MATERIAL SYSTEM ENGINEERING FOR ADVANCED ELECTROCALORIC COOLING TECHNOLOGY

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by

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ABSTRACT

Electrocaloric effect refers to the entropy change and/or temperature change in dielectrics caused by the electric field induced polarization change. Recent discovery of giant ECE provides an opportunity to realize highly efficient cooling devices for a broad range of applications ranging from household appliances to industrial applications, from large-scale building thermal management to micro-scale cooling devices. The advances of electrocaloric (EC) based cooling device prototypes suggest that highly efficient cooling devices with compact size are achievable, which could lead to revolution in next generation refrigeration technology. This dissertation focuses on both EC based materials and cooling devices with their recent advances that address practical issues. Based on better understandings in designing an EC device, several EC material systems are studied and improved to promote the performances of EC based cooling devices.

In principle, applying an electric field to a dielectric would cause change of dipolar ordering states and thus a change of dipolar entropy. Giant ECE observed in ferroelectrics near ferroelectric-paraelectric (FE-PE) transition temperature is owing to the large dipolar orientation change, between random-oriented dipolar states in paraelectric phase and spontaneous-ordered dipolar states in ferroelectric phases, which is induced by external electric fields. Besides pursuing large ECE, studies on EC cooling devices indicated that EC materials are required to possess wide operational temperature window, in which large ECE can be maintained for efficient operations. Although giant ECE was first predicted in ferroelectric polymers, where the large effect exhibits near FE-PE phase transition, the narrow operation temperature window poses obstacles for these
normal ferroelectrics to be conveniently perform in wide range of applications. In this dissertation, we demonstrated that the normal ferroelectric polymers can be converted to relaxor ferroelectric polymers which possess both giant ECE (27 Kelvin temperature drop) and much wider operating temperature window (over 50 kelvin covering RT) by proper defect modification which delicately tailors ferroelectrics in meso-, micro- and molecular scales. In addition, in order to be practical, EC device requires EC material can be driven at low electric fields upon achieve the large ECE. It is demonstrated in this dissertation that by facially modifying materials structure in meso-, micro- and molecular scale, low-field ECE can be greatly improved. Large ECE, induced by low electric fields and existing in wide temperature window, is a major improvement in EC materials for practical applications.

Besides EC polymers, this thesis also investigated EC ceramics. Due to several unique opportunities offered by the EC ceramics, Ba(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} (BZT), that is studied. (i) This class of EC ceramics offers a possibility to explore the invariant critical point (ICP), which maximizes the number of coexistent phase and provides a nearly vanishing energy barrier for switching among different phases. As demonstrated in this thesis, the BZT bulk ceramics at x~ 0.2 exhibits a large adiabatic temperature drop $\Delta T_c=4.5$ K, a large isothermal entropy change $\Delta S = 8$ Jkg$^{-1}$K$^{-1}$, a large EC coefficient ($|\Delta T_c/\Delta E| = 0.52 \times 10^{-6}$ KmV$^{-1}$ and $\Delta S/\Delta E=0.93 \times 10^{-6}$ Jmkg$^{-1}$K$^{-1}$V$^{-1}$) over a wide operating temperature range $T_{span}>30$K. (ii) The thermal conductivity of EC ceramics is in general, much higher than that of EC polymers, and consequently they will allow EC cooling configurations which are not accessible by the EC polymers. Moreover, in the same device configuration, the
high thermal conductivity of EC ceramics (κ > 5 W/mK, compared with EC polymer, ~ 0.25 W/mK) allows higher operation frequency and therefore a higher cooling power. (iii) Well-established fabrication processes of multilayer ceramic capacitor (MLCC) provide a foundation for the EC ceramic toward mass production. In this thesis, BZT thick film double layers have been fabricated and large ECE has been directly measured. EC induced temperature drop (ΔT) around 6.3 °C and entropy change (ΔS) of 11.0 Jkg⁻¹K⁻¹ are observed under an electric field of ΔE=14.6 MV/m at 40 °C was observed in BZT thick film double layers. The result encourages further investigations on ECE in MLCC for practical applications.

This thesis also explores ECE in dielectric fluids and asks the question of whether a high ECE is possible in dielectric fluids. Compared with solid state EC materials, dielectric fluids that possess large ECE would provide unique routes to design a cooling device. Fluids are widely used in industrial communities for passive cooling and thermal management, for which it is also known as coolants or heat exchange fluids. If there is a dielectric fluid that can provide active cooling by responding to external electric field, such fluid can thus provide functionalities of both active refrigerant and heat exchange media, opening grand opportunities to design much simpler cooling devices. In this dissertation, we demonstrated that ECE indeed exists in a class of fluid, liquid crystals, which possess large dielectric anisotropy and several first-ordered phase transitions near RT, i.e. smectic, nematic and isotropic phases. Large ECE is demonstrated in a widely studied liquid crystal, 5CB, near its nematic-isotropic (N-I) transition temperature that is near RT. An isothermal entropy change of more than 24 Jkg⁻¹K⁻¹ and an adiabatic
temperature change of 5.2 K was observed near 39 °C, which is slightly above the N-I transition temperature. The studies suggest that great potential of refrigeration designing lies in small molecules with functional group of large dipole moment and liquid or liquid crystal phases.

Previous reported ECE generates cooling and heating cyclically in response to an electric pulse (normal or negative ECE). This thesis asked the question that whether the cooling and heating signals can be unbalanced and even generate only cooling under and electric pulse. Since ECE is dipolar entropy in responses to electric field induced polarization change, there is no fundamental reason for ECE to always generate balanced cooling and heating signals. In the last chapter, an anomalous ECE (A-ECE) that exhibit only cooling but without subsequent heating, under an small electric pulse, is demonstrated, which may provide instant cooling with high reliability for applications such as the thermal management for on-chip hot-spots. The A-ECE is observed in internal-biased normal ferroelectric/relaxor ferroelectric composites. When such composites are de-poled, the dipolar-ordering in the internal-biased composites becomes random, and stay random when electric field is removed owing to the existence of randomness induced by relaxor ferroelectric participant. The observation of A-ECE is consistent with detailed polarization study. Upon de-poling such a polymer blend, the remnant polarization reduced to zero and stayed at zero-state. Therefore, the instant cooling ($\Delta S=10$ J/kgK) without subsequent heating is realized. The observation paves a way to produce anomalous, large EC effect through engineering inhomogeneous dipolar interactions, and thus could lead to many device applications. These devices would
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Chapter 1

Introduction

1.1 Background

One key component of a cooling device is the transportation of heat from the cold end to the hot end. The objective is to cycle between two entropy states from one temperature level to another temperature level in a reversible manner, that is, to transport the heat without generating any additional heat in the process. This requires a substance whose entropy depends on some properties other than temperature. In the electrocaloric (EC) based cooling, this substance is the EC material, in which entropy can be changed by external electric fields. All steady state converters must be cyclic since the heat carrying substance is not consumed. In a practical device, the irreversible leaking of heat down the temperature gradient by conduction and various losses can generate excess heat for cold end of the device. Such a cyclic device is essentially a heat pump that delivers heat from cold end to hot end. A simple and maybe the most outstanding example is the vapor compression refrigeration (VCR) technology. By employing the VCR, mechanic work is put into compressor to reduce the entropy of the vapor, causing it to eject heat into a heat sink, in reverse, expand and increase the entropy of the vapor so that it can absorb heat from the heat load. To evaluate the performance of heat pumps, the term coefficient of performance (COP) is normally used to describe the ratio between heat that is absorbed at cold end $Q_c$ and total input work. In a Carnot cycle, where cold end and hot
end have fixed temperature, $T_c$ and $T_h$, respectively, the Carnot COP, which is the maximum COP of a heat pump, is reduced to $T_c/(T_h-T_c)$. It should be noted that for different temperature spans between the two ends of the cooling device, Carnot COP are different. For example, Carnot COP for a heat pump that is pumping heat from 300 K to 320 K is 15. The Carnot COP is suggesting that the heat pumping can be quite efficient, i.e., 15 Joule heat can be pumped to $T_h$ per 1 Joule work input. However, since 1755, when the first know artificial refrigeration was demonstrated by William Cullen at University of Glasgow,[1] the technology hasn’t been significantly improved. Nowadays, 90% commercialized household freezers and air-conditioners have COPs below 3.5. Considering the huge amount of electricity consumption each year, which is approximately 4000 terawatt hours (TWh), and the fact that more than 30% of annual electricity is consumed in space cooling and refrigeration in US, only 10% COP improvement would save 110 terawatt hours energy that is almost the annual electricity consumption in Mexico. [2]
Figure 1-1. US electricity consumption according to the US Dept. of Energy. [3]

Besides the large annual consumption on electricity, space cooling and refrigeration cost much more electricity power in summer for those countries and areas in tropical and subtropical zones. Especially for developing countries, the electricity consumption by air-conditioning (A/C) and refrigeration in summer is a huge problem.
which leads to suddenly increased electricity consumption and thus leads to electricity outage.[4] Highly efficient cooling device would turn the situation around by maintaining the cooling function and reducing the electricity consumption.

Besides the general market of air conditioning and refrigeration, a highly compact and very efficient cooling device will also stimulate an emerging field of air conditioning, known as localized thermal management. One simple localized thermal management would be the heated seats in vehicles. Heating seat creates a localized environment that achieves human comfort very fast and without heating up the whole vehicle. Similarly, localized thermal management device can be more helpful in achieving higher energy efficiency in a much larger space such as buildings. A major factor impacting building energy efficiencies is the operating temperature range or the “neutral-band”, which is the temperature range in which no heating or cooling is required by centralized HVAC (heating, ventilating and air conditioning) systems. Neutral band is usually set between 70 and 75 °F. As show in Figure 1-2, wider neutral band setpoints would greatly reduce the energy cost in a building. Setpoint expansions of only 4 °F in each direction will yield more than 15% energy savings. However, it would inevitably cause a wider temperature gradient in the building thus human comfort is harder to be maintained. Localized cooling could provide additional thermal management where the centralized building thermal management system cannot reach. In other words, the localized thermal management device allows lower electricity consumption in building cooling and heating. The potential energy saving can be huge. Building heating and cooling represents more than 13% of domestic energy use in the US. This translates to, about 12 Qbtu of energy annually and 13% of domestic greenhouse gas emissions. Consequently, a technology
reducing this heating and cooling energy consumption by a large amount, such as 30%, would have transformative national impacts on electricity usage, fuel consumption, and greenhouse gas emissions.

![Diagram showing energy savings for widened air temperature setpoints relative to conventional setpoints in four cities.](image)

Figure 1-2. Percentage energy savings for widened air temperature setpoints relative to conventional setpoints in four cities.[5]

Without large compressors and greenhouse gas emission, EC-based cooling technology offers opportunity to develop small, localized and efficient thermal management device to address the issue such as energy efficiency in building thermal management. EC based Localized Thermal Management Systems (LTMS) modify the local thermal environment surrounding the human body rather than throughout the building, enabling wider neutral band temperature setpoints without loss of human comfort. An EC thermal management device that can be applied locally and efficiently
provide enough cooling/heating for people’s comfort is important to ease the electricity burden in weathers with very high or very low temperatures.

Besides providing the high efficiency and potential to work with current VCR to reduce the electricity consumption, the next generation thermal management is required to do more in a much smaller scale, such as integrated circuit thermal management or on-chip cooling for hot spots that occasionally strike in CPUs and cause instability in the operation of processors. [6] Compared to solely using current passive cooling methods, i.e., fan-based cooling and coolant-based cooling, EC based cooling device may work with conventional passive approach to manage ever growing heat dissipation from CPUs.

It is essential for the next generation cooling devices to be environmentally friendly. Current VCR employs HFCs as the refrigerants, which are strong greenhouse gases. The leakage of such HFCs during refrigeration processes contributed to 25% of greenhouse gas emission annually. Especially after the Copenhagen Accord was signed in 2009, reducing the greenhouse gas emission became an issue that is treated more seriously and leading to a more stringent government regulations as a part of international efforts to combat the global warming. All major countries and areas, US, China, EUs, etc., are agreed on reducing the greenhouse gas emission to control the global warming. Air-conditioning and refrigeration technologies without any greenhouse gas emission during the operation would be in great appreciation in the environmental consideration.

As stated above, there is a great demand of next generation thermal management device which should possess: (i) higher coefficient of performance (COP), compared with VCR based cooling system, (larger than 50% of Carnot COP); (ii) high cooling power to enable effective operation; (iii) potential to be applied in different dimension scales, i.e.,
from chip-scale cooling for integrated circuits to large scale building thermal management; (iv) good compatibility with electricity input; (v) environmentally friendliness. The question is how to develop such technologies to meet these ever increasing demands.

In this chapter, current developed or on-developing alternative thermal management technologies, which are dedicated to address above issues, will be presented. Then, electrocaloric effect, as the most promising advanced thermal management solution that can be highly efficient, highly scalable, environmentally friendly and at low cost, will be introduced from the device engineering and materials science point of views. The concurrent study of EC devices and materials introduced several device requirements in EC materials, which can be rationally designed and modified accordingly to different device configurations. The research objectives, which are developed early on in this PhD study, will be discussed at end of this chapter.

1.2 Alternative Refrigeration Solutions

In order to address above issues, several alternative refrigeration solutions have been investigated and developed. From the working principles, those technologies are named thermoelectric refrigeration, thermoacoustic refrigeration, caloric refrigeration, to name a few. These alternatives at current stage have their advantages as well as shortcomings compared to the current VCR technology. Here we will introduce these technologies briefly.
1.2.1 Thermoelectrics

The thermoelectric effect refers to a phenomenon by which either a temperature difference creates an electric potential or an electric potential creates a temperature difference. Thermoelectric cooling is based on the Peltier effect, which creates the temperature difference at an electrified junction of two different conductors. For example, when a voltage is applied to the free ends of the two semiconductors there is a flow of DC current across the junction of the semiconductors causing a temperature difference., [7] as shown in Figure 1-3.

Figure 1-3. Schematic of (a) one thermoelectric unit and (b) one cooling device based on thermoelectrics. [8]

The amount of heat has been pumped at the junction per second, which is essentially the cooling power, is noted as,

\[ P_c = (S_P - S_N) \cdot I \cdot T, \]

where \( S_N \) and \( S_P \) are the Seebeck coefficient of the N and P type semiconductors. \( I \) is the current that flow across the junction, and \( T \) is the temperature at the heat load. As shown in Eq. 1.1, larger difference of Seebeck coefficients between P type and N type
semiconductor and larger driving current would be expected to provide larger cooling power.

In a real device, it is a general approach to connect many of these thermoelectric modules electrically in series and thermally in parallel to add up cooling power and extent the cooling contact surfaces, as shown in Figure 1.4b. In addition, the positive heat flow (from high temperature to low temperature) and the extra heat caused by current flow (Joule heating) are taken into account. Thus the total cooling power of such device can be written as,

$$ P_c = N [(S_p - S_N)I T_c - K(T_h - T_c) - \frac{1}{2} I^2 R], $$  

where $N$ is the number of total thermoelectric modules in the device. $T_c$ and $T_h$ are the temperature in cold end and hot end, respectively. $K$ is the effective thermal conductance and $R$ is the electric resistance of the device. For a cooling device that pumps heat from cold end to hot end, the efficiency of such device is given by the ratio between cooling power and total input power. The total input power is given by,

$$ W = N [(S_p - S_N)I(T_h - T_c) + I^2 R] $$

As a result, the coefficient of performance (COP) of such heat pump can be expressed as

$$ COP = \frac{PC}{W} = \frac{N [(S_p - S_N)I T_c - K(T_h - T_c) - \frac{1}{2} I^2 R]}{N [ (S_p - S_N)I(T_h - T_c) + I^2 R]} $$

Compared to cooling devices that require thermodynamically cyclic operation, thermoelectric based refrigeration technology is of great interest owing to that there is no moving part in the device. When attached to the heat load, which is the object that is
intent to be cooled, driven with proper amount of current flow, the device is working. It is also noted that the fabrication of such cooling device has great compatibility with current micro-scale fabrication methods, which make thermoelectric refrigeration attractive for mass production and commercialization.

However, owing to the generation of large Joule heating during the operation, which is inevitable because of the necessities of current flowing, the thermoelectric refrigeration technology suffers from very low efficiency (COP). To evaluate the performance of the given thermoelectric cooling device, one figure of merit was brought up, \( Z \), which is given by,

\[
Z = \frac{S^2}{\rho \kappa},
\]

where \( \rho \) and \( \kappa \) are the electric resistivity and thermal conductivity, respectively. In order to obtain higher efficiency, both electric resistivity and thermal conductivity are required to be small. In practical applications, \( Z \) normally works with \( T \), the temperature, to produce a dimensionless quantity. The current advances in thermoelectric refrigeration devices indicate a production of \( ZT \) is still less than 1, although in nano-structured films, \( ZT > 1 \) has been reported. However, that is still less than 10\% of the Carnot COP. [7, 9-15] How to enhance the efficiencies of thermoelectric refrigeration devices is remained a challenge to be addressed.
1.2.2 Thermoacoustics

Thermoacoustic refrigeration is another developed heat-pump-like thermal management device.[16-26] Analogy to VCR, instead of using mechanic pump to press working refrigerant, HFCs, into fluids, thermoacoustic refrigeration technology utilizes acoustic power to compress a gas and induces a mechanic-thermal energy conversion. More interestingly, the acoustic wave provides not only the pressure for the energy conversion, but also the capability to move the compressed gas inside the device. By delicately control the compression and the gas movement, a heat-pump which absorb heat and one end and eject heat at the other can be designed, as schematically shown in Figure 1-4.

![Schematic of heat pumping in a standing-wave thermoacoustic device.](image)

Figure 1-4. Schematic of heat pumping in a standing-wave thermoacoustic device. [16]

Due to the behavior of applied acoustic field, the thermoacoustic devices can be divided into two types, standing-wave device and traveling wave device. Figure 1-4
schematically shows a typical standing-wave device. In this design, a loudspeaker is placed at one end of a tube in which the other end is closed. When the loudspeaker is operation in proper wavelength, a standing acoustic wave can be generated owing to resonation. In this case, a package of gas in the tube is oscillating between a series of plate, which is normally indicated as a stack, where the each end of the stack is subjected to different acoustic pressure. As a result, the gas package is expended at low pressure end to absorb heat, and pressed at high pressure end to eject heat. Hence the device can work as a heat pump as what is happening in VCR technology. In standing-wave thermoacoustic device, the displacement of each gas package is limited to a small fraction of the length of the stack, however, we can imagine many of such packages adding together, moving back and forth along the length direction of the stack. The combined effect makes sure an effective cooling capability across the stack.

Figure 1-5. Schematic of heat pumping in a traveling-wave thermoacoustic device.[16]
Traveling-wave thermoacoustic device, on the other hand, energy carried by gas packages is flowing in a loop instead of moving back and forth in a small fraction along a stack in the case of standing-wave. In addition, traveling-wave thermoacoustic devices accumulate heat with a regenerator rather than a stack. A well designed regenerator can thoroughly exchange heat with gas and has limited heat leakage. During operation, each gas package would go entirely through the regenerator and finish the heat exchange during the process, accompanied by volume changes in respond to traveling acoustic wave. A typical traveling-wave device is shown in Figure 1.6.

Running with a loudspeaker and almost any kind of gas, thermoacoustic refrigerator has been proved to achieve low cost and reliable operation. Also, without involving of any environmentally harmful gas, such heat pump has no threat to global ecology and environment. However, the device dimensions of such devices cannot be scaled down. The requirement of generate certain wavelength of acoustic wave has to be met in order to maintain the cooling power density provided by the system. Hence the tube has to be made in certain dimension to allow the acoustic wave generation.

1.2.3 Caloric Effect Based Refrigeration

Caloric effect based refrigeration is referring to magnetocaloric (MC)\cite{27}, electrocaloric (EC)\cite{28, 29}, elastocaloric (eC) /barocaloric (BC)\cite{30, 31} effects based refrigeration technologies, which are not new but recently attracting a lot of attention in both academia and industrial world. In principle, the caloric effects are external general forces (magnetic, electric, mechanic field) induced reversible thermal energy change
(cooling and heating) while phase transitions are happening. Such effects are normally not a result of energy direct conversion but internal energy release and absorb stimulated by external fields. This grants the caloric refrigeration opportunities to reach higher COP compared to above mentioned alternatives which are based on direct energy conversions.

Let’s take magnetocaloric refrigeration as an example. MC cooling is referring to entropy/temperature change of a material in respond to a changing magnetic field. When a MC material is entering a magnetic field zone, it experiencing magnetic field change applied to it and temperature would rise owing to the reducing of magnetic moment entropy. When it is leaving the zone, the magnetic field applied to it is reducing thus the temperature of MC material will drop. Such reversible temperature change provides the opportunity to operate such material in a heat pump cycle. [32-38] The MC effect can be large if it is near the material’s Curie temperature near which the magnetic moment is starting to demagnetized and thus is easier to be affected by external magnetic fields.

By operating the MC materials in the thermodynamic cycle and employing regenerator to facilitate the temperature gradient accumulation, MC based cooling devices were developed in many different designs.[39-42] Especially in last two decades, MC cooling devices utilizing active magnetic regenerator (AMR) have been intensively studied and lot of them are prototyped.
However, MC materials, such as gadolinium or its alloys, are normally required huge magnetic field to generate large MC effects, i.e., 1.5 Tesla. However, to generate such high magnetic field is normally not an efficient process. Superconducting magnets are good to provide large magnetic field but it will consume huge amount of electric energy which will dramatically reduce the energy efficiency of such device. Permanent magnets may do their job well but they can also be bulky, heavy and space consuming. In addition, devices running by magnetic field is hard to put near any electronic device and even harmful for human health.

Barocaloric and elastocaloric cooling make use of mechanic field to induce structure phase transition in order to generate caloric effects. Such effects are still low
compared to MC materials. However, it is exciting to find people have been starting to prototype devices based on these effects (see Figure 1-6). [44]

Table 1-1. Comparison of different refrigeration technologies.

<table>
<thead>
<tr>
<th>Technology</th>
<th>State of Development</th>
<th>Cooling Power Density</th>
<th>COP</th>
<th>Scalability</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCR</td>
<td>Commercial</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Thermoelectric</td>
<td>Commercial</td>
<td>High</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Thermoacoustic</td>
<td>Prototype</td>
<td>Low</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Magnetocaloric</td>
<td>Prototype</td>
<td>Medium</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Mechanocaloric</td>
<td>Prototype</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Electrocaloric</strong></td>
<td><strong>Prototype</strong></td>
<td><strong>High</strong></td>
<td><strong>High</strong></td>
<td><strong>High</strong></td>
</tr>
</tbody>
</table>

Electrocaloric (EC) refrigeration, on the other hand, has been demonstrated to possess giant effect and expected to exhibit much better COP. Analogy to MCE, ECE is an entropy/temperature change in respond to an electric field induced polarization change. Besides the potential to achieve high efficiency and cooling power density cooling devices, ECE is much more compatible with electricity and therefore household environment. It also shows great scalability owing to the large EC induced temperature/entropy change and the ease to apply electric field in different scales. Adding together, EC refrigeration is the most promising alternative technology which could pave the way to high cooling power density and high COP cooling devices, as summarized in Table 1-1.
1.3 Prediction and Demonstration of Giant Electrocaloric Effect in Ferroelectric Polymers

Electrocaloric effect (ECE) is not a newly found phenomenon. The first study can be dated back to 1930, however, there was no numerical data reported. [45] In 1963, Wiseman and Kuebler characterized ECE in Rochelle salt and reported $\Delta T = 0.003$ K. Later in 1980s, a series of studies were carried out on SrTiO$_3$, BaTiO$_3$, KTaO$_3$, PZT, KDP, TGS, $\Delta T \leq 1$ °C. For PbScTaO$_3$, $\Delta T \approx 1.5$ K. A relatively large ECE ($\Delta T=2.5$ K at temp. > 200 °C) was reported by Tuttle and Payne in Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.75}$Sn$_{0.20}$Ti$_{0.05}$)O$_3$ ceramic in 1981.[46] Indeed, the small ECEs, where the adiabatic temperature changes $\Delta T$ were less than or around 2 K, make the ECE not attractive it for practical applications. In order to be attractive to practical applications, it is better for EC induced temperature range to exceed 5 K to be considered as large ECE.

In 2004, Zhang predicted a large ECE in ferroelectric P(VDF-TrFE) based polymers, based on the general materials consideration and Landau-Devenshire thermodynamic Theory.[47] The free energy $G$ of a ferroelectric material in the thermodynamic Landau-Devonshire theory can be written as, [48]

$$G = G_0 + \frac{1}{2} a D^2 + \frac{1}{4} b D^4 + \frac{1}{6} c D^6 - ED$$  \hspace{1cm} (1.6)$$

where $G_0$ is the free energy of the non-ferroelectric phase, $D$ is the polarization, and $E$ is the electric field. For normal ferroelectrics, $a = \beta (T-T_c)$, where $b$, $c$, $\beta$ and $T_c$ are constants. From $\Delta S = - (\partial G/\partial T)_E$, the isothermal entropy change $\Delta S$ due to the change of spontaneous polarization is

$$\Delta S = - \frac{1}{2} \beta D^2$$  \hspace{1cm} (1.7)$$
From $\Delta Q = C_E \Delta T = T \Delta S$, the adiabatic temperature change can be expressed as

$$\Delta T = \frac{1}{2} T \beta D^2 / c_E,$$  \hspace{1cm} (1.8)

where $c_E$ is the specific heat. For the P(VDF-TrFE) 65/35 mol% ferroelectric polymers, relevant parameters are $\beta = 3.5 \times 10^7 \text{ JmK}^{-1} \text{C}^{-2}$, $D = 0.1 \text{ C/m}^2$, yielding $\Delta S = -96 \text{ J/kgK}$.

Taking the FE-PE transition of $100 \degree \text{C}$ and the specific heat of $c_E = 1.4 \times 10^3 \text{ J/kgK}$, it can be deduced that $\Delta T = 26 \degree \text{C}$. This analyses suggest that a giant ECE in ferroelectric P(VDF-TrFE) polymers when operating near the FE-PE transition. Zhang further suggested in 2004 that the relaxor ferroelectric polymers, may also exhibit a giant ECE near room temperature. [47]

These predictions are consistent with the Maxwell relation, which relates the electrocaloric effect to the pyroelectric effect. [48]

$$\left( \frac{\partial S}{\partial E} \right)_{T,y} = \left( \frac{\partial P}{\partial T} \right)_{E,y},$$ \hspace{1cm} \hspace{1cm} (1.13)

and

$$-\left( \frac{\partial T}{\partial E} \right)_S = T \left( \frac{\partial D}{\partial T} \right)_E = \frac{T p_E}{c_E},$$ \hspace{1cm} (1.14)

where $c_E$ is the specific heat. Under a constant stress $X$, the isothermal entropy change $\Delta S$ and adiabatic temperature change $\Delta T$ of an ECE material as the $E$ is changed from $E_1$ to $E_2$ can be expressed as [48]

$$\Delta S = \int_{E_1}^{E_2} \left( \frac{\partial D}{\partial T} \right)_E dE$$ \hspace{1cm} (1.15)
For ferroelectric materials, the pyroelectric coefficient $p_E$ reaches a large value near FE-PE transition, suggesting a large ECE near FE-PE transition. Moreover, the relaxor ferroelectric polymers also exhibit a large ($\frac{\partial D}{\partial T}$) their broad dielectric constant peak which is near room temperature, suggesting a large ECE.

\[
\Delta T = -T \int_{E_1}^{E_2} \frac{1}{c_E} \left( \frac{\partial D}{\partial T} \right)_E dE
\]

Figure 1-7. Electrocaloric Effect reported in ferroelectric polymer P(VDF-TrFE) 55/45 mol%.[49]

These predictions have been demonstrated by a series experiments starting from 2008.[28, 49-59] As presented in Figure 1-7, an electric field induced temperature change of nearly 12 °C has been obtained in the P(VDF-TrFE) 55/45 mol% copolymer near FE-PE transition.[49]
The prediction and observation of giant ECE stimulated great interests in EC material study. As a result, direct EC characterization is quite important as will be introduced in the following section.

### 1.4 Measurement Methods

#### 1.4.1 Direct EC Characterization

ECE direct characterization set-ups are usually including two key components: sensors and temperature controlled chambers. By different sensors, the direct measurement can be categorized into two groups: temperature measurement (thermocouple) and heat measurement (heat flux sensor). Owing to different sensing mechanism and nature of ECE, EC samples should be held in the temperature controlled chamber accordingly. For direct temperature sensor such as a thermocouple or infra-red sensors, it is required a fast data acquiring response time, smaller than 1 ms, in order to acquire the sharp temperature rising peak.[60] In addition, for temperature sensing, EC samples should be held freestandingly in air or vacuum in order to reduce any unnecessary thermal load that would reduce the measured temperature data. Induced by a very fast electric field change, the freestanding EC sample would exhibit a temperature change which happens fast enough to be considered as adiabatic temperature change. On the other hand, when utilizing a heat flux sensor, it is better for the EC samples to lying on the heat flux sensor which is attaching to a huge thermal load, as shown in Figure 1-8. Heat generated in an under testing EC sample would quickly go through the heat flux sensor and diffusion into the heat load, owing to the asymmetric thermal boundary
condition on the two surfaces of the EC sample. To ensure a good thermal contact, high thermal conductivity paste is applied between sample and sensor. The huge thermal load would minimize the temperature change of the sample and create a scenario close to isothermal condition for directly measuring the EC induced entropy change.

One major issue in direct ECE measurements is the accuracy of measurements. In case of direct temperature measurement, although the EC sample is holding freestandingly, the metal electrodes would still act as thermal loads that reduce the measured adiabatic temperature change. When measuring with heat flux sensor, heat leaking from top of the sample is also a problem. In addition, different level of thermal contact between samples and the heat flux sensor would result in different recorded signal which pose challenges to compare result from different measurements.

![Figure 1-8. A schematic of heat flux sensor based EC direct measurement setup.](image)

We addressed the issue by introduce a real-time calibration method. A reference heater, based on resistivity Joule heating, is attached to an EC sample that needs to be measured. The resistive heater can be one of the electrodes, which would be good because it will well-attached to the sample, or a reference heat fabricated on a thin film
material. Attaching reference heater to the sample, it forms a standalone entity that contains both heater and sample. During the measurement, the heat generated by the ECE sample was compared with the heat generated by a standard reference resistor $R$, from which $\Delta S$ is determined. When a voltage, $V$, with a pulse time duration, $t$, applies to the resistor heater, it would produce a joule heat $Q_h = (V^2/R)t$. The heat generated is detected by a heat flux sensor directly attached to the sample surface. Now if the ECE film under an applied electric field also generates the same amount of heat as detected by the same flux sensor, then the heat $Q_{ECE}$ from the ECE material is equal to $Q_h$. From $Q_h = Q_{ECE} = T\Delta S$, thus $\Delta S$ can be obtained. If the ECE material has a heat capacity of $c_E$, a density $\rho$, and a volume of $U$, then the adiabatic temperature change can be obtained, $\Delta T_{ECE} = \frac{Q_{ECE}}{c_E \rho U}$, where $c_E$ is specific heat and can be considered as a constant between ambient temperature $T$ and $T \pm \Delta T_{ECE}$, in which plus or minus sign is determined by heating or cooling of the studied signal. If the specific heat is varying a lot in the temperature range (from $T$ to $T \pm \Delta T_{ECE}$), the adiabatic temperature change, $\Delta T_{ECE}$, can be calculated from $Q_{ECE} = \int_0^T c_E dT$.

As briefly stated above, for different thermal scenario, in which ambient temperature, thermal contact of entities, sample thickness and masses would all act as variables, the calibration needs to be performed again to ensure a well-defined heat reference for each specific thermodynamic scenario. The reference heater calibration can also be applied to EC direct temperature measurement to calibrate the effect of excess thermal load from electrodes and heat leaking to the surrounding. A special designed EC measurement setup with a temperature controlling chamber in Zhang’s lab at Penn State University is shown in Figure 1-9. If not specifically indicated, direct EC measurement conducted in this
thesis are using reference heater calibration. Heat flux sensor (RdT P/N 27134-3) is used for the measurement.

It worth mentioning that the direct measurement method can be accurate on calibrating the entropy change, however, it may cause certain errors on deducing the $\Delta T_{ECE}$, owing to the field-dependency of specific heat $c_E$. In order to accurately characterize EC induced temperature change $\Delta T_{ECE}$, further studies is needed to investigate how specific heat of the EC material changes during the EC operation.

![Figure 1-9. A special designed ECE direct measurement setup.](image)

Commercial Differential Scanning Calorimetry (DSC) machine can also be utilized to direct measure ECE with modifications of electric connection to external power source. [61] Such modification is required to (i) have good electric insulation to safely apply high voltage to the DSC chamber and (ii) maintain the thermal environment of the DSC sample chamber. It is worth noticing that the real-time calibration method
with a reference heater can still be used to calibrate the endothermic and exothermic signals measured by DSC.

1.4.2 Other material characterizations

If not specifically indicated, the dielectric properties were investigated using an LCR meter (HP4284A) equipped with a temperature controlled chamber (Delta9023), which is provided by MRI at Penn State University.[62] Polarization-electric field (D-E) loops were measured using a Sawyer–Tower circuit. A differential scanning calorimetry (DSC) (TA Q100) was employed to characterize the thermal properties and information of phase transitions of the EC samples. X-Ray diffraction measurements are conducted by PANalytical Empyrean X-Ray Diffractometer which is also provided by MRI at Penn State University.

1.5 Materials with Giant Electrocaloric Effect

1.5.1 Electrocaloric Polymers

PVDF, especially P(VDF-TrFE) based ferroelectric polymers are the best known ferroelectric polymers which also exhibit large electromechanical responses and have been used widely for sensors and actuators.[63-67] Figure 1-10 presents the phase diagram of P(VDF-TrFE) copolymer.
Figure 1-10. Phase diagram of P(VDF-TrFE) copolymer with varying mol% of VDF.

After giant ECE has been reported in PVDF based polymers in 2008 by Neese et al., [28] it became interesting to notice that, by making use of FE-PE phase transition, such polymer would experience not only large dimension change, but also a giant thermal energy change owing to the latent heat that is accompanied by this first-order phase transition. (see Figure 1-11)

Figure 1-11. FE-PE transition heat measured in P(VDF-TrFE) 65/35 mol% copolymer.
PVDF ferroelectric polymers have been reported to possess at least five crystalline phases.\cite{68,69} The most interesting one is the β phase which exhibits all-trans (TTTT) polymer chain conformation, where all the fluorine atoms are on one side of the chain and all the hydrogen atoms are on the other side, as illustrated in Figure 1-12. The ordered molecular structure produced a net dipole moment that is around 2.2 Debye per unit cell. That is the molecular origin of ferroelectric phenomenon in such polymer. Upon heated up, the polymer will undergo a phase transition and turn into α phase which consists random sequence of trans-gauche (TG) bonds, such as TGTG’, and T3GT3G’ isomers (also shown in Figure 1-12). Hence the dipoles in the polymer will cancel each other to generate a paraelectric phase with no spontaneous polarization. As a result, a dipolar order-disorder phase transition can be expected.

Near the FE-PE transition temperature, where the ferroelectric phase starts to become unstable, it is possible to apply electric field to induce a disorder to order
(paraelectric to ferroelectric) phase transition. By electrically controlling the transition, one can expect to manipulate the latent heat, an internal thermal energy, which is corresponding to this transition. For instance, P(VDF-TrFE) 68/32 mol% copolymer shows a heat of FE – PE transition of more than $2.1 \times 10^4 \text{ Jkg}^{-1}$ (or $\Delta S \sim 56.0 \text{ Jkg}^{-1}\text{K}^{-1}$).[70] This is approximately 10 times larger than its inorganic counterparts.

Based on Landau thermodynamic theory, one can expect P(VDF-TrFE) copolymer to possess large ECE. As shown in Eq 1.4, the ECE is direct related to electric displacement $D$. Inheriting the large dielectric strength as a polymer, P(VDF-TrFE) can withstand over 600 MV/m without causing breakdown. Besides the high dielectric strength, PVDF based polymers also exhibit a large electric displacement $D$ which would serve as an indication of large ECE (see D-E loops in Figure 1-13).

![Figure 1-13. Typical D-E loops of copolymer P(VDF-TrFE).](image)

For example, P(VDF-TrFE) 65/35 mol% copolymer, with $\beta = 3.5 \times 10^{-7} \text{ Jm} \,(\text{C}^{-1}) \text{m}^{-1}$.
and \( D = 0.1 \text{ Cm}^{-2} \), will exhibit a \( \Delta S = 96 \text{ J/kg-K} \). Making use of its specific heat of \( c_E = 1.4 \times 10^3 \text{ J/kg-K} \) [71] and Curie temperature \( T_c = 100 \text{ °C} \) [72], it can be deduced that \( \Delta T = 26 \text{ °C} \), which is even larger than the recently reported “giant” magnetocaloric effect.

However, as temperatures move away from the FE-PE transition, ECE reduces rapidly, as inevitably happening in every phase-transition-related response. Although copolymers with higher TrFE content would reduce the transition temperature, it is still at 50 °C for P(VDF-TrFE) 55/45 mol% copolymer (see phase diagram in Figure 1-10). A large ECE has been demonstrated in such copolymer system with a \( \Delta S \) of more than 55 Jkg\(^{-1}\)K\(^{-1}\) and a \( \Delta T \) of more than 12 °C under an electric field of 209 MVm\(^{-1}\) at temperatures around 80 °C. However, the narrow operation temperature range (5-10 K near transition temperature) would still pose challenge in designing high performance EC based cooling devices. In this thesis, we focus on engineering the materials to meet the requirements of EC refrigerators.

1.5.2 Electrocaloric Ceramics

Giant ECE in inorganic materials was first reported in 2006 by Mischenko et al. [29] A \( \Delta T = 12 \text{ K} \) under an electric field change of 48 MV/m was estimated from Maxwell relation in 350 nm thick \( \text{Pb(Zr}_{0.95}\text{Ti}_{0.05})_3 \) (PZT) ceramic thin film at temperatures near 230 °C. After that, a temperature change of 11 K was also reported in a 700 nm \( \text{PbZrO}_3 \) thin film near its phase transition temperature around 235 °C. Those giant ECE in ceramics thin films would be interesting to some high temperature applications.
In order to investigate giant ECE at room temperature, La doped to PZT (PLZT) thin films were studied by Lu et al.[60] The results show PLZT thin films exhibit a direct measured ECE of $\Delta T=40$ °C under an electric field of 120 MV/m and at 45 °C. Moreover, the large ECE occurs over a relatively wider operation temperature range that covers room temperature. PbSc$_{0.5}$Ta$_{0.5}$O$_3$ thin films were also studied which exhibit a large ECE and wide operation temperature range, i.e., a $\Delta T=6.2$ °C under an electric field of $\Delta E=77.4$MV/m.[73]

Some inorganic solid solutions have also been studied for large ECE in form of thin films. For example, 0.93PMN-0.07PT thin films exhibited $\Delta T=9$ °C under an electric field of 72.3 MV/m. The peak ECE was observed at 18 °C where dipolar glass-relaxor transition takes places. For PMN-PT solid solution, composition plays an interesting role to modify ECE properties. The 0.9PMN-0.1PT thin film exhibited a maximum ECE of $\Delta T=5$ K at 75 °C, which indicates that the large ECE was benefited from a pseudocubic to cubic phase transition. Keep increasing concentrations of PT would introduce morphotropic phase boundary (MPB) that can also contributed to ECE.

Thin films, with their thicknesses in 100s nm range and deposited on substrates which are normally in mm thickness, can be good material systems to study ECE and assess the ultimate ECE that can be achieved in a dielectric material because they normally possess very high dielectric strength compared to bulk samples. It would be also interesting to make use of substrate effect to induce additional stress/strain to modulate ECE. However, it would not be very promising for practical applications. First, the amount of EC material in thin films is too tiny and the thick substrate serves as a huge...
thermal load. Due to above reasons, it is already very hard to directly measure ECE induce temperature change. One could imagine that it would be even harder for thin film ceramics to cool the environment temperature down.

However, bulk ceramics suffers from low dielectric strength. For a 0.1 mm thick bulk ceramic, the typical breakdown field is around 10 MV/m, which is 10% of that in thin films. As a result, the ECE reported in those bulk ceramics are normally below $\Delta T=3$ K. Some lead-free bulk ceramics such as $\text{Ba}_{0.73}\text{Sr}_{0.27}\text{TiO}_3$, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, and $\text{Ba}_{0.3}\text{Na}_{0.7}\text{Ti}_{0.3}\text{Nb}_{0.7}\text{O}_3$ are investigated for their ECE.[74, 75] Lead-based bulk ceramics perform a little better ECE, such as a high temperature annealed $\text{PbZr}_{0.75}\text{Sn}_{0.2}\text{Ti}_{0.05}\text{O}_3$ bulk ceramic for which a $\Delta T = 2.6$ K was reported. [46] It should be noted that previously reported ECE in bulk ceramics are still too low to become attractive for practical cooling applications. In order to provide competitive cooling performance, large ECE, i.e., $\Delta T>5$ K, should be required.

Figure 1-14. Schematic fabrication processes of MLCC. [76]
Possessing the advantages of both thin-film and bulk ceramics, thick film multilayer ceramic capacitors (MLCC) are the most promising in practical applications. First of all, there is existing technology for MLCC mass production (see Figure 1-12). Commercially available MLCC can be made with each layer thickness down to 1 \( \mu \)m which allows them to stand much higher electric fields, thus generate more ECE. In addition, it is possible to introduce strain modulation in the multilayer EC elements to further enhance ECE. As a well-developed fabrication technology, EC multilayer elements with a large ECE can be made at very low cost which makes this material system more attractive for practical deployment.

1.6 Research Objectives

The goal of this dissertation is to explore general material requirements in the designing of electrocaloric-based thermal management devices and refrigerator, bridging the material development and device designing.

Based on the goal, this dissertation is organized as follows:

- In Chapter 2, several existing electrocaloric cooling devices are presented, analyzed and compared. Device figures of merit are introduced and basic designing idea is summarized. Most importantly, the material requirements in designing such devices are introduced, paving the way to following chapters which are working on improving the materials properties to meet the device designing requirements for different functionalities.
• In Chapter 3, PVDF-based relaxor ferroelectric polymers are introduced. In this chapter, we show that ferroelectric polymer, although showing large electrocaloric effect near ferroelectric-paraelectric phase transition temperatures, can be further improved by modifying the material to relaxor ferroelectrics. Such defect-modified ferroelectric polymer exhibit giant electrocaloric effect covering a much wider temperature window at room temperature, which is promising for easily design room temperature cooling device based on such material system. We also discuss several issues in device design with such polymers, such as mechanic modulus, thermal conductivity, etc.

• In Chapter 4, electrocaloric ceramics are studied and presented. The reasons that ceramic materials are interesting for practical cooling device design are discussed. The main challenge, how to enhance the electrocaloric effect in ceramics are addressed by modifying one traditional ceramic material BaTiO$_3$ to its invariant critical points and hence promoting multiphases coexistence.

• In chapter 5, electrocaloric fluids are introduced and analyzed. The advantages for a fluid material to possess large electrocaloric effect are discussed. Detailed phenomenon demonstration was carried on several typical nematic liquid crystals, such as 5CB. Polymer Stabilized LC (PSLC) is also discussed. Potential to further enhance the electrocaloric effect in such materials and how to apply LCs to practical devices are discussed.

• In Chapter 6, recently observed anomalous electrocaloric effect is presented. We show that the observed anomalous electrocaloric effect, which exhibit an
irreversible thermal responses with respect of electric field change, open opportunities to design more reliable and effective cooling devices for applications such as on-chip cooling and circuit management.

- In Chapter 7, we summarize this thesis study and prospect the future development in this area in both academia and industrial point of views.
Chapter 2

From Cooling Device Designs to Material Properties

2.1 Introduction: Basic Thermodynamics of EC Cooling Cycle

Observation of giant ECE in dielectric materials could open up opportunities to design novel refrigeration devices and systems with high cooling power, high efficiency and environmental friendliness. However, without further understanding on EC based cooling device design, it would be difficult to assess the performance of an EC material or find direction to future material improvement.

Figure 2-1. Entropy-temperature plot of a Carnot cycle for electrocaloric thermal management device.
In a normal ECE, material ejects heat when dipolar ordering is promoted by the increasing of external electric field and absorbs heat when the dipoles become random-oriented as the field decreasing. Owing to the reversible thermal responses under an electric pulse, it is convenient to design EC cooling devices as heat pumps. One example of the highest COP is the EC based Carnot cycle, as illustrated in Figure 2.1. The cooling cycle consists of four steps, (i) Applying an electric field adiabatically raises the EC element temperature to $T_H$ (ii) then the EC material in thermal contact with the heat sink will eject heat at $T_H$ while the field is further increased to its maximum value, (iii) the temperature of the material will reduce to $T_C$ when the applied electric field is reduced adiabatically, (iv) the EC element is in thermal contact with the heat load and absorbs heat $Q_c$ from the load as the electric field is reduced to zero, where $Q_c = T_C \Delta S$.

As has been introduced earlier, Carnot cycle possesses the highest COP, which is $COP = T_c / (T_H - T_C)$. On the other hand, Figure 2-1 indicates that the temperature span of $T_H - T_C$ of an EC cooling device, if it can be operating as a Carnot cycle, is smaller than the adiabatic temperature change $\Delta T_{ECE}$ of the EC materials. A material with a large ECE is highly desirable. In addition, since $Q_c = T_C \Delta S$ and the cooling power is directly proportional to $Q_c$, besides a large $\Delta T_{ECE}$, an EC material should also exhibit a large $\Delta S_{ECE}$. Hence both the adiabatic temperature and isothermal entropy change are important parameters to characterize an EC material for cooling applications. As will be presented in the following paragraph, a regenerative process is often employed in the caloric cooling system which can greatly expand the temperature span $T_H - T_C$ and also improve the cooling system COP.
Regenerative process is a general approach to extend the temperature span of such cooling devices beyond the adiabatic temperature change of the caloric materials. Regenerative process, also known as regeneration or heat recovery, employs a regenerative medium (fluid or solid) that exchanges heat with active cooling agent, EC materials in this case, and serves as a heat storage to prevent the heat that been dumped in the heat sink (the hot end) to flow back to the heat load (the cold end). As an example, a Brayton cycle with regenerative process is shown in Figure 2-2. By employing regenerator, the heat pump can achieve wider temperature span $T_{\text{span}}$ compared to what can be realized in single EC material (red square). Such process is widely used in industrial applications especially in heat pumps and engine thermal management, e.g. air preheater in engines. It is also not uncommon to find regenerative process in newly
developed heat pumps, i.e., active magnetic regenerators (AMR) are applied to magnetocaloric cooling devices from late 1990s to now. [40-42]

2.2 General Design Considerations of EC based Cooling Devices

As discussed in the Chapter 1, the volumetric cooling power density \( P_c \) and COP are two fundamental parameters in assess a heat pump. Here \( P_c = \frac{Q_c}{t-V} \), where \( Q_c \) is the cooling capacity that is the heat absorbed at heat load, \( t \) is time and \( V \) is the volume of the EC cooling agent. Cooling power density is the cooling power per unit volume that can be absorbed from the heat load. COP is the ratio between the heat that absorbed from the heat load and all of the input work to the system. Ideally, the highest COP can only be achieved in Carnot cycle which has been shown in Figure 2.1. Figure 2.1 indicates that Carnot COP can be calculated by the lighter gray area divided by the darker gray area that squared by blue arrows. We can write,

\[
Q_c = \Delta S \cdot T_c, \tag{2.1}
\]

\[
COP = \frac{Q_c}{W} = \frac{T_c}{(T_H - T_C)}, \tag{2.2}
\]

where \( W \) is the external work put into the system, \( T_H \) is temperature at hot end (heat sink) and \( T_C \) is temperature at cold end (heat load), respectively. However, comprising two adiabatic processes and two isothermal processes, Carnot cycle is hard to control by applying external electric fields and thus it is not practical.

Considering the fact the EC cooling effect is generated by applying electric fields to the EC material, Ericsson cycle, which is containing two isothermal processes and two iso-field processes could be more close to practical operation. A schematic of Ericsson
cycle employing regenerative process is shown in Figure 2-3. In this case, cooling capacity and COP can be expressed as,

\[
Q_C = \Delta S_{ECE} \cdot T_C ,
\]

\[
COP = \frac{Q_C}{W} = \frac{\Delta S_{ECE} \cdot T_C}{W} ,
\]

where \( \Delta S_{ECE} \) is the EC induced entropy change.

It is a special case for the Ericsson cycle to achieve Carnot COP, \( T_C/(T_H-T_C) \), if the two iso-field entropy-temperature (S-T) curves are parallel. It is essentially indicating that temperature invariant ECE is a preferred feature of an EC material in order to reach high COP. In addition, larger isothermal entropy change can lead to higher cooling capacity and also the cooling power density.

However, the two isothermal processes in Ericsson cycle require entropy changes happening at a same temperature. In real application, since every material has a finite value of thermal conductivity and heat capacity, such isothermal entropy change could
take a long time to happen, which would dramatically reduce the cooling power density, $P_c$. Instead, Brayton cycle, which contains two adiabatic temperature change processes and two isothermal processes and shown in Figure 2.2, can be a more proper cycle compared to real applications. In Brayton cycle, cooling capacity and COP is,

$$Q_c = \Delta S_{ECE} \cdot (T_c - \Delta T_{ECE} / 2),$$ \hspace{1cm} 2.5

$$COP = \Delta S_{ECE} \cdot (T_c - \Delta T_{ECE} / 2) / W,$$ \hspace{1cm} 2.6

where $\Delta T_{ECE}$ is the EC induced adiabatic temperature change. As we can find, the COP of Brayton cycle can never achieve Carnot COP but it provides much faster heat exchange owing to the suddenly generated temperature differences between hot/cold end and external environment. Both Ericsson and Brayton cycles are suggesting that higher thermal conductivity and both hot/cold ends are helpful to enhance the cooling power density of the cooling device. The actual EC cooling devices are normally running in thermodynamic cycles that in between of Ericsson cycle and Brayton cycle.

Above analysis on thermodynamic cycles are useful when considering general heat pump or refrigerators in a thermal static condition.

### 2.3 EC Refrigeration Prototypes

In 1992, Sinyavsky and his colleagues designed a refrigerator that making use of electrocaloric effect in ceramics. [77, 78] The device operated as a typical regenerative heat pump by employing fluid as the regenerative medium. Pb(Sc0.5Ta0.5)O3 (PST) ceramics were utilized as active cooling agent which has an EC induced temperature
change ($\Delta T_{ECE}$) around 1.3-1.5 K at room temperature, under an external electric field of 2.5 MV/m. The prototype is schematically illustrated in Figure 2-4.

![Figure 2-4. Schematic of EC cooling device developed by Sinyavsky et al. in 1992. [77]](image)

The refrigerator is comprised of two stacks of PST as active cooling agents shown as 1 and 2 in the schematic. External electric fields are applied on the two stacks of PST periodically with 180° out of phase. During the periodically applied electric field, regenerative fluid is pumping through the ceramic stacks back and forth with a frequency that is synchronized with that of application of electric fields. As a result, heating and cooling caused by ECE are taken to heat sink and heat load by the regenerative fluid, respectively. The device achieved 5 °C temperature-span around the room temperature. Owing to the poor heat exchange between fluid and PST ceramics and the low operating frequency (0.6-0.9 Hz), the device didn’t exhibit optimal performance as predicted in theoretical analysis. The performance may not be optimal but it successfully provided
continuous cooling at room temperature. In addition, considering low EC temperature change of PST at room temperature, 5 °C temperature span has already proved the capability of regenerative process and provide insight of future designing of regenerative based EC cooling devices.

Upon discovery of giant ECE in polymers and ceramics, it is stimulated a great amount of interests in designing EC based cooling devices. Many groups have reported their device simulations and prototypes of EC based cooling devices. [33, 79-86] However, most of those demonstrated prototypes did not provide satisfactory performance even compared to previous design in 1992.

Figure 2-5. Schematic of a regenerative based rotary electrocaloric cooling device. [87]

In 2013, based on the giant ECE in PVDF based ferroelectric polymers, Zhang’s research group at Penn State University demonstrated an all-solid cooling devices which
employed a thermal conductivity modified solid regenerator (See Figure 1-6).[43, 88] By theoretically and numerically analyzing the device configuration, the demonstrated cooling device, electrocaloric oscillatory refrigerator (ECOR) was thoroughly studied.[43, 88]

Based on the study of ECOR, an EC rotary cooling device, which is without any regenerative layer, has been proposed, simulated and experimentally examined. The device configuration is schematically shown in Figure 2-5. Instead of operating in one-dimensional oscillatory cycles on a regenerative layer, rotary EC refrigerator consists of stacked double-rings which are coaxial rotating. One EC ring is composed of a number of EC elements which are thermally insulated from each other. One EC ring in a double-ring system is in good thermal contact with and is rotating in a counter direction to the other, coaxially with same rotary speed. Many of these double-ring systems can stack together with heat exchange layer in between in order to exchange heat with ambient.

Figure 2-6. Simulated $T_{\text{span}}$ of the rotary EC ring device as a function of EC induced temperature change $\Delta T$ from the EC elements for different number of elements in the ring. The simulated EC elements is using parameters from $\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$. [87]
During the operation, it is important to ensure all EC element are rotating-in the electric field region (eject heat) at one position and rotating out of the electric field region (absorb heat) at the other position. The two positions are collecting heating and cooling and form hot end and cold end of the device. Owing to the rings in one double-ring system are rotating in different directions, the electric field region in one ring of the double-ring system will not overlap with that in the other, in order to eject and absorb heat in one position for the both rings.

Simulation results suggest several general requirements that are essential to achieve better performances of EC cooling devices. (i) Temperature span of the device $T_{\text{span}}$ is directly depending on EC induced temperature change from the EC material and the level of thermal insulation in planar directions. As shown in Figure 2-6, larger $\Delta T$ would induce larger $T_{\text{span}}$ of the device. The enhancement is due to the larger cooling power $P_{c}$ that can be supplied by the larger ECE (see Figure 2-3). During the continuous rotation, there are times when the EC elements from upper and lower rings are not perfectly overlapped. The mismatching in position would allow heat flow through the bridges formed by mismatched EC elements in the double-ring system. More number of EC elements would reduce surface area of the EC elements and provide better thermal insulation that prevents heat flow from the hot end to the cold end of the device, effectively enhancing the regeneration process and leading to higher efficiency.
Figure 2-7. Simulated (a) $P_c$ and (b) COP of the rotary EC ring device as a function of rotation speed for different EC element thickness. The simulation is using parameters from $\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$.\cite{87}

(ii) Rotation speed and thickness of the EC elements are also critical to device performances. Considering a case that EC elements possess infinity thermal conductivity in vertical direction of the device, the heat exchange between neighboring EC rings can finish immediately. Higher rotation speed of the device can certainly enhance the cooling power linearly and thickness of the EC element won’t affect the device performance. With a giving material with finite thermal conductivity, thickness of the EC element would direct related to the heat exchange speed between one EC element and elements
from the neighboring ring and therefore set a limit of the rotation speed for device operation with high performances. Figure 2-7 presents the simulated performances of such a rotary EC device with its EC elements made of $\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$. Thicker EC element reduce both $P_c$ and COP rapidly. Above numerical analysis give general ideas of how material properties affect the device performances.

Figure 2-8. EC rotary device prototype and preliminary results.
Prototype of the rotary EC ring device has been fabricated and tested. From practical consideration, commercially available EC ceramics, doped BaTiO$_3$ MLCC (manufacture number C5750Y5V1C107Z), have been employed as EC elements. The MLCC has the dimension of 5.7 mm by 5mm by 2 mm in length, width and thickness. The preliminary results prove the fundamental of the device design as shown in Figure 2-8.

2.4 Material Properties Desired for EC Refrigerator Designs

Although through carefully modification of device configurations, e.g., dimensions, thermal contacts, electric field ramp rates, can optimize the device performance, the enhancement of material properties would fundamentally improve the performance. In addition, unique features of different EC materials may lead to novel EC cooling device designs. Here we list several EC material properties that are recognized as key parameters to EC cooling devices. In addition of theoretically enhance the device performance, some practical-issues-related material properties are also included here for discussion.

1. EC induced adiabatic temperature change and isothermal entropy change, $\Delta T$ and $\Delta S$.

   It is not surprise at all that EC induced $\Delta T$ and $\Delta S$ are listed here as the first material parameters. According to schematic of both Brayton cycle and Ericsson cycle, cooling capacity is direct related to EC induced entropy change, as shown in Figure 2-2.
and Figure 2-3. Higher ECE would directly result in higher $Q_c$ which gives rise of possibility of higher cooling power density, according to Eq. 2.3 and 2.5. EC induced adiabatic temperature change $\Delta T$ is equally important to $\Delta S$. As we all know, the heat is always flow from higher temperatures to lower temperatures. Without a large $\Delta T$, even a large $\Delta S$ would not be useful if the $\Delta T$ cannot exceed the hot end temperature $T_H$. Consequently, there would not be any heat pumping from cold end to hot end. Observation of giant ECE of both large $\Delta T$ and $\Delta S$ opens opportunities to achieve high $Q_c$ compared to previous observed smaller ECE.

2. Wide operation temperature range.

It has been also shown in Figure 2-2 and 2-3 that higher heat pump efficiency can be achieved if the two iso-field curves are parallel. The requirement is essentially asking for the ECE, $\Delta T$ and $\Delta S$, to be temperature independent across the temperature range that has been focused on. Here we define a parameter $T_{\text{width}}$ to describe the width of temperature window in EC materials. $T_{\text{width}}$ is the temperature range of ECE when the ECE is reduced to 90% of its peak performance, analogy to fall width half maximum (FWHM). However, in most ferroelectric material, giant ECEs are correlated to FE-PE transition temperature and thus exhibiting narrow temperature window less than 10 K. As a result, although a cascaded cooling device can widen the $T_{\text{span}}$, as shown in Figure 2-9, the wide $T_{\text{span}}$ of devices made of material with narrow $T_{\text{width}}$ is posing more processing steps in designing and fabrication.
3. EC coefficients, $\Delta T/\Delta E$ and $\Delta S/\Delta E$. (field required to induce a large ECE, ECE is a non-linear function of the field...what is best parameter to describe this..., let’s discuss

Analogy to piezoelectric coefficients, EC coefficients depict the EC responses with regard to applied external electric field. It is highly preferred to use smaller electric fields to induce giant ECE, especially for thermal management applications that require low voltage and high reliability of operation. In practical application, in order to maintain a reliable working and long life time, it is suggested for a material to work under the 30% of its dielectric strength. However, most EC materials exhibit non-linear field-response. EC polymers exhibit high EC coefficient at very high field. EC bulk single crystals and ceramics show large EC coefficient at very low field, 0.1 MV/m, and significantly reduce with increasing electric field. A good EC materials should exhibit a large ECE, EC
induced temperature change larger than 5 K. Upon achieving the large ECE, high EC coefficient should be pursued.

4. Thermal conductivity.

Thermal conductivity is another key parameter for an EC based refrigerator to achieve both high cooling power density and high COP. As stated above, realistic EC heat pump like refrigerator operates in between Brayton cycle and Ericsson cycle, as shown in Figure 2-2 and 2-3. Although large Qc may be achieve by giant ECE, the cooling power density of the cooling device would still be low if the EC material possess a very low thermal conductivity. Low thermal conductivity would prevent the heat exchange between the EC material and external environments and therefore reduce the performances of the device. It would reduce COP dramatically due to the unfinished heat exchange and reduce the cooling power density because of the heat pumping rate is slow and inefficient. High thermal conductivity on cold end and hot end would promote the heat exchange and allow higher operating frequency thus enhance the cooling power density Pc, as shown in Figure 2-10.

Figure 2-10. COP (left) and cooling power density (right) of a rotary ECE refrigerator as a function of rotation speed, for EC polymers with different thermal conductivities. (Simulation results)
In addition, anisotropic thermal conductivity is preferred. Depending on the EC based cooling device configuration, thermal conductivity along the heat exchange direction between EC module and regenerator needs to be as large as possible. On the contrary, thermal conductivity along the heat exchange direction between hot and cold needs to be as small as possible in order to reduce the backward leakage heat flux from hot end to cold end.

In EC cooling device design, EC module thickness and working frequency can be determined by the thermal diffusion length in both EC modules and regenerative plates.

\[ \delta = \sqrt{\frac{2\alpha}{\omega}}, \quad 2.11 \]

where \(\omega\) is angular frequency and \(\alpha\) is thermal diffusivity and defined as

\[ \alpha = \frac{\kappa}{\rho c}, \quad 2.12 \]

Thermal diffusion length suggests proper thickness of an EC module under a certain operation frequency. In order to get larger cooling power density of the EC module by enhancing the operation frequency, it is desired for an EC material to possess high thermal conductivity. In addition, it is easier to reduce thermal conductivity of an EC module on one dimension than improve thermal conductivity. Hence, an EC material that exhibit inherent high thermal conductivity is utterly interesting to study.

5. Dielectric strength.

ECE is an electric field induced thermal response. Normally, \(\Delta S\) is proportional to electric displacement square. The fact suggests that the high ECE is normally a result of high electric field. Higher dielectric strength would allow higher reliable applied electric
field. However, a material with a high dielectric strength is normally possessing a small electric polarization that is not desired for achieving large ECE.

6. Mechanic properties.

Owing to the thermal exchange between EC material and regenerative plate or external environment, EC materials with better mechanic properties would help to make mechanically stronger EC modules. For example, polymers with Young’s modulus smaller than 100 MPa would be very hard to be used in an EC cooling device. Especially considering the fact that polymers possess a low thermal conductivity, the EC polymers are required to be made in thin film to ensure an effective heat exchange. A low elastic modulus will make it hard to include these thin film EC polymers in an EC cooling system. Higher modulus would facilitate the fabrication of multilayer polymer/ceramic thin films. Also, the mechanically modification on surface of EC module could be useful to reduce the friction during heat pump operation. Adding together, a mechanically strong material would reduce the difficulties in fabricating an EC polymer-based refrigerator.

2.4 Summary

In this chapter, operation principle of EC based refrigerator is thermodynamically analyzed. Three different thermodynamic cycles, Carnot, Ericsson and Brayton are briefly introduced. Based on theoretical analysis, regenerative EC cooling devices are introduced. Several EC based regenerative cooling device prototypes are introduced and discussed in detailed device configurations, operating protocols and performances.
Simulation and prototyping of EC based cooling devices lead to general ideas of how EC material properties interact with device configurations. Preferred material parameters are summarized and discussed. From next chapter, several studies are conducted to tackle the material issues and improve material parameters that in favor of EC cooling device performances, including high cooling powers and COPs, based on the study in this chapter.
Chapter 3
Enhancing ECE By Tailoring the Nano- and Meso-Structures of P(VDF-TrFE) Based Ferroelectric Polymers

3.1 Introduction

Enabling a concept to practical application takes great amount of efforts in developing science and engineering in both materials and devices. By studying several EC based refrigerator prototypes, it becomes clearer that there are several material properties are especially important in order to design a reasonably good device. As summarized in Chapter 2, the most straightforward requirements to design an EC cooling device are the amplitude of the ECE and wide operation temperature window $T_{\text{width}}$ for the ECE material. Fortunately, giant ECE has been observed in ferroelectric materials, which is a unique material system we would like to focus on, in most parts of this dissertation.

The intrinsic symmetry of the ferroelectric material enables not only ferroelectricity, which is associated with a spontaneous electric polarization in a material that can be switched by an electric field, but also coexisting piezoelectricity and pyroelectricity, which are the electro-mechanical energy conversion and electro-thermal energy conversion processes, respectively, as is illustrated in Figure 3-1. Ferroelectricity in polymers was discovered much later in 1970s in the polyvinylidene fluoride (PVDF)
homopolymer and later in PVDF based copolymers such as P(VDF-TrFE) (TrFE, trifluoroethylene).[48]

Figure 3-1. Heckmann diagram of coupling between electric energy to mechanic and thermal energy.

Figure 3-1. Electric field E and electric displacement D are linked with temperature and entropy in thermal energy form through a parameter, pyroelectric coefficient, $\partial D/\partial T$, which is essentially the dielectric property variation with temperature. Ferroelectric materials thus possess great potential to exhibit giant ECE owing to their potential to achieve large electric displacement and $\partial D/\partial T$ near their FE-PE phase transitions, as discussed in Chapter 1. And indeed, as first predicted in ceramics and polymers, more and more materials have been studied and demonstrated to present giant ECE.

However, only giant ECE is not enough to design an efficient refrigerator. Studies on thermodynamic cycles implicitly suggested that the cooling agent needs to exhibit
consistent cooling capability throughout a wide temperature range to maintain an efficient operation of thus made device, i.e., the two entropy-temperature curves are required to be paralleled. However, for the most ferroelectric material, including inorganic and organic ferroelectrics, the giant ECEs they achieved are possessing narrow temperature window $T_{\text{width}} < 10$ K, which is inevitably true if we noticed that ECE is essentially a phase transition related phenomenon.[29, 49] The tremendous entropy change, which is achieve from dipolar ordered phase to disordered phase, can only accessible near the phase transition temperature. In addition, for most ferroelectric materials, their FE-PE transition temperature is away from room temperature. Thus it is even harder to utilize the phenomenon to room temperature application that is in great demand in practical applications. The challenge is also existed in other phenomena such as magnetocaloric refrigeration, electrostriction, which are also relied on benefits originated from phase transition.

In this chapter, we will show that, by carefully material engineering, above challenge can be well addressed and giant ECE with wide operation temperature window covering room temperature can be realized.

### 3.2 Performance enhancement: Giant ECE with wide Operation Temperature Window

When a material is in its ferroelectric phase, in which a spontaneous polarization is holding, it is already in a relatively ordered phase after first electric poling. Such a hysteresis prevents the dipolar structure of the material to become disorder. After being
applied with an electric field, achieved unipolar electric displacement will not be too large owing to the hysteresis. According to thermodynamic theory,

\[ \Delta S = -\frac{1}{2} \beta D^2, \]

3.1

The EC induced entropy change is proportional to polarization (electric displacement) square, the ferroelectric material still cannot reach large ECE at ferroelectric phase owing to much smaller achievable polarization change caused by the huge polarization hysteresis, as shown in Figure 3.2.

![Figure 3-2](image.png)

Figure 3-2. Electric displacement-Electric field (D-E) loops of ferroelectric copolymer (red) and relaxor ferroelectric polymer (blue). The red dot is indicating the spontaneous polarization.

As one can find in Figure 3-2, although PVDF based ferroelectric copolymer can still reach high total polarization, the high spontaneous polarization renders a smaller
polarization change when an electric field is applied to the material. On the other hand, to
engineering a material with high total polarization but without any hysteresis may lead to
giant ECE at such temperature.

Through Landau theory, Pirc et al. derived the EC induced saturation $\Delta T$ in a
dipolar material:[90]

$$\Delta T_{sat} = \frac{7\ln \Omega}{3\epsilon_0\Theta C} P_s^2$$

where $P_s$ is the saturation polarization, $\Omega$ is the configuration number (number of
polar entities), $C$ is specific heat, $\epsilon_0$ is vacuum permittivity and $\Theta$ is the effective Curie
constant. Therefore, the development of polar-dielectrics with a large $\Omega$ as well as a small
$\Theta$ is highly desirable, especially if $P_s$ can be kept unchanged. However, for a ferroelectric
material sitting in a wide temperature range of ferroelectric phase, $\Theta$ is normally very
large owing to the strong polar correlation that is the very reason for forming the
ferroelectric hysteresis. So the question becomes that how to reduce the polar correlation
and eliminate the ferroelectric hysteresis?

Here we show that, through defect modification methods, resulted PVDF based
relaxor ferroelectric polymer show giant ECEs and a wide operation temperature window
$T_{width}$. The general idea is simple. By adding proper amount of random defects to the
ferroelectric polymer system, original bulky ferroelectric domain will experience size
reduction. As the domain sizes become smaller than a specific critical size, the
ferroelectric phase will be destabilized, as shown in Figure 3-3.
Destabilized ferroelectric phase forms random-oriented nano-polar regions and exhibit limited ferroelectric spontaneous polarization, as the D-E loop of P(VDF-TrFE-CFE) shown in Figure 3-2. In addition, those random-oriented nano-polar regions still possess relatively larger polar-correlation compared to pure dielectric polymers. As a result, those nano-sized domains will still in high response to external electric fields and can still reach large electric displacement Ps. There are typically two approaches to modify ferroelectric PVDF based copolymer with defects: polymerization copolymer with a third, bulkier monomer; and high energy electron irradiation. Both approaches are demonstrated to be quite effective to destabilize the ferroelectric phase and thus lead to the formation of relaxor ferroelectric polymers. In order to verify ECE directly, several direct measurement protocols have been developed in many groups including ours.

Figure 3-3. Schematic of destabilized ferroelectric phase, where dipoles are becoming random oriented.
3.2.1 Direct EC Characterization in P(VDF-TrFE) Copolymer

ECE in ferroelectric P(VDF-TrFE) copolymer were studied with direct measurement that is summarized in Chapter 1. The results verified the previously prediction that the ECEs are strongly depending on temperature. Figure 3.6 shows the direct measured heat flux signal for a P(VDF-TrFE) 65/35 mol% polymer film under an electric field of 60 MV/m through different temperatures. The data reveal a great enhancement of ECE when the sample is heated up to its FE-PE transition temperature.

![Diagram](image)

Figure 3-4. Directly measured EC induced heat flux in P(VDF-TrFE) 65/35 mol% sample.

The copolymer, as a ferroelectric material, also exhibit great temperature hysteresis for ECE. Direct measured ECE under ΔE=60 MV/m are compared with temperature dependent dielectric constant and shown in Figure 3-4, while the sample was measured during temperature ramping up and down, respectively.
Figure 3-5. The permittivity and ECE of P(VDF-TrFE) 65/35 mol% sample measured during cooling and heating. The electric field is 60 MV/m.

In addition of large thermal hysteresis that is confirmed by both temperature dependent permittivity and ECE, Figure 3-5 also demonstrates that ferroelectric copolymer show highly temperature-dependent ECE characteristics. Near phase transition, the ECE measured are quite high at this electric field level, whereas the ECE rapidly reduced when temperature is away from Curie temperature. The observed temperature width $T_{\text{width}}$ is less than 5 K.

### 3.2.2 Wide Operation Temperature Width in Relaxor Ferroelectric Polymers

As shown in Figure 3-6, ferroelectric copolymer P(VDF-TrFE) contains VF2 and VF3 monomers that are in a similar dimension. As a comparison, CFE
(Chlorofluoroethylene) exhibits a much larger size owing to the bulkier chlorine atom. Polymerization of VF2 and VF3 provides improvements of crystalline structures which are the key to form ferroelectric phase. However, after adding the CFE as third monomer, the presents of bulkier CFEs reduce the crystallinity and break the isomorphism in to apart. That is molecule origin of the reduction of dipolar correlation and ferroelectric domain sizes in such materials. Consequently, the terpolymer P(VDF-TrFE-CFE) exhibits a unique dielectric properties as a relaxor ferroelectrics.

![Figure 3-6. Schematic of VF2, VF3 and CFE that are polymerized in terpolymer P(VDF-TrFE-CFE) relaxor ferroelectric polymer.](image)

P(VDF-TrFE-CFE) terpolymers (e.g. P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol%) were synthesized using a suspension polymerization process by Piezotech (France). The films were fabricated using a solution-cast method by dissolving P(VDF-TrFE-CFE) powders in N,N-dimethyl formamide (DMF) solvent. Then, the polymer solution was cast onto clean glass plates. The terpolymer solution coated glass plates were dried at 70 °C for 22 hrs in an oven and then the terpolymer films were peeled off from the plates and annealed at 105 °C for over 10 hours to increase crystallinity and further remove the residual solvent. Some of the films were uniaxially stretched 4 times of the original
length while others remained non-stretched in order to study how the uniaxial stretching of the films affects various terpolymer properties. The thickness of non-stretched film was 30 μm and the thickness of stretched film was 7 μm. Gold electrodes were sputtered on both sides of the films for electric characterization.

![Graph](image)

**Figure 3-7.** Temperature dependent dielectric constant of P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer.

An example of temperature-dependent dielectric constant data of the terpolymer are plotted in Figure 3-7. The dielectric constant measurement was conducted using the facility at Dielectric Lab of Materials Research Institute. As one can direct identify, the dielectric peak temperature are dispersed with different frequencies. Such relaxor terpolymer shows great permittivity around the room temperature, which suggests a strong interaction between dipoles and electric fields. Indeed, low-field dielectric
constant may provide insight of the dielectric properties, however, high-field D-E loops may reveal more ECE-related information owing to the direct relationship between D and EC induced $\Delta S$ and $\Delta T$. Figure 3-8 presents the D-E loops of studied terpolymer, which exhibit large polarization of 10 $\mu$C/cm$^2$ under external field of 300 MV/m.

![D-E Loop Graph](image)

Figure 3-8. Typical D-E loops of a P(VDF-TrFE-CFE) terpolymer at room temperature.

Temperature dependent D-E loops were also studied in P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer. The induced polarizations under various unipolar electric fields were measured at frequency of 10 Hz, over a temperature range from 5 °C and 55 °C. The results are plotted in Figure 3-9, where the polarization didn’t show much variation over the studied temperature window and electric fields. The flat temperature
dependency of the terpolymer is vastly different from ferroelectric copolymer, which suggests Maxwell relation may need further modification to predict the ECE in relaxor ferroelectric polymers.

Figure 3-9. Temperature dependency of induced polarization in P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer under electric fields from 50 MV/m to 150 MV/m.

Large induced polarization suggests a giant ECE in this class of terpolymer. Temperature dependent ECEs under different applied electric fields in such terpolymers are presented in Figure 3.10(a). Besides a very large ECE, which is around 32 J/kgK entropy change at room temperature, the data reveal that the relaxor terpolymer maintains a high ECE over a broad temperature range, which is in sharp contrast to what is observed in the normal ferroelectric P(VDF-TrFE) copolymer, where ECE inevitably
shows a sharp peak at FE-PE temperature. The feature is perfectly fit into the requirement of achieving high COP in EC based cooling devices by generating a parallel entropy-temperature curves, as discussed in Chapter 2. Figure 3.10(b) presents the electric field dependency of ECE in P(VDF-TrFE-CFE) terpolymer measured at 30 °C. A giant ECE, $\Delta T=16$ K, is observed under an external electric field of 150 MV/m at room temperature. The above results indicate that by employing CFE as third participating monomer, the defect modified ferroelectric polymer can be destabilized and show a great EC enhancement at room temperature, which would serve as a strong stimulation to many room temperature thermal management applications. Such strong ECE ensures a potential for an EC based refrigerator to reach high cooling power density, at the studied temperature window.

Figure 3-10. (a) Isothermal entropy change of ECE as a function of sample temperature and (b) adiabatic temperature change as a function of electric field at 30 °C in non-stretched P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer under different constant electric field of 50 MVm$^{-1} - 100$ MVm$^{-1}$, while inset shows the adiabatic temperature change of ECE as a function of applied electric field.
The similar results were observed in high energy electron irradiated copolymer P(VDF-TrFE) 65/35 mol%. P(VDF-TrFE) 65/35 mol% copolymer powders were purchased from Solvay and Cie (Bruxelles, Belgium). Solution casting method was employed to prepare the copolymer films. The copolymer powders were dissolved in dimethylformamide (DMF) and then the solution was cast on a flat glass plate and dried in an oven. The temperature of the oven was intentionally set at a low value around 60 °C, which prevented high crystallinity in the copolymer films. Two types of films were used in this investigation: the uniaxial stretched and non-stretched. In stretched films, films made from solution cast were uniaxial stretched by a factor of 5 using zone stretching method. Both stretched and non-stretched films were annealed at 140 °C for a period between 16-20 hours in order to increase the crystallinity. To prevent shrinkage during the annealing for the stretched films, the two ends of the films were mechanically fixed during annealing. The thickness for both stretched and non-stretched films was in the range of 10 to 15 μm.

Figure 3-11. Temperature dependency in EC induced entropy change and D-E loops of electron irradiated copolymer P(VDF-TrFE) 65/35 mol% under 100MV/m.
The irradiation was carried out using the facility at National Institute of Standards and Technology, in a controlled atmosphere (Ar or N\textsubscript{2} gas) to avoid oxidation of the polymers in the irradiation. The specially designed setup allowed heating which provided high temperature above the phase transition of P(VDF-TrFE) 65/35 mol\%.

The electron energy about 1.2 MeV was used for the irradiation. The high energy electrons have large penetration depth so that many P(VDF-TrFE) copolymer layers (up to 0.5 mm in total thickness) can be irradiated at once. To avoid possible overheating of the polymer films in the irradiation process, the irradiation rate is maintained at 1 Mrad per minute. For a copolymer 65/35 mol\% irradiated at above FE-PE transition temperature (~ 100 °C). In this study, the irradiation doses at 20, 40, 60, 75 Mrads had been used to vary the defects concentration in the copolymer.

The results are shown in Figure 3.11(a), where one can find that the electron irradiated copolymer starts to exhibit relaxor ferroelectric properties after being irradiated with 40 Mrads dosage. It is worth mentioning that, for those relaxor ferroelectric irradiated copolymer, temperature stability is dramatically reduced that rendering electric breakdowns at temperature higher than 60 °C, similar to what we have observed in terpolymer P(VDF-TrFE-CFE). The slim D-E loops shown in Figure 3.11(b) are also suggesting a typical material featuring a destabilized ferroelectric phase.

As one can probably conclude, defect modification is effective to manipulate the ferroelectric stability and provide opportunity to electrically induce an transition from random-oriented, nano-sized domain to ordered dipolar configuration, analogy to what happens when a proper ferroelectric material go through its paraelectric-ferroelectric transition. In this way, giant ECE can be realized in wide temperature range owing to the
EC enhancement at those temperatures that are originally in ferroelectric phase. Such relaxor ferroelectric polymers possess great potential to be utilized as active cooling agent for EC refrigerators with high cooling power densities and COPs.

### 3.3 EC Enhancement at Lower Electric Fields

Wide operation temperature window of an EC material ensures higher COP in an EC based cooling device. It also simplifies the device designing and configuration to achieve wider $T_{\text{span}}$ of such a device, considering there is no need for design a cascade device that comprises a series of EC materials with narrow $T_{\text{width}}$.

Besides a great potential of enhance COP of a refrigerator, it is also of great interests that if one can keep improve the amplitude of ECE, especially get large ECE at a relatively low electric field. Reduce driving voltage is a key for a lot of electric field driven phenomena. As shown in Choi’s study at Samsung Advanced Institute of Technology, driving voltage can be dramatically reduced if a multilayer thin film polymer module can be employed. [65, 91] However, thinner polymer films are normally hard to handle owing to their inherent low Young’s modulus. Although fabricating multilayer thin film polymer is promising and effective in lowering the driving voltage, it would still be interesting to search routes to enhance ECE at lower electric fields. The two technologies, working concurrently, may provide a unique approach to greatly reduce the required driving voltage and required weight/size for power source.

However, as shown in Landau theory, giant ECE is proportional to electric displacement square, which indicates that the ECE will be low at low voltage. In order to
get larger ECE at lower electric field, we can either enhance the electric field response regardless of how much field that is applied or specially enhance the ECE at lower electric fields only.

3.3.1 Effect of the irradiation dose on the ECE response in P(VDF-TrFE) copolymer

In principle, ECE is the dipolar entropy difference between two states with applied fields of $E_2$ and $E_1$,

$$\Delta S = S(E_2,T) - S(E_1,T),$$

To enhance ECE of a material regardless the applied electric field amplitude, one can either enhance the randomness of dipolar conformation, enhancing $S(E,T)$, when there is no field applied to the material or enhance the dipolar ordering, reducing $S(0,T)$, when the material is in electric field on state, or both. In theory, paraelectric phase presents a total random dipolar orientation, which should possess the largest $S(E,T)$. However, for copolymer P(VDF-TrFE), the paraelectric phase is starting at a high temperature, normally near 100 ºC, at which thermally induced conduction loss is very strong. As a result, it is not reliable for such a polymer being operated at those temperatures. In addition, at high temperature, strong thermal vibration prevents external electric field to effectively order the dipoles. To achieve even higher ECE, it is required to tuning facially the material properties by material processes and proper modifications.
Figure 3-12. EC induced entropy change of copolymer P(VDF-TrFE) with different electron irradiation doses.

Figure 3-12 presents the EC properties for a P(VDF-TrFE) that has been through different electron irradiation doses that are above 40 Mrads. As discussed above, the irradiated copolymers show relaxor ferroelectric properties and a wide EC operation temperature window $T_{\text{width}}$ compared to non-irradiated copolymer samples. However, their ECE are lower too. Non-irradiated copolymer shows double the effect of those samples which are irradiated with an dose larger than 40 Mrads. Since the experiment was conducted during the cooling temperature ramp, the peak ECE is showing at around 65 ºC, which is still pretty high and the polymer starts to become mechanically unstable at the temperature.

However, the irradiate copolymer that have been through 20 Mrads electron irradiation is very interestingly showing a larger ECE and a lower peak temperature. At
100 MV/m, the EC induced entropy change was reaching 65 J/kgK, which is more than doubled compared to the samples with higher irradiation doses. Although the temperature window of such high ECE was narrow, it brings insights to achieve potential giant ECE in such a polymer system by introducing delicately controlled material modifications.

Electron irradiation offers the capability to reduce the size of the bulky ferroelectric domain by breaking the polymer main chain. The reducing of ferroelectric domain sizes would introduce more available dipolar regions and reduce the polar correlations. Both of them will contribute to generation of giant ECE at wider temperature window. However, it will also reduce the crystallinity of the polymer film, which will reduce the ordering for the material when it is in electric field on state. As shown in Table 3.1, the crystallinity of copolymer reduced dramatically between electron irradiation of 20 Mrads and 40 Mrads.

Table 3-1. Total enthalpy change of the melting peaks, DSC melting peak temperatures, and the crystallinity of the ferroelectric and irradiated P(VDF–TrFE) copolymer system

<table>
<thead>
<tr>
<th>Irradiated Copolymer</th>
<th>ΔH (J/g)</th>
<th>T_m (K)</th>
<th>X_c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 Mrad</td>
<td>-26.6</td>
<td>425.6</td>
<td>80</td>
</tr>
<tr>
<td>20 Mrads</td>
<td>-25.6</td>
<td>411.5</td>
<td>77</td>
</tr>
<tr>
<td>40 Mrads</td>
<td>-20.8</td>
<td>400.6</td>
<td>62</td>
</tr>
<tr>
<td>60 Mrads</td>
<td>-18.4</td>
<td>390.1</td>
<td>55</td>
</tr>
</tbody>
</table>

Table 3-1 also summarizes the transition temperatures and enthalpies for copolymers that have been irradiated with different dosage. We one can observe, 20 Mrads irradiated copolymer exhibit less reduced transition enthalpy and crystallinity, but
a more suitable transition temperature that is much closer to room temperatures. The above analysis indicate a much larger ECE could be generated in 20 Mrads irradiated copolymer P(VDF-TrFE) at 50 °C.

Electric field dependent ECE responses were measured on 20 Mrads irradiated P(VDF-TrFE) copolymer samples around its FE-PE transition temperature, i.e., 50 °C. Under the electric field $\Delta E = 180 \text{ MVm}^{-1}$, the sample exhibited a temperature change reaching 28 K, which is presented in Figure 3-13. To the best of my knowledge, the recorded results are the largest by far in the reported pristine polymer-based materials. The giant ECE responses may be attributed to multi-phases coexistence with reduced energy barrier in the partially irradiated copolymer. The giant EC induced entropy change would provide a large cooling power density, as discussed in Chapter 2, to exhibit great potential for compact cooling device with huge cooling capacity when the required ambient temperature range is around 50 °C. In addition, it is worth noticing that the low field ECE is also significantly enhanced. At electric field of 50 MV/m, the EC induced temperature change is reaching 5 K that is not too bad for some practical applications. When we considering these high electric field induced phenomenon, it is very important to emphasize that the driving field has certain requirement for a reliable, long life-time operation. Normally, the polymer cannot operate near its breakdown field. It is highly desired, as an engineering consideration, to reduce the driving electric field to 30% of its breakdown field. Upon such consideration, the enhancement at lower electric field is of great interests for designing EC cooling devices by the polymer.
Figure 3-13. Temperature change caused by electrocaloric effect as a function of electric field at 50 °C in irradiated copolymer with 20 Mrads.

Besides the giant ECE observed in the irradiated copolymer, the impact of correlation between electron irradiation and EC hysteresis heat has been studied. For a non-irradiated copolymer, large EC hysteresis is existed at ferroelectric phase temperatures and it would show up when the electric field applied on the film is larger than a critical field. The hysteresis would introduce the hysteresis heat that dramatically enlarges the heat signal difference between EC induced heat ejection (apply electric field) and heat absorption (remove electric field). The ECE signals obtained, at various temperatures below, near, and above the dielectric constant peak temperature (~ 90 °C), during the heating process (measurement started at lower temperature and keep elevating temperature) under a unipolar electric field of 100 MV/m are shown in Figure 3-14, where the positive voltage signal is indicating heat ejecting when electric field is applied and the negative voltage signal is referring to the case when the field is removed. It is
noted that there is a large difference between signals in the heat ejection and heat absorption.

![Graph showing ECE signals](image)

Figure 3-14. Directly recorded ECE signal from the flux sensor when the P(VDF-TrFE) 65/35 mol% films under an uni-polar electric field pulse of (a) 100 MVm⁻¹ with pulse width larger than 10 seconds measured at 60 °C, 90 °C, and 100 °C.

Partially irradiation on the copolymer would help to reduce the EC hysteresis heat. It is reducing the heat ejection and enhancing the cooling effect at the same time. Figure 3-15 presents a series of ECE signals at various temperature points in P(VDF-TrFE) 65/35 mol% copolymer, irradiated P(VDF-TrFE) 65/35 mol% copolymer with 20 Mrads irradiation dose. It is of great interests to notice that although the heat signal generation is still exhibiting a strong temperature dependency, the different between heat ejection and heat absorption is greatly reduced.
Figure 3-15. ECE signals (both when applying electric field and removing electric field) at various temperature points in irradiated P(VDF-TrFE) 65/35 copolymer with 20 Mrads.

Entropy change $\Delta S$ derived from the directly measured data at various temperatures are presented in Figure 3-16(a) for non-irradiated copolymer 65/35 mol%. Both heat ejection and heat absorption are summarized in order to highlight the difference between the two that are denoted as $\Delta S_h$ and $\Delta S_c$, respectively. The presented data suggest that the EC hysteresis is functions of temperature and electric fields. At 85°C, which is near the FE-PE transition, $\Delta S_h$ recorded from pristine copolymer films under 100 MV/m in heat ejection (heating) is $156 \pm 28$ Jkg$^{-1}$K$^{-1}$ (or a $Q = 56.6$ J/g) while in the heat absorption (cooling) $\Delta S_c = 48.9 \pm 0.4$Jkg$^{-1}$K$^{-1}$, which is still quite large albeit much smaller than the former. It is noted that $\Delta S_h$ exhibits a large variation among samples and hence exhibits a large data scattering, which is reasonable owing to operational history residue on EC hysteresis heat. On the other hand, $\Delta S_c$ does not show variation as much among samples tested. Figure 3-16(a) verifies that a large difference between $\Delta S_h$ and $\Delta S_c$ exists crossing the whole temperature window (35 °C to 100 °C) where the recorded data is the first drive of electric pulse after the sample is stabilized at each temperature.
The $\Delta S$ difference between the heat ejection and absorption under 50 MV/m (Figure 3-16(b)) becomes much smaller, which indicate an EC induced heat change dominated the process. For example, at 116 °C, $\Delta S_h$ is nearly the same as $\Delta S_c$. As discussed above, at a lower electric field, which hasn’t reach the critical field, the EC hysteresis of the material is limited.

Through the large difference between $\Delta S_h$ and $\Delta S_c$ that are directly measure, we are allowed to quantitatively analyze the EC hysteresis heat in ferroelectric polymers. That is,

$$\Delta S_h = S_i(0, T) - \Delta S(E, T) + \Delta S_{\text{hys}(h)},$$  \hspace{1cm}  3.2

and

$$\Delta S_c = S_f(0, T) - \Delta S(E, T) - \Delta S_{\text{hys}(c)},$$  \hspace{1cm}  3.3

where $S_i(0, T)$ and $S_f(0, T)$ the initial (right after poling) and final (aged for long enough time) entropies, $\Delta S(E, T)$ the EC induced entropy change, respectively. The total polarization hysteresis loss is $\Delta S_{\text{hys}} = \Delta S_{\text{hys}(h)} + \Delta S_{\text{hys}(c)}$. $\Delta S_h - \Delta S_c$ under 100 MV/m and 85 °C can be directly observed as 107 Jkg$^{-1}$K$^{-1}$ (6.7 Jmol$^{-1}$K$^{-1}$) which is corresponding to $\Delta Q$ =38 Jg$^{-1}$ (or 70 Jcm$^{-3}$). $\Delta S_{\text{hys}(h)}$ and $\Delta S_{\text{hys}(c)}$ are polarization hysteresis loss of ejection and absorption. It is noted that the polarization hysteresis loss is much smaller than the EC hysteresis heat, less than 1 Jg$^{-1}$ (< 2.8 Jkg$^{-1}$K$^{-1}$) under 100 MVm$^{-1}$ at 85 °C. The result indicates that a large entropy variation between the initial and final states $S_i(0, T) - S_f(0, T)$ is existing. It is interesting to note that at 35 °C, which is well below the FE-PE transition, $S_i(0, T) - S_f(0, T) > 60$ Jkg$^{-1}$K$^{-1}$. The large $S_i(0, T) - S_f(0, T)$ exists well below the FE-PE transition indicates a low level of ordering in the ferroelectric phase, which is suggesting possible intermediate phases with different degree of polar-ordering in the
The phase (or state) of the copolymer right after the poling possesses exhibits low dipolar entropy, however if the film is aged without external electric field for a long enough time, the internal domain structures relaxes to a phase with high dipolar entropy. This is also explaining the observation of large data scattering of $S_i(0,T)$, which is owing to different film aging time. $\Delta S_h - \Delta S_c = 150 \text{ Jkg}^{-1}\text{K}^{-1}$ has been observed at 85 °C, suggesting a significant change in the molecular conformation between the poled state and aged state.

Above discussion suggests that when the neat copolymer is subject to repeated field pulses, $\Delta S_h$ and $\Delta S_c$ should be approaching to each other since the polymer does not have time to relax back to its disordered state. If that is the case, the heat ejection and absorption would become balanced after a series of repeated electric pulse. The scenario is indeed observed in the ECE data summary of P(VDF-TrFE) 65/35 mol% copolymers which are applied with repeated electric pulses, at 85 °C under 100 MV/m. As presented in Figure 3-18(c), $\Delta S_h - \Delta S_c$ decreases substantially even at the second pulse. When applied pulses are more than twenty, $\Delta S_h$ and $\Delta S_c$ becomes nearly the same, suggesting that the $\Delta S$ measured is approaching to the intrinsic isothermal entropy change and $\Delta S_{\text{int}} \geq 67 \text{ Jkg}^{-1}\text{K}^{-1}$ under 100 MVm$^{-1}$. Now the difference $\Delta S_h - \Delta S_c$ can be reduced to polarization hysteresis loss, which is very small compared to the intrinsic EC induced entropy change. $\Delta S_h - \Delta S_c$ would be enlarging again if there is no electric field that is applying to the sample. Ten minutes would be enough for the molecular conformation to relax back and large $\Delta S_h - \Delta S_c$ reinstated.
Figure 3-16. $\Delta S_h$ and $\Delta S_c$ (the isothermal entropy change during applying field and removing the electric field to the polymer film) of 65/35 ml% copolymer films (a) under 100 MVm$^{-1}$ uni-polar field (from the first field cycle at each temperature) as a function of temperature; (b) under 50 MVm$^{-1}$ uni-polar field (from the first field cycle at each temperature) as a function of temperature; and (c) under 100 MVm$^{-1}$ uni-polar square wave of 0.05 Hz and at 85 °C as a function of field cycle number. Dada points are shown and solid curves are drawn to guide eyes.
As shown in Figure 3-17, by irradiating the copolymer with 20 Mrad (1.2 MeV energy) of high energy electron, the hysteresis heat and also the dielectric hysteresis loss (much smaller as discussed) are significantly reduced. Transition temperature at the heating process is reduced to 49 °C, which can be noticed in Figure 3-17(a). $\Delta S_h$ and $\Delta S_c$ recorded in the first cycle of 100 MV/m electric pulse input at various temperatures near transition temperature are shown in Figure 3-17(a), indicating a significant reduction in $\Delta S_h - \Delta S_c$, compared to the case of normal ferroelectric P(VDF-TrFE) 65/35 mol% copolymer. Within the whole temperature window (from 25 °C to 60 °C), $\Delta S_c$ for the modified copolymer is higher than that of the normal ferroelectric 65/35 mol% copolymer. At 50 °C, $\Delta S_h$ and $\Delta S_c$ are 87 Jkg$^{-1}$K$^{-1}$ and 59 Jkg$^{-1}$K$^{-1}$, respectively. The differences between $\Delta S_h$ and $\Delta S_c$ become smaller and smaller with the increasing number of applied electric field pulses, as presented in Figure 3-17(b), which are similar to what was observed in non-irradiated ferroelectric copolymer case. At the 20th cycle, $\Delta S_h$=72.6 Jkg$^{-1}$K$^{-1}$ and $\Delta S_c$=71.6 Jkg$^{-1}$K$^{-1}$, suggesting intrinsic EC entropy change $\Delta S_{int}$ ~ 72 Jkg$^{-1}$K$^{-1}$ which is larger than the peak value of that of the non-irradiated ferroelectric P(VDF-TrFE) copolymer (65/35 mol%). It is noted that $\Delta S_{int}$ ~ 72 Jkg$^{-1}$K$^{-1}$ is also almost the same value to the average of $\Delta S_h$ and $\Delta S_c$(($\Delta S_h + \Delta S_c$)/2 induced by each electric pulse), indicating that one may use $\Delta S_{ave} = (\Delta S_h + \Delta S_c)/2$ of any electric pulse cycle to estimate $\Delta S_{int}$. Above findings suggest that even the first electric pulse input may cause large differences in EC induced heat ejection and absorption, continuously operating the EC material would reduce the differences significantly and thus can still be applied as EC refrigerant for solid state cooling application with high COP and cooling power density.
To investigate the electric field dependency of the partially irradiated copolymer, the directly measured ECE data under first electric pulse after aging at T=50 °C under various electric field for the 20 Mrads irradiated copolymer is presented in the inset of Figure 3-17(c), which indicated a high ECE, a $\Delta S_h = 190 \text{ Jkg}^{-1}\text{K}^{-1}$, $\Delta S_c = 130 \text{ Jkg}^{-1}\text{K}^{-1}$, $\Delta S_{int} \approx 160 \text{ Jkg}^{-1}\text{K}^{-1}$, can be achieved under 180 MV/m. In addition, the inset of Figure 3-19(c) presents a typical direct recorded heat flux signal of the 20 Mrad irradiated copolymer, which show no conduction heating owing to a reduced transition temperature (50 °C).
Figure 3-17. $\Delta S_h$ and $\Delta S_c$ of 20 Mrads irradiated 65/35 mol% copolymer films (a) under 100 MVm$^{-1}$ uni-polar field (from the first field cycle at each temperature) as a function of temperature; (b) under 100 MVm$^{-1}$ uni-polar square wave of 0.05 Hz at 50 $^\circ$C as a function of field cycle number, and (c) at 50 $^\circ$C under different electric field amplitude. $\Delta S_{ave}$ ($\sim \Delta S_{int}$) as a function of temperature is also presented in (c). Data points are shown and solid curves are drawn to guide eyes. At 180 MVm$^{-1}$, $\Delta S_h$ is 190 Jkg$^{-1}$K$^{-1}$ and $\Delta S_{int} \sim 160$ Jkg$^{-1}$K$^{-1}$.

It is noted that the dipolar entropy in the disordered phase of P(VDF-TrFE) copolymer (crystalline phase) have been evaluated by Furukawa and Takahashi by linking them to detailed molecular conformations of the polymer chains.[93] By simply assuming the molecular structure is a mix of trans-trans (TT), trans-gauches (TG), and TG’ with certain degree of correlations, the dipolar entropy $S(0,T)$ is estimated to be reaching 63 Jkg$^{-1}$K$^{-1}$, which is apparently smaller than what we observed here $\Delta S_h = 190$ Jkg$^{-1}$K$^{-1}$ in the non-irradiated ferroelectric polymer near the FE-PE transition under the first application of 100 MV/m. If the molecular conformation of dipolar-disordered phase contains a totally random mix of TT, TG, and TG’, the dipolar entropy $S(0,T)$ is estimated to increase to 141 Jkg$^{-1}$K$^{-1}$, which is closer to the 190 Jkg$^{-1}$K$^{-1}$ observed here. For the case of the conformation that is containing random T and G sequences, a $S(0,T)$ of 280 Jkg$^{-1}$K$^{-1}$ is estimated, which is more than what we have observed. The above
analysis suggests that there might exist multiple phases with different degrees of disordered dipolar conformation in the non-irradiated and partially irradiated ferroelectric copolymer, resulting in a large entropy $S(0, T)$ near their FE-PE transition due to coexistence of these polar-states.

To summarize, directly measured ECEs are performed on the P(VDF-TrFE) 65/35 mol% copolymers that display a FE-PE transition. The data reveals that there is a large difference between the EC induced heat ejection and heat absorption (an EC hysteresis), which can be reduced after a continuous electric pulse input. Near transition, a $\Delta S_h > 190$ Jkg$^{-1}$K$^{-1}$ is observed under 100 MV/m. After a few field pulses, $\Delta S_h$ and $\Delta S_c$ becomes nearly the same, suggesting an intrinsic $\Delta S_{int} = 67$ Jkg$^{-1}$K$^{-1}$ under 100 MV/m can be induced neat transition. By partially irradiating the copolymer with 20 Mrads of high energy electron, the hysteresis can be substantially reduced. Near the dielectric peak temperature at 50 $^\circ$C, $\Delta S_{int}$ becomes 72 Jkg$^{-1}$K$^{-1}$ under 100 MV/m. Field dependent investigation indicates that a $\Delta S_h = 190$ Jkg$^{-1}$K$^{-1}$, $\Delta S_{int} \sim 160$ Jkg$^{-1}$K$^{-1}$ and $\Delta T_{int} = 35$ $^\circ$C can be induced under a field of 180 MV/m. Besides the enhancement at high field, the low-field EC performances are also significantly improved. A $\Delta S=25$ Jkg$^{-1}$K$^{-1}$ or $\Delta T=5$ K was observed in the partially irradiated ferroelectric copolymer, which is much higher than that in relaxor ferroelectric polymers.

The experimental observation of large difference between $\Delta S_h$ and $\Delta S_c$ also suggests that there are multiple coexisted states with a large difference in degrees of dipolar ordering but a small variation in free energy. The mixture of large number of coexisting phases near the FE-PE transition leads to the ultra-high ECE as observed.
These results demonstrate a general approach to achieve a significant improvement of ECE in ferroelectric polymers by including as much multiple intermediate phases as possible. By properly tailoring the material structure in different dimension scales, generation of large ECE at relatively lower electric field is achievable with increasing knowledge on the material properties. However, the giant ECE is still strongly temperature-dependent within partially irradiated copolymer. In next chapter, we will focus on a general approach to enhance low-filed ECE for relaxor ferroelectrics that exhibit ECE with temperature-independent feature.

3.3.2 EC enhancement in internal biased ferroelectric/relaxor polymer hybrids

Besides modifying material properties to achieve much larger ECE no matter what are the applied electric fields, it is possible to manipulate dipolar material to exhibit larger EC responses only under lower electric fields. From the Landau thermodynamic theory of ferroelectrics, the strain and EC temperature change $\Delta T$ are proportional to the square of polarization,$[48, 90, 94]$ $\Delta T \propto P^2$ and hence $\Delta T \propto E^2$ because $P$ is approximately proportional to the applied electric field $E$ provided field is not high enough for nonlinear dielectric susceptibilities to become important contributors to polarizability. In this paper, this class of materials is referred to as the square law materials. The square law dependence on $E$ yields a high EC or EM response at high $E$ fields but when $E$ is low, these responses become small. This is why in many practical device applications, a DC bias field is applied to induce large responses under small AC (or changing fields).$[95]$ The external DC bias field causes complications in the system
design and may also cause dielectric breakdown when the field is too high. On the other hand, if an internal DC bias field $E_{\text{bias}}$ can be established in the material, $\Delta T = c(E_{\text{bias}} + E)^2 - cE_{\text{bias}}^2$ is larger than $cE^2$ when $E_{\text{bias}}$ and $E$ have the same polarity (along the same direction), where $c$ is an EC constant. The question is whether and how such an $E_{\text{bias}}$ be established in the EC materials. We note that in other functional material systems, similar questions have been asked and investigated. For example, in magneoelectric (ME) composites, utilizing the exchange bias in a multilayer structure, an internal small DC magnetic field (up to 10 mTesla) was established that eliminated the need of an external DC bias field in the magnetostrictive alloy for the ME composite sensors.[96]

Analogously, a normal ferroelectric thin film was also utilized in a photovoltaic (PV) device to establish an internal DC bias field in the device and improve the PV cell efficiency.[97] In this paper, we investigate a polymer blend approach (a nanocomposite approach), in which a normal ferroelectric component in the nanophase form is introduced into the EC relaxor polymer, and demonstrate that an internal DC bias field can be established in the blends by properly controlling the properties of the normal ferroelectric component. As a result, the EC response at low electric fields is enhanced markedly, that is, a $\Delta T = 4.9$ K and $\Delta S = 24.5$ Jkg$^{-1}$K$^{-1}$ can be induced under 50 MV/m, which is more than 40% higher than that in the blends without internal bias field.

The P(VDF-TrFE-CFE) (poly(vinyliden fluoride- trifluoroethylene-chlorotrifluoroethylene)) 59/33/8 mol% relaxor terpolymer was chosen for the study, because of its high EC response.[50] Figure 3-18(a) is the polarization loop of this terpolymer at room temperature, showing large and reversible polarization changes. Normal ferroelectric P(VDF-TrFE) was employed in the blends to induce internal DC
bias. The copolymers in the compositions from 50/50 mol% to 100/0 mol% (PVDF homopolymer) with weight percent from 5 wt% to 30 wt% in the blends were studied in order to examine how the copolymer composition (and hence the strength of normal ferroelectricity) and volume content influence the EC response and internal DC bias fields. The normal ferroelectric P(VDF-TrFE) does not show a high EC response except near the FE-PE transition and excess amount of P(VDF-TrFE) in the blends hence will reduce the EC response in the temperature of study, i.e., near room temperature.

Experimental results reveal that both the composition and concentration of the normal ferroelectric component affect the establishment of the internal bias field and EC response of the blend, indicating the delicate balance between the normal ferroelectric component which shows very weak EC response and relaxor ferroelectric which requires high fields to establish large EC response. Experimental results also show that terpolymer/copolymer blends display higher polarization (and EC) response compared with the neat terpolymer when the copolymer VDF/TrFE ratio is below 85/15 mol%. The blends with copolymers at VDF/TrFE ratio 85/15 mol% exhibit lower polarization (and EC) response. Among all the blends investigated, the one with 65/35 mo% P(VDF-TrFE) at 10 wt% exhibits the highest EC response. Hence, blends of this composition (blends with 90 wt%/10 wt% of terpolymer/65/35 mol% copolymer) are investigated further on how to establish an $E_{bias}$ so that a high EC response can be obtained at low electric fields. The results presented in the paper are for this terpolymer/copolymer blend except if otherwise specified. The normal ferroelectric P(VDF-TrFE) 65/35 mol% copolymer exhibits a near square polarization loop at room temperature, as shown in Figure 3-20(a).
Figure 3-18. The polarization hysteresis (D-E) loops of the normal ferroelectric P(VDF-TrFE) copolymer 65/35 mol.% and the relaxor ferroelectric P(VDF-TrFE-CFE) terpolymer. (b), The dielectric properties of blend (star) and internal-biased (int-biased) blend (square) as a function of temperature from -30 °C to 100 °C at 1 kHz. (c), Schematic illustration of the working mechanism of charge-neutrality in establishing the

The dielectric properties of the blend are shown in Figure 3-18(b), which exhibit a broad dielectric constant peak and typical relaxor dispersion.[98] Indeed, the FT-IR spectra of the blends does not display absorptions from the all-trans bonds of the normal ferroelectric phase. This is consistent with earlier experimental results, indicating that P(VDF-TrFE) in the blends at low wt% (10 wt%, for example) forms nano-phase dispersion in the relaxor terpolymer matrix and does not show normal ferroelectric characteristics.[98] To induce an $E_{bias}$ in the terpolymer, the preferentially oriented polarization of the normal ferroelectric P(VDF-TrFE) component in the blends should be established so that a compensating polarization can be induced in the terpolymer, even at the absence of external electric field, as schematically illustration in Figure 3-18(c). In our study, it was found that applying a DC field of 50 MVm$^{-1}$ at 85 °C, which is above the ferroelectric-paraelectric (FE-PE) transition of the 65/35 mol% copolymer, for more than 10 minutes on the blend film and then cooling down the film under the field at 1 °Cmin$^{-1}$ to room temperature yielded the significantly enhanced EC response at low fields.[99] Increasing the DC poling field beyond 50 MVm$^{-1}$ and/or to higher temperature did not make much difference in the EC response for this composition of blends. In this paper, the blends with an $E_{bias}$ are referred to as the internal-biased (int-biased) blends, in contrast to the blends which are not poled. The results presented in this paper on the int-biased blends were those obtained after the external DC field was removed at room temperature for more than one day.
Figure 3-19. The D-E loops of blend with the internal bias field. (a), The bipolar D-E loop of int-biased samples measured at room temperature. The data reveals a shift of electric filed due to the internal DC biasing in the blend. (b), Comparison of the unipolar D-E loops of int-biased blend with that of the blend under 100 MVm$^{-1}$. (c), Comparison of the maximum polarizations of blend (star) and int-biased blend (square) from the unipolar D-E loops as functions of electric fields measured at 25 °C. The curves are drawn to guide eyes. The D-E loops were measured at 10 Hz.
Both the dielectric and polarization responses indicate the presence of a DC bias field for the int-biased blends. For instance, the int-biased blend films exhibit a broad dielectric peak which is at higher temperature compared with the un-biased blend films. Earlier experiments have shown that applying DC fields to relaxor ferroelectric moves the broad dielectric peak to higher temperature while also reducing the dielectric peak height, consistent with observed results for the int-biased blends [100, 101]. In addition, the dielectric loss at high temperatures is also reduced markedly, for example, from 40% loss of the un-biased blends to below 10% for the int-biased blends at 100 °C. The increased dielectric loss at high temperature originates mainly from the increase in the conduction loss. The experimental data indicate that the int-biased blends can effectively cut down the conduction loss in the films, which is likely due to the presence of internal polar-interfaces in the blends between the copolymer and terpolymer in the int-biased blends, as schematically illustrated in Figure 3.18(c), that block the space charge conduction.[102] An $E_{\text{bias}} \sim 14$ MV/m can be seen in the bipolar polarization-electric field (D-E) loop in Figure 3.19(a) as the center of the loop is shifted horizontally.

To further study the internal bias field and its influence on the polarization and EC response, unipolar D-E loops were measured along the same direction as the $E_{\text{bias}}$ direction to investigate the polarization change in a heating-cooling cycle (measured at 10Hz) and presented in Figure 3.19(b). Figure 3.19(c) summarizes the increased polarization in the uni-polar D-E loops under different applied fields in the int-biased blends, compared with that of un-biased blends. The int-biased blends display higher polarization level, especially at low field range.
The EC responses (the adiabatic temperature change $\Delta T$ and isothermal entropy change $\Delta S$) of both int-biased and un-biased blends under electric fields of $\Delta E=50$ MVm$^{-1}$ and 100 MVm$^{-1}$, respectively, as functions of temperature are presented in Figures 3-20(b) and 3-20(c). A marked enhancement of the EC responses is obtained at 50 MVm$^{-1}$ where the peak values of $\Delta T = 4.9$ K and $\Delta S=24.5$ Jkg$^{-1}$K$^{-1}$ are obtained for the int-biased blends, compared with the peak values of $\Delta T = 3.4$ K and $\Delta S=17$ Jkg$^{-1}$K$^{-1}$. Presented in Figure 3-20(a) are the EC responses as functions of the applied field at room temperature (25 °C). As can be seen, the EC response of the int-biased blends under 50 MVm$^{-1}$ is the same as that of un-biased blends under 62 MVm$^{-1}$, which is consistent with that observed from the bi-polar D-E loop in Figure 3-19(a). The enhancement, which is more prominent at lower field, opens up opportunities to design EC based cooling devices with capabilities in low-field and reliable operation.

In order to understand the influence of internal $E_{bias}$ on the polarization and EC responses, the $\beta$ coefficient, from $\Delta S = -\frac{1}{2}\beta P^2$, is evaluated for the blends, using the data in Figure 3-19 and Figure 3-20, and presented in Figure 3-21(a). The internal DC bias field enhances $\beta$ at low electric fields ($< 40$ MVm$^{-1}$), while at high fields, $\beta$ of the int-biased blends becomes smaller compared with un-biased blends. The results indicate that the internal $E_{bias}$ approach indeed enhances ECE effectively at low electric fields ($\Delta E < 50$ MVm$^{-1}$).
Figure 3-20. The improvement of the ECE performance in the blends due to the internal biasing: the adiabatic temperature change $\Delta T$, isothermal entropy change $\Delta S$ of int-biased blend (circles) and blend (squares). (a) $\Delta T$ and $\Delta S$ as functions of electric field measured at room temperature. (b) and (c), $\Delta T$ and $\Delta S$ as functions of temperature under electric fields of 50 MVm$^{-1}$ and 100 MVm$^{-1}$, respectively.
Besides the peak ECE that an EC material can generate, high electrocaloric coefficients, such as $\Delta T/\Delta E$ and $\Delta S/\Delta E$, are also critical in order to measure EC behaviors versus different external electric fields. $\Delta S/\Delta E$ and $\Delta T/\Delta E$ for the int-biased blends and un-biased blends at different applied field are presented in Figure 3-21(b), which shows a large improvement compared with that of the un-biased blends, especially at low electric fields. These parameters are summarized in Table 7-1 and compared with other stand-alone EC materials reported in the literature (including the measuring fields and temperatures). [103-107] The $\Delta S/\Delta E$, which was measured in int-biased polymer blend, is comparable to that has been reported in inorganic ceramics and single crystals. The improvement of more than 40% in both ECE ($\Delta T= 5$ K) and EC coefficient ($\Delta S=0.5 \times 10^{-6}$ J/kg K$^{-1}$ V$^{-1}$) at 50 MVm$^{-1}$, which is far away from the breakdown field of such polymer blends, suggests a more effective, efficient and reliable electric operation on such material is achievable.
Figure 3-21. The EC performances of the int-biased blends and blends at room temperature. (a), The EC coefficient $\Delta S/\Delta E$ and $\Delta T/\Delta E$ and (b), coefficient $\beta$ as functions of electric field. Data points are shown and the curves are drawn to guide eyes.

The results indicate that with better understanding of how polarizations contributes to ECE induced entropy change, much larger ECE at lower electric fields could be achieved. Moreover, the work presented here represents a general approach to improve the performance of square law materials at low applied fields. This work as well a plethora of progresses made recently in EC materials suggest there are opportunities for further improving ECE as we develop our understanding of ECE and polar-dielectrics.
3.4 Summary

In this chapter, we focused on the challenge to generate better ECE performances in PVDF based ferroelectric polymers for practical cooling applications. The first requirement in designing high COP cooling device is wide operational temperature window of the EC material. By utilizing defect modification, we demonstrated that the ferroelectric copolymer P(VDF-TrFE) can be modified to relaxor ferroelectric and exhibit giant ECE covering a wide temperature window near room temperature. A 10 K EC induced temperature change can be realized from 0-50 ºC temperature range which opens opportunities for room temperature refrigerators with high COP. In addition, by carefully choosing the intensity of defect modification, giant ECE can be even more enhanced. We demonstrated a 35 K temperature change in 20 Mrads irradiated copolymer under and electric field of 180 MV/m. Furthermore, by establishing DC biased field in P(VDF-TrFE)/P(VDF-TrFE-CFE) 10/90 mol% blends, ECE at lower field can be enhance by 60% under electric field around 50 MV/m. The enhancement in ECE, especially at lower electric field would dramatically enhance the reliability of EC cooling devices owing to the capability to running at lower electric fields.
Chapter 4
EC Ceramics: Invariant Critical Point and Higher Thermal Conductivity

4.1 Introduction

After the giant ECE has been estimated in ceramic thin films from Maxwell relation, experimental demonstrations of giant ECE were limited in ceramic or single crystal thin films. Large ECE, $\Delta T>5\ \text{K}$, is still absence in bulk inorganic materials including both single crystals and ceramics. One alternative is making use of MLCC technology as mentioned in Chapter 1. MLCCs exhibit the both advantage of thin film ceramics and bulk ceramics as they are thin enough to handle high electric field and thick enough for easy handling and device processing. Large ECE has been observed in $\text{BaTiO}_3$ (BT) thick films, $|\Delta T| = 7.1\ \text{K}$ and $\Delta S = 10.1\ \text{Jkg}^{-1}\text{K}^{-1}$ were generated under the application of high electric fields change $\Delta E = 80\ \text{MVm}^{-1}$.[105] Although the applied electric field is still very high, the finding encouraged the studies in EC ceramic MLCCs for practical applications. As we starts to address EC materials for practical cooling devices applications, where both performance and cost should be considered, large ECE would be a first goal to achieve in bulk ceramics and MLCCs. Additional material parameters should also be considered besides a large $\Delta T$ and $\Delta S$ to assess the performance of the EC materials. For example, in order for a cooling device to be
operated at low voltage such as $< 200$ volts which is the normal input voltage range for most cooling devices, an EC material with a large ECE induced under low electric fields is also important. Furthermore, a wide operational temperature window near concerned temperature, room temperature for example, is highly desired to develop EC cooling devices with high performances.[43, 79, 81, 88] Therefore, one critical question is how to design and engineer a ceramic material which is capable to generate giant ECE over a broad operation temperature window stimulated by a relatively low applied electric field $\Delta E$.

Ceramics, compared to polymers, present much higher thermal conductivity if intentionally fabricated. For example, BaTiO$_3$, a well-known lead-free ferroelectric ceramic which has been intensively and extensively studied over hundred years, possess a thermal conductivity around 5-6 W/mK that is 25 times higher than PVDF based ferroelectric polymers. Higher thermal conductivity in ceramics would encourage heat exchange between EC materials and ambient environment thus lead to higher operational frequencies and cooling power, as shown in Figure 2-7. In addition, ceramic possess much larger modulus that could helpful for fabrication process and some device configurations. Considering the advantages that inherited in ceramics for practical applications, large ECE in bulk ceramics and MLCCs is of great interests and demands to investigate.

As a lead-free ferroelectric ceramic which is environmentally friendly and is as a matter of fact the most widely used ferroelectric material, BT has been studied for ECE quite intensively in the past decade by many groups and in various forms, e.g., thin films, bulk ceramics (including thick films, MLCCs), and single crystals.[105, 107-110] Large
ECE has been reported in BT ceramics at temperatures near its ferroelectric-paraelectric (FE-PE) transition.[105] It has been noted that, for BT, besides the high FE-PE transition temperature \( T_{FE-PE} > 100 \, ^\circ C \) between the tetragonal ferroelectric (Tet) and cubic paraelectric phase, it also exhibits an orthorhombic (O) and a rhombohedral (Rhom) phase as schematically illustrated in Figure 4.1.[111] As ECE is directly corresponding to the entropy changes of an insulation dielectric due to the change of an applied electric field, a ceramic with a polar phase that contains a large amount of polar-states with relatively similar energy levels would be introduced at a reasonable electric field from a non-polar phase (i.e., below the dielectric breakdown field of the dielectric) has the potential of exhibiting giant \( \Delta T \) and \( \Delta S \).[112, 113] In addition, a giant ECE can also be induced at a low electric field if the energy barriers of switching between different polar-states are vanishingly small. For pure BT ceramic or single crystal at the FE-PE transition, the ferroelectric tetragonal phase (Tet) has six equivalent polar-states and a large dielectric constant at FE-PE transition that induces a large \( \Delta T/\Delta E \) at temperatures slightly above the FE-PE transition, as has been observed in single crystal form of BT.[107] On the other hand, as discussed by Liu et al., by manipulating material systems to its invariant critical point (ICP) at which all the available phases (paraelectric cubic, Tet, O, and Rhom) can coexist, it is possible to have an increased number of available polar states, i.e., twenty-six states, that leads to a significant enhancement of entropy at the non-polar phases,[113] resulting to better ECE performance. Moreover, the near zero energy barriers near ICP suggest a low electric field for inducing switching among these various states and hence a giant ECE that can be stimulated at low operational electric fields.[113]
It has been extensively and intensively studied that the temperature of above mentioned phase transitions in BT can be easily modulated by rational chemical modifications in the BT.[111] As illustrated in Figure 4-1 (a), by modulating BT with Zr, i.e., a solid solution of Ba(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3}, all three transitions will merge into cubic phase to enable an ICP starting at x~ 0.15, near which the four phases can coexist and the transition temperature can be further moved to room temperature.[111, 114] In addition, as an early study has shown that BZT at compositions x>0.2 exhibits ferroelectric relaxor response,[114] one can expect the ECE in such solid solution can be improved as improvement in relaxor ferroelectric polymers, as discussed in Chapter 3. In this chapter, we experimentally demonstrate that indeed for BZT(x=0.2), a relaxor feature near ICP presents and a much more improved ECE property exhibits, i.e., both a larger ECE and EC coefficients, ΔT/ΔE and ΔS/ΔE can be obtained near room temperature over a broader temperature window in bulk ceramic samples compared to BT ceramics. The results
presented here indicate a general approach to significantly improve ECE in ferroelectrics (both ceramic and polymers) with lower applied electric fields, which addresses a critical issue in employing ceramic materials for practical refrigeration devices. A schematic of ICP is shown in Figure 4-1 (b).

4.2. ECE enhancement in Ba1-xZrxTiO3 Bulk Ceramic

The BZT ceramic samples were fabricated by conventional solid-state reaction approaches. All chemicals, including barium carbonate (BaCO₃, 99.8 %), zirconium dioxide (ZrO₂, 99.5 %), and titanium dioxide (TiO₂, 99.5 %), were purchased from Alfa Aesar and used as arrived and without further purification. Stoichiometric weights of all powders were ball-milled by zirconia balls for 24 hours to obtain a well-dispersed mixture. After the calcination at 1100 °C for 2 hours, sintering of the pellets was performed at 1360 °C in air for 2 hours with a heating rate of 3 °C/min. One wt% glass was added in before the sintering in order to enhance the breakdown strength of the resulting ceramic bulk samples. The final ceramic samples were 10 mm in diameter and about 1 mm in thickness. A typical top view of BZT(x=0.2) is shown in Figure 4-2 taken by Scanning Electron Microscopy (FEI NanoSEM 630 FESEM). For electric/dielectric/ECE characterization, the samples were polished to 100 μm thick with careful polishing procedures provided by Materials Research Institute at Penn State University. Au electrodes were sputtered on the sample surfaces for the electric characterizations. An image of a real tested BZT sample is shown in inset of Figure 4-2.
In order to study the modulation caused by different compositions, BZT ceramics at compositions of $x=0.15$, 0.2, and 0.25 were sintered and their ECE and related electric/dielectric properties were characterized over the temperature window of our interest (from 10 °C to 100 °C). Figure 4-3 shows that the specific heat data of the three compositions do not differ significantly with temperatures from 0 °C to 70 °C.
Figure 4-3. Modulated DSC measured specific heat of BZT in different composition.

Figure 4-4. Permittivity of BZT in different composition x.
Figure 4-4 presents the dielectric characteristics measured at 1 kHz of BZT ceramics for x=0.15, x=0.2, and x=0.25 compositions. The BZT(x=0.2) samples exhibit a broad dielectric constant peak at 25 °C and a relaxor dielectric response, which is consistent with earlier studies.[114] The induced polarization D versus temperature, obtained from the D-E loops acquired from BZT(x=0.2) sample at different applied field amplitudes at 100 Hz, is presented in Figure 4-5. The induced polarization decreases, as expected, with temperature continuously from 15 °C to 60 °C and does not exhibit any sudden drop around 25 °C, also consistent with the relaxor feature of the material. The permittivity peak of BZT(x=0.15) occurs at a temperature around 67 °C and peak is narrower compared to that of BZT(x=0.2). As shown in Figure 4-6, BZT samples at these compositions exhibit slim D-E loops at temperatures near their dielectric peaks, respectively.

Figure 4-5. Temperature dependent polarization in BZT x=0.2 from 15 °C to 60 °C.
Figure 4-6. D-E loops of BZT bulk samples in x=0.15 and x=0.2. Measured around their respective dielectric peak temperatures.

Directly measured ECE results of all three BZT compositions were characterized. Among them, BZT(x=0.2) exhibits the highest EC response that is also occurring near room temperature. BZT(x=0.15) samples display a slightly reduced ECE that reaches peak at 67 °C, compared with BZT(x=0.2), but is higher than the peak ECE measured from BZT(x=0.25) samples, which exhibits large ECE near -10 °C. Hence, detailed ECE studies were conducted for BZT(x=0.15) and BZT(x=0.2) samples which are presented in the chapter.
Figure 4-7. (a) The directly recorded ECE signal for BZT(x=0.2) as the electric field was turning on and off, respectively. The data were measured under $\Delta E=9.5$ MVm$^{-1}$ at 35 °C. Solid line is drawn to show the ambient temperature reading. (b) EC-induced temperature drop $\Delta T_c$ and isothermal temperature change $\Delta S$ as functions of $\Delta E$ for BZT(x=0.2) at 39 °C. The data were extrapolated (solid curve) to estimate $\Delta T_c$ at higher electric fields. (c) $\Delta T_c$ and $\Delta S$ as functions of temperature for BZT(x=0.2) under different electric fields. Solid curves are drawn to guide eyes.
The directly measured ECE signal from BZT(x=0.2) (at 35 °C under a ΔE = 5, 6, 8 MV/m) are presented in Figure 4-7(a), which shows the heat flux rise and drop as the field is applied to and removed from the ceramic sample. ΔS and ΔTc from the temperature decrease of the sample as the field is removed are presented in Figure 4-7(b) for the BZT(x=0.2) at 35 °C under different applied electric field ΔE. The result reveals that at ΔE = 14.5 MV/m, ΔTc = - 4.5 K and ΔS = 8 Jkg⁻¹K⁻¹ (Q = 2.5 Jg⁻¹) are observed. Here ΔTc is referring to the temperature decrease (cooling) of the sample as the applied electric field is removed. As shown in Figure 4-7(c), ΔTc and ΔS do not exhibit much change over a broad temperature window from 25 °C to 50 °C, and there is observed a very broad peak between 35 °C and 40 °C, which is than the broad dielectric constant peak temperature (around 25 °C). For the BZT(x=0.2) ceramic bulk samples in this ECE study, the highest field that can be applied without breakdown was 14.5 MV/m. To make a comparison with the results on non-modified BT thick films, extrapolated data is shown Figure 4-7(b) to higher fields and it is estimated that EC induced ΔTc = -7.1 K can be achieved for BZT(x=0.2) ceramics under an electric field of 31 MV/m, which is less than 40% of what is required to achieve the same ΔTc (=80 MVm⁻¹) in the pure BT ceramics. The extrapolation is well consistent with the polarization data of this BZT composition, following the assumption that ΔTc is proportional to the square of the polarization D,[94] which can be measured up to 35 MV/m. The results verified the prediction that giant ECE at low applied field can be achieved by operating the material system near ICP to involve
maximum number of coexisting phases that have vanishing energy barriers for dipole switching.[113, 115]

To quantitatively measure how effective an applied external electric field $\Delta E$ in stimulating ECE in studied ceramics, electrocaloric coefficients, the ratio of $\Delta T_c/\Delta E$, $\Delta S/\Delta E$ (or $Q/\Delta E$, where $Q=TS\Delta S$) have been introduced in early studies.[107, 116] In analogy to many material property coefficients of ferroelectrics such as the piezoelectric coefficients that vary with the driving field amplitude $\Delta E$, the EC coefficients for BZT($x=0.2$) also change with $\Delta E$. High EC coefficients, i.e., $|\Delta T_c/\Delta E| = 0.52 \times 10^{-6}$ KmV$^{-1}$ and $\Delta S/\Delta E=0.93 \times 10^{-6}$ Jmkg$^{-1}$K$^{-1}$V$^{-1}$, are observed at a relatively lower electric field $\Delta E = 2.1$ MV/m and $\Delta T_c= -1.1$ K. The coefficients reduce ($|\Delta T_c/\Delta E| = 0.31 \times 10^{-6}$ KmV$^{-1}$ and $\Delta S/\Delta E=0.54 \times 10^{-6}$ Jmkg$^{-1}$K$^{-1}$V$^{-1}$) at higher field $\Delta E=14.5$ MV/m and $\Delta T_c= -4.5$ K.

Figure 4-8. ECE measured in BZT $x=0.15$ samples. (a) Field dependent ECE at 69 °C, (b) Temperature dependent ECE under different electric fields.
Figure 4-8(a) presents EC induced $\Delta T_c$ and $\Delta S$ of BZT(x=0.15) measured at 69 °C vs. As usual, $\Delta E$ and the data were taken from the temperature lowering and backward heat flux signal of the sample when electric field was removed. A large ECE, $\Delta T_c = -4.2$ K and $\Delta S = 7.3$ Jkg\(^{-1}\)K\(^{-1}\) were measured under 15 MV/m. $\Delta T_c$ vs. ambient temperature measured under different electric fields are shown in Figure 4-8(b) and a slightly higher temperature dependency is noted, when compared with the data in Figure 4-7 for bulk BZT(x=0.2). Temperature dependent $\Delta T_c$ shows a broad peak near 69°C. The EC coefficients, $|\Delta T_c/\Delta E|=0.48 \times 10^{-6}$ KmV\(^{-1}\) and $\Delta S/\Delta E=0.85 \times 10^{-6}$ Jmkg\(^{-1}\)K\(^{-1}\)V\(^{-1}\) for the composition BZT(x=0.15) under $\Delta E=1$ MVm\(^{-1}\) was measured. The EC coefficients of BZT(x=0.15) is slightly lower than that of BZT(x=0.2). Similar to what has been observed in BZT(x=0.2), the EC coefficients are reduced to $|\Delta T_c/\Delta E|=0.28 \times 10^{-6}$ KmV\(^{-1}\) and $\Delta S/\Delta E=0.5 \times 10^{-6}$ Jmkg\(^{-1}\)K\(^{-1}\)V\(^{-1}\) under a higher electric field $\Delta E=15$ MV/m. The results here as well as earlier studies all suggest that BZT(x=0.15) is where the three transitions merge (ICP). Over that composition, BZT(x=0.2) exhibits “stronger” relaxor ferroelectric behavior compared with BZT(x=0.15).[114] The results suggest that it is the combination of ICP and ferroelectric relaxor behavior that leads to the giant $\Delta T_c$ and $\Delta T_c/\Delta E$ in the ceramic BZT over a wide temperature range near selectable center temperature.[106, 113] Above results are also consistent with the $\beta$ coefficient, where $\beta$ is defined in Landau theory, $\Delta S = -\frac{1}{2} \beta P^2$, from BZT with different compositions.[94] Figure 4-9 shows that $\beta$ value for BZT(x=0.2) can be more than 25% higher than that of BZT(x=0.15) composition. On the other hand, further increasing the composition to x=0.25 causes a decrease of EC coefficients compared with that at x=0.2 owing to the
further reduced dipolar correlation, i.e., higher electric field would be needed for aligning the dipoles.

Figure 4-9. $\beta$ coefficients in BZT x=0.15 and x=0.2.

Table 7-2 summarizes and compares the EC properties from this chapter with other EC ceramics that are reported to possess potential for practical refrigeration applications. The ECE results reported in single crystals and ceramic thin films are also included, which may also provide insight for material property point of view. It is worth noticing that both $\Delta T$ and $\Delta S$ may also be derived from the pyroelectric coefficient $(\partial P/\partial T)$ of Figure 4-5 using the Maxwell relation (the pyroelectric coefficient data for both BZT(x=0.15) and BZT(x=0.2) was characterized). It was noted that the $\Delta T$ and $\Delta S$ thus estimated (here the method is referred to as the indirect method) were very different from that directly measured data, likely caused by the fact that these BZT compositions show relaxor ferroelectric behavior and a broaden polarization variation with elevating
temperature. An earlier experimental study from our group also showed that such indirect method may not necessarily yield consistent ECE data with directly measured ones in the case of relaxors.[62] Hence, the ECE results deduced from the indirect method are not included in Table 7-2. For practical applications, the operational temperature window in that a large ECE can be maintained unchanged is also critical as we discussed in Chapter 2. In the Table, $T_{\text{width}}$ is introduced to identify this performance, which is the temperature span width over which the $\Delta T_c$ maintains $0.9 \times \Delta T_c$ (maximum). As can be seen, the BZT developed here possesses a giant ECE, i.e., large $\Delta T_c$, $\Delta T_c/\Delta E$, $\Delta S/\Delta E$ and $T_{\text{width}}$. The combination of these highly desired performances, including the ECEs, mechanic, and thermal conductivities inherited as ceramic materials, indicate the potential of the ceramic materials developed here for the ECE based cooling devices with high cooling power and efficiency.

### 4.3 ECE in Multilayer Ceramic Capacitors

As we shown in last section, the modified BZT, Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ (BZT) bulk ceramic exhibits giant ECE, i.e., large EC induced temperature drop about $\Delta T=4.5$ °C and large entropy change ($\Delta S = 8 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) under 14.5 MV/m owing to the fact that the operation is near its invariant critical point, where four different phases, including cubic, tetragonal, orthorhombic and rhombohedral phases can coexist.[104] Compared to BT, the highly enhanced ECE and the inherent high thermal conductivity and strong mechanic properties make the modified BT ceramic system especially promising for practical cooling devices.
However, beside of giant ECE, which is normally observed at high electric field in each material system, some realistic issues should be considered to reliably employ the EC materials as the solid-state refrigerant to ensure a long operation life time. For example, the operating voltage is demanded to be at least lower than 200 V for household applications and meanwhile EC induced temperature change or entropy change should be maintained. Furthermore, electrocaloric coefficient of an EC material is a key parameter to assess the material performance in practical cooling device. In the last section, we showed that the EC ceramics exhibit high cooling coefficient at lower electric fields, but reduce at higher fields. Therefore, there are two approaches to reduce the driving voltages of EC ceramics and maintain the ECE. First approach is that to keep working on material modifications and enhance both EC coefficients and ECE. The other one is more straightforward and would be valid for all EC materials. Since the voltage is not the electric field but the field times thickness, making EC material thinner would allow lower voltage to generate same amplitude of electric field. For example, 100 MV/m electric field applied to 1 µm ceramic thick film would require applied voltage of 100 V. For ceramics, 1 µm ceramic thick film is hard to be freestanding and also difficult to handle. Fortunately, multilayer ceramic capacitor MLCC fabrication is quite mature in industry that would open opportunities for EC ceramics to be applied as EC cooling refrigerant in novel solid state refrigeration technology. In addition, strain may introduce in the MLCC and can be controlled by fabrication processes. Strain offers material modification in more degree of freedom and may introduce more phase-coexistence that may further improve the ECE.
Bearing with the above concerns, we started to fabricate the BaZr$_{0.2}$Ti$_{0.8}$O$_3$ thick films MLCC by firstly making thick film double layers on bulk ceramic BZTs. As discussed before, the bulk BZT composition showed a large EC induced temperature drop under an electric field of 14.5 MV/m. It was expected that smaller thickness than that of bulk could yield better breakdown strength and linearly reduced the voltage required. In addition, the existence of metallic electrode between ceramic thick films would enhance effective thermal conductivity of the thick film module.

The BZT thick film was prepared by well-known tape casting method, which is followed by the structure forming that is schematic shown in Figure 4-10(a). Sinter aids were added in the system, in order to decrease the sintering temperature of BZT below 1200 °C. The reason for lower sintering temperature is that low cost metal electrode can thus be used. All the chemicals of barium carbonate (BaCO$_3$, 99.8 %, 1 micron), zirconium dioxide (ZrO$_2$, 99.5 %, 1 micron), and titanium dioxide (TiO$_2$, 99.5 %, 1 to 2 micron) were purchased from Alfa Aesar and used as soon as they arrived. Stoichiometric weights of all the powder were mixed with ethanol and milled by zirconia balls for 24 h. After the calcination at 1100 °C for 2 h, 0.5 mol.% MnO$_2$, 1 wt.% polyvinyl alcohol (PVA) binder solution and 1 wt.% sinter aids (PbO and B$_2$O$_3$) were added in. After well blended, mixture was sent in tape casting procedure to make green tape. The BZT green tapes with printed Pt electrodes were stacked layer by layer with precise alignment before the isostatic lamination. After sintering at 1200 °C in air for 1.5 h, silver epoxy was used to terminate the both ends as outer electrodes for the further electric/dielectric/ECE characterization.
Temperature dependent dielectric constant and loss with different driving frequencies were measured by a HP 4980A LCR meter equipped with a temperature-controlled oven (Delta 9023). Polarization (D)-electric field (E) loops were recorded by Sawyer-Tower circuit as functions of electric field and temperature. The cross-section SEM image of BZT multilayer films with two active layers is shown in Figure 4-10(b) by FEI NanoSEM 630 FESEM. As observed, the thickness of single layer is around 12 μm. Similar to ECE measurement setup we introduced before, here we use a similar measurement protocol but by employing DSC as calorimeter. The heat Q generated and absorbed by the BZT thick film sample were collected by an external power source enabled differential scanning calorimetry (DSC) (TA Q2000) developed at Zhang’s lab at Penn State University. In this set-up, two terminations are connected with two surface-insulated silver wires to a special designed interface board then to a power
supplier/amplifier (Trek 610C) that was utilized as power amplifier. The input voltage ramp was specially designed by an arbitrary function generator. Voltage ramps with constant rate were applied on the sample for different peak voltages throughout the whole test. While voltage is applying and removed to the measured sample that is sitting on one of the sensor in DSC, the temperature change of the sample causes respectively exothermic and endothermic heat flux signals which are recorded by the DSC. The thermal capacity of the BZT thick film was also obtained by the DSC. Reference heater is also sputtered on the sample to provide known amount of heat which can be recorded by DSC as a calibration.

![Figure 4-11. The dielectric constant and loss of BZT thick film for the temperature change.](image)

The temperature dependent dielectric constant and loss tangent under different frequencies from 100 Hz to 10 kHz are presented in Figure 4-11. As expected, the BZT thick film exhibits the relaxor behavior, with dielectric peaks dispersion with frequencies, and shows maximum dielectric constant of around 6500 at 20°C which is still can be
considered as the maintenance of high value compared to bulk samples. From the inset of Figure 4-10(b), the grain size of BZT is smaller, 2 to 3 μm, compared to that of bulk ceramic, and the phenomenon of small grain size is attributed to the low sintering temperature (1200 °C) and is also the reason of relatively lower dielectric constant as observed. The polarization D of the BZT thick film obtained at 10 Hz as function of temperature are presented in Fig. 4-12. It is noted that the polarization of the BZT thick film reaches 0.19 C/m² at 15 MV/m at room temperature. The induced polarization decreases with elevating temperature from 10 to 60 °C and exhibits no obvious suddenly rise or drop in the test temperature window, which is normally observed in the relaxor ferroelectric materials.[104]

![Figure 4-12. Polarization as a function of temperature for BZT thick film under 15 MV/m.](image)

The heat Q generated and absorbed by the BZT samples were detected with the electric power source enabled differential scanning calorimetry (DSC) (TA Q2000) to further deduce the temperature drop induced by ECE. As shown in Figure 4-13(a), EC induced temperature drop (ΔT) around 6.3 °C and entropy change (ΔS) of 11.0 Jkg⁻¹K⁻¹
are observed under an electric field of $\Delta E = 14.6$ MV/m at 40 °C, which is higher than that of bulk BZT ceramic samples measured the same condition. The maximum $\Delta T = 7.0$ °C is observed under $\Delta E = 19.5$ MV/m for the thick film samples. Here $\Delta T$ is referring to the temperature drop (cooling) when the electric field is removed. As shown in Figure 4-13(b), $\Delta T$ and $\Delta S$ are temperature independent over a broad range from 20 to 60 °C which suggested a broad temperature window for the material to be effective on a same level as EC modules for a heat pump (two parallel entropy-temperature curves). According to the thermodynamic phenomenological theory, EC performance can be further assessed by $\beta$ coefficient, $\Delta S = -\beta D^2/2$.\[120\] It is noted that $\Delta S$ is proportional to the square of the polarization as in theory which is consistent to what we have found in PVDF based ferroelectric polymers but a little variant from what we have observed in the ceramic cases. Employing the data of induced polarization and ECE of samples, the $\beta$ values of BZT thick film can be calculated and are shown in Figure 4-13(c). The value of $\beta$ is $3.5 \times 10^6$ J m K$^{-1}$C$^{-2}$ at 11.7 MV/m, which is much higher than bulk ceramic (less than $3.0 \times 10^6$ J m K$^{-1}$C$^{-2}$), which indicate the EC coefficients at lower fields are much more enhanced. Indeed the EC coefficient of BZT thick film multilayer is larger, $\Delta T/\Delta E = 0.50 \times 10^{-6}$ KmV$^{-1}$ and $\Delta S/\Delta E = 0.88 \times 10^{-6}$ J m kg$^{-1}$K$^{-1}$V$^{-1}$ at 9.8 MV/m, respectively. The field applied here is especially interesting owing to the fact that is corresponding to an input voltage of around 120 V. From Table 7-2 that is shown in the Chapter 7 that summarize previous reported EC ceramic properties, it can be observed that the BZT thick film discussed in this section exhibits enhanced ECE performance, such as high temperature change $\Delta T$, large EC coefficients $\Delta T/\Delta E$, $\Delta S/\Delta E$ and especially large EC
performances under low ΔE, which may lead to a general solution for utilizing EC material in the practical cooling device.

Figure 4-13. (a) EC-induced temperature drop ΔT and isothermal entropy change ΔS for the different electric fields at 40 °C. (b) EC-induced temperature drop ΔT and isothermal entropy change ΔS for the temperature changes under different electric fields. (c) β coefficient for the electric fields change at 40 °C. Solid, dash and dot curves are drawn to guide eyes.
Besides the combination of invariant critical point and ferroelectric relaxor behavior around room temperature, such enhancement can be also attributed to smaller grain sizes, strain effect and thinner samples. In this study, two EC ceramic thick film layers were stacked on the same composition of BZT substrate. Internal strain is generated inside the thick film layers and the BZT substrate corresponding to the sintering procedure. Internal strain could provide more degrees of freedom to manipulate the material structure to further increase the coexisting phases and hence improve the ECE. The internal strain resulted from the mechanical between layers and the substrate plays a key role in the generating larger ECE of ceramic thick film. The improved ECE, which is operated by near invariant critical points where all phases coexisted, could be tuned by the second kind of field, the strain. The total pyroelectric coefficient measured at constant stress $p^X$ can be expressed as,

$$ p^X_i = p^r_i + d^X_{ijk} c^{X,E}_{jklm} \alpha^{E}_{lm}, \quad (4.1) $$

where $d^X_{ijk}$ is the piezoelectric strain tensor at a constant stress, $c^{X,E}_{jklm}$ the elastic stiffness tensor at constant stress and electric field, $\alpha^{E}_{lm}$ the thermal expansion tensor at a constant electric field. The second term in the equation is the secondary effect, which also significantly contributes to the ECE as discussed by Li et al.[121]. This may be another reason for the enhancement of ECE in the BZT thick film as presented in this section.
4.4 Summary

Several unique properties of ceramics, such as high thermal conductivity, strong mechanic modulus and mature fabrication processes, bring great amount of attention to employing them as EC devices for practical application. This chapter is dedicated to improve the ECE in the bulk ceramics and probe the material fabrication process of MLCCs. Our work demonstrates that both ECE and EC coefficient can be greatly enhanced in lead-free bulk ceramics by modifying the BT ceramics to its ICP and, during the same procedure, turning it to relaxor ferroelectrics. BZT bulk ceramics were air-environmentally sintered and their EC performances were directly characterized. Large improvement of EC-induced temperature change $\Delta T$ of 4.5 K and large EC coefficients, $\Delta T/\Delta E$ around $0.5 \times 10^{-6}$ K m V$^{-1}$, were observed. Multi-phase coexistence near ICP allows more randomness in the material system and hence more available polar-states. Furthermore, the BT ceramics were meanwhile tailored from ferroelectrics to relaxor ferroelectrics after Zr was occupying the B site of the system. The resulting ceramic relaxor BZT($x=0.2$) exhibits a giant ECE around room temperature and a wide EC operating temperature window that is promising in designing cooling devices. In addition, BZT thick film multilayers were fabricated for ECE characterization owing to the benefits it provides such as low driving voltages for longer and reliable operation life time. ECE at room temperature was investigated in BZT thick film. The fabricated thick film double layer module exhibits a large $\Delta T= 7.0$ °C, large entropy change of 12.2 J kg$^{-1}$K$^{-1}$, and large EC coefficients ($\Delta T/\Delta E = 0.50 \times 10^{-6}$ K m V$^{-1}$ and $\Delta S/\Delta E = 0.88 \times 10^{-6}$ J m kg$^{-1}$K$^{-1}$V$^{-1}$) over 40 K temperature window covering room temperature. These
properties, adding together with ceramic’s inherent features, indicate a general solution of the EC ceramics with high performance for practical cooling applications.
Chapter 5
EC fluids – Potential for Realizing EC Active Regenerative Refrigeration
Without External Heat Exchange Fluid

5.1 Introduction

The advances of ECE offering opportunities to operate compact and light-weighted cooling devices with great electrical efficiency which is of great benefit to practical applications such as electrical vehicles since the mechanical compressor required for conventional vapor compression technology is an extra-burden in electrical vehicles. The recent findings of giant ECEs in ferroelectric polymers and ceramic thin films have attracted great interest for developing new cooling cycles which are environmental friendly, mechanical-compressor-free, and have the potential to reach better efficiency.[28, 29, 50, 60, 94, 122, 123]

Up to now, ECE is limited in studies of solid-state materials. However, there is no fundamental reason that large EC responses can occur only in the solid state dielectrics. Indeed, considering the conventional vapor compression refrigeration (VCR) technology, which is running a vapor/fluid transporting in systems, it may provide more compatibilities if an novel EC based cooling device is operating an EC cooling fluid which can provide active heat pumping with response to electric fields. Benefits of such an EC fluid cooling device is obvious, besides all the benefits that are inherited as an EC based refrigerator, such as no need for bulky and noisy compressor, high efficiency and cooling power density, the EC fluid cooling devices can be designed in much
complicated geometries in much smaller scales, because the fluid can simply flow in the
designed channels. The lab-on-chip ECE device hasn’t been demonstrated but it is
certainly of great interests to look into.

As discussed in Chapter 2, one key component of a cooling device is the
transportation of heat from the cold end to the hot end. The objective is to transport
entropy from one temperature level to another temperature level in a reversible and cyclic
manner. This requires a substance (refrigerant) whose entropy depends on some
properties other than temperature. In solid-state ECE materials, this substance is an
insulating dielectric, in which entropy can be changed by external electric fields. Various
methods have been proposed to transport entropy from the cold end to the hot end in
cooling cycles with ECE.[81, 83, 124, 125] Among them, in analogous to the magnetic
cooling cycles built upon the magnetic alloys with giant magnetocaloric effect
(MCE)[42], using heat exchange fluid is still the only one that is realizable with the
present technologies to achieve high efficiency and high cooling power. Compared with
solid state ECE materials, a dielectric fluid with a large ECE can be more interesting
since it can be used as both the refrigerant and heat exchange fluid, which could lead to
new cooling cycles with simpler structures and even better performance than these based
on solid state ECE materials.

In theory, an EC fluid cooling device operation should be similar to what we
discussed in Chapter 2. A Carnot cooling cycle using ECE fluids is illustrated in Figure
5-1. In general, a cooling device should comprise of two main components (functions): a
refrigerant whose entropy depends on some properties other than temperature, and the
transport of entropy from the cold end to the hot end. Compared with the solid state ECE materials, liquid ECE materials have the advantage of being used as both the refrigerant and heat exchange fluid to transport entropy from the cold to hot ends.

![Figure 5-1. Schematic illustration of the Carnot cycle based on ECE effect.](image)

In practical cooling devices employing ECEs, the Ericsson cycle as illustrated in Figure 5-2, which consists of two isothermal processes (at $T_h$ and $T_c$) and two constant field processes (at $E_H$ and $E_L$), is more convenient to use and also $T_h - T_c$ is not limited by the adiabatic temperature change of the ECE materials.[126] If the heat ejected in the $E_H$ process $Q_2$ can be absorbed in the $E_L$ process $Q_1$ (if $Q_1 = Q_2$), the COP (coefficient of performance) of Ericsson cycle is the same as the Carnot COP. Such a cooling cycle also enables a larger temperature span $T_h - T_c$ and a higher cooling power than that of Carnot cycle. For EC fluids, the heat capacity can be tuned by compositions so that $Q_1$ and $Q_2$ can be nearly the same, resulting in a high COP.
Figure 5-2. An ECE Ericsson cycle, consisting of two isothermal and two constant field processes.

A design of EC cooling device employing EC fluid is presented in Figure 5-3 in which the ECE fluid is pumped (flow) along one direction (in the figure, it is in counterclockwise flow direction). The ECE fluid in the left channel is subject an E field (the blue region with the red arrow) and there is no electric field on the ECE fluid in the right channel. As the ECE fluid from the right channel (no field) enters the left channel (under field), there is an increase in temperature and heat is rejected at $T_h$. As the ECE fluid flows from $T_h$ to $T_c$ in the left channel, there is a heat transfer between the ECE fluid in the left channel (under $E_H$) to the right channel ($E=0$), a heat regenerative process similar to that in rotary EC devices employing solids (Chapter 2). At $T_c$, the field in the ECE fluid is removed and there is a reduction of temperature (and absorbs heat at the cold end). Owing to the fluidity, EC fluid can flow in one direction in a designed channel and achieve regeneration during the circulation, as shown in Figure 5-3.
Figure 5-3. A (Left) Schematic of a cooling cycle (Ericsson) employing an ECE fluid. The ECE fluid in the left channel is under $E_H$ and no field in the right channel. The ECE fluid flows counter clockwise. (Right) Finite Element Method simulation result.

It is clear that such a cooling cycle (device configuration) can’t be accomplished using a solid state ECE material. For the solid state ECE material, the most convenient cooling cycle is that analogous to the active magnetocaloric regenerative refrigeration (AMRR), which has been extensively investigated by the magnetocaloric cooling community[42, 126]. In general, AERR (active electrocaloric regenerative refrigeration) consists of two ECE banks and uses an additional heat exchange fluid for transporting entropy from the cold end to the hot end (see Figure 5-4)[125, 127]. One challenge for such a cooling cycle is the bi-directional flow of the heat exchange fluid. That is, in one-half cycle, the heat exchange fluid flows clockwise and in another half cycle, it flows in
counter clockwise. This severely limits the operation frequency of the cooling device (since the fluid channels have small size for the effective heat exchange between the ECE material and heat exchange fluid and a high flow resistance for fast reversing the flow direction). An EC based cooling device is hence promising due to the fact that EC fluid can serve as both active cooling agent and heat exchange fluid.

![Schematic of an AERR](image)

**Figure 5-4.** Schematic of an AERR. In the AERR, due to the cyclic nature of the ECE, the heat exchange fluid has to flow bi-directionally. For example, clockwise in one half cycle ($E=0$) and counterclockwise in the other half cycle ($E=E_h$).

### 5.2 ECE in Liquid Crystals with Large Dipole Moments

Basic materials consideration and experimental results indicate that in order to achieve a large ECE, a dielectric fluid should possess a high density of dipoles which can provide direct and strong coupling to applied electrical fields. Moreover, operating the
dipolar materials near dipolar order-disorder transitions, where a dipolar ordered state can be most easily induced from a dipolar disordered state, will make it more likely to realize a large ECE. For practical applications, it is important that the dielectric fluid can withstand a relatively high electric field (> 100 V) in order to induce a dipolar order state in a practical device configuration with a long electric field cycling life. Although there are many dielectric liquids such as water which possesses high dielectric constants, the relatively low electrochemical window of these fluids, often less than 2 or 3 volts, make them not possible to reach a large ECE for practical applications.[128, 129] On the other hand, liquid crystals (LCs), which have been used widely in optic displays, are dipolar liquids in which the molecular orientation and consequently dipolar states can be easily controlled by external electric signals with a long operation life under high voltage.[130-132] Hence LCs may be ideal dielectric liquids to realize large ECE. For example, as illustrated in Figure 5.5(a), rodlike, anisotropic liquid crystal molecules, the mesogens, will form a randomly oriented state, the isotropic phase, at high temperatures. As the temperature is lowered, LC molecules can transform into a nematic phase or a smectic phase, (see Figures 5.5(b) and 5.5(c)). In the nematic phase, the mesogens are aligned, on average, along a preferred direction as defined by a director \( \mathbf{n} \). In a smectic phase, the mesogens, besides aligned along a preferred direction, form a layered structure while in each layer, the molecular centers are randomly arranged (two-dimensional liquids). Applying electrical fields may induce a transition from an isotropic (I) phase to a nematic (N) or smectic (S) phase when near the N-I or S-I transition, thus may lead to a large ECE.[133, 134]
In this paper, we investigate the ECE in LC 5CB (4-n-pentyl-4'-cyanobiphenyl, see Figure 5.5(d) for the molecular structure) near its N-I transition. LC 5CB is chosen because it has the N-I transition near room temperature (~ 35 °C) and the mesogens also possess a large dielectric anisotropy.[135, 136] The dielectric constant parallel to the director ($\varepsilon_{\parallel}$ >18.5) is much larger than that perpendicular to the director (~7.5) (see Figure 5-6), which provide a strong orientation force to align the mesogens along $\mathbf{n}$ by external electric field ($\mathbf{E} \parallel \mathbf{n}$).

![Figure 5-5](image)

Figure 5-5. Schematic of various mesophases for rodlike LC molecules which are of interest for generating large ECE: (a) an isotropic, (b) nematic, and (c) smectic A phases, (d) Molecular structure of 5CB.

The isothermal entropy change of an ECE material when the electric field is increased from $E_1$ to $E_2$ is,

$$\Delta S = S(E_1, T) - S(E_2, T)$$

5.1
Therefore, the initial conditions of the ECE material at $E_1$ (in most cases, $E_1=0$) will directly affect the ECE. For LCs, the molecular orientations can be strongly influenced by the surface conditions of substrates with which LC molecules are in contact and consequently the entropy of the LCs.\cite{137-139} In order to study the effect of preferred molecular orientations on the ECE, two groups of LC cells, i.e., homogeneously aligned cells (HA-Cells) and no-aligned cells (NA-Cells), were purchased. In the HA-Cells, the rod-like LC molecules are aligned preferentially along the surface of the substrates. In this study, the HA-Cells have a thickness of 3.2 $\mu$m. In the cell without surface alignment layer, the cell is made by two transparent ITO electrode coated glass substrates separated by glass fiber spacers with a thickness $d = 4$ $\mu$m (NA-Cells). Figure 5-7 (a) and (b) present the polarizing microscopic images of 5CB in NA-cells without and with electric field (10 MV/m), respectively. The purchased LC cell is shown in Figure 5-7 (c).
LC 5CB was purchased from Merck. Two groups of LC cells were purchased from Instec for HA-Cells (parts No. SA025A032uG180) and NA-Cells (SA100A040uNOPI). In the homogeneous cell the electrodes on the glass substrates were first coated with an alignment layer, e.g., polyvinyl alcohol (PVA), to introduce a small pretilt angle when contact with LC molecules. Then the top and bottom electrodes were rubbed in opposite direction. The cell gap of HA-Cells and NA-Cells is 3.2 μm and 4 μm, respectively.

Presented in Figure 5-8 are the polarization responses (electric displacement-electric field loops, D-E loops) of HA-Cells and NA-Cells, respectively, measured under 50 MV/m and 100 Hz AC field at temperatures near the N-I transition. The data reveal that there is very little hysteresis in the D-E loops. Reversible isothermal entropy change ΔS and adiabatic temperature change ΔT for a dielectric film as the electric field changes from E₁ to E₂ can be deduced from the pyroelectric coefficient ∂D/∂T as a function of electric field, i.e,

$$\Delta S = \int_{E_1}^{E_2} \left( \frac{\partial D}{\partial T} \right)_E dE$$  \hspace{1cm} 5.2(a)

and

$$\Delta T = -\int_{E_1}^{E_2} \frac{T}{c_E} \left( \frac{\partial D}{\partial T} \right)_E dE$$  \hspace{1cm} 5.2(b)
where $c_E$ is the specific heat of the ECE material. These equations are based on the Maxwell equation

$$\left(\frac{\partial D}{\partial T}\right)_E = \left(\frac{\partial S}{\partial E}\right)_T.$$ 

Figure 5-8. D-E loops of 5CB under 50 MV/m AC field of 100 Hz at temperatures near the N-I transition for the HA-Cells (a-c) and NA-Cells (e-g). (d) and (h) present the D vs. temperature curves under different constant E fields ($\geq 25$ MV/m), which show no discontinuous change of D vs. temperature in this field range.
Figure 5-9. (a) DSC data of 5CB liquid crystal measured during the heat and cooling runs. The DSC peak corresponding to the N-I transition is at 34.7°C in heating and 34.07°C in cooling processes. Scan rate is 1 °C/min. (b) The specific heat data of 5CB, measured during heating. The heating rate is 1°C/min.

In general, the Maxwell equation is valid only for a reversible thermodynamic process. For the LC 5CB studied here, it has a weak first order N-I transition around 34.5 °C which has a small thermal hysteresis of 0.7 °C between the N-I transitions measured in heating and cooling runs (see Figure 5-9). Hence only at temperatures above the critical point, which is about 0.6 °C above the N-I transition (> 35 °C) and/or electric fields well above the hysteresis, the Maxwell relation can be used. In the experimental study here, the applied electric field E is well above the D-E loop hysteresis at the temperature of study (>32 °C). As shown in Figure 5.8 (h), the curves of D vs. temperature under different electrical fields do not display signs of discontinuous chance of D around the N-I transition. The temperature differentiation of polarization, dD/dT, under different electric field is plotted in Figure 5-10. Under these experimental conditions, the Maxwell relation can be approximated to deduce the ECE at temperatures around the N-I transition. The LCs in the experiment are confined by the glass plate cells which have fixed
electrode area $A$ and dielectric film thickness $d$. The area $A$ (~ $1 \text{ cm}^2$) is much larger than $d$ (= 4 $\mu\text{m}$). Consequently $\Delta S$ and $\Delta T$ thus deduced for the LCs here are these under the constant strain condition. It is also noted that the peak of $dD/dT$ for each $E$ in Figure 5-10 moves progressively towards higher temperature with the field $E$, which is expected since a higher field will stabilize the nematic phase to higher temperatures.

![Graph](image)

Figure 5-10. Pyroelectric coefficient $dD/dT$ measured for different temperatures and different electric fields for 5CB.

The isothermal entropy change $\Delta S$ and adiabatic temperature change $\Delta T$ deduced as a function of the temperature are presented in Figure 5-11 for these two groups of LC samples (the specific heat data used is presented in Figure 5-9). The data reveal that ECE peaks near N-I transition which has $\Delta S = 24 \text{ Jkg}^{-1}\text{K}^{-1}$ and $\Delta T=5.2 \text{ K}$ under 90 MV/m applied electric field for the LCs in the NA-cells. The ECE observed here is nearly the same as that observed in the polar-fluoropolymers under the same electric field level,
which also exhibit very large ECE near room temperature. As has been pointed out earlier, increasing applied field will stabilize the nematic phase to higher temperatures. As a result, the ECE peak will shift progressively towards higher temperature as observed experimentally in Figure 5-11.

Figure 5-11. The electrocaloric effect deduced from the Maxwell relations for (a) isothermal entropy change $\Delta S$ and (b) adiabatic temperature change $\Delta T$ of 5CB LCs in NA-Cells, and (c) $\Delta S$ and (d) $\Delta T$ of 5CB LCs in homogeneously aligned LC cells (HA-Cells). Data points are shown and solid curves are drawn to guide eyes.

Figure 5-12 presents $\Delta S$ as a function of applied field amplitude for the two groups of LC cells at 39 °C which is above the N-I transition. The LC cells without
surface alignment display larger $\Delta S$ than that with homogeneous surface alignment. This is understandable since surface alignment induces partial ordering of molecular alignment in the LC films and reduces the dipolar entropy in $E=0$ state; consequently, $\Delta S$ is reduced. On the other hand, Figure 5-11 shows that the homogeneous surface alignment broadens the ECE peak, i.e., the FWHM ($\sim 8 ^\circ C$) (full width at half maximum) of $\Delta S$ vs. temperature curves for the homogeneously aligned cells is slightly larger than that (FWHM $\sim 7 ^\circ C$) of the randomly oriented cells.

![Image of graph showing comparison of $\Delta S$ as a function of electric field $E$ of 5CB at 39 °C in NA-Cells (crosses) and in HA-Cells (squares). Data pointes are shown and solid curves are drawn to guide eyes.]

Figure 5-12. Comparison of $\Delta S$ as a function of electric field $E$ of 5CB at 39 °C in NA-Cells (crosses) and in HA-Cells (squares). Data pointes are shown and solid curves are drawn to guide eyes.
The ECE in LCs can also be estimated from the phenomenological Landau-de Gennes formulation (LG). [130] According to the LG phenomenological theory, the isothermal entropy change $\Delta S$ of a nematic liquid crystal at temperatures above the N-I transition critical point is related to the change of the order parameter $Q$ (0 ≤ $Q$ ≤ 1) as ($Q$ is used instead of $S$, which is normally used for order parameter, in order to distinguish from the denote of entropy $S$.)

$$\Delta S = (a/2)(Q_2^2 - Q_1^2)$$

(5.3)

where $Q_1$ and $Q_2$ are the order parameter at electric fields $E_1$ and $E_2$, and $a$ is a constant. For nematic liquid crystals, $Q=1$ corresponds to a perfect LC molecular alignment which may be achieved under a very high electric field $E$ while $Q = 0$ corresponds to molecular random orientation as in the isotropic phase. From the $a$ value reported in the literature for 5CB,[135] $a = (1.1\pm0.4) \times 10^5$ J/Km$^3$ and the density $\rho = 1$ g/cm$^3$, a very large $\Delta S = 55$ J kg$^{-1}$ K$^{-1}$ can be deduced when $Q$ is changed $Q_1=0$ to $Q_2=1$. For the study here $Q_2=0.65$ is induced under 90 MV/m at the critical temperature which yields $\Delta S = (23 \pm 8.5)$ J kg$^{-1}$ K$^{-1}$ (see Figure 5-13 and Figure 5-14). Considering the uncertainty of the coefficient $a$ and the possible substrate effects in the thin LC cells here, the agreement between the experimental data and LG phenomenological theory estimation is quite good. These results indicate that giant ECE can be obtained from electrical field induced orientational order-disorder transition in LCs near the N-I and S-I transitions.
Following the Landau-de Gennes phenomenological theory of a nematic liquid crystal in the presence of a stabilizing electric field $E \parallel n$, the free-energy $f$ can be written as [136]

$$f = f_0 + \frac{1}{2} a(T - T^*) Q^2 - \frac{1}{3} b Q^3 + \frac{1}{4} c Q^4 - \delta E^2 Q$$

5.4

where $\delta = \varepsilon_{ad}/12\pi$, $\varepsilon_{ad} = \varepsilon_{a}/Q$ is the dielectric anisotropy for $Q=1$, $T$ is the absolute temperature, $T^*$ is the lowest temperature at which the isotropic phase is metastable, $f_0$ is the free-energy density of the isotropic phase for $E=0$, $a$, $b$, $c$ are supposed constants, and $Q = Q_0 + Q(E)$ is the sum of the field-induced order $Q(E)$ and $Q_0 = Q(0)$.

Assuming the phenomenological coefficient $a$, $b$, $c$ and $\delta$ are temperature independent, then the isothermal entropy change at the phase transition can be expressed as

$$\Delta S = - \left( \frac{\partial f}{\partial T} \right)_E = - \frac{1}{2} a Q^2$$

5.5

5CB has a weak first-order N-I transition. At the equilibrium state, $\partial f/\partial Q = 0$, which leads to

$$a(T - T^*) Q - b Q^2 + c Q^3 - \delta E^2 = 0$$

5.6

Equation 5.6 has at least a real solution with different $E$. The order parameter $Q$ displays a discontinuous change when $T < T_c$ and the critical behaviors at $T = T_c$. At the critical point $T_c$ and field $E_c$, $dQ/dT$ reaches its maximum. The order parameter $Q$ as a function of temperature and electric field at temperatures above the N-I transition can be
calculated using the parameters for the Landau-de Gennes phenomenological theory of 5CB published by Coles[135], Ledlidis and Durand[136]. Results are shown in Figure 5-13. Using the Q values in Figure 5-13, ΔS for 5CD at temperatures above the critical temperature (~ 35 °C) can be deduced from Eq. 5.5, which is presented in Figure 5-14.

![Figure 5-13. Order parameter Q as a function of temperature under different electric fields for 5CB. Parameters used here are from ref. S8. The electric field changes from 14 MV/m (critical electric field) to 100 MV/m.](image-url)
Figure 5-14. Isothermal entropy change as a function of temperature under different electric fields for 5CB. Parameters used here are from Ref. S8 and Figure S7. The electric field changes from 14 MV/m (critical electric field) to 100 MV/m.

It should be pointed out that there are a broad range of LCs available in which the N-I and S-I transition temperatures cover a broad temperature range.\textsuperscript{[29]} Moreover, for a given LC, its transition temperature can be tuned by, for example, mixing with other LCs with different transition temperatures.\textsuperscript{[30]} For cooling devices to be operated over a broad temperature range, LCs with large ECE at different temperature regions may be cascaded to cover the required temperature range. This is analogues to the cooling devices based on the magnetic alloys exhibiting giant magnetocaloric effect (MCE) in which the giant MCE occurs near the ferromagnetic-paramagnetic transition and the MCE alloys are cascaded to generate cooling over a broad temperature range.\textsuperscript{[19,20]} Compared with the conventional cooling cycles based on MVCC and the cooling devices under development employing solid state ECE and MCE, dielectric liquids with giant ECE will create totally
new cooling device cycles which have potential to expand the cooling device application ranges and improve the performance.

5.3 Challenge and Opportunities of ECE in LCs

As an electro-thermal response that is corresponding to a first ordered phase transition, the ECE in a LC is inevitably restrained at its N-I transition temperature. The narrow EC operational temperature window poses challenges for an EC fluid based cooling device to work at a temperature away from the transition temperature. The challenge can be addressed in both device configuration and material modifications.

It is not new scenario in which a cooling device design is employing a caloric material with narrow cooling temperature window. In magnetocaloric (MC) refrigeration, MC materials are also featuring limited operation temperature range. In order to design a cooling device that can work in wider temperature range, cascade cooling cycles are normally designed with multiple cooling agents, which are in charge of certain temperature ranges and connected from high temperature to low temperature, as schematically shown in Figure 5-15.
This design can work well on LCs because of the N-I transition temperature of LCs can be easily manipulated by simply mixing two different LCs, which possess different transition temperature, as a mixture. By linearly tuning the composition of the LC mixture, N-I transition temperature present linear shift between the two transition temperatures of participating LCs.

It is also possible to directly enlarge the temperature window my material modification. Analogy to relaxor ferroelectric materials, which de-stabilizes ordered ferroelectric phase by reducing the domain size, the ordered nematic phase can also be de-stabilized by dispersing LCs in cured polymer matrix. Polymer stabilized LC (PSLC) is a composite of polymer and LC in which a diffuse network of polymer chains can penetrate throughout the volume. Normally PSLC contains 1-10 wt% polymers and the major content is still LC so that the composite exhibits form of a viscous liquid or gel.
The existence of polymer matrix creates domains in the PSLC and as a result, randomness of molecular orientation may be relatively maintained even at nematic phase temperature.

A simple PSLC gel was fabricated in order to verify above prediction. 5CB, which is used in ECE study as pure LC, and UV-curable epoxy NOA65 are mixed in 90/10 wt%. After stirred in dark overnight, the mixture was constrained in a non-aligned (NA) LC cell and cured under UV illumination in CL-1000 UV crosslinker for 10 min (254nm). Similar to indirect EC measurement details provided in the last section, the temperature-dependent D-E loops were measured and the total polarizations were plotted as shown in Figure 5-16.

![Figure 5-16. Polarization D plotted as a function of temperatures, under various electric fields in 5CB/NOA65 PSLC.](image)

It is noted that the PSLC exhibit slightly higher breakdown field than pure 5CB, which is reasonable owing to the low dielectric constant of cured NOA65. Additionally,
at high field, the decrease of polarization is nearly linear with rising temperature, suggesting a temperature invariant dD/dT. Indeed, the PSLC gel exhibit a much wider EC temperature window than the pure 5CB as presented in Figure 5-17.

Figure 5-17. Indirect characterized ECE in 5CB/NOA65 PSLC and the comparison with pure 5CB.

It is interesting to notice that the ECE in the PSLC is reduced almost 50% than that in pure 5CB. An EC induced $\Delta S=12.5\text{J/kgK}$ is predicted under electric field $\Delta E=75 \text{MV/m}$ compared to 20 J/kgK in the case of pure 5CB. It should also important to note that the ECE enhancement is not only showing below N-I transition temperature of 5CB (in nematic phase) but also much more enhanced in isotropic fluid phase. The results imply that the form of LC small droplets, separated by polymer matrix, may enhance the
electric response in isotropic phase as well by reducing the molecular thermal vibration energy level that is very high for input electric field to align those molecules in the case of pure 5CB.

5.4 Summary

In summary, we present indirectly measured ECE in LC 5CB that displays an N-I transition temperature around 35°C through Maxwell relations. An isothermal entropy change of more than 24 Jkg⁻¹K⁻¹ and an adiabatic temperature change of 5.2 K was observed near 39 °C, which is slightly above the N-I transition temperature. The limitation in EC operation temperature window has also been discussed. To address that issue, we discussed it in device configuration point of view and material science point of view. A cascade cooling device can be designed by making use of multiple EC fluids which have different N-I transition temperatures. The transition temperature can be tuned by mixing two or more LCs. Thus formed mixture shows continuous transition temperature shift by linearly varying the composition of participated LCs. In addition, the PSLC, a 5CB/NOA65 90/10 wt% cured mixture which shows much wider EC temperature window, is studied by indirect method. The PSLC, analogy to ferroelectric de-stabilization in relaxor ferroelectric case, features smaller sized droplets which are in relatively disordered phase in nematic temperature range. The ECE results indicate that such a PSLC gel shows slightly reduced ECE but exhibits much wider EC operation temperature window.
It should be noted that, LC is only one class of fluid-like material. There are still thousands of organic fluids out there for study. It is important to focus on fluids that exhibit relatively larger dielectric constant and smaller molecular dimensions, where the large dielectric constant implies a large response of those fluid molecules to the electric fields and smaller molecular dimensions ensures more available polar-states that introduce larger entropy when there is no electric field applied.
Chapter 6
Cool Without Subsequent Heating: Anomalous ECE

6.1 Introduction

The electrocaloric effect (ECE) is an electrical energy induced thermal energy responses in which insulation materials exhibit temperature/entropy changes when subjected to external electric fields.[28, 29, 48, 141-143] In an ECE we have discussed above, an insulation material may release or absorb heat when an electric field is applying and may absorb or release heat when the field is removing, which is known as positive or negative ECE[36, 144-146]. It is noticed that EC refrigeration devices are more likely to be designed as a heat pump by making use of EC materials to absorb heat at one place and eject heat to the other, owing to the reversible heat processes in the normal EC materials. That is implying that 1. A movement of EC material or heat exchange media is needed for the heat pump to work; 2. An electric field needs to be maintained for some time before the cooling actually taking places. The cooling and heating effects are taking turns in both normal ECE and inverse ECE that has been observed. However, in some applications where instant and reliable cooling are needed, neither of above is desired. Here we present an anomalous ECE in a normal ferroelectric/relaxor ferroelectric polymer hybrid blend: when applied of an short electric pulse, the hybrid blend exhibits a large cooling effect (an isothermal entropy change $\Delta S=11.5 \text{ J/(kgK)}$) without the following-up heating signal. We show that such an
anomalous ECE in the hybrid blend can be generated by the mesoscale dipolar interactions between the ferroelectric component and the relaxor ferroelectric polymer. The normal ferroelectric component introduces dipole ordering in the hybrid blend matrix after poling, which can be later switched to a de-poled state by an external field pulse on the opposite direction to the poling field; more interestingly, when the de-poling field pulse is finished, this de-poled state (randomness) can be maintained by the relaxor component hence there is no subsequent heating signals showing up.

In general, applying an electric field to a polar dielectric material enhances dipole ordering, as illustrated in Figure 6-1(a). This ordering reduces the dipolar entropy of the dielectric and leads to a heat ejection (red peak in Figure 6-1(a)). When the field is removed, the dipoles return to their less ordered state and lead to a heat absorption, shown as the blue peak in Figure 6.1a. The recent demonstration of giant ECE in dielectric materials has stimulated great interests in developing refrigeration technologies that are environmentally friendly and have the potential to achieve higher COP compared with the century-old, vapor compression based refrigeration technology[28, 29, 43, 50, 79, 87, 104, 141-143, 147, 148]. Analogous to the inverse magnetocaloric effect reported earlier[36], the inverse (or negative) ECE (N-ECE) has also been predicted and observed in normal ferroelectric materials in which an external electric field causes a reduction of dipole ordering, generating heat absorption, and the removal of the electric field causes heat ejection in the dielectric material (see illustration in Figure 6.1b)[75, 144, 149, 150]. Both the normal ECE and N-ECE features periodic heat ejection and absorption during the application of an electric field pulse. That is a heating (cooling) is always accompanied by a cooling (heating) effect.
Here we report an anomalous inverse (negative) ECE in a series of ferroelectric/relaxor ferroelectric polymer hybrid blends that do not show follow-up heating as the field is removed, as schematically shown in Figure 6-1(c). We here refer
the observed EC phenomenon as anomalous ECE (A-ECE) to distinguish it from the ECE and N-ECE. Dielectric materials exhibiting the A-ECE are attractive for applications where an electric pulse induces cooling effect of the ambient environment without any heat ejection [6, 142, 151, 152]. In contrast to the normal (positive) ECE (Figure 1a), the dipole ordering is diminished in the N-ECE when an electric field applied is increasing. There are several polarization mechanisms in ferroelectric materials that can lead to the N-ECE[75, 144, 149, 150]. However, to realize an A-ECE (without heating under an electric pulse), the dielectric material (1) should be in a dipole-ordered state initially, which can be later switched by an external field to a dipolar-disordered state; and (2) more significantly, as the applied electric field is removed, the dielectric material can maintain this less-ordered state without recovering to a dipole ordered state hence showing no heat ejection during the process.

6.2 Materials Preparation and Measurement Methods

P(VDF-TrFE-CFE) terpolymer (59/33/8 mol.%) was synthesized with suspension polymerization[153]. P(VDF-TrFE) copolymers (65/35, 55/45, 75/25 mol.%) were purchased by Measurement Specialties. The density of the copolymer and terpolymer is nearly the same (~ 1.75 g/cm$^3$). The polymer films were fabricated via solution casting method that is discussed in previous chapters. The P(VDF-TrFE-CFE) and P(VDF-TrFE) were separately dissolved in N,N-dimethylformamide (DMF) solvent and stirred overnight. Then the solutions with proper weight ratio were mixed and stirred for 12 hours. The final solution was filtered with 0.2 μm sized polytetrafluoroethylene (PTFE)
syringe filters before pouring on a pre-cleaned silica quartz plate, on which the solution was dried at 70 °C for 12 h in a temperature controlled oven and cooled slowly to room temperature. In order to further remove residual solvent and increase crystallinity, the films were peeled from the plates and annealed at 110 °C for 12 h. The thickness of the blend films is around 6-10 μm. Sputtered aluminum layers of 20 nm thickness deposited on the polymer films were used as the electrodes for all the electric characterization (dielectric/electric/ECE).

The temperature dependent dielectric property was characterized by an LCR meter (HP4284A) equipped with a Labview-controlled temperature chamber (Delta 9023). Polarization (D)-electric field (E) loops were recorded using a Sawyer-Tower circuit. For the N-ECE and A-ECE study, the polymer films were pre-poled by an electric pulse of 100 MV/m and 5 seconds duration time.

Differential Scanning Calorimetry (DSC) was conducted by employing a TA Q-2000 DSC Instrument. Specific heat was measured with the same equipment using a modulated DSC mode. The measuring temperature scan rate is 2 °C/min, and the modulate period is 60 seconds.

6.3 Anomalous ECE in Ferroelectric/Relaxor Ferroelectric Polymer Hybrids

The A-ECE was observed in the hybrid blends of ferroelectric P(VDF-TrFE) (polyvinylidene fluoride-trifluoroethylene) copolymers and the relaxor ferroelectric P(VDF-TrFE-CFE) (CFE: chlorofluoroethylene) 59/33/8 mol% terpolymer. It has been shown in Chapter 1 and 3 that the normal ferroelectric P(VDF-TrFE) copolymer does not
exhibit a large ECE except at temperatures near its ferroelectric-paraelectric (FE-PE) phase transition [28, 49], while the relaxor ferroelectric terpolymer exhibits a giant ECE over a broad temperature range near room temperature due to the proper defect modifications. [50, 60, 103].

Figure 6-2. D-E loop comparison among neat copolymer P(VDF-TrFE) 65/35 mol%, neat terpolymer P(VDF-TrFE-CFE) and their 50/50 wt% blend.

In a ferroelectric P(VDF-TrFE) copolymer, which has been pre-poled to a poled state (for example, at point A of the electric displacement (D)-electric field (E) loop in Figure 6-2 which is its spontaneous polarization), applying an electric field to de-pole the ferroelectric polymer (the de-poling field is in the opposite direction that is against the original poling field, which is in the positive direction) may reduce the dipole ordering compared with that of the pre-poled state, which is essentially a N-ECE.
Figure 6-3. The N-ECE for the copolymers of 55/45 mol%, 65/35 mol%, and 75/25 mol%. $\Delta S$ from the cooling peak is shown in the figure.

This is indeed observed, as shown in Figure 6-3, where the pre-poled copolymers absorb heat as a field is applied and eject heat as the field is removed. It is noted that, when the electric field is reduced to zero, these normal ferroelectric materials display a subsequent heating peak (eject heat), presenting the typical N-ECE. For the ferroelectric copolymer P(VDF-TrFE), the N-ECE is small, i.e., $\Delta S \leq 1$ J/(kgK) at room temperature owing to the strong dipolar confinement deep inside the ferroelectric phase. This is understandable due to the normal ferroelectric materials are featured by the presence of large remnant polarization and large macroscopic polarization domains. When a normal ferroelectric is pre-processed to the poled state, the polarization directions of the ferroelectric domains are aligned to be close to the pre-poling field direction[48, 154, 155]. While in the de-poled state, the polarization directions of the polar domains are tend to oriented randomly in the material and the polar domain size may be reduced, which
suggests less dipolar ordering in some parts of the material, such as near the domain walls[48], yielding a small cooling peak. As shown in Figure 6-3, the ferroelectric copolymer P(VDF-TrFE) 55/45 mol% exhibits the largest N-ECE among the three compositions investigated (65/35 mol% and 75/25 mol% are the other two). This is highly related to its high TrFE content, which reduces its ferroelectric ordering and lowers its FE-PE transition temperature compared with the other two copolymers[154, 155]. The 75/25 mol% copolymer has a high ferroelectric dipolar ordering and exhibits the smallest N-ECE[154, 155], i.e., $\Delta S = 0.5$ J/(kgK), at room temperature. When the depoling field is removed, the normal ferroelectric P(VDF-TrFE) copolymers recover most of their macroscopic domain conformation and generate an equally small heating peak, as shown in Figure 6-3.

In contrast, the relaxor ferroelectric polymers do not possess macroscopic polarization domains and remnant polarization at zero electric field[100, 156], as shown in the slim D-E loop in Figure 6-2 for the relaxor terpolymer P(VDF-TrFE-CFE). Hence, applying an electric field will induce ordering of dipoles from a disordered polar state, ejecting heat (or causing temperature rise of the material if it is not in the isothermal condition), while removing the field will return the material to its original dipolar-random state, absorbing heat as a result. Owing to the large difference in the dipole conformations between the dipolar-ordered and dipolar-disordered states of the relaxor ferroelectric polymers, a giant ECE (positive ECE) can be stimulated, i.e., an adiabatic temperature change $\Delta T > 16^\circ$C and $\Delta S > 75$ J/(kgK), under a field higher than 150 MV/m[28, 50, 60, 103], which has been discussed in previous chapters.
Now if one can design and fabricate a dielectric material in which, at the poled state, the dipoles are holding in an ordered orientation exhibiting relatively large remnant polarization, and the ordered state can be converted to and maintained at a dipole random state when subjected to a field in opposite direction of the original poling direction, absorbing heat, then one can overcome the limitations of conventional dielectric materials (periodic heating and cooling). Because this de-poling process involves a transition from a strongly dipolar-ordered to a strongly dipolar-random state, the N-ECE can be much larger than that in a normal ferroelectric. Moreover, upon decreasing the de-poling field to zero, the dipolar conformation can still retain its dipolar-disordered state, which will diminish the follow-up heating signal that is typically observed in the normal ferroelectric polymers. In this chapter, we demonstrate that such a polar-dielectric material can be realized in normal ferroelectric/relaxor ferroelectric polymer hybrid blends, in which the coupling between the two constituents (ferroelectrics and relaxors) stabilizes the dipolar-ordering in the relaxor ferroelectric region in the pre-poled state, see Figure 6.3 of the D-E loop of the hybrid blend, while in the de-poled state, the dipolar-random state can be retained by the relaxor ferroelectric terpolymer in the blends after the de-poling field is reduced to zero.
Figure 6-4. (a) The dielectric constant vs. temperature measured at 1 kHz for the 65/35 mol% copolymer, the terpolymer, and the TC50-65/35 blend. (b) D-E loop of TC50-65/35 blends. The blue arrow points out the de-poling direction from spontaneous polarization.

Figure 6-4(a) and Figure 6-4(b) present the temperature dependent dielectric constant and the D-E loop of the hybrid blends with 65/35 mol% copolymer. The weight ratio between the two polymers is 50/50, presenting a lower remnant polarization $P_r$ and coercive field $E_{coer}$ than those of the pure ferroelectric copolymer, which is understandable because of the presence of 50 wt% of dipolar-random terpolymer in the blends. Here we denote this hybrid as TC50-65/35, where T and C are referring to terpolymer and copolymer, respectively; 50 refers to the wt% of the terpolymer inside the hybrid blends; and 65/35 refers to composition of the ferroelectric copolymer. Since the densities of the two polymers are nearly the same, i.e., 1.75g/cc, the volume ratio of the two polymers participates in the hybrid blend is nearly the same as the weight ratio.
Figure 6-5. A bipolar D-E loop (first poling) and a series of unipolar loops that induced by different de-poling fields (0.1 Hz). Each de-poling loop was measured after a 100 MV/m poling (0.1Hz).

A comparison in D-E loops shown in Figure 6-3 implies that TC50-65/35 blends have a remnant polarization of \( P_r = 0.044 \, \text{C/m}^2 \), which is not far from that of the copolymer \( P_r = 0.054 \, \text{C/m}^2 \). Considering that the terpolymer content is 50 wt% in the blends, the observed large ratio of \( P_r(\text{blends})/P_r(\text{copolymer}) \) suggests that the normal ferroelectric copolymer induces dipola-ordering in the terpolymer regions as well, in the poled state, resulting in a larger \( P_r \) rather than 50% of \( P_r(\text{copolymer}) \). The detailed poling and de-poling operation were recorded by a series of D-E loops presented in Figure 6-5. Each de-poling loop was performed after a 100MV/m poling. At 40 MV/m de-poling field, the polarization reduced from spontaneous polarization, reduced and maintained at
zero-polarization state. The de-poling D-E loops indicate that ordering of dipolar orientation states in such ferroelectric/relax blends can be tuned into disordered state from ordered state (after the first poling). In addition, when the proper de-poling field is removed, the dipolar orientation state is maintained as a disordered state. As indicated in Figure 6-6, higher de-poling field would result in an ordering of dipoles again, to the opposite direction from the original poled direction. The related EC response will be discussed in following paragraphs and here we note this as field-overshoot.

Differential scanning calorimetry was performed to characterize the phase transition behavior in the terpolymer, copolymer and blends. The results are presented in Figure 6-6 for the terpolymer, the 65/35 mol% copolymer, blends of TC50-65/35, respectively. The blends display two distinguishable melting peaks, corresponding to those of the copolymer and terpolymer, and also a FE-PE transition peak, due to the ferroelectric copolymer, albeit the FE-PE transition peak is broader in the blends compared with the neat copolymer, owing to the structure interactions between the copolymer to the terpolymer.
Figure 6-6. (a) DSC scans taken during heating and cooling runs, showing the melting of the copolymer (~ 151 °C), the terpolymer (~ 120 °C), and the FE-PE transition of the copolymer. (b) Copolymer DSC scans taken during heating and cooling runs. (c) Terpolymer DSC scans taken during heating and cooling runs. (d) Specific heat data measured during cooling using a modulated DSC.

In pre-poled TC50-65/35 hybrid blends, applying a de-poling field will transfer the material to a dipolar-random state, yielding a large N-ECE, as shown in Figure 6-7, where the TC50-65/35 blends exhibit an A-ECE and display an EC induced entropy change $\Delta S = 11.5$ J/(kgK) ($\Delta T = -2.1$ K) when the de-poling electric field = $E_{coer}$, the coercive field, indicated by the blue arrow in the D-E loop in Figure 6-5(b). More interestingly, the hybrid blend does not show a follow-up heating peak when the de-
poling field is removed, yielding a new class of EC material which displays a large N-ECE without the follow-up heating peak under a complete electric pulse, i.e., the A-ECE.

Figure 6-7 presents the A-ECE for the hybrid blends in different P(VDF-TrFE) copolymer compositions. It is noted that the TC50-65/35 hybrid blends exhibit the largest A-ECE. The TC50-55/45 blends show a smaller A-ECE, which is majorly owing to their low dipole ordering in the poled state (see the D-E loop in Figure 6-8(a)). On the other hand, TC50-75/25 exhibits an N-ECE as appears in normal ferroelectrics, i.e., a small cooling peak ($\Delta S = 1.8 \text{ J/(kgK)}$) as the de-poling field is applied, followed by a weak heating peak ($\Delta S < 1 \text{ J/(kgK)}$) upon the removal of the de-poling field, which is also consistent with the D-E loop of TC50-75/25 shown in Figure 6-8(b).

![Figure 6-7](image-url)  

Figure 6-7. The anomalous ECE in TC50-55/45 and TC50-65/35, and the N-ECE in TC50-75/25.
The D-E loops in Figure 6-8 indicate that the blends with 55/45 mol% copolymer display a very low remnant polarization, i.e., $P_r$ of the blends is less than 50% of $P_r$ exhibited in the neat 55/45 mol% copolymer, suggesting that in the TC50-55/45 blends, the weak ferroelectric ordering in the 55/45 mol% copolymer is too weak to stabilize the polarization in the terpolymer in the poled state and instead being dominated by terpolymer contents, resulting in a weak polar-ordering in the poled state and a smaller A-ECE, compared with the scenario of TC50-65/35. On the other hand, the blends with 75/25 mol% copolymer (TC50-75/25) display a D-E loop not much different from that of the neat copolymer and hence display an N-ECE as the copolymer P(VDF-TrFE) exhibit a quite strong ferroelectric phase owing to the less TrFE presented in the copolymer.

Figure 6-8. Comparison of the D-E loops: (a) 55/45 mol% copolymer and TC50-55/45 blends, and (b) 75/25 mol% copolymer and TC50-75/25 blends.
Figure 6-9 presents the de-poling field-dependence of A-ECE. The data indicate that the A-ECE induced entropy change keep increasing with the intensity of the de-poling (or “negative”) field till it reaches the coercive field $E_{\text{coer}}$. As the “negative” de-poling field increases beyond $E_{\text{coer}}$, the blends will be poled to the negative direction to induce a field overshoot, as arrows in D-E loops presented in Figure 6-10, generating a heating peak again due to the increased ordering, as shown in Figure 6-9 (a) for the de-poling field = 40 MV/m. When the de-poling field is applied, the blends will exhibit cooling first and then heating as the field is further extended to become higher than coercive field $E_{\text{coer}}$. After the field becomes larger than $E_{\text{coer}}$, the total polarization of the blend is oriented to the negative direction (polarization reverse) and hence shows a positive ECE, i.e., a cooling peak as the field is removed, as shown in experimental data in Figure 6-9 (a) for the de-poling field is 40 MV/m, 10 MV/m higher than the coercive field of the blends. Figure 6-9(b) summarizes this field dependence of the A-ECE as well as the case when de-poling fields is larger than $E_{\text{coer}}$, i.e., the field overshoot region, for the TC50-65/35 blends. An A-ECE of $\Delta S=11.5$ J/(kgK), which is corresponding to $\Delta T=-2.1$K temperature change, is recorded when the de-poling field is right at the $E_{\text{coer}}$, which is 30 MV/m.
Figure 6-9. Temperature and electric field dependences of A-ECE. (a) Evolution of the A-ECE vs. de-poling field strength for TC50-65/35, from the A-ECE at E < E_{coer} to the field overshoot region (40 MV/m) where the applied field first induces a cooling peak and then, immediately, a heating peak as the field exceeds E_{coer}. As a result of the poling under E=40 MV/m, the blends also show a heating peak upon reducing the field to zero. (b) $\Delta S$ and $\Delta T$ vs. the applied de-poling field at 24 °C, showing the evolution from the A-ECE to the field overshoot ECE. The $\Delta S$ for the field overshoot ECE is the combination of the cooling and heating peaks at the application of the de-poling field. (c) $\Delta S$ vs. temperature under 30 MV/m. Increasing temperature causes a reduction of E_{coer} and hence a crossover from the A-ECE to the field overshoot when measured under a fixed field. (d) 2-D plot (temperature and de-poling field) of the A-ECE and field overshoot regions for the TC50-65/35 blends. The black curve indicates the boundary between the A-ECE and field overshoot ECE.

For ferroelectric materials, E_{coer} is dependent on temperature, and hence the A-ECE response changes with temperature under a given de-poling field. Figure 6-9(c) plots the A-ECE vs. temperature for blends TC50-65/35 under the same de-poling field of 30 MV/m. At temperatures below 28 °C the blends show features of A-ECE, while
above that temperature, field overshoot ECE behaviors are observed owing to $E_{\text{coer}}$ become smaller than 30 MV/m at temperatures higher than 28 °C. A 2-dimensional graph of the evolution of A-ECE as functions of both the de-poling field and temperature is presented in Figure 6-9(d).

![Graph of polarization vs electric field](image)

**Figure 6-10.** Schematic illustration of (a) the de-poling field $< E_{\text{coer}}$, and (b) the de-poling field $> E_{\text{coer}}$, the field overshoot case.

The evolution of the EC response under the de-poling field at each individual $E_{\text{coer}}$ of different compositions in blends, from the N-ECE of the neat copolymer (Figure 6-3) to the A-ECE (Figure 6-7) of the TCx -65/35 blends with the terpolymer content $x$, was investigated and exhibited in Figure 6-11. As the relaxor ferroelectric terpolymer content $x$ in the blends increases beyond zero, the N-ECE induced cooling peak ($\Delta S$) increases while the follow-up heating peak decreases. At $x=50$ wt% (TC50-65/35), the cooling peak reaches the maximum while the heating peak disappears that is where the A-ECE
reaches its maximum. Beyond \( x = 50 \text{ wt}\% \), the blends exhibit the A-ECE as well. Because \( E_{\text{coer}} \) reduces (and hence the applied de-poling field also decreases) with \( x \), the A-ECE (cooling peak covered area) becomes smaller with \( x \) for \( x > 50 \text{ wt}\% \). For TC75-65/35, the cooling peak becomes smaller than the instrument resolution. One extreme case that the “blends” with \( x=100 \text{ wt}\% \) are the pure terpolymers, which have \( E_{\text{coer}} = 0 \) at room temperature and exhibit giant positive ECEs\cite{28, 50}.

![Graph showing ECE vs. terpolymer content](image)

**Figure 6-11.** The evolution of the ECE vs. the terpolymer content, \( x \), in the blends of TC\( x \)-65/35 for the de-poling field = \( E_{\text{coer}} \). With increased \( x \), the blends evolve from the N-ECE to the A-ECE, i.e., the cooling peak (\( \Delta S \)) of the N-ECE increases and the heating peak decreases till TC50-65/35, at which point no heating peak is detected. For \( x>50 \text{ wt}\% \), the blends show the A-ECE, and now the cooling peak decreases with \( x \). The blends TC50-65/35 show the largest \( \Delta S \) of the cooling peak. Measurements were carried out at different temperatures for different compositions so that the \( \Delta S \) of the cooling peak is the largest for a given composition.
6.4 Summary

As a short summary, an anomalous EC effect, in which an electric pulse applied to a dielectric material to instantly generate cooling without follow-up heating, is observed in a normal ferroelectric/relaxor ferroelectric polymer hybrid blend. It is believed that the effect is a result of the mesoscale dipolar coupling between the two participants, i.e., the normal ferroelectric component induces dipolar-ordering in the relaxor polymer matrix in the poled state, which can be switched to a de-poled state (dipolar-random state) by an external field; when the de-poling field is reduced to zero, this de-poled state can be maintained by the relaxor component. This newly demonstrate phenomenon paves a way to produce anomalous, large EC effect through engineering inhomogeneous dipolar couplings, and thus could lead to many potential device applications. These devices are capable to absorb heat from the surroundings without subsequent heat release to the surroundings. It is utterly interesting to probe the dipolar conformations by enabling two or more very different dipolar materials, through which new modulation method could be revealed and hence lead to novel application with such new phenomenon observed.
Chapter 7
Conclusions and Future Works

7.1 Conclusions

In conclusion, this dissertation is focus on concurrent investigation on both electrocaloric (EC) based thermal management devices/refrigerators and related material systems engineering for the need of various device configurations. By first studying the possible device configuration theoretically, numerically and experimentally, preferred material figures of merit thus can be summarized in order to achieve better performances in devices, i.e., higher COPs and cooling power densities.

Electrocaloric effect (ECE) is a reversible temperature/entropy change in a dielectric material induced by an external electric field. In general, such electric field induced thermal responses is exhibiting only when the electric field is varying, e.g., heat ejection as applying an electric field and heat absorption as removing an electric field for the normal ECE case. The periodical heat release and absorption is always occurring in pairs in normal or inverse ECEs. The unique nature of ECE determined that the ECE based refrigeration devices is more relevant to a heat pump that absorb heat at one end and dump the heat to another places. Owing to the nature of the ECE, several material properties are utterly important in order to design an effective and efficient ECE based cooling device after carefully studied the our ECE cooling device prototypes. (i) Giant ECE, i.e., large EC induce temperature change, entropy change, and large EC coefficients, $\Delta S/\Delta E$ and $\Delta T/\Delta E$. (ii) Wide EC operational temperature window $T_{width}$ for operation
between wide temperature difference between cold end and hot end. (iii) High thermal conductivity and thermal conductivity anisotropy in different heat transfer directions in order to maximum the operation frequencies and hence then cooling power densities while reduce the backward heat flows that reduces COPs. (iv) Dielectric strengths and mechanic strengths for a reliable and long-life time operation.

With the further understandings in requirements of device engineering, material parameters can thus be modified. In Chapter 3, we first demonstrated that by making use of defect modifications, ECE operational temperature window Twidth can be significantly widened as a ferroelectric material is tuning into a relaxor ferroelectrics. It is developed a general solution to extend the high ECE performance, which is normally exhibited at a temperature slightly higher than phase transition temperature in ferroelectric materials, to its ferroelectric phase temperature range by introducing random defects (bulkier third monomer or high energy electron irradiation) to reduce the size of the dipolar-ordered phase domains and diminish the dipolar correlations among dipolar states. As a result, terpolymer P(VDF-TrFE-CFE) and irradiated copolymer P(VDF-TrFE) show giant ECE in wide temperature windows that covers the room temperature which is promising in practical cooling applications.

Also from practical point of view, a reliable and long life-time operation in these dielectrics requires an operation electric field below 30% of their breakdown field. It is essentially asking for a high ECE at lower electric field for a given dielectric. In Chapter 3, we further discussed that at partially irradiated copolymer P(VDF-TrFE) where multiple phase may coexist and maintain a delicate degree of correlations, ECE can be dramatically enhanced in all applied field range. We demonstrated that a 20 Mrads
irradiated copolymer exhibit 35 K temperature drop under and electric field of 180 MV/m, which is the highest at the field range in all reported pristine polymer system. The low-field performances are also improve to 5 K under 50 MV/m. Beside the EC enhancement regardless of the applied electric field, we further revealed a general approach that is effective on low-field EC performance only. We showed that by blend 10 mol% of ferroelectric copolymer in a 90 mol% relaxor terpolymer matrix, the blend is dominated by the features of relaxor. However, after employing a pre-poling to the system, an internal field can be established in the matrix that is owing to the present of ferroelectric contents, which exhibit a remnant polarization. As a result, the internal electric fields work with external fields, significantly enhanced the ECE especially at low fields. A 40% enhancement at 50 MV/m has been observed.

Ferroelectric polymer is promising in designing EC base cooling device owing to its large ECE, however, it is also features low thermal conductivity and soft mechanic properties. In order to ensure a thorough heat exchange between the polymer-made EC module and external environment, the module cannot made very thick due to the small thermal diffusion length. Additionally, the soft polymer presents a mechanic issue especially when a relative movement is always needed in the heat pump operation. On the other hand, the ceramic features high thermal conductivity and strong mechanic properties, which make it promising as a material candidate of EC cooling devices.

However, previously reported ECE in bulk ceramics are very low, around 1-2 K, which is not practical for real devices. In Chapter 4 we addressed the challenge by modifying the ferroelectric ceramic BaTiO3 to its invariant critical point (ICP). By adding Zr atoms to occupy the B site of the ceramic, the resulted Ba(ZrxTi1-x)O3 (BZT)
exhibited significant enhancement in ECE and EC coefficients. In addition, the modification manipulates the ferroelectric BT to a relaxor-like BZT, which extend the EC operational temperature window. As a result, 4.5 K EC induced temperature change is observe at 14.5 MV/m and the $T_{\text{width}}$ is wider than 20 °C near the room temperature. In order to be more practical, multilayer ceramic capacitor (MLCC) based on modified BT is fabricated to generate large ECE at low voltage. The MLCC is fabricated in facilities at MRI, Penn State University. As expected, thus fabricated ceramic thick films (20 µm thick) double layer ceramic features higher breakdown field and a better EC coefficients compared with BZT bulk ceramic which has a thickness around 100 µm. EC induced temperature change is recorded to above 6.5 K under and electric field of near 20 MV/m.

We extend the ECE study from solid to fluid dielectrics in Chapter 5. The reason for fluid EC material is interesting is its capability in flow. As a solid EC material which is employed to move back and forth on a regeneration layer, the EC fluid can be designed to flow in a circle and exchange heat with itself, employing the fluid flowing in the other half circle as regeneration layer. An fluid EC material enables new design of cooling device which can be flowing in micro-fluidic channels to perform cooling effect for lab-on-chip systems. However, normally dielectric fluid possessing high dipole moment has a low chemical window and very high dielectric loss. And a low dielectric constant fluid would exhibit limited responses to external electric field owing to the low dipole moments. In Chapter 5 we demonstrated that, utilizing indirect ECE measurement, a large ECE is presented in one class of dielectric fluid, nematic liquid crystals (LCs). As a demonstration, a typical nematic LC, 5CB, is picked for study, also owing to the suitable nematic-isotropic transition temperature (35 °C). Indeed, a large ECE is observe at a
temperature that is slightly higher than N-I transition temperature. Inside a thin LC cell, an EC induced temperature change of 5 K was predicted under an electric field of 90 MV/m. The finding reminds us that it is possible to make use of fluid like material to generate large thermal responses directly with electric fields.

At last but not the least, we first observed an anomalous ECE (A-ECE) which only generate cooling peak under a complete electric pulse without any thermal ejection accompanied. By delicately modified a normal ferroelectric/ relaxor ferroelectric polymer hybrid blend, a large A-ECE, $\Delta S=11.5$ K, was directly recorded. In such a blend, the ferroelectric participant serves as a dipolar-ordering maintainer which converts terpolymer content into a relatively ordered phase upon pre-poling. As the blend is de-poled at an electric field near the coercive field, the ferroelectric phase losing control of ordering and the relaxor ferroelectric terpolymer dominates that matrix and prevent a subsequent heating from happening which is normally the case in inverse ECE. Although the A-ECE induced entropy change is still small compared to ECE and N-ECE in polymers, the instant cooling feature and low operation electric field open opportunities to exploring the new material systems that possess much larger A-ECE for particular applications where instant cooling under a short electric pulse and without subsequent heating is desired. Such a phenomenon leads to new designs of EC-based cooling and provides flexibility when integrated with materials with normal ECE and N-ECE.

At the end of the summary, we summarize EC properties of different organic and inorganic materials in Table 7-1 and 7-2, respectively. EC features that are critical to EC cooling device engineering are listed.
Table 7-1. Summary of the electrocaloric properties among different organic materials.

<table>
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<tr>
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<td>50</td>
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<td>0.72</td>
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<td>Direct</td>
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<td>100</td>
<td>60</td>
<td>12</td>
<td>0.60</td>
<td>&gt;40</td>
<td>Direct</td>
<td>[This work]</td>
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<td>P(VDF-TrFE-CFE)</td>
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<td>0.18</td>
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<td>100</td>
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<td>7.6</td>
<td>0.38</td>
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<td>100</td>
<td>50</td>
<td>10</td>
<td>0.50</td>
<td>&gt;40</td>
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<td>&gt;40</td>
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<td>10</td>
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<td>100</td>
<td>18</td>
<td>0.18</td>
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<td>&gt;20</td>
<td>Indirect</td>
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Table 7-2. Summary of EC properties of BZTs developed in this thesis with other direct measured EC properties of inorganic materials in literatures.

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<td>2.1</td>
<td>0.93</td>
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<td>69</td>
<td>4.2</td>
<td>15</td>
<td>0.5</td>
<td>&gt;30</td>
<td>Direct</td>
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<td>40</td>
<td>4.9</td>
<td>9.7</td>
<td>0.88</td>
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<td>DSC</td>
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<td>0.75</td>
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<td>Ceramic MLCC</td>
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<td>0.7</td>
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<td>1</td>
<td>2.13</td>
<td>5</td>
<td>DSC</td>
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<td>1.1</td>
<td>2.5</td>
<td></td>
<td></td>
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<td>1</td>
<td></td>
<td></td>
<td>DSC</td>
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7.2 Future Works

The objective of this dissertation is to explore material-device relations in designing an EC based thermal management device. The advances in devices and materials are always coupled and it is not wise to separately consider each one of them. From device designing point of view, currently developed materials have already possessed great potentials of practical device demonstration. By further understanding the device operation and especially the regeneration process, more compact cooling device with higher theoretical COPs and cooling power densities can thus be expected. For example, recently a multilayer EC ring rotatory cooling devices has been proposed which is predicted to possess much larger COP than one-dimensional oscillatory EC cooling device, which is discussed in Chapter 2. Figure 7.1 presents a finite element method simulated results of such a device.

![Figure 7-1. COMSOL simulated result of a rotary EC cooling device. (a) Temperature distribution on the EC ring. (b) Average temperature on each plate.](image)

Figure 7-1. COMSOL simulated result of a rotary EC cooling device. (a) Temperature distribution on the EC ring. (b) Average temperature on each plate.

The preliminary experimental results, using commercial BT MLCCs, already proved that fundamentals such a rotary device. Device dimensions and configurations can be further optimized such as surface area, number, and thickness of EC elements. By
utilizing the device configuration, new EC materials with much better EC performances, such as, BZT near ICP, modified PVDF-based polymers, PVDF-based nanocomposites, may be planted into the system to maximize the device performance in future study.

It is very interesting and fundamentally of great importance to bring up a standard parameter, a figure of merit in order to evaluate the performance of EC based cooling device. Future study is demanded to consider extract each unique parameters and combine them into one figure of merit. It should be noted that there exist two basic heat pump mechanisms. One is cyclic mechanism, such as cooling devices based on VCR, MCE and ECE, which were discussed in previous chapters; the other is based on thermoelectric effect. The latter can be evaluated by ZT, as the figure of merit of the device. The energy efficiency of the former is normally direct given by COP. It requires further study on EC device prototypes to fully evaluate the COP which can be given by the cooling power density over all power put into the system, including electric power for charging and discharging the EC modules and the power for moving the modules.

From the material science point of view, it has been clearer that although giant ECE is still very interesting in scientific regime, high ECEs at low-fields, or at electric fields much lower than the breakdown field of the dielectric, are more promising in practical applications. In addition, a good EC material may not be the material that possesses the highest EC induced temperature change and entropy change, but a material with a reasonably large ECE and desired material properties as a whole. Such as high thermal conductivity, mechanic durability and low cost.

Compared to PVDF based relaxor ferroelectric polymers, ceramic is generally recognized to possess above three features. However, the EC induced temperature
changes in bulk ceramics and MLCCs are still much smaller than polymers, even when
the ceramic system has been modified to its ICP. For example, BZT at its ICP, x=0.2, the
achieve EC temperature drop is still less than 5K. In this case, theoretically, there is four
individual phases coexisted at the ICP. To induce more ECE, key is to maximize the
participating phases that provide more degrees of freedoms. In Landau theory, more-
phase coexistence is possible. A more complicated ceramic solid solution may provide
more degree of freedom if properly designed.

Based on discussion in Chapter 3 and 4, it should be noted that PVDF-based
ferroelectric polymer feature large ECE but a low thermal conductivity. On the other
hand, BZT ceramics possess a much smaller ECE compared to polymer but a very high
thermal conductivity. Therefore, it is a reasonable idea to make polymer/ceramic
nanocomposites by rationally selecting the material participants and their forms in order
to make use of the benefits of all material contents. It has been reported that a P(VDF-
TrFE-CFE)/BST/BNNS nanocomposite exhibits giant ECE owing to the modified
polymer/ceramic nanoparticle interfaces, where BST is referring to Ba(Sr,Ti_{1-x})O_{3} solid
solution and BNNS refers to Boron Nitride nanosheet. Moreover, the nanocomposite
feature improved thermal conductivity owing to the presents of BST and BNNS. The
breakdown strength of the material is also improved. However, the low vol% of inorganic
parts prevents to keep improve ECE of the nanocomposite. In addition, BST does not
perform large ECE at room temperature. A nanocomposite with high vol% of ECE active
inorganic nanoparticles such as BZT nanocomposite may be a practical approach to form
an EC material with high thermal conductivity, mechanically strong and reasonable ECE.
Challenges are how to fabricate the nanocomposite with evenly distributed high vol%
nanocomposite and how to prevent the conduction and dielectric loss induced by space charge polarization and conduction channel. Recently, a bio-inspired approach is introduced to reduce the issues caused by organic/inorganic interfaces. Dopamine, a hormone which is secreting in brain and play important roles in motor control, motivation, arousal, cognition, and reward of human being, is applied to coat nanoparticles for a better connection with organic matrix. It is expected that the high vol% nanocomposites (30-50 vol%) could lead to a good EC material in which ECE, thermal properties and mechanic properties can be reasonably balanced.

Practical material parameters should also be carefully studied in future. Such as degradation and fatigue of the material, these properties hasn’t been studied for EC cooling device design but is utterly important for designing an real EC device practically. In addition, mechanic wearing and friction issues should be put into great attention in order to design a material with capabilities to operate for a long life-time reliably.

Fluid-like EC material is promising owing to its ability to flow in formed channels and provide cooling. In ideal case, such a fluid can work with solid EC material to serve as both heat transfer fluid and active cooling agent. However, the liquid crystal, 5CB, studied in this dissertation only shows a large ECE at narrow temperature range near its N-I transition temperature. It is understandable considering the ECE in the 5CB is also a presentation of the transition heat from isotropic to nematic phases. In addition, the required electric field is still too large for generating such an ECE. It is highly desired to dramatically extend the operational temperature window and reduce the operation electric fields.
Blue phase LCs (BPLC), an optic isotropic phase in between nematic and isotropic phase, may provide opportunity to reduce the electric field required for generation of large ECE. On one hand, the macro-scale isotropic phase indicates a random conformation of the molecular structure. On the other hand, using electric field to align molecules in blue phase (BP) is obviously much easier than that in isotropic liquid phase. The challenge is normally blue phase has a temperature range of only several degree wide. To address that, polymer stabilized BPLC has been demonstrated to stabilize the BP in a much wider temperature window. In such PSBPLC, it is possible to apply smaller electric field to introduce large ECE in a much wider temperature range. However, owing to the fact that the fluid is confined in thick glass LC cells, direct measurement of ECE in fluid is yet to be demonstrated.

Other organic fluids which may possess large ECE have been summarized in Table 7-3. High permittivity organic fluid may be a direction to investigate potential large ECE in fluids which would enable simple and more compact cooling devices.
<table>
<thead>
<tr>
<th></th>
<th>Formula</th>
<th>Density</th>
<th>Dielectric constant</th>
<th>Boiling Point / °C</th>
<th>Melting point / °C</th>
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</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>C2H3N</td>
<td>0.786</td>
<td>37.5(20)</td>
<td>81.6</td>
<td>-46</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>C3H3N</td>
<td>0.81</td>
<td>33(20)</td>
<td>77</td>
<td>-84</td>
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<tr>
<td>Benzonitrile</td>
<td>C7H5N</td>
<td>1.01</td>
<td>25.9(20)</td>
<td>191</td>
<td>-13</td>
</tr>
<tr>
<td>Butanenitrile</td>
<td>C4H7N</td>
<td>0.7954</td>
<td>24.83(20)</td>
<td>117.5</td>
<td>-112</td>
</tr>
<tr>
<td>N,N-Dimethylacetamide</td>
<td>C4H9NO</td>
<td>0.9429</td>
<td>38.85(20)</td>
<td>166</td>
<td>-20</td>
</tr>
<tr>
<td>N,N-Dimethylformamide</td>
<td>C3H7NO</td>
<td>0.944</td>
<td>38.25(20)</td>
<td>153</td>
<td>-61</td>
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<tr>
<td>Dimethyl Sulfoxide</td>
<td>C2H6OS</td>
<td>1.092</td>
<td>47.24(20)</td>
<td>189</td>
<td>18.4</td>
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<tr>
<td>Ethylene carbonate</td>
<td>C3H4O3</td>
<td>1.321</td>
<td>89.78(40) 69.4(91)</td>
<td>246.7</td>
<td>34-37</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>C2H6O2</td>
<td>1.115</td>
<td>41.4(20) 37.1(25)</td>
<td>195</td>
<td>-13</td>
</tr>
<tr>
<td>Formamide</td>
<td>CH3NO</td>
<td>1.133</td>
<td>111(20) 103.5(40)</td>
<td>210</td>
<td>2-3</td>
</tr>
<tr>
<td>N-Methylacetamide</td>
<td>C3H7NO</td>
<td>0.946</td>
<td>178.9(30)</td>
<td>204 - 206</td>
<td>26 - 28</td>
</tr>
<tr>
<td>N-Methylformamide</td>
<td>C2H5NO</td>
<td>1.003</td>
<td>200.1(15) 189(20)</td>
<td>198-200</td>
<td>-3</td>
</tr>
<tr>
<td>N-Methylpropionamide</td>
<td>C4H9NO</td>
<td>0.931</td>
<td>170(20) 151(40)</td>
<td>146</td>
<td>-43</td>
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<tr>
<td>Nitrobenzene</td>
<td>C6H5NO2</td>
<td>1.205</td>
<td>35.6(20) 34.82(25)</td>
<td>210-211</td>
<td>5-6</td>
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<tr>
<td>Nitroethane</td>
<td>C2H5NO2</td>
<td>1.045</td>
<td>29.11(15) 28.06(30)</td>
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<tr>
<td>Nitromethane</td>
<td>CH3NO2</td>
<td>1.1371</td>
<td>37.27(20) 35.87(30)</td>
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<td>-29</td>
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<tr>
<td>1-Nitropropane</td>
<td>C3H7NO2</td>
<td>0.993</td>
<td>24.74(15) 23.24(30)</td>
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<td>-108</td>
</tr>
<tr>
<td>Propanenitrile</td>
<td>C3H5N</td>
<td>0.77</td>
<td>29.7(20)</td>
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<td>-93</td>
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<tr>
<td>Propylene carbonate</td>
<td>C4H6O3</td>
<td>1.21</td>
<td>66.14(20)</td>
<td>240</td>
<td>-55</td>
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Reference

1. Arora, R.C., Refrigeration and air conditioning. 2010, New Delhi.


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134. !!! INVALID CITATION !!!


VITA

Xiaoshi Qian

Xiaoshi Qian obtained his B.S. and M.S. at Nanjing University, China, majoring in materials science and engineering. In 2010, he joined Dr. Qiming Zhang’s research group at Penn State University to pursue his Ph.D. in electrical engineering. Extensively trained during his master and Ph.D. studies, in which he learned fundamentals to conduct a proper research along with various hands-on, characterization, simulation skills, he devoted himself intensively to giant electrocaloric effect related researches in multiple material systems and device engineering, which is regarded as emerging science and technology that would lead to revolution in thermal management technology such as refrigeration, air-conditioning, on-chip cooling and bio-medical thermal treatment. He authored 24 journal papers which have been cited over 300 times. As a Ph. D. student, he served as a peer reviewer for technical journals such as Nature Communications, Applied Physics Letters, Journal of Materials Chemistry A &C, Physical Chemistry Chemical Physics, RSC Advances. For his Ph. D. thesis study, he is awarded Dr. Nirmal K. Bose Dissertation Excellence Award in 2014.