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Layered ceramic structure based on the electrocaloric elements working as a solid state cooling line

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Abstract

The temperature response in the solid state cooling line composed of electrocaloric (EC) and thermoconductive elements was investigated using analytical approach and computational experiment. A periodical bias electric field applied to ferroelectric capacitor caused their heating and cooling, however, alternative adiabatic and isothermal switching of the EC elements allowed to generate the directed heat flux and the temperature decrease ΔT at one edge of the solid state structure. Thin film topologies are expediently to be used because thin electrocaloric elements are most appropriate to enhance switching frequency and increase ΔT. The temperature decrease $\sim 20^{\circ}$ was obtained at one edge of the cooling line with (Ba,Sr)TiO_3 EC elements. The serial connection of the EC lines can give a considerable cooling effect.

Keywords: Films; Composites; Ferroelectric properties; Perovskites; Electrocaloric cooling

1. Introduction

The search of new cooling principles based on solid state phenomena and development of ecologically friendly refrigerators with lowest power consumption are very important tasks for modern society and it can be solved on the basis of a complex approach including solid state material science, molecular physics and low temperature engineering. The effective heat transformation could be implemented in the solid state structures using magnetocaloric (MCE)[1,2] and electrocaloric effects (ECE)[3–5]. The comparison of such characteristics as applied electric power, material and device cost leads to a conclusion that ECE heat transformer is considerably more effective than MCE one. The ceramics based on Pb(Zr,Ti)O_3, PMN-PT, (Ba,Sr)TiO_3 compounds and other perovskite materials are perspective for the refrigerating application based on ECE.[5,6] The temperature effect ΔT was not more than 1 K under action of bias electric field of several volts per micrometer. This fact and low effective thermodynamic cycles restricted the developments of cooling devices based on ECE. Novel ferroelectric compounds revealing ECE ~ 3–4 K, such as in reference[6] and thin film technologies change the relation of the cryogenic engineers to EC cooling systems. In 2005–2006 the essential $\Delta T \sim 12$ K was demonstrated for Pb(Zr,Ti)O_3 films.[7] Nowadays the important improvements were achieved including synthesis of novel materials, development of reliable film technologies, modeling of effective thermodynamic cycle. This work is devoted to the investigation of EC cooling cycle, solution of the analytical heat tasks for the layered structure composed of heat transferring and electrocaloric elements subjected to periodical switching.

2. Electrocaloric effect in ferroelectric materials

The temperature variation in the periodical electrical field applied to dielectric is a basis of EC effect, which has the thermal yield determined by the following expression:[8]

$$dQ = -T\varepsilon_0 \frac{d\chi}{dT} E\, dE \quad (1)$$

where $\chi(E, T)$ is a dielectric susceptibility dependent on electric field intensity E and temperature T. A change of the specific heat energy dQ is caused by a variation of electrical field dE. The expression (1) for dQ (J/m^3) can be transformed using the following equations: $\gamma(E, T) = T\varepsilon_0\, d\chi/dT$; $E\, dE = 1/2\, dE^2$,

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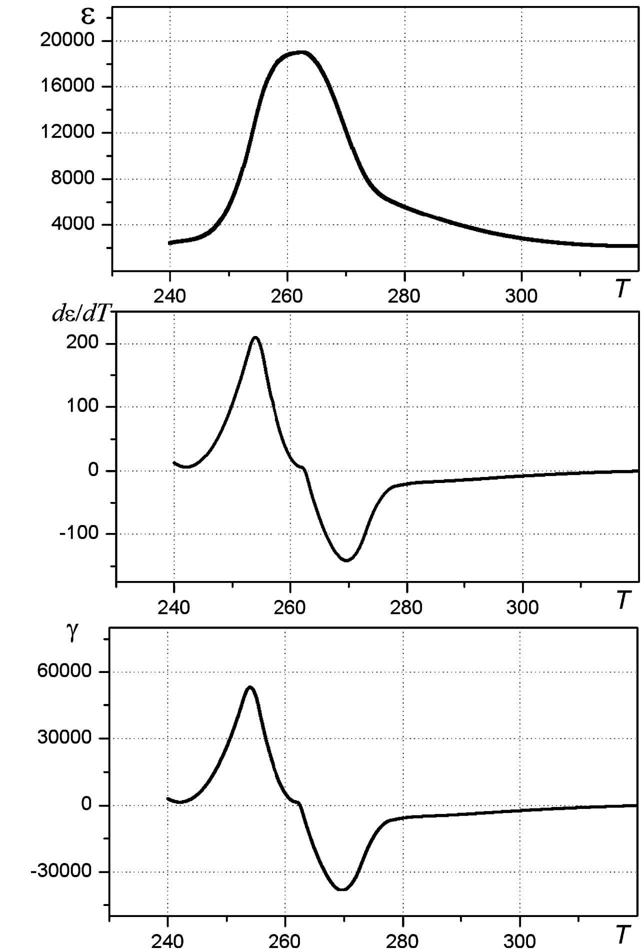

Fig. 1. The temperature dependence of the dielectric constant and its derivatives for $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics (the $\varepsilon(T)$ dependence was taken in[9]).

then $\mathrm{d}Q = -(1/2)\gamma(E, T)\mathrm{d}E^2$, and thermal power P proceeding through EC element is determined such as follows:

$$P = \frac{\mathrm{d}Q}{\mathrm{d}\tau} = \frac{1}{2}\gamma(E, T)\frac{\mathrm{d}E^2}{\mathrm{d}\tau} \tag{2}$$

The behavior of dielectric susceptibility $\chi(E, T)$ determines $\mathrm{d}Q$ value. Static dielectric permittivity $\varepsilon(E, T)$ of a ferroelectric material has practically the same physical meaning as a susceptibility from the point of view of its temperature dependence. As the example we have chosen the well-studied ferroelectric ceramics $(Ba,Sr)TiO_3$—BST. It is expedient to use the ferroelectric ceramics with the highest value of $\partial\varepsilon/\partial E$ and $\partial\varepsilon/\partial T$ in paraelectric phase. Fig. 1 shows the temperature dependence of the dielectric constant, $\partial\varepsilon/\partial T$ and its derivatives for $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics.[9] Ferroelectric phase is distinguished by a property of a residual polarization, which decreases a heat effect at the switching of the ferroelectric capacitor. Big value of $\partial\varepsilon/\partial T$ is also demanded for electrocaloric heat transformers. The region on right from the maximum is most appropriate for electrocaloric refrigerator. The appropriate choice of the BST composition and the processing route allows select the ceramics with maximal ΔT for the chosen operational temperature region. For example, in Fig. 1 the chosen range (275–300 K) includes room temperature which has big practical importance. At present a wide set of novel ferroelectric compounds revealing considerable electrocaloric effect was synthesized. Along with the materials revealing big ECE the effective thermodynamic cycle are also very important to implement effective refrigerator. This work presents a novel approach to the formation of the solid state refrigerator based on electrocaloric elements.

3. Periodical switching of the electrocaloric elements

The switching can be executed in various modes: adiabatic (iso-entropic) and isothermal ones. The electric field is switched by jump from 0 up to E_1 in the adiabatic thermal regime. The characteristic time of the front of this switching process is about $\Delta\tau = 10^{-12}$ s. During this short period the electrocaloric element cannot change its temperature immediately, because the characteristic time of the thermal processes is about $10^{-6}c$. The adiabatic heat density Q_1 can be absorbed, or it can be extracted according to the formula:

$$Q_1 = \pm\frac{1}{V}\gamma(T_1)E^2 \tag{3}$$

where T_1 is the initial temperature of the electrocaloric element. Final temperature of the nonlinear element after switching pulse is T_2. If we would use the isothermal switching mode, then electrical field passes slowly enough, and the isothermal heat density Q_2 can be expressed by the following formula:

$$Q_2 = -\int_{t_1}^{t_2}\frac{1}{V}\gamma(T)E\frac{\partial E}{\partial T}\,\mathrm{d}t = -\frac{1}{V}\gamma(T_a)E^2 \tag{4}$$

where t_1 is the initial moment and t_2 is the final moment of the switching process, and T_a is some average temperature between T_1 and T_2. Fig. 2 shows schematic representations of various switching processes in EC element. The variation of the electric

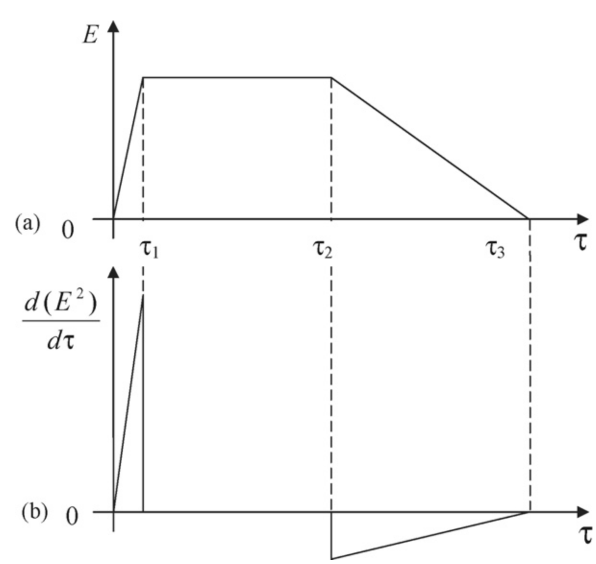

Fig. 2. The different temperature modes (adiabatic and isothermal), which were used for the switching of EC elements: (a) the variation of the electric field applied to ferroelectric capacitor; (b) the derivative of electric field on a time.

field applied to ferroelectric capacitor is presented in Fig. 2(a). Initially electric field grows relatively fast. This is an adiabatic process, which takes a short period $(0-\tau_1)$. Then electric field is kept on the EC element and from the moment τ_2 electric field is switched using isothermal regime. The duration of the adiabatic and the isothermal pulse fronts is distinguished approximately in 10^3 times. The time derivative of electric field, which is shown in Fig. 2(b), enters in the formula (3) for heat power proceeding in the cooling line, and it reflects the shape of adiabatic and isothermal pulses applied to EC element. In order to obtain integral heat effect (ΔQ) one may incorporate two EC elements, which should be switched with application of the alternative switching modes, and thermal conductor elements. The composed cooling line gives a possibility obtaining heat effect $\Delta Q = |Q_1| - |Q_2| \neq 0$, which is a difference between heat extracted and absorbed during various switching modes in the separate EC elements of the cooling line. The implementation of the cooling process requires to ensure the difference between the extracted and absorbed heat fluxes owing to nonlinear $\gamma(T)$ dependence for the taken ferroelectric material.

4. Heat transfer line and cycling procedure

Fig. 3 presents the simple model, which was used for the description of the operational principles of the solid state cooling line based on EC elements. The line consisted of five serial layers—two EC elements (2 and 4) and three heat conductors.

We studied temperature variations only along the x-axis (1D model). This linear task used also the following assumptions: the boundary $x = 0$ has thermal isolation, i.e. heat flux at this point was absent. The temperature at $x = L$ had the value T_0, which had the temperature of the environmental medium and the initial temperature of the line. We expressed the heat conductance equation with using the following designations: $C(x)$ и $\lambda(x)$—heat capacitance and heat conductance of the line, respectively:

$$C(x)\frac{\partial T}{\partial \tau} = \frac{\partial}{\partial x}\lambda(x)\frac{\partial T}{\partial x} + P(x, \tau, T) \qquad (5)$$

with the following boundary conditions:

$$\lambda(0)\left.\frac{\partial T}{\partial x}\right|_{x=0} = 0, \quad T|_{x=L} = T_0 \qquad (6)$$

and initial condition: $T(x,0) = T_0$. The $C(x)$ и $\lambda(x)$ values were constant inside the limits of one layer (element). The parameter $P(x, \tau, T)$ is the heat source, which expressed specific thermal capacity extracted or absorbed in EC element:

$$P(x, \tau, T) = P_1(x, \tau, T) + P_2(x, \tau, T),$$
$$P_i(x, \tau, T) = \gamma(T)E_i\frac{\partial E_i}{\partial \tau}l_i, \quad i = 1, 2 \qquad (7)$$

where $E_i(\tau)$ is the electrical field intensity on EC element with number i, and $l_i = x_{2i} - x_{2i-1}$ is the thickness of EC element, and function P_i is different from zero at the required electric field only. The functions P_1 and P_2 were not strictly periodical ones owing to the nonlinear dependence $\gamma(T)$. We have obtained the analytical solution for the temperature distribution along the cooling line presented in Fig. 3 for the equilibrium regime. There are linear $T(x)$ dependencies for the parts 1, 3 and 5, however (dT/dx) is different for every indicated parts. At narrow sections of EC elements we had some temperature jumps. It is necessary to note that analytical decision gives the approximate solution only, and basing on the analytical solution, we can estimate the character of temperature evolution in the solid state cooling line along its length and in the equilibrium regime. The correct solution of the Eq. (5) could be obtained using numerical approach and modern computational procedures.

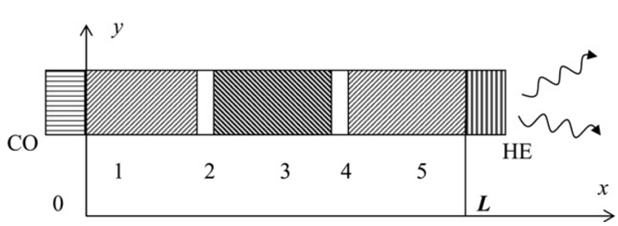

Fig. 3. The sketch of solid state cooling line with EC elements, where CO: cooling object; HE: hear exchanger; the length of the solid state line is L.

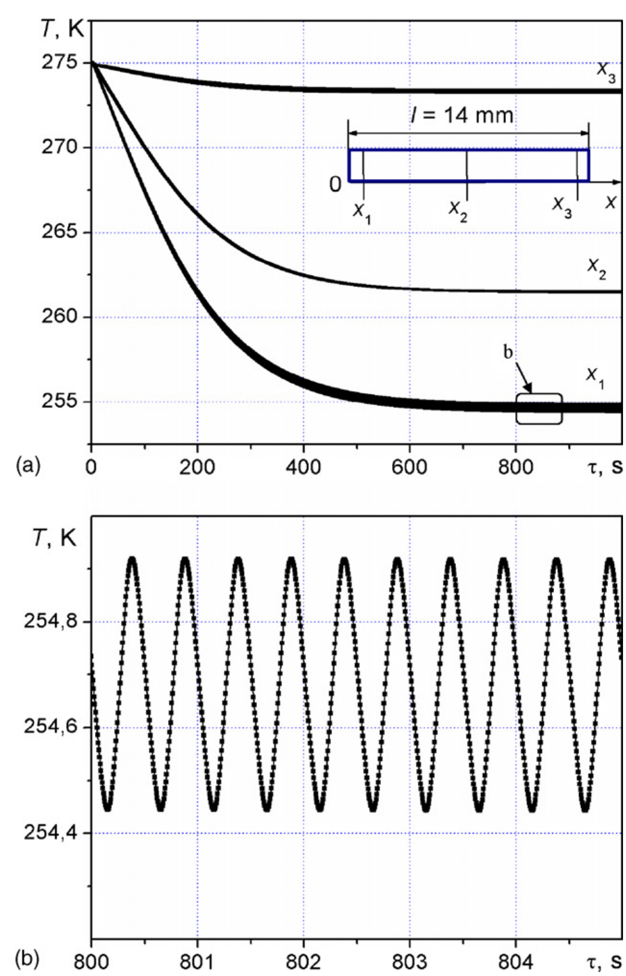

Fig. 4. The results of the computational experiment for the temperature variation along the solid line length ($L = 14$ mm). The experiment was carried out for the following distances: $x_1 = 0.7$ mm; $x_2 = 7$ mm; $x_3 = 13.3$ mm.

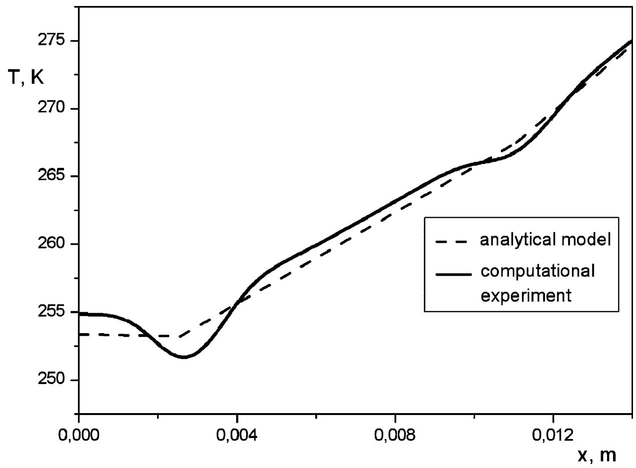

Fig. 5. The comparison of the temperature distribution along the thermoconductive elements of the cooling line using analytical and computational approaches.

5. Computational experiment

The numerical modeling of the cooling procedure was based on the method of finite elements and software FEMLAB. As the initial temperature we used $T_0 = 275$ K at one edge of the cooling line; another edge had the thermal isolation from the environment. The amplitude of the electric field pulse was chosen equal 1 mV/mm. We have taken the BST compound, which temperature dependence of dielectric constant is presented in Fig. 1. The thermal conductivity is $\lambda = 10$ W/(m K); thermal capacity is $c = 900$ J/(kg K), and mass density $\rho = 6000$ kg/m^3. Using these experimental data we calculated the value of $\gamma(E, T)$ coefficient, which was introduced in the formula (3). We selected the defined regions on the dependence $\varepsilon(T)$ and $\gamma(E, T)$, where the module of $\gamma(T)$ dependence had the decreasing character, that means $\mathrm{d}|\gamma(T)|/\mathrm{d}T < 0$. Therefore, the temperature band (270–280) K was chosen for the investigations. We have taken the linear approximation of the $\gamma(T)$ dependence. The periodical pulses were applied to the EC elements and the defined frequency $f = 1/\tau_3$ (see Fig. 2). In our experiments we varied the frequency in the region (1–10) Hz. The periodical switching causes the heating and cooling of EC elements in accordance with expression (3) and this led to the temperature field redistribution in the nearest parts of the solid state line. In the experiments we applied 2000 pulses. At the initial moment the line had the temperature 275 K. Fig. 4 presents the results of the computational experiment for the temperature variation along the solid line length in the equilibrium regime. The figure shows the essential temperature decrease at the thermally isolated edge. The equilibrium regime is achieved in the system after about 1000 pulses, and the temperature is oscillated at some average value. This result corresponds to the temperature distribution obtained from the analytical considerations using formula (5)–(7). Fig. 5 presents the linear temperature distribution along the thermoconductive elements of the cooling line, and the analytical and computational results are in a good coincidence.

6. Conclusion

Basing on the analytical and computational approaches, we showed that directed heat flux is formed in state layered structure composed of two EC elements, which can be periodically switched under action of adiabatic and isothermal modes, and thermoconductive elements. The linear temperature dependence is evidenced in every thermoconductive part. The (Ba,Sr)TiO_3 ceramics was chosen for every element of the solid state cooling line, which was used in the computational experiment. The analytical and computational analysis showed that temperature difference about 20 K between the edges of the cooling line could be achieved in the equilibrium regime at the distance14 mm, if the effective heat transfer would be organized on the edge, which plays a role of a heat exchanger.

Acknowledgement

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References

1. Warburg, E., Magneto-caloric effect. *Ann. Phys. Chem.*, 1981, **13**, 141–146.
2. Tegus, O., Bruck, E., Buschow, K. H. J. and de Boer, F. R., Transition-metal-based magnetic refrigerants for room-temperature applications. *Nature*, 2002, **415**, 150–151.
3. Borisovski, K. E. and Prudan, A. M., Electrocaloric coefficients of strontium titanate at cryogenic temperatures. *Solid State Phys.*, 1989, **31**, 53–56.
4. Lawless, W.N., Electrocaloric device and thermal transfer system employing the same. US Patent 6,877,325 B1, April 12, 2005.
5. He, J., Chen, J., Zhou, Y. and Wang, J., Regenerative characteristics of electrocaloric Stirling or Ericsson refrigeration cycles. *Energy Convers. Manage.*, 2002, **43**, 2319–2327.
6. Zhang, R., Peng, S., Xiao, D., Wang, Y., Yang, B., Zhu, J., Yu, P. and Zhang, W., Preparation and characterization of $(1-x)Pb(Mg_{0.33}Nb_{0.67})O_{3-x}PbTiO_3$ electrocaloric ceramics. *Cryst. Res. Technol.*, 1998, **33**, 827–832.
7. Mischenko, A., Zhang, Q., Scott, J. F., Whatmore, R. W. and Marhur, N. D., Giant electrocaloric effect in thin film $PbZr_{0.05}Ti_{0.05}O_3$. *Science*, 2006, **311**(5765), 1270–1271.
8. Ryogo, K., *Thermodynamics. An Advanced Course with Problems and Solutions*. North-Holland Pub. Co, Amsterdam, New York, 1976.
9. Vendik, O. G., ed., *Ferroelectric at Microwaves*. Soviet Radio, Moscow, 1979.