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Kinetic electrocaloric effect and giant net cooling of lead-free ferroelectric refrigerants

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The electrocaloric effect of BaTiO₃ multilayer thick film structure was investigated by direct measurement using differential scanning calorimeter. The samples show a giant electrocaloric effect of 0.89 J/g under $E=176$ kV/cm, which also depends on the varying rate of applied field, following a general power-law relation. Based on the large net-cooling (0.37 J/g) resulting from the difference in the varying rates of rising and falling fields, the kinetic electrocaloric effect provides a solution for the design of refrigeration cycle in ferroelectric microrefrigerator. © 2010 American Institute of Physics. [doi:10.1063/1.3511342]

I. INTRODUCTION

Solid state refrigeration based on ferroelectric refrigerants has attracted considerable attention in recent years because of its high reversible adiabatic temperature change, good efficiency, and feasible miniaturization. In particular, the ferroelectric microrefrigerator is the best solution for the cooling of microelectronic devices and microelectromechanical systems.¹ The ferroelectric refrigeration is based on the electrocaloric (EC) effect, which is referred to the heat exchange resulting from the electric field induced paraelectric-ferroelectric (P-F) phase transition. Recently, the giant EC effect is obtained in some ferroelectric thin films successively,¹⁻⁸ and was studied in various ferroelectric materials based on thermodynamics.⁹⁻¹³ The large EC reversible adiabatic temperature change (>10 °C) of those ferroelectric thin films makes them most desirable to be used as refrigerants in ferroelectric microrefrigerators. In spite of encouraging progresses, there are several critical issues that have hindered the practical application of those ferroelectric thin films as refrigerants in ferroelectric microrefrigerators. First, the heat absorption capacity of a thin film is too small for practical application due to the tiny volume of working medium. Second, how to effectively implement the refrigeration cycle of the ferroelectric refrigerants is still an open question. Although Ericsson cycle has been used in the designs of ferroelectric refrigeration, complex and expensive heat switches or mechanical shifters¹⁴⁻¹⁶ have to be involved.

We solve the above-mentioned first issue by developing the BaTiO₃ multilayer thick film structure (MLTFS) as ferroelectric refrigerants. Considering that the giant EC effect of thin films mainly depends on the ultrahigh applied electric field (600–900 kV/cm), dozens times higher than the breakdown field of bulk ceramics, in our work, alternatively, the ferroelectric thick films with multilayer structure is selected as the refrigerant for ferroelectric microrefrigerator, which

has the advantages of both ultrahigh breakdown electric field and large volume of working medium. Our previous work¹⁷ and Kar-Narayan's report¹⁸ both demonstrated the high EC effect in MLTFS under ultrahigh electric field.

In this paper, we solve the second problem based on the kinetics control of EC cycles. Considering that the P-F phase transition is a typical first-order phase transition (FOPT) and its energy conversion involved is always determined by the kinetic process of EC effect,¹⁹ which has not been well understood up to date, we focus our research on the kinetics of heat exchanges during the EC processes by direct measurement using differential scanning calorimeter (DSC), and demonstrate a giant net cooling in one EC cycle without the aid of any other accessory.

II. EXPERIMENTAL PROCEDURE

The MLTFS was fabricated by the tape-casting method. The sample had a multilayered structure similar to that of a multilayer chip capacitor. The ferroelectric medium of the BaTiO₃ (EYANG Technology Development Co., Ltd.) and the inner Ni electrode were printed alternately and cofired. In the structure, two groups of interpenetrating electrodes led to two terminals, respectively. The average thickness of the BaTiO₃ layers was 1.4 μm and the total number of dielectric layers was 180.

The direct measurement of the heat flow was conducted as an isothermal process using a DSC (TA Instruments Q200), and a dc power supply (Agilent N8741) was used to apply the electric field to the sample. The sample was connected to the dc power by two vanished wires, which were too thin ($d\sim 0.01$ mm) to change the thermal isolation of the testing cell. The sample was attached to the DSC pan with insulating glue. As the connection between DSC and dc power supplier and the heat conduction of the sample cell were well designed, the system could perform a precise heat flow measurement with high sensitivity (~ 0.2 μW) and low noise (peak to peak value ~ 1 μW). In the experiment, the start and end electric field intensities were fixed to 0 kV/cm

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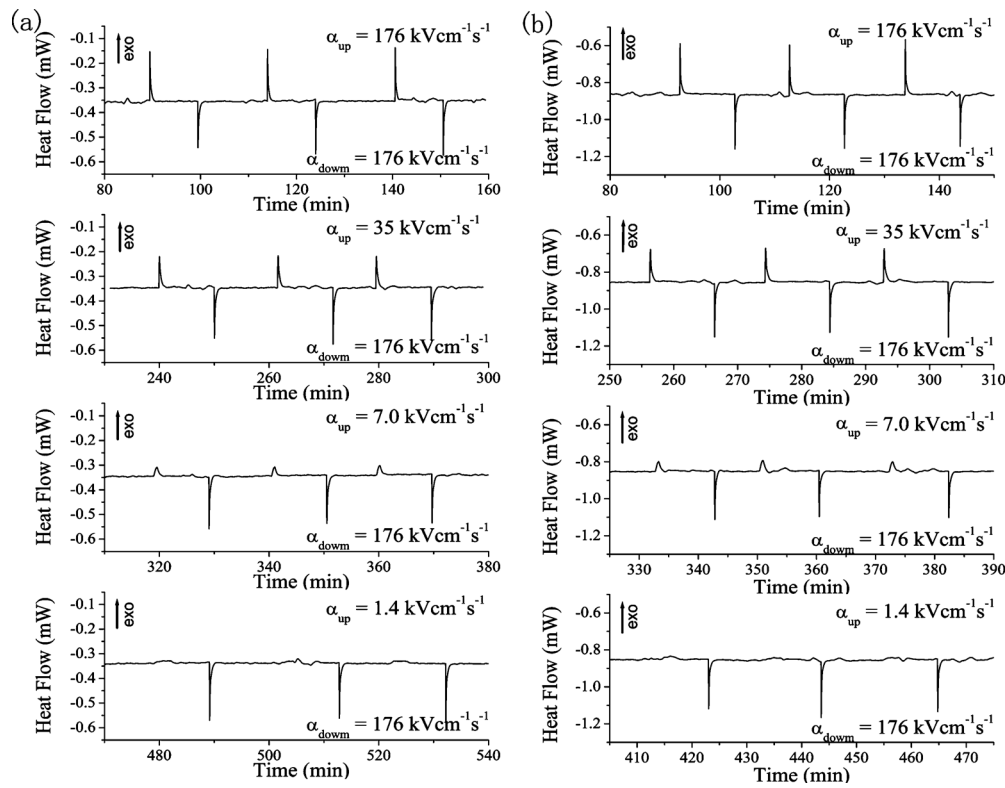


FIG. 1. The DSC heat flow of the sample under 176 kV/cm at (a) 40 °C and (b) 80 °C. The sample is a parallel connection of eight BaTiO₃ MLTFSs.

and 176 kV/cm, respectively. The rising rate of the driving field varied from 1.4 to 176 kV cm⁻¹ s⁻¹, and the falling rate was kept constant at 176 kV cm⁻¹ s⁻¹.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the DSC measurements of the MLTFS sample at 40 °C and 80 °C, respectively, where the rising field rate varies from 1.4 kV cm⁻¹ s⁻¹ to 176 kV cm⁻¹ s⁻¹ and the falling field rate is kept at 176 kV cm⁻¹ s⁻¹. There are obvious exothermic and endothermic peaks corresponding to the application and removal of the electric field, respectively. The EC endothermal values, i.e., the integral of downward peak in the heat flow versus time curve, is 0.70 J/g at 40 °C and 0.89 J/g at 80 °C under a falling field rate of 176 kV cm⁻¹ s⁻¹, which are much stronger than that in most reported ferroelectric ceramics, either lead-free or lead-based. The corresponding temperature change ΔT are 1.3 K and 1.8 K, respectively. Under higher electric field, the EC effect can be further improved. A heat absorption of 2.02 J/g ($\Delta T=4.0$ K) is obtained at 80 °C under 352 kV/cm. The giant EC effect in MLTFS is caused by the ultrahigh electric field, which is much higher than the applied field in ceramics (~ 30 kV/cm). During the EC process, phase transition is induced by an external electric field, the work of which is converted into lattice elastic energy and polarization energy through lattice deformation and the generation and reorientation of polarization. Hence, the higher the field intensity, the higher the latent heat of the phase transition. In addition, the results demonstrate that the Joule heating during the measurement is negligible because the exothermic and endothermic heat value is almost the same under same driving field rates, and in the two processes the

heat flows both return to the baseline very well after enough thermal equilibrium time. The large EC temperature change in MLTFS samples suggests that they are suitable and practical for ferroelectric refrigeration application.

It is clear from Fig. 1 that the exothermic value decreases as the rising field rate drops, whereas the endothermic value remains constant under a fixed falling field rate. Considering that the instrumental error of *heat value* induced by different driving field rate is very small ($\sim 3\%$), the dependence of EC heat value on electric field application rate could originate from the kinetics of the EC effect. The difference in the endothermic and exothermic values in an electric field cycle suggests that the EC effect is determined not only by static parameters, such as electric field intensity and temperature but also by kinetics processes, such as the rising and falling rates of electric field. Net cooling in a single EC cycle can be realized by controlling the driving field rate. Table I lists the heat values of the exothermic and endothermic

TABLE I. The measured exothermic and endothermic values under different driving field rates.

	α_{up} (kV cm ⁻¹ s ⁻¹)	H_{exo} (J/g)	α_{down} (kV cm ⁻¹ s ⁻¹)	H_{endo} (J/g)
40 °C	176	0.69 ± 0.01	176	0.70 ± 0.03
	35	0.64 ± 0.03	176	0.70 ± 0.02
	7.0	0.42 ± 0.02	176	0.68 ± 0.03
	1.4	0.38 ± 0.05	176	0.69 ± 0.04
80 °C	176	0.92 ± 0.03	176	0.89 ± 0.02
	35	0.83 ± 0.03	176	0.87 ± 0.05
	7.0	0.59 ± 0.03	176	0.89 ± 0.04
	1.4	0.50 ± 0.09	176	0.87 ± 0.05

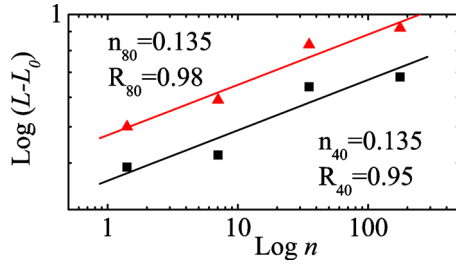


FIG. 2. (Color online) Double logarithmic graph of $(L-L_0)$ and driving electric field rate n .

mal processes under different driving field rates. The net heat adsorption value, the difference of absorbed and released heat, in an electric field cycle is as high as 0.37 J/g, which is calculated from the area difference between the endothermal peak and exothermal peak. The value of 0.37 J/g is even higher than the EC heat absorption value reported for most lead-based ferroelectric ceramics.^{10–13}

The relation between the varying rate of electric field and the heat value of exothermal or endothermal process can be fitted using a general power-law relation,

$$L = L_0 + A\alpha^n, \quad (1)$$

where α is the varying rate of the linear driving field, n is the scaling exponent, L_0 is the value of heat exchange in a quasistatic case ($\alpha \sim 0$), and A is a constant. Figure 2 plots the linear relation between $\log(L-L_0)$ and $\log \alpha$, and shows them to have a good linear correlation of $R_{40}=0.95$ and $R_{80}=0.98$ at working temperatures of 40 °C and 80 °C, respectively. The scaling exponents n for these two temperatures are both 0.135.

The ferroelectric phase transition is a typical FOPT related to nucleation and growth kinetics of polarization domains. We further explain the kinetics of the EC effect by using the Landau theory of ferroelectrics. Under the time-dependent rising or falling electric field, the free energy of the materials is expressed as

$$F = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 - PE(t), \quad (2)$$

where P is the polarization, $a=a_0(T-T_c)/T_c$, and T_c is the Curie temperature. a_0 , b , and c are coefficients independent of temperature. We assume $E(t)$ varies linearly with time t with a varying rate of α , as it was in our experiment. Because of the nonequilibrium relaxation of the polarization during FOPT,^{19–21} its kinetics can be described by the Ginzburg–Landau equation as follows:

$$\frac{dP}{dt} = -\frac{\delta F}{\delta P} = -aP - bP^3 - cP^5 + E(t). \quad (3)$$

From Eq. (2), the entropy can be expressed as

$$S = -\frac{\partial F}{\partial T} = -\frac{a_0}{2T_c}P^2. \quad (4)$$

The endothermal or exothermal heat resulting from the removal or application of an electric field can be calculated by

$$\begin{aligned} \Delta Q &= T \int_{S_0}^{S_1} dS = -\frac{a_0}{T_c} T \int_{E_0}^{E_1} P \left(\frac{dP}{dE} \right) dE \\ &= -\frac{a_0}{T_c} T \int_0^\Gamma P \left(\frac{dP}{dt} \right) dt, \end{aligned} \quad (5)$$

where E_0 and E_1 are the applied fields at time $t=0$ and Γ , respectively, and corresponding entropies of the materials are S_0 and S_1 , respectively. By solving Eq. (3), the relation between heat conversion ΔQ and varying rate α of the electric field is found to follow a power law when E_0 and E_1 are fixed:

$$(\Delta Q - \Delta Q_0) \propto \alpha^{2/3}, \quad (6)$$

where ΔQ_0 is an α independent heat conversion during static F–P transition. Although the exponent $n=2/3$ is different with that of $n=0.135$ in Eq. (1), Ginzburg–Landau theory predicts the same scaling relation between the endothermal or exothermal heat and α as that [Eq. (2)] observed in experiment

The scaling coefficient $n=0.135$ is also much smaller than the value of 1/2 obtained from a phenomenological ferroelectric phase transition models which considers the effect of impurities on the energy conversion.²² The difference could be caused by the significant lattice deformation and the resulted changes in polarization under ultrahigh electric field applied on BaTiO₃ thick films, which cannot be well described by either Landau theory or phenomenological model.

The kinetics studies of the EC effect are very important for the practical application of EC refrigeration. Because ferroelectric refrigeration is based on a solid-state phase transition, the ferroelectric material acts as both a warm junction and a cold junction in different sections of the refrigeration cycle. In previous design^{14–16} of refrigeration cycle, a micro-mechanical shifter, or heat switch was necessary to control the direction of heat flow. The mechanical shifters work by opening and closing the thermal contact between the cooler and the object. The heat switches made from semiconductor or liquid crystal are operated by varying the heat conductance under different conditions.^{14–16} Obviously, those designs have complex structure, high cost, low reliability, and poor robustness for microrefrigerators. Instead, from our work, a feasible alternative method of refrigeration is provided using a simple ferroelectric MLTFS based on the scaling relation between EC heat and the driving field rate. Giant net cooling (~ 0.37 J/g) in an electric field cycle can be achieved by controlling the driving electric field rates. A schematic of the design based on the kinetic EC effect of the MLTFS ferroelectric refrigerant is shown in Fig. 3. Because the rate of rising electric field is smaller than that of the falling field, there is a net cooling in an electric field cycle (time interval $\Delta t=2\Gamma$). Such design for ferroelectric refrigeration can significantly reduce the accessory used to accomplish a full refrigeration cycle. For example, it is not necessary to use micromechanical shifter or heat switch since the ferroelectric MLTFS elements can acts as heat switches as well.

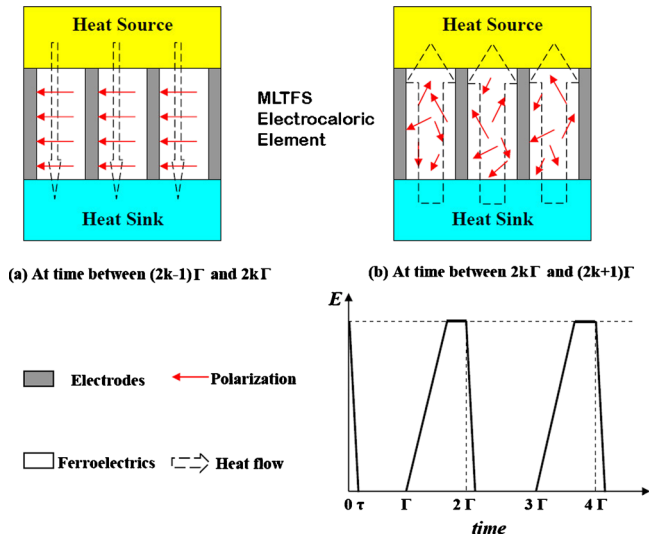


FIG. 3. (Color online) Schematic of BaTiO_3 MLTFS used as refrigerants. Net cooling in one electric field cycle (2Γ) is achieved: heat dissipation of MLTFS element at time interval 0 to Γ (a) is smaller than heat adsorption at time interval Γ to 2Γ (b). k is an integer.

IV. CONCLUSIONS

In summary, we demonstrate the giant EC effect of BaTiO_3 MLTFS by direct DSC measurement and characterize the scaling relation between the EC heat and the driving field rate. The MLTFS samples show a giant EC effect with heat absorption values of 0.70 J/g at 40°C and 0.89 J/g at 80°C under an electric field of 176 kV/cm . The measured EC heat is much higher than that of most reported ferroelectric ceramics because of the ultrahigh applied electric field. The exothermal and endothermal values during the application and withdrawal of electric field are, respectively, determined by the rising and falling rate of electric field, and the driving field rate dependence of heat value follows a general power-law relation. A giant net cooling ($\sim 0.37 \text{ J/g}$) in one electric field cycle can be obtained by applying different rising and falling rates of electric field. This work provides a feasible method to implement net cooling in one electric field cycle without the aid of any other accessory, which will lead to a practical application of lead-free ferroelectric microrefrigerator in near future.

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