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Large Electrocaloric Effect in a Dielectric Liquid Possessing a Large Dielectric Anisotropy Near the Isotropic–Nematic Transition

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The recent findings of large electrocaloric effects (ECEs) in ferroelectric polymers and in ferroelectric ceramic thin films have attracted great interest for developing new cooling cycles that are environmental friendly and have the potential to reach better efficiency than the existing vapor-compression approach. Compared with these solid state ECE materials, a dielectric fluid with a large ECE can be more interesting because it may lead to new cooling cycles with simpler structures than these based on solid state ECE materials. Here it is shown that a large ECE can be realized in the liquid crystal (LC) 5CB near its nematic–isotropic (N-I) phase transition. 5CB has 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 23.6 J kg^{-1}K^{-1} is observed just above the N-I transition.

1. Introduction

Applying an electrical field to an insulating polar material will increase the dipolar ordering and, as a result, will cause a reduction of dipolar entropy. In reverse, as the field is removed, the dielectric material will relax back to a less ordered dipolar state and consequently cause an increase in the dipolar entropy.[1–5] This electrical field induced dipolar entropy change in dielectric materials is known as the electrocaloric effect (ECE). Dielectrics with a large ECE are attractive for developing new cooling devices for air conditioning and refrigeration, which provide an alternative to the existing mechanical vapor compression cycle (MVCC) based cooling technologies that use strong greenhouse gases as the refrigerant. Operating cooling devices with electrical power only is also of great benefit to electrical vehicles since the mechanical compressor required for MVCC is an extra burden in electrical vehicles. The recent findings of giant ECEs in ferroelectric polymers and ceramic thin films have attracted great interest for developing new cooling cycles, which are environmental friendly, mechanical-compressor-free, and have the potential to reach better efficiency.[3–13]

One key component of a cooling device is the transportation of entropy from the cold end to the hot end. The objective is to transport entropy from one temperature level to another temperature level in a reversible and cyclic manner. This requires a substance (refrigerant) whose entropy depends on some properties other than temperature. In ECE materials, this substance is an insulating dielectric material, in which entropy can be changed by external electric fields. Various methods have been proposed to transport entropy from the cold end to the hot end in cooling cycles with ECE.[14–17] Among them, in analogous to the magnetic cooling cycles built upon the magnetic alloys with giant magnetocaloric effect (MCE),[18,19] using heat exchange fluid is still the only one that is realizable with the present technologies to achieve high efficiency and high cooling power.[14,15] Compared with solid state ECE materials, a dielectric fluid with a large ECE can be more interesting since it can be used as both the refrigerant and heat exchange fluid, which could lead to new cooling cycles with simpler structures.

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.[1–9] 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.[1–5] For practical applications, it is important that the dielectric fluid can withstand a relatively high voltage(>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 V, make them not possible to reach a large ECE for practical applications.[10,20] On the other hand, liquid crystals (LCs), which

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DOI:10. 1002/adfm.201202686

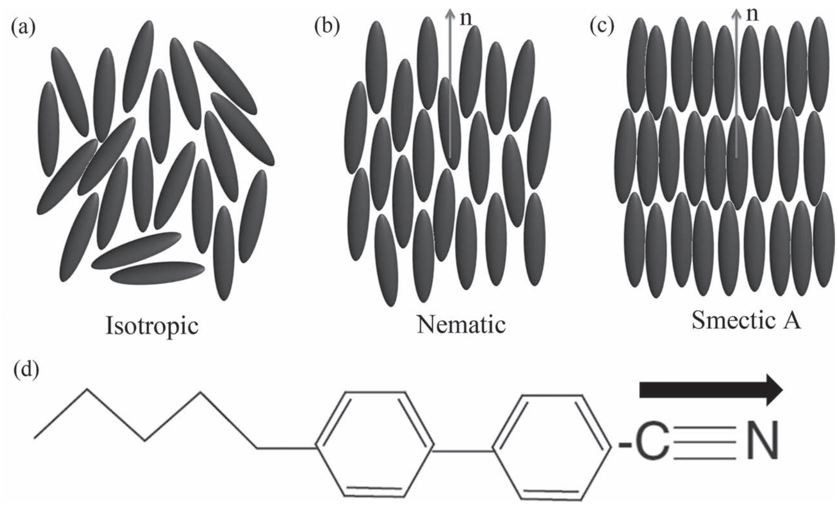

Figure 1. Schematic of various mesophases for rodlike LC molecules which are of interest for generating large ECE: a) an isotropic, b) nematic, and c) smectic A phases. d) Molecular structure of 5CB.

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.[2–23] Hence LCs may be ideal dielectric liquids to realize large ECE. For example, as illustrated in **Figure 1**a, rodlike, anisotropic LC 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 Figure 1b,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 (2D 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.[21,22,24]

In this paper, we investigate the ECE in LC 5CB (4-n-pentyl-4′-cyanobiphenyl, see Figure 1d for the molecular structure) near its N-I transition. LC 5CB is chosen because it has the N-I transition near room temperature (≈35 °C) and the mesogens also possess a large dielectric anisotropy.[25–27] The dielectric constant parallel to the director ($\varepsilon_{\parallel} > 18.5$) 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 ($E//\mathbf{n}$).[25–27]

2. Results and Discussion

The isothermal entropy change of an ECE material when the electric field is increased from E_1 to E_2 is,[5]

$$\Delta S = S(E_{1,} T) - S(E_2 T) \tag{1}$$

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.[28–30] 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 indium tin oxide (ITO) electrode coated glass substrates separated by glass fiber spacers with a thickness $d = 4$ μm (NA-Cells).

Presented in **Figure 2** are the polarization responses (electric displacement–electric field loops, D–E loops) of HA-cells and NA-cells, respectively, measured under 50 MV/m and 100 Hz AC field at temperatures near the N-I transition. The data reveal that there is very little hysteresis in the D–E loops. Reversible isothermal entropy change ΔS and adiabatic temperature change ΔT for a dielectric film as the electric field changes from E_1 to E_2 can be deduced from the pyroelectric coefficient $\partial D/\partial T$ as a function of electric field, i.e,[1–5]

$$\Delta S = \int_{E_1}^{E_2} \left(\frac{\partial D}{\partial T}\right)_E \mathrm{d}E \tag{2a}$$

and

$$\Delta T = -\int_{E_1}^{E_2} \frac{T}{c_E}\left(\frac{\partial D}{\partial T}\right)_E \mathrm{d}E \tag{2b}$$

where c_E is the specific heat of the ECE material. These equations are based on the Maxwell relation $(\frac{\partial D}{\partial T})_E = (\frac{\partial S}{\partial E})_T$.

In general, the Maxwell relation is valid only for a reversible thermodynamic process.[1,4,5,31] For the LC 5CB studied here, it has a weak first-order N-I transition around 34.5 °C, which has a small thermal hysteresis of 0.7 °C between the N-I transitions measured in heating and cooling runs (see Figure S1, Supporting Information). Hence, Maxwell relation, Equation (2), is used here to deduce the ECE at temperatures above 35 °C. The LCs in the experiment are confined by the glass plate cells which have fixed electrode area A and dielectric film thickness d. The area A (≈1 cm^2) is much larger than d (4 μm). Consequently ΔS and ΔT thus deduced for the LCs are these under the constant strain condition. It is also noted that the peak of $\mathrm{d}D/\mathrm{d}T$ for each E in Figure 2 moves progressively towards higher temperature with the field E, which is expected since a higher field will stabilize the nematic phase to higher temperatures.

The isothermal entropy changes ΔS deduced as a function of the temperature (>35 °C) are presented in **Figure 3** for these two groups of LC samples. The data reveal that ECE peaks above N-I transition, which has $\Delta S = 23.6$ J kg^{-1} K^{-1} under

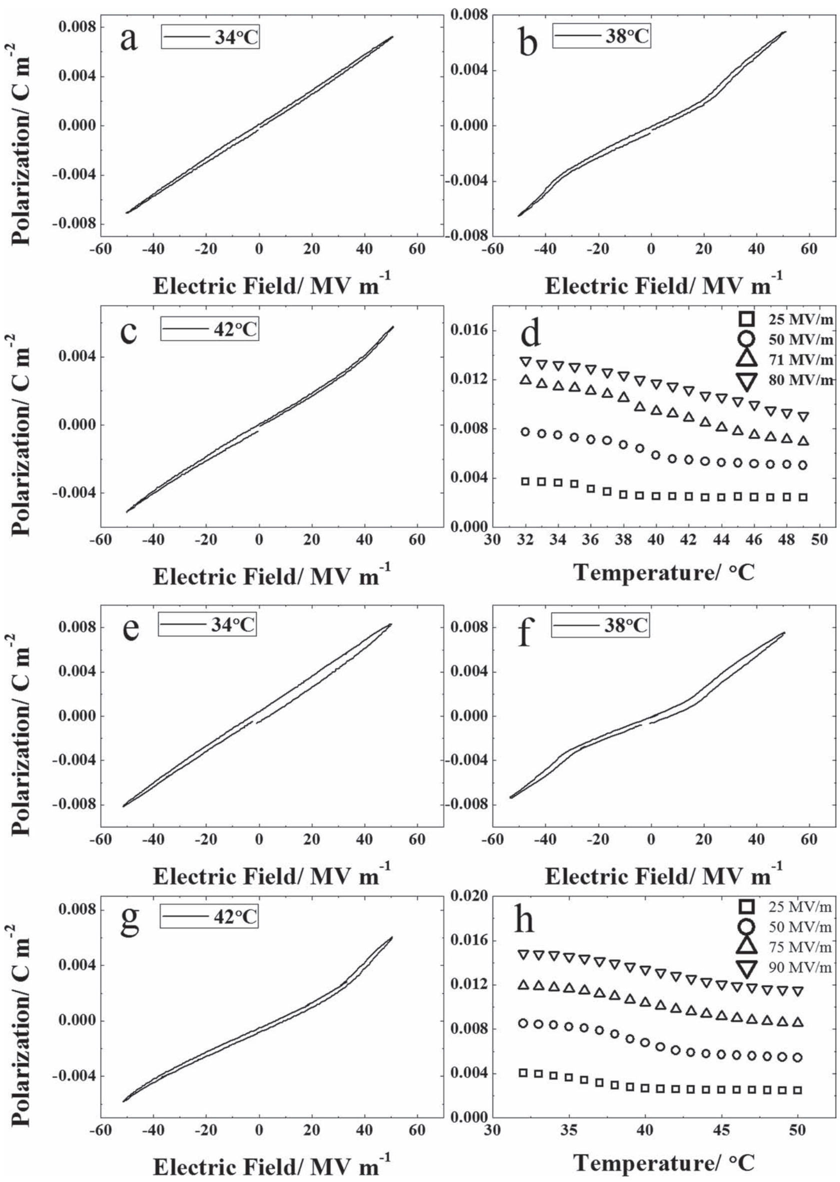

Figure 2. *D*–*E* loops of 5CB under 50 MV/m AC field of 100 Hz at temperatures near the N-I transition for a–c) the HA-cells and e–g) NA-cells. d,h) The *D* vs. temperature curves under different constant *E* fields (≥25 MV/m), which show no discontinuous change of *D* vs. temperature in this field range.

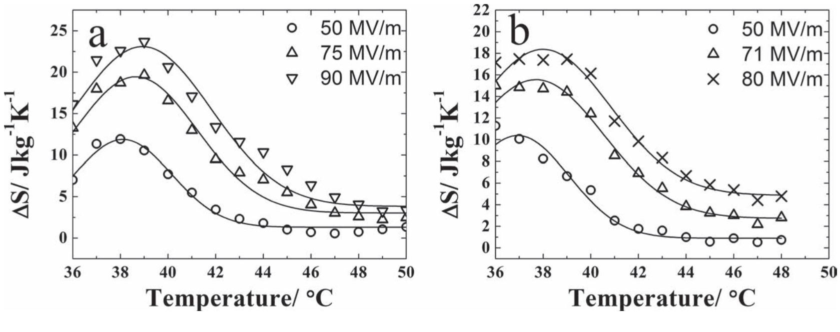

Figure 3. The electrocaloric effect deduced from the Maxwell relations for a) isothermal entropy change ΔS of 5CB LCs in NA-cells and b) ΔS of 5CB LCs in homogeneously aligned LC cells (HA-cells). Data points are shown and solid curves are drawn to guide the eyes.

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.[4,8] 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 3.

Figure 4 presents ΔS as a function of applied field amplitude for the two groups of LC cells at 39 °C, which is above the N-I transition. The LC cells without surface alignment display larger 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 full width at half maximum (FWHM) (≈8 °C) of ΔS vs. temperature curves for the homogeneously aligned cells is slightly larger than that (FWHM ≈ 7 °C) of the randomly oriented cells.

To deduce the adiabatic temperaure change ΔT from the Maxwell relation requires the specific heat data under different electric field (see Equation (2b)), which are not available. Hence we use the specific heat data measured under zero electric field (Figure S2, Supporting Information) to estimate the upper and lower bounds of ΔT. Above the N-I transition at temperatures higher than 37.5 °C, the specific heat is 1.4 J g^{-1} K^{-1}, while at 35 °C the specific heat has its peak value of 2.2 J g^{-1} K^{-1}. Using these values and ΔS at 39 °C (Figure 4) yield the bounds of $3.35\text{ K} < \Delta T < 5.26\text{ K}$ under a 90 MV/m field.

The ECE in LCs can also be estimated from the phenomenological Landau-de Gennes formulation (LG).[21] 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 ($0 \le Q \le 1$) as[21,24]

$$\Delta S = (a/2)\left(Q_1^2 - Q_2^2\right) \tag{3}$$

where Q_1 and Q_2 are the order parameter at electric fields E_1 and E_2, and a is a constant (see Supporting Information). For nematic liquid crystals, $Q = 1$ corresponds to a perfect LC molecular alignment, which may be

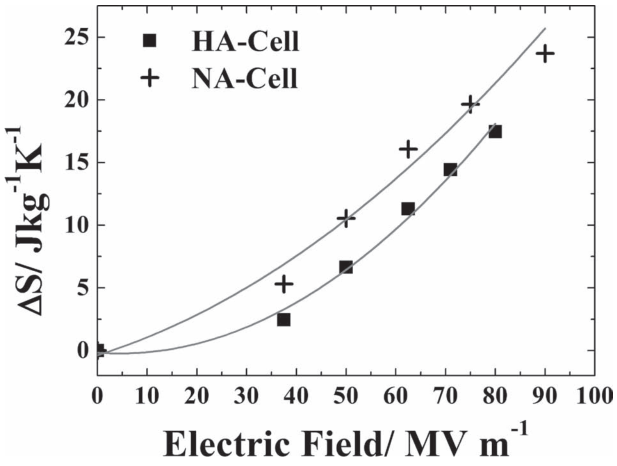

Figure 4. Comparison of ΔS as a function of E of 5CB at 39 °C in NA-cells (crosses) and in HA-cells (squares). Data points are shown and solid curves are drawn to guide the eyes.

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,[26,27] $a = (1.1 \pm 0.4) \times 10^5$ J K^{-1} m^3 and the density $\rho = 1$ g cm^{-3}, a very large $\Delta S = 55$ J kg^{-1} K^{-1} can be deduced when Q is changed $Q_1 = 0$ to $Q_2 = 1$. For the study here $Q_2 = 0.65$ is induced under 90 MV m^{-1} at the critical temperature that yields a $\Delta S = 23 \pm 8.5$ J kg^{-1} K^{-1} (see Figure S3,S4, Supporting Information). 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.[26,27] These results indicate that giant ECE can be obtained from electrical field induced orientational order-disorder transition in LCs near the N-I and S-I transitions.

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.[32] Moreover, for a given LC, its transition temperature can be tuned by, for example, mixing with other LCs with different transition temperatures.[33] 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.[18,19] Compared with the conventional cooling cycles based on MVCC and the cooling devices under development employing solid state ECE and MCE, dielectric liquids with giant ECE will create totally new cooling device cycles which have potential to expand the cooling device application range and improve the performance.

3. Conclusions

In summary, we have presented indirectly measured ECE from LC 5CB, which displays a N-I transition temperature around 35 °C. An isothermal entropy change of 23.6 J kg^{-1} K^{-1} and an adiabatic temperature change of $3.35 \text{ K} < \Delta T < 5.26$ K under 90 MV m^{-1} electric field was observed near 39 °C. A dielectric fluid, e.g., LCs with a large ECE, could be more promising to be cooling-active materials for ECE-based refrigerators because it gives rise to new cooling cycles with simpler designs than those based on solid-state ECE materials.

4. Expremimental Section

LC 5CB was purchased from Merck. Two groups of LC cells were purchased from Instec for HA-cells (part no. SA025A032uG180) and NA-cells (SA100A040uNOPI). In the homogeneous cell the electrodes on the glass substrates were first coated with an alignment layer, e.g., polyvinyl alcohol (PVA), to introduce a small pretilt angle when contact with LC molecules. Then the top and bottom electrodes were rubbed in opposite directions. The cell gaps of HA-cells and NA-cells were 3.2 μm and 4 μm, respectively. The dielectric properties as a function of temperature were characterized using a multifrequency LCR meter (HP 4284A) equipped with a temperature chamber. The electric displacement vs. electric field (D–E) loops at different temperatures were measured using a Sawyer-Tower circuit with a temperature chamber. The differential scanning calorimetry (DSC) data were taken using a TA Instrument (TA Q100), which also had a modulated mode for measuring the specific heat. Hermetic pans and lids purchased from TA Instrument were used in the LC measurement. For the data shown in Figure S1,S2 (Supporting Information), the sample mass was 8 mg, temperature scanning rate was 1 °C/min, and temperature modulation period was 60 s.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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 grant W911NF-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.

Received: September 16, 2012
Revised: November 11, 2012

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