

Theoretical investigation on polar dielectric with large electrocaloric effect as cooling devices

Liwu Liu,¹ Yanju Liu,^{1,a)} Bo Li,² and Jinsong Leng^{3,a)}

¹Department of Astronautical Science and Mechanics, Harbin Institute of Technology (HIT), P.O. Box 301, No. 92 West Dazhi Street, Harbin 150001, People's Republic of China

²School of Mechanical Engineering, Xi'an Jiaotong University, No. 29 Xianning West Road, Xi'an 710049, People's Republic of China

³Centre for Composite Materials, Science Park of Harbin Institute of Technology (HIT), P.O. Box 3011, No. 2 Yikuang Street, Harbin 150080, People's Republic of China

(Received 23 March 2011; accepted 1 October 2011; published online 4 November 2011)

Polar dielectric based cooling devices are modeled as a system with two degrees of freedom and represented by either an entropy-temperature or electric displacement-electric field plane. A typical thermodynamic energy cyclic path is proposed for polar dielectric as cooling devices to experience. With the influence of temperature taken into consideration, the free energy of a thermal electrical coupling system of polar dielectrics is formulated, and the variation of temperature and entropy, the absorption of heat, and the work under different electric fields are calculated for BaTiO_3 , $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, $\text{P}(\text{VDF}-\text{TrFE})$, and water. And the simulation results obtained agree well with the recently published experimental data [B. Neese, *et al.*, Science **321**, 821 (2008)]. It is, therefore, suggested that the high polar liquid dielectrics may possess a large electrocaloric effect. © 2011 American Institute of Physics. [doi:10.1063/1.3655327]

Due to the change in dipolar states, a change in entropy or a change in temperature will be induced under isothermal or adiabatic condition, respectively, when an electric field is applied to a polar dielectric, and this is known as electrocaloric effect (ECE).¹⁻⁹ In practical applications, the former can be used to design and manufacture cooling devices.¹⁻⁹

The electrocaloric effect of solid polar dielectric is extensively investigated in recent years.^{2,8} It is found that the change in adiabatic temperature and the change in isothermal entropy of initially explored electrocaloric materials, such as ferroelectric ceramic BaTiO_3 , KTaO_3 , and SrTiO_3 are moderate, which restricts their applications in practical cooling devices.^{2,8}

However, recent experimental results indicate that the antiferroelectric ceramic PbZrTi (PZT) thin film and ferroelectric polymer thin film have a large electrocaloric effect when the temperature range is above ferroelectric (polarization-ordered)–paraelectric (polarization-disordered) (F–P) phase transition.^{1-3,5-7,9,15,16}

For example, Mischensko *et al.* demonstrated a large electrocaloric effect in antiferroelectric ceramic $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ above F–P phase transition at a ferroelectric Curie temperature of 222 °C, and observed a change in adiabatic temperature of more than 12 °C and a change in isothermal entropy of over 8 J/(KgK).³

Zhang *et al.* observed a change in isothermal entropy of more than 55 J/(KgK) and a change in adiabatic temperature of over 12 °C. They also showed that the relaxor ferroelectric polymer of $\text{P}(\text{VDF}-\text{TrFE}-\text{chlorofluoroethylene})$ has a large electrocaloric effect.¹ They also showed that the relaxor ferroelectric polymer of $\text{P}(\text{VDF}-\text{TrFE}-\text{chlorofluoroethylene})$ has a large electrocaloric effect.¹

By taking into consideration, the effect of temperature on a polar dielectric thermodynamics system, the thermal contribution, and the free energy function of a thermal-electric coupling system are proposed in this paper to describe the relations of electric displacement-electric field, entropy-temperature. The changes in entropy, temperature, and absorption of heat, are calculated together with the work when the polar dielectric is subjected to different electric fields and temperatures.

Figure 1 sketches the working principle of polar dielectric as cooling devices. Electric displacement and electric field are used in Figure 1(a) and entropy and temperature are used in Figure 1(b) to describe a thermodynamic cycle. The working material experiences four thermodynamic paths which compose an analog to the Carnot cycle of a steam engine.

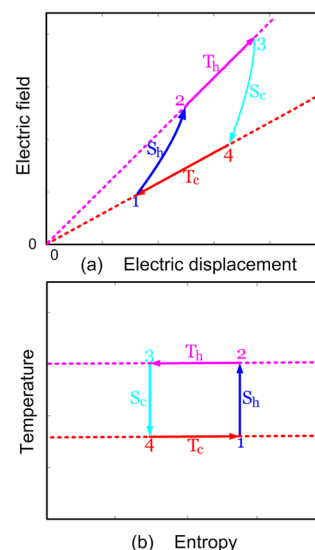


FIG. 1. (Color online) Working cycle of polar dielectric as cooling devices.

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: yj_liu@hit.edu.cn (Tel./FAX: +86-451-86414825) and lengjs@hit.edu.cn (Tel./FAX: +86-451-86402328).

- (1) Applied electric field on polar dielectric E_1 increases in the adiabatic temperature rising process 1→2. Due to the electrocaloric effect, the temperature of material rises, and the material changes from state 1 (E_1, T_c, S_h) to state 2 ($E_1 \uparrow, T_h, S_h$). ΔT represents the change in adiabatic temperature from T_c to T_h , and $\Delta T = T_h - T_c$, which is an isentropic process.
- (2) The applied electric field on polar dielectric increases to E_2 in the isothermal heat release process 2→3. Material changes from state 2 ($E_1 \uparrow, T_h, S_h$) to state 3 (E_2, T_h, S_c) as entropy decreases, and heat is ejected into environment. ΔS denotes the change in isothermal entropy from S_h to S_c , i.e., $\Delta S = S_h - S_c$.
- (3) The applied electric field on polar dielectric decreases from E_2 in adiabatic temperature decreasing process 3→4. Material changes from state 3 (E_2, T_h, S_c) to state 4 ($E_2 \downarrow, T_c, S_c$) as temperature decreases.
- (4) The applied electric field on polar dielectric decreases to E_1 in isothermal heat absorbing process 4→1. Material changes from state 4 ($E_2 \downarrow, T_c, S_c$) to state 1 (E_1, T_c, S_h) as entropy increases, and heat is absorbed by dielectric material.

Upon the completion of a cycle, working material returns to its original state and the another cycle is initiated. The heat that polar dielectric absorbs from environment in isothermal decalescence process 4→1, is $\Delta q = T_c \Delta S$, which indicates its capability to absorb heat energy. The heat ejected into environment in isothermal releasing process 2→3, is given as $\Delta q' = T_h \Delta S$. According to the first law of thermodynamics, the work that environment does on the working material is $\Delta q' - \Delta q$, thus, $\Delta W = \Delta T \Delta S$, which is known as refrigerant capacity (RC) value.⁶

Polar dielectric and battery constitute a thermodynamic system, which is characterized by two generalized coordinates: electric displacement D and temperature T and two control parameters: electric field E and entropy S . When generalized coordinates are varied by small amounts, dD and dT , the variation in free-energy can be expressed as

$$dW = EdD - SdT. \quad (1)$$

Two independent variables (D, T) characterize the state of polar dielectric as cooling devices. The Helmholtz free energy of polar dielectric cooling devices is a function of two independent variables $W(D, T)$. Associated with small variations dD and dT , the free energy varies by

$$dW = [\partial W(D, T)/\partial D]dD + [\partial W(D, T)/\partial T]dT. \quad (2)$$

Therefore, electric field E and entropy S in the thermodynamics system of polar dielectric are partial derivative coefficients of $W(D, T)$,

$$E = \partial W(D, T)/\partial D, \quad (3)$$

$$S = -[\partial W(D, T)/\partial T]. \quad (4)$$

The thermal contribution can be expressed as $U(T) = Q(T) - TS$, where $Q(T)$ is the internal energy.¹⁰⁻¹³ As the temperature rises, internal energy $Q(T) = c_0(T - T_0)$. According to the relation of specific heat for constant volume and entropy, $c_0 = T \frac{\partial S}{\partial T}$, we obtain $S = c_0 \ln \frac{T}{T_0}$, where c_0 is the specific heat of polar dielectric, T_0 and T are the temperatures in reference and current states, respectively. Therefore, the thermal contribution of a thermodynamic system related to temperature is $U(T) = c_0[(T - T_0) - T \ln \frac{T}{T_0}]$, which reflects the effect of temperature on the free energy of a polar dielectric thermo-electric coupling system.

The free energy function of a polar dielectric thermo-electric coupling system is expanded near $D \approx 0$.¹⁴ Due to symmetry, the even powers of D is preserved. When $T > T_c$, the free energy function of polar dielectric can be expressed as

$$W(T, D) = c_0[(T - T_0) - T \ln(T/T_0)] + 1/2[\beta(T - T_c)D^2], \quad (5)$$

where β is a phenomenological parameter.

The electric field and entropy of polar dielectric can be obtained by inserting Eq. (5) into Eqs. (3) and (4), respectively,

$$E = \beta(T - T_c)D, \quad (6)$$

$$S = c_0 \ln(T/T_0) - 1/2(\beta D^2). \quad (7)$$

Considering the relation of specific heat,

$$c_0(T_h - T_c) = T_c[S_h^{(h)} - S_c^{(c)}], \quad (8)$$

where $S_c^{(c)}$ is the entropy at T_c and under low voltage, and $S_h^{(h)}$ is the entropy at T_h and under high voltage. The relationship between the electric field and temperature of polar dielectric can be established

$$\left| c_0 \ln(T_h/T_c) + 1/2 \left\{ \beta \{ [\varepsilon(T_c)]^2 E_1^2 - [\varepsilon(T_h)]^2 E_2^2 \} \right\} \right| T_c = c_0(T_h - T_c). \quad (9)$$

TABLE I Material parameters of electrocaloric materials.

Material	Specific heats 10^3 (J/kgK)	Densities 10^3 (kg/m ³)	Phenomenological parameter β 10^7 (mF ⁻¹ K ⁻¹)	Phase transition temperature T_c (K)	Permittivity (F/m)
P(VDF-TrFE) 55/45 copolymer	1.8 (Refs. 1 and 2)	1 (Refs. 1 and 2)	2.4 (Refs. 1 and 2)	341 (Refs. 1 and 2)	$70-0.77 \times (T-72)$ Te[70,93] $58-0.6 \times (T-90)$ Te[93,120] (Refs. 1 and 2)
P(VDF-TrFE) 65/35	1.4 (Refs. 1 and 2)	1.886 (Refs. 1 and 2)	3.5 (Refs. 1 and 2)	375 (Refs. 1 and 2)	$\frac{1}{\beta(T - T_c)}$
BaTiO ₃	0.407 (Refs. 1 and 2)	6.02 (Refs. 1 and 2)	0.067 (Refs. 1 and 2)	380 (Refs. 1 and 2)	
Pb(Zr _x Ti _{1-x})O ₃	0.35 (Refs. 1 and 2)	7.5 (Refs. 1 and 2)	0.0188 (Refs. 1 and 2)	523 (Refs. 1 and 2)	
Water	4.2	1	$\frac{1}{(87.08 - 0.32T)(T - T_c)}$	273	(87.08-0.32T) (Ref. 17)

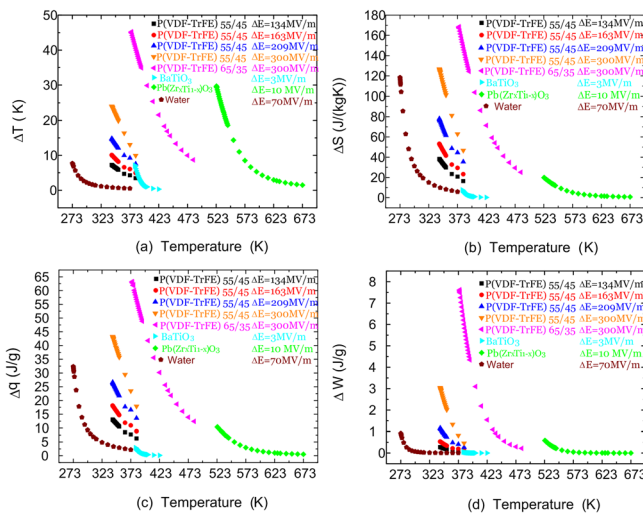


FIG. 2. (Color online) Changes in temperature and entropy, absorption of heat, and work of polar dielectric as cooling devices in paraelectric state.

Due to the electrocaloric effect of working material, the temperature reaches T_h from T_c when the electric field applied on polar dielectric rises to E_2 from E_1 under adiabatic condition. According to Eq. (9), T_h can be induced, once E_1 , E_2 , and T_c are given, and change in temperature ΔT can be obtained. Entropy change ΔS can be obtained using Eq. (8). And according to the definition before, absorption of heat Δq and work ΔW can be further obtained as well.

Table I material parameters used for numerical calculations. Applied electric field ΔE ($E_1 = 0$ here) for material are as shown in Figure 2, and the relevant data are taken from Refs. 1, 2 and 17.

Figure 2 illustrates ΔT , ΔS , Δq , and ΔW of several typical polar dielectric as cooling devices in the paraelectric phase when an electric field is applied on the working material. With the same electric field ΔE applied, ΔT , ΔS , Δq , and ΔW of working material get higher as the temperature gets closer to Curie temperature. ΔT , ΔS , Δq , and ΔW decline as temperature increases because the electric field induced in the polar phase is lower. It can be seen through comparison between a particular polar dielectric material including BaTiO_3 , $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, P(VDF-TrFE) with water, that ΔT of ferroelectric polymer P(VDF-TrFE) and antiferroelectric ceramic $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, ΔS of ferroelectric polymers P(VDF-TrFE) and liquid polar dielectric water, Δq of $[\text{P(VDF-TrFE)}]$ and water, and ΔW of P(VDF-TrFE) are higher. Furthermore, high polar liquid dielectrics may process a large ECE because within a specified temperature range, the molecule dipole disordering-ordering processes can be induced by an electric field and associated with this process is a large change in entropy.

Figure 3 illustrates the theoretical simulation results agree well with the published experimental results.¹

In summary, polar dielectric is modeled as a system with two degrees of freedom and represented by either an entropy-temperature or electric displacement-electric field plane, to describe the thermodynamic cycle of polar dielectric as cooling devices. With the effect of thermal contribution taken into consideration, the free energy model of a thermal-electric coupling system is developed for study of the electrocaloric effect of polar dielectric, and the calculation of changes temperature

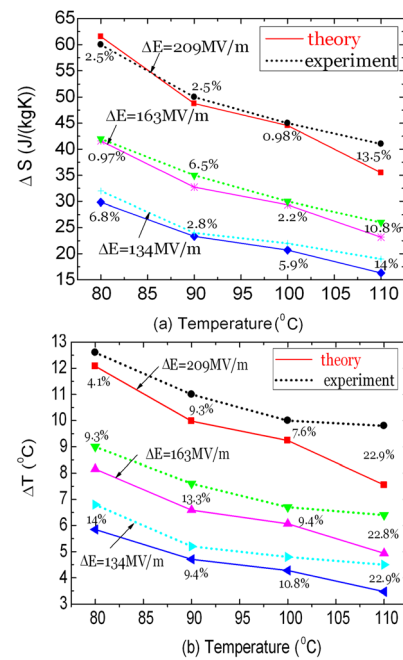


FIG. 3. (Color online) Comparison between theoretical and experimental results of changes in temperature and entropy of $[\text{P(VDF-TrFE)}]$ 55/45 mol. % copolymer.

and entropy, absorption of heat and work under different electric field and temperature. From what has been demonstrated on P(VDF-TrFE) 55/45 mol. % is applicable to other polar dielectric. Results show that high polar liquid dielectrics may possess a large electrocaloric effect.

The authors would like to appreciate the esteemed guidance of Professor Zhigang Suo at Harvard University in the theories of electrocaloric energy conversion as well as the meaningful discussions in electrocaloric materials with Professor Qiming Zhang at Pennsylvania State University.

- ¹B. Neese, B. Chu, S. G. Lu, Y. Wang, E. Furman, and Q. M. Zhang, *Science* **321**, 821 (2008).
- ²S. G. Lu and Q. M. Zhang, *Adv. Mater.* **21**, 1983 (2009).
- ³S. Mischenko, Q. Zhang, J. F. Scott, R. W. Whatmore, and N. D. Mathur, *Science* **311**, 1270 (2006).
- ⁴S. Mischenko, Q. Zhang, R. W. Whatmore, J. F. Scott, and N. D. Mathur, *Appl. Phys. Lett.* **89**, 242912 (2006).
- ⁵B. Neese, S. G. Lu, B. J. Chu, and Q. M. Zhang, *Appl. Phys. Lett.* **94**, 042910 (2009).
- ⁶B. Li, W. J. Ren, X. W. Wang, H. Meng, X. G. Liu, Z. J. Wang, and Z. D. Zhang, *Appl. Phys. Lett.* **96**, 102903 (2010).
- ⁷J. F. Scott, *Science* **315**, 954 (2007).
- ⁸J. H. Qiu, and Q. Jiang, *Eur. Phys. J. B* **71**, 15 (2009).
- ⁹P. F. Liu, J. L. Wang, X. J. Meng, J. Yang, B. Dkhil, and J. H. Chu, *New J. Phys.* **12**, 023035 (2010).
- ¹⁰J. L. Wegner, J. B. Haddow, *Elements of Continuum Mechanics and Thermodynamics* (Cambridge University Press, New York, 2009), pp. 202–219.
- ¹¹G. A. Holzapfel, *Nonlinear Solid Mechanics: A Continuum Approach for Engineering* (Wiley, Chichester, 2000), pp. 306–357.
- ¹²C. O. Horgan and G. Saccomandi, *Rubber Chem. Technol.* **79**, 152 (2006).
- ¹³S. Baek and A. R. Srinivasa, *Math. Probl. Eng.* **4**, 153 (2003).
- ¹⁴D. Damjanovic, *Rep. Prog. Phys.* **61**, 1267 (1998).
- ¹⁵S. G. Lu, B. Rožič, Q. M. Zhang, Z. Kutnjak, X. Li, E. Furman, L. J. Gorny, M. Lin, B. Malič, M. Kosec, R. Blinc, and R. Pirc, *Appl. Phys. Lett.* **97**, 162904 (2010).
- ¹⁶S. G. Lu, B. Rožič, Q. M. Zhang, Z. Kutnjak, R. Pirc, M. Lin, X. Li, and L. Gorny, *Appl. Phys. Lett.* **97**, 202901 (2010).
- ¹⁷H. M. Jones and E. E. Kunhardt, *IEEE Trans. DEI-1*, 1016 (1994).