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The electrocaloric effect around the orthorhombic-tetragonal first-order phase transition in BaTiO₃

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This paper demonstrates the electrocaloric effect (ECE) around BaTiO₃'s orthorhombic-tetragonal first-order phase transition. By manipulating a field-induced transition of a metastable phase in the thermal hysteresis zone, a huge exothermic or endothermic peak appears after first applying or removing electric fields because of the energy change of lattice structure. A large ECE of $\Delta T/E = 1.4\text{K} \cdot \text{m/MV}$, equaling to latent heat, is achieved under 10kV/cm at 10°C. The entropy change for polarization ordering alone induces an ECE two orders of magnitude lower under the same condition. It confirms the dominant factor to ECE of the energy flow due to the structural phase transition. *Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License.* [<http://dx.doi.org/10.1063/1.4732146>]

The electrocaloric effect (ECE), a fundamental property of ferroelectrics, is a temperature change that occurs in a polar material upon application of an electric field, which reflects the energy change related to the polarization states, such as the generation and reorientation of dipoles. In principle, some thermal effect can be produced by any change of polarization state, but it is usually very small until a phase transition is involved. Although ECE research has been carried out for several decades,¹⁻³ the underlying physics behind ECE and its relation with phase transition are not yet completely understood. The thermodynamic theory based on the Maxwell relation was widely used in the characterization and analysis of ECE,⁴⁻¹⁹ but recent reports revealed that it is unsuitable for ferroelectric relaxors with non-ergodic glassy state^{11,12} and becomes invalid near phase transitions^{5,12} or under ultrahigh electric field,¹⁴ which are two keys to achieve giant ECE.

Since the origination of giant ECE has not been properly interpreted, the development of highly-efficient ferroelectric refrigeration is put off. Early researches attempted to enhance ECE by increasing entropy change of dipole ordering, and focused on ferroelectric relaxors, but the ECE obtained in bulk samples was always not satisfying, $\Delta T < 2.5\text{K}$.¹⁻⁵ Since 2006, a giant ECE with $\Delta T = 5\sim 40\text{K}$ was subsequently observed in ferroelectric films under ultrahigh electric fields.⁶⁻¹⁴ Although ECE ΔT and/or ΔS of thin films under high fields is much higher than that of bulk samples, the effect under unit field is weakened significantly,⁴ about one order of magnitude (from $0.2\sim 1.0\text{K} \cdot \text{m/MV}$ to $0.01\sim 0.1\text{K} \cdot \text{m/MV}$). In this paper, we quantitatively distinguish the dominant factor of ECE near a phase transition, and achieve a large effect of $\Delta T/E = 1.4\text{K} \cdot \text{m/MV}$ in BaTiO₃ near room temperature (RT).

Considering BaTiO₃ is the best known lead-free ferroelectric material with a typical first-order phase transition, this work was focused on its orthorhombic-tetragonal (O-T) phase transition near RT. The (001) BaTiO₃ single crystals, a commercially available product (Phscience Opto-electronics

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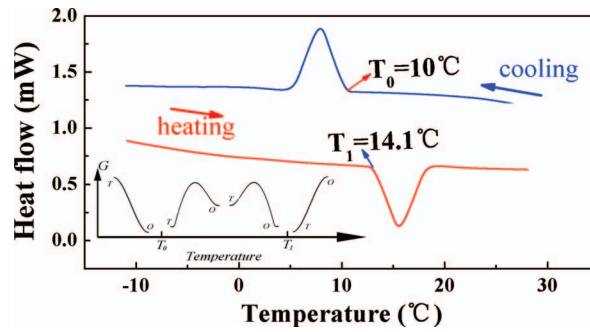


FIG. 1. The DSC curves of BaTiO₃ single crystal during heating and cooling process in a temperature range of $-10\sim 30^{\circ}\text{C}$. The inset illustrates the meaning of T_1 and T_0 .

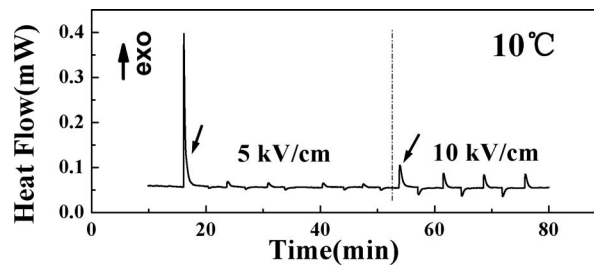


FIG. 2. The overall variation of heat flow for BaTiO₃ ceramics after zero-field-cooling from 20°C to 10°C . ($E = 5$ and 10kV/cm)

Co., Ltd., Beijing), were produced by a top seeded solution growth method. The ceramics were fabricated by a solid-state reaction method using analytic reagent grade BaCO₃ and TiO₂ as raw materials. The thermal characters of phase transition were measured using a differential scanning calorimeter (DSC, TA Instruments Q200). The ECE was characterized in isothermal process using a DSC accompanied with a DC power supply.¹⁴

Fig. 1 shows the heat flow curve of BaTiO₃ single crystal during heating and cooling process within a temperature range of $-10\sim 30^{\circ}\text{C}$. The endothermic and exothermic peaks are related to the **O-T** phase transition, and the obvious thermal hysteresis reflects characteristic feature of a first-order phase transition. The phase transition points are respectively 14.1°C and 10.0°C in the heating and cooling runs, corresponding to the T_1 and T_0 in the Landau-Ginzburg-Devonshire theory. As illustrated in Fig. 1 inset, T_0 and T_1 are the lower and upper temperature limits for which the tetragonal or orthorhombic phase can remain in a metastable state in the cooling or heating process, in the absence of an applied field.

The ECE reflects the energy change of different polarization states, where the generation of dipoles is affected by the phase structure and their reorientation is related to the ordering entropy. To clarify their contributions to the ECE, a series of experiments were performed to manipulate the phase transition by electric fields. A ceramic sample was cooled from 20°C to 10°C under zero-field, and an electric field was applied to and removed from it repeatedly at 10°C . Fig. 2 shows the overall variation of heat flow. A large exothermic peak appears immediately after first applying an electric field, while the followed endothermic and exothermic peaks decrease dramatically. If the applied field is enhanced further, for example from 5kV/cm to 10kV/cm , another large exothermic peak appears accordingly. The sum of these two large exothermic peaks under 5kV/cm and 10kV/cm is equal to that of the large exothermic peak which occurs when a field of 10kV/cm is initially applied. Furthermore, a contrast experiment is performed in a reverse process. The sample was warmed from 0°C to 15°C under a field of 5kV/cm , and experienced the process of removal and application of the electric fields repeatedly at 15°C . As shown in Fig. 3, a large endothermic peak appeared after first removing the field, and the following exothermic and endothermic peaks became much smaller.

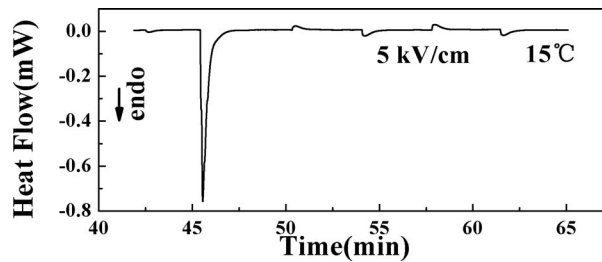


FIG. 3. The overall variation of heat flow for BaTiO₃ ceramics after field-heating under 5kV/cm from 0°C to 15°C.

For a first-order phase transition, two phases coexist in the thermal hysteresis zone defined by $T_0 < T < T_1$, where the potential barrier for phase transition reflects the additional energy needed by the nucleation and growth of the new phase. The tetragonal phase is stable near T_1 , and turns metastable near T_0 . When cooled from 20°C to 10°C, BaTiO₃ maintains a metastable tetragonal phase. As an electric field is applied, the occurrence of **T-O** phase transition induces a large exothermic peak, because the energy change associated with the field-induced structural phase transition is involved. When the field is removed, the stable orthorhombic phase cannot transform reversibly to the metastable tetragonal phase, so the corresponding endothermic peak is much smaller, because it only originates from the entropy change of dipole reorientation. In the subsequent cycles, both exothermic and endothermic peaks keep their low values because no further phase transition is induced under such applied field, and ECE is dominated by the ordering entropy change. In the reverse process, BaTiO₃ keeps a metastable orthorhombic phase at 15°C with the aid of the electric field. The large endothermic peak appears after first removing the applied field, thanks to the energy change of the **O-T** phase transition. The results demonstrate that the energy variation of the lattice structure gives a much larger contribution to the ECE near a phase transition than the ordering entropy change of dipole reorientation. It proves a previous view that the pure dipole reorientation does not generate a large entropy change as the field-induced phase transition.⁸ This was not experimentally confirmed previously, because the discontinuity of thermodynamic characters, especially the order parameter of polarization **P**, makes the theoretical calculation invalid to predict the ECE near a first-order phase transition.^{12,20,21}

The inhomogeneity and defects in real materials will induce the energy fluctuation, so the potential barrier of lattices has a distribution, not an identical value. Considering the phase transition only occurs in the lattices with potential barrier lower than the applied field, no further phase transition is induced in lattices under a same field, unless the applied field is further enhanced.

To quantitatively analyze the effects of two factors, a BaTiO₃ single crystal sample was characterized in the same way and the field was applied along the (001) direction. Fig. 4 plots the temperature dependence of the exothermic value in first cycle under different fields. The exothermic value in first cycle is 0.56J/g under 5kV/cm at 10°C, which refers to $\Delta T = 1.2\text{K}$; while that in subsequent cycles is only 0.006J/g, about two orders of magnitude lower. It substantially proves that the energy variation of the lattice structure is the dominant factor for giant ECE near phase transition, when compared with the ordering entropy change. The exothermic value in first cycle under 10kV/cm indicates a large RT ECE of $\Delta T = 1.4\text{K}$ and $\Delta T/E = 1.4\text{K} \cdot \text{mm/kV}$, which is the highest ECE per unit field known in ferroelectric material. The corresponding ECE heat of 0.64J/g is equal to the latent heat of O-T phase transition (as obtained from Fig. 1), which means most lattices are involved in phase transition under this condition. With the rise of temperature, the exothermic value decreases slowly at first, and drops suddenly at 10.7°C for 5kV/cm and at 13°C for 10kV/cm. It is because the potential barrier for **T-O** phase transition increases with the rise of temperature. Once the driving force is lower than the potential barrier of most lattices, much fewer lattices can be involved in the phase transition and the exothermic value drops remarkably.

Except for the large exothermic (or endothermic) peak in first cycle, the exothermic and endothermic values in following cycles are identical (as shown in Fig. 5 inset), and their temperature dependence is shown in Fig. 5. The maximum occurs above T_1 , and it enhances and moves to higher

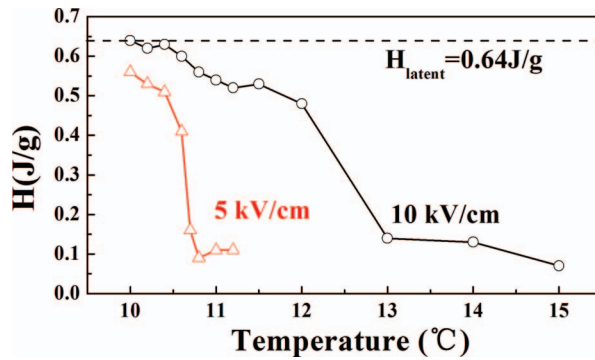


FIG. 4. The temperature dependence of ECE exothermic values in first cycle under different fields for BaTiO₃ single crystal. The dash line indicates the latent heat value.

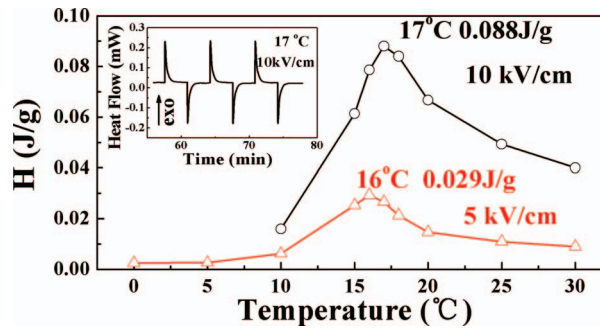


FIG. 5. The temperature dependence of ECE endothermic values except for first cycle of BaTiO₃ single crystal. The inset shows the DSC heat flow curve under 10kV/cm at 17°C.

temperature with increasing applied field. Since the ordering entropy change is dominant here, the maximum ECE occurs above the phase transition temperature due to the combination effect of the applied field and the thermal excitation, which play inverse roles for the polarization ordering. Its variation with applied field is accompanied by the shift of field-induced phase transition, which can be described as $\partial T_c/\partial E = -(\Delta D_{O-T}/\Delta S_{O-T}) > 0$ according to the Devonshire theory. The maximum ECE is 0.06K at 16°C under 5kV/cm, and 0.19K at 17°C under 10kV/cm, still much lower than the exothermic (or endothermic) values in first cycle.

The experimental results indicate that energy change of lattice structure has much larger contribution to the ECE than the ordering entropy change, so it is the key for giant ECE. The phase transition of a ferroelectric relaxor is diffused, so the ECE has a fairly-high value in a wide temperature range. For ferroelectrics under an ultrahigh electric field, the lattices were seriously deformed, far beyond the spontaneous polarization state, so large lattice energy involved results in a giant ECE several times higher than that of the latent heat. However, the efficiency under unit field is not as high as where the latent heat is involved. In addition, this work suggests that a large ECE can be achieved by manipulating phase transition in a proper refrigeration cycle, where a well controlled field-induced phase transition could bring a significant energy flow associated with a change of lattice structure to produce a large ECE.

In conclusion, this paper demonstrates the electrocaloric effect around the orthorhombic-tetragonal phase transition in BaTiO₃. The experimental results quantitatively confirm the dominant contribution to ECE of the energy flow due to the structural phase transition. Through manipulating a field-induced phase transition, a large exothermic or endothermic peak appears after first application or removal of field, due to the contribution of lattice energy, and a large effect of 0.64J/g ($\Delta T = 1.4K$) is achieved under 10kV/cm at 10°C. By comparison, the ECE associated with the entropy change of polarization ordering is two orders of magnitude lower under the same conditions. This work provides a new route to achieve large ECE through manipulating the transition of metastable phases

by fields, which can promote the development of the application of highly-efficient ferroelectric refrigeration.

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