Synchronous Temperature-Voltage Cycle Instigated Memory Effects: Experimental Analysis of SmC* Phase in SiO₂ Dispersed Ferroelectric Liquid Crystals

Aradhana Roy, Atul Srivastava, and Rajiv Manohar*

Liquid Crystal Research Lab, Physics Department, University of Lucknow, Lucknow-226007, India

Email: rajiv.manohar@gmail.com (R. M.)

The present investigation explores memory behavior in pristine ferroelectric liquid crystals (FLC) and their composites. The induced non-volatile memory traces back its origin from the reconfiguration of helical arrangement of LC molecules under the influence of synchronous cycle of temperature-voltage. The addition of SiO₂ quantum dots provides pronounceable memory behavior, which can be applied for coding optical or electrical field motivated LC based storage devices. The measurement of the polarized state of the FLC molecules and their composites has been carried out dielectrically upto 1 h projecting non-volatile memory effects. The analysis of geometrical arrangement of LC molecules and surface effects due to the incorporation of quantum dots and simultaneous stimulations of temperature and voltage cycle has been reckoned in the study. The traps on the surface of the dispersed quantum dots capture mobile ions and force the LC molecules in the vicinity of quantum dots to display reminiscences of switched state. The dispersion of SiO₂ ensures efficient memorized orientation in the formulated composites resulting in steady memory behavior.

Keywords ferroelectric liquid crystals, SiO₂, quantum dots, memory effects, surface effects

Introduction

Liquid crystals (LC) stands as both fundamentally evolved and technologically successful branches of soft matter physics since the discovery of ferroelectric state of LC's by Meyer.^[1] Ferroelectric liquid crystals (FLC) provide a platform for innovative applications explored from scientific disciplines. The spiral organization of molecules, where the orientational director composes patterned tilt phase angle with smectic layer normal, is a fascinating characteristic of FLC. This helical structure of FLC promotes high contrast ratio, faster response, lower threshold voltage and remarkable dielectric properties, portraying the existence of assortment of modes. FLC is utilized in advancement of flat panel displays, optical antennas, spatial light modulators, and other industrial applications. Due to the applicative demand, the research arena bubbles with investigations on new functional FLC materials and their various dispersed state.^[2,3]

In recent years, the analysis of numerous physical and biological mechanisms at nano level has gained a lot of attention. The introduction of nanoparticles to any state of matter modifies and enhances material parameters such as elastic constants, viscosity, birefringence, polarization, and response time. Following the progression of nano-science, the symbiotic relationship of LC and nanoparticles is the catch during the past decade. The dispersion of nanoparticles in pristine LC tailors various properties of the latter exhibiting enhanced features.^[4,5] The improvement of orientational order and elevation of response parameter along with enrichment of dielectric and optical factors are few significant alterations, which are fashioned by the addition of nanoparticles in LC. Because of efficient interaction with LC matrices, quantum dots (QD) are now fre-

quently employed in the development of LC based photovoltaic applications, optical devices, and memory retainers.^[6] QD, designed in spherical shape with diameter of nano scale range, prevents aggregation when it is added in the system promoting "QD memory".^[7] Recently, popular QD, namely CdTe, CdSe, TiO₂, graphene, ZnO, has acquired credits for harnessing the ground qualities of LC and recreating them in more improved approach. Due to ionic impurities and modification in ionic or molecular relaxation mechanisms, the suppression of screening effect has been observed with adding TiO₂ QD to FLC.^[8] The development of holographic stature is obtained in LC, which is doped with CdSe QD.^[9] The addition of ZnS QD to FLC has produced alterations in photoluminescence behavior.^[10] CdSe QD facilitates faster electro-optical response in LC,^[11] and energy storing aspect generated in CuInS₂/ZnS core-shell QD added to FLC matrix^[12] is salient contributions of QD in pure LC. One of the uprising phenomenons promoted by the helicoidal arrangement of FLC molecules is the existence of memory effect.

Kaur *et al.*^[13] has realized thickness independent memory behavior of LC samples, whereas Kumar *et al.*^[14] has detected the preservation of memory owing to the concentration of external dopants in LCs. Both the investigations point to volatile memory effect. Pandey *et al.*^[15] identified this dielectric polarized state as transient referring to charge leakage tendency of dispersed nanoparticles, and Chandran *et al.*^[16] has noticed gradual tenfold relaxation of the molecules in a short period of time. Basu *et al.*^[17] established an aspect of non-volatile memory in nematic LC, which was described by electromechanical process exhibited by the LC-CNT hybrid system. In this paper, our group is able to deduce experimentally the existence of stable memory state for a planned interval of time in contrast to described FLC possessing transitory memory. The

Report

measurement of the polarized state of FLC molecules and their composites has been carried out dielectrically upto 1 h projecting non-volatility.

Experimental

$^{\circ}\text{C}$ FLC material coded as W327, provided to us by Military University of Technology Liquid Crystal group, Warsaw, Poland, is a multicomponent mixture of pyrimidine and pyridine organic compounds with a chiral dopant and their composition is based on results referenced here.^[18,19] Mixture W327 has following transition scheme.

A small amount of SiO_2 QD dispersed in *N,N*-dimethylformamide (DMF) has been ultrasonicated for 2 h followed by magnetic stirring. The homogeneously dispersed solution of SiO_2 is exercised to formulate 0.2 wt% and 0.4 wt% composites from pristine FLC sample. Sample holders are designed by ITO (indium tin oxide) coated photolithographic techniques treated conductive glass plates. Nylon 6/6 polymer layered glass plates are then rubbed unidirectionally to supply alignment to the investigated sample molecules. The planer aligned glass plates are then supported by Mylar spacers to sustain even distance. The thickness of the experimental cells, determined dielectrically on principle of Wheatstone bridge, is maintained at 8.3 μm .

The experimental sample holders are filled with pure FLC and their composites through capillary action at isotropic temperature to ensure homogeneity of filled samples and eradication of additional impurities. The fabricated cells are then subjected to cross state of polarized microscope (Radical RXLr-5) to observe any kind of agglomeration of added QD. The electronic microscope is fitted with an inbuilt camera (Jenoptik ProgresCT3) and a temperature controller hot plate stage (Instec mk1000). The textures of the composites generated by computer interface displayed prominent alignment order indicating a homogenous dispersion of QD and enhancement of orientational order of LC molecules. Dielectric study of the sample holders are then carried out by software programme attributed Impedance/Gain Phase Analyser (HP-4194 A) having frequency range 100 Hz to 40 MHz in the provided transition scheme. Broadband spectroscopy of the pure and composites presented a low frequency mode followed by consecutive Goldstone mode and Soft mode. The above measurements techniques have been conducted by our group and the detailed description has been provided in the papers.^[8,10-12,15,20-21]

Results and Discussion

The bistable switching tendency of FLC refers to the rotator torque exerted on helicoidal conformation of the molecules in the smectic layering by external force. Unwinding of helix in presence of applied bias voltage releases a significant characteristic of FLC termed as memory effect. The terminology coined addresses to the suppression of the phason mode in presence of externally applied electric field accompanied by the relaxation of the molecules in absence of the field. The reminiscences of the polarized state sustaining in the sample after the removal of bias voltage defines memory behavior. In present experiment to observe memory effect, the LC sample is heated to isotropic temperature 87 $^{\circ}\text{C}$ and cooled to 65 $^{\circ}\text{C}$ in attendance of 10 V bias electric field. The investigational temperature is maintained at 65 $^{\circ}\text{C}$, where the pure as well as composites displayed highest value of trans-

verse component of relative permittivity of goldstone mode with respect to frequency in SmC^* phase during dielectric examination. Memory behavior in FLC is studied by following mechanism: Firstly, 0 V reading is taken at 65 $^{\circ}\text{C}$ before application of bias voltage; Then, the sample is heated and cooled from isotropic temperature to 65 $^{\circ}\text{C}$ in presence of externally operated DC (direct current) electric field and dielectric reading at 0 V is immediately recorded. At an interval of 5, 10, 15, and 60 min, relative permittivity at 0 V is registered. Figure 1 presents the relative permittivity of pure at 0 V before and after the application of 10 V bias voltage. After 5 min, the polarized state of pristine FLC is stored about 12.3% and the same observations are recorded of dielectric spectra at 10, 15, and 60 min in Figure 1, which displays retention of memory behavior of 7.6%, 5.5% and 5.3%, respectively. Figures 2 and 3 account the identical experimental treatment for composite 1 and composite 2. However, the graphical descriptions generate reports of pronounced memory alignment. In Figure 2, the relaxation value of dielectric constant of composite 1 is much less than the original kindled value of 0 V showing about 25.3% retention of memory state after 5 min. Further evaluation of dielectric constant after 10, 15 and 60 min coincides together, displaying 22.2%, 21.5% and 21.9% memories of switched polarized state of molecules. Figure 3 relays 21.5% of memory behavior in composite 2 after a time interval of 5 min. Observations monitored illustrate 18.9%, 18.5%, 18.6% of memory study at an interval of 10, 15 and 60 min. Herein, the prominent inference can be drawn that helix of FLC molecules relaxes back immediately near to its original value after removal of bias voltage at a particular temperature in beginning. After that, the helix is temporarily deformed. This deformation in helicoidal arrangement of molecules signals towards the induced non-volatile memory effect in FLC composites. The dispersion of QD ensures decrement in the rate of degradation of memory state of the composites after the removal of bias voltage as can be witnessed in the above reported value.

Figure 1 Variation of dielectric permittivity of pure FLC with time (minutes) after removal of field.

The gradual slackening of helicoidal assembly of FLC molecules after prompt relaxation is illustrated here via following reasons. Considering from geometrical viewpoint, FLC is regarded as 1D solid due to possessing directorial as well as angular symmetry reflected as helical arrangement of molecules. The orientational director of FLC can be perturbed in two ways: Firstly, in course of cooling, the sample is cooled from isotropic temperature while approaching to mesogenic phase;

Figure 2 Variation of dielectric permittivity of FLC + 0.2 wt% SiO₂ with time (minutes) after removal of field.

Figure 3 Variation of dielectric permittivity of FLC + 0.4 wt% SiO₂ with time (minutes) after removal of field.

Secondly, after the immediate removal of applied electric field, the sample is cooled at any fixed experimental temperature. In both the processes, the reorientation of director takes place in smectic layering of molecules. While analyzing the present observations, we note that the simultaneous effect of temperature and voltage perturbs the reorientation of the helix director, which generates a constrained activity of molecules giving rise to durable non-volatile dielectric memory state. The experiment is carried out in SmC* phase, where goldstone mode is predominant. Therefore, we need to consider the role played by arrangement of tilt angle made by smectic layer normal and orientational director. The placement of QD within the smectic layers of FLC hinders the general alignment of phase angle and controls the tilt fluctuations. The applied field in the cooling cycle in presence of dispersed QD intervenes with the reconstruction of phase angle and constrains it to exist in a particular state. The alteration in geometrical array redefines the molecular consortium fixed in a state presenting reminiscences of polarized state. This temporal deformation of helicoidal array of molecules can be erased by heating the sample to isotropic temperature.

The anchoring of the LC molecules to the alignment polymer layer is modified in this voltage-temperature treatment, giving rise to surface dependent memory phenomenon.^[22]

When the system is cooled in presence of magnetic field, Clark *et al.*^[23] has deduced that the bulk alignment of the system imprinted on surface polymer layer exhibiting surface memory effect (SME). In the present scenario, this polymer imposed surface alignment hampers the motion of helically arranged molecules close to the glass plane resulting in memory behavior. When the system is cooled from isotropic temperature, reorientation of the molecules takes place near the surface of the sample holder. However, the application of voltage in presence of heating-cooling cycles modulates the FLC molecular configuration, which forces parallel dielectric component of LC molecules to stay in the direction of applied field. After the removal of field, the restoring torque forces the helical structure to wind back in stability. However, the effect of heating-cooling cycle constraints the molecular motion, which results in memorisability. One advantage of using QD is that it possesses great surface to volume ratio. Jakli *et al.*^[24] found that repeated heating and cooling cycles reduces the average size of the silica aggregates, which resulted in increased surface to volume ratio and enhanced the surface effects. Based on the above evidence, herein, we can deduce that high surface to volume ratio of SiO₂ QDs enhances in heating cooling cycle in presence of external bias voltage. The impurity charge carriers, originated during rubbing of the polymeric layer on ITO glass plates and while infusion of LC sample by capillary actions into the sample holders, are trapped on the surface of the nanoparticle. Under the influence of simultaneous temperature and voltage cycles, the charge is occupied by these impure thermal-ionic charge carries. Thus, the FLC molecules in the vicinity of QD retain the charge and stays in polarized condition restraining from restoring back to helix arrangement. Prominence of these surface effects amplifies the memorising ability of the LC composites. Under the influence of these surface effects, the observed memory can be designated as Voltage driven SME.

Figure 4 is dedicated to time analysis of memory behavior in order to elaborate the significance of the applied mechanism. Under the influence of present methodology, pristine FLC displays non-volatile memory behavior for a long duration along with composites in contrast to reported FLC displaying transient memory.^[15] However, in time frame, steep fall in relative permittivity is noticed in pure FLC in comparison to its dispersed state owing to the presence of QD. Earlier various memory observations of the LC molecules have been reported under the effect of applied external field but portraying insufficient align-

Figure 4 Time analysis of memory effect in pure FLC and composites to display significance of the applied mechanism.

ment. The application of cooling cycle from isotropic temperature along with DC electric field on FLC sample induces stable memory orientation. Thus, the technique of synchronous thermal and voltage cycle introduced in the study ensures stability in the system projecting a steady memory performance.

Relative permittivity defines the polarization response of the dielectric material determined through broadband dielectric spectroscopy. Variation in the polarization state of the FLC molecule has been reported in graphical plot of Figure 5. Relative permittivity of the composite FLC sample has increased in comparison to pure FLC. Dielectric permittivity attains maximum value at SmC*-SmA* transition temperature for the investigated samples, which indicate the change in the geometrical arrangement of the FLC molecules. With increase in temperature, pure FLC molecules attain high polarized state at SmC*-SmA* transition temperature and low frequency of 500 Hz. However, with increase in temperature, the layer by layer stacking geometry of SmA* phase transforms to thread like molecular arrangement of nematic phase, which is witnessed as rapid fall in polarizability of the system. Similar results have been obtained for composite 1 and composite 2 as depicted in Figure 5. Relative permittivity shows a sharp increase at 65 °C for composite 1 in deep SmC*, where the memory effect of the composites has been investigated showing very promising result. For composite 2, a continuous increase in dielectric permittivity is observed with sharp drop at SmA*-Nematic transition temperature.

Figure 5 Variation of relative permittivity with respect to temperature at fixed frequency 500 Hz observed for pure FLC, composite 1 and composite 2.

A textural study has been conducted to ensure the homogeneous alignment of the pristine FLC sample and its respective SiO₂ doped composites. As witnessed from Figure 6, pure FLC displays broken focal conic texture signifying the presence of Smectic A phase in the studied FLC sample. The tilted geometrical arrangement of FLC molecules representing helical structure casts a significant role in formation of broken focal conic polygonal texture. This helicoidal arrangement has been heavily perturbed on addition of SiO₂ QD, as can be seen from the optical micrographs of composite 1 and composite 2 captured at fixed interval of temperature. Planar alignment of composite 1 is reported at Figure 7 at (a) 35 °C, (b) 50 °C, (c) 65 °C and (d) 80 °C. Broken focal conic structure has completely disappeared, which supports the argument mentioned above that dispersed QD has constrained the FLC helix resulting in homogeneous alignment of molecules. For composite 2, again optical micrographs have been reported Figure 8 at (a) 35 °C,

(b) 50 °C, (c) 65 °C and (d) 80 °C, respectively. Pronounced change in the optical hue of the texture has been observed from 35 to 80 °C in composite 2. The constrained arrangement of FLC molecules under the influence of synchronous cycle of temperature and voltage depicts non-volatile memory effect.

Figure 6 POM images captured for pure FLC at temperature (a) 35 °C, (b) 50 °C, (c) 65 °C and (d) 80 °C.

Figure 7 POM images captured for pure FLC + 0.2 wt% at temperature (a) 35 °C, (b) 50 °C, (c) 65 °C and (d) 80 °C.

Figure 8 POM images captured for pure FLC + 0.4 wt% at temperature (a) 35 °C, (b) 50 °C, (c) 65 °C and (d) 80 °C.

Conclusions

In brevity, the manipulation created by nanodynamics on the memory characteristic of FLC has been studied in the present experiment. The investigation demonstrates clearly the increase of memory retaining ability of SiO₂ dispersed FLC under the influence of synchronous cycle of temperature and bias field in comparison to only application of externally applied field at a given temperature. The memory behaviour shows uncanny resemblance monitored for designed interval of time as value of dielectric constant resonates for a given composite. With increasing the concentration of dopants, there is decrement in memory retainment of dispersed FLC due to aggregation of QD resulting in disturbance of ordering of orientational director. The influences of molecular arrangement and surface effects have been discussed sponsoring up the derived conclusion. This reliability of the memory effect can be utilized in temperature dependent optical memory storage and image recorder. Further work in future prospective includes textural analysis and polarization-tilt effect of the observed mechanism.

Acknowledgement

A. Roy is sincerely thankful to UGC (F-25-1/2014-2015/7-177/2007 BSR) in New Delhi for providing financial assistance in the form of UGC-BSR Fellowship. Authors are also grateful to DST/INT/13/2014 for the grant of funds in the form of SERB and INDOPOLISH project. R. Manohar is thankful to UGC for MID Career award. Authors are also thankful to APJ Kalam centre for innovation for experimental facilities.

Special Issue

This paper is dedicated to the special issue of "Liquid Crystals".

References

[1] Meyer, R. B.; Liebert, L.; Strzelecki, L.; Keller, P. *Journal de Physique Lettres* **1975**, 36, 69.
 [2] Kurp, K.; Czerwiński, M.; Tykarska, M. *Liq. Cryst.* **2015**, 42, 248.
 [3] Kurp, K.; Czerwiński, M.; Tykarska, M.; Bubnov, A. *Liq. Cryst.* **2017**, 44, 748.

[4] Yadav, S. P.; Singh, S. *Prog. Mater. Sci.* **2016**, 80, 38.
 [5] Roy, J. S.; Majumder, T. P.; Dabrowski, R. *J. Mol. Struct.* **2015**, 1098, 351.
 [6] Mirzaei, J.; Reznikov, M.; Hegmann, T. J. *Mater. Chem.* **2012**, 22, 22350.
 [7] Lundstrom, T.; Schoenfeld, W.; Lee, H.; Petroff, P. M. *Science* **1999**, 286, 2312.
 [8] Gupta, S. K.; Singh, D. P.; Manohar, R. *Adv. Mater. Lett.* **2015**, 6, 68.
 [9] Anczykowska, A.; Bartkiewicz, S.; Nyk, M.; Myśliwiec, J. *Appl. Phys. Lett.* **2011**, 99, 191109.
 [10] Vimal, T.; Singh, D. P.; Agrahari, K.; Srivastava, A.; Manohar, R. *Photonics Lett. Pol.* **2016**, 8, 23.
 [11] Singh, D. P.; Gupta, S. K.; Manohar, R.; Varia, M. C.; Kumar, S. *J. Appl. Phys.* **2014**, 116, 034106.
 [12] Singh, D. P.; Vimal, T.; Mange, Y. J.; Varia, M. C.; Nann, T.; Pandey, K. K.; Manohar, R.; Douali, R. *J. Appl. Phys.* **2018**, 123, 034101.
 [13] Kaur, S.; Thakur, A. K.; Bawa, S. S.; Biradar, A. M. *Appl. Phys. Lett.* **2006**, 88, 122905.
 [14] Kumar, A.; Prakash, J.; Khan, M. T.; Dhawan, S. K.; Biradar, A. M. *Appl. Phys. Lett.* **2010**, 97, 163113.
 [15] Pandey, S.; Singh, D. P.; Agrahari, K.; Srivastava, A.; Czerwinski, M.; Kumar, S.; Manohar, R. *J. Mol. Liq.* **2017**, 237, 71.
 [16] Chandran, A.; Prakash, J.; Gangwar, J.; Joshi, T.; Srivastava, A. K.; Haranath, D.; Biradar, A. M. *RSC Adv.* **2016**, 6, 53873.
 [17] Basu, R.; Iannacchione, G. S. *Appl. Phys. Lett.* **2008**, 93, 183105.
 [18] Czerwiński, M.; Tykarska, M.; Dąbrowski, R.; Żurowska, M.; Kowrdziej, R.; Jaroszewicz, L. R. *Liq. Cryst.* **2012**, 39, 1498.
 [19] Tykarska, M.; Dąbrowski, R.; Czerwiński, M.; Chelstowska, A.; Piecek, W.; Morawiak, P. *Phase Transit.* **2012**, 85, 364.
 [20] Pathak, G.; Pandey, S.; Katiyar, R.; Srivastava, A.; Dabrowski, R.; Garbat, K.; Manohar, R. *J. Lumin.* **2017**, 192, 33.
 [21] Roy, A.; Pathak, G.; Herman, J.; Inamdar, S. R.; Srivastava, A.; Manohar, R. *Appl. Phys. A* **2018**, 124, 273.
 [22] Ouchi, Y.; Feller, M. B.; Moses, T.; Shen, Y. R. *Phys. Rev. Lett.* **1992**, 68.
 [23] Clark, N. A. *Phys. Rev. Lett.* **1985**, 55, 292.
 [24] Jakli, A.; Almasy, L.; Borbely, S.; Rosta, L. *Eur. Phys. J. B* **1999**, 10, 509.

Received April 24, 2018

Accepted April 27, 2018