



# Electrical field dependence of electrocaloric effect in relaxor ferroelectrics

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## Abstract

Relaxor ferroelectrics demonstrate great potential in achieving large electrocaloric effect (ECE) which could be used as cooling devices in microelectronics industry as well as in daily life. The electrical field dependence of ECE, however, remains unclear, especially for relaxor ferroelectrics. The electrical field dependence of ECE can help to predict the ECE characteristics of cooling devices, and facilitate the design of highly efficient refrigerators. In this work, relaxor ferroelectric  $0.71\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.29\text{PbTiO}_3$  (PMN–PT) (011) single crystals,  $(\text{PbLa})(\text{ZrTi})\text{O}_3$  ceramic thin films, and poly(vinylidene fluoride–trifluoroethylene–chlorofluoroethylene) (P(VDF–TrFE–CFE))/poly(vinylidene fluoride–trifluoroethylene) (P(VDF–TrFE)) terpolymer/copolymer blends were used to investigate the electrical field dependence of ECE. Direct method was used to measure the ECE adiabatic temperature change as a function of electrical field. Results indicate that, the ECE temperature change tends to show quadratic relationship, i.e.,  $\Delta T-E^2$ , at lower electrical fields. At higher fields, however, the temperature change has a tendency towards saturation in terms of the relationship, i.e.,  $\Delta T-E^{2/3}$ . In the intermediate electrical fields, the temperature change shows a roughly linear relationship with electrical field. The above phenomena could be illustrated in the frame of approximately continuous phase transition derived Belov–Goryaga equation, which can be modified for ferroelectrics.

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## 1. Introduction

Electrocaloric effect (ECE) is the inverse of pyroelectric effect occurred in polar materials due to the change of polarization states when applied with an external electrical field [1–3]. Both ECE and magnetocaloric effect (MCE) [4,5] are associated with the solid state phase transition of materials in terms of the transformation of ordering to disordering, or vice versa. Both of them can be used as cooling devices. The MCE devices, however, cannot be miniaturized too much due to the large size of magnets used, which limits their applications. For ECE devices, it is pretty easy to design the electrode tips. Hence, ECE cooling devices can be used for microelectronic circuits situations in which small size is needed.

The study of ECE can be traced to 1930s when two German scientists measured the ECE of Rochelle salt, but no numerical data were published [6]. Later on Wiseman and Kuebler re-measured the ECE in Rochelle salt, they obtained the temperature change of  $0.0036\text{ }^\circ\text{C}$  [7]. The revisit to ECE in large scale worldwide was due to the two papers published in Science on Pb  $(\text{ZrTi})\text{O}_3$  ceramic thin films and P(VDF–TrFE) 55/45 mol% copolymer films [8,9]. An adiabatic temperature of  $12\text{ }^\circ\text{C}$  was obtained respectively. Up to now, research works cover almost all the ferroelectric categories, such as, ceramics, single crystals, thin films, polymers, and even liquid crystals. Of all the studies, the electrical field dependence of ECE is still unclear, especially for relaxor ferroelectrics due to the catastrophe of thermodynamics applied in these materials. Relaxor ferroelectrics are different from the normal ferroelectrics, which demonstrate first-order or second-order phase transitions. Due to nonergodicity, relaxor ferroelectrics cannot be applied by thermodynamic relations, e.g.,

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Maxwell relations. In this work, we report the electrical field dependences of ECE in 0.71 Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>–0.29PbTiO<sub>3</sub> (PMN–PT) single crystals, (PbLa)(ZrTi)O<sub>3</sub> ceramic thin films, and poly(vinylidene fluoride–trifluoroethylene–chlorofluoroethylene) (P(VDF–TrFE–CFE)) /poly(vinylidene fluoride–trifluoroethylene) (P(VDF–TrFE)) terpolymer/copolymer blends, and illustrate the experimental results in terms of the approximately continuous phase transition derived Belov–Goryaga equation.

## 2. Material and methods

The 0.71PMN–0.29PT (011) single crystals were grown using a modified Bridgman method [10]. The grown crystal was cut into small pieces. Before the electrical measurement, gold was sputtered on both surfaces to be used as contact electrode. (Pb<sub>0.88</sub>La<sub>0.08</sub>)(Zr<sub>0.65</sub>Ti<sub>0.35</sub>)O<sub>3</sub> (8/65/35 PLZT) thin films were fabricated using a sol–gel method and the thickness of ceramic thin films was ~0.45 μm. The PLZT thin films were covered with platinum electrodes [11]. Terpolymer P(VDF–TrFE–CFE) 62.5/29.5/8 mol% (Piezotech, France) and copolymer P(VDF–TrFE) 55/45 mol% (Solvay) were used as the batch materials. A certain ratio of terpolymer and copolymer were weighed and dissolved in N,N-dimethyl formamide, and stirred for 12 h at room temperature, respectively. Then the terpolymer and copolymer solutions were mixed and stirred for several hours. The final solution was filtered using a 0.2 μm sized polytetrafluoroethylene filter and then cast onto the cleaned glass plates and dried at 70 °C for 24 h in an oven. Afterwards, the films were peeled off from the glass plates and further annealed at 110 °C for 24 h in an oven. The final films obtained have thicknesses of 8–10 μm [12].

By employing a high-resolution calorimeter [13,14], the ECE in PLZT thin films was directly measured. Details are presented in Ref. [11]. A specially designed calorimeter was also developed at Penn State to directly measure the temperature change due to ECE in polymer films. In this calorimeter, the heat generated by the ECE sample is compared with the heat generated by a reference resistor  $R$ , from which  $\Delta S$  is determined. When a voltage  $V$  with a pulse time duration  $t$  is applied to the resistor heater, it will produce a joule heat  $Q_h = (V^2/R)t$ . The heat will generate a temperature change in the sample system and this temperature change is detected by an infrared (IR) temperature sensor. For PMN–PT single crystals, the ECE was directly measured using a thermocouple connecting to a preamplifier and an oscilloscope to record the adiabatic temperature change profile. An exponential function was fitted and extrapolated to its origin ( $t=0$ ) to get the temperature change due to the ECE. The dielectric properties as a function of temperature were characterized using a multi-frequency LCR Meter (HP 4284A). The electric displacement versus electrical field ( $D$ – $E$ ) hysteresis loops at different temperatures were measured using a Sawyer–Tower circuit. A differential scanning calorimeter (TA Instrument TA Q100) in modulated mode was used to measure the specific heat capacity.

## 3. Results and discussion

For relaxor ferroelectrics, thermodynamics cannot be applied due to nonergodicity in some temperature range [15]. Outside this range, the ferroelectric behavior, such as the order parameter polarization versus temperature, could be approximated by the second-order phase transition. For a second-order transition, Landau–Devonshire phenomenological expansion of Gibbs free energy is [1–3]

$$G = \frac{1}{2}\beta(T - T_c)P^2 + \frac{1}{4}\gamma P^4 - EP, \quad (1)$$

where  $\beta$  and  $\gamma$  are assumed to be temperature-independent phenomenological coefficients, both  $\beta > 0$  and  $\gamma > 0$ .  $T_c$  is the Curie temperature.

For simplicity in the general discussions here, we assume that the polymer is a uniaxial ferroelectric and hence  $\vec{P}$  in the free energy expression is written as a scalar. The entropy can be obtained from  $S = -(\partial G / \partial T) = -1/2\beta P^2$ , then  $\Delta T = \frac{1}{2} \frac{\beta T}{C_E} P^2$ . Differentiating  $G$  with respect to  $P$  yields the relationship between  $E$  and  $P$

$$E = \beta(T - T_c)P + \gamma P^3. \quad (2)$$

Substituting  $\Delta T = \frac{1}{2} \frac{\beta T}{C_E} P^2$  into Eq. (2) yields

$$\frac{a}{k^{1/2}} \Delta T^{1/2} + \frac{b}{k^{3/2}} \Delta T^{3/2} = E. \quad (3)$$

where  $k = \beta T / (2c_E)$ ,  $a = \beta(T - T_c)$ ,  $b = \gamma$ . Eq. (3) is analogous to the Belov–Goryaga equation for the magnetocaloric effect [16,17]. At lower electric fields, the first term on the left side of Eq. (3) dominates, one has

$$\Delta T = \frac{\beta T}{2c_E [\beta(T - T_c)]^2} E^2. \quad (4)$$

This means that the ECE has a quadratic relationship with the electric field. At higher electric fields, the second term on the left side of Eq. (3) dominates, then

$$\Delta T = \frac{\beta T}{2c_E \gamma^{2/3}} E^{2/3}. \quad (5)$$

Thus the ECE temperature change is proportional to  $E^{2/3}$  at higher electric fields. In between the two extreme cases, usually a quasi-linear profile can be obtained.

Fig. 1 shows the ECE temperature change as a function of electric field for PMN–PT (011) single crystal. At low electric fields, the experimental data can be fitted by a quadratic relation of electric field. In this region, there is a sharp increase of ECE temperature change at certain electric fields, which is a good indication that the ECE temperature change could rise rapidly. At higher electric fields, the ECE temperature change still increases in the form of  $E^{2/3}$ . But the material is easy to breakdown in this range. In between the two extreme cases, an almost linear relationship can be utilized, which might facilitate the design of ECE device to control the adiabatic temperature change versus electric field. Based on Eq. (3), a crossover electric field could be obtained for PMN–PT single crystals, which strongly depends on the phenomenological coefficients for PMN–PT crystals. At this time, due to the lack

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