Progress Report

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The Pennsylvania State University

Giant Electrocaloric Effect
In Ferroelectrics With Tailored Polar-Nanostructures

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Summary of Accomplishments

Electrocaloric effect (ECE) is the temperature and/or entropy change in a dielectric material caused by an electric field induced polarization change. Although ECE has been studied since 1930s, the very small ECE observed in earlier studies in bulk materials before 2007 makes it not attractive for practical cooling applications. The objectives of this DOE program are to carry out a systematical scientific research on the entropy change and ECE in polar-dielectrics, especially ferroelectrics based on several fundamental hypotheses and to search for answers on a few scientific questions. Especially, this research program developed a series of polar-dielectric materials with controlled nano- and meso-structures and carried out studies on how these structures affect the polar-ordering, correlations, energy landscapes, and consequently the entropy states at different phases and ECE. The key hypotheses of the program include:

(i) Whether a large ECE can be obtained near the ferroelectric-paraelectric (FE-PE) transition in properly designed ferroelectrics which possess large polarization P and large β (the coefficient in the thermodynamic Landau theory where the Gibbs free energy G = $G = G_0 + \frac{1}{2} a P^2 + 1/4\ b P^4 + 1/6\ c P^6 - EP$, *and* $a = \beta (T - T_c)$, where b,c,β and T_c are constants)?
(ii) What determines/determine β? Whether a ferroelectric material with built-in disorders, which disrupt the polar-correlations and enabling a large number of local polar-states, such as a properly designed ferroelectric relaxor, can achieve a large ECE?
(iii) How to design a ferroelectric material which has flat energy landscape so that the energy barriers for switching among different phases are vanishingly small? What are the necessary conditions to maximize the number of coexisting phases?
(iv) How to design ferroelectric materials with a large tunable dielectric response? That is, at zero electric field, the material possesses very low polar-correlation and hence a very small dielectric constant, under the application of electric field, the material develops long range polar-correlation and hence a high dielectric response. Studying and developing these materials will deepen our understanding on the polarization responses in strongly coupled materials and the roles of molecular and nano, meso-, and micro-scale defects and structures on the polarization responses. On the application front, besides ECE, these dielectrics will also have great impact on micro-electronics and communications.
(v) The multi-field effect, besides the electric, elastic and even magnetic effects, could be made use of to tune the energy landscape of polar-materials and hence enhance the ECE. Hence the question is what are the suitable material systems to develop and maximize the multi-field effects?
(vi) Besides solid dielectric, liquid dielectrics with properly designed molecular structures and dipolar coupling can also exhibit a large ECE near the dipolar order-disorder transition. The study of order-disorder transition and their influence on entropy change and ECE will provide additional avenue to study dielectrics and understand relationship between the polar-ordering and dipolar entropy in dielectrics.
(vii) Besides the regular ECE in which applying an electric field will induce dipolar ordering, there are dielectric material systems which can exhibit negative ECE in which the applied field will reduce the dipolar ordering and anomalous ECE in which applying an electric field pulse will generate cooling only. The question is how to control and balance the nano- and meso-scale polar coupling in dielectrics to achieve such effects?

ECE in dielectrics provides an interesting and effective avenue to probe the polar-correlation in dielectrics. Thus the study of ECE in polar-dielectrics, besides the application values, will also deepen our understanding of strongly coupled materials systems, phase transitions, and materials systems with nano- and meso-scale disorders.

Through the efforts of this DoE program, we have developed understandings for many questions and materials approaches for many hypotheses listed above. The major accomplishments include:
(i) The first one to show that a giant ECE can be obtained in bulk materials of ferroelectric P(VDF-TrFE) copolymer, which has a large β coefficient and high polarization, near FE-PE transition.[1,3,12]
(ii) The first who developed the theoretical analyses on the upper bound of dipolar entropy change in polar-materials and the general approach to maximize the coexisting phases with vanishingly small switching fields among the coexisting phases[10,23] Experimental results confirm these theoretical predictions.[24]
(iii) The first to show that the relaxor ferroelectrics, due to built-in defects structures at nano- and meso scale, exhibit a giant ECE over a broad temperature range.[1,3,7,14]
(iv) The first to show that a large ECE can be obtained near order-disorder transition in dielectric fluids such as liquid crystals with large dielectric anisotropy. Also the study developed a general approach for developing dielectric fluids to achieve a large electric field induced entropy change.[26]
(v) We are starting to explore the multi-field effect (multiferroic effect) in nanocomposites in which there exist large dielectric contrasts between the matrix and nanofilelrs and showed that a significantly enhanced ECE compared with polymer matrix.[36]
(vi) By facially tuning the nano- and meso-scale dipolar coupling, we are the first to show that an anomalous ECE can be obtained in a relaxor/normal ferroelectric blend.[39]
(vii) Introduced and demonstrated that the internal bias field approach can be effective in enhancing the EC response at low electric field. The result is significant since for practical applications, a low applied field is highly desired.
(viii) A high sensitivity ECE characterization system has been developed.

This program has made major contributions to the advancement of the EC materials and understandings of EC phenomena. To reflect the advancement in the EC materials development and scientific understandings on ECE through in this time period (from Sept. 1, 2007 to May 2015), this final report is written based on the reports complied each year through the program. Some early works on the ECE which were obtained using the indirect method are not included in this report.

Major Accomplishments

I. (2007 -2008)

1.1. Electrocaloric effect in the normal ferroelectric P(VDF-TrFE) (55/45) copolymers

We first investigate the ECE in normal ferroelectric P(VDF-TrFE) 55/45 mol% at temperatures near the FE-PE transition. We choose P(VDF-TrFE) 55/45 mol% copolymer because the FE-PE transition is continuous which avoids the hysteresis effect associated with a first order FE-PE transition even at temperatures above the FE-PE transition. Furthermore, among all the P(VDF-TrFE) compositions, 55/45 mol% is the one exhibiting the lowest FE-PE transition temperature (~70°C, see Figure 1) since we are interested in refrigerants for near room temperature operation.

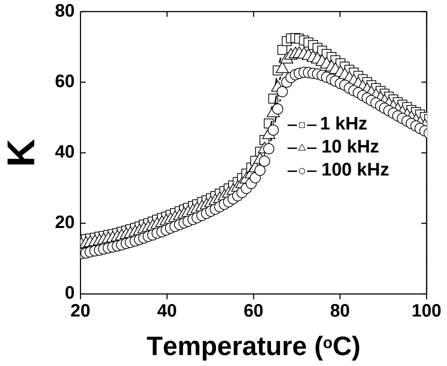


Figure 1 Dielectric constant K of P(VDF-TrFE) (55/45) copolymer under different temperatures and frequencies

The polymer films used in this investigation were made by spin cast method. In general, there are two methods to characterize ECE in dielectrics. One is based on the Maxwell relation (indirect method)

$$\left(\frac{\partial D}{\partial T}\right)_E = \left(\frac{\partial S}{\partial E}\right)_T . \quad (1)$$

where D and T are electric displacement and temperature, S and E are entropy and electric field, respectively. This method is simple. The other method is the direct method which measures directly the isothermal entropy change and adiabatic temperature change due to ECE. In 2007 and 2008, there were very few groups in the world who could directly characterize the ECE.

On the other hand, for the thermodynamically reversible system, the Maxwell relation should be valid for characterizing the ECE. During this DoE project, a high precision direct ECE measurement system was developed. A direct comparison between the indirect and direct method confirmed that the indirect method can be used to characterize the ECE in the normal ferroelectric materials.

To obtain temperature and entropy change of the copolymer, the electric displacement vs. electric field (D-E) loops at different temperature were measured using a Sawyer-Tower circuit with a temperature chamber at 100 Hz. The typical D-E loops of P(VDF-TrFE) (55/45) copolymer under various temperature by applying a maximum voltage of 209MV/m are shown in Figure 2. At 70°C, which is at the FE-PE transition, the D-E loop still exhibits some hysteresis while at 80°C the copolymer exhibits a slim hysteresis loop. Reversible isothermal entropy change ΔS and adiabatic temperature change ΔT as the electric field changes from E_1 to E_2 can be found from,

$$\Delta S = -\int_{E1}^{E2} \left(\frac{\partial D}{\partial T}\right)_E dE \qquad (2a)$$

and

$$\Delta T = -\frac{1}{\rho}\int_{E1}^{E2} \frac{T}{C}\left(\frac{\partial D}{\partial T}\right)_E dE \qquad (2b)$$

where ρ is the density and C is the specific heat.

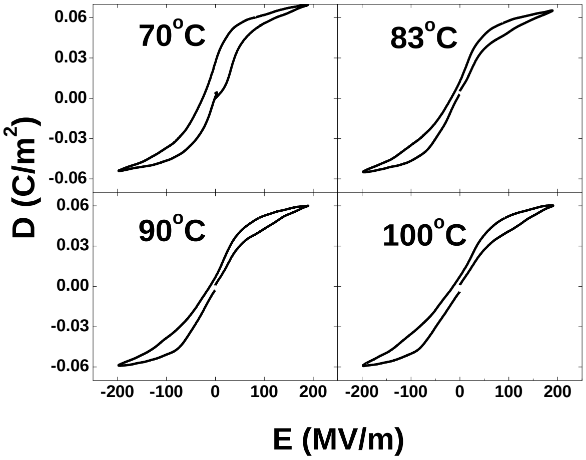


Figure 2 D-E loops of P(VDF-TrFE) copolymer at different temperatures

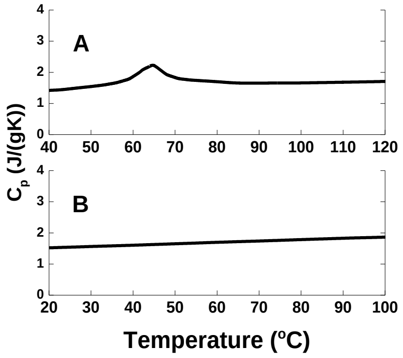


Figure 3 Specific heat for (A) the P(VDF-TrFE) 55/45 mol% copolymer and (B) the P(VDF-TrFE-CFE) terpolymer.

The heat capacity of copolymer was characterized by modulated DSC, as shown in Figure 3 (a). In deducing ΔT from Eq. 2, the heat capacity measured at zero electric field was used. In the temperature range from 80 °C to 110 °C, there is not much change in the heat capacity with temperature, as seen from the figure, which suggests that it will not change with the field very much.

The electric displacement versus temperature taken at different electric fields for the copolymer is shown in the inset of figure 4(a) for data at temperatures above the FE-PE transition where the copolymer displays slim polarization hysteresis loops. The ΔS and ΔT at several electric field levels thus derived are presented in figures 4(a) and 4(b), respectively. The data reveal that the copolymer exhibits a giant ECE, i.e., ΔS of the copolymer is more than 55 J/kgK and ΔT is more than 12°C under an electric field of 209 MV/m in the temperatures around 80 °C. In the whole temperature range from 80°C to 110°C, ΔT is more than 10 °C and ΔS is more than 45 J/kgK.

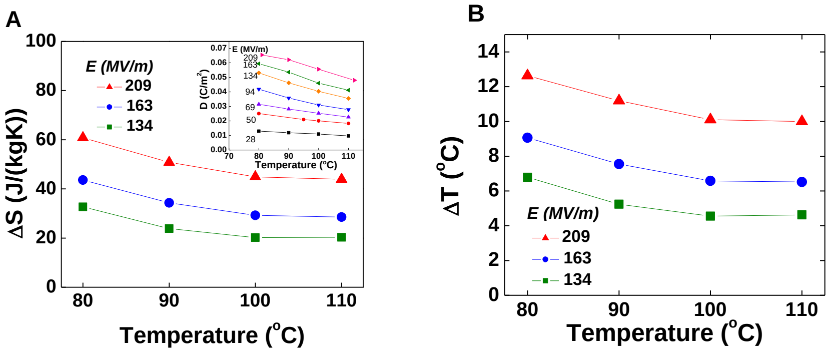


Figure 4 (a) The isothermal entropy change ΔS at temperatures from 80°C to 110°C and different electric fields. The insert shows the displacement vs. temperature taken from the D-E loops at different temperatures. (b) The adiabatic temperature change ΔT of the copolymer films.

1.2. Phenomenological theory of electrocaloric effect of P(VDF-TrFE) (55/45) copolymer

The ferroelectric-paraelectric phase transition of P(VDF-TrFE) 55/45 copolymer is second order. The free energy can be expressed as:

$$G=G_0+1/2\beta(T-T_c)P^2+1/4\xi P^4-EP \qquad (3)$$

where G_0 is the free energy of paraelectric phase; β and ξ are phenomenological parameters, and assumed temperature independent; T_c is the Curie temperature; E is electric field; and P the polarization response.

By differentiating G with respect to P, and dG/dP=0, we get

$$E=\beta(T-T_c)P+\xi P^3 \qquad (4)$$

At zero field,

$$P^2=\beta(T-T_c)/\xi \qquad (5)$$

Further differentiating the Eq. (4) by P yields the reciprocal permittivity,

$$1/\varepsilon=\beta(T-T_c)+3\xi P^2 \ (T<T_c). \qquad (6)$$

and

$$1/\varepsilon=\beta(T-T_c) \quad (T\geq T_c). \qquad (7)$$

Using Eqs. (5) and (7) and the permittivity versus temperature (Figure 1), and the D-E loops under different temperatures, β and ξ can be obtained:

$$\beta=2.4\times10^7\ (K^{-1}) \text{ and } \xi=3.9\times10^{13}\ (m^4C^{-2})$$

The polarization change with temperature under different DC field can be further calculated with Eq. (4). It should be noted that T_c also changes with bias field:

$$\Delta T_c \sim E^{2/3} \qquad (8)$$

From Eq. (3), we can get

$$\Delta S=1/2\beta P^2 \qquad (9)$$

Based on the above equations, the temperature and entropy change under an electric field of 209 MV/m is shown in Figure 5. The calculation results are close to experiment results, but a little higher.

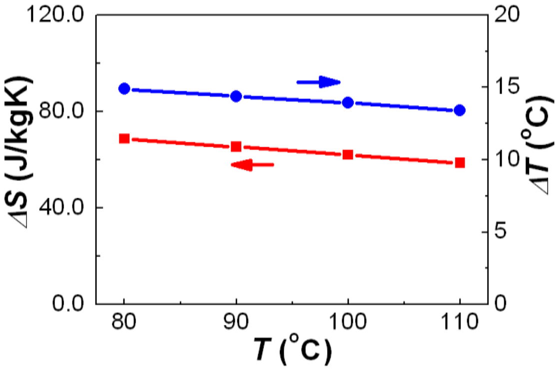


Figure 5. Entropy and temperature change under an electric field 209 MV/m of P(VDF-TrFE) (55/45) copolymer calculated from the phenomenological theory.

1.3. Electrocaloric effect in the ferroelectric relaxor P(VDF-TrFE-CFE) terpolymers

For P(VDF-TrFE) copolymers, experimental results have shown that by defects modification, either through the copolymerization with a bulky monomer such as CFE or CTFE (chlorotrifluoroethylene) to form a terpolymer or by direct high energy irradiation on copolymer films, the normal ferroelectric P(VDF-TrFE) polymer can be converted into a ferroelectric relaxor, which exhibits a large room temperature dielectric constant (~ 55 @ 1 kHz, see Figure 6). At near room temperature, these polymers exhibit a large change of electric displacement with

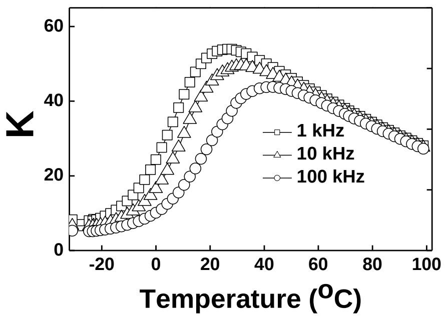


Fig. 6. Dielectric constant of the P(VDF-TrFE-CFE) 58.5/34.3/7.2 mol% terpolymer

temperature, suggesting a high ECE in these polymers at near room temperature.

Here the ECE was characterized by employing the indirect method. The D-E loops for a P(VDF-TrFE-CFE) 58.5/34.3/7.2 mol% terpolymer are presented in Figure 7, from which ΔS and ΔT are determined as shown in Figure 8(a) and (b), respectively. The specific heat used for calculation is shown in Figure 3(b). At 30 °C, ΔS is 20 J/kgK and at 40 °C, it is increased to more than 45 J/kgK and 55 J/kgK at 45 °C to 55 °C, respectively. ΔT for the terpolymer increases from ΔT=4°C at 30°C to more than 12°C at 55°C. All of these values are comparable to that observed in the P(VDF-TrFE) 55/45 mol% copolymer. The difference is that a higher field is required to induce these changes. For the terpolymer, the field is ~ 307 MV/m while for the copolymer it is about 209 MV/m to induce these changes. It is understandable since in the terpolymer, the defects modification lowers the peak dielectric constant and consequently in order to induce the same amount of polarization change, a higher field is required. In addition to P(VDF-TrFE-CFE) 58.5/34.3/7.2 mol% terpolymer, we also studied the electrocaloric effect in terpolymer with the composition of 64.3/27.6/8.1. The terpolymer with this composite exhibits the similar temperature and entropy change as 58.5/34.3/7.2 mol% terpolymer. The maximum entropy and temperature changes are about 63 J/kgK and 12°C at 60°C by applying an electric field of about 300MV/m.

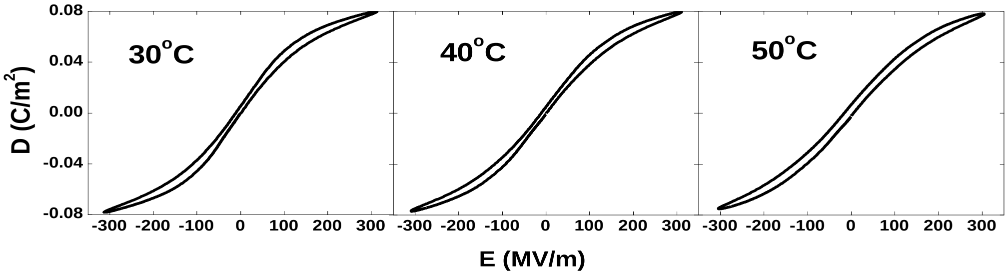


Figure 7 D-E loops of P(VDF-TrFE-CFE) (58.5/34.3/7.2 mol%) terpolymer at different temperatures

As will be shown later in this report, the directly measured ECE in these relaxor terpolymer, in fact, is much higher than that presented in Fig. 8, deduced from the indirect method. The results indicate that for relaxor ferroelectrics, or in general, for no ergodic dielectric materials, the Maxwell relation should be used with caution (or should not be used) since the Maxwell relation is derived based on reversible

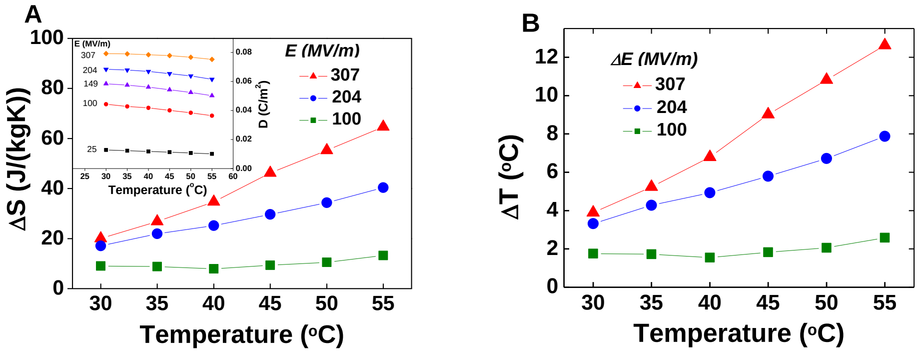


Figure 8 (a) The isothermal entropy change ΔS at temperatures from 30 °C to 55 °C and different electric fields. The insert shows the displacement vs. temperature taken from the D-E loops at different temperatures. (b) The adiabatic temperature change ΔT of the terpolymer films.

(ergodic) thermodynamic relation.

1.4. Electrocaloric effect of PVDF terpolymer/copolymer blend

Previous study showed that by addition of a small amount of P(VDF-CTFE) copolymer into terpolymer, the breakdown field of terpolymer can be greatly improved with reduction of polarization response, which can improve the reliability of terpolymer under high voltage operation. The maximum entropy and temperature change in the blend of P(VDF-TrFE-CFE) terpolymer (58.5/34.3/7.2mol%) and P(VDF-CTFE) (91/9 mol%, 5 wt% copolymer in the blend) copolymer can be as high as about ΔS=50 J/kgK and ΔT=12°C, re at 50 °C.

II 2008-2009

2.1. Large ECE in the high energy electron irradiated P(VDF-TrFE) 68/32 mol% relaxor ferroelectric copolymers.

High energy electron irradiated P(VDF-TrFE) copolymer is another class of relaxor ferroelectric polymers. The effects of different irradiation dosage on the room temperature dielectric properties of P(VDF-TrFE) 68/32 mol% are presented in Figure 1. It is obvious that small amounts of irradiation have a dramatic effect on the dielectric constant of the polymer with the dielectric constant at 1 kHz increasing from 11.7 to 46.2 going from unirradiated to irradiated with a dose of 50 Mrad. This effect is consistent with that previously observed in studies of converting P(VDF-TrFE) to a relaxor by irradiation. As the dosage is increased to 75 and 100 Mrad, the dielectric constant is reduced, due to high levels of crosslinking creating disorder in the crystalline phase and reducing molecular mobility.

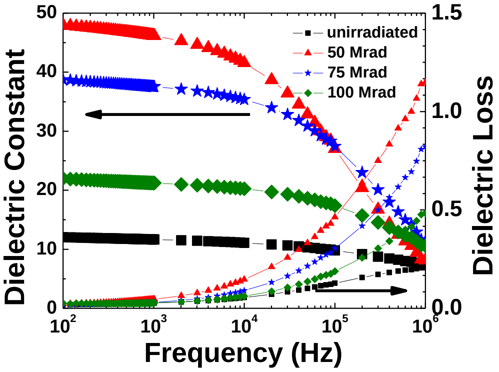


Figure 1. Dielectric constant as a function of frequency for the copolymer treated with different doses

The ECE was characterized using the indirect method (Maxwell relation) on the irradiated copolymer treated with 50 Mrad dose and is presented in figure 2. The results show that the irradiated copolymer exhibits a little bit smaller level of ECE compared with that of the relaxor ferroelectric terpolymer. It is likely that the crosslinking introduced in the irradiation process

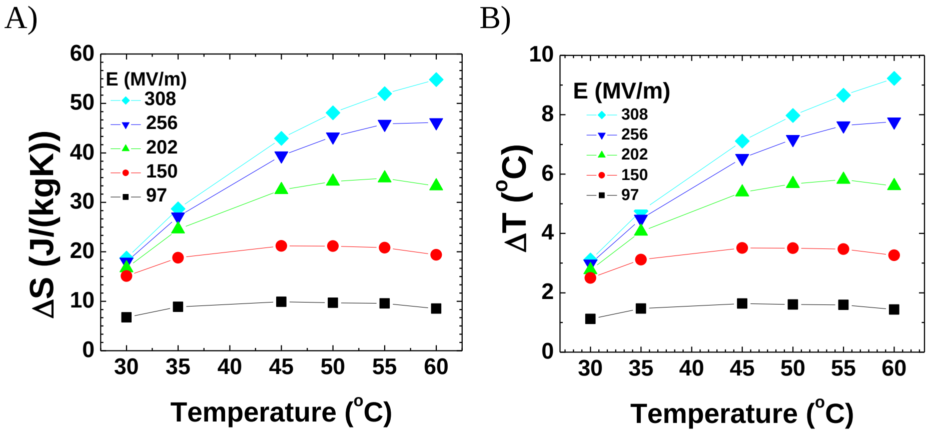


Figure 2: Entropy change (A) and temperature change (B) as a function of temperature measured for P(VDF-TrFE) 68/32 mol% irradiated at 50 Mrad.

restricts the chain motion at high electric field and consequently results in smaller ECE effect.

2.2 Investigation of ECE in crystalline and amorphous phases in the relaxor ferroelectric terpolymer

PVDF based polymers are semicrystalline polymers and how the crystalline and amorphous phases contribute to the ECE is investigated by varying the crystallinity of the polymer. One effective means of varying the crystallinity is to prepare the samples under different annealing and quench conditions. Quenched samples of 59.2/33.6/7.2 mol% terpolymer were prepared by heating the samples to over 200 ℃ where all crystallites were melted and then quickly quenched the samples in ice water.

The DSC analysis shows a difference in the crystallinity between the quenched and annealed samples, with a heat of fusion of 19.8 J/g for the quenched sample in contrast to 23.4 J/g for the annealed sample, indicating a 15% reduction in the crystallinity of the quenched samples compared with the annealed samples

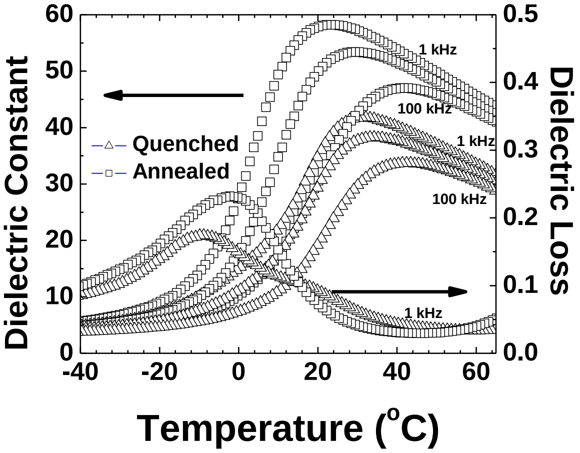


Figure 3: Temperature dependence of permittivity for P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% quenched and annealed.

The dielectric properties as a function of temperature for both quenched and annealed terpolymer films are presented in Figure **3**. Quenched samples exhibit a large reduction in the dielectric constant due to reduced crystallinity. Moreover, the broad dielectric constant peak also moves to higher temperature, occuring at 23.3 ℃ for the annealed sample and 31.6 ℃ for the quenched one, which is related to the dipolar ordering-disordering transition. This may be related to more crystallization in the P(VDF-TrFE) portion than the CFE portion in the quenched sample and thus moving the transition temperature closer to that of the P(VDF-TrFE) copolymer. This is consistent with the phenomenon observed in an early study of the influence of crystallization conditions on

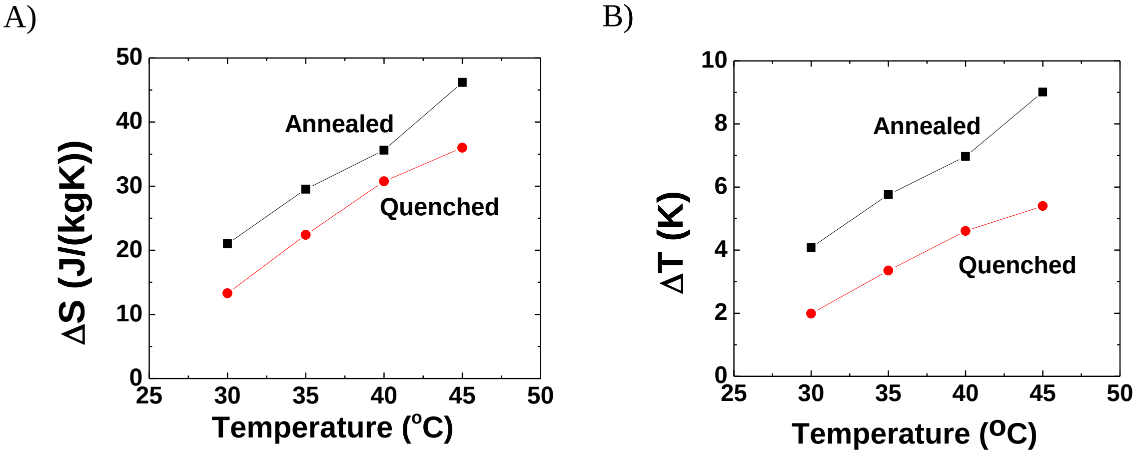


Figure 4. The isothermal entropy A) and adiabatic temperature change B) for the annealed and quenched samples as a function of temperature for the relaxor ferroelectric terpolymer.

the microstructure of the terpolymer where results suggest that within the same crystallite there are some regions with higher CFE content and other regions with lower CFE content.

ECE was evaluated and due to lower crystallinity, the quenched samples show lower ECE as presented in figure 4. The ratio of entropy change of the annealed sample to quenched is 1.58, 1.32, and 1.16 at 30 ℃, 35 ℃, and 40 ℃, respectively, which is consistent with the ratio of crystallinity of 1.18 between the two samples. The results indicate that the major contribution in these ferroelectric polymers to ECE is from the crystalline phase.

To quantify temperature dependence behavior, we plot the ΔS=1/2 βD^2 for the normal ferroelectric P(VDF-TrFE) 55/45 mol% copolymer. As shown in figure 5, for the copolymer, β is nearly a constant for the normal ferroelectric copolymer. For the normal ferroelectric polymer at temperatures above the FE-PE transition, the polarization response is from the dipolar order-disordering process, which is responsible for the temperature independent β and consistent with the thermodynamic phenomenological theory.

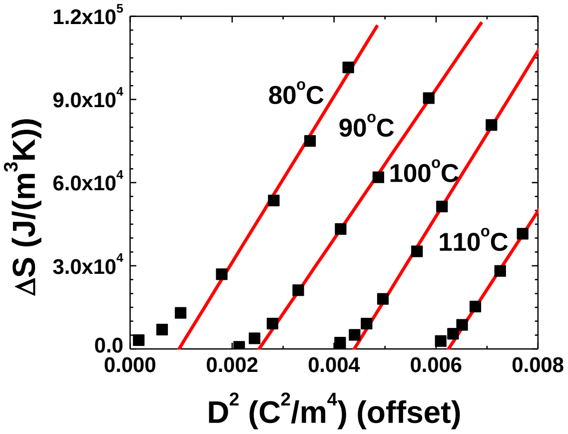


Figure **5**. ΔS ~ D^2 for the normal ferroelectric copolymer

2.4. Preliminary work on elastocaloric effect in shape memory polymers

Based on the Maxwell equation for entropy S, temperature T, strain x, and Stress X,

$$\left(\frac{\partial S}{\partial X}\right)_T = \left(\frac{\partial x}{\partial T}\right)_X . \tag{1}$$

and since **X**=Y**x,** the entropy change can be expressed as

$$\Delta S = -\int_{X_1}^{X_2} \frac{1}{Y^2}\left(\frac{\partial Y}{\partial T}\right)_X XdX . \tag{2}$$

These results indicate that the shape memory polymers developed recently (see figure 6) may provide a material system to realize high elastocaloric effect, attractive for solid state refrigeration.

Based on materials parameters from MM4500, it can be deduced that the isothermal entropy change for this SMP can reach: ΔS = 59.92 J/(kgK). Taking into account the relationship between the temperature change and entropy change, the adiabatic temperature change is ΔT = T_g·ΔS/c_p= 12.68 °C. These preliminary studies reveal the potential of SMP for large elastocaloric effect.

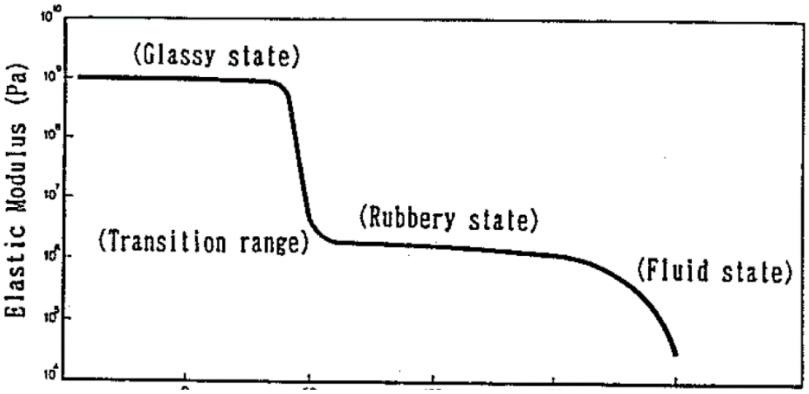


Figure 6: Dynamic characteristic of a SMP (polyurethane MM-4500).

III. 2009-2010

A high resolution calorimetry was developed during this time period, which enabled us to directly measure ECE of various polymeric materials. The capability of directly measuring ECE over a broad temperature and electric field, with high precision and time resolution created a unprecedented opportunity for studying various EC phenomena, many of which could not be studied by the Maxwell relation, and EC materials.

3.1 P(VDF-TrFE) 55/45 copolymers

Direct measurements of ΔS and ΔT have been carried out. Presented in Fig. 1 are some results of ΔS and ΔT thus obtained from P(VDF-TrFE) 55/45 mol% copolymers. For comparison, the data deduced from Maxwell relation at E=134 MV/m are also presented (open circles, indirect data from Science paper). It confirms that a ΔS > 30 J/(kgK) and ΔT ~9 °C could be achieved at E=150 MV/m. The direct measured ECE results are consistent with the results deduced from the Maxwell relations which were reported last year. Hence, these results indicate that the Maxwell relations can be used to reliably deduce ECE in normal ferroelectric materials in the paraelectric phase.

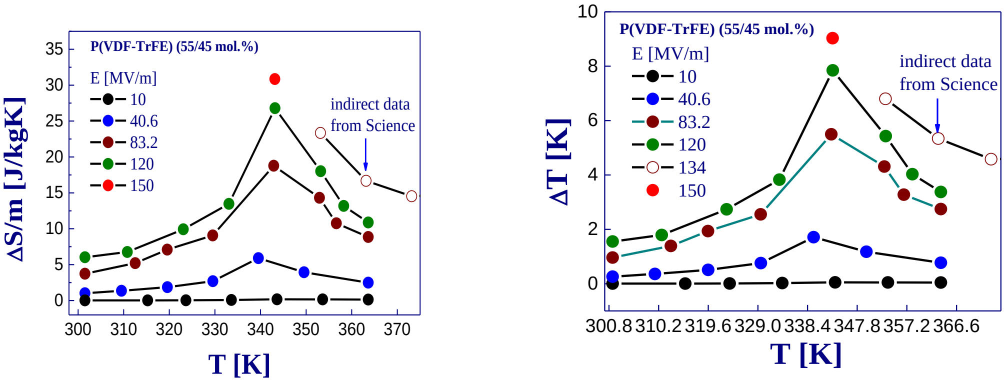


Fig. 1. Direct measured ΔS and ΔT vs T for 55/45 copolymers. For comparison, the results deduced from the Maxwell relation under 134 MV/m (open circles) are also shown.

3.2 P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymers and terpolymer blends with P(VDF-CTFE) 91/9 mol% copolymers

For the P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% relaxor terpolymer, it was observed that by blending it with a small amount of P(VDF-CTFE) 91/9 mol% copolymer, the polarization level is increased, which may result in an increase of the electrocaloric effect. Therefore, both the neat terpolymer and terpolymer blends with P(VDF-CTFE) were studied.

The solution casting method was used to prepare the P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer and blends with P(VDF-CTFE) 91/9 mol% copolymers. It was observed that (i) the ECE measured from the direct method for the terpolymer is much larger than that deduced from the Maxwell relation, which indicates that for the relaxor ferroelectric polymer, even at temperatures higher than the broad dielectric constant peak, the Maxwell relations can’t be used to derive the ECE. This is in sharp contrast to that in the normal ferroelectric polymer P(VDF-TrFE) 55/45%. Since the Maxwell relations are only valid for thermodynamic equilibrium systems (ergodic systems), the results indicate that the relaxor ferroelectric, even at temperatures far above the broad dielectric constant peak still exhibits the non-ergodic behaviour. We note that recently there have been several reports of large ECE in relaxor ferroelectrics, based on the Maxwell relations. The observation here indicates that there results should be treated with great caution. (ii) The ECEs from the neat terpolymer and blends with 5% and 10% of P(VDF-CTFE) are near the same. Since the blends with 5% of P(VDF-CTFE) show higher breakdown strength and hence, it was chosen for detailed study. Fig. 2(a) presents the direct measured ΔT as a function of electric field for P(VDF-TrFE-CFE)-P(VDF-CTFE) 95/5 wt% blends at 45 °C. Figure 2(b) summarizes the directly measured ΔT on the blends with 5% of P(VDF-CTFE), acquired from many film samples. The data show that the ECE of the terpolymer blends does not change much with temperature, which is highly desirable for practical cooling device applications.

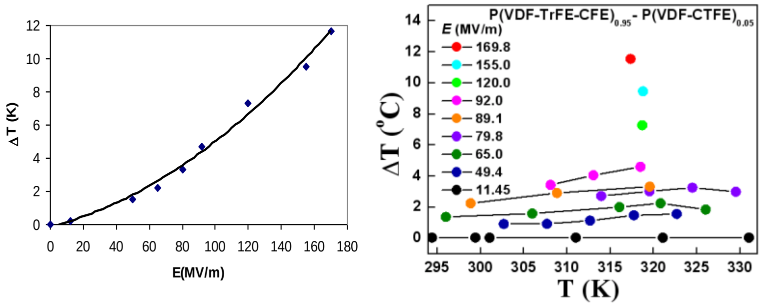


Figure 2. (a) Direct measured ΔT vs E for P(VDF-TrFE-CFE)-P(VDF-CTFE) blends at 45 °C. (b) Summary of direct measured ΔT vs temperature for P(VDF-TrFE-CFE)-P(VDF-CTFE) blends under different electric field

3.3 Irradiated P(VDF-TrFE) 68/32 mol% copolymers

Basic materials considerations and experimental results all indicate that a large polarization change between dipolar ordered and disordered states has a potential to reach high ECE. The high dielectric constant near the broad dielectric constant peak of relaxor ferroelectric materials create a scenario of achieving large ECE over a broad temperature range.

However, in the ferroelectric materials, there exist different types of polarization responses and their contribution to the ECE is different. This is also true for the relaxor ferroelectric materials in which the polarization response can be from the nano-domain re-orientations, which may not generate much ECE, and/or from the intrinsic field induced change between the order and disorder molecular structures, which should have the potential to generate large ECE. For the relaxor ferroelectric polymers, how to engineer the materials to generate large ECE will be a focus in next year's research. Preliminary experimental results in this year show that the relaxor polymers based on the high energy electron irradiated P(VDF-TrFE) copolymers have their polarization responses at temperatures near the broad dielectric constant peak (at room

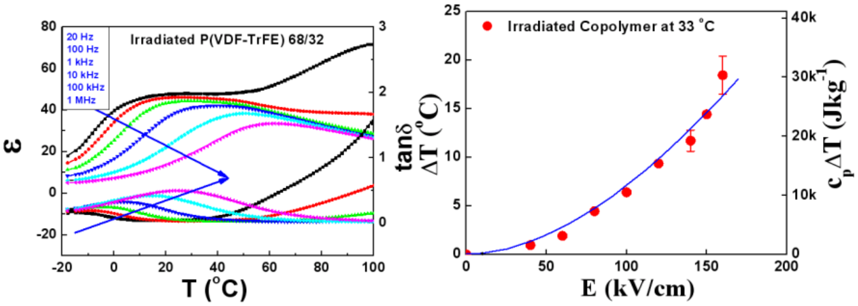


Figure 3. (a) Permittivity (ε) and loss tangent (tanδ) as a function of temperature and (b) Directly measured ΔT and effective heat ($c_p\Delta T$) vs E for irradiated P(VDF-TrFE) 68/32 mol% copolymers at 33 °C.

temperature) mainly from the field induced change between the non-polar and polar molecular conformations, which is different from the relaxor P(VDF-TrFE-CFE) terpolymers, in which there is a large contribution of nano-polar domain reorientations to the polarization responses.

Figure 3(a) presents the permittivity (ε) and loss tangent (tanδ) as a function of temperature, showing that the permittivity peak at 1 kHz is at 32 °C. This permittivity peak is very broad and peak position shifts to higher temperature with frequency, a key characteristics of relaxor ferroelectrics. ECE of the irradiated copolymers was directly measured using the calorimeter developed in our lab. Figure 3(b) shows that the irradiated copolymer exhibits the largest ΔS and ΔT at room temperature: ΔT=18 °C and ΔS= 99 J/(kgK) under an electric field of 160 MV/m. This is by far the largest ECE reported at room temperatures and is much higher than any reported giant magnetocaloric effect. Since this is only the very preliminary study, the results reveal the potential of ferroelectric materials in achieving even large ECE at room temperature. The investigations on the basic mechanisms responsible for the ECE in the irradiated copolymer, compared with the relaxor terpolymer, are still in progress.

3.4. ECE in the defects modified PVDF polymers – P(VDF-CTFE) copolymers

Besides the defects modified P(VDF-TrFE) copolymers, i.e., high energy electron irradiated P(VDF-TrFE) copolymers, we also studied the ECE in defects modified PVDF polymers. P(VDF-CTFE) copolymer exhibits a very large electric energy density (~ 30 J/cm^3) due to its high polarization and electric breakdown, which makes it worthy study of ECE since thermal energy and electric energy, to some extent, are correlated. We used the Maxwell relations to deduce the ECE in P(VDF-CTFE) 91/9 mol% copolymers.

Figure 4 presents the D vs. temperature under different electric fields, obtained from a series of D~E loops measured at different temperatures and electric field, for the copolymers and based on the, the ECE deduced. Very large ECE was deduced for the copolymer of P(VDF-CTFE) 91/9 mol%. To check whether the large ECE is real or due to the limitation of the Maxwell relations, more recently, a direct measurement of ECE in the P(VDF-CTFE) was carried and experimental results indicates that the ECE in the P(VDF-CTFE) copolymers is not as large as that in figure 13, although ΔT = 5.6 ^{o}C and ΔS ~26.3 J/(kgK) were obtained under 300 MV/m which is still quite large.

These results indicate that the defects modified P(VDF-TrFE), such as the irradiated P(VDF-TrFE), is much more promising in realizing giant ECE at room temperatures compared with defects modified PVDFs. In the future, our efforts will focus on these relaxor ferroelectric polymers.

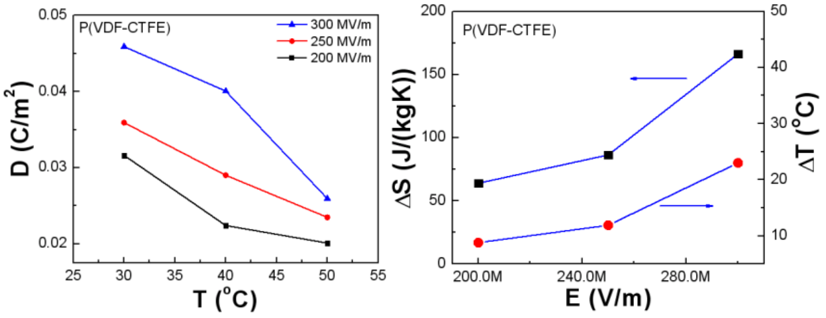


Figure 4. The D vs. Temperatures at different electric fields and the ECE deduced from the Maxwell relations for the P(VDF-CTFE) 91/9 mol% copolymer films at room temperature as a function of electric field.

3.5 Magnetocaloric and pyroelectric coupling for a new class of magnetgoelectric multiferroics

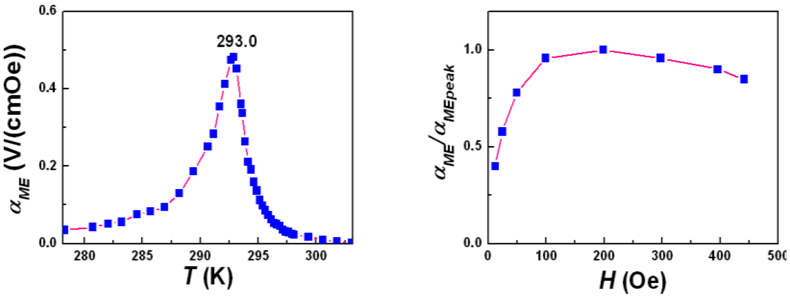
During the past two years, we have devoted a small effort in studying the multiferroic magnetoelectric composites which explore the magnetocaloric and electrocaloric coupling, i.e., the magnetocaloric effect in the magnetic materials and pyroelectric effect (inverse of the electrocaloric effect) in the ferroelectric materials. The study has the potential of creating a new class of multiferroics, which are attractive from the fundamental understanding and practical applications

The magnetoelectric effect in the composite investigated here can be expressed through the thermal coupling, i.e.

$$\alpha_{ME}=\frac{dE}{dH}=\left(\frac{\partial E}{\partial T}\right)_D\left(\frac{\partial T}{\partial H}\right) . \tag{1}$$

Equation (1) indicates that both large $\left(\frac{\partial E}{\partial T}\right)_D$ and $\frac{dT}{dH}$ for this type of ME multiferroic composite (MMC) will lead to a large ME coupling coefficient α_{ME}. Gd crystal with high purity (99.87%) was chosen as the MCE material because it has a MCE peak (or phase transition temperature) near room temperature (21 °C), and it has a large temperature change (~ 3 °C/T when B=2 T). The pyroelectric material used the relaxor ferroelectric polymer which was prepared by irradiating P(VDF-TrFE) 68/32 mol% copolymer films with 1.2 MeV electron first at 100 °C by 35 Mrad and then at 90 °C by 40 Mrad due to the depolarization temperature (~ 21.8 °C) approached the phase transition temperature of Gd, and the polymer has a very high pyroelectric coefficient over permittivity ratio.

Fig. 5 (a) shows that the thermally coupled MMC exhibits a large α_{ME} near room temperature, as we have designed, where α_{ME}=0.5 V/(cm·Oe) was observed for H_0 =180 Oe. Fig. 5 (b) shows that α_{ME} increases with H till 200 Oe and beyond that α_{ME} shows a slight decrease with H. This behavior is consistent with the thermodynamic model of the magnetocaloric effect, which indicates that at low magnetic fields ΔT is proportional to the square of the magnetic field ($\Delta T \sim H^2$). While at high magnetic fields, $\Delta T \sim H^{2/3}$. Thus, $dT/dH \propto H$ at low magnetic fields, resulting in an increase of dT/dH with H; while at high magnetic fields, $dT/dH \propto 1/H^{1/3}$, leading to a decrease of dT/dH with H, as observed in figure 5(b).



(a) (b)

Fig. 5. (a). ME coupling coefficient of the MMC as a function of temperature. An a.c. magnetic field of 2.4 Hz with the amplitude H_0=180 Oe was applied to the composite. (b). Reduced ME coefficient as a function of the applied magnetic field amplitude measured at 292.5 K (the data are presented in reduced unit, α_{ME}/α_{ME}(peak), where α_{ME}(peak) is at H_0=200 Oe).

IV. 2010-2011

4.1 A novel calorimeter based on heat flux sensors

A calorimeter to directly measure the ECE in polymer films has been developed. The calorimeter was based on direct characterization of temperature of the ECE films under different applied electric field and hence a small bead thermistor was used to reduce the thermal load of the temperature sensor. This characterization method is difficult due to the attachment of the bead thermistor to the thin film samples which can cause damage to the thin film samples (~ 4 to 5 μm thick) and limit the measurement to low fields (due to electric breakdown). To obtain a complete set of ECE data, especially to high fields (>100 MV/m), requires measurements on many thin film samples and takes long experimental time. In order to overcome this difficulty, we searched for new methods to directly characterize ECE in polymer thin films and other dielectrics during the 4th year and was successful in finding a high sensitivity flux sensor which can directly measure the heat flux. Making use of the heat flux sensors, a new calorimeter was developed. At first, we measure the heat flux versus time of a reference (e.g. a resistor with resistance R) at an applied voltage V, in which the heat power per unit area ($V^2/(AR)$, V-applied voltage, A-area) is known. Thus the calibration factor for a fixed time period (e.g. 10 s) can be obtained. Then the heat flux versus time of ECE material is measured at an electric field for the same time period (10 s). The real heat flux from ECE material can be obtained by multiplying the measured one with the calibration factor. *This new calorimeter is much easier to use and offers higher sensitivity than the first generation of the calorimeter at Penn State.*

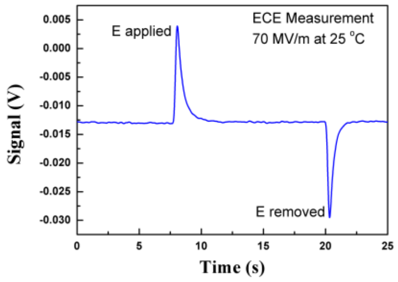


Fig. 1. The ECE signal recorded from the calorimeter developed at at Penn State.

Present in Fig. 1 is the ECE signal recorded from the calorimeter. The data were acquired from a P(VDF-TrFE-CFE) terpolymer when a field is applied (eject heat due to a reduction of dipolar entropy) and removed (absorb heat due to an increase in dipolar entropy).

4.2 ECE in normal ferroelectric P(VDF-TrFE) copolymers, a composition study

Making use of a high resolution calorimeter, we refined the measurement of ECE in 55/45 mol% copolymers and expand the study to P(VDF-TrFE) copolymers with higher VDF/TrFE ratio, such as 65/35 mol% copolymers. Figure 2 presents the ECE results for the 55/45 mol% copolymer which shows that ECE peaks at the FE-PE transition. A ΔT ~ 12 °C can be induced under 120 MV/m and ΔT ~ E^2 as indicated in figure 2(b). P(VDF-TrFE) 55/45 copolymer has a continuous FE-PE

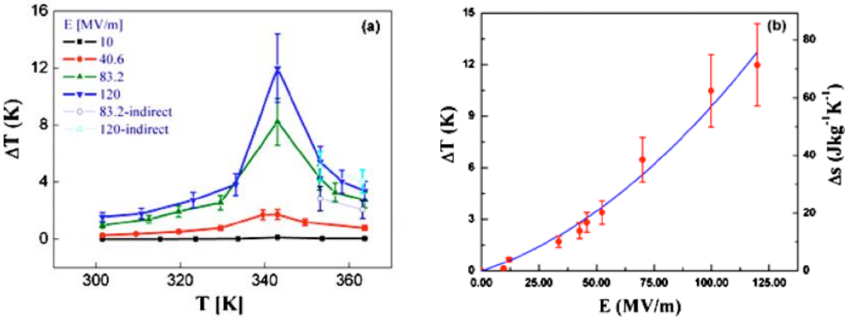


Fig. 2. (a) ECE ΔT versus sample temperature and (b) ΔT and ΔS versus applied electric field for P(VDF-TrFE) 55/45 mol% copolymer at FE-PE transition temperature (67 °C).

transition and there is no thermal hysteresis between measurement carried out in heating and cooling runs.

Figure 3 presents the preliminary ECE results for the 65/35 mol% copolymer (figure 2(a)), along with the dielectric data (figure 2(b)). P(VDF-TrFE) 65/35 mol% copolymer exhibits a first order FE-PE transition and hence the data show hysteresis between the heating and cooling runs. What is interesting is that the 65/35 mol% copolymer exhibits much higher ECE than that from 55/45 mol% copolymer. For example, under a field of 50 MV/m, a ΔT of >7 ^{o}C can be obtained for 65/35 mol% copolymer while the maximum ΔT under the 50 MV/m field for 55/45 mol% copolymer is 4 ^{o}C. The results indicate the potential of using copolymer with higher VDF/TrFE ratio to achieve very large ECE under lower applied field, which is of great interest for practical cooling applications. We plan to carry out this composition study in the future. By defects modifications, the hysteresis associated with FE-PE transition can be reduced or even eliminated.

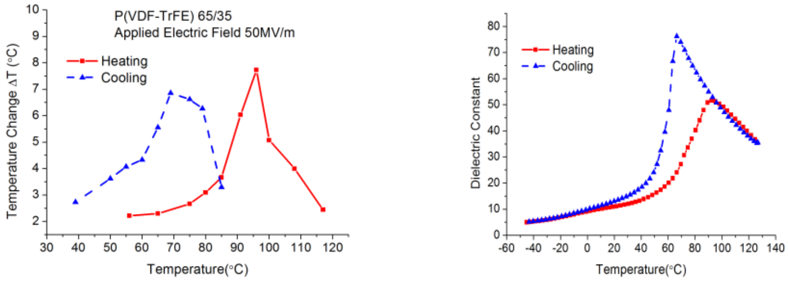


Fig. 3. (a) ECE ΔT versus T at 50 MV/m; (b) Dielectric constant versus T at 1 kHz for P(VDF-TrFE) 65/35 mol%.

4.3 Studies on direct and indirect ECE measurements for relaxor ferroelectric polymers

It is significant to compare the direct and indirect ECE measurement to further understand the mechanism behind the ferroelectric polymer materials. Especially the relaxor ferroelectric becomes a non-ergodic system in some temperature range, in which the Maxwell relation may not be used. Further, the newly developed calorimeter at Penn State allows us to measure ECE in thin polymer films to high fields. Presented in figure 4 is the ECE measured on the terpolymer of P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol%. The terpolymer exhibits a very large ECE (ΔT >15 ^{o}C at 150 MV/m). What is more interesting is that, *the large ECE in the relaxor terpolymer is nearly*

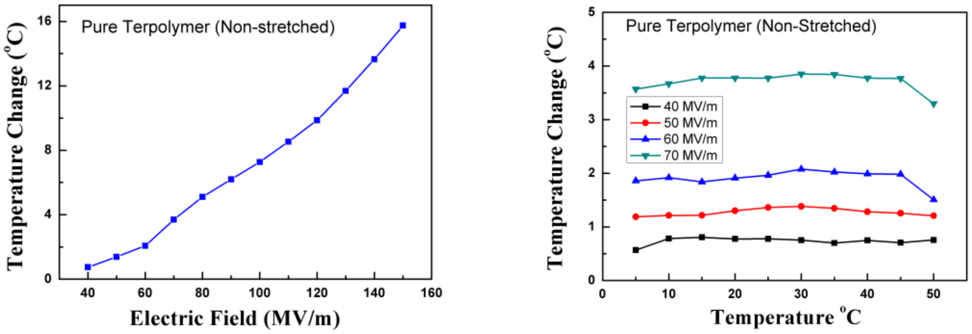


Fig. 4. (Left) ΔT versus applied field at 30 °C and (right) ΔT versus sample temperature under different applied field of the P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer.

temperature independent over a broad temperature range from 5 °C to 45 °C which is highly desired for practical devices. This is in sharp contrast to the normal ferroelectrics (see figures 2 and 3) which have ECE peak at FE-PE transition and display strong temperature dependence. We will develop further understanding on the fundamentals of ECE in the relaxors and their temperature dependence.

We compare the directly measured ECE of the relaxor terpolymer with that deduced from the Maxwell relation, which is presented in figure 5. The results show a large difference in the ECE directly measured and deduced. For example, the deduced ECE in figure 5 shows that ΔT increases with temperature in the same temperature range and is much smaller than that directly measured. The larger difference between the two methods indicates that the Maxwell relation, which is derived for ergodic systems, is not suitable for deducing ECE in the relaxor ferroelectric polymers. The results further indicate that even at temperatures far above the relaxor freezing temperature (~ 277 K) and the broad dielectric constant peak temperature (~ 300 K), the Maxwell relation cannot be used to deduce the ECE reliably in the relaxor ferroelectric polymers. In viewing of the fact that the convenience of the Maxwell relation in deducing ECE makes it widely used in the research community to study ECE from a broad range of ferroelectric materials, the results here indicate that the Maxwell relation should be used with great caution.

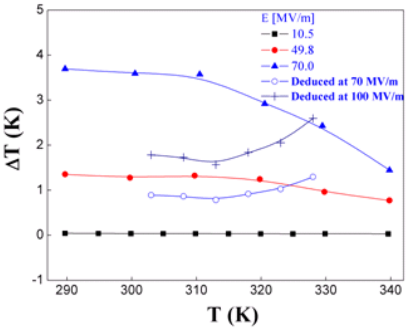


Fig. 5. Directly measured ECE ΔT versus T of the terpolymer. The ΔTs deduced from the Maxwell relation at 70 and 100 MV/m are also shown for comparison.

4.4. Study of fundamentals of ECE in polar-dielectrics and giant ECE in relaxor ferroelectric polymers

In polar-dielectrics, as the electric field is increased from 0 to E, the isothermal entropy change ΔS and adiabatic temperature change ΔT can be expressed as,

$$\Delta S = S(E,T) - S(0,T) \text{ and } \Delta T = T\Delta S/c_E$$

where c_E is the specific heat and S(E,T) is the total entropy at a temperature T and electric field E. Since the lattice entropy is field independent, ΔS is determined by the dipolar entropy S_{dip}. In order to maximize ΔS, it is necessary to maximize the entropy $S_{dip}(0,T)$ at E=0 and minimize $S_{dip}(E,T)$, occurring in a field E sufficiently large to induce polarization saturation. As shown in a recent thermodynamic and statistical analysis, for a system of N dipolar entities, each having Ω discrete equilibrium orientations, the maximum entropy corresponds to the case where all directions i are equally populated or $N_i = N/\Omega$, where N_i is the number of dipoles along symmetry direction i with the condition $\sum_i N_i = N$,

$$\Delta S = \frac{\ln \Omega}{3\varepsilon_0 \Theta} P^2 \qquad (1)$$

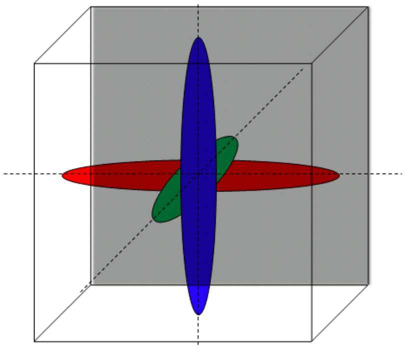


Fig. 6. Schematic of 6 possible polarization directions in a tetragonal ferroelectric phase.

where Θ is the Curie constant in the asymptotic behavior of the linear dielectric susceptibility, $\chi=\Theta/(T-T_0)$, and T_0 the Curie-Weiss temperature for a ferroelectric, ε_0 is the vacuum permittivity. In deriving Eq. (1), it was assumed that $S_{dip}(E,T)=0$, corresponding to the minimum of entropy occurring when all dipoles are aligned along the field E. For normal ferroelectrics such as a tetragonal ferroelectric phase, $\Omega=6$ due to 6 possible polarization directions (see schematic in Fig. 6). Therefore, a dipole system with a larger number of dipole entities Ω and small dipole correlation (small Θ) will have the potential to realize very large ECE.

Relaxor ferroelectrics in which the long-range polarization correlation is disrupted by random defects field, leading to polar-glass states which can be switched to polar-state with high polarization (large P in Eq. (1)), may provide dipolar systems to realize high ECE. The defect fields also break up the global symmetry of lattice, causing large number of disordered fluctuating polarization entities (local polar-states) and nano-polar-regions, which may lead to larger number of Ω. One measure of increased effectiveness of the ECE response is the β coefficient ($\Delta S = -1/2\beta D^2$) which is directly related to the microstructures of a dielectric as indicated by Eq. (1). Figure 7 presents the comparison of the β coefficient between the normal ferroelectric P(VDF-TrFE) copolymer and the defects modified copolymer (high energy electron irradiated) which shows that $\beta=9.3\times10^7$ Jm/KC^2 for the relaxor polymer is larger than that in the normal ferroelectric copolymer ($\beta=5.4\times10^7$ Jm/KC^2).

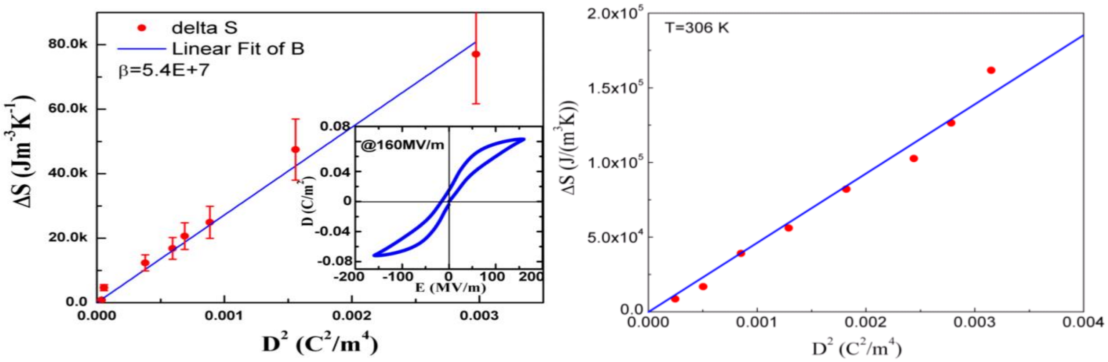


Fig. 7. Comparison of the β coefficient between the normal ferroelectric P(VDF-TrFE) 55/45 copolymer ($\beta=5.4\times10^7$ Jm/KC^2) and the high energy electron irradiated relaxor P(VDF-TrFE) 68/32 copolymer ($\beta=9.3\times10^7$ Jm/KC^2).

V. 2011-2012

5.1 Tuning the electrocaloric effect in the relaxor P(VDF-TrFE-CFE) terpolymer

The ECE in the P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer was studied using the newly developed calorimeter. The ECE as a function of temperature under different applied electric fields for non-stretched films is presented in figure 1(b). The inset shows the adiabatic temperature change ΔT as a function of applied field acquired at 30 ^oC, where a $\Delta T > 15$ K is induced under 150 MV/m. Besides a very large ECE, the data reveal that the relaxor terpolymer maintains a high ECE over a broad temperature range, which is in sharp contrast to what observed in the normal ferroelectric polymer where ECE shows a sharp peak at the FE-PE temperature. Figure 1(c) presents ΔT for 4X uniaxially stretched terpolymer films as a function of temperature under 100 MV/m field and inset shows the field dependence of ΔT measured at 30 ^oC. At 30 ^oC, both non-stretched and 4X uniaxially stretched films display nearly the same ECE. What interesting is that in the same temperature range (from 0 ^{o}C to 55 ^{o}C), the uniaxially stretched films display much prounced temperature variation and at 5 ^{o}C and 55 ^{o}C, ΔT of the uniaxially stretched films is more than 15% smaller, compared with that of the non-stretched films.

The ECE in a dielectric is determined by the dipolar entropy change ΔS_p between the polar- and non-polar states, i.e.,

$$\Delta S_p = S_p(0,T) - S_p(E,T) \qquad (1)$$

where $S_p(0,T)$ is the dipolar entropy when E=0 and $S_p(E,T)$ corresponds to the dipole aligned state when external electric field E is applied. For a dipolar disordered state at E=0 such as the relaxor at temperatures above the broad dielectric constant peak here, $S_p(0,T)$ is proportional to $P^2\ln(\Omega)$, where Ω is the number of possible polar states in the dielectrics, while $S_p(E,T)$ can be approximated as zero (much smaller than $S_p(0,T)$) when E is high.

Therefore, in general, ΔS_p or ΔT under a given field E will increase as temperature is reduced towards the broad dielectric constant peak of the realxor terpolymer (~ 30 ^{o}C) (P increases with reduced temperature). As the temperature is further lowered towards the freezing temperature of the relaxor, remanent polarization will be developed after application of high electric fields, which will result in a decrease of ΔS_p with reduced temperature. Uniaxial stretching of terpolymer films causes preferred polymer chain orientation and hence reduces the number of possible polar states in the dipolar-disordered states and hence Ω. Consequently, ΔS_p is reduced due to a reduced Ω at temperatures above the broad dielectric peak. In addition, uniaxial stretching in general will favor all-trans molecular conformation and hence increase the polar-correlation. Increasing polar-correction in the relaxor polymer at E=0 state will cause a reduction of $S_p(0,T)$. These results indicate that ECE temperature behavior of relaxor polymer or even normal ferroelectric polymer can be tailored by controlling the polymer film processing conditions.

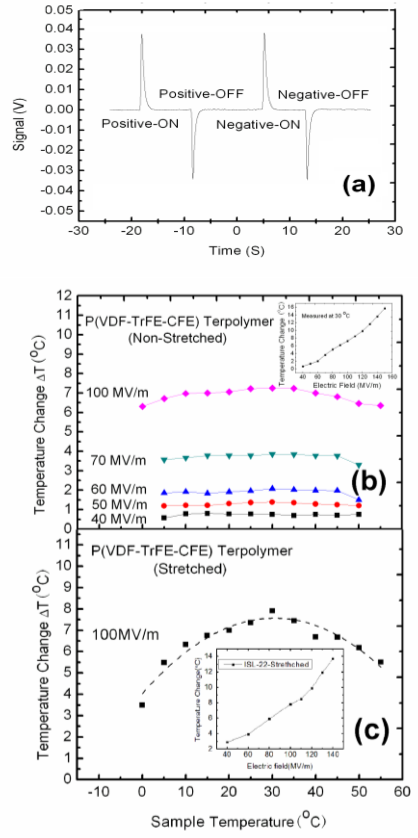


Figure 1. **(a)** ECE signal directly measured **(b)** ΔT as a function of temperature in non-stretched terpolymer under different electric field of 50 MV/m – 100 MV/m, while inset shows the ΔT as a function of applied field. **(c)** ΔT as a function of sample temperature in stretched terpolymer under a constant electric field of 100 MV/m, while the inset shows the ΔT as a function of applied electric field at 30 ^{o}C.

5.2 Electrocaloric effect in ferroelectric P(VDF-TrFE) copolymer with high degree of polar disorder in the ferroelectric phase near a first order transition

As shown in Eq. (1), a large ECE requires the dielectric material possessing a large S(0,T). Several recent studies have demonstrated that polar-dielectrics with a large number of equivalent polar-orientations and short polar-correlation can lead to large dipolar-entropy $S_p(0,T)$ and consequently a large ECE. Near first order ferroelectric-paraelectric (FE-PE) phase transitions, it has also been shown that many intermediate phases with small energy difference among them may exist and the easy polarization switch facilitated by these "bridging" phases can lead to large electromechanical responses. Since entropy is directly related to the "randomness" of a system, increasing the number of coexisting phases, for example, from the intermediate phases with very small energy differences among them, in a ferroelectric material may lead to marked enhancement in the ECE.

In this program, the ECE in a ferroelectric polymer, P(VDF-TrFE) copolymer at the composition of 65/35 mol%, near its first order ferroelectric-paraelectric (FE-PE) phase transition (~ 90 ^{o}C in heating run) was chosen for investigation. Earlier studies have revealed that in this copolymer, besides the normal paraelectric and ferroelectric phases, there exist low temperature phases below the FE-PE transition which contain high degrees of trans-gauche bonds (high degree of disorder), suggesting possible presence of intermediate phases near the FE-PE transition. Increasing the number of coexisting phases at the E=0 state can lead to large ECE. In this study, utilizing the recently developed calorimeter, the ECE in the two half cycles, i.e., the heating half-cycle in which an electric field is applied to the polymer film that causes reduction of entropy in and rejection of heat from the polymer films and the cooling half-cycle in which the field is removed that causes an increase in entropy in and absorbing heat by the polymer films, is directly characterized. The results reveal that there is a large difference between the isothermal entropy changes in the two half cycles and ΔS_h in the heating half-cycle can be much larger than ΔS_c in the cooling half-cycle, might be caused by the presence of intermediate phases. More significantly, the copolymer slightly modified by low dosage of high energy irradiation exhibits a very large ECE (ΔS ~ 160 $Jkg^{-1}K^{-1}$) which is substantially higher than those reported earlier.

A typical ECE signal thus obtained is presented in figure 2(b), where the positive voltage signal is from the heating half-cycle and the negative voltage signal is from the cooling half-cycle. It is apparent that there is a large different between signals in the positive (heating) and negative (cooling) half-cycles and the signals from the positive half-cycle is larger than that of the negative half-cycle. ΔS_h and ΔS_c deduced from the data in the two half-cycles at various temperatures is presented in figure 2(a). At 85 ^{o}C, near the first order FE-PE transition, ΔS_h acquired from several films under 100 MV/m is 156 ± 28 $Jkg^{-1}K^{-1}$ (or a Q = 56.6 Jg^{-1}) while in the cooling $\Delta S_c = 48.9 \pm 0.4$ $Jkg^{-1}K^{-1}$, still quite large albeit much smaller than ΔS_h.

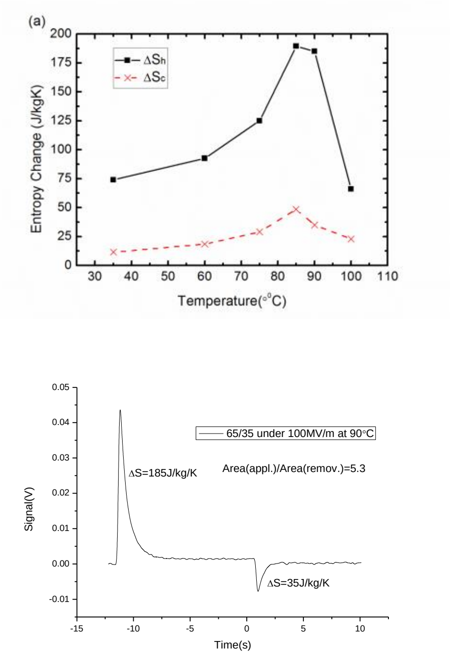


Figure 2. (a) ΔS_h and ΔS_c under 100 MV/m field as functions of temperature and (b) directed measured ECE signal at 90 ^{o}C for P(VDF-TrFE) 65/35 copolymer.

Interestingly, by irradiating the copolymer with 20 Mrads dose of high energy electron (1.2 MeV energy), the dielectric hysteresis is significantly reduced along with a marked reduction in the dielectric peak temperature. T_m at the heating run is reduced to 49 ^{o}C. In the whole temperature range measured (from 25 ^{o}C to 60 ^{o}C), ΔS_c for the modified copolymer is higher than that of normal ferroelectric 65/35 mol% copolymer. At 50 ^{o}C, ΔS_h and

ΔS_c are 87.1 $Jkg^{-1}K^{-1}$ and 59.2 $Jkg^{-1}K^{-1}$, respectively. The difference between the two becomes small with the field cycle and at twentieth cycle, ΔS_h and ΔS_c become 72.6 $Jkg^{-1}K^{-1}$ and 71.6 $Jkg^{-1}K^{-1}$, respectively, implying ΔS_{int} ~ 72 $Jkg^{-1}K^{-1}$ which is larger than the peak value of ΔS_{int} of the normal ferroelectric P(VDF-TrFE) 65/35 mol% copolymer. ΔS_{int} ~ 72 $Jkg^{-1}K^{-1}$ is also very close to the average of ΔS_h and ΔS_c (($\Delta S_h + \Delta S_c$)/2 of the first cycle is 73.1 $Jkg^{-1}K^{-1}$).

The large ΔS_{int} and much smaller hysteresis loss in the modified copolymer are highly desirable for practical cooling device applications. *The directly recorded first cycle ECE data at T = 50 ^oC under 180 MV/m for the copolymer irradiated with 20 Mrads is presented in the inset of figure 3, which has a ΔS_h = 190 J $Jkg^{-1}K^{-1}$, ΔS_c = 130 $Jkg^{-1}K^{-1}$, ΔS_{int} ~ 160 $Jkg^{-1}K^{-1}$ as presented in figure 3*. The inset in figure 3 also shows that the irradiated copolymer with 20 Mrads dose does not show much conduction loss at 50 ^oC, which is very attractive for practical applicatoins. *Combining ΔS_{int} with the DSC data yields a ΔT_{int} = 35 ^oC and ΔT_c = 28 ^oC under 180 MV/m (Fig. 3).* Irradiating the copolymer with higher than 20 Mrad dose causes a reduction of ΔS_h and ΔS_{int}.

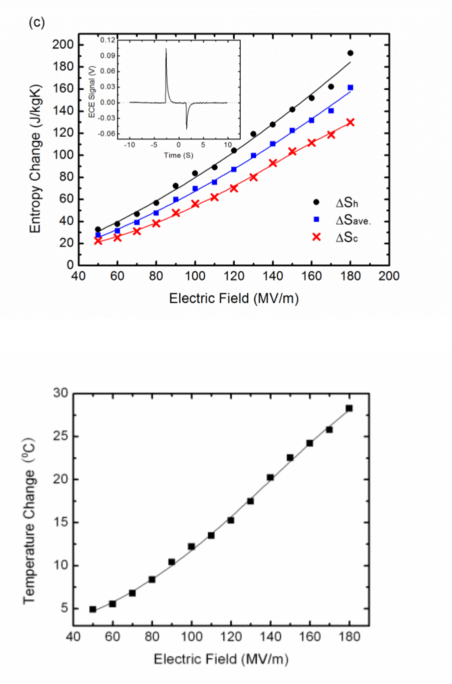


Figure 3. Isothermal entropy change ΔS (top) and ΔT (bottom) of 20 Mrad irradiated P(VDF-TrFE) 65/35 mol% copolymer at 50 C under different electric fields, upto 180 MV/m.

The large difference in ΔS_h and ΔS_c suggests that there are intermediate states with large difference in dipolar ordering but small free energy difference, which is consistent with earlier experimental observations. The mixing of large number of coexisting phases near the first order FE-PE transition leads to high ECE observed. These results demonstrate the promise of achieving significant ECE in ferroelectric polymers or ferroelectrics in general by operating near first order FE-PE transition in which multiple intermediate phases can exist. By properly modifying (or tailoring) these materials, the hysteresis losses can be significantly reduced while significant ECE can be maintained.

5.3 Engineering EC materials near invariant critical point to maximize the number of coexisting phases and minimizing the energy barriers for switching among different phases

One critical challenge in developing ferroelectric materials is to identify promising approaches to achieve high material responses. Recently, it has been demonstrated that by operating near phase transitions, giant EC response can be realized. It has also been shown that the giant electromechanical (EM) response in $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) is a manifestation of two-phase critical points (CPs) that define a line of critical end points (LCEP) in the electric-field–temperature–composition ($E - T - x_{PT}$) phase diagram. Here we developed a theoretical framework to show that not all the points along a LCEP are equal and much larger EM or EC can be realized by maximizing the number of coexisting phases near invariant critical points (ICP).

The Gibbs energy for a ferroelectric is defined with its natural variables being temperature, 6 stresses, 3 electric field, and *c* chemical components with their conjugate quantities being entropy, strains, electric displacement, and the chemical potentials. The Gibbs phase rule of the system is written as, $\nu = c + 1 + 6 + 3 - p = c + 10 - p$, where p denotes the number of phases co-existing at equilibrium. A critical point is defined when the following condition is fulfilled

$$\left(\frac{\partial^2 G}{\partial (X^a)^2}\right)_{Y^{b\neq a}} = \left(\frac{\partial Y^a}{\partial X^a}\right)_{Y^{b\neq a}} = \mathbf{0} \qquad (2)$$

where Y^a and X^a represent a natural variable and its conjugate variable, respectively. Eq. (2) contains c + 9 equations, and consequently the degree of freedom of the system at a critical point becomes zero, i.e. $\nu = c + 10 - 1 - (c + 9) = 0$. We name such a critical point in this c + 10 dimensional space an invariant critical point (ICP). Let n_S represent the number of natural variables fixed in the system, the maximum number of phases that can co-exist is $p_{max} = c + 9 - n_s$, before an ICP is reached. For example, in the $T - x_{PT}$ phase diagram of PMN-PT under the ambient pressure and a given electric field ($c = 2$ and $n_s = 9$ for six stress and 3 electric field components), $p_{max} = 2 + 9 - 9 = 2$, i.e. two phases. In the thin film engineering of a binary system with two in-plane stress components, one has $n_s = 6$ (4 stress and 2 electric field components), $c = 2$ and $p_{max} = 5$. The larger number of coexisting phases at ICP increases the entropy change of ferroelectric and paraelectric transition and results in larger ECe responses.

Considering the EC response, the entropy of a dipolar system can be written as $S_p = -\sum_i \frac{k}{v_i} c_i \ln (c_i/\Omega_i)$, with k, c_i, Ω_i and v_i being Boltzmann constant, volume fraction, number of polar-states, and average volume associated with each dipolar unit in the ith phase, respectively. For PMN_{1-x}-PT_x thin films near the ICP, $p_{max} = 5$, which may include rhombohedral (Rh, Ω=8), two monoclinic (M, Ω=8 for both), orthorhombic (O, Ω=12), tetragonal (T, Ω=6). Assuming c_i =1/5 and $v_i = v_0$ for all the phases one has $S_p = 3.71\ k/v_0$, which is much larger than a composition near pure PMN, (Rh phase), i.e., $S_p = 2.08 k/v_0$, thus achieving a much higher entropy change near ICP than other CPs along LCEP. The result here is consistent with the available experimental results. For example, entropy change ΔS for PMN_{1-x}-PT_x thin films near pure PMN was reported in the range of 1.7 J mol^{-1}K^{-1} to 3.6 J mol^{-1}K^{-1} induced under E > 720 kV/m, in contrast, PMN_{1-x}-PT_x thin films near MPB (x ~ 0.3) exhibit a much higher ΔS, from 3.7 J mol^{-1}K^{-1} to 8.7 J mol^{-1}K^{-1} with E > 600 kV/m. Systematic studies, based on these considerations and guidelines, will be carried out to develop and tailor polar-dielectric material systems.

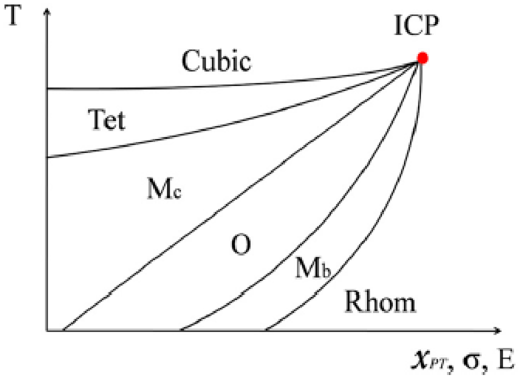


Fig. 4. Schematic of an E-T-σ1-σ2-χ_{PT}-χ_{PM} multidimensional phase diagram with an invarant critical point, using PMN-PT as an example.

VI. 2012-2013

6.1 ECE in liquid crystals with nematic-isotropic phase transition near room temperature

Liquid crystals offer an attractive material system with the potential to achieve high electrocaloric effect. Compared with solid state ECE materials, a dielectric fluid with a large ECE can be more interesting since it could lead to new cooling cycles with simpler structures and even better performance than these based on solid state ECE materials.

In this program we show that a large ECE can be realized in the liquid crystal (LC) 5CB near its nematic-isotropic (N-I) phase transition (see figure 1). The LC 5CB possesses a large dielectric anisotropy which facilitates the electric field induced large polarization change. As a result, a large ECE, i.e., an isothermal entropy change of more than 24 Jkg^{-1}K^{-1} was observed near 39 ^{o}C, near the N-I transition (see figures 2 and 3), which is comparable to these obtained in dielectric polymers with giant ECE.

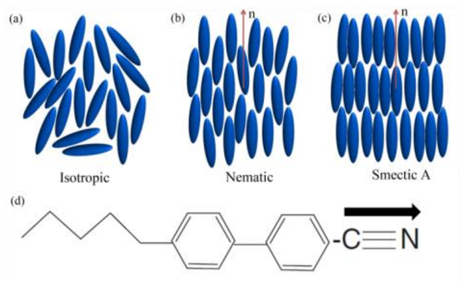


Figure 1. Schematic of various mesophases for rodlike LC molecules which are of interest for generating large ECE: (a) an isotropic, (b) nematic, and (c) smectic A phases, (d) Molecular structure of 5CB.

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. 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. Hence LCs may be ideal dielectric liquids to realize large ECE. For example, as illustrated in Figure 1(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 1(b) and 1(c)). In the nematic phase, the mesogens are aligned, on average, along a preferred direction as defined by a director **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.

In this program, we investigate the ECE in LC 5CB (4-n-pentyl-4'-cyanobiphenyl, see Figure 1(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 ^{o}C) and the mesogens also possess a large dielectric anisotropy. The dielectric constant parallel to the director ($\varepsilon_{\|}$>18.5) is much larger than that perpendicular to the director (~7.5), which provide a strong orientation force to align the mesogens along **n** by external electric field (E // **n**).

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

$$\Delta S = S\left(E_{1,}\ T\right) - S\left(E_2\ T\right) \qquad (1)$$

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. 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), are prepared. In the HA-Cells, the rodlike LC molecules are aligned preferentially along the surface of the substrates. In this study, the HA-Cells have a thickness of 3.2 μm. 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 μm (NA-Cells).

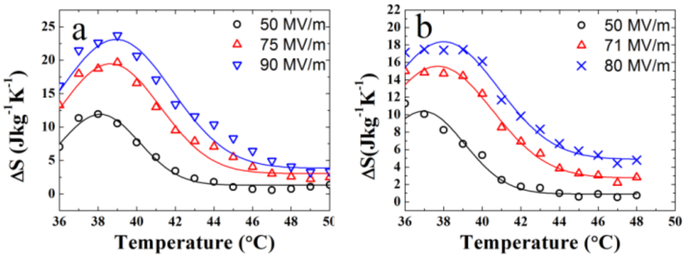


Figure 2. The electrocaloric effect for (a) isothermal entropy change ΔS of 5CB LCs in NA-Cells, and (b) ΔS of 5CB LCs in homogeneously aligned LC cells (HA-Cells) as functions of temperature.

The isothermal entropy change ΔS and adiabatic temperature change ΔT deduced as a function of the temperature are presented in Figure 2 for these two groups of LC samples. *The data reveal that ECE peaks near N-I transition which has ΔS= 24 J/kgK and ΔT=5.2 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 2.

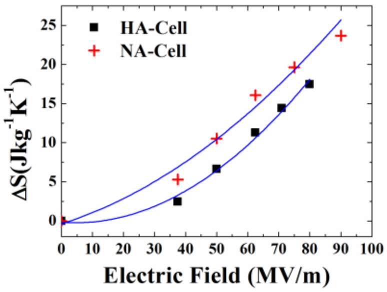


Figure 3. Comparison of ΔS as a function of electric field E of 5CB at 39 ℃ in NA-Cells (crosses) and in HA-Cells (squares).

Figure 3 presents ΔS as a function of applied field amplitude for the two groups of LC cells at 39 ^{o}C which is above the N-I transition. The LC cells without surface alignment display larger ΔS 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, ΔS is reduced. On the other hand, Figure 3 shows that the homogeneous surface alignment broadens the ECE peak, i.e., the FWHM (~ 8 ^{o}C) (full width at half maximum) of ΔS vs. temperature curves for the homogeneously aligned cells is slightly larger than that (FWHM ~ 7 ^{o}C) of the randomly oriented cells.

The ECE in LCs can also be estimated from the phenomenological Landau-de Gennes formulation (LG). According to the LG phenomenological theory, the isothermal entropy change ΔS of a nematic liquid crystal at temperatures above the N-I transition critical point is related to the change of the order parameter Q ($0 \leq Q \leq 1$) as

$$\Delta S = (a/2)\left(Q_1^2 - Q_2^2\right) \tag{2}$$

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, a very large ΔS =55 Jkg^{-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 a $\Delta S = (23 \pm 8.5)$ J kg^{-1}K^{-1}. 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.

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. Moreover, for a given LC, its transition temperature can be tuned by, for example, mixing with other LCs with different transition temperatures. 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. Compared with the conventional cooling cycles, 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.

6.2 Internal DC bias field in the blends of the ECE terpolymer and normal ferroelectric polymer to significantly enhance the ECE at low electric fields.

In the past several years, we have demonstrated giant ECE in several relaxor ferroelectric polymers, which represent the best ECE materials reported in the literature, including polymers, ceramics, and thin films. On the other hand, all the dielectric materials which exhibit substantial ECE display square dependence on the applied field E, i.e.,

$$\Delta S \text{ and } \Delta T \sim E^2 \qquad (3)$$

Hence at low E, the ECE is low, as illustrated in figure 4, which is not desired for practical applications. On the other hand, if there is already an internal DC bias field E_0 in the ECE material, i.e.,

$$\Delta T = \beta E^2 = b\,(E + E_0)^2 \qquad (4)$$

If the applied field is along the same direction as E_0, a large ΔT can be induced at a low E (since $E + E_0$ can be high). For example, for E_0 = 40 MV/m, an E= 40 MV/m is equivalent to a total of 80 MV/m and as seen in figure 4, a ΔT > 5 °C can be induced at 40 MV/m if there is an E_0 = 40 MV/m which is highly desired for practical applications.

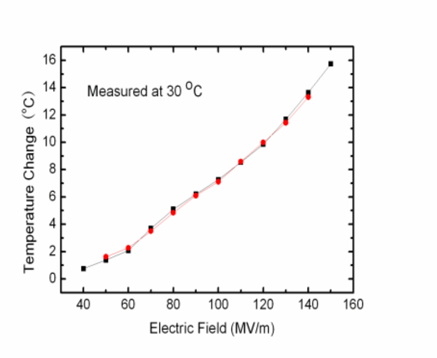


Fig. 4. ΔT as a function of applied field for an ECE P(VDF-TrFE-CFE) terpolymer. Although ΔT is quite high at high field (150 MV/m), at low field such as 40 MV/m, ΔT is near zero

In this program, we first investigate the blends of of P(VDF-TrFE-CFE) with small amount of P(VDF-TrFE) copolymer, which also provide a model system to study how the random defects in the terpolymer influence the polarization response in the copolymer and consequently ECE in the blends. Since P(VDF-TrFE) copolymer belongs to normal ferroelectrics, in which large remanent polarization will exist after poling, the copolymer may provide an internal electric field in the blends, thus generating higher polarization and enhanced ECE. The internal EC bias field can be more effective, as illustrated in figure 5(b), which was prepared to study the poling effect in the terpolymer/copolymer bilayer system.

Figure 6 presents the SEM image of the blends samples. As can be seen, the terpolymer and copolymer are not completely miscible, and possibly the copolymer forms nano-sized crystallites, whose size varies between 30 nm to 100 nm, in the terpolymer matrix. One interesting result of the terpolymer/copolymer blends is the observation of the increase in the polarization response and ECE of the blends, compared with the neat terpolymer, when the amount of copolymer is low < 10 mol% in spite of the fact that the copolymer has a low ECE due to its normal ferroelectric nature. The results suggest that through interfacial effects (which will be studied) the defects in the terpolymer convert the normal ferroelectric copolymer into relaxor.

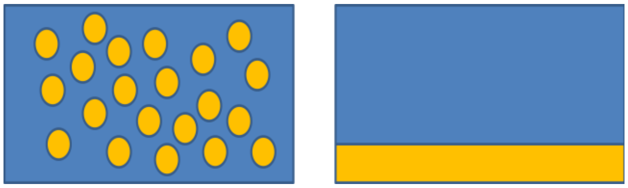


Figure 5 (a) terpolymer/copolymer blends, in which the blue matrix represents terpolymer, and the yellow dots respresents copolymer dispersed in terpolymer, (b) terpolymer/copolymer tandem bilayer, where the blue represents the terpolymer layer and the yellow represents the copolymer layer.

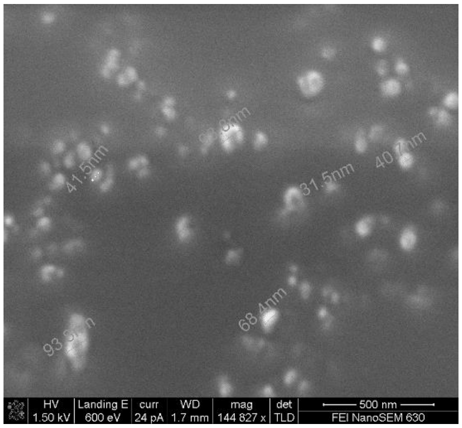


Figure 6. SEM image of terpolymer/copolymer blends surface.

Moreover, figure 7 reveals that the enhancement of ECE in the blends (with 10% P(VDF-TrFE) 55/45 mol% copolymer) is more higher at low electric fields (< 50 MV/m for example) compared with that at the high fields. The results indicate that the P(VDF-TrFE) copolymer act as an effective local DC bias field source to increase the ECE at low fields. To confirm this hypothesis, blends of P(VDF-TrFE-CFE) terpolymer with 10% of P(VDF-TrFE) 65/45 mol% copolymer were studied. As shown in figure 8, the blend exhibits a significant ECE response at 40 MV/m (better than that in figure 4 and even figure 7). The blends in figure 8 differ from the neat terpolymer and also the blends in figure 7 in (i) because of the high VDF ratio (65/35 mol% copolymer) compared with that in figure 7, the copolymer has stronger normal ferroelectric response; (ii) the blend in figure 8 has been subjected to a DC poling field to further enhance the local DC bias field. To further examine the DC bias field effect, bilayers of P(VDF-TrFE-CFE) (62.5/29/8.5 mol%)/P(VDF-TrFE) (65/35 mol%)

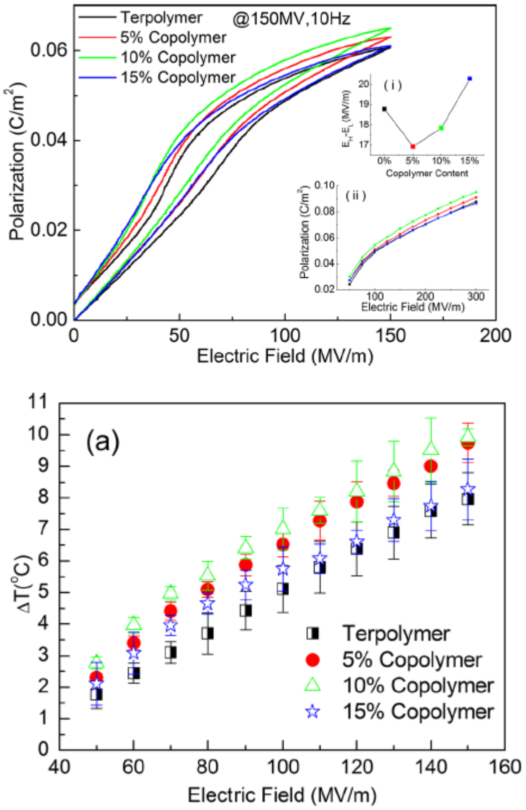
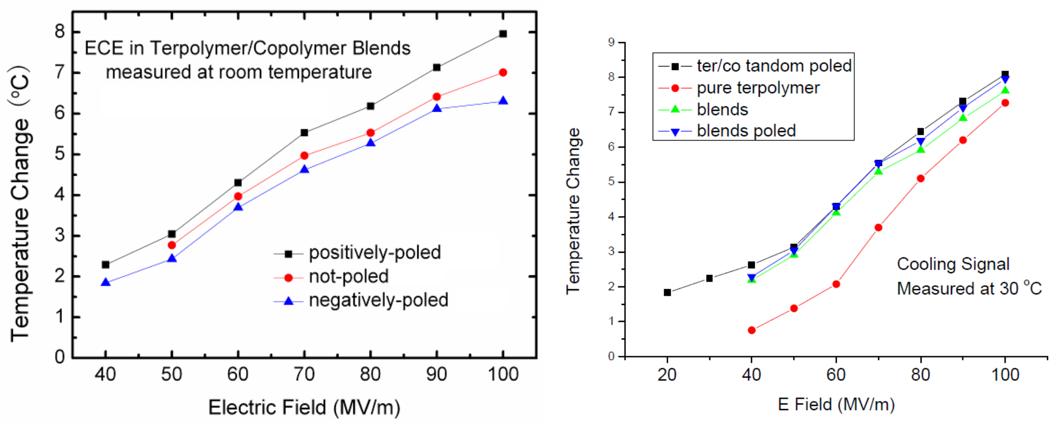


Figure 7. Comparison of (a) the polarization response and (b) ECE of the blends of P(VDF-TrFE-CFE)/P(VDF-TrFE) with that of the neat terpolymer of P(VDF-TrFE-CFE). All measured at room temperature. 55/45 mol% copolymer was used in the blends.

bilayer with 90/10 ratio between the two were fabricated and ECE was investigated. As shown in figure 8(b), the terpolymer/copolymer bilayer exhibits a high ECE even at 20 MV/m field (ΔT ~ 2 °C) while in the neat terpolymer, ΔT is near zero at 20 MV/m.



(a) (b)

Figure 8. The adiabatic temperature change ΔT of the poled blend of P(VDF-TrFE-CFE)/P(VDF-TrFE) 90/10 (a) blends and (b) bilayer as functions of the applied field.

VII. 2013-2014

7.1 Internal DC bias field in the blends of the ECE terpolymer and normal ferroelectric polymer to significantly enhance the ECE at low electric fields.

Here, we continue the study of internal DC bias field to enhance the ECE at low electric fields. As we have shown, all the polar-dielectric materials which exhibit substantial ECE display square dependence on the applied field E, i.e.,

$$\Delta S \text{ and } \Delta T \sim E^2 \qquad (1)$$

(these dielectrics are referred to as the square law dielectrics). Hence at low E, the ECE is low, as illustrated in figure 1, which is not desired for practical applications. On the other hand, if there is already an internal DC bias field E_0 in the ECE material, i.e.,

$$\Delta T = \beta E^2 = b\,(E + E_0)^2 \qquad (2)$$

If the applied field is along the same direction as E_0, a large ΔT can be induced at a low E (since $E + E_0$ can be high). For example, for E_0 = 40 MV/m, an E= 40 MV/m is equivalent to a total of 80 MV/m and as seen in figure 1, a ΔT > 5 °C can be induced at 40 MV/m if there is an E_0 = 40 MV/m built-in in the material, which is highly desired for practical applications.

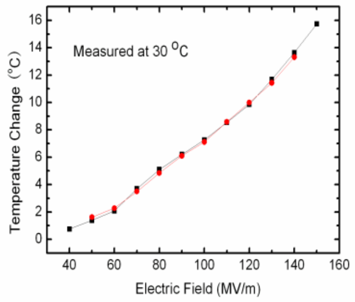


Fig. 1. ΔT as a function of applied field for an ECE P(VDF-TrFE-CFE) terpolymer. Although ΔT is quite high at high field (150 MV/m), at low field such as 40 MV/m, ΔT is near zero

In this program, we have investigated the blends of of P(VDF-TrFE-CFE) with small amount of P(VDF-TrFE) copolymer, which also provide a model system to study how the random defects in the terpolymer influence the polarization response in the normal ferroelectric copolymer and consequently ECE. Since P(VDF-TrFE) copolymer belongs to normal ferroelectrics, in which large remanent polarization will exist after poling, the copolymer can provide an internal electric field E_{bias} in the blends, thus generating higher polarization and enhanced ECE.

The P(VDF-TrFE-CFE) 59/33/8 mol% relaxor terpolymer was chosen for the study, because of its high EC response (see Fig. 1). The P(VDF-TrFE) copolymers in 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, if existing in large volume.

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%. 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.

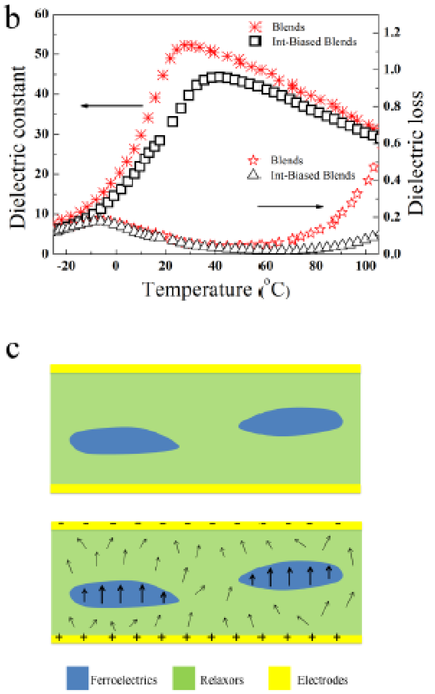


Fig. 2. **a**, The dielectric properties of blend (stars) and internal-biased (int-biased) blend (squares) as a function of temperature at 1 kHz. **b**, Schematic illustration of the working mechanism of charge-neutrality in establishing the internal DC biasing in the blends. Top: The un-biased blends. Bottom: Int-biased blends. Arrows represent dipole alignments in the normal ferroelectric and relaxor ferroelectric components.

The dielectric properties of the blend are shown in Fig. 2a, which exhibit a broad dielectric constant peak and typical relaxor dispersion. Indeed, the FT-IR spectra of the blends does not display absorptions from the all-trans bonds of the normal ferroelectric phase. The result indicates 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. 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 (see schematics in Fig. 2b).

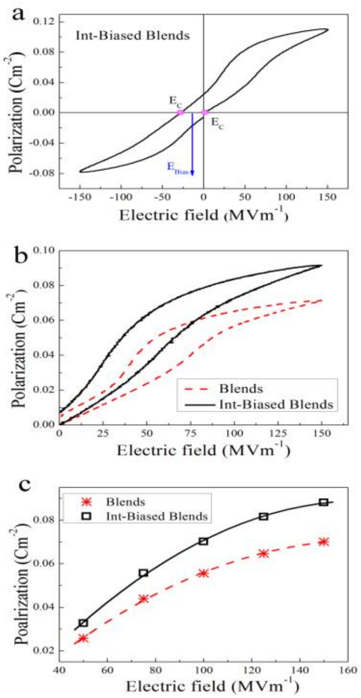


Fig. 3. **a**, The P-E loops of blend with the internal bias field. **b**, Comparison of the unipolar P-E loops of int-biased blend with that of the blend under 100 MVm^{-1}. **c**, Comparison of the maximum polarizations of blend (star) and int-biased blend (square) from the unipolar P-E loops as functions of electric fields measured at 25 ℃.

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. 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 ^{o}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 Fig. 2b, that block the space charge conduction. An E_{bias} ~ 15 MVm^{-1} can be seen in the bipolar polarization-electric field (P-E) loop in Fig. 3a as the center of the loop is shifted horizontally. The establishment of an effective DC bias field in the blends was confirmed by the FT-IR spectra, where an absorption peak corresponding to the all-trans polar conformation (at 1280 cm^{-1}) is observed for the int-biased blend films (See Fig. 4).

To further study the internal bias field and its influence on the polarization and EC response, unipolar P-E loops were measured along the same direction as the E_{bias} direction to investigate the polarization change in a heating-cooling cycle (measured at 10Hz) and presented in Fig. 3b. Fig. 3c summarizes the increased polarization in the uni-polar P-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.

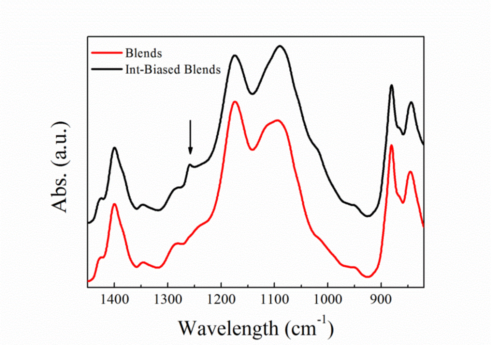


Fig. 4. FT-IR spectra of terpolymer/copolymer blend and internal-biased blend (10 wt% of P(VDF-TrFE) 65/35 mol% copolymer).

The EC responses (the adiabatic temperature change ΔT and isothermal entropy change ΔS) of both int-biased and un-biased blends under electric fields of ΔE=50 MVm^{-1} and 100 MVm^{-1}, respectively, as functions of temperature are presented in Figs. 5a and 5b. A marked enhancement of the EC responses is obtained at 50 MVm^{-1} where the peak values of ΔT = 4.9 K and ΔS=24.5 Jkg^{-1}K^{-1} are obtained for the int-biased blends, compared with the peak values of ΔT = 3.4 K and ΔS=17 Jkg^{-1}K^{-1}. Presented in Fig. 5c are the EC responses as functions of the applied field at room temperature (25 ^{o}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}, consistent with that observed from the bi-polar P-E loop in Fig. 3a.

Besides the large ECE that an EC material can generate, high electrocaloric coefficients, such as ΔT/ΔE and ΔS/ΔE, are also critical measures when considering EC materials for practical cooling devices. ΔS/ΔE and ΔT/ΔE for the int-biased blends at different applied field are presented in Fig. 6, which shows a large improvement compared with that of the un-biased blends, especially at low electric fields. The results show that the int-biased EC polymer blends exhibit both ECE, ΔS/ΔE and ΔT/ΔE.

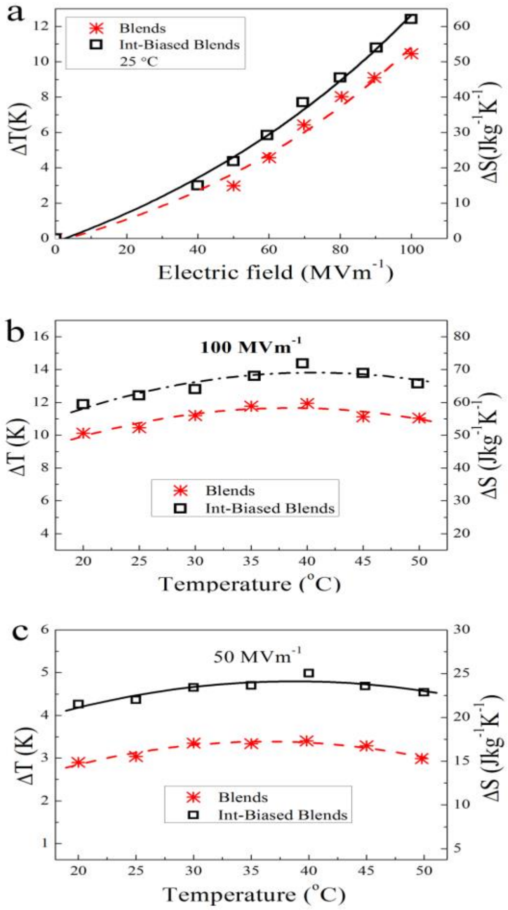


Fig. 5. The improvement of the ECE performance in the blends due to the internal biasing: the adiabatic temperature change ΔT, isothermal entropy change ΔS of int-biased blend (squares) and blend (stars). **a** and **b**, ΔT and ΔS as functions of temperature under electric fields of 50 MVm^{-1} and 100 MVm^{-1}, respectively. **c**, ΔT and ΔS as functions of electric field measured at room temperature.

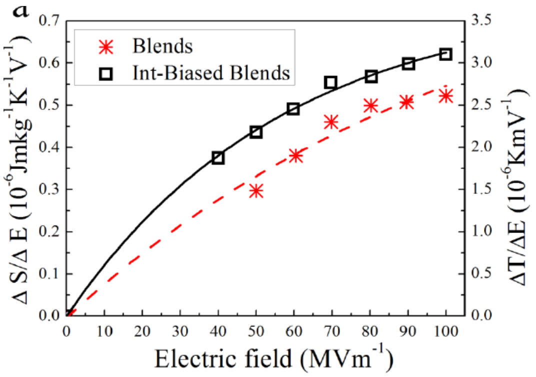


Fig. 6. The EC coefficients *ΔS/ΔE* and ΔT/ΔE of the int-biased blends and blends.

7.2. Inorganic/organic nanocomposites consisting of ferroelectric ceramic BST nano-particles and high thermal conductivity BN nano-sheets and the relaxor P(VDF-trFE-CFE) terpolymer.

Past studies on inorganic/organic nanocompsoites with relaxor terpolymers were mainly focused on inorganic nanofillers such as ZrO_2 and TiO_2, which have similar dielectric constant K as that of the terpolymer and hence improve the dielectric strength. In addition, earlier studies have shown these nanofillers also led to an increased polarization and ECE compared with neat terpolymer, at low nanofiller volume fraction (< 20 vol%). In this study, we expand the study to include ferroelectric ceramic nano-fillers such as modified $BaTiO_3$ which have much higher dielectric constant compared with the terpolymer and shows relatively high ECE. The preliminary experimental results show that the nanocomposites exhibit much higher ECE than the nanocompsoites with low K nanofillers composites (See Fig. 7). One penalty of including high K nanofillers in the terpolymers is the reduction of the dielectric strength. By including another low K nano-fillers, here BN nano-sheets, the nanocomposites of BST and BN (9 vol%) in P(VDF-TrFE-CFE) matrix exhibit an extremely high dielectric strength, a marked improved ECE, and a much higher thermal conductivity (~ 1 W/mK) compared with the neat terpolymer (~ 0.25 W/mK). Such a multi-component nanocomposite approach opens up a new avenue to synthesize EC polymer based materials with optimized performance.

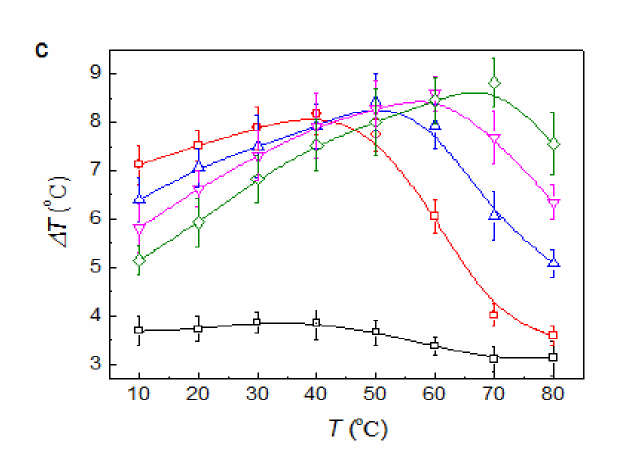


Fig. 7. Improved EC performance in the new three-component terpolymer nanocomposites (under 75 MV/m) where the black squares are the data from the neat terpolymer.

One interesting aspect of a high dielectric contrast nanocomposites is the high field concentration in the polymer matrix near the high-K inorganic nanofillers. Such a field concentration may cause local and large elastic stress/strain field. The EC polymer is also a ferroelastic material and the elastic field could also drive the conformation changes between the polar- and non-polar forms. This additional degree of freedom will provide additional synthesis parameter to tailor the composite properties. The observed very large enhancement of ECE in this three component nanocomposites suggest that this additional ferroelastic coupling may play a role in the observed polarization and EC response.

In general, the inclusion of very high dielectric constant nano-fillers into polymer matrix will cause a reduction of the dielectric breakdown field E_b, due to the large local electric field concentration. In this three phase nanocomposite, it was found that the inclusion of BN nano-sheets in the composites, in addition to improve the thermal conductivity of the nanocomposites, also improves the dielectric breakdown strength. For the three phase nanocomposites, E_b reaches 450 MV/m at 9 vol% of BN nano-sheets in the composites, which is much higher than E_b=350 MV/m of the neat terpolymer.

VIII. 2014-2015

Anomalous Electrocaloric Effect

All the EC responses presented in the report upto 2014 are based on the normal ECE, which are the most commonly observed polar dielectric response under application of electric field. That is, applying an electric field to a polar dielectric increases dipole ordering, as illustrated in **Figure 1a**, this ordering reduces the dipolar entropy of the dielectric and leads to a heat release (red peak in **Figure 1a**). As the field is removed, the dipoles return to their less ordered state and the dielectric absorbs heat, shown as the blue peak in **Figure 1a**. The discovery of dielectric materials with giant ECE as shown in this report has stimulated great interest in developing cooling technologies that are environmental friendly and have the potential to achieve higher efficiency compared with the century-old, vapor compression based cooling technology.

In addition to the normal ECE, the negative (or inverse) ECE (N-ECE) has also been observed in ferroelectric materials in which an applied electric field causes a reduction of dipole ordering, generating cooling, and the removal of the electric field causes heating in the dielectric material (see illustration in **Figure 1b**).

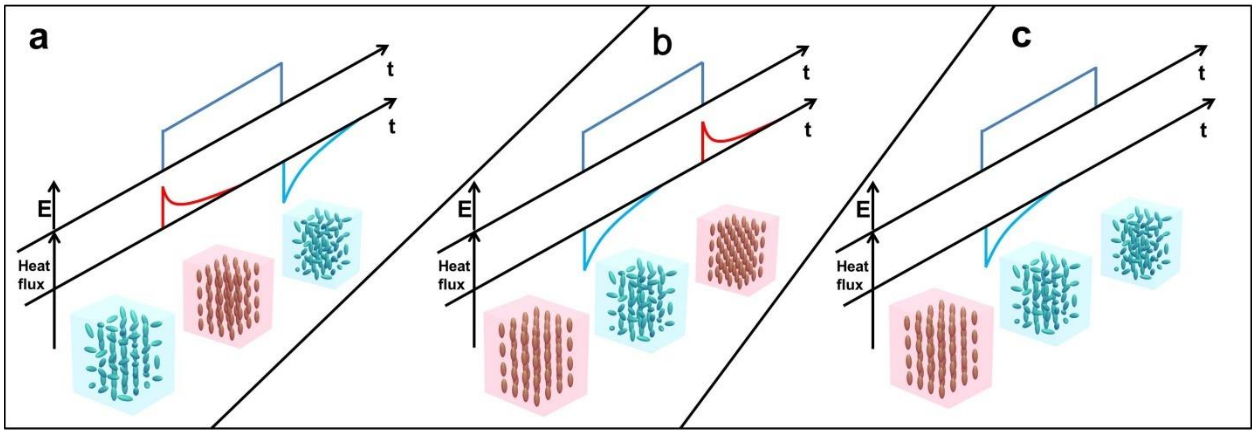


Figure 1. Schematics of positive/negative electrocaloric effect (ECE) and proposed anomalous ECE (A-ECE). (a) The normal ECE in which the dielectric material ejects heat (red peak, referred to as the heating peak in the paper) when a field is applied and absorbs heat (blue peak, referred to as the cooling peak in the paper) when the field is removed. The applied field E, the ECE signal recorded (heat flux, the integrated area is the total heat Q ejected or absorbed), and the schematics of the change of ordering of a polar-dielectric due to change of applied field vs. times. Schematic of dipole ordering: ordered (red) and disordered (less ordered) (blue). (b) The negative ECE in which the dielectric material absorbs heat (blue peak) when a field is applied and ejects heat (red peak) when the field is removed. In the N-ECE, the dipoles in the dielectric becomes less ordered (or disordered) under an applied field and returns to the ordered state after the field is removed. (c) Anomalous ECE in which the dielectric material absorbs heat (blue peak) under an electric pulse, and there is no heating peak as the field is removed. The dipoles in the dielectric become disordered upon application of an electric field. However, different from the negative ECE, the dipoles remains disordered after the electric field is removed. Hence the A-ECE generates cooling only after an electric pulse.

Here we report an anomalous N-ECE in a class of hybrid normal ferroelectric/relaxor ferroelectric polymer blends that does not show subsequent heating as the field is removed, as illustrated in **Figure 1c**. We refer the observed EC phenomenon here as the anomalous ECE (A-ECE) to distinguish it from the ECE and N-ECE. Dielectrics showing the A-ECE are attractive for applications where an electric pulse causes cooling of the surroundings without any heating. In contrast to the normal ECE (**Figure 1a**), the dipole ordering is reduced in the N-ECE when an electric field is applied. There are several polarization mechanisms in ferroelectric materials that can lead to the N-ECE. However, in order to realize an A-ECE (without heating under an electric pulse), the material (i) should be in a dipole ordered state initially, which can be switched by an external field to a less ordered state; and (ii) more importantly, as the electric field is removed, the dielectric can maintain this less ordered state without recovering to a dipole ordered state.

The A-ECE was observed in the hybrid blends of normal 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 that the normal ferroelectric P(VDF-TrFE) copolymer does not display a large ECE except near its ferroelectric-paraelectric phase transition (FE-PE), while the relaxor ferroelectric terpolymer exhibits a giant ECE over a broad temperature range near room temperature. In a normal ferroelectric P(VDF-TrFE) copolymer, which has been processed to a poled state (for example, at point A of the electric displacement (D)-electric field (E) loop in **Figure 2a**), applying an electric field to de-pole the ferroelectric polymer (the de-poling field is in the negative direction against the original poling field, which is in the positive direction) may reduce the dipole ordering compared with that of the poled state. This is indeed observed, as shown in **Figure 2b**, where the copolymers absorb heat as a field is applied. However, when the electric field is reduced to zero, these normal ferroelectric materials display a subsequent heating peak (eject heat), exhibiting the typical N-ECE. For the normal ferroelectric P(VDF-TrFE), the N-ECE is small, i.e., $\Delta S \leq 1$ J kg^{-1} K^{-1}. This is understandable since the normal ferroelectric materials are featured by the presence of remnant polarization and macroscopic polarization domains. When a normal ferroelectric is in the poled state, the polarization directions of the polar-domains are aligned to be closer to the original poling field direction. While in the de-poled state, the polarization directions of the polar domains are oriented randomly in the material, and the polar domain size may be smaller than that in the poled state, which means less dipole ordering in some part of the material, such as near the domain walls, yielding a small cooling peak. As shown in **Figure 2b**, the P(VDF-TrFE) 55/45 mol% copolymer exhibits the largest N-ECE among the three compositions studied (65/35 mol% and 75/25 mol% are the other two). This is likely due to its high TrFE content, which reduces its ferroelectric ordering and lowers its FE-PE transition temperature compared with the other two copolymers. The 75/25 mol% copolymer has a high ferroelectric ordering and hence the smallest N-ECE value, i.e., $\Delta S = 0.5$ J kg^{-1} K^{-1}.When the de-poling field is removed, the normal ferroelectric P(VDF-TrFE) copolymers recover most of their macroscopic domain structure and generate a small heating peak, as observed in **Figure 2b**.

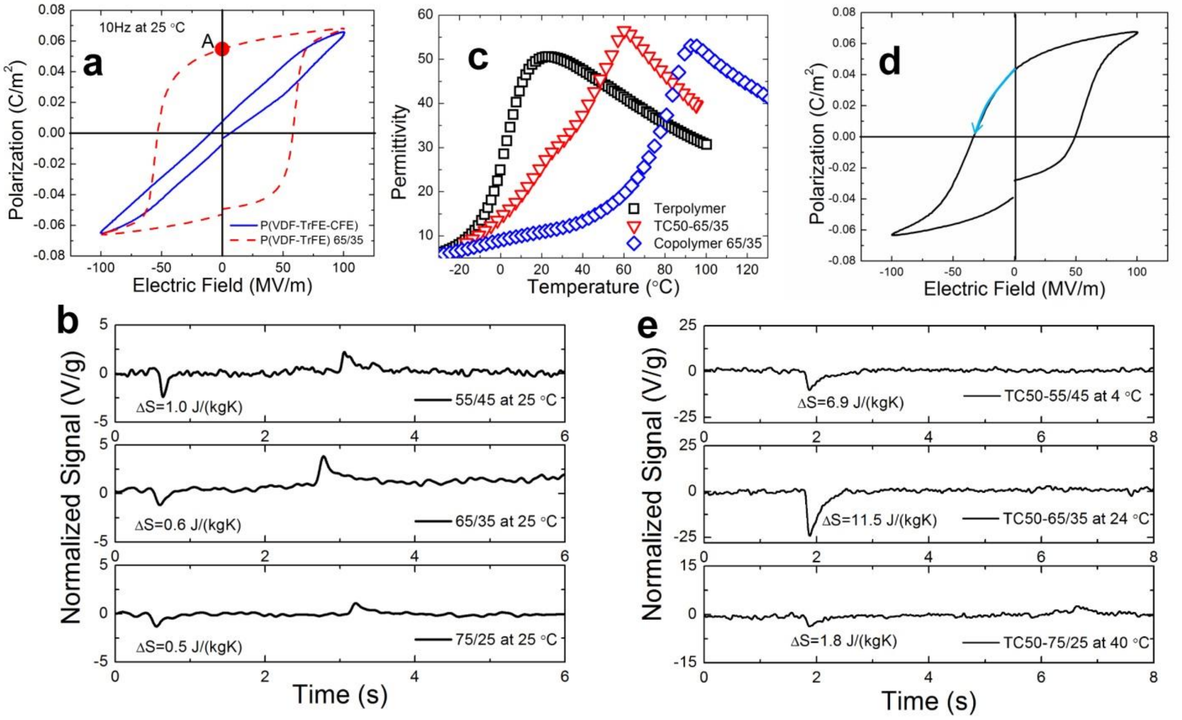


Figure 2. Comparison of dielectric properties and direct-measured ECE signals between neat copolymers and blends.(a) The D-E hysteresis loops for the normal ferroelectric 65/35 mol% copolymer and the relaxor P(VDF-TrFE-CFE) terpolymer. Applying a de-poling field in the copolymer generates an N-ECE. (b) The N-ECE for the copolymers of 55/45 mol%, 65/35 mol%, and 75/25 mol%. ΔS from the cooling peak is shown in the figure. (c) The dielectric constant vs. temperature measured at 1 kHz for the 65/35 mol% copolymer, the terpolymer, and the TC50-65/35 blend. (d) The D-E

loop of the blends TC50-65/35, where the arrow indicates the de-poling field = E_{coer}, the coercive field. (e) The anomalous ECE in TC50-55/45 and TC50-65/35, and the N-ECE in TC50-75/25.

In contrast, the relaxor ferroelectric polymers do not possess macroscopic polarization at zero electric field, as shown in the slim D-E loop in **Figure 2a** for the terpolymer P(VDF-TrFE-CFE). Hence, applying an electric field will induce ordering of dipoles, ejecting heat (or causing temperature rise of the material when not in the isothermal condition), while removing the field will return the material to its original dipole random state, absorbing heat. Due to the large difference in the dipole ordering between the dipole ordered and disordered states in the relaxor ferroelectric polymers, a giant ECE (positive ECE) can be induced, i.e., an adiabatic temperature change $\Delta T > 16$ K and $\Delta S > 75$ J kg^{-1} K^{-1}, under a field higher than 150 MV m^{-1}.

Now if one can design a polar-dielectric in which, at the poled state, the dipoles are in an ordered state with relatively large remnant polarization, and the ordered state will be converted to a dipole random state when subjected to a de-poling field, absorbing heat, then one can overcome the limitations of conventional polar-dielectrics. Because this de-poling process involves a transition from a dipole ordered to a dipole random state, the N-ECE can be much larger than that in a normal ferroelectric. Moreover, upon reducing the de-poling field to zero, the material can still retain its dipole disordered state, which will remove the subsequent heating peak as observed in the normal ferroelectric polymers. In this paper, we show that such a polar-dielectric material can be realized in hybrid normal ferroelectric/relaxor ferroelectric polymer blends, in which the coupling between the two constituents stabilizes the polar-ordering in the relaxor ferroelectric region in the poled state, see **Figure 2d** of the D-E loop of the hybrid, while in the de-poled state, the dipolar random state can be retained by the relaxor terpolymer in the blends after the de-poling field is reduced to zero.

Figure 2c and **Figure 2d** present the dielectric constant vs. temperature and the D-E loop of the hybrid blends with 65/35 mol% copolymer. The weight ratio between the two polymers is 50/50, displaying a lower remnant polarization P_r and coercive field E_{coer} than those of the normal ferroelectric constituent, which is understandable because of the presence of 50 wt% of relaxor terpolymer in the blends. Here we denote this hybrid as TC50-65/35, where T and C denote terpolymer and copolymer, respectively: 50 refers to the wt% of the terpolymer in the blends; and 65/35 refers to composition of the copolymer. Since the densities of the two polymers are nearly the same, the volume ratio of the two polymers in the hybrid is nearly the same as the weight ratio.

A comparison of **Figure 2a** and **Figure 2d** reveals that TC50-65/35 blends have a P_r=0.044 C/m^2, which is not far from that of the copolymer (P_r=0.054 C m^{-2}). Considering that the copolymer content is 50 wt% in the blends, the observed large ratio of P_r(blends)/P_r(copolymer) suggests that the normal ferroelectric copolymer induces polarization in the terpolymer regions in the poled state, resulting in a large P_r. The results here are confirmed by a phase field simulation, presented in **Figure S1**, which shows that the local fields of the copolymer constituent in the poled state induce polarization in the terpolymer regions in the blends.

In such a hybrid, applying a de-poling field will transition the material to a dipole random state, yielding a large N-ECE, as shown in **Figure 2e**, where the TC50-65/35 blends display an isothermal entropy change $\Delta S = 11.5$ J kg^{-1} K^{-1} ($\Delta T = -2.1$ K) when the de-poling field = E_{coer}, the coercive field, indicated by the arrow in the D-E loop in **Figure 2d**. More interestingly, the hybrid does not show a subsequent heating peak when the de-poling field is reduced to zero, yielding a new class of EC material which exhibits a large N-ECE without the subsequent heating peak under an electric pulse, i.e., the A-ECE.

Figure 2e presents the A-ECE for the hybrid blends with different P(VDF-TrFE) copolymer compositions, among which the TC50-65/35 blends exhibit the largest A-ECE. The TC50-55/45 blends show a smaller A-ECE, due to their low dipole ordering in the poled state. On the other hand, TC50-75/25 exhibits an N-ECE as appears in normal ferroelectrics, i.e., a small cooling peak (ΔS = 1.8 J kg^{-1} K^{-1}) as the de-poling field is applied, followed by a weak heating peak (ΔS < 1 J kg^{-1} K^{-1}) upon the removal of the de-poling field. This is also consistent with the D-E loop of TC50-75/25. The D-E loops in **Figure 2** show 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 of the 55/45 mol% copolymer, indicating that in the TC50-55/45 blends, the weak ferroelectric ordering in the 55/45 mol% copolymer is not strong enough to stabilize the polarization in the terpolymer in the poled state, resulting in a weak polar-ordering in the poled state and a smaller A-ECE, compared with that 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.

Figure 3 presents the dependence of A-ECE on the de-poling field. The data shows that the A-ECE increases with the de-poling (or "negative") field till it reaches the coercive field E_{coer}. As the "negative" field increases beyond E_{coer} (field overshoot), the blends will be poled to the negative direction, generating a heating peak due to the increased ordering, as shown in **Figure 3a** for the de-poling field = 40 MV m^{-1}. That is, as the de-poling field is applied, the blends will generate cooling first and then heating as the field is further increased to higher than E_{coer}. After the field becomes > E_{coer}, the polarization of the blend is poled 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

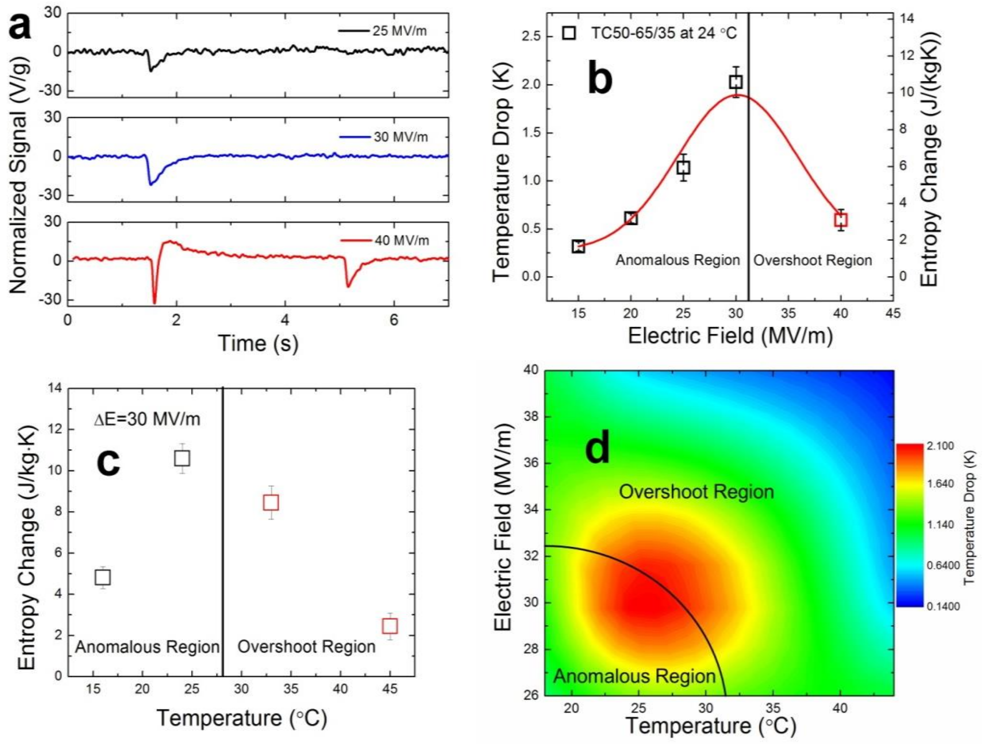


Figure 3. Temperature and electric field dependences of A-ECE.(a) Evolution of the A-ECE vs. de-poling field strength for CT50-65/35, from the A-ECE at E <E_{coer} to the field overshoot region (40 MV/m) where the applied field first induces a cooling peak and then, immediately, a heating peak as the 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) ΔS and ΔT vs. the applied de-poling field at 24 ºC, showing the evolution from the A-ECE to the field overshoot ECE. The ΔS for the field overshoot ECE is the combination of the cooling and heating peaks at the application of the de-poling field. (c) ΔS 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.

experimental data in **Figure 3a** for the de-poling field = 40 MV m^{-1}. **Figure 3b** summarizes this field dependence of the A-ECE as well as the conversion to the positive ECE at de-poling fields > E_{coer}, i.e., the field overshoot region, for the TC50-65/35 blends. An A-ECE of ΔS=11.5 J kg^{-1} K^{-1}, which corresponds to ΔT=-2.1 K temperature drop, is observed when the de-poling field = $E_{coer,}$ which is 30 MV m^{-1}.

For ferroelectric materials, E_{coer} changes with temperature, and hence the electrocaloric response will change with temperature under a given applied de-poling field. **Figure 3c** presents the A-ECE vs. temperature for TC50-65/35 under the de-poling field of 30 MV/m. At temperatures below 28 ^{o}C the blends show the A-ECE, and above that temperature, a field overshoot ECE behavior is observed because E_{coer}< 30 MV m^{-1} at temperatures higher than 28 ^{o}C. A 2-dimensional plot of the evolution of A-ECE as a function of the de-poling field and temperature is presented in **Figure 3d**.

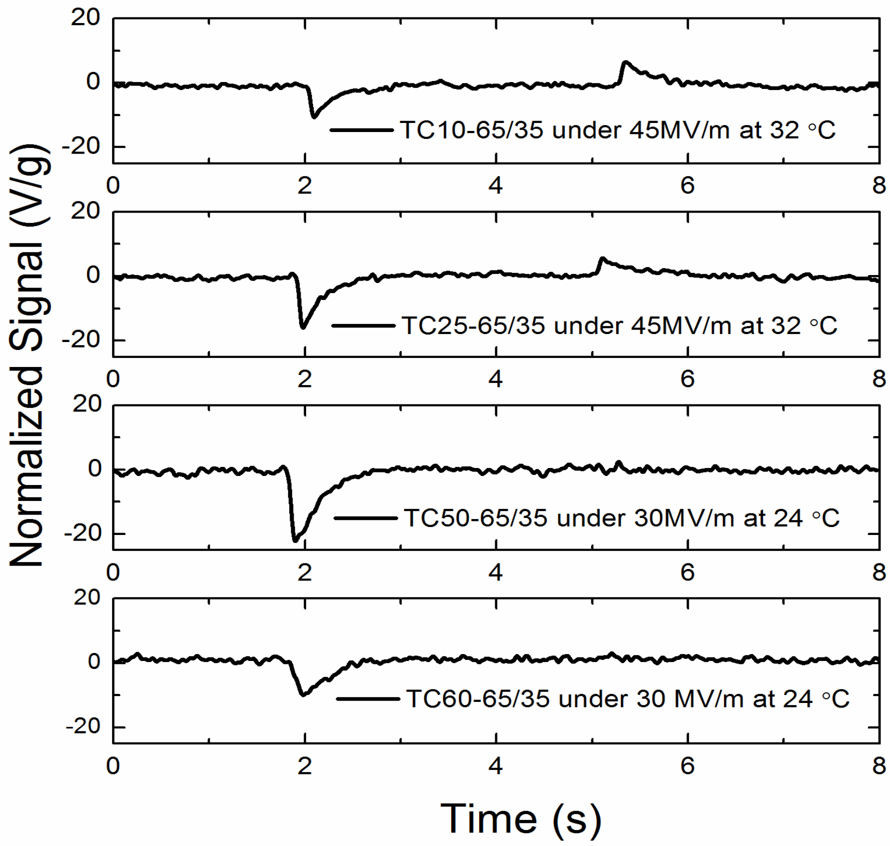


Figure 4. The evolution of the ECE vs. the terpolymer content, *x*, in the blends of TC*x*-65/35 for the de-poling field = E_{coer}. With increased *x*, the blends evolve from the N-ECE to the A-ECE, i.e., the cooling peak (ΔS) of the N-ECE increases and the heating peak decreases till TC50-65/35, at which point no heating peak is detected. For *x*>50 wt%, the blends show the A-ECE, and now the cooling peak decreases with *x*. The blends TC50-65/35 show the largest ΔS of the cooling peak. Measurements were carried out at different temperatures for different compositions so that the ΔS of the cooling peak is the largest for a given composition.

The evolution of the EC response under the de-poling field = E_{coer}, from the N-ECE of the neat copolymer (**Figure 2b**) to the A-ECE (**Figure 2e**) of the TCx-65/35 blends with the terpolymer content *x*, was investigated and presented in **Figure 4**. As the terpolymer content *x* in the blends increases beyond zero, the cooling peak (ΔS) increases while the heating peak decreases. At x=50 wt% (TC50-65/35), the cooling peak reaches the maximum while the heating peak disappears. Beyond x = 50 wt%, the blends exhibit the A-ECE. Because E_{coer} decreases (and hence the applied de-poling field also decreases) with x, the A-ECE (cooling peak) becomes smaller with x for x> 50 wt%. For TC75-65/35, the cooling peak becomes smaller than the instrument resolution. The “blends” with x=100 wt% are the pure terpolymers, which have E_{coer} = 0 at room temperature and exhibit giant positive ECEs.

An anomalous EC effect, in which an electric pulse applied to a dielectric material generates cooling, is observed in a hybrid normal ferroelectric/relaxor ferroelectric polymer blend. The effect is produced by the mesoscale dipolar interactions between the two components, i.e., the normal ferroelectric component induces dipole ordering in the relaxor polymer in the poled state, which can be switched to a de-poled state by an external field; when the de-poling field is removed, this de-poled state can be maintained by the relaxor component. This work 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 absorb heat from the surrounding area without subsequent heat release to the surrounding area.

--- Papers published in refereed journals:

1. Bret Neese, Baojin Chu, Sheng-Guo Lu, Yong Wang, and Q. M. Zhang, Giant Electrocaloric Effect in Ferroelectric Polymers at Near Room Temperature, *Science*, 321, 821-823 (2008).
   “The work was supported by the U.S. Department of Energy through grant number DE-FG02-07ER46410”

2. S. G. Lu, B. Neese, B. Chu, Y. Wang, and Q. M. Zhang, Large electric tunability in P(VDF-TrFE) based polymers, *Appl. Phys. Lett*. 93, 042905 (2008).
   “This work was supported by the U.S. Department of Energy through Grant No. DE-FG02-07ER46410.”

3. Sheng-Guo Lu and Q. M. Zhang, Electrocaloric Materials for Solid State Refrigeration, *Adv. Mater*. 21, 1 (2009).
   “We would like to thank Bret Neese, Yong Wang, B. Chu, and E. Furman for their contributions. The work was supported by the US Department of Energy through grant number DE-FG02-07ER46410.”

4. Bret Neese, S. G. Lu, Baojin Chu, and Q. M. Zhang, Electrocaloric Effect of the Relaxor Ferroelectric P(VDF-TrFE-CFE) Terpolymer. *Appl. Phys. Lett*. 94, 042910 (2009).
   “The authors wish to thank Eugene Furman for discussions. This work was supported by the Department of Energy through Grant No. DE-FG02-07ER46410.”

5. S. G. Lu, Z. Fang, E. Furman, Y. Wang, Q. M. Zhang, Y. Mudryk, K. A. Gschneidner, Jr.,V. K. Pecharsky, and C. W. Nan. Thermally mediated multiferroic composites for the magnetoelectric materials. *Appl. Phys. Lett*. 96, 102902 (2010).
   “The work at The Pennsylvania State University was supported by U.S. Department of Energy through Grant No. DE-FG02-07ER46410 and NSF through Grant No. ECCS-0824202. The

work at Ames Laboratory was supported by the Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-07CH11358 with Iowa State University. The work at Tsinghua University was supported by the NSF of China through Grant No. 50621201 and the State Key Project of Fundamental Research of China through Grant No. 2009CB623303."

6. S. G. Lu, B. Rožič Q. M. Zhang, Z. Kutnjak, R. Pirc, Minren Lin, Xinyu Li, and Lee J. Gorny, "Comparison of directly and indirectly measured electrocaloric effect in the relaxor ferroelectric polymers". *Appl. Phys. Lett.*, 97, 202901 (2010).

"Research at The Pennsylvania State University was supported by the U.S. DOE, Office of Basic Energy Sciences, and Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410. Research at JSI was supported by the Slovenian Research Agency under Grant Nos. P1-0125, P2-0105, and J1-2015."

7. S. G. Lu, B. Rožič Q. M. Zhang, Z. Kutnjak, Xinyu Li, E. Furman, Lee J. Gorny, Minren Lin, B. Malič, M. Kosec, R. Blinc, and R. Pirc, "Organic and Inorganic Relaxor Ferroelectrics with Giant Electrocaloric Effect", *Appl. Phys. Lett.*, 97, 162904 (2010).

"Research at The Pennsylvania State University was supported by the U.S. DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410. Research at JSI was supported by the Slovenian Research Agency under Grant Nos. P1-0125, P2-0105, and J1-2015."

8. B. Rozic, Z. Kutnjak, B. Neese, S. G. Lu, and Q. M. Zhang, "Electrocaloric effect in the relaxor ferroelectric polymer composition P(VDF-TrFE-CFE)$_{0.90}$ - P(VDF-CTFE)$_{0.10}$", *Phase Transitions*, 83, 819 (2010).

"This study was supported by the Slovenian Research Agency under program P1-0125 and the projects J1-9368 and J1-2015." B. Neese, S. G. Lu, and Q. M. Zhang are from Penn State and we forgot to acknowledge the DoE support.

9. B. Rozic, B. Malic, H. Ursic, J. Holc, M. Kosec, B. Neese, Q. M. Zhang, and Z. Kutnjak, "Direct measurements of the giant electrocaloric effect in soft and solid ferroelectric materials." *Ferroelectrics*, 405, 26 (2010).

"This work was supported by the Slovenian Research Agency under program P1-0125 and the projects J1-9368 and J1-2015." B. Neese and Q. M. Zhang are from Penn State and we forgot to acknowledge the DoE support.

10. R. Pirc, Z. Kutnjak, R. Blinc, and Q. M. Zhang, "Upper bounds on the electrocaloric effect in polar solids." *Appl. Phys. Lett.*, 98, 021909 (2011).

"This work was supported by the Slovenian Research Agency through Grant Nos. P1-0044, P1-0125, P2-0105,J1-0155, and J1-2015. Research at the Pennsylvania State University was supported by the U.S. DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410."

11. S. G. Lu, B. Rožič, Z. Kutnjak, and Q. M. Zhang, "Electrocaloric effect in ferroelectric P(VDF-TrFE) copolymers", *Integrated Ferroelectrics*, 125, 176 (2011)

"The works at Penn State University was supported by the US Department of Energy, Division of

Materials Sciences, under Grant No. DE-FG02-07ER46410. The work at Jozef Stefan Institute was supported by the Slovenian Research Agency. The authors thank B. Neese, B. Chu, Y. Wang, and E. Furman for their contributions to ECE work and Xiaoshi Qian for his assistance in the preparation of manuscript."

12. S. G. Lu, B. Rožič Q. M. Zhang, Z. Kutnjak, and B. Neese, "Enhanced Electrocaloric Effect in Ferroelectric Poly(vinylidene-fluoride/trifluoroethylene) 55/45 mol% Copolymer at Ferroelectric-Paraelectric Transition", *Appl. Phys. Lett.*, 98, 122906 (2011).

" Research at The Pennsylvania State University was supported by the U.S. DoE, Office of Basic Energy Sciences,Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410. Research at JSI was supported by the Slovenian Research Agency under Grant Nos. P1-0125, P2-0105, and J1-2015"

13. S. G. Lu, B. Rozic, Z. Kutnjik, and Q. M. Zhang, Electrocaloric Effect in Ferroelectric P(VDF-TrFE) Copolymers, *Integrated Ferro*. 125, 176 (2011).

"The works at Penn State University was supported by the US Department of Energy, Division of Materials Sciences, under Grant No. DE-FG02-07ER46410. The work at Jozef Stefan Institute was supported by the Slovenian Research Agency."

14. Xinyu Li, Xiao-shi Qian, S. G. Lu, Jiping Cheng, Zhao Fang and Q. M. Zhang. Tunable Temperature Dependence of Electrocaloric Effect in Ferroelectric RelaxorP(VDF-TrFE-CFE) Terpolymer. *Appl. Phys. Lett*. 99, 052907 (2011).

"This research was supported by the US DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410".

15. Brigita Rozic, Marija Kosec, Hana Ursic, Janez Holc, Barbara Malic, Q. M. Zhang, Robert Blinc, Rasa Pirc, and Zdravko Kutnjak, Influence of the critical point on the electrocaloric response of relaxor ferroelectrics. *J. Appl. Phys*. 110, 064118 (2011).

"This work was supported by the NAMASTE Centre of Excellece and the Slovenian Research Agency through Grants P1-0044, P1-0125, P2-0105, J1-0155, and J1-2015. The work at Penn State was supported by the US Department of Energy, Division of Materials Sciences, under Grant No. DE-FG02-07ER46410."

16. R. Pirc,Z. Kutnjak, and R. Blinc, Q. M. Zhang. Electrocaloric effect in relaxor ferroelectrics. *J. Appl. Phys*. 110, 074113 (2011).

"This work was supported by the Slovenian Research Agency through Grants P1-0044, P1-0125, P2-0105, J1-0155, and J1-2015. Research at the Pennsylvania State University was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410."

17. B. Rozic, B. Neese, S. G. Lu, Q. M. Zhang, and Z. Tutnjak, Direct Measurements of the ELectrocaloric Effect in P(VDF-TrFE) 68/32 Copolymer Ferroelectric Films. Ferro. 416, 139-143 (2011) .

"This work was supported by the Slovenian Research Agency under program P1-0125 and the projects J1-9368 and J1-2015. The work at Penn State was supported by the US Department of Energy, Division of Materials Sciences, under Grant No. DE-FG02-

07ER46410."

18. B. Rozic, S. G. Lu, Z. Kutnjak, B. Neese, and Q. M. Zhang. Electrocaloric Effect in the Relaxor Ferroelectric Terpolymer P(VDF-TrFe-CFE). *Ferro*. 422, 81 (2011).
    "This work was supported by the Slovenian Research Agency under program P1–0125 and projects J1-9368, J1-2015. The work at Penn State was supported by the US Department of Energy, Division of Materials Sciences, under Grant No. DE-FG02-07ER46410"

19. S. G. Lu, J. Z. Jin, X. Zhou, Z. Fang, Q. Wang, and Q. M. Zhang. Large magnetoelectric coupling coefficient in poly(vinylidene fluoride-hexafluoropropylene)/Metglas laminates. *J. Appl. Phys.*110, 104103 (2011).
    "The work (Z. F. and X. Z) was partially supported by NSF under Grant No. ECCS-0824202 and (S.G.L. and Q.M.Z) partially by the US DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410."

20. S. G. Lu, B. Rozic, Q. M. Zhang, Z. Kutnjak, R. Pirc. Electrocaloric Effect in Ferroelectric Polymers. *Applied Physics A*106(4) (2012).
    "Research at The Pennsylvania State University was supported by the US DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410. Research at JSI was supported by the Slovenian Research Agency under grants P1-0125, P2- 0105, and J1-2015."

21. V. Bobnar, X. Li, G. Casar, A. Erste, S. Glinsek, X. Qian, and Q. M. Zhang. Tailoring electrically-induced properties by stretching relaxor polymer**.** *J. Appl. Phys*. 111, 083512 (2012).
    "This research was supported by the Slovenian Research Agency under program P1-0125 and by the U.S. DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410."

22. R. Pirc , B. Rozic , R. Blinc , Xinyu Li , Q. M. Zhang, ELECTROCALORIC EFFECT AND DIPOLAR ENTROPY CHANGE IN FERROELECTRIC POLYMERS. *Ferro*. 426, 38 (2012).
    "This work was supported by the Slovenian Research Agency through Grants P1-0044, P1-0125, P2-0105, J1-0155, and J1-2015. Research at the Pennsylvania State University was supported by the US DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410."

23. Z. K. Liu and Q. M. Zhang, Maximizing Coexisting Phases Near Invariant Critical Points For Giant Electrocaloric and Electromechanical Responses in Ferroelectrics. *Appl. Phys. Lett*. 101, 082904 (2012).
    "Z.K.L. is supported by National Science Foundation through Grant DMR-1006557 and Office of Naval Research under the Contract Number N0014-07-1-0638. Q.M.Z. is supported by Army Research Office under Grant W911NF-11-1-0534, and X.L. is supported by the U.S. Department of Energy Division of Materials Sciences through Grant No. DE-FG02-07ER46410. We thank to Y. Wang, Z. Kutnjak, R. Pirc, and S. G. Lu for discussions."

24. Xinyu Li, Xiaoshi Qian, Haiming Gu, Xiangzhong Chen, S. G. Lu, Minren Lin, Fred Bateman,

and Q. M. Zhang, Electrocaloric effect in ferroelectric poly(vinylidenefluoride-trifluoroethylene) copolymers with a high degree of polar disorder in the ferroelectric phase near a first order transition. . *Appl. Phys. Lett*. 101(13), 132903 (2012).

"X. Li, X. Qian, M. Lin, S. Lu and Q. M. Zhang were supported by the US DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410 and X. Chen by Army Research Office under Grant No. W911NF-11-1-0534."

25. Xinyu Li, Sheng-Guo Lu, Xiang-Zhong Chen, Haiming Gu, Xiao-shi Qian and Q. M. Zhang. Pyroelectric and electrocaloric materials, *J. Mater. Chem. C*. **1**, 23 (2013) (Feature Article, DOI: 10.1039/c2tc00283c (Invited))

"Xinyu Li, Xiaoshi Qian, Q. M. Zhang were supported by the US DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410. Sheng-Guo Lu and Xiangzhong Chen were supported by Army Research Office under Grant No. W911NF-11-1-0534. Haiming Gu was supported by a DOE SBIR Phase II, Contract No.DE-SC0003340 (subcontract from Strategic Polymers, Inc.) We thank Quinn Burlingame and Shan Wu for assistance in preparing the manuscript."

26. Xiao-Shi Qian, S. G. Lu, Xinyu Li, Haiming Gu, L-C Chien, Q. M. Zhang, Large Electrocaloric Effect in A Dielectric Liquid Possessing A Large Dielectric Anisotropy Near the Isotropic-Nematic Transition. *Adv. Funct. Mater*. DOI: 10.1002/adfm.201202686 (2013).

"X.-S.Q., X.L., and Q.M.Z. were supported by the U.S. Department of Energy Division of Materials Sciences through grant No. DE-FG02-07ER46410. S.G.L. and H.G. were supported by the Army Research Office under grantW911NF-11-1-0534. The authors thank Antal Jakli and I-C Khoo for stimulating discussions. They also thank William C. Kinsman for his assistance in this work."

27. S. G. Lu and Q. M. Zhang, LARGE Electrocaloric Effect In Relaxor Ferroelectrics. *J. Adv. Diel*. 2(3), 1230011 (2012).

"Research at The Pennsylvania State University was supported by the US DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410."

28. S. G. Lu, B. Rozic, Q. M. Zhang, Z. Kutnjak, and R. Pirc, Electrocaloric effect in ferroelectric polymers, *Applied Physics A: Materials Science & Processing* 107, 559-566 (2012).

"Research at The Pennsylvania State University was supported by the US DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410. Research at JSI was supported by the Slovenian Research Agency under grants P1-0125, P2- 0105, and J1-2015."

29. Xinyu Li, Xiao-shi Qian, Haiming Gu, Xiangzhong Chen, S. G. Lu, Minren Lin, Fred Bateman, and Q. M. Zhang. Giant electrocaloric effect in ferroelectric P(VDF-TrFE) copolymers near a first-order ferroelectric transition. *Appl. Phys. Lett*. 101(13), 132903(2012).

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30. B. Rozic, B. Malic, H. Ursic, J. Holc, M. Kosec, S.-G. Lu, Q. M. Zhang, and Z. Kutnjak. The Giant Electrocaloric Effect in Inorganic and Organic Ferroelectric Relaxor Systems. *Ferro*. 430, 98-102 (2012).
"This work was supported by the Slovenian Research Agency under program P1-0125 and projects J2-3633, J1-2015 and Slovenian National UNESCO-L'OREAL grant"

31. Xiang-Zhong Chen, Xinyu Li, Xiao-Shi Qian, Minren Lin, Shan Wu, Qun-Dong Shen, and Q. M. Zhang. A nanocomposite approach to tailor electrocaloric effect in ferroelectric polymer. *Polymer*, 54, 5299 (2013).
" This research was supported by Army Research Office under Grant No. W911NF-11-1-0534 (X. Z. Chen, M. Lin, and Q. Zhang) and by the U.S. DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410 (X. Li and X. Qian). X. Z. Chen was also partially supported by Nanjing University, China."

32. Sheng-Guo Lu, Hui Xiong, Aixiang Wei, Xinyu Li and Q. M. Zhang. Electrocaloric and electrostrictive effect of polar P(VDF-TrFE-CFE) terpolymers. *JOURNAL Of ADVANCED DIELECTRICS*, 3, (2013) 1350015.
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33. Goran Casar, Xinyu Li, Jurij Koruza, Qiming Zhang, Vid Bobnar, Electrical and Thermal Properties of Polymer Systems With Coexisting Ferroelectric and Relaxor States. *J. Mater Sci.* 48, 7902 (2013).
"This research was supported by the Slovenian Research Agency under program P1-0125 and by the U.S. DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410."

34. S. Pamir Alpay, Joseph Mantese, Susan Trolier-McKinstry, Q. M. Zhang, Roger W. Whatmore, Next Generation Electrocaloric and Pyroelectric Materials for Solid State Electrothermal Interconversion. *MRS Bulletin* 39, 1099 (Dec. 2014) (Invited review article).
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35. G. Casar, X. Li, Q. M. Zhang, and V. Bobnar, Influencing dielectric properties of relaxor polymer by blending PVDF-TrFE-based terpolymer with a ferroelectric copolymer. *J. Appl. Phys.* 115, 104101 (2014).
"This research was supported by the Slovenian Research Agency under program P1-0125 and by the U.S. DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410."

36. Guangzu Zhang, Qi Li, Haiming Gu, Shenglin Jiang, Kuo Han, Matthew R. Gadinski, M. A.

Haque, Q. M. Zhang, and Qing Wang. Ferroelectric Polymer Nanocomposites for Room-Temperature Electrocaloric Refrigeration. *Adv. Mater*. 27, 1450-1454, DOI: 10.1002/adma.201404591 (2015).

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37. G. Casar, Xinyu Li, B. Malic, Q. M. Zhang, and V. Bobnar, Impact of structural changes on dielectric and thermal properties of vinylidene fluoride-trifluoroethylene-based terpolymer/copolymer blends, *Physica B*. 461, 5-9 (2015).

"This research was supported by the Slovenian Research Agency under program P1-0125 and by the US DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award no. DE-FG02-07ER46410."

38. Xiaoshi Qian, Shan W, Eugene Furman, Ji Su, and Q. M. Zhang, Ferroelectric polymers as multi-functional electroactive materials: Recent advances, Potentials, and Challenges, *MRS Communications*, In print (2015).

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39. Xiaoshi Qian, Tiannan Yang, Tian Zhang, Long-Qing Chen, Q. M. Zhang, Anomalous Electrocaloric Effect In A Relaxor/Normal Ferroelectric Polymer Blend With Controlled Nano- and Meso-Dipolar Couplings, Submitted to *Adv. Mater* (2015)

"The work was supported by the US DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410 (X.Q. and Q. M. Z.), Army Research Office grant W911NF-11-1-0534 (T.Z.), and NSF under Grant No. DMR-1410714 (T.Y. and L.Q.C.). The authors thank Dae-Yong Jeong for discussions."

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--- Book chapters published:

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"The works at Penn State University was supported by the US Department of Energy, Division of Materials Sciences, under Grant No. DE-FG02-07ER46410. The work at Jozef Stefan Institute was supported by the Slovenian Research Agency."

- *Electrocaloric Polymers*, Xinyu Li, Sheng-Guo Lu, Xiaoshi Qian, Minren Lin, and Q. M. Zhang. Chapter 5 in *Electrocaloric Materials: New Generation of Coolers*. Tatiana Correia and Qi Zhang, Ed. Springer (2014).

"We acknowledge the support of the US Department of Energy, Division of Materials Sciences, under Grant No. DE-FG02-07ER46410 (X.L. X. Q., M. L., and Q.M.Z). US Army Research Office under grant W911NF-11-1-0534 (S. L.)."

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"This work was supported by the US DoE, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46410."

--- **Patent**:

Q. M. Zhang, S.-G. Lu, Xinyu Li, Lee Gorny, and Jiping Cheng, Breet Neese, and Baojin Chu. Polymer-Based Electrocaloric Cooling Devices. US Patent. No. 8,869,542 (2014).

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