Abiding Electro-Optic Memory Effect Based on Deformed Helix Ferroelectric Liquid Crystal

Ajay Kumar, Jai Prakash[1], Ashok M. Biradar*, and Wolfgang Haase[2]

Liquid Crystal Group, National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi-110012, India
[1] *Instrument Design Development Center, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India*
[2] *Institute of Physical Chemistry, Technical University Darmstadt, Petersenstr. 20, 64287 Darmstadt, Germany*

The characterization of a newly synthesized deformed helix ferroelectric liquid crystal (DHFLC) namely LAHS18 has been presented. The material LAHS18 has been found to possess ultrashort helical pitch, large optical tilt, high spontaneous polarization and large rotational viscosity. A long-lasting memory effect has been shown in this material by electro-optical measurements. It has been demonstrated that why does pure LAHS18 material exhibit a long-lasting memory effect. These studies will certainly provide an understanding of the memory effect in DHFLC (LAHS18).

The introduction of ferroelectricity in liquid crystal (LC) materials has attracted a great deal of interest from researchers around the world.[1)] Ferroelectric liquid crystals (FLCs) have been found to be more advantageous than nematic LCs due to their good optical contrast, low threshold voltage, and faster electro-optical response. Some boundary conditions have been imposed to make FLC cells to achieve bistable switching, which led to an important discovery of surface-stabilized FLCs (SSFLCs).[2)] The discovery of the deformed helix FLCs (DHFLCs) has ruled out the constraint on the cell thickness as the optical bistability is independent of the cell thickness in these materials. DHFLCs have many applications in display devices because of their low driving voltage, gray scale generation capability, easily achievable alignment, fast response, etc.[3,4)] The averaged optical indicatrix of the helical structure in DHFLCs has been found to depend almost linearly on the applied electric field and, hence, these materials are enriched with the gray scale generation capability. The bistability in DHFLCs arose due to the fact that the modulated planar LC conformation hinders the helix formation in DHFLC layers.[5)] In DHFLCs, a low field causes only a deformation of the helix, whereas a larger field unwinds the helix and provides a quasibistable switching.[4,6)] The phenomenon of bistability and memory effect in DHFLC (FLC 6304) has been studied in detail recently by our group.[7)]

In present studies, we report the characterization of a newly synthesized DHFLC material, namely, LAHS18. A long-lasting memory effect has been observed in LAHS18 by electro-optical methods. It has also been shown why LAHS18 possesses such a long-lasting memory effect.

For this study, highly conducting indium tin oxide (ITO)-coated glass substrates were used to fabricate the sample cells. Photolithographic technique was employed to achieve the desired electrode patterns (with electrode area of $4.5 \times 4.5\,\mathrm{mm}^2$) on the ITO. The rubbed polyimide technique was used to obtain homogeneous alignment of the DHFLC cells. The thickness of the DHFLC cells was maintained by using 3.5-µm-thick Mylar spacers. For optical response, the time-delayed square pulse generated by the pulse generator was applied to the sample and studied by using a storage oscilloscope (HAMEG HM 1507-3) interfaced with a computer via SP-107 software. The material parameters such as spontaneous polarization (P_S), rotational viscosity (η), and switching time (τ_R) of the LAHS18 material were determined using an automatic LC tester (Instec ALCT-P). The measurement of P_S is based on the basic principle discussed earlier.[8)] The optical micrographs of the material were recorded using a polarizing optical microscope (Carl Zeiss) fitted with a charge coupled device camera.

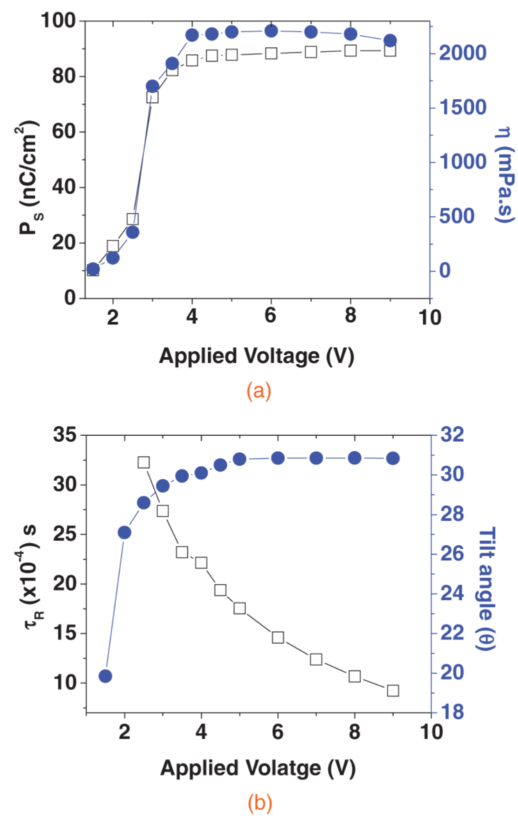
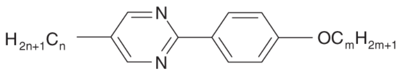


Fig. 1. Behaviors of (a) spontaneous polarization (P_S) (open squares), rotational viscosity (η) (filled circles), (b) response time (τ_R) (open squares), and Optical tilt (θ) (filled circles) of LAHS18 material with applied voltage at room temperature (RT).

Figure 1 shows the variation of P_S, η, τ_R, and optical tilt angle (θ) of the LAHS18 material with applied voltage at room temperature (25 °C). The saturation value of P_S has been observed at around $90\,\mathrm{nC/cm^2}$, whereas the magnitude of η has been observed at $\sim$2100 mPa·s [Fig. 1(a)]. The value of τ_R has been calculated using the formula used in ref. 9. The variation of τ_R and optical tilt angle (θ) with

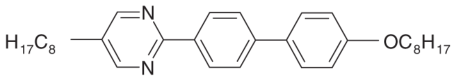
*E-mail address: abiradar@mail.nplindia.ernet.in

Three phenylpyrimidine compounds



m=6, n=8: 19.4% m=8, n=8: 17.5% m=9, n=8: 6.5%

One biphenylpyrimidine (21.6%)



Chiral compound (35%)

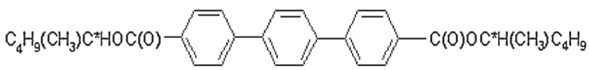


Fig. 2. Molecular formulae and concentration of constituent compounds of DHFLC material (LAHS18) used.

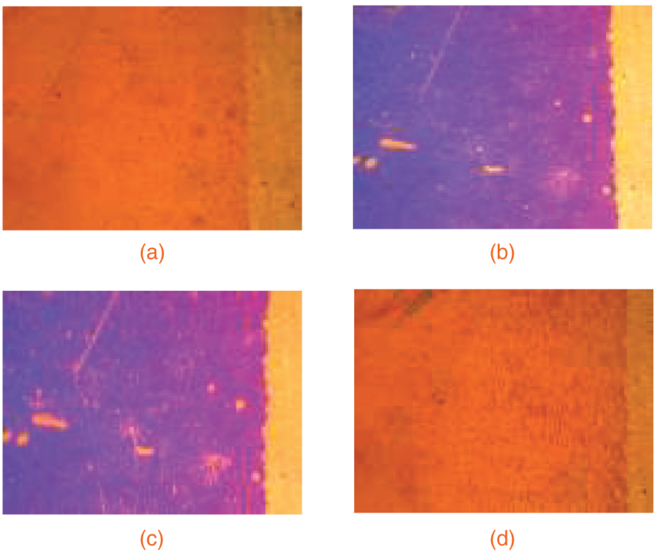


Fig. 3. Optical micrographs of LAHS18 material at RT at (a) 0 V, (b) 8 V, (c) after 80 h of removal of bias, and (d) scattering state achieved upon applying low voltage and high-frequency ac field.

applied voltage is shown in Fig. 1(b). The LAHS18 material possesses large optical tilt (~30°), which has been clearly reflected in Fig. 1(b). The phase transitions of the material used were determined at atmospheric pressure by differential scanning calorimetry. The SmC*–SmA* and SmA*–Iso. phase transition temperatures of the material have been observed at 58 and 64 °C, respectively. The material LAHS18 is a mixture of three phenylpyrimidine compounds, one biphenylpyrimidine, and a chiral compound. The molecular formulae and concentration of these constituent compounds are shown in Fig. 2. The LAHS18 material comprises almost similar compounds that were used to prepare LAHS19.[10)] The difference in the mixing ratios of core compounds and chain length of the chiral compound has resulted in the form of long-lasting memory effect in LAHS18, unlike in LAHS19 in which the memory effect was completely absent. The observance of memory effect in the LAHS18 material can be clearly seen from Fig. 3. Figure 3(a) shows the optical micrograph of the material when no bias was applied across the cell and it was called

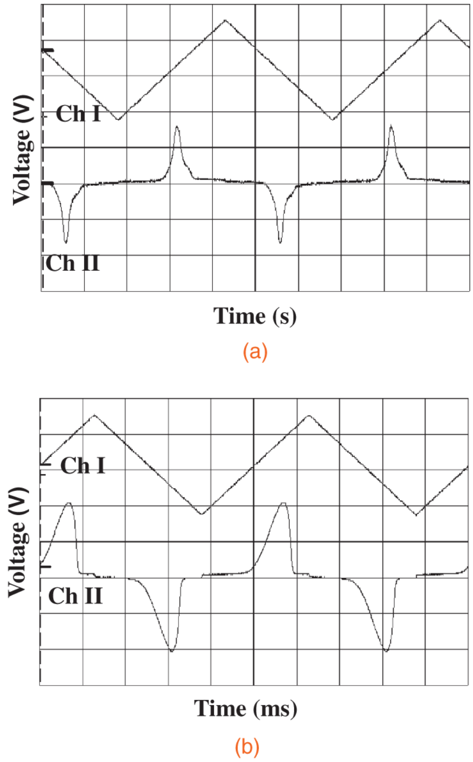


Fig. 4. Electrical response of LAHS18 sample cell at RT at frequencies of (a) 200 mHz [Ch I-10 V/div, Ch II-0.1 V/div, Time-1 s/div] and (b) 10 Hz [Ch I-10 V/div, Ch II-2 V/div, Time-20 ms/div].

scattering state. A completely switched state of the cell was achieved by the application of 8 V bias [Fig. 3(b)]. Figure 3(c) shows that the memory was retained for 80 h after the removal of bias. Once the cell switches, it tends to remain in that state for a long time (for many days). The memory state in LAHS18 samples was switched back forcibly to the original state (scattered state) upon application of a sinusoidal field of low amplitude (1 V) and high frequency (30–50 Hz), which is shown in Fig. 3(d). The occurrence of memory effect has also been confirmed by taking the electrical response of the material. The occurrence of a single peak in the electrical response of a DHFLC material clearly indicated the complete resonance between helix unwinding–winding and molecular reorientation processes, and whenever such a resonance took place, the material showed the memory effect.[7)] Figure 4 shows the electrical response of the LAHS18 sample cell upon application of a triangular pulse of 20 V_{pp} amplitude. In the output response, a single peak has been observed over the whole frequency range (200 mHz–10 Hz). The observance of the single peak clearly depicts the resonance between helix unwinding–winding and molecular reorientation processes and, hence, the memory effect is observed in LAHS18 over a wide frequency range.[7)] Figure 5 shows the optical response of the LAHS18 material at different frequencies and at a fixed voltage. The optical response of the sample was observed by applying time-delayed positive and negative square pulses. As seen in Fig. 5, the optical transmission changes from maximum to minimum as the applied field reverses its polarity, and there is almost no change when the applied field attains its 0 V state, which confirms the memory effect.

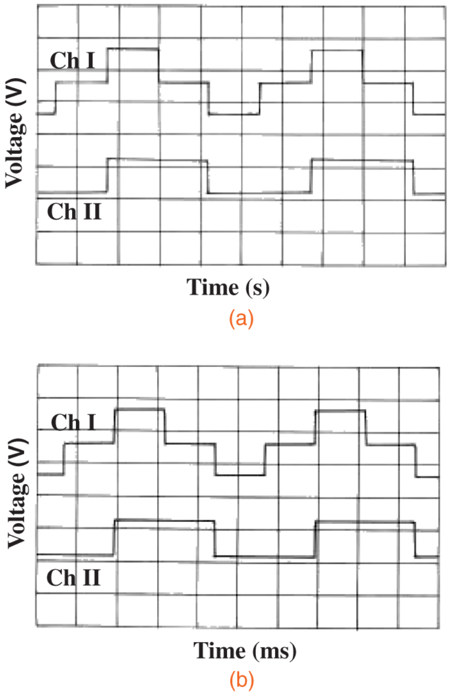


Fig. 5. Optical response of LAHS18 sample cell at RT at frequencies of (a) 200 mHz [Ch I-10 V/div, Ch II-0.02 V/div, Time-1 s/div] and (b) 10 Hz [Ch I-10 V/div, Ch II-0.02 V/div, Time-20 ms/div].

In conventional FLCs, the memory effect has been found to be related to the interactions of FLC molecules with different surfaces. However, the occurrence of the memory effect in DHFLCs has been found to have different origins. Recently, the occurrence of the memory effect in DHFLCs has been studied and the results were demonstrated by taking different aspects into account in the case of pure as well doped with nanomaterials.[11–13] To understand the possible reason for the memory effect shown by LAHS18, we conducted comparative studies of the two DHFLC materials (LAHS18 and LAHS19) having slightly different chemical compositions. We made the sample cells for both materials while keeping the parameters, such as rubbing strength, active electrode area, sheet resistance, and thickness of the cells, almost the same to observe the memory behavior of the materials. The various material parameters of LAHS19 were determined by electro-optical studies.[10] We have also performed electro-optical and dielectric measurements to observe the memory effect in LAHS19 and found that LAHS19 did not show memory effect. The mechanism of the memory effect in LAHS18 and LAHS19 mixtures could be understood by taking into account the stochiometric ratio of different components in both systems. The mixing ratio of the phenylpyrimidine host has minutely been reduced, whereas the chiral compound has been mixed in slight excess in the case of LAHS18. It has been observed that the FLC mixtures containing the chiral dopant with a longer aliphatic chain exhibit low η due to stronger lateral intermolecular interactions.[14] It has been found that the strong lateral intermolecular interaction produced by the long alkyl chain can provide low η and more stable smectic phases in the case of chiral-compound-doped systems.[15] The alkyl chain length of the chiral dopant and the mixing ratio of core compounds are smaller by one carbon unit and 2.1 wt % respectively, in the case of LAHS18. It has been demonstrated that as the terminal chain is extended, it is forced by the steric constraints of a neighboring molecule to lie closer to the long axis of the molecule and this increases the effective dipole at the centre, which increases the intrinsic polarization.[16] The increase in chiral compound concentration in the mixture reflected the contribution of alkyl chains. Thus, the modification of the mixing ratios of constituent compounds has resulted in the form of smaller P_S and higher η values of the LAHS18 material. The higher value of η of the LAHS18 material is one of the reasons for the long-lasting memory effect. It has also been observed that the compactness of packing of the DHFLC molecules increases by increasing the concentration of the chiral dopant.[17] The concentration of the chiral dopant in LAHS18 is 2 wt % higher than that in LAHS19 and, hence, the molecules of LAHS18 are tightly packed. The dipolar interactions between the molecules are more prominent due to the tight packing of the molecules of LAHS18. This prominent dipolar interaction has provided remarkable assistance in balancing the elastic deformation caused by the application of electric field and, hence, favored the memory state. However, the mechanism of the memory effect in DHFLC materials is rather unclear and leaves further space for LC researchers to think in this direction.

The characterization of a newly synthesized DHFLC, namely, LAHS18 has been presented. A long-lasting memory effect in the LAHS18 material has been observed by dielectric and electro-optical measurements, and the observed memory effect has been attributed to the combination of smaller values of spontaneous polarization and higher rotational viscosity of the LAHS18 material. These parameters also depend on the chemical composition of the LC/FLC materials, which is responsible for memory behavior and needs to be investigated by chemists in order to have a clear understanding of the phenomenon. The promising applications of this long-lasting memory effect can be in personal computers, data storage electronic devices, and zero power LC display devices etc.

Acknowledgments The authors sincerely thank Professor R. C. Budhani, Director, National Physical Laboratory, for continuous encouragement and interest in this work. We also sincerely thank Mr. A. Lapanik, Technical University Darmstadt, Germany for providing the DHFLC (LAHS18) material. The authors (A.K. and J.P.) are thankful to University Grants Commission and Council of Scientific and Industrial Research, New Delhi, respectively, for financial assistance.

1) R. B. Meyer *et al.*: J. Phys. Lett. **36** (1975) 69.
2) N. A. Clark and S. T. Lagerwall: Appl. Phys. Lett. **36** (1980) 899.
3) J. Fuenfschilling and M. Schadt: J. Appl. Phys. **66** (1989) 3877.
4) L. A. Beresnev *et al.*: Liq. Cryst. **5** (1989) 1171.
5) J. Fuenfschilling and M. Schadt: Jpn. J. Appl. Phys. **30** (1991) 741.
6) A. Jakli *et al.*: J. Appl. Phys. **79** (1996) 1891.
7) J. Prakash *et al.*: J. Appl. Phys. **103** (2008) 044103.
8) K. Miyasato *et al.*: Jpn. J. Appl. Phys. **22** (1983) L661.
9) B. Bahadur: *Liquid Crystals—Applications and Uses* (World Scientific, Singapore, 1990) Vol. 1.
10) A. Kumar *et al.*: Appl. Phys. Lett. **95** (2009) 023117.
11) A. Mukherjee *et al.*: Chem. Phys. Lett. **443** (2007) 71.
12) J. Prakash *et al.*: Appl. Phys. Lett. **93** (2008) 112904.
13) S. Kaur *et al.*: Physica B **352** (2004) 337.
14) I. Nishiyama *et al.*: Jpn. J. Appl. Phys. **28** (1989) L1851.
15) I. Nishiyama *et al.*: Jpn. J. Appl. Phys. **29** (1990) L326.
16) J. W. Goodby *et al.*: J. Phys. Chem. **91** (1987) 5151.
17) M. D. Wand *et al.*: U.S. Patent 5539555 (1996).