Low Temperature and High Frequency Effects on Blue Phase Liquid Crystals

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Abstract

We report the low temperature and high frame rate operation limits of a polymer-stabilized blue phase liquid crystal (BPLC). Debye relaxation sets another practical application limit even the temperature is still above melting point. Doping a diluter compound to the BPLC host greatly extends this low temperature operation range in terms of dielectric relaxation frequency and response time.

1. Objectives and Background

Polymer-stabilized blue phase liquid crystal (PS-BPLC) [1-4] holds great promises for color sequential displays because of its submillisecond gray-to-gray response time [5,6]. In order to reduce operation voltage, the host BPLC compounds usually possess a huge dielectric anisotropy ($\Delta \approx 100$) [7]. As a result, its viscosity is ~10X higher than that of a commonly used nematic LC. Two problems associated with such a high viscosity BPLC: 1) a fairly low Debye dielectric relaxation frequency ($f_r \sim 1-2 \text{ kHz}$ vs. ~100kHz for a low viscosity nematic), and 2) increased response time at low temperatures. For color sequential displays [8,9], the required frame rate is 3X higher than normal, i.e., at least 360Hz. As the operation frequency approaches f_r , $\Delta \varepsilon$ would decrease dramatically, which translates into unmanageably high operation voltage. This effect becomes more serious in the low temperature region, where the viscosity increases exponentially and f_r further decreases. Therefore, dielectric relaxation could set another practical operation limit even the temperature is still above the melting point of the BPLC material.

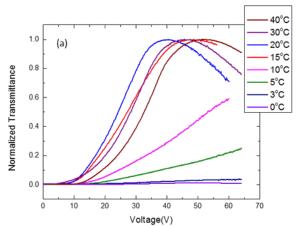
To overcome these problems, in this paper we develop a model to correlate the temperature and frequency effects on the Kerr constant (K) of BPLC materials. Excellent agreement between model and experimental data is obtained. Based on our model, we find that for each BPLC there is an optimal operation temperature at which the Kerr constant has a maximum value, i.e., the device operation voltage is the lowest. Moreover, by doping a diluter compound to our BPLC we can greatly extend the low temperature operation limit, which is imposed by the low f_r .

2. Experiment and results

In our experiment, we prepared two samples employing JC-BP06N and JC-BP07N as LC hosts. While $\Delta\varepsilon$ at low frequency limit of JC-BP06N is 648, which is almost twice of JC-BP07N ($\Delta\varepsilon$ -332). The BPLC precursors consist of 88.17 wt% LC host with 2.92 wt% of chiral dopant R5011, 9 wt% of monomers (5.24 wt. % RM257 & 3.46 wt. % TMPTA (1,1, 1-Trimethylolpropane Triacrylate)) and 0.21 wt% photoinitiator. Samples were filled into two in-plane-switching (IPS) cells whose electrode width is 8µm, electrode gap is 12µm, and cell gap is 7.34µm. Both cells were cooled to BP-I phase and cured by an UV light with λ -365nm and intensity ~2mw/cm² for 30 min. After UV curing, the PS-BPLC composite was self-assembled. For convenience, we call two cells as JC-BP06 and JC-BP07. Next, both cells were

placed on a Linkam heating/freezing stage controlled by a temperature programme (Linkam TMS94). We measured the voltage-dependent transmittance (VT) by sandwiching the heating stage between two crossed polarizers at two frequencies: 240Hz and 480Hz (square-wave AC voltage). A He-Ne laser (λ =633nm) was used as probing beam and the transmitted light was focused by a lens, so that different diffraction orders can be collected by the detector. [10]

Figure 1(a) shows the normalized VT curves of JC-BP06 measured from 40°C to 0°C at 480 Hz. As the temperature decreases, the VT curves shift left first and then rightward, indicating V_{on} bounces back at low temperatures. The lowest V_{on} occurs at 20°C. As the temperature is below 3°C, which is still above the melting point of the BPLC (T_{mp} = -2°C), the transmittance is lower than 5% even the applied voltage (V_{app}) has reached 65V. Therefore, this imposes a practical low temperature operation limit of PSBP. Similar phenomenon was also observed for JC-BP07. We will further discuss this temperature limit later.



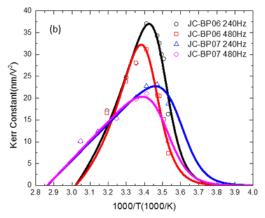


Figure 1. (a) VT curves of JC-BP06 at different temperatures with 480Hz AC voltage signal, and (b) Kerr constants for each temperature of JC-BP06 and JC-BP07 and fitting curves using Eq. (3).

2.1 Optimal operation temperature

We fitted each VT curve for both cells with extended Kerr effect model [11] and obtained K values. Results are plotted in Fig. 1(b). As the temperature decreases from clearing point (left side), K increases linearly ($\sim 1/T$), reaching a maximum, and then declines steeply. The first part agrees well with the results published in Ref. [5], but the second part is new. There exists an optimal operating temperature (T_{op}) where the Kerr constant has a maximum value. From Fig. 1(b), T_{op} depends on the BPLC material and frequency. To better understand the observed phenomena, we analyze the temperature effect of Kerr constant.

Based on Gerber's model [12], K is governed by birefringence (Δn) , average elastic constant (k), $\Delta \varepsilon$ and pitch length (p) of the chiral LC host as:

$$K \sim \Delta n \frac{\varepsilon_0 \Delta \varepsilon P^2}{k \ \lambda (2\pi)^2}.$$
 (1)

Here Δn , k and $\Delta \varepsilon$ are all temperature dependent because they are related to the nematic order parameter $[S = (1 - T/T_{cn})^{\beta}]$ as: $\Delta n \sim \Delta n_0 S$, $\Delta \varepsilon \sim S \exp(E_1/k_B T)$, and $k \sim S^2$ [13,14], where T_{cn} is the clearing point of nematic host, β is a material constant, Δn_0 is the extrapolated birefringence at T=0K, E_I is a parameter related to dipole moment, and k_B is the Boltzmann constant. On the other hand, pitch length is not sensitive to the temperature [15]. From Eq. (1), the frequency effect of K originates from $\Delta \varepsilon$ because the remaining parameters are all independent of frequency in the low frequency region. Based on Debye relaxation model, $\Delta \varepsilon$ has following form:

$$\Delta \varepsilon = \Delta \varepsilon_{\infty} + \frac{\Delta \varepsilon_0 - \Delta \varepsilon_{\infty}}{1 + (f/f_r)^2},$$
(2)

where $\Delta \varepsilon_{\infty}$ and $\Delta \varepsilon_{0}$ are the dielectric anisotropy at high and low frequency limits respectively, f is the operation frequency, and f_{r} is the relaxation frequency. For a low viscosity nematic LC host, f_{r} is usually over 100kHz, which is much higher than the operation frequency (e.g. 120Hz –480Hz), so the denominator in Eq. (2) can be regarded as 1. Therefore, we can treat $\Delta \varepsilon = \Delta \varepsilon_{0}$ which means $\Delta \varepsilon$ would increase as T decreases. However, this approximation would be invalid when f approaches f_{r} . For a large $\Delta \varepsilon$ BPLC its f_{r} is in the 1 kHz region [16].

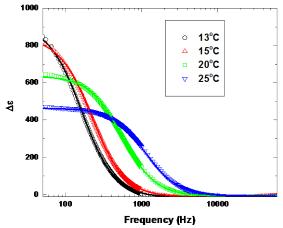


Figure 2. Frequency-dependent $\Delta\epsilon$ of JC-BP06N at four specified temperatures

In experiment, we measured the capacitance of a homogeneous cell and a vertical-alignment cell to determine the $\Delta \varepsilon$ of JC-BP06N and JC-BP07N at different temperatures ¹. Figure 2 depicts the measured $\Delta \varepsilon$ (dots) and fitting curve (solid lines) with Eq. (2) for JC-BP06N. Through fittings, f_r at each temperature is obtained. Results indicate that f_r decreases exponentially with T as $f_r = (1/D) \cdot exp(-E_{\chi}k_BT)$ [17]. Here, E_2 is the activation energy and 1/D is a proportionality constant. Once f_r gets close to f, $\Delta \varepsilon$ decreases as T decreases because of the slow dielectric relaxation time. As Fig. 2 shows, at 480 Hz $\Delta \varepsilon$ decreases $\sim 2X$ as T decreases from 20°C to 13°C. This explains well why V_{on} 'bounces back' as the temperature decreases [Fig. 1(a)]. Thus, the frequency effect should be taken into consideration. Substituting Eq. (2) to Eq. (1) and satisfying the boundary condition that K vanishes when $T=T_c$, we derive following equation for K:

$$K = \mathbf{A} \frac{\exp\left[\frac{E_1}{k_B} \left(\frac{1}{T} - \frac{1}{T_C}\right)\right] - 1}{1 + \left[\mathbf{f} \cdot \mathbf{D} \cdot \exp(\mathbf{E}_2 / \mathbf{k}_B \mathbf{T})\right]},\tag{3}$$

where A is a proportionality constant. We fitted K at various T with Eq. (3) for both JC-BP06 and JC-BP07. Good agreement is obtained as depicted in Fig. 1(b). The optimal operation temperature (T_{op}) can be obtained by setting $\partial K / \partial T = 0$. From Fig. 1(b), T_{op} of JC-BP06 at 240Hz and 480Hz are 18.79°C and 22.53°C, respectively. Based on the extended Cole-Cole model 2 , Kerr constant decreases as frequency increases. Frequency effect on T_{op} is also investigated.

Figure 3 depicts the temperature dependent K at different frequencies for JC-BP06 and BPLC2. BPLC2 has a relatively small Kerr constant because of its small $\Delta\varepsilon$ (~50). As a result, its V_{on} >100V at 25°C and f= 100Hz. However, its viscosity is much lower than that of JC-BP06N so that its f_r ~15 kHz at 25 °C, which is more than 10X higher than that of JC-BP06N. For these two BPLC samples as Fig. 3 shows, the RGB curves overlap in the high temperature region, which means their Kerr constant is quite insensitive to the frequencies. This can be explained by Eq. (3): when $f_r >> f$, the frequency part can be ignored and K becomes inert to frequency. In the low temperature region, the curve with high frequency (blue) bends down first due to the plunge of $\Delta\varepsilon$. Thus, T_{op} decreases as the frequency decreases.

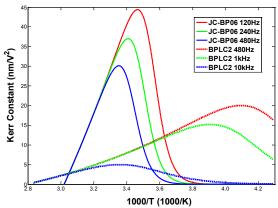


Figure 3. Temperature dependent Kerr constant of JC-BP06 ($f_r \sim 1.2 \text{ KHz}$) and BPLC2 ($f_r \sim 15 \text{ KHz}$) at the specified frequencies.

2.2 Extending low temperature operation limit

Melting point sets the ultimate low temperature operation limit for a BPLC device. However, in this study we find another practical limitation. Even the temperature is still above the melting point of a blue phase, the dramatic plunge of makes the device difficult to drive, which in turn limits the operation temperature range. Let us take JC-BP06 as an example. As the temperature decreases from 25°C to 5°C, its *Von* increases dramatically and the decay time increases exponentially to 17ms. These problems could hinder the BPLC application at low temperatures.

To overcome these problems, we doped 13% diluter 5CC3: 4-pentyl-4'-propyl-1, 1'-bi (cyclohexyl) into JC-BP06N, which shifts f_r from 1.1 kHz to 4.85 kHz at 25°C. We call the new mixture as BPLC3. Although the Von of BPLC3 is somewhat higher than that of JCBP-06 at 25°C, its performance in the low temperature region is much better than that of JC-BP06. Figure 4(a) depicts the measured VT curves and 4(b) shows the response time at 5°C. With diluter, both V_{on} and decay time are decreased significantly. Thus, doping diluter helps to maintain the high performance of BPLC at low temperatures.

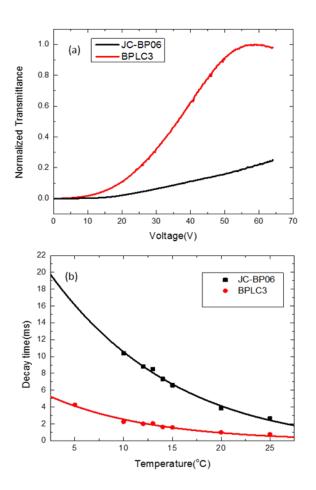


Figure. 4. (a) VT curves of JC-BP06 and BPLC3 at $5\,^{\circ}$ C with f=480 Hz; (b) Temperature dependent response time of JC-BP06 and BPLC3.

3. Conclusion

In this paper, we report two major discoveries: 1) for a given BPLC material and frequency, there exists an optimal operation temperature where the Kerr constant has a maximum value, or Von is the lowest. 2) Although the melting point of a BPLC sets its ultimate operation limit, we found another practical limit which originates from the Debye relaxation of $\Delta \varepsilon$ at low temperatures. By doping a diluter to BPLC helps extend the low temperature operation range.

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5. References

- H. Kikuchi, M. Yokota, Y. Hisakado, H. Yang, and T. Kajiyama, "Polymer-stabilized liquid crystal blue phases," Nat. Mater. 1, 64–68 (2002).
- [2] Y. Hisakado, H. Kikuchi, T. Nagamura, and T. Kajiyama," Large Electro-optic Kerr Effect in Polymer-Stabilized Liquid-Crystalline Blue Phases," Advanced Materials 17, 96-98 (2005).
- [3] J. Yan and S. T. Wu, "Polymer-stabilized blue phase liquid crystals: a tutorial [Invited]," Optical Materials Express 1, 1527-1535 (2011)
- [4] J. Yan, L. Rao, M. Jiao, Y. Li, H. C. Cheng, and S. T. Wu, "Polymer-stabilized optically isotropic liquid crystals for next-generation display and photonics applications," Journal of Materials Chemistry 21, 7870-7877 (2011).
- [5] L. Rao, J. Yan, S. T. Wu, S. Yamamoto, and Y. Haseba," A large Kerr constant polymer-stabilized blue phase liquid crystal," Applied Physics Letters 98, 081109 (2011)
- [6] Y. Chen, J. Yan, M. Schadt, S. H. Liu, K. L. Cheng, J. W. Shiu, and S. T. Wu," Diluter Effects on Polymer-Stabilized Blue Phase Liquid Crystals," Journal of Display Technology 9, 592-597 (2013).
- [7] Y. Chen, D. Xu, S. T. Wu, S. Yamamoto, and Y. Haseba, "A low voltage and submillisecond-response polymer-stabilized blue phase liquid crystal," Applied Physics Letters 102,141116 (2013)
- [8] S. Gauza, X. Zhu, W. Piecek, R. Dabrowski, and S. T. Wu, "Fast Switching Liquid Crystals for Color-Sequential LCDs," Journal of Display Technology 3, 250-252 (2007).
- [9] M. Kobayashi, A. Yoshida, and Y. Yoshida, "A Basic Assessment for Color Break-Up on a Field-Sequential Color Display,"SID Internaltional Symposium Digest Technology Papers 41, 1434-1437 (2010).
- [10] J. Yan, Y. Chen, S. T. Wu, and X. Song, "Figure of Merit of Polymer-Stabilized Blue Phase Liquid Crystals," Journal of Display Technology 9, 24-29 (2013).
- [11] J. Yan, H. C. Cheng, S. Gauza, Y. Li, M. Jiao, L. Rao, and S. T. Wu," Extended Kerr effect of polymer-stabilized blue-phase liquid crystals," Applied Physics Letters, 96, 071105 (2010)

- [12] P. R. Gerber," Electro-Optical Effects of a Small-Pitch Blue-Phase System," Molecular Crystals and Liquid Crystals, 116, 197-206 (1985)
- [13] S. T. Wu and C. S. Wu, "Experimental confirmation of the Osipov-Terentjev theory on the viscosity of nematic liquid crystals," Physical Review A 42, 2219-2227 (1990).
- [14] S. T. Wu," Birefringence dispersions of liquid crystals" Physical Review A 33, 1270-1274 (1986).
- [15] F. Zhang and D. K. Yang," Temperature dependence of pitch and twist elastic constant in a cholesteric to smectic A phase transition," Liquid Crystals 29, 1497-1501 (2002).
- [16] Y. Li, Y. Chen, J. Sun, S. T. Wu, S. H. Liu, P. J. Hsieh, K.

- L. Cheng, and J. W. Shiu," Dielectric dispersion on the Kerr constant of blue phase liquid crystals,"Applied Physics Letters **99**, 181126 (2011)
- [17] M. Schadt," Dielectric Properties of Some Nematic Liquid Crystals with Strong Positive Dielectric Anisotropy," The Journal of Chemical Physics **56**, 1494-1497 (1972).