Effects of ferroelectric nanoparticles on ion transport in a liquid crystal

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A small quantity of $BaTiO_3$ ferroelectric nanoparticles (FNPs) of 50 nm diameter was doped in a nematic liquid crystal (LC), and the free ion concentration was found to be significantly reduced in the LC + FNP hybrid compared to that of the pure LC. The strong electric fields, due to the permanent dipole moment of the FNPs, trapped some mobile ions, reducing the free ion concentration in the LC media. The reduction of free ions was found to have coherent impacts on the LC's conductivity, rotational viscosity, and electric field-induced nematic switching. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4898581]

Almost all liquid crystals (LCs) contain mobile ions[1,2] that influence the LCs' conductivity and field-induced switching phenomena. These ions are generated as impurities during the LC's production process. In other cases, ions can also come from the LC cell's polymer alignment layers, the surrounding glue of the cell, and the filling process.[3–5] In LC displays, the presence of excess ions causes several problems such as slow responses, long-term image sticking effects, and short-term flicker effects.[6–11] Understanding the ion transport phenomenon in an LC and the principles governing their subsequent effects on the LC's electrical and electro-optical properties is an important and active area of research.[12–19] In another direction, LCs have been exploited very effectively over the past decade to impose their long-range orientational order onto various nanoparticles.[20–24] Interestingly, the interactions between the LCs and nanomaterials are multifaceted, as the nanoparticles significantly alter some LC-properties. For example, the presence of carbon nanotubes has a favorable impact on LCs' electro-optical responses,[25–27] quantum dots modify the chiral pitch in cholesteric LCs,[28] and *ferroelectric nanoparticles* (FNPs) significantly enhance the orientational order and electro-optical response, reducing the orientational threshold voltage.[29–41] In this letter, we experimentally demonstrate that when $BaTiO_3$ FNPs are dispersed in a nematic LC, the *free ion concentration* in the LC + FNP system is significantly reduced. Consequently, the hybrid system shows a faster field-induced switching effect with a reduced rotation viscosity.

$BaTiO_3$ FNPs, obtained from US Research Nanomaterials, Inc., had a diameter in the range 50 ± 5 nm. A small amount of $BaTiO_3$ sample was first dispersed in acetone and shaken on a vortex mixer for 8 h, followed by sonication for 5 h. This process reduces the aggregation tendency of the FNPs. The liquid crystal 4-cyano-4'-pentylbiphenyl (5CB) then was added to the acetone + FNP mixture and sonicated for 5 h, allowing the LC to dissolve completely into the solution. Finally, the acetone was evaporated at an elevated temperature, leaving a pure LC + FNP mixture. The process was repeated to produce several known concentrations of FNPs in the LC. Commercially manufactured planar LC cells (SA100A200uG180) from Instec, Inc., with a $1.5°$ pre-tilt angle, 1 cm^2 indium tin oxide

(ITO) coated area, and a $d = 20 \pm 0.5 \, \mu m$ spacing were used for our experiments. The cells were filled with the pure LC or the LC + FNP mixtures at temperature $T > 46 °C$ in the isotropic phase by capillary action. The LC 5CB shows nematic to isotropic transition at $T_{NI} = 36.0 °C$. Note that the small cell spacing tends to filter out any aggregates larger than d.

The presence of free ions in the pure LC and LC + FNP mixtures was measured by detecting the ion-bump[42] in a transient current generated by inverting the voltage at opposite electrodes of the LC cell. The nematic phase of an LC shows dielectric anisotropy $\Delta\varepsilon$ and experiences a torque proportional to $\Delta\varepsilon E^2$ (Ref. 43) in an external electric field E. Thus, the *director* (average direction of LC molecules) can rotate from planar to homeotropic configuration above some critical E. This reorientation process depends on the *magnitude* of E and not on its *sign*. Therefore, when a constant square wave is applied across a nematic LC cell (i.e., the voltage is inverted at opposite electrodes), the LC molecules do not rotate. However, positive and negative ions in the LC cell are initially separated at opposite electrodes. After the voltage is inverted, the ions start to move towards the opposite electrodes in response to E, causing an ion current, I_{ion} in the cell. When the positive and negative ions meet approximately at the middle of the cell, I_{ion} reaches its peak value at peak time, $t_{ion-peak} = \frac{d^2}{2\mu E}$, where μ is the mobility.[42] Finally, I_{ion} drops to zero when the positive ions reach the negative electrode and the negative ions reach the positive electrode of the cell. The total ion transport in the cell then can be calculated by taking the area under the I_{ion} vs. time curve. A square wave of 18 V at 1 Hz was applied using an Automatic Liquid Crystal Tester (Instec, Inc.) to detect I_{ion} for the pure LC and LC + FNP hybrids. The ion concentration, n_i (C/m^3) was extracted using the cell's known dimension.

Figure 1(a) shows n_i as a function of temperature in the nematic phase for 5CB and three 5CB + $BaTiO_3$ mixtures. The inset in Figure 1(a) shows the time dependent I_{ion} for 5CB and a mixture of 0.275 wt. %. Note that for all measurements, we have used the same type of commercially available cells from Instec, Inc. For consistency and to eliminate any experimental error, our experiments with all three concentrations were repeated with new but the same type of LC cells. Results were reproducible with a variation in between 2% and 5%. Also, multiple samples of the same FNP
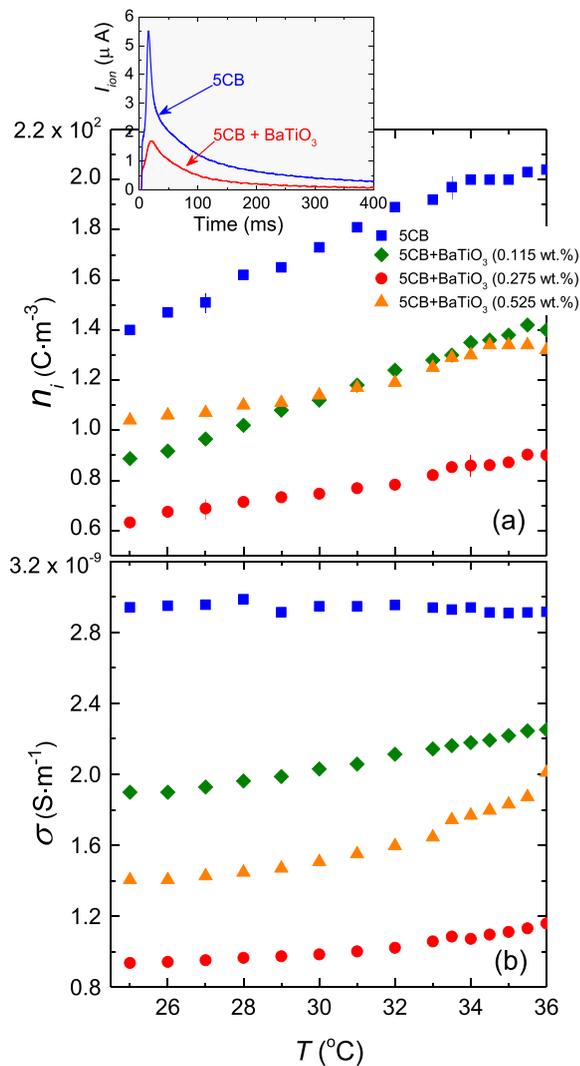
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FIG. 1. (a) Free ion concentration, n_i as a function of temperature for 5CB and three different 5CB + BaTiO$_3$ mixtures listed in the legend. Typical error bars are shown. Inset: Ion current, I_{ion} as a function of time for 5CB and 5CB + BaTiO$_3$ (0.275 wt. %) at 26 °C after the voltage is inverted across the cells. The peak represents the ion-bump when positive and negative ions meet at the middle of the cell. (b) Conductivity, σ as a function of temperature for 5CB and three different 5CB + BaTiO$_3$ mixtures listed in the legend.

concentration gave the same results within the same experimental error. Therefore, if there are any ions generated from the cell's polymer alignment layers or/and the surrounding glue, they must be consistent in all cells, and thus, the observed change in n_i is only due to the presence of the BaTiO$_3$ FNPs. Figure 1(a) depicts that n_i is greatly reduced when BaTiO$_3$ FNPs are doped in 5CB. For the lower two concentrations, 0.115 wt. % and 0.275 wt. %, n_i decreases; and interestingly, at a higher concentration of 0.525 wt. %, n_i is more than that of the other two lower concentrations. However, for this higher concentration (0.525 wt. %), n_i is still smaller than that of the pure 5CB sample. Note that n_i increases with increasing temperature because of more ion transport at high temperature.

The electrical conductivity, σ in a solution is proportional to the ion concentration. Thus, measuring σ is another reliable way of measuring the ionic content in a solution.[44] Figure 1(b) illustrates σ as a function of temperature in the

nematic phase for 5CB and three 5CB + BaTiO$_3$ mixtures. Clearly, the presence of FNPs reduces the conductivity, revealing the presence of fewer mobile ions in the three hybrids. Note that at the higher concentration, 0.525 wt. %, σ increases but stays smaller than that of pure 5CB–similar to the behavior observed for n_i.

Spherical BaTiO$_3$ FNPs possess a spontaneous permanent polarization, $P = 0.26$ C m^{-2}.[45] The local field due to this polarization at a radial distance r around an FNP can be written as $\vec{E}_{FNP} = \frac{R^3 P}{3\varepsilon_o r^3}(2\cos\theta\,\hat{r} + \sin\theta\,\hat{\theta})$, where the radius of the particle $R = 25$ nm and ε_0 is the free space permittivity. The average E_{FNP} at a distance $\xi = r - R = 5$ nm (i.e., $r = 30$ nm) from the surface of the particle is $\sim 10^{10}$ V m^{-1}. This local field, however, rapidly drops to $\sim 10^7$ V m^{-1} at $\xi = 200$ nm and to $\sim 10^6$ V m^{-1} at $\xi = 500$ nm. Consequently, these strong local fields can trap the mobile ions near the FNPs, decreasing n_i in the LC. This ion trapping process is schematically shown in Figure 2.

It is expected that more FNPs would trap more ions, reducing n_i in the LC, which is consistent with our results at low FNP concentrations (0.115 wt. % and 0.275 wt. %), reported in Figures 1(a) and 1(b). Now, for a 0.525 wt. % sample the average separation between the FNPs would be of order 500 nm, and they would be in each other's electric field, $E_{FNP} \sim 10^6$ V m^{-1}. At this length scale, it is possible that the nanoparticles start to interact with each other. This would eventually increase the number, and perhaps the size, of FNP-aggregates. The aggregates, however, remain sufficiently small ($< 0.5\,\mu m$) that they are not visible under the optical microscope. The presence of the aggregates might result in antiparallel dipole configurations, causing a decrease in the resultant electric fields of the particles. An antiparallel-dipole configuration can be treated approximately as a quadrupole, whose field magnitude drops as $\sim 1/r^4$—which is still strong close to the aggregates, but decreases more rapidly as r increases. Moreover, the FNPs present in the aggregates are not completely exposed to the LC media. We thus believe that due to the less exposed surface area and weaker E fields at larger r, these aggregates do not contribute substantially to the ion trapping process; hence the observed increase in n_i and σ
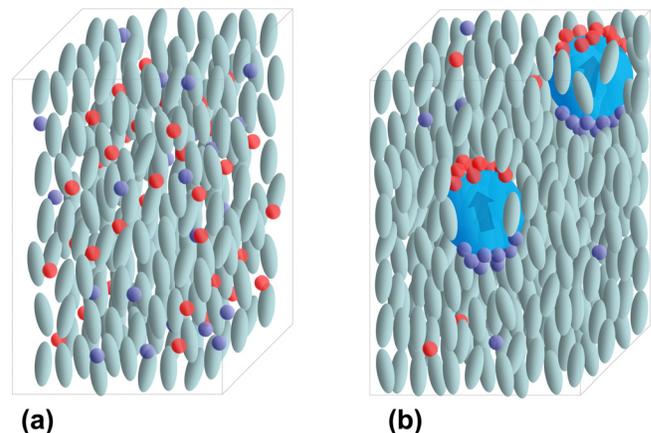

FIG. 2. A schematic illustration of the presence of ions and BaTiO$_3$ FNPs in the nematic phase. The *small spheres* represent the ions, the *ellipsoids* represent LC molecules, and the *big spheres* represent the FNPs. (a) Random distribution of free ions in a nematic phase. (b) FNPs' ion trapping process in a nematic phase.

for the 0.525 wt. % sample in Fig. 1. Since the behavior of n_i is not linear with the FNP concentration, perhaps the aggregation at the 0.275 wt. % is already setting in leading to a higher measured n_i than would be expected from the linearly extrapolated value.

Rotational viscosity, γ_1 of an aligned LC represents an internal friction among LC molecules during the rotation process. The presence of free ions can greatly enhance this internal friction, increasing γ_1 of the LC.[25] Therefore, we performed experiments to measure γ_1 for the pure LC and LC + FNP hybrids to understand if the reduction of ions had any consequent effects on γ_1. This was obtained by measuring the transient current induced by a dc voltage across a planar-aligned configuration.[46,47] When a dc voltage (much higher than the threshold voltage) is applied across a planar LC cell, the director goes through the dynamic rotation, inducing a transient current, $I(t) = \frac{A(\Delta\varepsilon\,\varepsilon_o)^2 E^3}{\gamma_1}\sin^2[2\varphi(t)]$ through the cell, where A is the area of the cell and φ is the angle the director makes with the electrodes/substrate at a given time, t. Figure 3 represents γ_1 as a function of FNP concentration at a constant temperature. The inset in Fig. 3 shows $I(t)$, induced by 25 V, as a function of time for 5CB and one 5CB + BaTiO$_3$ sample. The way to extract γ_1 from $I(t)$ is explained elsewhere.[25,26]

Figure 3 reveals that at low concentrations (0.115 wt. % and 0.275 wt. %) γ_1 decreases with increasing concentration. We attribute this phenomenon to the ion trapping process by the dispersed FNPs. The presence of fewer ions reduces the internal friction of the nematic media, allowing the nematic director to rotate faster. However, being embedded in the LC, the FNPs themselves act as *external additives* and can increase the internal friction. Therefore, in one direction, the reduction of free ions tends to decrease γ_1 and in the opposite direction, higher FNP concentrations tend to increase γ_1. When the concentration of FNPs increases above a certain limit, the presence of FNPs (perhaps due to aggregations) overmatches the effect of the reduction of ions on γ_1. It is experimentally observed that at a higher concentration (0.525 wt. %) γ_1 is more than that of the pure LC, see Fig. 3.
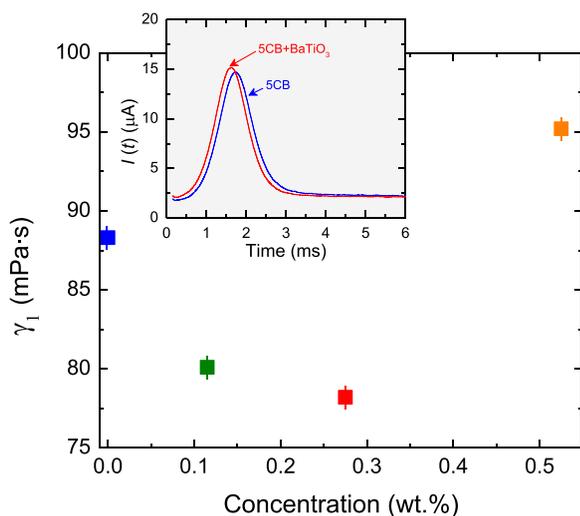
Rotational viscosity is an important parameter for many electro-optical applications employing LCs, because the response time of the LC devices is linearly proportional to this parameter. For a planar aligned LC cell, the director's response to an external field is given by[48] $\tau_{rise} = \frac{\gamma_1 d^2}{\Delta\varepsilon\,\varepsilon_o V^2 - K_{11}\pi^2}$, where K_{11} is the splay elastic constant and V is the applied voltage. We performed experiments to study the electro-optical response of the pure LC and LC + FNP hybrids to understand the effect of ion reduction (hence, a decrease in γ_1) on the field-induced director rotation. The optical setup consisted of a beam from a 5-mW He-Ne laser at wavelength 633 nm that passed through a polarizer, the cell, a crossed analyzer, and into a detector. The beam was polarized at an angle of 45° with respect to the cells' rubbing direction. The output of the detector was fed into a digital storage oscilloscope. A dc voltage pulse of 45 V (much higher than the threshold switching voltage) at a pulse interval of 25 Hz was applied across the cell, and the change in transmittance intensity as a function of time (when the voltage was turned on) was detected by the oscilloscope. The response time was studied as a function of temperature.

Figure 4 shows the electro-optical response of the field-induced switching for 5CB and 5CB + BaTiO$_3$ (0.275 wt. %) at 26 °C. These responses reveal that the hybrid cell responses faster when the field is turned on at $t = 0$ s. The response time, τ_{on} for each sample is obtained from the time the cell takes to drop to 10% of its maximum transmittance intensity and is plotted for all the samples as a function of temperature in Figure 5. Note that τ_{rise} is not directly the electro-optical response. It is the time the director takes to rotate from planar to homeotropic configuration without any backflow in the cell. However, since the optical response is mainly due to the director's rotation after the field is turned on, one can write $\tau_{rise} \propto \tau_{on}$, neglecting the backflow in the cell. From the equation of τ_{rise} (in the previous paragraph), for a constant d and V, the director's response would be faster for a reduced γ_1, an enhanced $\Delta\varepsilon$, and a reduced K_{11}. We empirically show that γ_1 has more pronounced effect on the response time, compared to the other two. Our
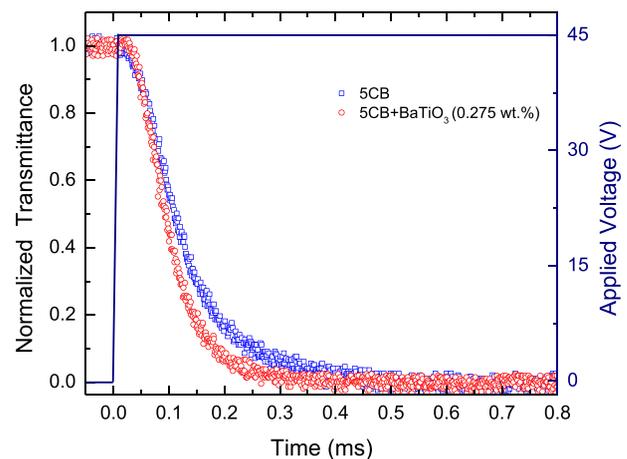
FIG. 3. Rotational viscosity, γ_1 as a function of BaTiO$_3$ concentration in the nematic phase at 26 °C. Typical error bars are shown. Inset: Transient current, $I(t)$ as a function of time for 5CB and 5CB + BaTiO$_3$ (0.275 wt. %).

FIG. 4. Left axis: Normalized transmittance as function of time for 5CB and 5CB + BaTiO$_3$ (0.275 wt. %) at 26 °C after the voltage is turned on. Right axis: The lines represent the applied voltage profile across the cell as a function of time. Note, as the applied voltage is turned on to 45 V at $t = 0$, the transmittance starts to drop.
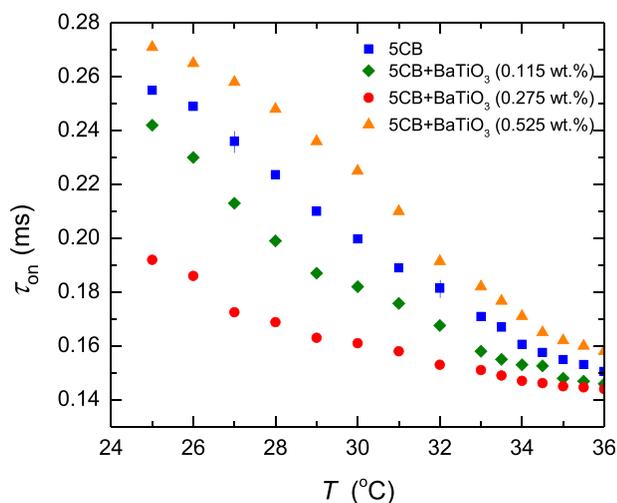
FIG. 5. Electro-optical response time, τ_{on} as a function of temperature for 5CB and three different $5CB + BaTiO_3$ mixtures listed in the legend. Typical error bars are shown.

measurements[40,49] show that, the presence of FNPs (0.275 wt. %) increases both $\Delta\varepsilon$ and K_{11} of the mixture at 26 °C; $\Delta\varepsilon$ (5CB) = 12.1, $\Delta\varepsilon$ ($5CB + BaTiO_3$) = 12.7, K_{11} (5CB) = 5.7 pN, and K_{11} ($5CB + BaTiO_3$) = 7.1 pN. Using these values and keeping γ_1 unchanged, we find only a 2% faster τ_{rise} for the 0.275 wt. % hybrid. When we incorporate the observed change of γ_1, we obtain a 14% faster τ_{rise}, which is closer to the change we experimentally observe in τ_{on} for the 0.275 wt. % mixture at 26 °C (see Fig. 5). Thus, the response time is mainly driven by γ_1 at constant temperature. Figure 5 demonstrates that τ_{on} is consistent with γ_1 (Fig. 3) for each sample. The faster response observed at low concentrations (0.115 wt. % and 0.275 wt. %) strongly suggests that the presence of fewer ions significantly reduces the internal friction between the LC molecules, facilitating the nematic director to respond quicker. The higher concentration of FNPs, as discussed before, increases γ_1 of the system, slowing down the response time in the nematic phase.

It has been theoretically predicted before that some concentration of mobile ions in the LC can redistribute in response to the FNPs electric fields,[32] which is consistent with our experimental observations in the sense that some ions are trapped by the FNPs' electric fields. The observed electro-optical effect at a low concentration is also consistent with a report in the literature,[37] where a ferroelectric LC was found to switch faster in the smectic-C^* phase when doped with $BaTiO_3$ FNPs.

To summarize, we have experimentally demonstrated that when a small quantity of $BaTiO_3$ FNPs is dispersed in 5CB LC, the free ions near the nanoparticles are trapped by the strong local fields of the FNPs. By sweeping some concentration of free ions, FNPs make positive impacts on the LC's electro-optical and mechanical properties—which may have potential applications in LC based electro-optic devices. These results are also important for purifying LCs from excess ions without additional chemical synthesis. At higher concentrations, however, these effects are reversed, perhaps due to the formation of nanoscale FNP-aggregates. Several experiments are planned for the future to study the impact of the size of FNPs on this ion trapping process.

[1]G. H. Heilmeier and P. M. Heyman, Phys. Rev. Lett. **18**, 583 (1967).
[2]G. Briere, F. Gaspard, and R. Herino, Chem. Phys. Lett. **9**, 285 (1971).
[3]N. A. J. M. Van Aerle, Mol. Cryst. Liq. Cryst. **257**, 193 (1994).
[4]S. Murakami and H. Naito, Jpn. J. Appl. Phys., Part 1 **36**, 773 (1997).
[5]S. Naemura and A. Sawada, Mol. Cryst. Liq. Cryst. **346**, 155 (2000).
[6]S. Takahashi, J. Appl. Phys. **70**, 5346 (1991).
[7]H. De Vleeschouwer, B. Verweire, K. D'Have, and H. Zhang, Mol. Cryst. Liq. Cryst. **331**, 567 (1999).
[8]H. De Vleeschouwer, F. Bougrioua, and H. Pauwels, Mol. Cryst. Liq. Cryst. **360**, 29 (2001).
[9]H. De Vleeschouwer, A. Verschueren, F. Bougrioua, R. van Asselt, E. Alexander, S. Vermael, K. Neyts, and H. Pauwels, Jpn. J. Appl. Phys., Part 1 **40**, 3272 (2001).
[10]K. H. Yang, J. Appl. Phys. **67**, 36 (1990).
[11]N. Sasaki, Mol. Cryst. Liq. Cryst. **367**, 671 (2001).
[12]K. Neyts, S. Vermael, C. Desimpel, G. Stojmenovik, R. van Asselt, A. R. M. Verschueren, D. K. G. de Boer, R. Snijkers, P. Machiels, and A. van Brandenburg, J. Appl. Phys. **94**, 3891 (2003).
[13]M. Yamashita and Y. Amemiya, Jpn. J. Appl. Phys., Part 1 **17**, 1513 (1978).
[14]V. Novotny, J. Appl. Phys. **50**, 2787 (1979).
[15]A. Sugimura, N. Matsui, Y. Takahashi, H. Sonomura, H. Naito, and M. Okuda, Phys. Rev. B **43**, 8272 (1991).
[16]H. Naito, M. Okuda, and A. Sugimura, Phys. Rev. A **44**, R3434 (1991).
[17]H. Naito, K. Yoshida, and M. Okuda, J. Appl. Phys. **73**, 1119 (1993).
[18]C. Colpaert, B. Maximus, and A. De Meyere, Liq. Cryst. **21**, 133 (1996).
[19]A. Sawada, A. Manabe, and S. Naemeura, Jpn. J. Appl. Phys., Part 1 **40**, 220 (2001).
[20]M. D. Lynch and D. L. Patrick, Nano Lett. **2**, 1197 (2002).
[21]I. Dierking, G. Scalia, and P. Morales, J. Appl. Phys. **97**, 044309 (2005).
[22]R. Basu and G. Iannacchione, Appl. Phys. Lett. **93**, 183105 (2008).
[23]In.-Su. Baik, S. Y. Jeon, S. H. Lee, K. A. Park, S. H. Jeong, K. H. An, and Y. H. Lee, Appl. Phys. Lett. **87**, 263110 (2005).
[24]R. Basu and G. S. Iannacchione, Phys. Rev. E **80**, 010701 (2009).
[25]H.-Y. Chen, W. Lee, and N. A. Clark, Appl. Phys. Lett. **90**, 033510 (2007).
[26]R. Basu, Appl. Phys. Lett. **103**, 241906 (2013).
[27]R. Basu, K. A. Boccuzzi, S. Ferjani, and C. Rosenblatt, Appl. Phys. Lett. **97**, 121908 (2010).
[28]A. L. Rodarte, C. Gray, L. S. Hirst, and S. Ghosh, Phys. Rev. B **85**, 035430 (2012).
[29]G. Cook, V. Yu. Reshetnyak, R. F. Ziolo, S. A. Basun, P. P. Banerjee, and D. R. Evans, Opt. Express **18**, 17339 (2010).
[30]A. N. Morozovska, M. D. Glinchuk, and E. A. Eliseev, Phys. Rev. B **76**, 014102 (2007).
[31]M. Copic, A. Mertelj, O. Buchnev, and Y. Reznikov, Phys. Rev. E **76**, 011702 (2007).
[32]L. M. Lopatina and J. V. Selinger, Phys. Rev. Lett. **102**, 197802 (2009).
[33]F. Li, O. Buchnev, C. Il Cheon, A. Glushchenko, V. Reshetnyak, Y. Reznikov, T. J. Sluckin, and J. L. West, Phys. Rev. Lett. **97**, 147801 (2006).
[34]Y. Reznikov, O. Buchnev, O. Tereshchenko, V. Reshetnyak, A. Glushchenko, and J. West, Appl. Phys. Lett. **82**, 1917 (2003).
[35]Y.-S. Ha, H.-J. Kim, H.-G. Park, and D.-S. Seo, Opt. Express **20**, 6448 (2012).
[36]J.-F. Blach, S. Saitzek, C. Legrand, L. Dupont, J.-F. Henninot, and M. Warenghem, J. Appl. Phys. **107**, 074102 (2010).
[37]A. Rudzki, D. R. Evans, G. Cook, and W. Haase, Appl. Opt. **52**, E6 (2013).
[38]S. A. Basun, G. Cook, V. Yu. Reshetnyak, A. V. Glushchenko, and D. R. Evans, Phys. Rev. B **84**, 024105 (2011).
[39]M. R. Herrington, O. Buchnev, M. Kaczmarek, and I. Nandhakumar, Mol. Cryst. Liq. Cryst. **527**, 72/[228] (2010).
[40]R. Basu, Phys. Rev. E **89**, 022508 (2014).
[41]A. Mikulko, P. Arora, A. Glushchenko, A. Lapanik, and W. Haase, Europhys. Lett. **87**, 27009 (2009).
[42]Z. Zou, N. A. Clark, and M. A. Handschy, Ferroelectrics **121**, 147 (1991).

[43]P. G. De Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford University Press, New York, 1994).

[44]J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry 1: Ionics*, 2nd ed. (Kluwer Academic Publishers, New York, 2000).

[45]B. Jaffe, W. R. Cook, Jr., and H. Jaffe, *Piezoelectric Ceramics* (Academic Press, New York, 1971).

[46]M. Imai, H. Naito, M. Okuda, M. Okuda, and A. Sugimura, Jpn. J. Appl. Phys., Part 1 **33**, 3482 (1994).

[47]M. Imai, H. Naito, M. Okuda, and A. Sugimura, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **259**, 37 (1995).

[48]E. Jakeman and E. P. Raynes, Phys. Lett. A **39**, 69 (1972).

[49]R. Basu, unpublished data (2014).