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The giant electrocaloric effect and high effective cooling power near room temperature for $BaTiO_3$ thick film

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The electrocaloric effect (ECE) of $BaTiO_3$ multilayer thick film was investigated by direct calorimetric measurement. The ECE increases monotonically with the enhancement of applied field. The maximum ECE occurs above T_c and shifts to higher temperature with increasing applied field. Under an ultrahigh field of 800 kV/cm, it exhibits a giant ECE of $\Delta T = 7.1$ K and $\Delta S = 10.1$ J/kg · K at 80 °C. The ECE heat follows a general power-law relation with the varying rate of applied field within a certain range. A high cooling power (~50 W/kg) is achieved based on the net-cooling resulting from the different varying rates of rising and falling fields. © *2011 American Institute of Physics*. [doi:10.1063/1.3658251]

I. INTRODUCTION

The electrocaloric effect (ECE), the inverse of pyroelectric effect, is a basic characteristic of ferroelectric materials, which refers to a reversible temperature and/or entropy change of a ferroelectric material during the application or removal of applied electric field. Recently, the ECE solid-state cooling technology arouses more attention with the rapid development of portable electronic products and the attention to environmental protection.[1] Compared with Peltier solid-state refrigerator, ECE refrigerator involves in a reversible process with higher coefficient of performance and without parasitical thermal and electrical resistances.[2] Compared with magnetocaloric refrigerator, ECE refrigerator does not need huge field supplier, so it is much easier to be miniaturized. Hence, the ECE refrigerator is the most feasible candidate for microelectronic devices and microelectromechanical systems.

Since 2006, the giant ECE ($\Delta T_{max} > 5$ K) was reported successively in various ferroelectric ceramics or polymer films,[3–12] where the ultrahigh applied field played a key role. Up to now, intense research and development efforts are still on-going and there are many blank, especially on the kinetics problem. As corresponding to the field-induced paraelectric-ferroelectric (**P-F**) phase transition, ECE is determined by the kinetics process in addition to the start and end thermodynamic states.[13] The previous research revealed a power-law relation between the ECE heat value and the varying rate of applied field,[14] but the detail was not clear yet due to the conflict of high phase transition temperature (~125 °C) and relatively low temperature limit of testing system. Here, we demonstrate the ECE of $BaTiO_3$ multilayer thick film, which peaks near room temperature, and especially discusses its relation with temperature, field intensity, and the varying rate of applied field.

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II. EXPERIMENTAL

The $BaTiO_3$ multilayer thick film was fabricated by the tape casting method and had Ni as inner electrode. The paste of $BaTiO_3$ and Ni were printed alternately and cofired. In the structure, two groups of interpenetrating Ni electrodes were led to two terminals, respectively. The $BaTiO_3$ layers have an average thickness of 3 μm and a total number of 63. The temperature dependence of permittivity was measured at 1 kHz using HP4192 equipped with a temperature controller and exhibited a peak (T_c) at about 50 °C (not shown here). The direct measurement of heat flow was measured in isothermal process using a differential scanning calorimeter (DSC, TA Instruments Q200) and a DC power supplier (Agilent N8741) was used to apply electric field on the sample. The sample was solidified with the DSC pan by insulating glue and connected with the DC power by two thin vanished wires.

III. RESULTS AND DISCUSSION

Fig. 1 shows the DSC measurement of the sample at 40 °C, where both rising and falling field rates are 200 kV/cm · s. There are obvious exothermal and endothermal peaks corresponding to the application and removal of applied fields. Under the same conditions (field intensity and varying field rate), the upward peak has same area as the downward peak, i.e., the ECE exothermal and endothermal values are same. With the enhancement of applied field, the ECE exothermal and/or endothermal value increases monotonically. The ECE depends on the change of ordering entropy, lattice elastic energy and electric polarization energy during the application or withdrawal of field. The field-induced dipole

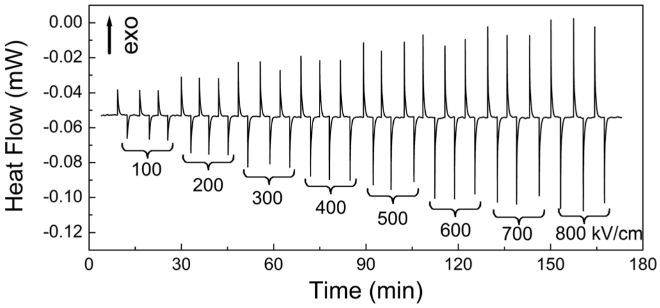

FIG. 1. The DSC heat flow measurement of the sample at 40 °C under different field intensities ($\alpha_{up} = \alpha_{down} = 200$ kV/cm · s).

reorientation and lattice deformation result in the enhancement of ECE with increasing field. In addition, the former factor is finished gradually with the increase of applied field and only the later one dominates the process, so the rise of ECE heat value slows down to a saturated value under ultrahigh field, as shown in Fig. 2.

Fig. 3 plots the temperature dependence of ECE endothermal values. The maximum ECE occurs above the zero-field T_c and tends to move to higher temperature with increasing applied field due to the field-induced shift of phase transition temperature. Under an ultrahigh field of 800 kV/cm, the sample exhibits a giant electrocaloric effect of $\Delta T = 7.1$ K and $\Delta S = 10.1$ J/kg · K at 80 °C,[15] which exceeds the ECE value in most ferroelectric ceramics in previous reports.[5–10] Although the $PbZr_{0.95}Ti_{0.05}O_3$ thin film in Ref. 3 has higher ECE ΔT of ~12 °C, its ΔS of ~8 J/kg · K is smaller due to high operating temperature of 222 °C. Because (1) large entropy change is more practical for the refrigerating application, (2) low working temperature would open up wider application prospect, and (3) large effective volume of multilayer thick film produces huger heat absorption capacity, the $BaTiO_3$ multilayer thick film has more promising application future.

Fig. 4 shows the DSC measurement of the sample at 80 °C, where the field intensity is 500 kV/cm, the rising field rate α_{up} varies from 10 kV/cm · s to 500 kV/cm · s and the falling field rate α_{down} is kept at 200 kV/cm · s. It is clear that

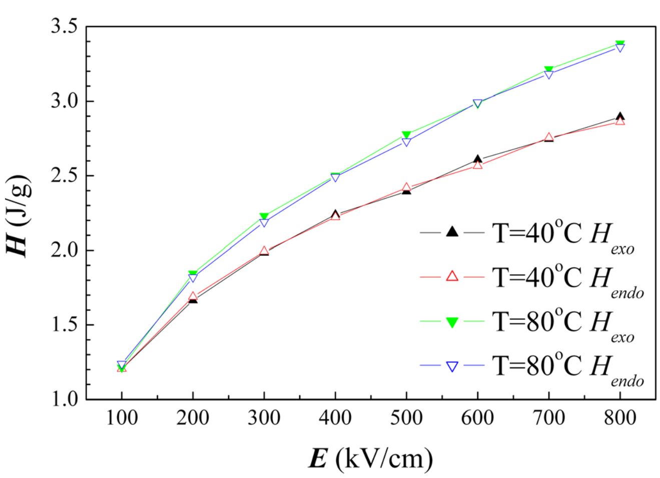

FIG. 2. (Color online) The field dependence of exothermal and endothermal values of the sample at 40 °C.

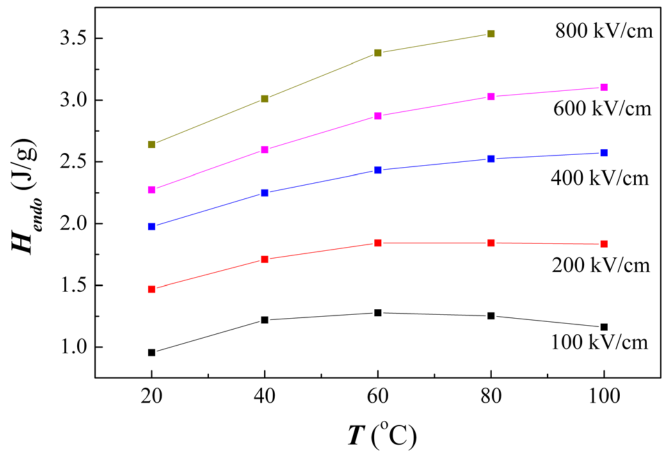

FIG. 3. (Color online) The temperature dependence of endothermal values of the sample at different applied field.

the exothermal peak shrinks with the reduction of α_{up}, while the endothermal value still keeps constant under a fixed α_{down}. That implies that ECE is determined not only by thermodynamic states, such as field intensity and temperature, but also by kinetic processes, such as the varying rate of applied field. Fig. 5 plots the double logarithmic graph of exothermal value and driving electric field rate α_{up}. The Log H_{exo} increases linearly as $\alpha_{up} < 100$ kV/cm · s, while it almost keeps constant as $\alpha_{up} > 100$ kV/cm · s. That means ECE heat value and varying rate of applied field follows a general power-law relation only under a moderate varying rate. As $\alpha_{up} < 10$ kVcm^{-1}s^{-1}, the exothermal signal is too weak to be distinguished with noise, so the data are not included in the discussion.

The **P-F** phase transition of normal ferroelectrics, such as $BaTiO_3$, is a first-order phase transition, which is always accompanying some fundamental characteristics, including the co-existence of phases and the moving interphase boundary. During the phase transition, the moving interphase boundary can be regard as a source or sink of heat, and alter the temperature distribution near the boundary. The heat generated during the interphase boundary motion accelerates the interface, which in turn increases the heat production rate. Then, the system is involved in an avalanche-like process, which can be stabilized by heat conductivity and heat exchange.[16–18] For the ferroelectric phase transition, the

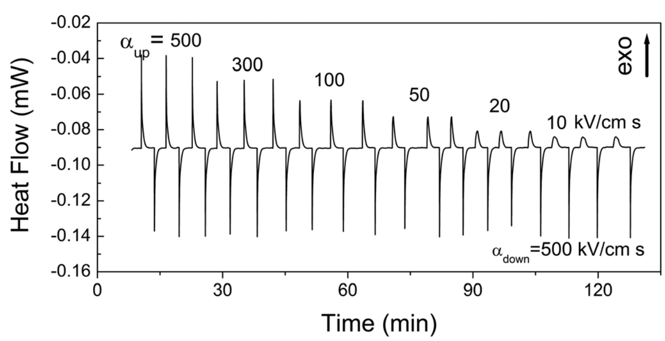

FIG. 4. The DSC heat flow of the sample under 500 kV/cm at 80 °C, where α_{up} varies from 10 kV/cm·s to 500 kV/cm·s and α_{down} is kept at 200 kV/cm·s.

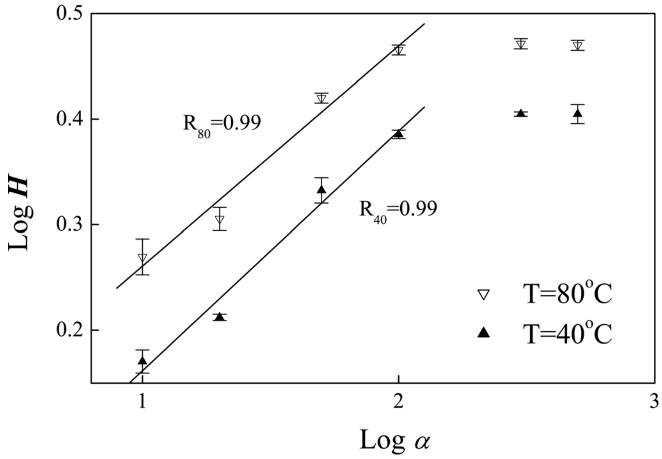

FIG. 5. The double logarithmic graph of exothermal value and rising field rate α_{up}.

slow interphase boundary dynamics can be described by using the time-dependent Ginzburg-Landau equation, which treats it as the nonequilibrium relaxation of polarization.[13,19,20] This theory predicts a general power-law relation between the endothermal or exothermal heat and the varying rate of applied field, whose derivation of equation was provided in our previous work.[14] As the velocity of the moving interphase boundary increases with the rise of varying field rate, the ECE heat value increases accordingly, that is well proved by our experimental results in Fig. 5. However, the ECE heat value will not increases consistently because the velocities of the moving interphase boundary and the heat transfer are finite. The ECE exothermal value reaches a saturated value as the rising field rate is large enough ($\alpha_{up} > 100$ kV/cm · s).

The ECE exothermal and endothermal values are determined by the rising and falling rate of applied fields, so the net-cooling in one cycle can be achieved by controlling the applied field. Under this route, the cooling power can be calculated according to Fig. 5. In addition, to evaluate the real refrigerating ability of material, the cooling power is normalized by the mass of the constituent layers. As $E = 500$ kV/cm, the maximum cooling power is ~40 W/kg at $\alpha_{up} = 20$ kV/cm · s and $\alpha_{down} = 500$ kV/cm · s; while it increases to ~50 W/kg as E rises to 800 kV/cm. The ECE performance can be further improved by material and structure optimization. For example, replacing Ni electrodes by Ag electrodes with higher thermal conductivity ($\kappa_{Ni} = 94$ W/m · K, $\kappa_{Ag} = 428$ W/m · K) will increase the cooling power by a factor of 4.5.[21]

IV. CONCLUSIONS

In summary, this paper demonstrates the giant ECE near room temperature in $BaTiO_3$ thick film, as well its relationship with temperature, field intensity, and varying field rate. The ECE increases monotonically with the enhancement of applied field. The maximum ECE occurs above T_c and shifts to higher temperature with increasing applied field. Under an ultrahigh field of 800 kV/cm, it exhibits a giant ECE of $\Delta T = 7.2$ K and $\Delta S = 10.7$ J/kg · K at 60 °C. The ECE heat follows a general power-law relation with the varying rate of applied field within a certain range. A high cooling power (~50 W/kg) is achieved based on the net-cooling resulting from the different varying rates of rising and falling fields. The obtained giant ECE near room temperature and high effective cooling power will promote the practical application of lead-free ferroelectric microrefrigerator possible in the near future.

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