Giant isothermal entropy change In (111)-oriented PMN–PT thin film

Mahmoud A. Hamad

Physics Department, Faculty of Science
Tanta University, Tanta, Egypt
m_hamad76@yahoo.com

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An isothermal entropy change of 240 nm (111)-oriented PMN–PT 65/35 film near the ferroelectric Curie temperature, relative cooling power (RCP) and change of heat capacity have been investigated. The extracted data characterized giant isothermal entropy change of more than 16 J/kg K in electric field shift ΔE of 455 kV cm⁻¹, which is nearly twice than that found for PbZr_{0.95}Ti_{0.05}O₃ thin film at 492 kV cm⁻¹ near the Curie point. Furthermore, the RCP $\approx$ 700 J/kg and change of heat capacity $\approx$ 233 J/kg K in electric field shift ΔE of 747 kV cm⁻¹.

Keywords: Electrocaloric effect; PMN–PT thin film; polarization; entropy change; heat capacity change.

The search for materials showing caloric effects has become a challenge in modern materials physics and it is expected that such a group of materials will give a way to renovate present cooling devices that are based on the vapor compression of hazardous gases. Till now, the most promising materials are electrocaloric and magnetocaloric materials.^{1–13} Ferroelectric materials (1 – x)PbMg_{1/3}Nb_{2/3}O₃ – xPbTiO₃ with the compositions near the morphotropic phase boundary are promising for microelectro-mechanical systems and high-strain actuators/transducers due to their well-known ferroelectric, dielectric, and piezoelectric properties.^{14–20}

The electrocaloric effect (ECE) of (111) 0.65PbMg_{1/3}Nb_{2/3}O₃ – 0.35PbTiO₃ (PMN–PT 65/35) thin films near the Curie point has been studied.²¹ This study reported an electrocaloric temperature change ΔT of 31 K ($\Delta E = 747$ kV/cm) for a (111) PMN–PT 65/35 thin film deposited on a substrate (Pt(111)/TiO₂/SiO₂/Si). This paper computes the electrocaloric properties of ferroelectric (111) PMN–PT 65/35 thin film such as entropy changes, heat capacity changes, and relative cooling power (RCP) at various applied electric field shifts that were not included in Ref. 21.

According to the phenomenological model,²² the dependence of polarization on variation of temperature and Curie temperature (T_c) is presented by

$$P = \left(\frac{P_i - P_f}{2} \right) [\tanh(A(T_c - T))] + BT + C, \quad (1)$$

where P_i is an initial value of polarization at ferroelectric–paraelectric transition and P_f is a final value of polarization at ferroelectric–paraelectric transition as shown as in Fig. 1.

$A = \frac{2[B - \frac{dP}{dT}|_{T=T_c}]}{P_i - P_f}$, B is polarization sensitivity $\frac{dP}{dT}$ at ferroelectric state before transition, $\frac{dP}{dT}|_{T=T_c}$ is polarization sensitivity $\frac{dP}{dT}$ at Curie temperature T_c , and $C = \frac{P_i + P_f}{2} - BT_c$.

A result of this phenomenological model, the electrocaloric entropy change ΔS^E caused by variation of the external electric field from E_1 to E_2 is given by

$$\Delta S^E = \left(-A \left(\frac{P_i - P_f}{2} \right) \times \text{sech}^2(A(T_c - T)) + B \right) \times \frac{\Delta E}{\rho}, \quad (2)$$

where ρ is the mass density and $\Delta E = E_2 - E_1$.

Fig. 1. Dependence of polarization as a function of temperature is described by Eq. (1).

A main result of Eq. (2) is maximum entropy change ΔS_{Max}^E (where $T = T_c$), is expressed as follows:

$$\Delta S_{\text{Max}}^E = \left(-A \left(\frac{P_i - P_f}{2} \right) + B \right) \times \frac{\Delta E}{\rho}. \quad (3)$$

According to the phenomenological model, a full-width at half-maximum δT_{FWHM} can be calculated as follows²²:

$$\delta T_{\text{FWHM}} = \frac{2}{A} \cosh^{-1} \left(\sqrt{\frac{2A(P_i - P_f)}{A(P_i - P_f) + 2B}} \right). \quad (4)$$

An electrocaloric cooling efficiency is calculated by considering the magnitude of maximum electrocaloric entropy change, $-\Delta S_{\text{Max}}^E$ and its full-width at half-maximum (δT_{FWHM}).²³ A product of $-\Delta S_{\text{Max}}^E$ and δT_{FWHM} is called RCP based on electrocaloric entropy change.

$$\begin{aligned} \text{RCP} &= -\Delta S_{\text{Max}}^E(T, \Delta E) \times \delta T_{\text{FWHM}}, \\ &= \left(P_i - P_f - 2 \frac{B}{A} \right) \times \frac{\Delta E}{\rho} \\ &\quad \times \cosh^{-1} \left(\sqrt{\frac{2A(P_i - P_f)}{A(P_i - P_f) + 2B}} \right). \end{aligned} \quad (5)$$

A polarization-related change of heat capacity is given by

$$\Delta C_{P,E} = T \frac{\delta \Delta S^E}{\delta T}. \quad (6)$$

According to this phenomenological model, a change of heat capacity is given by

$$\begin{aligned} \Delta C_{P,E} &= -TA^2(P_i - P_f) \text{sech}^2(A(T_c - T)) \\ &\quad \times (\tanh(A(T_c - T))) \frac{\Delta E}{\rho}. \end{aligned} \quad (7)$$

A temperature change of a polar system under adiabatic electric field variation from an initial value E_1 to final value E_2 , can be written in the form

$$\begin{aligned} \Delta T &= -\frac{T}{C_E \rho} \int_{E_1}^{E_2} \left(\frac{\partial P}{\partial T} \right)_E dE, \\ &= \frac{AT(P_i - P_f)}{2C_E \rho} [\text{sech}^2(A(T_c - T)) + B] \Delta E. \end{aligned} \quad (8)$$

C_E is a heat capacity per mole at constant electric field.

The refrigerant capacity (RC) is, the amount of heat that can be transferred in one thermodynamic cycle.²⁴ Here, RC values can be obtained as follows.²²

$$\begin{aligned} \text{RC} &= \int_{T_c - \frac{\delta T_{\text{FWHM}}}{2}}^{T_c + \frac{\delta T_{\text{FWHM}}}{2}} \Delta S^E dT, \\ &= \left[-(P_i - P_f) \times \tanh \left(A \frac{\delta T_{\text{FWHM}}}{2} \right) \right. \\ &\quad \left. + B \delta T_{\text{FWHM}} \right] \frac{\Delta E}{\rho}. \end{aligned} \quad (9)$$

From this phenomenological model, the values of δT_{FWHM} , $|\Delta S_E|_{\text{Max}}$, $|\Delta T|_{\text{Max}}$, RCP, RC, and ΔC for (111) PMN-PT 65/35 thin film due to applied electric field shift ΔE can be easily calculated.

In order to apply the phenomenological model, five parameters versus applied electric field were determined as displayed in Table 1. In the temperature range of interest, a heat capacity of $C_p = 120 \text{ J mol}^{-1} \text{ K}^{-1} = 377 \text{ J Kg}^{-1} \text{ K}^{-1}$ and mass density $\rho = 8.08 \text{ g} \cdot \text{cm}^{-3}$ for PMN-PT 65/35 thin film has been considered.²¹

Figure 2 shows polarization variation induced by temperature change at different electric fields for (111)-oriented PMN-PT 65/35 film. The symbols in Fig. 2 represent experimental data from Ref. 21 and the dashed lines represent simulated data. It is clear that Fig. 2 shows a good agreement between simulated results and experimental data. EC entropy changes associated with the ferroelectric-paraelectric transition are shown in Fig. 3. The extracted data characterized giant isothermal entropy change of more than 16 J/kg K in electric field shift ΔE of 455 kV cm^{-1} , which is nearly twice than that found for $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ thin film in 492 kV cm^{-1} near the Curie point.¹

In Fig. 4, the predicted heat capacity changes and temperature changes are shown as functions of temperature under different electric field shifts, calculated from Eqs. (7) and (8), respectively.

The extracted data characterized the electrocaloric temperature change, up to 31.21 K at 17.928 V (i.e., 1.74 KV^{-1}) near the Curie point at temperatures around 138°C . This value is closer to the previous work ($\Delta T = 31 \text{ K}$).²¹

From Fig. 4, the (111)-oriented PMN-PT 65/35 film has a giant change in heat capacity to more than 200 J/kg K . At an electric field shift of 747 kV cm^{-1} , using Eqs. (5) and (9), the

Table 1. Model parameters for (111) PMN-PT 65/35 thin film at various applied electric fields.

E (kV cm ⁻¹)	T_c (°C)	P_i ($\mu\text{C} \cdot \text{cm}^{-2}$)	P_f ($\mu\text{C} \cdot \text{cm}^{-2}$)	B ($\mu\text{C} \cdot \text{cm}^{-2} \cdot ^\circ\text{C}^{-1}$)	$\frac{dP}{dT} _{T=T_c}$ ($\mu\text{C} \cdot \text{cm}^{-2} \cdot ^\circ\text{C}^{-1}$)
455	138	38.36	33.11	-0.011	-0.31
502	138	40.12	34.4	-0.011	-0.31
554	138	42.38	35.94	-0.011	-0.31
605	138	44.21	37.45	-0.011	-0.31
654	138	45.55	38.43	-0.011	-0.31
747	138	47.46	39.43	-0.011	-0.31

Fig. 2. Polarization variation induced by temperature change under different electric field for (111) PMN-PT 65/35 thin film. The dashed lines are modeled results by Eq. (1) and symbols represent experimental data from Ref. 21.

Fig. 3. Absolute values of electrocaloric entropy changes versus temperature at various applied electric field shifts for (111) PMN-PT 65/35 thin film.

values of RCP and RC are 698.6 and 559.3 J/kg, respectively. Therefore, (111) PMN-PT 65/35 thin film shows a giant ECE near the Curie point. This may be attributed to the significant contribution of the latent heat from the field-induced phase transition and the choice of the substrate (Pt(111)/TiO₂/SiO₂/Si) which has, through the interfacial strain, enhanced the ECE. The control of the misfit strain by appropriate choice of substrate provides potential means to vary both the magnitude and the temperature sensitivity of the ECE for use in cooling or thermoelectric power conversion devices.²⁵ Another contributing factor can be the orientation of the epitaxial films that activates the strongest EC tensor element, as well as the high film crystallinity.²⁶ Furthermore, PMN-PT thin-film processing is a challenge due to the persistence of a pyrochlore phase and high porosity. Pyrochlore phases and porosity have been pointed out as the main factors contributing to the decrease of dielectric and ferroelectric properties.^{27–30}

The addition of the (111) PMN-PT 65/35 shows a giant ECE, the pyroelectric effect of (111) PMN-PT 65/35 thin

(a)

(b)

Fig. 4. (a) Heat capacity changes and (b) Electrocaloric temperature changes for (111) PMN-PT 65/35 thin film at various applied electric field shifts versus temperature.

film can recover useful electrical power from waste heat. Therefore, electrical triggering of the cooling of (111) PMN-PT 65/35 thin film is more practical. Finally, in phenomenological model, it can calculate the electrocaloric properties of (111) PMN-PT 65/35 thin film with limited processing time. Moreover, the model does not add any auxiliary computational efforts to the numerical simulation. Our results resolve the controversy surrounding macroscopic models of the ECE and may inspire *ab initio* calculations of electrocaloric parameters and thus a targeted search for new materials.

In conclusion, ECE of (111)-oriented PMN-PT 65/35 is calculated showing promising results. The extracted data characterized an isothermal entropy change of more than 28 J/kg K, RCP $\approx$ 700 J/kg and change of heat capacity $\approx$ 233 J/kg K in electric field shift ΔE of 747 kV cm⁻¹.

In conclusion, a giant ECE in this sample suggests that a large family of layered perovskite oxides might exhibit analogous feature. The simulation shows more potential of ECE by this model can be easily worked out, which constitutes the main originality.

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