECE}), and barocaloric (ΔT_{AD}^{BCE}) effects in the regions of (a, b) ferromagnetic phase transition and (c, d) ferroelectric phase transition in two-phase mixed composites $x\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3-(1-x)\text{PbTiO}_3$ with $x = (1)$ 0.85, (2) 1, (3) 0.18, and (4) 0.

magnetic phase transition in $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ under the action of H and p .

5. CONCLUSIONS

In this paper, we considered the main problems of the current state-of-the-art research into the caloric effects (ECE, MCE, BCE) in oxygen mono- and multiferroic materials. It was noted that undeservedly little attention has been paid to the universal and very promising barocaloric effect caused by uniaxial or hydrostatic pressure.

The performed analysis revealed the following possible ways to increase the caloric efficiency of oxygen ferroics:

- (1) use of paired caloric effects (BCE + ECE, BCE + MCE) in monoferroics;
- (2) hydrostatic or chemical pressure induced displacement of the phase transition toward the tricritical point, which is accompanied by an increase of the temperature derivative of the order parameter and,

accordingly, by an increase in the extensive and intensive caloric effects;

- (3) use of anisotropy of the caloric effects, which provides a means for sequentially heating and cooling a single-crystal sample either by rotating it in the field of a permanent magnet, or by applying a polarization canted electric field, or by alternately applying a uniaxial pressure along the axes with different signs of the barocaloric effect;

- (4) use of the direct relationship between order parameters with a different physical nature in single-phase multiferroics, which makes it possible to induce multicaloric effects in response to a single field;

- (5) design and synthesis of composite magneto-electric materials in which caloric effects with a different physical nature are induced by a single field due to a combination of striction and piezoelectric effects generated by the mechanical coupling between the components.

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REFERENCES

1. M. Tishin and Y. Spichkin, *The Magnetocaloric Effect and Its Applications* (Institute of Physics, Bristol, Philadelphia, United States, 2003).
2. Yu. V. Sinyavskii, *Khim. Neft. Mashinostr.*, No. 6, 5 (1995).
3. A. Smith, C. R. H. Bahl, R. Bjørk, K. Engelbrecht, K. K. Nielsen, and N. Pryds, *Adv. Energy Mater.* **2**, 1288 (2012).
4. V. K. Pecharsky and K. A. Gschneidner, Jr., *J. Magn. Magn. Mater.* **200**, 44 (1999).
5. V. K. Pecharsky and K. A. Gschneidner, Jr., *Adv. Mater. (Weinheim)* **13**, 683 (2001).
6. M. Valant, *Prog. Mater. Sci.* **57**, 980 (2012).
7. J. F. Scott, *Annu. Rev. Mater. Res.* **41**, 229 (2011).
8. K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, *Rep. Prog. Phys.* **68**, 1479 (2005).
9. A. Planes, L. Manosa, and M. Acet, *J. Phys.: Condens. Matter* **21**, 233201(1–29) (2009).
10. Zhong Wei, Au Chak-Tong, and Du You-Wie, *Chin. Phys. B* **22**, 057501 (2013).
11. Sheng-Guo Lu and Qiming Zhang, *J. Adv. Dielectr.* **2** (3), 1230011 (2012).
12. Th. Strässle, A. Furrer, Z. Hossain, and Ch. Geibel, *Phys. Rev. B: Condens. Matter* **67**, 054407 (2003).
13. I. N. Flerov, M. V. Gorev, A. Tresso, and N. M. Laptash, *Crystallogr. Rep.* **56** (1), 9 (2011).
14. L. Mañosa, D. González-Alonso, A. Planes, E. Bonnot, M. Barrio, J.-L. Tamarit, S. Aksoy, and M. Acet, *Nat. Mater.* **9**, 478 (2010).
15. A. V. Kartashev, E. A. Mikhaleva, M. V. Gorev, E. V. Bogdanov, A. V. Cherepakhin, K. A. Sablina, N. V. Mikhashonok, I. N. Flerov, and N. V. Volkov, *J. Appl. Phys.* **113**, 073901 (2013).
16. P. Lampen, N. S. Bingham, M. H. Phan, H. Kim, M. Osofsky, A. Pique, T. L. Phan, S. C. Yu, and H. Srikanth, *Appl. Phys. Lett.* **102**, 062414 (2013).
17. L. Shaobo and L. Yanqiu, *Mater. Sci. Eng., B* **113**, 46 (2004).
18. J. Peräntie, J. Hagberg, A. Uusimäki, and H. Jantunen, *Phys. Rev. B: Condens. Matter* **82**, 134119 (2010).
19. B. Rožič, M. Kosec, H. Uršič, J. Holc, B. Malič, Q. M. Zhang, R. Blinc, R. Pirc, and Z. Kutnjak, *J. Appl. Phys.* **110**, 064118 (2011).
20. Z. Feng, D. Shi, and S. Dou, *Solid State Commun.* **151**, 123 (2011).
21. G. C. Lin, X. M. Xiong, J. X. Zhang, and Q. Wei, *J. Therm. Anal. Calorim.* **81**, 41 (2005).
22. E. A. Mikhaleva, I. N. Flerov, V. S. Bondarev, M. V. Gorev, A. D. Vasil'ev, and T. N. Davydova, *Phys. Solid State* **53** (3), 510 (2011).
23. M. V. Gorev, I. N. Flerov, E. V. Bogdanov, V. N. Voronov, and N. M. Laptash, *Phys. Solid State* **52** (2), 377 (2010).
24. H. Y. Lee, K. H. Cho, and H.-D. Nam, *Ferroelectrics* **334**, 165 (2006).
25. E. P. Gorzkowski, M.-J. Pan, B. Bender, and C. C. M. Wu, *J. Electroceram.* **18**, 269 (2007).
26. I. Ponomareva and S. Lisenkov, *Phys. Rev. Lett.* **108**, 167604 (2012).
27. R. Pirc, Z. Kutnjak, R. Blinc, and Q. M. Zhang, *Appl. Phys. Lett.* **98** (2), 021909 (2011).
28. S. G. Lu, B. Rožič, Q. M. Zhang, Z. Kutnjak, R. Pirc, M. Lin, X. Li, and L. Gorný, *Appl. Phys. Lett.* **97**, 202901 (2010).
29. A. G. Gamzatov, A. B. Batdalov, A. M. Aliev, P. Amirzadeh, P. Kameli, H. Ahmadvand, and H. Salamati, *Phys. Solid State* **55** (3), 476 (2013).
30. T. Kinoshita, S. Seino, H. Maruyama, Y. Otome, K. Okitsu, T. Nakayama, K. Niihara, T. Nakagawa, and T. A. Yamamoto, *J. Alloys Compd.* **365**, 281 (2004).
31. K. A. Gschneidner, Jr. and V. K. Pecharsky, *Annu. Rev. Mater. Sci.* **30**, 387 (2000).
32. E. Mikhaleva, I. Flerov, A. Kartashev, M. Gorev, A. Cherepakhin, K. Sablina, N. Mikhashonok, N. Volkov, and A. Shabanov, *J. Mater. Res.* **28**, 3322 (2013).
33. L. N. Dzhavadov and Yu. I. Krotov, *Prib. Tekh. Eksp.*, No. 3, 168 (1985).
34. I. N. Flerov, M. V. Gorev, and Ph. Sciau, *J. Phys.: Condens. Matter* **12**, 1 (2000).
35. L. Shebanovs, K. Borman, W. N. Lawless, and A. Kalvane, *Ferroelectrics* **273**, 137 (2002).
36. R. Zhang, D. Peng, D. Xiao, Y. Wang, B. Yang, J. Zhu, P. Yu, and W. Zhang, *Cryst. Res. Technol.* **33**, 827 (1998).
37. N. S. Akulov and L. W. Kirensky, *J. Phys.* **3**, 31 (1940).
38. M. D. Kuz'min and A. M. Tishin, *J. Phys. D: Appl. Phys.* **24**, 2039 (1991).
39. J.-L. Jin, X.-Q. Zhang, G.-K. Li, Zh.-H. Cheng, L. Zheng, and Y. Lu, *Phys. Rev. B: Condens. Matter* **83**, 184431 (2011).
40. J.-L. Jin, X.-Q. Zhang, H. Ge, and Zh.-H. Cheng, *Phys. Rev. B: Condens. Matter* **85**, 214426 (2012).
41. M. Balli, S. Jandl, P. Fournier, and M. M. Gospodinov, *Appl. Phys. Lett.* **104**, 232402 (2014).
42. M. V. Gorev, E. V. Bogdanov, I. N. Flerov, A. G. Kocharova, and N. M. Laptash, *Phys. Solid State* **52** (1), 167 (2010).
43. L. G. Medeiros, N. A. Oliveira, and A. Troper, *J. Appl. Phys.* **103**, 113909 (2008).

44. E. A. Mikhaleva, I. N. Flerov, M. V. Gorev, M. S. Mollokeev, A. V. Cherepakhin, A. V. Kartashev, N. V. Mikhashenok, and A. K. Sablina, *Phys. Solid State* **54** (9), 1832 (2012).
45. S. Lisenkov, B. K. Mani, C.-M. Chang, J. Almand, and I. Ponomareva, *Phys. Rev. B: Condens. Matter* **87**, 224101 (2013).
46. H. Schmid, *Ferroelectrics* **162**, 317 (1994).
47. C.-W. Nan, L. Liu, N. Cai, J. Zhai, Y. Ye, Y. H. Lin, L. J. Dong, and C. X. Xiong, *Appl. Phys. Lett.* **81**, 3831 (2002).
48. W. Eerenstein, N. D. Mathur, and J. F. Scott, *Nature (London)* **442**, 759 (2006).
49. K. Zvezdin and A. P. Pyatakov, *Phys.—Usp.* **47** (4), 416 (2004).
50. M. M. Vopson, *Solid State Commun.* **152**, 2067 (2012).
51. M. I. Bichurin and V. M. Petrov, *Low Temp. Phys.* **36** (6), 544 (2010).
52. Sh. Binek and V. Burobina, *Appl. Phys. Lett.* **102**, 031915 (2013).
53. M. H. Phan, Sh. B. Tian, S. C. Yu, and A. N. Ulyanov, *J. Magn. Magn. Mater.* **256**, 306 (2003).

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