Chapter 4

Experimental Results

4.1 Introduction

Novel ferroelectric glassy liquid crystal (FGLC) processed the wide chiral smectic C mesophase, both net compounds and diluted FGLCs mixtures were investigated using W206A as host. We discuss the experimental results of FGLCs and their mixtures, the thermal properties were characterized with differential scanning calorimetry (DSC). Electro-optical characteristics and the alignment textures were characterized under 2 um pre-made cell (from EHC) with optical system and polarizing optical microscope (POM), respectively. And the spontaneous polarization was characterized under 5 um pre-made cell with field reversal method.

4.2 Thermal Properties

Various FLC materials have drawn much attention with their numerous molecular designs to enhance SmC* mesophase temperature since then [21-22]. The limited working temperature makes it less suitable for displays. In the following result, phase transition temperature of FGLC compound and their mixtures were characterized with DSC, and the temperature dependent liquid crystal mesophases were confirmed under POM.

4.2.1 Thermal Properties of FGLC Compounds and SmC Host

Thermal properties of low molecular weight ferroelectric glassy liquid crystals (FGLCs) and smectic C host (W206A) were summarized in Table 4.1. The mesophases of nematic, smectic A, and smectic C (15 ℃-85.7 ^{o}C) were presented in W206A. Among these FGLC compounds, the unidentified smectic mesophase was appeared at the first generation glassy FLC, FGLC-1, and the crystalline stage was presented at low temperature. The following FGLC-2 compound possessed short chiral smectic C phase at elevated temperature which was not used as chiral dopant in this experiment with its short chiral smetic C working temperature, and the glassy stage was appeared. The widest chiral smectic C mesophase from 15.7 ^{o}C to 115.4 ^{o}C was possessed in FGLC-3 covering all the phase transition temperature of W206A, and the glassy stage was also presented.

Table 4.1 Phase Transition and Phase Transition Enthalpies for pure compounds obtained from DSC at heating and cooling rate at 20 ^{o}C /min.

Material	Phase transition temperature (^{o}C)
W206A	Heating：*Cr* 14-15 *SmC* 85.7-86.4 *SmA* 90.1-90.6 *N* 99.4-102 *I*
	Cooling：*I* 101.4-98.4 *N* 90.4-89.9 *SmA* 86.3-85.6 *SmC* -0.65 *Cr*
FGLC-1	Heating：*Cr* 78 *I*
	Cooling：*I* 52 *SmX* 29 *Cr*
FGLC-2	Heating：*G* 12 *SmX* 66 *SmX* 109 *SmC** 125 *SmA* 145 *I*
	Cooling：*I* 140 *SmA* 119 *SmC** 103 *SmX* 11 *G*
FGLC-3	Heating：*G* 15.7 *SmC** 115.4 *SmA** 146.1 *I*
	Cooling：*I* 141.3 *SmA** 109.9 *SmC** 14

Cr : Crystalline, *Sm* : Smectic, *N* : Nematic, *I* : Isotropic, *G* : Glassy, * : chiral

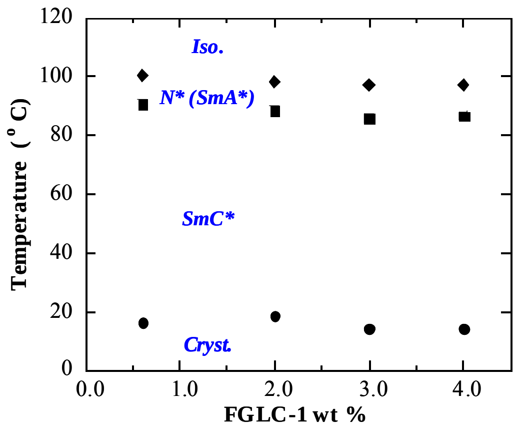
Tab. 4.2 Thermal property of FGLC-1 and FGLC-3 mixtures.

Heating 20 ^{o}C /min	Cr	SmC*	N*	I
W206A	15.37	89.17	99.57	
0.6%FGLC-1	16.38	90.85	100.64	
2%FGLC-1	18.7	88.5	98.23	
3%FGLC-1	14.36	85.81	97.22	
4%FGLC-1	18.7	86.82	97.22	
2% FGLC-3	14.2	89.4	98.79	
4.3%FGLC-3	13.93	90.77	99.16	
9% FGLC-3	16.06	96.91	102.94	
12%FGLC-3	16.93	97.92	103.62	
23%FGLC-3	15.08	95.27	99.96	

Cooling 20℃/min	I	N*	SmC*	Cr
W206A	98.15	88.76	-0.65	
0.6%FGLC-11	98.83	89.1	-0.32	
2%FGLC-1	97.14	87.41	-1.64	
3%FGLC-1	95.81	86.08	-1.65	
4%FGLC-1	96.81	86.74	-1.66	
2% FGLC-3	98.25	88.19	-0.88	
4.3%FGLC-3	98.51	89.8	-1.5	
9% FGLC-3	102.2	95.49	0.7	
12%FGLC-3	102.87	96.5	1.02	
23%FGLC-3	98.86	93.49	-0.95	

4.2.2 Thermal Properties of FGLC Mixtures

Both FLGC-1 and FGLC-3 used as chiral dopant were diluted in W206A, FGLC mixtures with different concentration were prepared, and the better aligned one was utilized and characterized the electro optical characteristics. Thermal properties of both mixtures were listed in Tab.4.2, FGLC-1 mixtures with different weight percentage, ranging from 0.6, 2, 3, and 4%, were measured by DSC at 20 ^{o}C/min heating and cooling rate. As shown in Fig. 4.1, a broad transition peak from DSC data covered the phase transition temperature from SmC* to N* in FGLC-1 mixtures. There was a small SmA* phase transition occurred, in which it can be identified under polarizing optical microscope (POM) inside the broad transition peak. In contrast, SmA* mesophase was completely suppressed in all FGLC-3 mixtures, the success of suppressing SmA* can be contributed to the wide SmC* mesophase of FGLC-3. Thermal transition properties of 2, 4.3, 9, 12, and 23% FGLC-3 mixtures were shown in Fig. 4.2. In particular, 12% FLGC-3 possessed the widest SmC* phase of mixtures with temperature range from 16.9 ^{o}C to 97.9 ^{o}C.



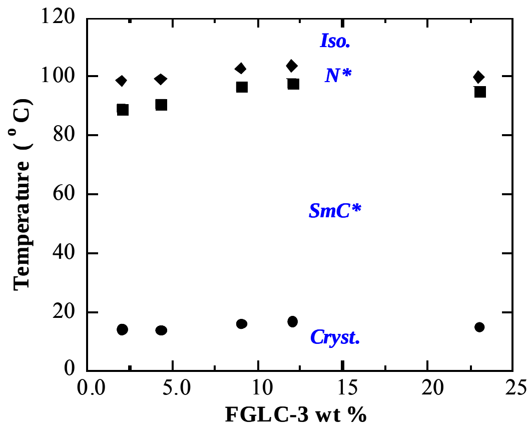


Fig. 4.1. Thermal properties of FGLC-1 mixtures.

Fig. 4.2. Thermal properties FGLC-3 mixtures.

4.3 Alignment

Glassy liquid crystal generally shows good alignment ability with larger domain size in previous study on fused silica substrates [29-31]. The patterned ITO, parallel rubbed pre-made cells (2±0.5μm, from EHC) were used without pre-treatment in this study. All liquid crystal textures in this chapter were captured under POM with the magnification of 100X. Fig. 4.3 presented the ON/OFF states of FLC materials, the bright state was driven by 30V, 1 kHz square wave. Pure FGLC-2 was studied in its SmC* mesophase (120 °C) as shown in Fig.4.3 (a), the pin holes defects occurred due to the trapped air bubbles existed in the filling process. 2% FGLC-1 mixture showed better aligned result (without applying V_{DC}) in the pre-made cell for large area as shown in Fig. 4.3(b) comparing to that of the commercial FLC material (R2301, from Clariant, Japan) in Fig. 4.3(d). 4.3% FGLC-3 mixture, however, showed zigzag defects in Fig. 4.3(c).

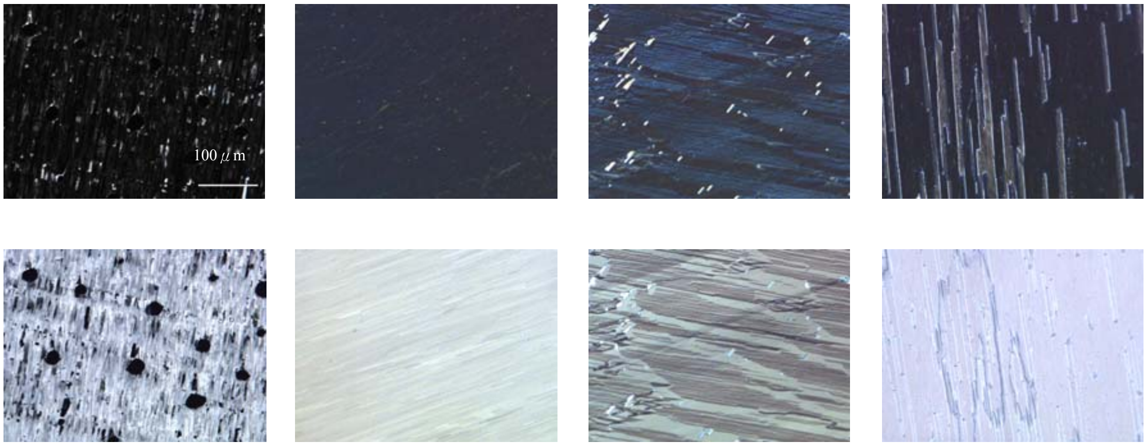


Fig. 4.3 Microscopic textures of alignment and ON /OFF (upper one) states of (a) FGLC-2, 120 °C; (b) 2% FGLC-1, 25 °C (c) 4.3% FGLC-3, 25 °C; (d) R2301, 25 °C

4.4 Response Time

Response time was characterized with optical system by applying 30V, 1 KHz bipolar square wave as shown in Fig. 4.4 (a), which was designed with the software of waveform generator, WFG500. The response time of various FGLC samples were listed at Table 4.3, and the data was defined from the transmittance of 10% to 90%. Pure FGLC-2 compound showed an extremely fast response time at 120 °C with bistability. As to FGLC-1 mixture, the rise time was under 700 μs and fall time was near 1 ms. In 4.3% FGLC-3 mixture, the rise and fall time were 580 μs and 760 μs, respectively. Both mixtures were suitable for color sequential displays. No over driving technique was utilized to characterize the optical response, since the response time would be reduced by over driving technique as shown in Fig. 4.6 (b), the shorter rise time of FGLC2 under high frequency over driving scheme was 280 μs [32], even it was measured form the transmittance of 0% to 100%.

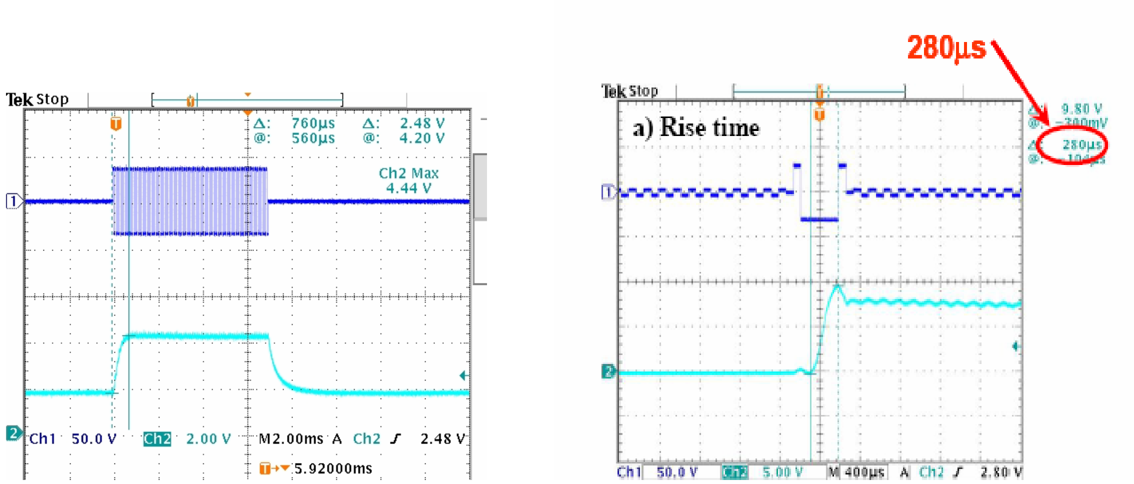


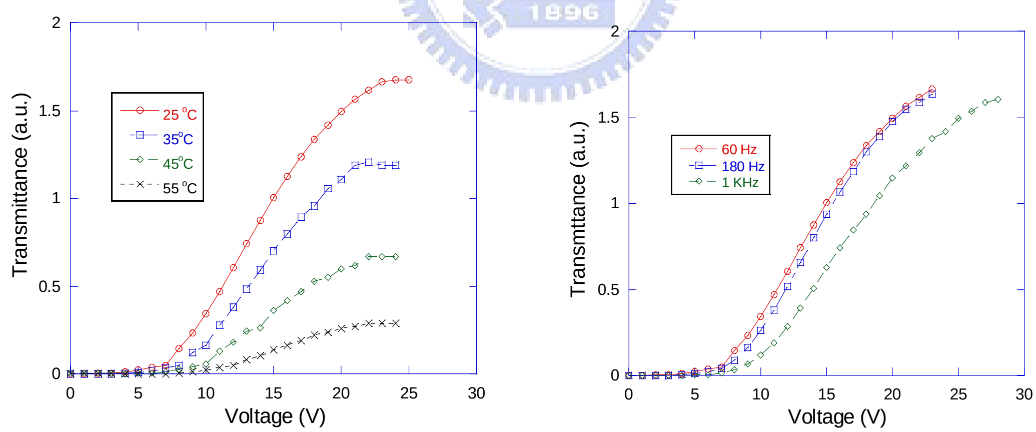
Fig. 4.4 (a) Driving scheme of response time measurement (b) Optical response of FGLC2 with over drive and high frequency driving scheme [32].

Table 4.3 Response time of various FLC samples
in 2±0.5 μm cell, driven by 1 kHz 30V square wave.

Material	Rise Time ($\tau_{10} \rightarrow \tau_{90}$, us)	Fall Time ($\tau_{90} \rightarrow \tau_{10}$, us)
FGLC-2 (120℃)	400	296
2% FGLC-1	680	1100
4.35% FGLC-3	580	760

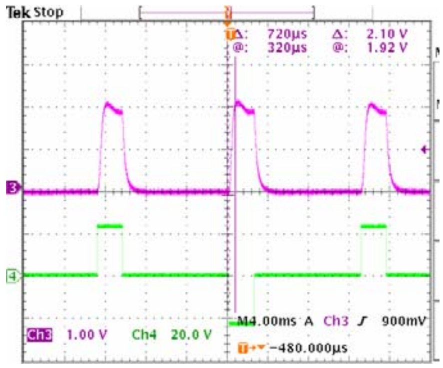
4.5 Electro Optical Characteristics of the 2% FGLC-1 Mixture

The electro optical characteristics of the better aligned 2% FGLC-1 mixture was characterized by applying 60 Hz bi-polar square wave and the temperature dependent results were shown in Fig. 4.5 (a). To get the temperature dependent data, LC cell was heated with hot stage at the heating rate 3 ^{o}C/min and hold at experimental temperature for more than 5 minutes before measuring. It was obviously that the transmittance was reduced with increasing temperature, and the result indicated that the material was weak at thermal stability. And the frequency dependent transmittance was shown in Fig. 4.5 (b), driving frequency of 60, 180, 1KHz were applied, respectively. The transmittance of 2% FGLC-1 driven by 60 Hz driving scheme was slightly larger than it of 180 Hz, and both driving voltages saturated at 23V. As to the electro optical characteristics of 1 KHz driving frequency, higher saturated voltage and lower transmittance were presented. It was supposed that to compare with the 1 KHz square wave, the rise time (680 μs) of 2% FGLC-1 mixture was not fast enough to be fully rotated. To confirm it, the single pulses were given as following, 2% FGLC-1 mixture was driven by 23 V, 2 ms pulses as shown in 4.6 (a). If the driving pulsed were reduced to 400 μs, the LC molecules couldn't be fully rotated and the transmittance was reduced as shown in Fig. 4.6 (b). To achieve to same transmittance, higher voltage (28 V) should be applied as shown in Fig. 4.6 (c).

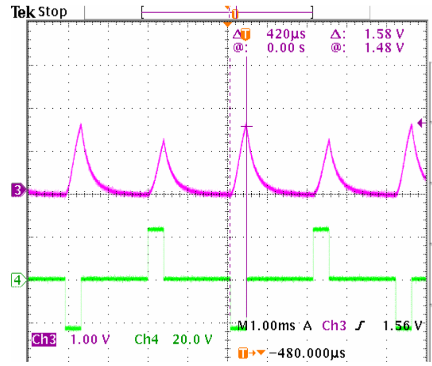


(a) (b)

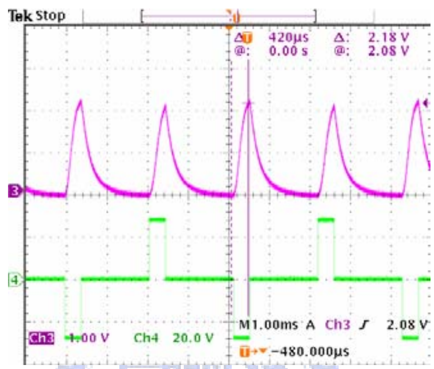
Fig. 4.5 (a) EO characteristics of the 2% FGLC-1 mixture driven by 60 Hz bi-polar square wave at different temperature. (b) frequency dependent EO characteristics at 25 °C



(a)

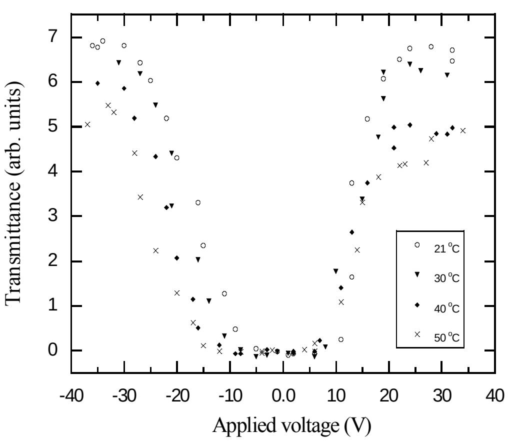


(b)



(c)

Fig. 4.6 Electro optical characteristics of 2%FGLC-1 mixture driven by single pulses. (a) 23 V, 2 ms. (b) 23 V, 400 µs. (c) 28 V, 400 µs.



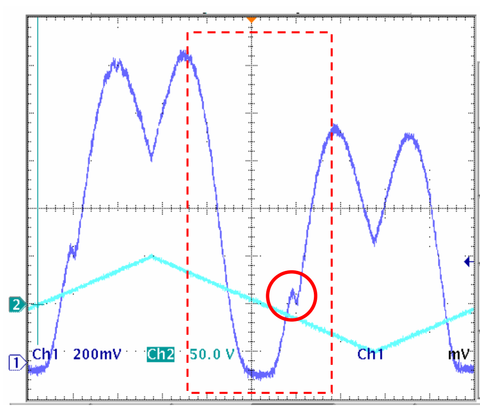


Fig. 4.7 Electro-optical characteristics of the 2% FGLC-1 mixture applied by (a) 10 Hz, (b) 0.5 Hz triangular wave.

Two kinds of switching modes, half V and V switching modes were studied in FLC materials. To realize the switching mode of 2% FGLC-1 mixture, the low frequency triangular wave was applied. Thus, the continuous voltage form positive to negative could be achieved from peak to peak of the triangular wave. The electro-optical characteristics of the 2% FGLC-1 mixture was characterized by applying a continuous 10 Hz triangular wave at different temperature as shown in Fig. 4.7 (a), a continuous V shaped switching with the threshold voltage about 8 V was presented. Lower driving frequency was still investigated, as the 0.5 Hz triangular wave was applied, a strange peak was presented as shown in Fig. 4.7 (b). In the observation under POM it was realized as the speedy domain growth.

Domain growth was appeared at low frequency triangular wave, to investigate it, the DC voltage was applied. In the beginning, a dark state was formed as shown in Fig. 4.8 (a), to induce domain growth, DC voltage with its threshold voltage of 6 V was applied. Then, the textures were gradually reversed into bright state like a flow as shown in Fig. 4.8 (b-e), and it took about 1 second. The applied V_{DC}, 6 V was not strong enough to reverse all the domains as shown in Fig. 4.8 (e), to overcome it, V_{DC}, 15V was applied as shown in Fig. 4.8 (f). The domains were switched from one sable state to the other with inversed DC voltage. Usually the domain growth takes place via nucleation and expansion of domains under one of both states. Once domain growth takes place, it would gradually reverse like a flow and the speed depends on driving voltage. And the flow stopped when the applied voltage was removed during domain growth and gave the impression of a quasi-continuous gray scale.

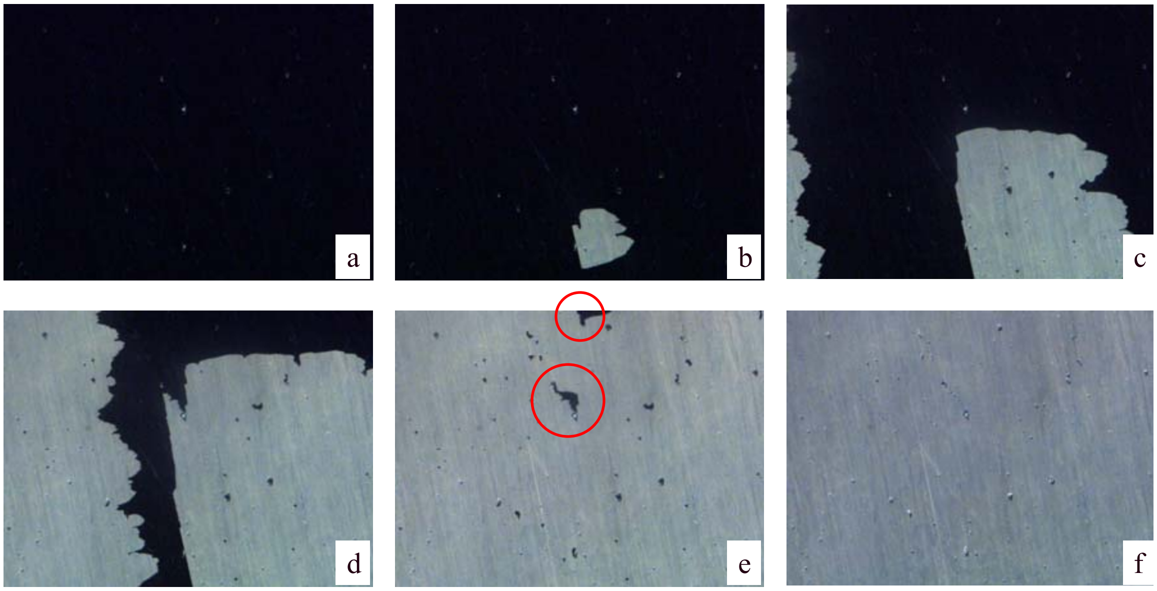
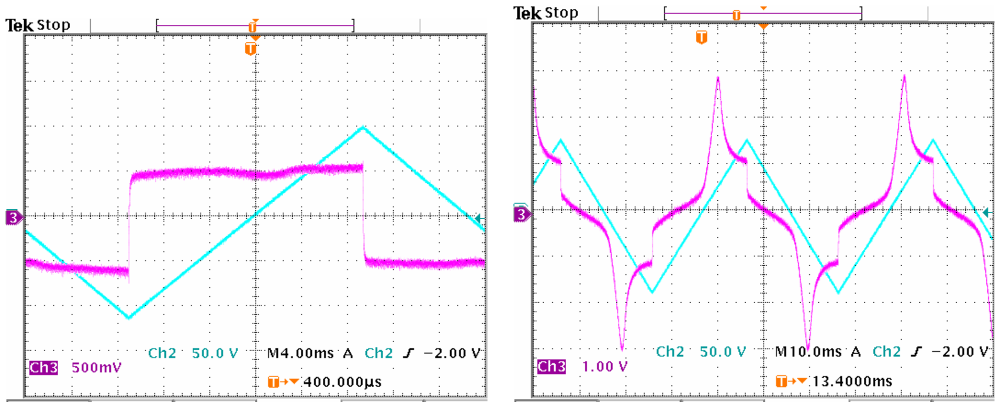


Fig. 4.8 (a) dark state without applying voltage. (b-e) the transition states by applying V_{DC}, 6V, (f) texture after applying $V_{DC,}$ 15V.

4.6 Spontaneous Polarization

Spontaneous polarization was characterized with field reversal method by applying 25Hz triangular wave across 5 μm cell. Small peaks were appeared in the result of 2% FGLC-1 mixture at 25 ^{o}C as shown in Fig. 4.9(a), and the cell was heated up to isotropic to confirm the peaks were due to spontaneous polarization or ions as shown in Fig. 4.9 (b). It could be easily observed that the peak area was increased with increasing temperature and still existed at isotropic, thus the peaks might be due to ions instead of spontaneous polarization. It was also supposed that the value of spontaneous polarization might be too small to be characterized (between 0 to 1 nC/cm^2), thus, higher concentration 4% FGLC-1 and 4.3%, 9% FGLC-3 mixtures were characterized, and the results were the same to 2% FGLC-1.



(a) (b)

Fig. 4.9 Spontaneous polarization results of 2% FGLC-1 mixture, (a) 25Hz, 100V triangular wave, at 25 °C. (b) 25Hz, 100V triangular wave, at 120 °C (isotropic).

The Ps value of net FGLC-2, R2301, and R3206 were 40.3, 4.2, and 21.2 nC/cm^2, respectively. Since net FGLC-1 compound couldn't be switched at its mesophase, and the unidentified Ps results were appeared in FGLC-1 mixtures. Thus, the other host, R3206 was chose. 2%, 5%, and 11% FGLC-1 mixtures (host: R3206) were prepared, and characterized the value of spontaneous polarization as shown in Fig. 4.10. The linear dependent results seem to demonstrate that the tendency toward lower spontaneous polarization with increasing the concentration of FGLC-1, and the chirality of FGLC-1 and R3206 were opposite to each other. It can be briefly supposed that the spontaneous polarization of FGLC-1 was -70 nC/cm^2 by extrapolation.

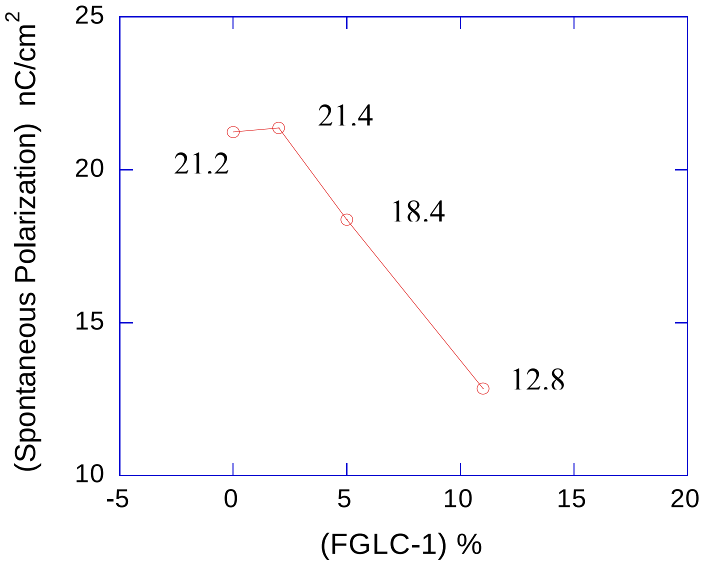


Fig. 4.10 Ps value of FGLC-1 mixtures doped in R3206

4.7 Summary

A series of ferroelectric glassy liquid crystals (FGLCs) were synthesized and evaluated their potential for wide SmC* mesophase and fast switching ability less than 1 ms. The latest developed FGLC possesses wide chiral smectic C mesophase over 100 ^{o}C. In the series of FGLC-3 mixtures, the chiral smectic A phase was completely suppressed within all concentrations. And 2% FGLC-1 mixture obtained better alignment than R2301 (Clariant, Japan) in the same pre-made 2μm cell (from EHC). As to its optical response, the rise time of FGLC-1 mixture was under 700 μs and fall time was near 1ms. In 4.3% FGLC-3 mixture, the rise and fall time were 580 μs and 760 μs, respectively. Both mixtures are suitable for color sequential displays. 2% FGLC-1 mixture was a V switching mode material, and it showed frequency dependent electro-optical characteristic, by applying 60Hz bi-polar square wave, the threshold voltage and saturation voltage were 6 V and 23 V, respectively, and the electro optical characteristics were weak at thermal stability. As to the spontaneous polarization, the unidentified Ps results of FGLC mixtures diluted in W206A were still investigated, it were supposed to be ion effects or small Ps value between 0 to 1nC/cm^2. The Ps value of pure FGLC-2 was

40.3 at 120 ^{o}C, and the Ps value of FGLC-1 was briefly supposed to be -70 nC/cm^2 by extrapolation.

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Chapter 5

Conclusions

5.1 Conclusions

FGLCs as chiral dopant have been demonstrated to maintain chiral smectic C mesophase. SmA* mesophase can be suppressed by large SmC* mesophase FGLC-3 compound. And the novel FGLCs have potentials in preparing a relatively good domain in SSFLC. Several groups have obtained mono-domain with FLC material R2301 by utilizing hybrid alignment [33] or asymmetrical cell with liquid crystal polymers (LCPs) and linearly-photo-polymerized polymers (LPPs) [34]. Since larger domain sizes were able to achieve by 2% FGLC-1 cell, we believe that the criteria to obtain mono-domain FGLC or FGLC mixture could be less strict than R-2301. These advantages may lead to a simpler manufacturing process or simpler cell structure in the future.

5.2 Future Work

Several issues are concerned for developing FLC materials, such as, wider chiral smectic C mesophase, thermal stability, long helical pitch, alignment ability, fast switching, low viscosity and large cone angle. Among this all, our 2% FGLC-1 mixture has the potential to get better alignment, and the FGLC-3 compound as well as FGLC-3 mixtures possess the wide chiral smectic C mesophase. And both 2% FGLC-1 and 4.3% FGLC-3 mixture show fast response, which are suitable for full color field sequential displays. To get a poly-functionalized FLC material, our FGLC mixtures still need to be further improved.

To combine both the advantages of FGLC-1 and FGLC-3, a wide SmC* mesophase and well-aligned material is desired. 2% FGLC-1 mixture has the potential to perform better alignment and FGLC-3 compound possesses the wide chiral smectic C mesophase. Base on the mentioned advantages above, a mixture with 1% FGLC-1 and 2% FGLC-3 was prepared, however the results with alignment defects and short working temperature with SmA* mesophase were presented. The other mixtures with different concentration will be continuous investigated to obtain the suitable materials.

Spontaneous polarization is an important parameter of FLC, which is related to the response time, rotation viscosity and so on. However, the unidentified Ps results were presented in FGLC mixtures, which were supposed to be ion effects or small Ps value between 0 to 1 nC/cm^2. Base on these issues, chemical process to eliminate ions is required. Also, the other method is studied to characterize spontaneous polarization as shown in Fig. 5.1. The Diamant bridge method [25] was developed by Diamant in 1957, which was studied base on a technique of hysteresis compensation. The voltage appearing across a reference capacitor represents the charge flow during switching is displayed as a function of drive voltage to form a hysteresis loop, the Ps value can be defined as,

$$\mathbf{Ps = C_o \, (V_{0B}) / \, 2A} \qquad (5.1)$$

Where, C_o is the value of fixed capacitor.

V_{0B} is the V_{PP} of compensated hysteresis loop.

A is ITO area of the sample.

The Ps results between 0 to 1 nC/cm^2 have been characterized and published, thus, the supposed small Ps value FGLC mixtures are probably to be characterized by Diamant bridge method.

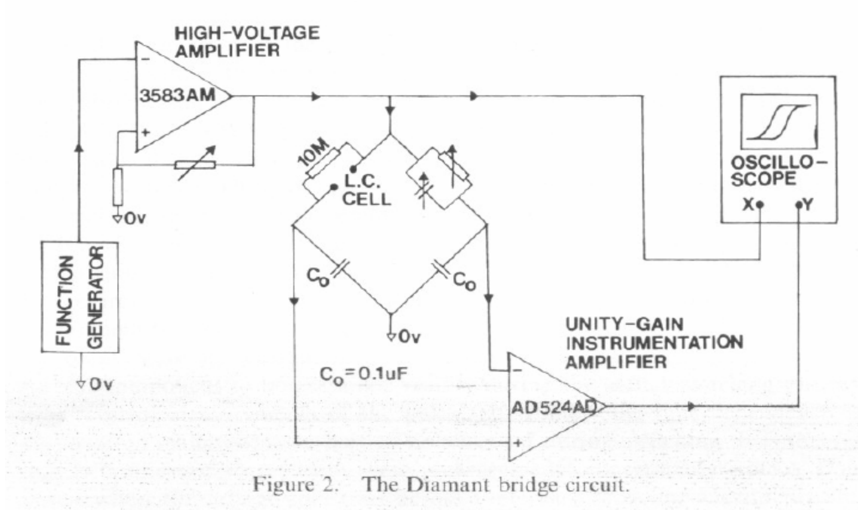

Fig. 5.1 Circuits of Diamant bridge method.

Reference

[1] G. W. Gray ed., *Thermotropic liquid crystals,* Wiley (1987)

[2] H. G. Kuball, H. Bruning, et al, *J. Mater. Chem.*, **5** , 2167 (1995).

[3] J. W. Goodby, R. Blinc, N.A. Clark, S.T. Lagerwall, et al., *Ferroelectric Liquid Crystal Principles, Properties and Applications,* Gordon and Breach Science (1991)

[4] S. Kobayashi, J. Xu, H. Furuta, et al., *Opt. Eng.* **43**, 290 (2004).

[5] N. A. Clark, S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).

[6] K. Takatoh, M. Hasegawa, M. Koden, et al, *Alignment Technologies and Applications of Liquid Crystal Devices*, Taylor and Francis (2005)

[7] H. Kamiya, et al., SID Symposium Digest **32**, 1354 (2001).

[8] R. B. Meyer, L. Liebert, L. Strzelecki, P. Keller, *J. Phys. Lett.* **36**, L69 (1975).

[9] J. S. Patel, J. W. Goodby, *Chem. Phys. Lett.* **137**, 91 (1987).

[10] PLC Virtual Text Book: http://plc.case.edu/tutorial/enhanced/files/textbook.htm.

[11] W. V. Verlag GmbH, C. KGaA, Weinheim, *Textures of Liquid Crystal*, Wiley (2003)

[12] J. S. Patel, J. W. Goodby, *J. App. Phys*. **59,** 2355 (1986).

[13] K. Kondo, H. Takazoe et al., *Jpn. J. App. Phys. Lett.* **22**, L85 (1983).

[14] B. Maximus, C. Colpaert et al., *Liq.Cryst.* **15**, 871 (1993).

[15] T. C. Chieu, H. K. Yang, *Jpn. J. App. Phys. Lett.* **28**, 2240 (1989).

[16] S.T. Lagerwall, "*Ferroelectric and antiferroelectric liquid crystals*, Wiley-Vch (1999)

[17] A. Tagawa, P. Bonnett et al., *Jpn. J. Appl. Phys.* **42**, 1675 (2003).

[18] H. Matsui, T. Miyata, S. Kobayashi et al., *Jpn. J. Appl. Phys.* 38, L136, (1999).

[19] H. Fujikake, T. Aida et al., *Electron. Comm. Jpn. 2,* **82**, N. 8 (1999).

[20] H. Hasebe, S. Kobayashi, *SID Digest of Tech-Papers* **16**, 81 (1995).

[21] C. S. Hsu, L. J. Shih, G. H. Hsiue, *Macromolecules*, ***26***, 3161 (1993).

[22] G. H. Hsiue, C. P. Hwang et al., *Liq. Cryst.* **20**, 45 (1996).

[23] K. H. Yang, *J. Appl. Phys.* **64**, 4680 (1988).

[24] C. B. Sawyer, C. H. Tower, *Rhys. Rev.* **35**, p369 (1930).

[25] H. Diamant, *Rev. Scient. Instrum.* **28**, 30 (1957).

[26] K. Miyasato, S. Abe, H. Takezoe et al., *Jpn. J. Appl. Phys. Lett.* **22**, L661 (1983).

[27] Martinot-Lagarde, *J. Phys. Lett.*, Paris **38**, L17 (1977).

[28] G. Spruce, R. D. Pringle, *J. Phys. E: Sci. Instrum.* **21,** 268 (1988).

[29] S. H. Chen, H. M. P. Chen, D. Katsis, J. C. Mastrangelo, *ACS Symposium Series* 888, 290 (2005).

[30] H. M. P. Chen, D. Katsis, S. H. Chen, *Chem. Mater.* **15**, 2534 (2003).

[31] H. P. Chen, D. Katsis, J. C. Mastrangelo, S. H. Chen, S. D. Jacobs, P. J. Hood, *Adv. Mater.* **12**, 1283 (2000).

[32] H. M. Philip Chen, K. G. P. Kumar, C. W. Lin, C. K. Kim, S. H. Chen, SPIE 587204-1 (2005).

[33] Y. Murakami, H. Furuta, J. Xu, H. Endoh, H. Fukuro, S. Kobayashi, *Jpn. J. App. Phys.* **42**, 2759 (2003).

[34] M. Okabe, N. Sawatari, M. Ishikawa, H. Hama, *SID 2005 Digest*, 1084