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Anomalous negative electrocaloric effect in a relaxor/normal ferroelectric polymer blend with controlled nano- and meso-dipolar couplings

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In general, a dielectric material will eject (or absorb) heat when an electric field is applied and absorb (or eject) heat when the field is removed, under isothermal condition, which is known as the normal (or negative) electrocaloric (EC) effect. For some applications, it is highly desired that an EC material will absorb heat (cooling the surrounding) without subsequent heating under an electric pulse. Here, we show that such an EC material can be realized in a properly designed hybrid normal ferroelectric/relaxor ferroelectric polymer blend in which 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. More importantly, the de-poled state can be maintained by the relaxor component when the de-poling field is removed. Consequently, the hybrid blend exhibits a large cooling (an isothermal entropy change $\Delta S = 11.5\,\mathrm{J\,kg^{-1}\,K^{-1}}$) without the subsequent heating upon the application of an electric pulse. *© 2016 AIP Publishing LLC.*
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The electrocaloric effect (ECE) is a phenomenon in which a dielectric material exhibits a temperature/entropy change in response to polarization change that is induced by an applied electric field.[1–6] Enabled by an electric-field-induced polarization change, ECE is directly related to dipolar entropy change. Heat will be ejected from the electrocaloric (EC) material if dipolar entropy is reducing. The EC material will absorb heat if its dipolar entropy is increased.[2–13] Since applying external electric field can both reduce and, in some cases,[14–19] increase the dipolar entropy, ECE and negative (or inverse) ECE (N-ECE) can be induced, as schematically shown in Figures 1(a) and 1(b), respectively. The recent discovery of dielectric materials with giant ECE 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.[6–8]

Many EC materials, in response to one electric pulse, exhibit reversible thermal processes, i.e., heating as the field is applied and cooling as the field is reduced. The amount of heating and cooling is nearly the same in these EC materials when the dielectric loss is small, as observed in the relaxor ferroelectric polymers.[7,20–22] Besides normal ECE, reversibility in negative ECE was directly characterized by de-poling ferroelectric polymer P(VDF-TrFE).[19] Such a reversibility responding to one electric pulse grants the promise of operating the EC materials as a high efficiency cyclic heat pump which features continuous cooling capacity.[9,23] On the other hand, applying an electric pulse to produce only cooling effect without generating any subsequent heating is essential for some applications such as on-chip hotspot striking. Such a cooling device can work on-demand with instant cooling pulse.

Here, we report an anomalous N-ECE (AN-ECE) in a class of hybrid normal ferroelectric/relaxor ferroelectric polymer blends that does not show subsequent heating as the field is removed, as shown schematically and experimentally in Figures 1(c) and 1(d), respectively. In the EC material exhibiting AN-ECE, the experimental cycle consists of two electric pulses which operate in bipolar direction. A first electric pulse poles the hybrid into a macroscopic polar-state. Then, applying a de-poling field pulse will transition the material to a dipole random state, yielding a large cooling effect where the polymer blends display a large entropy increase. Moreover, the dipolar random state can be maintained after removing the field, when the de-poling field is

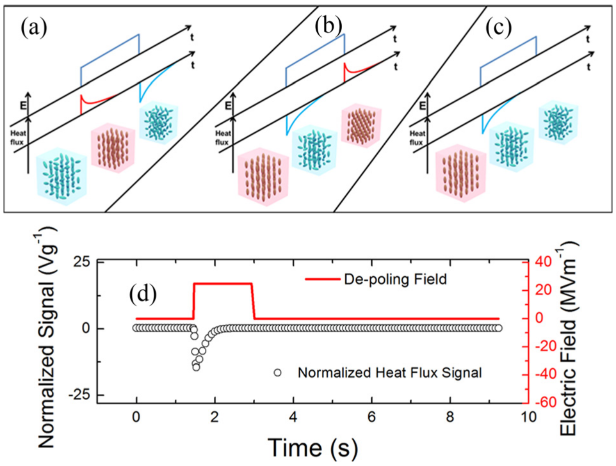

FIG. 1. Schematics of (a) positive ECE, (b) negative ECE, (c) proposed AN-ECE and weight-normalized heat-flux signal of directly measured AN-ECE. The heat-flux plot is fitted. Applied electric pulse is $25\,\mathrm{MV\,m^{-1}}$.

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lesser than E_{coer}, the coercive field. The full process cycle is illustrated in Figure S1. Thus, the hybrid does not show a subsequent heating peak when the field is reduced to zero, yielding an interesting phenomenon in which a large N-ECE exhibits only cooling under the de-poling electric pulse, i.e., the AN-ECE. It is also interesting to note that the hybrids after the first high field poling can remain in the macroscopically poled state, and in our experiment time (more than one month after the high field poling), no change was observed for the AN-ECE.

It should be emphasized that, in order to restore the AN-ECE, the hybrid needs to be conditioned (re-poled) to its macroscopic polarization state, before the next demand of AN-ECE arises. Thus, EC hybrid polymer exhibiting such a cooling response may find applications such as on-chip hotspot cooling. When the hotspot strikes, the pre-processed polymer hybrid can be de-poled to generate cooling power instantly.[24–26]

In order to realize an AN-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 dipolar disordered state; and (ii) more importantly, as the electric field is removed, the dielectric can maintain in this dipolar disordered state without recovering to a dipole ordered state. As stated above, this cooling effect can be repeated after the poling the hybrid under an electric pulse with the field amplitude several times larger than E_{coer}, as illustrated in Figure S1. The large poling pulse and the smaller de-poling pulse form a complete cycle of bipolar operation. The total heating and total cooling from the two pulses are the same when the EC material reaches the steady state operation.

The AN-ECE was observed in the hybrid blends of normal ferroelectric P(VDF-TrFE) (polyvinylidene fluoride-trifluoroethylene) copolymers (55/45, 65/35 and 75/25 mol. %) and the relaxor ferroelectric P(VDF-TrFE-CFE) (CFE: chlorofluoroethylene) 59/33/8 mol. % terpolymer. Here, we denote these hybrids as TC50-55/45, TC50-65/35 and TC50-75/25, where T and C denote terpolymer and copolymer, respectively: 50 refers to the wt. % of the terpolymer in the blends; 55/45, 65/35, and 75/25 refer to the composition of each copolymer, respectively. The detailed material process and measurements can be found in supplementary materials.[27] For the three P(VDF-TrFE) copolymers in this study, it is well known that the ferroelectricity, such as the coercive field and FE-PE transition temperature, becomes stronger with VDF/TrFE ratio, which affects the D-E loops of the blends, as shown in Figure S2.[28–30] 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. D-E loops of the neat copolymers, terpolymer, and their TC50 blends are shown in Figure S2. In such blends, normal ferroelectric copolymers will impart dipolar ordering and relaxor ferroelectric terpolymer will serve to stabilize the dipolar randomness.[28–30] It is the balance of these two effects in the hybrids that leads to a large AN-ECE.

In a normal ferroelectric P(VDF-TrFE) copolymer, which has been processed to a poled state, applying an electric field to de-pole the ferroelectric polymer at room temperature may reduce the dipolar ordering compared with that of the poled state, thus the material would absorb heat.[19] Due to the strong macroscopic ferroelectric state, the reduction in dipolar ordering is small, and hence, the amount of heat absorbed is small. The reduction of dipolar ordering can be recovered to the macroscopically dipolar ordered states when the electric field is removed, even when the polymer does not display macroscopic polarization, thus ejecting small amount of heat, causing a small N-ECE as observed in all three normal ferroelectric copolymers, see Figure 2(a), where $\Delta S \leq 1\,\mathrm{J\,kg^{-1}\,K^{-1}}$. In contrast, the relaxor ferroelectric polymers, which are ferroelectrics comprising nano-polar domains under the constraint of random local polarization field, do not possess macroscopic polarization at zero electric field,[28,29,31] as shown in the slim D-E loop in Figure S2 for the terpolymer P(VDF-TrFE-CFE). Hence, applying an electric field will induce dipole ordering, 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 $\Delta T > 16\,\mathrm{K}$ and $\Delta S > 75\,\mathrm{J\,kg^{-1}\,K^{-1}}$, under a field higher than $150\,\mathrm{MV\,m^{-1}}$.[30,32,33]

Figure S2 reveals that the D-E loops of the blends depend critically on the copolymer's compositions. At room temperature, TC50-55/45 exhibits the lowest hysteresis, whereas TC50-75/25 exhibits the D-E loop not very much different from that of the pure copolymer. Figure 2(b) presents the AN-ECE for the hybrid blends with different P(VDF-TrFE) copolymer compositions, which shows that the TC50-65/35 blends exhibit the largest AN-ECE, i.e., $\Delta S = 11.5\,\mathrm{J\,kg^{-1}\,K^{-1}}$, corresponding to an $\Delta T = -2.1\,\mathrm{K}$ temperature drop, when the de-poling field $= E_{coer} = 30\,\mathrm{MV\,m^{-1}}$. TC50-55/45 blends display a smaller AN-ECE, due to their low dipole ordering in the poled state (see the D-E loop in Figure S2(b)), compared with that of TC50-65/35. For these two blends, the data were taken at temperatures where the blends exhibit the highest AN-ECE. In contrast, TC50-75/25 exhibits an N-ECE as what has been observed in the pure copolymers, i.e., a small cooling peak ($\Delta S = 1.8\,\mathrm{J\,kg^{-1}\,K^{-1}}$) as the de-poling field is applied, followed by a weak heating peak ($\Delta S < 1\,\mathrm{J\,kg^{-1}\,K^{-1}}$) upon the removal of the de-poling field. This is also consistent with the D-E loop of TC50-75/25 shown in Figure S2, which is not much different from that of the neat copolymer.

For the blends with 65/35 mol. % copolymer, the evolution of the EC response with the terpolymer content x under the de-poling field $= E_{coer}$ was investigated. The results are presented in Figure 2(c), showing an evolution from N-ECE to AN-ECE. As the terpolymer content x 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 an AN-ECE. Because E_{coer} decreases (and hence the applied de-poling field also decreases) with x, the AN-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

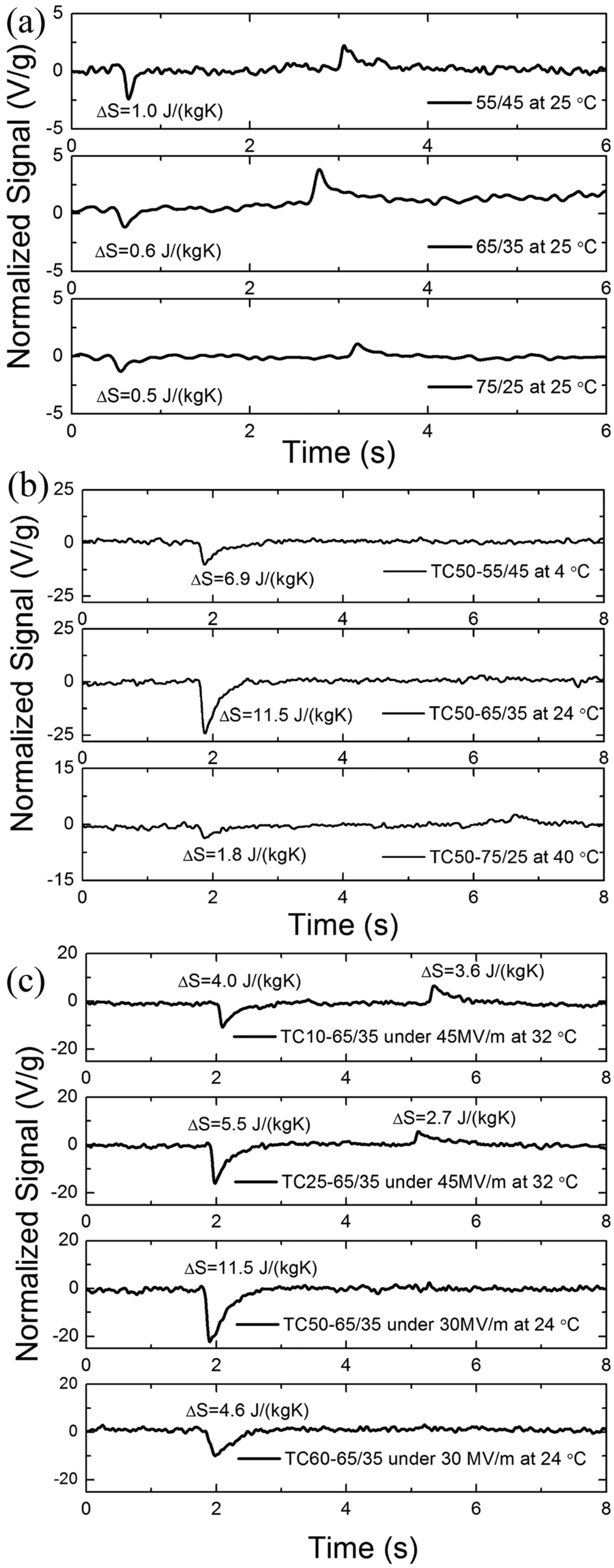

FIG. 2. (a) N-ECE for the copolymers of 55/45 mol. %, 65/35 mol. %, and 75/25 mol. %. ΔS from the cooling peak is shown in the figure. Applying a de-poling field in the copolymer generates an N-ECE. (b) The AN-ECE in TC50-55/45 and TC50-65/35, and the N-ECE in TC50-75/25. (c) The evolution of the ECE vs. the terpolymer content, x, in the blends of TCx-65/35 for the de-poling field = E_{coer}. With increased x, the blends evolve from the N-ECE to the AN-ECE. The data in (b) and (c) are shown at the temperatures, where the blends exhibit the highest AN-ECE. The duration of the square electric pulse is in the range of 2.5–3 s.

have $E_{coer} = 0$ at room temperature and exhibit giant positive ECEs.

The EC response on the magnitude of the de-poling field for the TC50-65/35 blends was further investigated. As the room-temperature DE loops shown in Figure 3(a), de-poling the TC50-65/35 blend with 30 MV m^{-1} results in a large polarization reduction which is in sharp difference from de-poling a normal ferroelectric where the spontaneous polarization is maintained after the de-poling, as shown in Figure S3. Further increasing the de-poling field causes the blend to be 100% de-poled (D = 0), and the blend maintains the de-poled state rather than returning to its remnant polarization. Above this field, the blend is poled to the opposite direction along which the dipolar ordering will increase. The direct measured heat-flux data confirm the polarization study. Figure 3(b) presents the dependence of AN-ECE on the de-poling field measured at room temperature. Data show that the AN-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 (Figure 3(a)), generating a heating peak due to the increased ordering, as shown in Figure 3(b) for the de-poling field = 40 MV m^{-1}. That is, as the de-poling field is applied, the blends will generate cooling (endo peak in the data) first and then heating (exo peak) as the field is further increased to higher than E_{coer} and, hence, show a positive ECE, i.e., a cooling peak as the field is removed. It is noted that the over-shoot de-poling field from the ECE measurement is lower than that from the D-E loop measurements. The difference is probably caused by different electric field wave forms used in the two studies. It is a sine wave for polarization study and a square wave in ECE measurements. Figure 3(c) summarizes this field dependence of the AN-ECE as well as the conversion to the positive ECE when the de-poling fields > E_{coer}, i.e., the field overshoot region, for the TC50-65/35 blends.

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 3(d) presents the AN-ECE vs. temperature for TC50-65/35 under the de-poling field of 30 MV m^{-1}. At temperatures below 28 °C, the blends show the AN-ECE, and above that temperature, a field overshoot ECE behavior is observed because that the E_{coer} reduces to below 30 MV m^{-1} at temperatures higher than 28 °C. The entropy change in the overshoot region is the summation of the endo and exo peaks.

A comparison of D-E loops in Figure S2(a) 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,[34–38] presented in Figure S4, which shows that the local fields of the copolymer constituent in the poled state induce polarization in the terpolymer regions in the blends. Simulation details can be found in

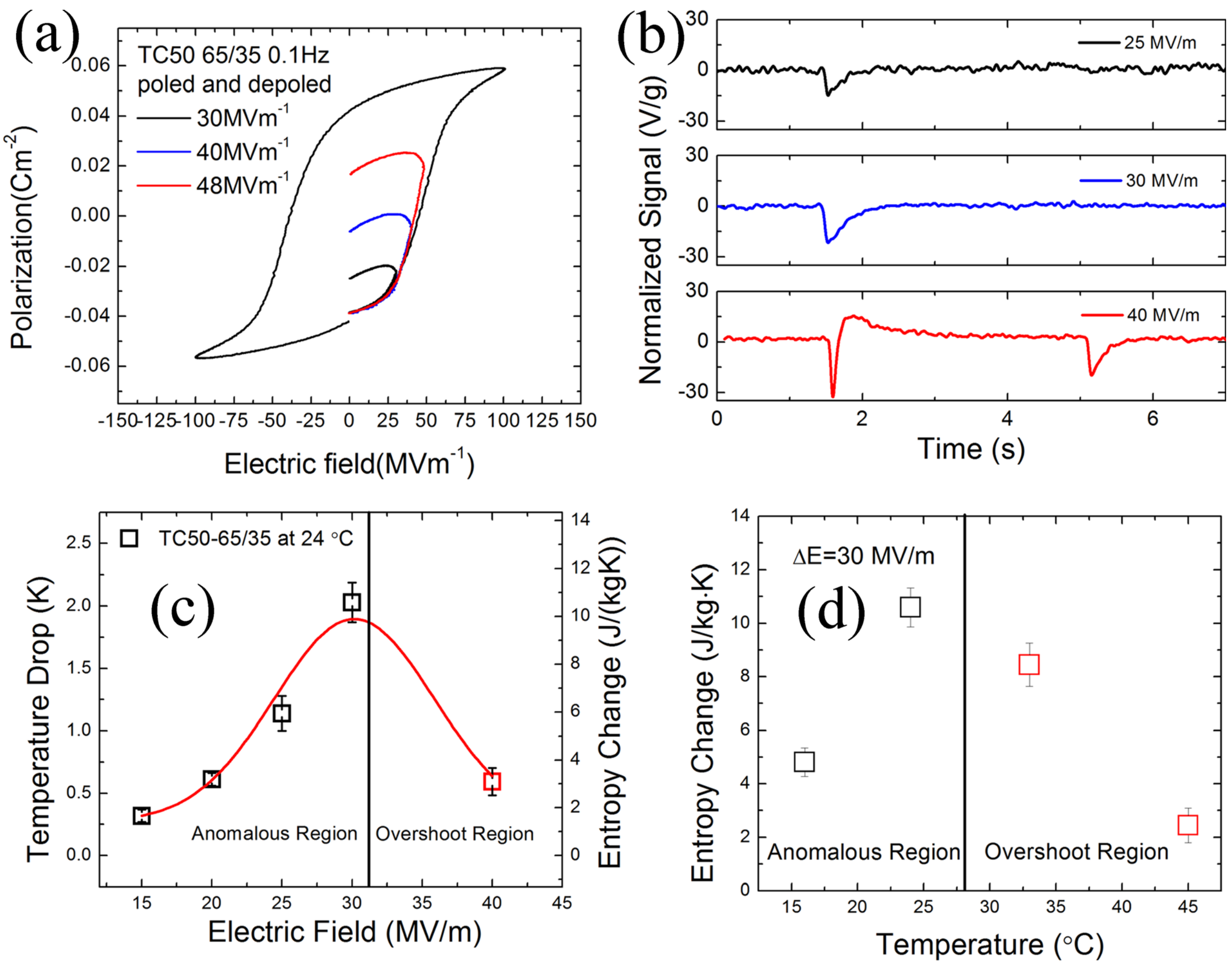

FIG. 3. Temperature and electric field dependences of AN-ECE. (a) Bipolar and unipolar P-E loop of TC50-65/35 blends at room temperature. Each unipolar P-E loop (depoling) was measured after a pre-poling on the opposite direction under 100 MV m^{-1}. (b) Evolution of the AN-ECE vs. de-poling field strength for TC50-65/35 at room temperature, from the AN-ECE at $E < E_{coer}$ to the field overshoot region (40 MV m^{-1}) 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^{-1}, the blends also show a heating peak upon reducing the field to zero. (c) ΔS and ΔT vs. the applied de-poling field at 24 °C, showing the evolution from the AN-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. (d) ΔS vs. temperature under 30 MV m^{-1}. Increasing temperature causes a reduction of E_{coer}, and hence, a crossover from the AN-ECE to the field overshoot when measured under a fixed field.

supplementary online materials. Differential scanning calorimetry was carried out to characterize the phase behavior of the blends. The results are presented in Figure S5 for the blends of TC50-65/35, the terpolymer, and the 65/35 mol. % copolymer, respectively. The blends display two distinctive melting peaks, corresponding to those of the copolymer and terpolymer, and a FE-PE transition peak, due to the copolymer, albeit the FE-PE transition peak is broader in the blends compared with the copolymer, owing to the coupling of the copolymer to the terpolymer.

The importance of dipolar randomness stabilization provided by P(VDF-TrFE-CFE) terpolymer is further confirmed by a comparison between ferroelectric copolymer at higher temperature and TC50-65/35 blends in both polarization study and ECE measurement, which is presented in Figure 4. At 81 °C, P(VDF-TrFE) copolymer exhibits a D-E loop with reduced hysteresis compared with that at room temperature. Its E_{coer} is smaller and its spontaneous polarization is at the same level as those of TC50-65/35 blends at room temperature, respectively. However, the heat-flux signals indicate that the normal ferroelectric P(VDF-TrFE) 65/35 mol. % at 81 °C does not show AN-ECE. Without the dipolar randomness introduced by the terpolymer, the neat copolymer will be first de-poled and then recovered to dipolar ordered states and thus present an N-ECE, owing to its macroscopic ferroelectric domains.

An anomalous negative ECE, in which an electric pulse applied to a dielectric material generates cooling only, is observed in a poled hybrid normal ferroelectric/relaxor ferroelectric polymer blend. The effect originates from 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 without macroscopic polarization by an external field; when the de-poling field is removed, this dipole random state can be maintained by the relaxor component. Based on this principle, we expect that the AN-ECE should have also been present in inorganic counterparts. By exploring more material systems, such as materials possessing anti-ferroelectric-ferroelectric transition, and their dipolar interactions with relaxor ferroelectrics, the AN-ECE may be further enhanced.

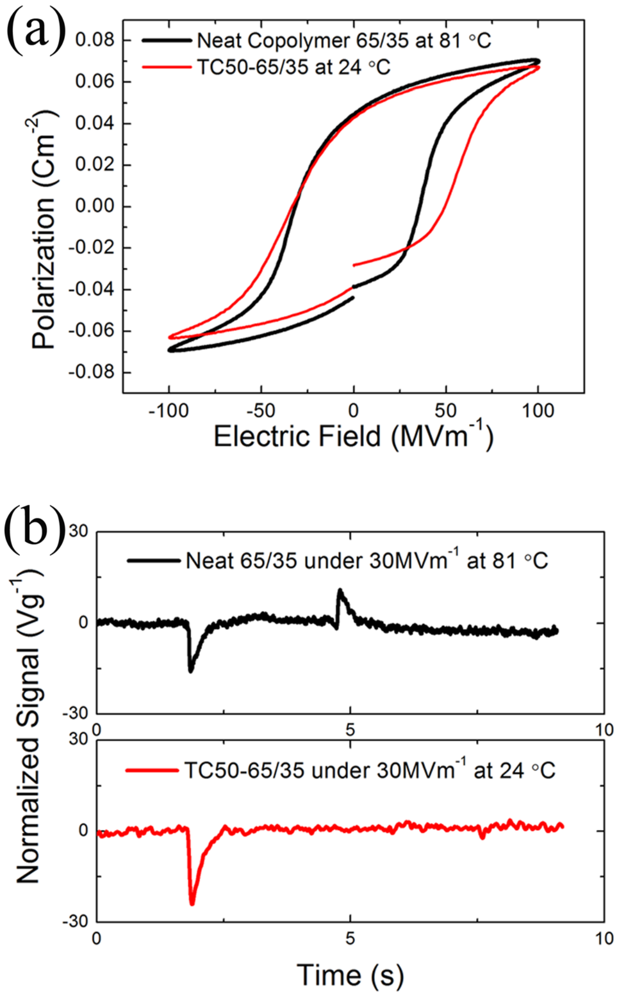

FIG. 4. Comparison of (a) polarization-electric field (P-E) loops and (b) directly measured heat-flux signals between TC50-65/35 blends and neat copolymer P(VDF-TrFE) 65/35 mol. %.

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[1] M. Lines and A. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Larendon, Oxford, 1977).
[2] A. S. Mischenko, Q. Zhang, J. F. Scott, R. W. Whatmore, and N. D. Mathur, Science **311**, 1270 (2006).
[3] B. Neese, B. Chu, S.-G. Lu, Y. Wang, E. Furman, and Q. M. Zhang, Science **321**, 821 (2008).
[4] S. G. Lu and Q. M. Zhang, Adv. Mater. **21**, 1983 (2009).
[5] J. F. Scott, Science **315**, 954 (2007).
[6] X. Moya, S. Kar-Narayan, and N. D. Mathur, Nat. Mater. **13**, 439 (2014).
[7] X. Li, X.-s. Qian, S. G. Lu, J. Cheng, Z. Fang, and Q. M. Zhang, Appl. Phys. Lett. **99**, 052907 (2011).
[8] X.-S. Qian, H.-J. Ye, Y.-T. Zhang, H. Gu, X. Li, C. A. Randall, and Q. M. Zhang, Adv. Funct. Mater. **24**, 1300 (2014).
[9] H. Gu, X. Qian, X. Li, B. Craven, W. Zhu, A. Cheng, S. C. Yao, and Q. M. Zhang, Appl. Phys. Lett. **102**, 122904 (2013).
[10] H. Gu, X.-S. Qian, H.-J. Ye, and Q. M. Zhang, Appl. Phys. Lett. **105**, 162905 (2014).
[11] Y. Jia and Y. Sungtaek, Appl. Phys. Lett. **100**, 242901 (2012).
[12] B. Peng, H. Fan, and Q. Zhang, Adv. Funct. Mater. **23**, 2987 (2013).
[13] G. Akcay, S. P. Alpay, G. A. Rossetti, Jr., and J. F. Scott, J. Appl. Phys. **103**, 024104 (2008).
[14] Y. Bai, G.-P. Zheng, and S.-Q. Shi, Mater. Res. Bull. **46**, 1866 (2011).
[15] A. K. Axelsson, F. Le Goupil, L. J. Dunne, G. Manos, M. Valant, and N. M. Alford, Appl. Phys. Lett. **102**, 102902 (2013).
[16] I. Ponomareva and S. Lisenkov, Phys. Rev. Lett. **108**, 167604 (2012).
[17] R. Pirc, B. Rozic, J. Koruza, B. Malic, and Z. Kutjnjak, Europhys. Lett. **107**, 17002 (2014).
[18] W. Geng, Y. Liu, X. Meng, L. Bellaiche, J. F. Scott, B. Dkhil, and A. Jiang, Adv. Mater. **27**, 3165 (2015).
[19] V. Basso, J. F. Gerard, and S. Pruvost, Appl. Phys. Lett. **105**, 052907 (2014).
[20] X. Li, S.-G. Lu, X.-Z. Chen, H. Gu, X.-s. Qian, and Q. M. Zhang, J. Mater. Chem. C **1**, 23 (2013).
[21] X. Qian, S. Wu, E. Furman, Q. M. Zhang, and J. Su, MRS Commun. **5**, 115 (2015).
[22] Y. Jia and Y. S. Ju, Appl. Phys. Lett. **103**, 042903 (2013).
[23] U. Plaznik, A. Kitanovski, B. Rozic, B. Malic, H. Ursic, S. Drnovsek, J. Cilensek, M. Vrabelj, A. Poredos, and Z. Kutjnjak, Appl. Phys. Lett. **106**, 043903 (2015).
[24] S.-C. Lin and K. Banerjee, IEEE Trans. Electron Devices **55**, 245 (2008).
[25] A. Bar-Cohen and P. Wang, J. Heat Transfer **134**, 051017 (2012).
[26] M. Redmond, K. Manickaraj, O. Sullivan, S. Mukhopadhyay, and S. Kumar, IEEE Trans. Compon., Packag., Manuf. Technol. **3**, 759 (2013).
[27] See supplementary material at http://dx.doi.org/10.1063/1.4944776 for material process, phase field simulation and measurement details.
[28] L. E. Cross, Ferroelectrics **76**, 241 (1987).
[29] Q. M. Zhang, V. Bharti, and X. Zhao, Science **280**, 2101 (1998).
[30] X. Li, X.-S. Qian, H. Gu, X. Chen, S. G. Lu, M. Lin, F. Bateman, and Q. M. Zhang, Appl. Phys. Lett. **101**, 132903 (2012).
[31] D. Wang, X. Ke, Y. Wang, J. Gao, Y. Wang, L. Zhang, S. Yang, and X. Ren, Phys. Rev. B **86**, 054120 (2012).
[32] S. G. Lu, B. Rozic, Q. M. Zhang, Z. Kutjnjak, X. Li, E. Furman, L. J. Gorny, M. Lin, B. Malic, M. Kosec, R. Blinc, and R. Pirc, Appl. Phys. Lett. **97**, 162904 (2010).
[33] F. Bauer, E. Fousson, Q. M. Zhang, and L. M. Lee, IEEE Trans. Dielectr. Electr. Insul. **11**, 293 (2004).
[34] L.-Q. Chen, J. Am. Ceram. Soc. **91**, 1835 (2008).
[35] Y. L. Li, S. Y. Hu, Z. K. Liu, and L. Q. Chen, Acta Mater. **50**, 395 (2002).
[36] L. Q. Chen and J. Shen, Comput. Phys. Commun. **108**, 147 (1998).
[37] For P(VDF-TrFE), $a_1^C = 1.412 \times 10^7(\mathrm{T}/°\mathrm{C} - 42)\mathrm{C}^{-2}\mathrm{m}^2\mathrm{N}$, $a_{11}^C = -1.842 \times 10^{11}\mathrm{C}^{-4}\mathrm{m}^6\mathrm{N}$, $a_{111}^C = 2.585 \times 10^{13}\mathrm{C}^{-6}\mathrm{m}^{10}\mathrm{N}$, $g_{11}^C = 5 \times 10^{-7}\mathrm{C}^{-2}\mathrm{m}^4\mathrm{N}$, $g_{44}^C = g_{44m}^C = 2.5 \times 10^{-7}\mathrm{C}^{-2}\mathrm{m}^4\mathrm{N}$. For P(VDF-TrFE-CFE), $g^T = 0$, $\kappa_r^T = 68.8 - 0.412\mathrm{T}/°\mathrm{C} - 6.20 \times 10^{-3}(\mathrm{T}/°\mathrm{C})^2 + 5.26 \times 10^{-5}(\mathrm{T}/°\mathrm{C})^3$ (15 °C $\leq T \leq$ 70 °C).
[38] Y. L. Li, S. Y. Hu, Z. K. Liu, and L. Q. Chen, Appl. Phys. Lett. **81**, 427 (2002).