Control of haze value by dynamic scattering in a liquid crystal mixture without ion dopants

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We report a method to control the haze value by dynamic scattering in a liquid crystal mixture without ion dopants. The liquid crystal (LC) mixture consists of chiral smectic C (SmC\(*\)) and nematic (N) LC molecules. In the absence of an electric field, LC molecules in the SmC\(*\) phase are oriented by the neighboring vertically-aligned N-LC molecules so that the LC cell is transparent. When a vertical electric field is applied to the LC cell, N-LC molecules with negative dielectric anisotropy tilt down in a random direction parallel to the two substrates, whereas SmC\(*\)-LC molecules are rotated with the polarity reversal of the applied field. During the switching process, we observed dynamic scattering because the random orientation of N-LCs is maintained via the rotation of SmC\(*\)-LCs, resulting in a high-haze translucent state without the use of ionic dopants. The LC mixture exhibited a very high haze of 96.1% in the translucent state while maintaining the haze-free (<1%) transparent state owing to the use of an LC layer without a polymer structure. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5030764

I. INTRODUCTION

Liquid crystal (LC) materials have been widely used for photonic devices and display applications because their optical characteristics can be controlled by applying an electric field. Recently, LC technologies have been widely studied for smart window or see-through display applications, because haze or transmittance can be controlled using the LC materials. Smart windows can replace blinds or curtains used to block excessive sunlight or to provide privacy, whereas see-through displays with a light shutter can be selectively operated in the see-through or high-visibility mode.\(^1\)\(^-\)\(^4\)

Various LC light shutter technologies have been actively studied for the control of the haze value. Haze can be controlled by either light scattering or diffraction.\(^5\)\(^-\)\(^7\)\(^-\)\(^17\) Light shutters using LC/polymer composites based on light scattering, such as polymer-stabilized LCs and polymer-dispersed LCs, can be switched between the transparent and translucent states by applying an electric field.\(^5\)\(^-\)\(^12\) However, light shutters using LC/polymer composites suffer from several disadvantages, such as high haze, low transmittance, and narrow viewing angle in the transparent state despite being able to provide a high-haze translucent state. Unexpected haze in the transparent state of the devices is caused by the refractive index mismatch between the LC and polymer matrices.\(^11\)\(^,\)\(^12\) In addition, these light shutters require the UV curing process for the polymerization of reactive monomers, which leads to an increase in the manufacturing cost. On the other hand, LC phase grating devices based on light diffraction can provide a haze-free transparent state as well as a high-haze translucent state because they do not contain any polymer matrices.\(^13\)\(^-\)\(^15\) However, these devices require a photolithography process to form patterned electrodes, which results in a higher manufacturing cost.

Meanwhile, it has been reported that haze can be controlled by light scattering caused by the electro-hydrodynamic effect simply by adding ionic dopants in LCs.\(^16\)\(^,\)\(^17\) A device using ion-doped

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LCs can be switched between the haze-free transparent and high-haze translucent states without a polymer structure or patterned electrodes. However, it suffers from long-term stability, heating, and high power consumption due to the ionic charges accumulating at the interface between the LC and alignment layers or the movement of ions in the cell. These challenges can hinder their use in a wide range of applications.

In this paper, we report a method to control the haze value using an LC mixture, consisting of chiral smectic C (SmC*) and nematic (N) LC molecules. In a SmC*/N-LC cell, N-LC is used as a host material while SmC*-LC is used as a guest material. It is switchable between the haze-free transparent and high-haze translucent states without using the polymer structures or ionic dopants. Initially, the LC mixture is aligned perpendicular to the two substrates so that the cell is transparent. A vertical electric field applied to the LC cell attempts to orient the N-LC molecules with negative dielectric anisotropy along the directions perpendicular to the applied electric field, whereas SmC*-LC molecules are rotated upon the polarity reversal of the applied electric field. Therefore, the guest SmC*-LC molecules induce random orientation of the host N-LC molecules in planes parallel to the substrates. The LC cell can be switched to a good translucent state owing to the strong light scattering by the randomly oriented LCs. The device exhibits a high haze of 96.1% in the translucent state while maintaining the haze-free (<1%) transparent state.

II. OPERATIONAL PRINCIPLE

The schematic representation of the switching of SmC*-LCs used as a guest material in this study is shown in Fig. 1. The SmC*-LC molecules are tilted away from the director n, which is defined as the average direction of the long molecular axis, by θ and form the helical structure along the director n, as shown in Fig. 1(a). The spontaneous polarization, \( P_s \), is perpendicular to the long molecular axis. In the tilted SmC* phase, the molecular chirality results in the formation of a helical structure, canceling the ferroelectricity. The direction of polarization P is determined by the interaction between the spontaneous polarization \( P_s \) and the external field E.

The linear coupling between the applied electric field and the permanent polarization causes active switching between the two opposite directions on field reversal, as shown in Fig. 1(b). The optic axis of the system, defined by the average direction of the long axis of the molecules, can be switched between the two states by an external electric field that acts on the local spontaneous polarization and rotates the molecules, hence the axis, around the cone. Based on this intrinsic switching principle of SmC*-LC, the SmC*-LC as a guest material can be substituted for the function of polymer structures or ionic dopants in the LC cell, as will be explained later.

The operation of a SmC*/N-LC cell is shown schematically in Fig. 2. Initially, N-LC molecules are vertically-aligned by the anchoring provided by the vertical alignment layer on each substrate. The SmC*-LC molecules are also aligned vertically by the interaction with the surrounding N-LC.

![FIG. 1. Schematic representation of the (a) helical structure of the SmC* phase and (b) molecular motion induced by an electric field in the tilted SmC*-LC. \( P_s \) is the spontaneous polarization, and \( \theta \) is the tilt angle of the LC molecules.](image)
molecules. Therefore, the SmC*/N-LC mixture is well-aligned perpendicular to the two substrates so that the cell is transparent, as shown in Fig. 2(a).

If we apply a vertical electric field to a pure N-LC cell, LC molecules with negative dielectric anisotropy start to tilt down in a random direction because their switching direction is not determined because of the absence of a pretilt angle. The LC molecules tend to be aligned in the direction of neighboring LC molecules to minimize the free elastic energy. During this process, light scattering occurs temporarily and gradually disappears. Various studies that pertain to maintaining light scattering by forming polymer structures\textsuperscript{5–12} or using ionic dopants\textsuperscript{16,17} have been reported. The polymer structures or ionic dopants scatter the incident light by creating random domains within the cell.

In contrast to a pure N-LC cell, a SmC*/N-LC cell can be switched to the translucent state by applying a vertical electric field, as shown in Fig. 2(b). When a vertical electric field is applied to the cell, N-LC molecules tilt down in a random direction while SmC*-LC molecules tend to be rotated upon the polarity reversal of the applied electric field. The rotation of SmC*-LC molecules depending on the polarity of the applied electric field prevents the neighboring N-LC molecules from being aligned with each other. Consequently, the incident light is strongly scattered by the randomly oriented LC molecules, which results in a high-haze translucent state.

III. EXPERIMENTAL RESULTS AND DISCUSSION

To investigate the electro-optical characteristics, we fabricated a SmC*/N-LC cell shown in Fig. 2. First, we prepared a host nematic LC (SPO-001, HCCH, China) with negative dielectric anisotropy, whose physical properties are as follows: the dielectric anisotropy $\Delta \varepsilon = -4.8$ ($\varepsilon_\parallel = 4.5, \varepsilon_\perp = 9.3$ at 1 kHz, 25 °C), optical anisotropy $\Delta n = 0.282$ ($n_e = 1.783, n_o = 1.501$ at 589 nm, 20 °C), nematic–smectic transition temperature $T_{SN} = -40$ °C, and nematic–isotropic transition temperature $T_{NI} = 114$ °C. We used SmC*-LC (Felix-017/100, Clariant, Germany) as a guest material to mix with the host LC. The phase sequence of SmC*-LC is given as follows: Cr $\leftrightarrow$ SmC$^*$ 73°C $\leftrightarrow$ SmA$^*$ 77°C $\leftrightarrow$ N$^*$ 85°C $\leftrightarrow$ Iso. The SmC*-LC has a spontaneous polarization $P_s = 47$ nC/cm$^2$ at 25 °C.

The LC mixtures with 15 wt%, 30 wt%, and 45 wt% of SmC*-LC were prepared. They were stirred for 24 h at 100 °C. To fabricate the LC cells, we coated a vertical alignment layer on each indium-tin-oxide substrate, which was baked for 1 h at 230 °C. The cell was assembled using silica spacers of diameter 20 µm. Finally, the LC mixtures were injected into empty cells at 100 °C; subsequently, the cells were slowly cooled to the room temperature of 23 °C.

To evaluate the optical performance of the fabricated LC cells, we measured the total transmittance, specular transmittance, diffuse transmittance, and haze using a haze meter (HM-65, Murakami Color Research Laboratory, Tokyo, Japan). The specular [diffuse] transmittance $T_s$ [$T_d$] refers to the ratio of the beam power that emerges from a sample cell, which is parallel (a small range of angles within 2.5°) [not parallel] to a beam entering the cell, to the power carried by the beam entering the cell, as shown in Fig. 3. The total transmittance $T_t$ is the sum of the specular transmittance $T_s$ and the diffuse transmittance $T_d$. The haze $H$ can be calculated as $H = T_d/T_t$. 
The concentration of the SmC*-LC is very important because it may determine the distance between the domain boundaries formed by the randomly oriented N-LCs. To confirm the effect of the SmC*-LC concentration, we measured the electro-optical characteristics of the fabricated cells with various SmC*-LC concentrations, as shown in Fig. 4. The optical characteristics were measured by applying the same 60 Hz square voltage wave to operate each LC cell. When the concentration of the SmC*-LC was 15 wt%, the measured specular transmittance and haze of the LC cell in the transparent state were 87.2% and 0.8%, respectively, whereas those of the cell in the translucent state (72 V) were 8.5% and 90%, respectively.

When the concentration of SmC* LC was increased from 15 wt% to 30 wt%, the haze in the translucent state increased by 6.8%. When the concentration of SmC* LC was 30 wt%, the measured specular transmittance and haze of the cell in the transparent state were 87.2 and 0.9%, respectively, whereas those of the LC cell in the translucent state (74 V) were 3.1% and 96.1%, respectively. Both cells exhibited the haze-free transparent state because the polymer structure was absent. The higher haze value in the translucent state of the cell with 30 wt% of SmC*-LC corresponds to the smaller domains originating from the randomly oriented N-LCs.

As the concentration of SmC*-LC was further increased to 45 wt%, the corresponding values in the transparent and translucent states were the same as those shown with 30 wt% of SmC*-LC, whereas the operating voltage was higher. These results show that we can choose a SmC*-LC concentration of 30 wt% because the domains were sufficiently small for light scattering.

The electro-optical characteristics of a SmC*/N-LC cell is dependent on its driving frequency, as shown in Fig. 5, because the switching speed of SmC*-LCs and N-LCs are significantly different. In a SmC*/N-LC cell, light scattering is caused by randomly oriented N-LCs, while the molecular rotation of SmC*-LCs due to the polarity reversal of the applied electric field serves to maintain the N-LCs randomly orientated. When a vertical electric field is applied to a SmC*/N-LC cell, SmC*-LC
molecules are rotated dominantly by the ferroelectric torque because of the spontaneous polarization while the dielectric torque rotates the N-LC molecules. In this case, the switching of SmC∗-LCs is very fast (~several tens of microseconds) whereas the switching of N-LCs is rather slow (~several tens of milliseconds). The latter is also dependent on the amplitude of the applied electric field.

To confirm the dependence of a SmC∗/N-LC cell on the driving frequency, we measured the optical characteristics as we varied the driving frequency from 30 Hz to 960 Hz, as shown in Fig. 5. As the driving frequency increases, the voltage-dependent specular transmittance and haze curves shifted to the right. In other words, both the threshold and operating voltages increased with the increase in the driving frequency. As the driving frequency increases, duration to maintain the polarity of the applied electric field becomes shorter, which may not be sufficient for the N-LC molecules to be switched fully for light scattering. Therefore, a relatively high applied voltage is required for the sufficient switching of N-LCs before the polarity of the applied electric field is reversed at a high driving frequency, as shown in Fig. 5. This is the reason why the operating voltage increases as the driving frequency is higher.

We can also identify these results through the specular transmittance measured at the same applied voltage of 74 V, as shown in Fig. 6. At low driving frequencies below 120 Hz, the N-LC molecules were completely switched so that the specular transmittance was very low. In contrast, at relatively high driving frequencies, such as 240 Hz and 480 Hz, a specular transmittance fluctuation was observed, and the time-average transmittance was relatively high because the duration between

![FIG. 5. Measured voltage-dependent (a) specular transmittance and (b) haze of a SmC∗/N-LC cell with the driving frequency as a parameter.](image)

![FIG. 6. Measured specular transmittance of a SmC∗/N-LC cell with the driving frequency as a parameter. The amplitude of the applied voltage wave was fixed at 74 V. The results are normalized by the specular transmittance in the transparent state of the cell.](image)
the polarity reversal of the applied electric field is insufficient to stabilize the N-LC reorientation. At 960 Hz, the time-averaged specular transmittance in the transparent state decreased slightly, as shown in Fig. 6. These results show that the operating voltage can be significantly reduced by operating the device at a low driving frequency.

Although the reduced driving frequency is highly favorable for a low operating voltage, it may cause a flicker in the LC cell, which depends on the human eye sensitivity. For a lower driving frequency, each period has a longer duration, which would result in a higher specular transmittance or haze difference in a SmC*/*N-LC cell. Therefore, to obtain a non-obvious flicker, the cell is to be operated at frequencies higher than 60 Hz, which is typically the driving frequency used in LC devices. In our experiments, the flicker was not noticeable when a SmC*/N-LC cell was driven at 60 Hz.

In addition to the threshold and operating voltages, the haze value achievable in the translucent state depends slightly on the driving frequency, as shown in Fig. 5. As shown in Fig. 5(b), the maximum haze value in the translucent state is the highest at the driving frequency of 60 Hz, and the cell showed a high haze of 96.1% at 74 V. It is comparable to that of previously reported LC light shutters with polymer structures or ionic dopants. This means that the driving frequency of 60 Hz allows the N-LC molecules to complete the randomly oriented state and the SmC* molecules to maintain the state well.

To observe the switching process of SmC* and N-LC molecules in a SmC*/N-LC cell, we measured the specular transmittance as we vary the applied voltage from 0 V to 80 V at a fixed driving frequency of 60 Hz, as shown in Fig. 7(a). We also recorded the polarizing optical microscopy (POM) images of the fabricated LC cell at each applied voltage, as shown in Fig. 7(b). In the absence of an applied voltage, the cell is transparent because both SmC* and N-LC molecules are vertically aligned between the two substrates. Therefore, the cell is in the dark state between the crossed polarizers, as shown in Fig. 7(b).

When a relatively low voltage of 20 V is applied to the cell, only a slight decrease is observed in the specular transmittance when compared to that of the transparent state, because the N-LCs start to rotate but are not fast enough to switch to a randomly oriented state before the polarity reversal of the applied electric field. We confirmed that no domains are observed through the POM images, as shown in Fig. 7(b).

As the applied voltage was increased to 40 V, more N-LCs are randomly oriented before the polarity reversal of the applied electric field owing to their faster switching time so that the specular transmittance decreased, and fluctuated with the polarity reversal of the applied electric field. In this case, the random domains whose sizes are relatively large were observed, as shown in Fig. 7(b).

![Figure 7](image_url)
FIG. 8. Photographs of a SmC∗/N-LC cell in the (a) transparent and (b) translucent states.

As the applied voltage was further increased to 60 V, more N-LCs are rotated before the polarity reversal of the applied electric field so that the very small domains were formed. Consequently, the specular transmittance was dramatically decreased, and the specular transmittance fluctuation was also decreased. For a higher applied voltage (80 V), the N-LCs are sufficiently switched for strong light scattering, resulting in a very low specular transmittance, as shown in Fig. 7(a).

Thus far, we have demonstrated the switching between haze-free (<1%) transparent and high-haze (96.1%) translucent states in a SmC∗/N-LC cell without any polymer structures or ionic dopants. In the transparent state, the background image can be observed owing to the high transmittance of the cell from using an LC layer without a polymer structure, as shown in Fig. 8(a). When the cells are switched to the translucent state, the background image can be completely hidden, as a result of strong light scattering due to the randomly oriented N-LCs, as shown in Fig. 8(b).

In a previous study, it was demonstrated that an ion-doped LC cell could be switched between the haze-free transparent and high-haze translucent states owing to the absence of the polymer structure. Although the ion-doped LC cell exhibited excellent electro-optical characteristics, it still suffers from several drawbacks, such as long-term stability, performance degradation after long-time driving, heating, and high power consumption, which are caused by the residual charges owing to the movement of ions in the LC cell. In contrast, a SmC∗/N-LC cell is robust against such problems because it exhibits dynamic scattering without the movement of ions. Table I shows the measured resistivity of cells with pure N-LCs, ion-doped N-LCs, and the SmC∗/N-LC mixture. For comparison, we fabricated a pure N-LC cell and an LC cell doped with a small amount (0.1 wt%) of ionic materials (tetra-n-butylammonium bromide, Sigma-Aldrich, Korea). The parameters used in the cell fabrication were the same as those used for a SmC∗/N-LC cell. The size of all the fabricated LC cells was 1.3 cm × 1.3 cm.

We measured the resistivity of the fabricated cells using an LCR meter (LCR-817, Instek, Taiwan). The resistivity of an ion-doped N-LC cell was much lower than that of a pure N-LC cell because of the net current formed by the added ion dopants. In contrast, a SmC∗/N-LC cell showed a higher resistivity than a pure N-LC cell, which accompanies lower power consumption. The resistivity of the SmC∗/N-LC mixture higher than that of the pure N-LC may originate from the SmC∗ LC with a higher resistivity than that of the pure N-LC. Moreover, the haze in the transparent and translucent states of the SmC∗/N-LC cell remained the same after repeated switching of over 30 times, as shown in Fig. 9.

Finally, we measured the response time of a SmC∗/N-LC cell, as shown in Fig. 10. Initially, the cell is transparent. For the switching from the transparent to translucent state, a 60-Hz square voltage wave with an amplitude of 74 V was applied to the fabricated cell for turn on and then removed after several seconds. The measured turn-on and turn-off times were 6.8 ms and 323.2 ms, respectively.

| TABLE I. Resistivity of cells with pure N-LC, ion-doped N-LC, and SmC∗/N-LC mixture. |
|---------------------------------|-----------------|-----------------|
| Resistivity (Ω·m)               | Pure N-LC       | Ion-doped N-LC  |
|                                 | 7.24 × 10³      | 6.15 × 10²      | 4.10 × 10⁴ |
| SmC∗/N-LC mixture              |                 |                 |            |
The turn-on switching was fast because it is controlled by applying an electric field whereas the turn-off switching was rather slow because it is limited by the slow relaxation of the SmC* and N-LC molecules. During the turn-off process, the N-LC molecules are relaxed by the vertical alignment layers, and then SmC* LC molecules are also oriented by the interaction with the vertically aligned N-LC molecules. Further study is necessary to reduce the slow turn-off time of the device.

IV. CONCLUSION

We investigated the electro-optical characteristics of a SmC*/N-LC cell for haze control. In this device, light scattering was induced by randomly oriented N-LCs, while the molecular rotation of SmC*-LCs due to the polarity reversal of the applied electric field maintained the N-LCs randomly orientated. In addition, we investigated the driving frequency effects on the electro-optical characteristics of the device. As the driving frequency decreases, both the threshold and operating voltages decreased. Although the reduced driving frequency is highly favorable for a low operating voltage, it may cause a flicker in the LC cell. In our experiments, no flicker was observed when the device was operated at driving frequencies above 60 Hz.

We demonstrated a SmC*/N-LC cell switchable between the transparent and translucent states. The transparent state of the device was haze-free (<1%) from using an LC layer without polymer structures. In the translucent state, the device exhibited a very high haze of 96.1% owing to the strong light scattering based on the switching of SmC*/N-LCs without using polymer structures or the movement of ions. In addition, the device is free from concerns such as long-term stability, heating, and performance degradation after long-time driving.
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1 G. Gu, V. Bulovic, P. E. Burrows, and S. R. Forrest, Appl. Phys. Lett. 68(19), 2606–2608 (1996).
2 C.-H. Lin, W.-B. Lo, K.-H. Liu, C.-Y. Liu, J.-K. Lu, and N. Sugiura, SID Symp. Dig. Tech. Pap. 43(1), 1159–1162 (2012).
3 J. Yeon, T.-W. Koh, H. Choi, J. Chung, S. Yoo, and J.-B. Yoon, Opt. Express 21(8), 10358–10366 (2013).
4 J.-H. Huh, B.-H. Yu, J. Heo, S.-M. Ji, and T.-H. Yoon, Mol. Cryst. Liq. Cryst. 644, 120–129 (2017).
5 R. A. M. Hikmet, J. Appl. Phys. 68, 4406–4412 (1990).
6 H. Ren and S.-T. Wu, Appl. Phys. Lett. 81(8), 1432 (2002).
7 H. Ren, Y.-H. Lin, Y.-H. Fan, and S.-T. Wu, J. Appl. Phys. 96, 3609–3611 (2004).
8 M. Kim, K. J. Park, S. Seok, J. M. Ok, H.-T. Jung, J. Choe, and D. H. Kim, ACS Appl. Mater. Interfaces 7(32), 17904–17909 (2015).
9 B.-H. Yu, S.-M. Ji, J.-H. Kim, J.-W. Huh, and T.-H. Yoon, J. Inf. Disp. 18(1), 13–17 (2016).
10 A. Lorenz, F. Omairat, L. Braun, and V. Kolosova, Mol. Cryst. Liq. Cryst. 646, 220–225 (2017).
11 S.-W. Oh, J.-M. Baek, J. Heo, and T.-H. Yoon, Dyes Pigm. 134, 36–40 (2016).
12 J.-H. Lee, J. J. Lee, Y. J. Lim, S. Kundu, S.-W. Kang, and S. H. Lee, Opt. Express 21(22), 26914–26920 (2013).
13 T.-H. Choi, J.-H. Woo, J.-M. Baek, Y. Choi, and T.-H. Yoon, IEEE Trans. Electron. Dev. 64(8), 3213–3218 (2017).
14 T.-H. Choi, J.-W. Huh, J.-H. Woo, J.-H. Kim, Y.-S. Jo, and T.-H. Yoon, Opt. Express 25(10), 11275–11282 (2017).
15 T.-H. Choi, J.-H. Woo, B.-G. Jeon, J. Kim, M. Cha, and T.-H. Yoon, Liq. Cryst. (2018).
16 G. H. Heilmeier, L. A. Zanoni, and L. A. Barton, Proc. IEEE 56(7), 1162–1171 (1968).
17 J.-H. Huh, J.-H. Kim, S.-W. Oh, S.-M. Ji, and T.-H. Yoon, Dyes Pigm. 150, 16–20 (2018).
18 S. H. Perlmutter, D. Doroski, and G. Moddel, Appl. Phys. Lett. 69(9), 1182–1184 (1996).
19 D. Xu, F. Peng, H. Chen, J. Yuan, S.-T. Wu, M.-C. Li, S.-L. Lee, and W.-C. Tsai, J. Appl. Phys. 116, 193102 (2014).
20 H. R. Brand, P. E. Cladis, and P. L. Finn, Phys. Rev. A 31, 361 (1985).
21 N. A. Clark and S. T. Lagerwall, Appl. Phys. Lett. 36, 899 (1980).
22 L. Sirleto, G. Coppolar, G. Breglio, G. Abbate, G. C. Righini, and J. M. Oton, Opt. Eng. 41(11), 2890–2898 (2002).
23 F. Araoka and H. Takezoe, Jpn. J. Appl. Phys. 53, 01AA01 (2014).