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**ELECTRICALLY AND MAGNETICALLY
INDUCED CRYOGENERATION IN CRYSTALLINE
DIELECTRICS**

Thermodynamic analysis of the induced caloric response of dielectric materials to the application of the electric and magnetic fields is performed. Quantitative characteristics of the electrocaloric and magnetocaloric effects are determined. It is shown that the electrocaloric effect (ECE) is not reverse to the pyroelectric effect, and the magnetocaloric effect (MCE) is not reverse to the pyromagnetic effect. For this reason the electrocaloric effect can be observed in nonferroelectric dielectrics, and the magnetocaloric effect can be observed in nonferromagnetic materials.

Key words: cryogeneration, electrocaloric effect, magnetocaloric effect.

Introduction

One of the promising directions of thermoelectricity development is creation of new types of thermoelements that can expand the range of technical capabilities implemented nowadays by means of “classical” thermoelements [1, 2]. This applies especially to the development of new cooling element designs.

The need for them is caused by increasing miniaturization of microelectronic elements whose stable operation requires extraction of rather large (up to 1 kW/cm^2) heat flows from very small areas on the surface of microcircuit. At the present time this technical task is successfully solved by thermoelectric methods [3], however in the future the application of thermoelectric elements for cooling and thermal stabilization of microelectronic devices may run into limitations caused by relatively low cooling capacity of such elements [4].

A possible way to overcome this difficulty is cryogeneration due to electrically and magnetically induced caloric effects in crystals. Many specialists are convinced (see, for instance [5, 6]) that solid-state cryogenerators are capable of supplanting traditional vapor compression refrigerating units. For that reason a search for materials suitable for creation of working media of such cryogenerators has become much more active.

It must immediately be emphasized that this search is pursued exceptionally among substances having a domain structure, namely ferroelectric and ferromagnetic materials. It is commonly supposed [5, 7] that the efficiency of material application as electrocaloric (or magnetocaloric) is determined by its structure capacity for spontaneous electrical (or magnetic) ordering. In light of this, electrocaloric materials are traditionally selected from among ferroelectric materials, and magnetocaloric materials – from among ferromagnetic materials. In so doing, for cryogeneration use is made of the temperature region close to the point of ferroelectric (or ferromagnetic) conversion. In this region, the domaining materials have extremely high susceptibility to application of electromagnetic field. However, the temperature instability of characteristics of such materials is also

very high. As a result, it appears that efficient cryogeneration requires unique materials with practically incompatible characteristics.

L.P. Bulat was the first to call attention to this peculiarity [4, 6] and he suggested that highly intensive magnetocaloric effect is also possible in nonferromagnetic materials. This idea was further developed in the present paper. In the following we will carry out the thermodynamic analysis of the caloric properties of crystalline materials induced by the electromagnetic effect, and reveal a number of nontrivial qualitative and quantitative regularities of the electrocaloric and magnetocaloric effects in crystalline dielectrics.

Thermodynamic analysis

On introducing the sample substance into electric or magnetic field, an own field is created in the bulk of the sample which differs from the initial field affecting the sample from the outside. If the sample substance in electric field of intensity E is quasi-two-dimensional (single-crystal plate perpendicular to field E), the intensity E' of electric field in the bulk of such sample is determined by the equality [8]

$$E' = \frac{E}{\varepsilon}, \quad (1)$$

where ε is dielectric permeability of the substance. If, however, the sample substance in the electric field is not quasi-two-dimensional, the electric field intensity in the bulk of this substance can be estimated by the formula [8]

$$E' = \frac{3\bar{\varepsilon}}{\varepsilon + 2\bar{\varepsilon}} E, \quad (2)$$

where $\bar{\varepsilon}$ is dielectric permeability of the medium surrounding the sample substance. In the case when the sample substance is exposed to a magnetic field with induction B , in the bulk of this substance the magnetic induction B' and magnetic field intensity h' will be, respectively [9]

$$B' = \mu B, \quad h' = \frac{B}{\mu_0(1 + \iota\zeta)}. \quad (3)$$

Here μ_0 is magnetic permeability of vacuum, $\mu = (1 + \zeta)$ is magnetic permeability of the substance, ζ is magnetic susceptibility of the substance, ι is degaussing factor governed by the sample substance geometry (see [9]).

Elementary work δR to create own fields in the substance is expressed through volume integrals in the form of the following equality [10]:

$$\delta R = \int_{\upsilon} E' \delta D d\upsilon + \int_{\upsilon} h' \delta B' d\upsilon, \quad (4)$$

where $D = \varepsilon_0 \varepsilon E'$ is electric induction, ε_0 is dielectric permeability of vacuum. As long as the values E' , D , h' and B' in Eq. (4) refer to the unit volume of the substance, the expression for differential of molar internal energy U of homogeneous substance in electromagnetic field is given by:

$$dU = TdS - p_0 dV + VE' dD + Vh' dB', \quad (5)$$

where T is temperature, S is molar entropy, V is molar volume of substance, p_0 is pressure of medium surrounding the sample substance.

The sample on which work δR is performed is not in thermally isolated state. Therefore, said work determines not only a change in the bulk of the sample substance, but also a change in its entropy. Indeed, substituting (1) – (3) into (5), we get that when the substance is exposed to electric field

$$dU = TdS - p_e dV + V d(LE^2) = TdS - (p_e + LE^2)dV + d(VLE^2), \quad (6)$$

and when it is exposed to magnetic field

$$dU = TdS - p_e dV + V d(\ell B^2) = TdS - (p_e + \ell B^2)dV + d(V\ell B^2), \quad (7)$$

where

$$\ell = \frac{\mu}{2\mu_0(1 + \nu\zeta)}. \quad (8)$$

In so doing, for quasi-two-dimensional single-crystal dielectrics

$$L = \frac{\varepsilon_0}{2\varepsilon}. \quad (9)$$

If, however, the sample substance cannot be considered quasi-two-dimensional, then

$$L = \frac{9\varepsilon_0 \varepsilon \bar{\varepsilon}^2}{2(\varepsilon + 2\bar{\varepsilon})^2}. \quad (10)$$

From (6) and (7) it follows that increments in molar internal energy and molar entropy of substance due to electric field (Δ_e) and magnetic field (Δ_m) are expressed by the equalities

$$\Delta_e U = VLE^2, \quad \Delta_m U = V\ell B^2, \quad (11)$$

$$\Delta_e S = \frac{VLE^2}{T}, \quad \Delta_m S = \frac{V\ell B^2}{T}. \quad (12)$$

Pressure $p = -(\partial U / \partial V)_S$ corresponding to thermodynamic equilibrium of the sample substance in electromagnetic field is determined by the equality

$$p = p_e + p_e + p_m \quad (13)$$

where

$$p_e = LE^2, \quad p_m = \ell B^2. \quad (14)$$

The isobaric-isothermal increments of molar enthalpy $H = U + pV$ and molar Gibbs energy $G = U + pV - TS$ caused by exposure to electric and magnetic fields are expressed by the equalities

$$\Delta_e G = p_e V, \quad \Delta_m G = p_m V; \quad (15)$$

$$\Delta_e H = 2p_e V, \quad \Delta_m H = 2p_m V, \quad (16)$$

and molar free energy $A = U - TS$ of substance in electromagnetic field is not changed.

Discussion of the results

A quantitative characteristic of ECE is electrocaloric coefficient $\Xi_e = (\partial T / \partial E)_S$. Let us use formal thermodynamic equations

$$\left(\frac{\partial T}{\partial E}\right)_S = -\left(\frac{\partial S}{\partial E}\right)_T \frac{T}{C_E}, \quad (17)$$

$$C_E = C_p - T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_E, \quad (18)$$

where C_p is isobaric heat capacity, C_E is heat capacity at constant electric field. From (13), (14) it follows that

$$\left(\frac{\partial p}{\partial T}\right)_E = E^2 \cdot \left(\frac{\partial L}{\partial T}\right)_E.$$

The value $(\partial L/\partial T)_E$ is governed by the temperature dependence of dielectric permittivity ε . However, if a dielectric is not ferroelectric, the above temperature dependence can be neglected: $(\partial L/\partial T)_E \approx 0$. Therefore, for nonferroelectric dielectrics instead of (18) we will have $C_E = C_p$. Then coming back to equality (17), with regard to (12) we will get:

$$\Xi_e = -\frac{2VLE}{C_p}. \quad (19)$$

From (19) it follows that if electric field intensity changes with time t by the law $E(t)$, by the moment $t = \tau$ the temperature of nonferromagnetic crystal will change by the value

$$\Delta T_e(\tau) = -\frac{2VL}{C_p} \int_0^\tau E(t) \frac{dE}{dt} dt, \quad (20)$$

where the moment of onset of electric field intensity variation is taken to be time reference point ($t = 0$).

Similarly, using the equalities

$$\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial S}{\partial B}\right)_T \frac{T}{C_B}, \quad C_B = C_p - T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_B,$$

where C_B is heat capacity at constant magnetic induction, for magnetocaloric coefficient $\Xi_m = (\partial T/\partial B)_S$ we obtain:

$$\Xi_m = -\frac{2V\ell B}{C_p}. \quad (21)$$

Hence it follows that if magnetic induction changes with time t by the law $B(t)$, by the moment $t = \tau$ the temperature of nonferromagnetic substance will vary by the value

$$\Delta T_m(\tau) = -\frac{2V\ell}{C_p} \int_0^\tau B(t) \frac{dB}{dt} dt, \quad (22)$$

where the moment of onset of magnetic induction variation is taken to be time reference point.

Formulae (19) – (22) show that the intensity of induced caloric effects is the higher, the larger molar volume of caloric material and the lower its heat capacity, as it was to be expected on the basis of traditional crystallographic concepts (see, for instance, [11]). At the same time, the results

obtained encourage to reconsider common point of view that only substances having domain structure can be efficient caloric materials.

By tradition, ECE is considered as an effect opposite to pyroelectric effect [11]. In reality it is not the case. In conformity with general differential thermodynamic relations [12], we have the equality

$$\left(\frac{\partial P}{\partial T}\right)_E = \left(\frac{\partial S}{\partial E}\right)_T = -\frac{\Xi_e C_E}{T}. \quad (23)$$

It is essential that P value in Eq. (23) is full electric polarization of substance including not only spontaneous (pyroelectric) polarization, but also induced polarization, created by external electric field. For this reason ECE is not only an effect opposite to pyroeffect, but even is not in a direct relationship with it.

This conclusion has an important consequence: the possibility of ECE observation is not restricted by pyroelectric materials. On account of (9), (10) and (19), the requirement $\Xi_e \neq 0$ is met for all dielectric materials (for electrically conducting media $\Xi_e = 0$, since for such media $\varepsilon \rightarrow \infty$, in consequence of which $L = 0$). In so doing, ferroelectrics do not have evident advantages. As is seen from (20), the efficiency of electrocaloric cryogeneration is determined not only by own characteristics of material, but also by the shape of its sample {cf. formulae (9) and (10)}, as well as by the rate of increase of external electric field intensity.

Special attention should be paid to the above dependence of the efficiency of electrocaloric cryogeneration on the geometrical shape of working medium. In the course of experimental data processing [13 – 54] by formulae (9) and (10) we have calculated the values of parameter L for the best studied dielectric crystals (see the Table). Calculations show that the transition from a quasi-two-dimensional to a three-dimensional sample matches a change in the value of parameter L by a factor of 8 – 10.

Table

Dielectric properties of electrocaloric materials

Substance	Parameter L		Substance	Параметр L		Substance	Параметр L	
	Quasi-two-dimensional sample, $L \cdot 10^{13}$	Three-dimensional sample, $L \cdot 10^{12}$		Quasi-two-dimensional sample, $L \cdot 10^{13}$	Three-dimensional sample, $L \cdot 10^{12}$		Quasi-two-dimensional sample, $L \cdot 10^{13}$	Three-dimensional sample, $L \cdot 10^{12}$
<i>AgBr</i>	3.379	2.289	<i>CaCeO₃</i>	2.108	1.582	<i>GaP</i>	4.137	2.643
<i>AgCl</i>	3.599	2.397	<i>CaF₂</i>	5.251	3.088	<i>GaSb</i>	2.750	1.958
<i>AgI</i>	6.324	3.443	<i>Ca(NO₃)₂</i>	6.769	3.573	<i>Ge</i>	2.767	1.968
<i>Ag₂O</i>	5.031	3.006	<i>CaO</i>	3.752	2.469	<i>α-HIO₃</i>	1.581	1.240
<i>AlAs</i>	4.401	2.756	<i>CaWO₄</i>	1.346	1.076	<i>HgCl₂</i>	3.162	2.179
<i>AlP</i>	4.517	2.804	<i>CaZrO₃</i>	1.581	1.240	<i>HgSe</i>	1.723	1.335
<i>AlPO₄</i>	3.144	2.170	<i>CdO</i>	2.021	1.528	<i>HgTe</i>	2.108	1.582
<i>AlSb</i>	3.677	2.434	<i>CdS</i>	1.525	1.201	<i>InAs</i>	3.053	2.122
<i>(AlF)₂SiO₄</i>	2.197	1.636	<i>CdSe</i>	1.473	1.166	<i>InP</i>	3.525	2.361
<i>Al₂O₃</i>	1.595	1.249	<i>CdSnAs₂</i>	3.231	2.214	<i>InSb</i>	2.501	1.817
<i>BP</i>	3.816	2.499	<i>CdTe</i>	4.257	2.695	<i>KBr</i>	9.262	4.143

Table (continued)

Sub- stance	Parameter L		Substance	Параметр L		Substance	Параметр L	
	Quasi- two- dimen- sional sample, $L \cdot 10^{13}$	Three- dimen- sional sample, $L \cdot 10^{12}$		Quasi- two- dimen- sional sample, $L \cdot 10^{13}$	Three- dimen- sional sample, $L \cdot 10^{12}$		Quasi- two- dimen- sional sample, $L \cdot 10^{13}$	Three- dimen- sional sample, $L \cdot 10^{12}$
<i>BaCl₂</i>	4.513	2.802	<i>Co₂O₃</i>	4.616	2.844	<i>KCl</i>	9.459	4.179
<i>BaF₂</i>	6.048	3.358	<i>CsBr</i>	6.800	3.582	<i>KF</i>	7.317	3.720
<i>Ba(NO₃)₂</i>	8.943	4.083	<i>CsCl</i>	6.149	3.389	<i>KI</i>	8.962	4.087
<i>BaO</i>	1.302	1.045	<i>CsI</i>	7.835	3.847	<i>KNO₂</i>	1.771	1.366
<i>BaZrO₃</i>	2.214	1.646	<i>CuBr</i>	5.534	3.187	<i>KNO₃</i>	8.854	4.066
<i>BeO</i>	6.023	3.350	<i>CuCl</i>	4.427	2.767	<i>LaScO₃</i>	1.476	1.167
<i>Bi₄(GeO₄)₃</i>	2.767	1.968	<i>CuI</i>	6.811	3.584	<i>LiBr</i>	3.659	2.425
<i>Bi₁₂SiO₂₀</i>	1.265	1.019	<i>EuF₂</i>	5.749	3.261	<i>LiCl</i>	4.006	2.585
<i>C</i>	7.794	3.837	<i>GaAs</i>	3.379	2.289	<i>LiF</i>	4.776	2.908
<i>CaCO₃</i>	1.800	1.385	<i>GaN</i>	1.506	1.188	<i>LiGaO₂</i>	1.876	1.435
<i>LiI</i>	4.014	2.588	<i>PbBr</i>	1.476	1.167	<i>SrF₂</i>	5.757	3.263
<i>Li₂GeO₃</i>	1.652	1.287	<i>PbI₂</i>	2.128	1.594	<i>Sr(NO₃)₂</i>	8.306	3.952
<i>MgF₂</i>	8.943	4.083	<i>Pb(CO₃)₂</i>	1.845	1.415	<i>SrO</i>	3.329	2.264
<i>MgO</i>	4.517	2.804	<i>PbCl₂</i>	1.321	1.059	<i>SrSO₄</i>	3.850	2.514
<i>MgSO₄</i>	5.399	3.140	<i>PbF₂</i>	1.511	1.192	β - <i>Ta₂O₅</i>	1.845	1.415
<i>MgTiO₃</i>	2.459	1.793	<i>Pb(NO₃)₂</i>	2.635	1.894	<i>ThO₂</i>	2.342	1.724
<i>MnO</i>	2.446	1.785	<i>PbO</i>	2.012	1.522	<i>TlBr</i>	1.481	1.171
<i>NH₄Cl</i>	6.361	3.454	<i>PbO₂</i>	1.703	1.321	<i>TlCl</i>	1.388	1.106
<i>NH₄I</i>	7.633	3.798	<i>RbBr</i>	9.090	4.111	<i>TlNO₃</i>	2.683	1.921
<i>NaBr</i>	7.391	3.738	<i>RbCl</i>	9.016	4.097	<i>Tl₃TaS₄</i>	3.304	2.251
<i>NaBrO₃</i>	7.767	3.830	<i>RbF</i>	7.491	3.763	<i>Tl₃TaSe₄</i>	4.383	2.749
<i>NaCl</i>	7.877	3.856	<i>RbI</i>	8.962	4.087	<i>Tl₃VS₄</i>	3.162	2.179
<i>NaClO₃</i>	8.384	3.969	<i>RbInSO₄</i>	6.463	3.485	<i>UO₂</i>	1.845	1.415
<i>NaClO₄</i>	7.686	3.811	<i>S</i>	3.647	2.419	<i>Y₃Al₅O₁₂</i>	3.784	2.484
<i>NaF</i>	7.378	3.735	<i>Se</i>	7.378	3.735	<i>ZnO</i>	1.500	1.184
<i>NaI</i>	6.708	3.555	<i>Si</i>	3.720	2.454	α - <i>ZnS</i>	1.703	1.321
<i>NaSO₄</i>	5.604	3.212	α - <i>SiO₂</i>	3.196	2.197	β - <i>ZnS</i>	5.334	3.117
<i>NdAlO₃</i>	2.530	1.834	<i>Sm₂O₃</i>	2.059	1.551	<i>ZnSe</i>	4.865	2.943
<i>NdScO₃</i>	1.640	1.279	<i>SnO₂</i>	1.845	1.415	<i>ZnTe</i>	4.383	2.749
<i>Ni₂O₃</i>	3.440	2.319	<i>SrCl₂</i>	4.817	2.924			

Making evident formal replacements and redesignations in the reasoning related to Eq. (23), it is easy to show in a similar way that MCE is not an effect opposite to pyromagnetic effect, therefore it can be observed not only in ferromagnetic materials. From formulae (21), (22) it is seen that by the main formal signs MCE is similar to ECE: the efficiency of magnetocaloric cryogeneration is determined by the shape of time-based sweep of magnetic induction and the sample geometry. However, the governing factor is the type of the dependence $B(t)$. Due to the fact that in ferromagnetic materials the magnetic permeability μ is slightly different from unity, and the magnetic susceptibility $\zeta \ll 1$, own magnetic properties of

such materials scarcely affect MCE: according to formula (8) for nonferromagnetic materials

$$\ell \approx \frac{1}{2\mu_0} = 3.979 \cdot 10^5 \text{ m/H}.$$

The possibilities of electrically and magnetically induced cryogeneration described by formulae (20) and (22) are naturally compared to "classical" electrically induced solid-state cryogeneration due to the Peltier effect.

Dimensional factor is the main characteristic giving a clear advantage to thermoelectric coolers over the above described cryogeneration methods. Electrocaloric and, even more, magnetocaloric coolers are inferior to thermoelectric coolers in compactness, as long as in view of formulae (20) and (22) for the implementation of electrically and magnetically induced cryogeneration it is necessary to have devices assuring cyclic changes of the electrical and magnetic fields with the asymmetrical shape of time-base sweep.

In a variety of factors (noise-free operation, ecological safety, possibility of quick cooling and "cooling-heating" reversal) the electrically and magnetically induced cryogeneration is similar to thermoelectric cooling. Of greatest interest are the advantages of electrically and magnetically induced cryogeneration as compared to thermoelectric cooling.

These advantages are primarily due to the absence of the Joule losses owing to which the coefficient of performance η of corresponding generators can be much in excess of the coefficient of performance of the most efficient thermoelectric coolers. Namely, at electrocaloric cryogeneration

$$\eta_e = \frac{T_0 - \Delta T_e}{\Delta T_e}, \quad (24)$$

and at magnetocaloric cryogeneration

$$\eta_m = \frac{T_0 - \Delta T_m}{\Delta T_m}, \quad (25)$$

where T_0 is initial temperature (ambient temperature), and ΔT_e and ΔT_m are determined by formulae (20) and (22), respectively.

Another important advantage is a relatively weak dependence of the intensity of electrically induced and, in particular, magnetically induced cryogeneration on the properties of working medium. As mentioned above, the decisive factors are the geometrical shape of working medium and, even more, the shape of time-base sweep of electrical (or magnetic) field. The latter factor is of particular significance, since it eliminates not only the necessity of seeking "efficient" materials, but also the need for using superstrong fields. Indeed, optimizing the shape of time-base sweep of the field, i.e. increasing the value $\frac{dE}{dt}$ or $\frac{dB}{dt}$, one can achieve high values of coefficients of performance η_e and η_m even in relatively weak electromagnetic fields [see formulae (20), (22), (24), (25)].

Conclusion

1. A thermodynamic analysis of induced caloric response of dielectric materials to application of electric and magnetic field was performed [formulae (6) – (16)], which allowed quantitative description of ECE and MCE [formulae (19) – (22)].

2. It was shown that ECE is not an effect reverse to pyroelectric effect, and MCE is not an effect reverse to pyromagnetic effect. For this reason ECE can be observed in nonferromagnetic dielectrics, and MCE can be observed in nonferromagnetic materials.
3. It was established that the influence of caloric material own characteristics on the efficiency of cryogeneration through ECE and MCE is not critically important. The decisive factor is the rate of increase in the intensity of external electromagnetic field. This conclusion is in agreement with the results of [55], where the effect of influence of electric field timebase form on the intensity of ECE was experimentally observed.

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