

Non-volatile Memory Effect in Iron Nanoparticles Dispersed Ferroelectric Liquid Crystal.

Lucia Marino, Nicola Scaramuzza, Salvatore Marino

Physics Department, University of Calabria (UNICAL) Address: Via P. Bucci, Cubo 31C, 87036 Arcavacata di Rende, Cosenza, Italy.

luciamarino81@gmail.com, nicola.scaramuzza@fis.unical.it, smarino71@gmail.com

Abstract— *The research on new devices dedicated to the information storage represents a field in which the investments and the efforts of both industry and applied sciences are continuously growing in the last decades. This is due to the fact that the development of modern society is strictly connected with the need to increase the amount of information circulating at the global level. All this, increases the demand for increasingly efficient memory systems, both in terms of execution speed and energy consumption. To meet this demand, some frontier research is proposing various alternative solutions to the traditional silicon-based technology. The study proposed in this article is part of the trend of devices based on nanocomposed materials. In particular, a pronounced memory effect has been observed in a commercial ferroelectric liquid crystal doped with iron nanoparticles using a dielectric spectroscopy technique. The experimental data would lead to the hypothesis that this effect is due to a sort of switch between an initial phase, strongly distorted because the presence of the iron nanoparticles, to a restored smectic-C phase which take place by the application of a bias voltage.*

Keywords— *“non-volatile memory effect, iron nanoparticles, ferroelectric liquid crystals, dielectric spectroscopy, nanocomposed materials”*

I. INTRODUCTION

Non-volatile memories, that is, all those technological devices dedicated for the data and program code storage without the need of continuous power supply [1] represents a very wide and dynamic research field within which also the liquid crystalline materials have a substantial application potential.

Thanks to their peculiar properties such as the marked dielectric anisotropy and the collective response towards external electric or magnetic fields, liquid crystals (LCs) are among the best materials to be used as embedding matrix for nanocomposite materials synthesis and self-assembly of nanoscale materials [2]. The control of the orientation of the LCs molecules by external electric fields is the basis of the electro-optical effects and therefore of the most important technological applications of LCs such as displays, spatial light modulators, optical storage and non-volatile memory effect devices among many others [3-5]. It is precisely in these application fields that particular ferroelectric (FLCs) or chiral smectic liquid crystals, discovered in 1975 by Meyer [6], are very promising, especially when these are appropriately combined with metallic nanoparticles. In fact, a substantial number of publications confirms that FLCs mixtures doped with nanoparticles shows enhanced physical

properties like frequency modulation response, faster switching time, non-volatile memory effects and lower operating voltage [7-9]. This allows an easy and efficient way to obtain new functional materials without resorting to the chemical synthesis of new liquid crystal materials, which is a more complex and relatively expensive process.

Among all the emerging research fields based on the study of nanodoped liquid crystals, one of the most widespread is that related to the creation of new devices for permanent non-volatile memory. It is evident that in these research contexts the information about the dielectric response of materials, the orientational adjustment of dipoles and the translational adjustment of mobile charges present in a dielectric medium in response to an applied electric field represents a key point. For these reasons the dielectric spectroscopy is one of the most useful techniques for verifying the presence of significant memory effects in nanodoped FLCs. Dielectric spectroscopy allows the parameters determination of the various modes related to liquid crystal phase transitions including the very important permittivity which is a quantity that describe the ability of a material to polarize in response to an applied electric field, and thereby to cancel, partially, the field inside the material [10]. In the past years deformed helix ferroelectric liquid crystals (DHFLCs) doped with gold nanoparticles (GNPs) has been studied and long nonvolatile memory effect has been observed probably as a result of the electric field induced charge transfer effect from liquid crystal molecules to the GNPs and the stabilization of the helix deformation process [11]. As reported in our previous works, memory effects have been observed in both pure orthoconic smectic liquid crystal mixture and those doped with GNPs, indicative of the importance of the liquid crystal host [12,13]. Equally, promising results can be obtained by using composites of FLCs with dispersed magnetic/ ferromagnetic nanoparticles (NPs). In fact, improvement in spontaneous polarization and response time in this kind of nanocomposites, in addition to a phenomenon of static memory effect, were verified and attributed by Goel et al. to the magneto-electric coupling resulting from the strong interaction among the ferromagnetic nanoparticle's exchange field and the field of liquid crystal molecular director [14].

Another important effect, deriving from the addition of nanoparticles in the liquid crystal is the reduction in impurity ion concentration; more specifically, the nanoparticles act like a trap for such ionic impurities [12]. A variable amount of ionic impurities is always present in LCs, as a consequence of synthesis procedures and aging, and this causes various undesirable effects such as the decrement in contrast ratio, the enhancement in operating voltage, slower response time, image sticking and flickering, etc. which compromise the proper functioning of the LCs devices [15-18]. In recent years, various methods have been tested to overcome the effects of the impurities in LCs such as, for example, the doping of FLCs with diamond powders or using titanium dioxide nanoparticles [17-23]. On the other hand, recent studies revealed that nanoparticle doping can increase the conductivity of the nematic host by orders of magnitude [24-27]. All these results show that, despite the high activity in this field for over a decade, the complex interactions between dopant and host are not fully understood, yet.

In this paper, we report the effects of doping a commercial chiral smectic liquid crystal (SCE3) with iron nanoparticles on dielectric behavior and conductivity at two different temperatures inside the liquid crystalline SmC* phase. The attention has been particularly focused on the distorting effect that the iron nanoparticles exerts on the SmC* phase of the SCE3 and on how the application of an appropriate bias voltage can partially restore a more ordered SmC* phase giving rise to an evident non-volatile memory effect.

II. MATERIALS AND METHODS

Japanese planar aligned commercial cells (purchased from EHC Ltd, Tokyo, Japan) made of highly transparent indium tin oxide (ITO)-coated glass substrates of cell gap (2.0 ± 0.2) μm and an ITO resistance of $100 \Omega / \square$ were used. A sample (without doping) consisting of the pure FLCs SCE3, produced by Merck (some useful information and values for some of the elastic constants and other parameters of the FLCs SCE3 liquid crystal may be gleaned from the work of MacGregor [28], Stewart [29] and “Phase Transition in Liquid Crystals”, edited by S. Martellucci and A. N. Chester, Springer Science, 1992), see Table 1, was prepared and dielectrically characterized. The iron nanopowder obtained from PlasmaChem GmbH, (Fe - nanopowder with hydrophilic carbon shell, Purity: $> 97.0 \%$, Particle shape: spherical, Average particle size: 30 - 60 nm. Particle size full range: 5 - 200 nm, Fe-state: ferromagnetic, Specific surface area: $> 12 \text{ m}^2/\text{g}$, Bulk density: $> 0.5 \text{ g/cm}^3$, Functionality on C-shell: -COOH, -OH, C-content: 25 - 30 %. Controlled admixtures, %: Cu < 0.4 ; W < 0.2) were used to prepare a mixture of FLCs SCE3 + 0.1 wt % NPs. The mixture of FLCs SCE3 + 0.1 wt% NPs was selected for investigation after preliminary experiments on different percentages of Fe NPs in the FLCs SCE3, ranging between 0.05% wt and 0.2% wt. From this experiment, it was found that FLCs SCE3 + 0.1 wt % NPs was the most efficient mixture.

TABLE I

Phase sequence and some material parameters of FLCs SCE3. I is for liquid isotropic phase, Ch cholesteric liquid crystals, SA smectic A liquid crystals, SC smectic C liquid crystals, Cr crystal phase respectively (available from BDH).

$I \leftarrow 136 \text{ }^\circ\text{C} \rightarrow Ch \leftarrow 105 \text{ }^\circ\text{C} \rightarrow S_A \leftarrow 74 \text{ }^\circ\text{C} \rightarrow S_C$
Spontaneous polarization P_0 at $15 \text{ }^\circ\text{C} = 88 \mu\text{C}/\text{m}^2$
Dielectric constants at $15 \text{ }^\circ\text{C}$:
$\epsilon_{\parallel} = 3.10$
$\epsilon_{\perp} = 5.04$

To prepare the nanocomposite samples, the iron nanopowders were first mixed in chloroform and then were added to the FLCs SCE3. Thereafter the mixture was sonicated using ultrasonicator till the solution was visibly homogeneously mixed and after that, the solution was left for 3~4 hours at a temperature of $40\sim 45^\circ\text{C}$ till the chloroform evaporated completely. The obtained FLCs SCE3 - NPs mixture was then introduced into the cell via capillary suction. These filled LC cells were kept in a heating stage. The dielectric measurements were carried out on an EG&G 273A galvanostat-potentiostat/impedentiometer controlled by the impedance software M398 in order to acquire the real and imaginary part of

impedance in the frequency range of 1 Hz – 100 kHz with a maximum applied voltage of 20 mV (RMS). The measurements were carried out for temperature values ranging from room temperature (RT) up to 50 °C so as to remain in the smectic-C mesophase which is the one in which we are specifically interested in this work. In order to verify the presence of memory effect a dc bias was applied during the acquisition of dielectric spectra. The real (ϵ') and the imaginary (ϵ'') part of dielectric constant have been calculated from impedenziometric output by using the following equations:

$$\epsilon' = -\frac{\text{Im}Z}{(\text{Im}Z^2 + \text{Re}Z^2)} \frac{d}{\epsilon_0 A} \frac{1}{2\pi f} \quad (1)$$

$$\epsilon'' = \frac{\text{Re}Z}{(\text{Im}Z^2 + \text{Re}Z^2)} \frac{d}{\epsilon_0 A} \frac{1}{2\pi f} \quad (2)$$

being ImZ, ReZ, d, A and f are respectively the imaginary part of the impedance, the real part of the impedance, the cell thickness, the area of the (ITO)-coated glass substrates and the frequency of the applied electric field. The complex dielectric constant is:

$$\epsilon^* = \sqrt{(\epsilon')^2 + (\epsilon'')^2} \quad (3)$$

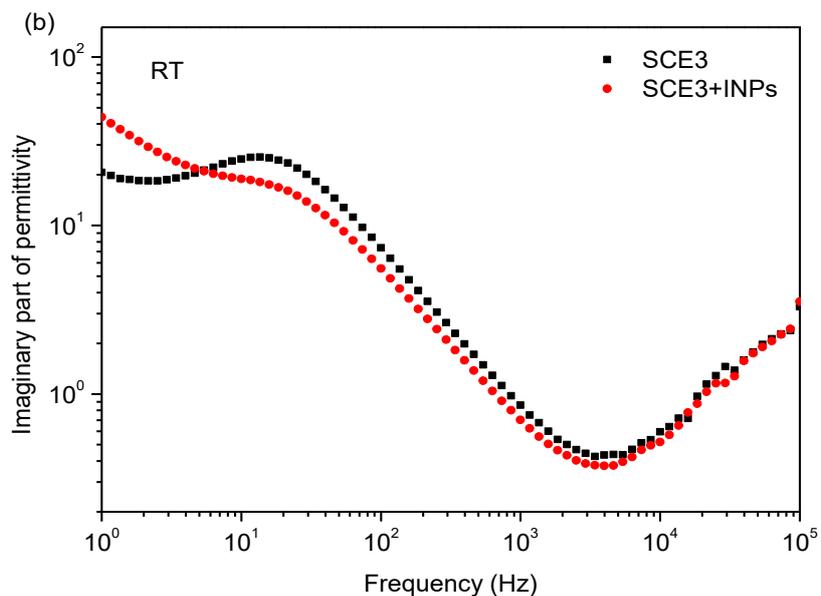
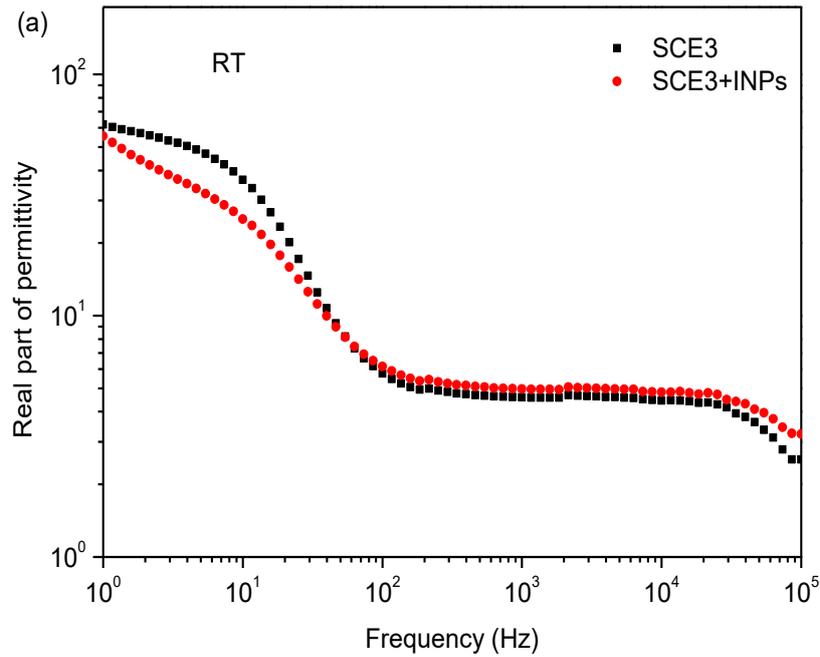
having verified that capacitor has negligible fringing capacitance, there are no air gaps between metal electrodes and sample under test and frequency is sufficiently low to neglect parasitic inductances.

III. RESULTS AND DISCUSSION

Dielectric spectroscopy represents one of the best techniques for the characterization of FLCs and for the detection of any memory effect that may be present in these materials. In FLCs, whether they are pure or doped with any kind of nanoparticles, the presence of non-volatile memory is usually studied by observing the Goldstone mode (GM). In fact, since the GM is related to the molecular oscillation around the azimuth angle, a suitable bias across the cell, which unrolls the helicoidal order, induces a reduction in the contribution of the GM and a decrease of the permittivity [30]. In absence of memory effects the FLC molecules returns to the initial order once the bias is removed due to the restoring forces, on the contrary, in presence of memory effects, the molecules remain in the switched state even for several days.

The frequency dependence behavior of dielectric permittivity at room temperature in the pure and doped samples is shown in Figure 1. Figure 1(a) shows that a considerable decrease in permittivity was observed in the doped sample on increasing the frequency up to 50 Hz. However, beyond 100 Hz the situation between pure and doped sample is slightly inverted. Figure 1(b) shows imaginary part of permittivity. The GM peak is around 10 Hz for pure sample while in the case of doped one is shifted to higher frequencies and it shows a lower

amplitude. After 100 Hz the trends of the two spectra are almost coincident (Fig.1(a) and 1(b)). Figures 1(c) and 1(d) show the trend to a fixed temperature of 50 °C. The real part shows that around 500 Hz the value of the doped FLCs SCE3 is slightly higher while the imaginary part shows a higher contribution of ionic currents at low frequencies; the doped sample shows also a less evident GM and a dielectric mode centered around 104 Hz more visible (Fig.1(d)).



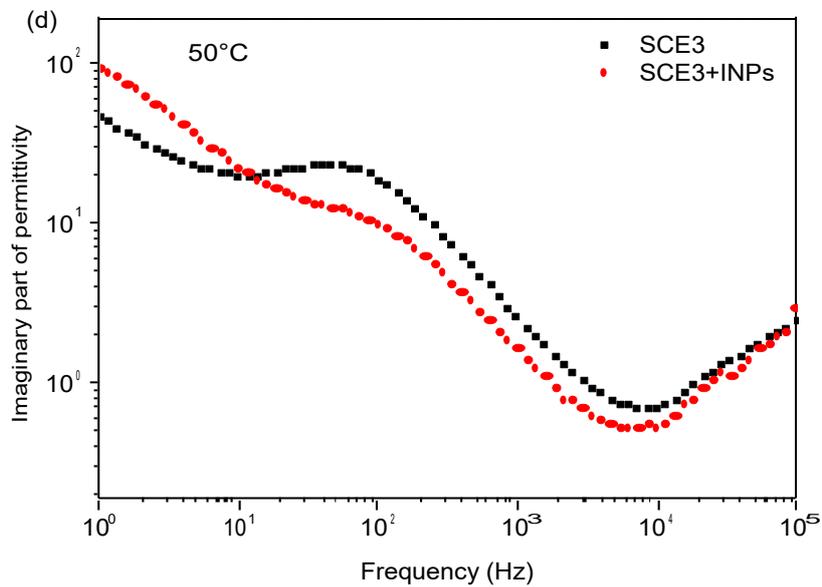
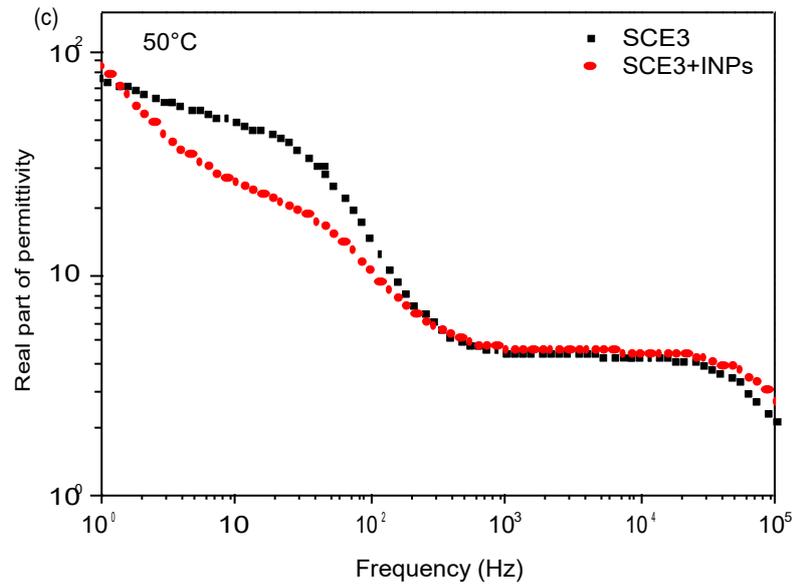
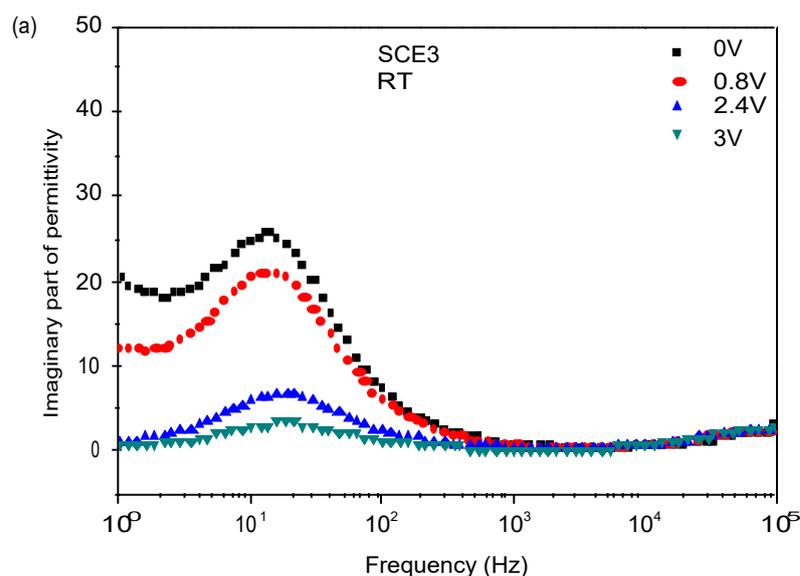


Fig. 1 Frequency dependence of the real part of dielectric permittivity in the pure and doped sample at room temperature (a). Frequency dependence of the imaginary part of dielectric permittivity in the pure and doped sample at room temperature (b). Frequency dependence of the real part of dielectric permittivity in the pure and doped sample at 50°C (c). Frequency dependence of the imaginary part of dielectric permittivity in the pure and doped sample at 50°C (d).

Figures 2(a) and 2(b) shows the effects of a voltage applied to the pure liquid crystal. It should be noted that the reduction of GM occurs around 3V both at room temperature (Fig.2(a)) and at 50°C (Fig. 2.(b)). In Fig. 2(c) and 2(d) the trend of the doped liquid crystal is shown. It is interesting to note that applying 0.8V (Fig. 2(c)) the GM tends to increase before starting the expected decrease with the increase of the applied voltage. This behavior could be attributed to an indirect coupling between the NPs magnetic moments and the FLCs electrical polarization [31], which would lead to a small decrease in the distortion of the ferroelectric structure and therefore to a small increase in the Goldstone mode. More in-depth investigations are underway to better clarify this behavior [32]. It is also plausible to hypothesize that the smectic-C phase of the FLCs is strongly distorted because of the polar group -COOH and -OH of the carbon shell which attract the polar ends of the FLCs. This fact, together with the randomness of the NPs distribution, leads to a waste loss of the smectic-C order. For the value of 0.8V a restore of the smectic-C order take place and, consequently, we observe an improved Goldstone mode that, we remember, is related to the oscillation of the molecular axis around the azimuth angle. Further increase of the applied voltage leads to the expected inhibition of the Goldstone mode due to the gradual decrease of the tilt angle. It is reasonable to suppose that, in the processes described above; the phenomenon of ion-trapping plays a negligible role. In fact, the phenomenon of ion trapping is strongly dependent on the level of ionic contamination of the sample [15]; however, as described in the previous paragraph, the level of purity of the NPs guaranteed by the manufacturer is quite high, as is the level of purity of the FLCs. Furthermore, the applied voltage and temperature values used during the measurements are not such as to cause an important phenomenon of ionic injection from the aligning substrates. Therefore, we argue that the absorption sites of the carbon shells remain mostly free. As a consequence of this, the NPs-FLCs polar interactions and/or the coupling between the NPs magnetic moment and the FLCs electrical polarization are preponderant with respect to the ion-NPs interaction.



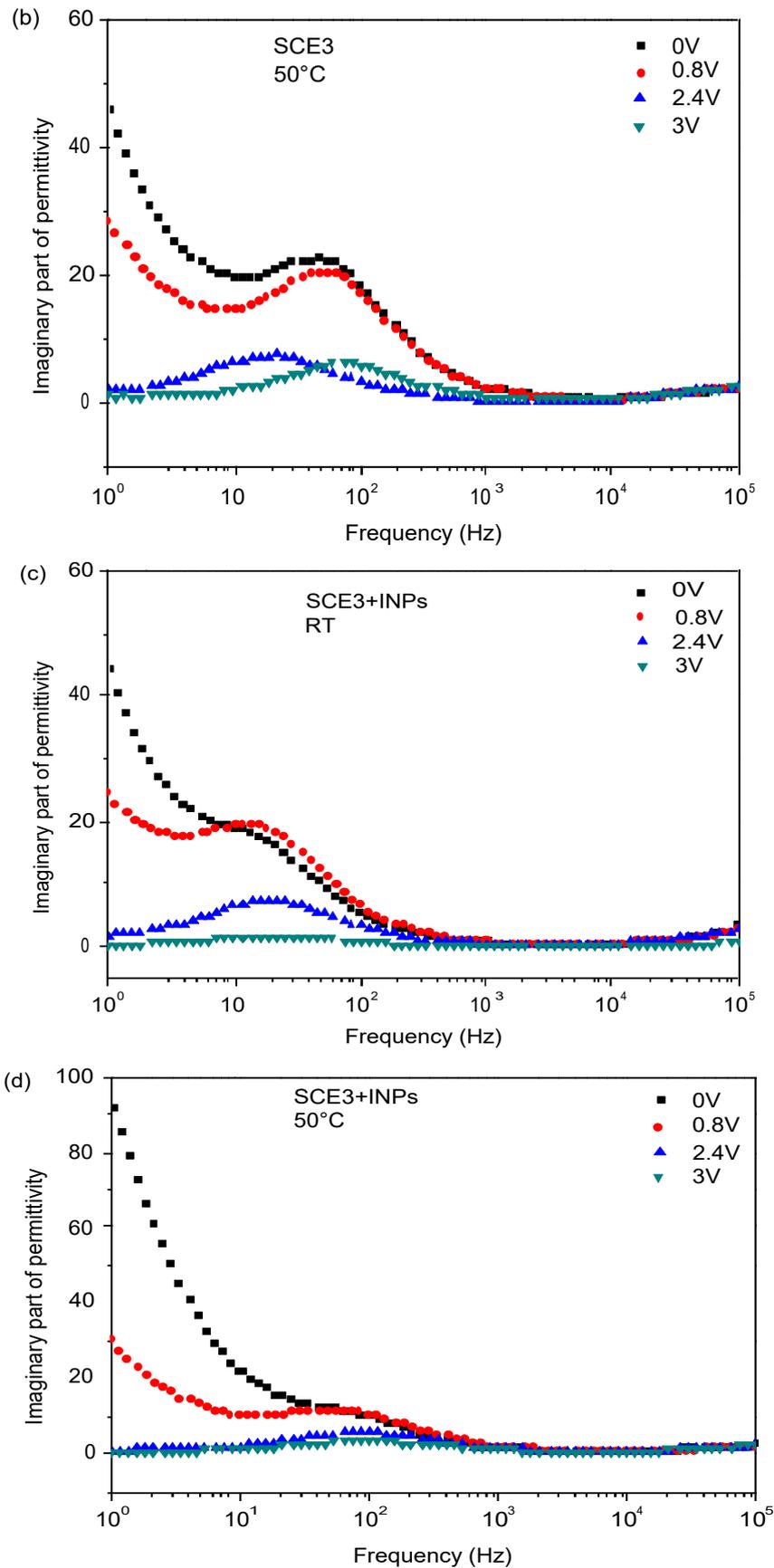
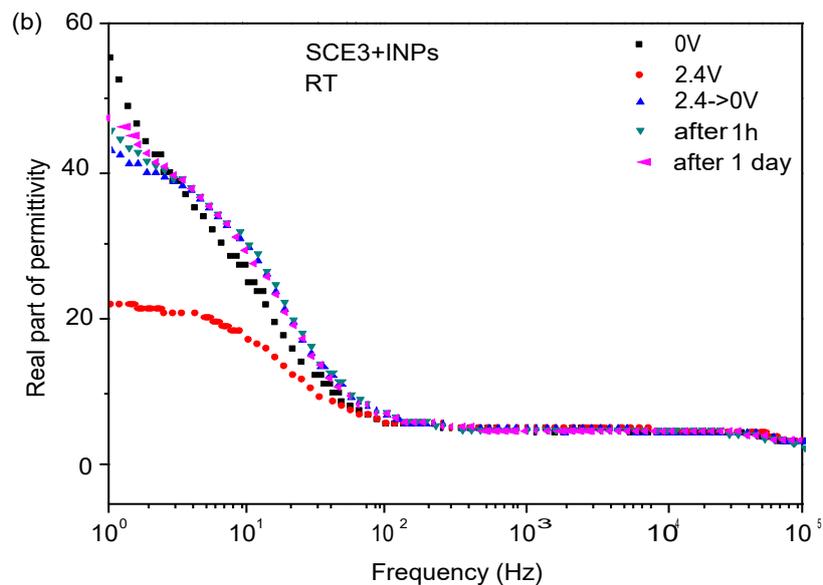
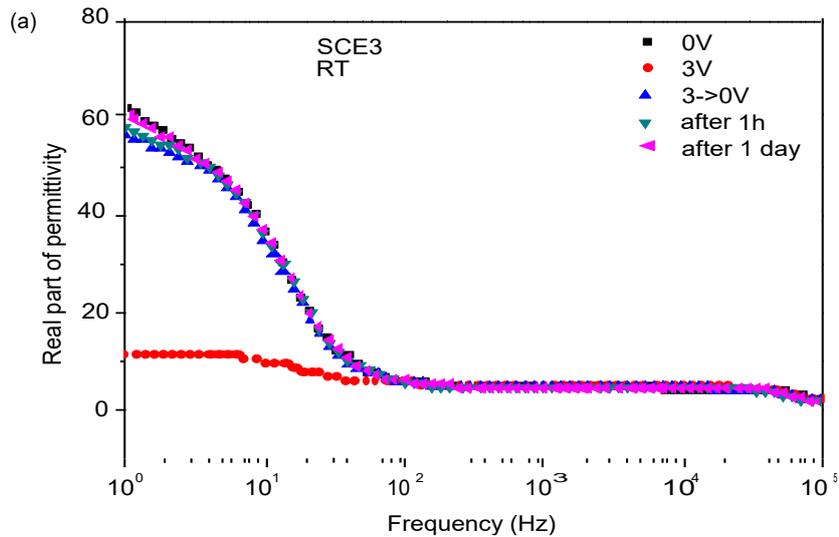


Fig. 2 Effects of a bias voltage applied to the pure liquid crystal at room temperature (a), at 50°C (b). Effects of a bias voltage applied to the doped liquid crystal at room temperature (c), at 50°C (d).

The memory effect in pure liquid crystal is almost absent at room temperature and rather weak at 50°C; in fact, the trend after 10 Hz is almost coincident before and after the application of the bias at room temperature and at 50°C (Fig. 3 (a) and 3 (c)); in any case, over time the values of the permittivity tend to the starting values before the application of the bias. In the case of the doped liquid crystal, there is an evident memory effect that remains even after days at room temperature (Fig.3 (b)) and at 50 ° C (Fig.3 (d)).



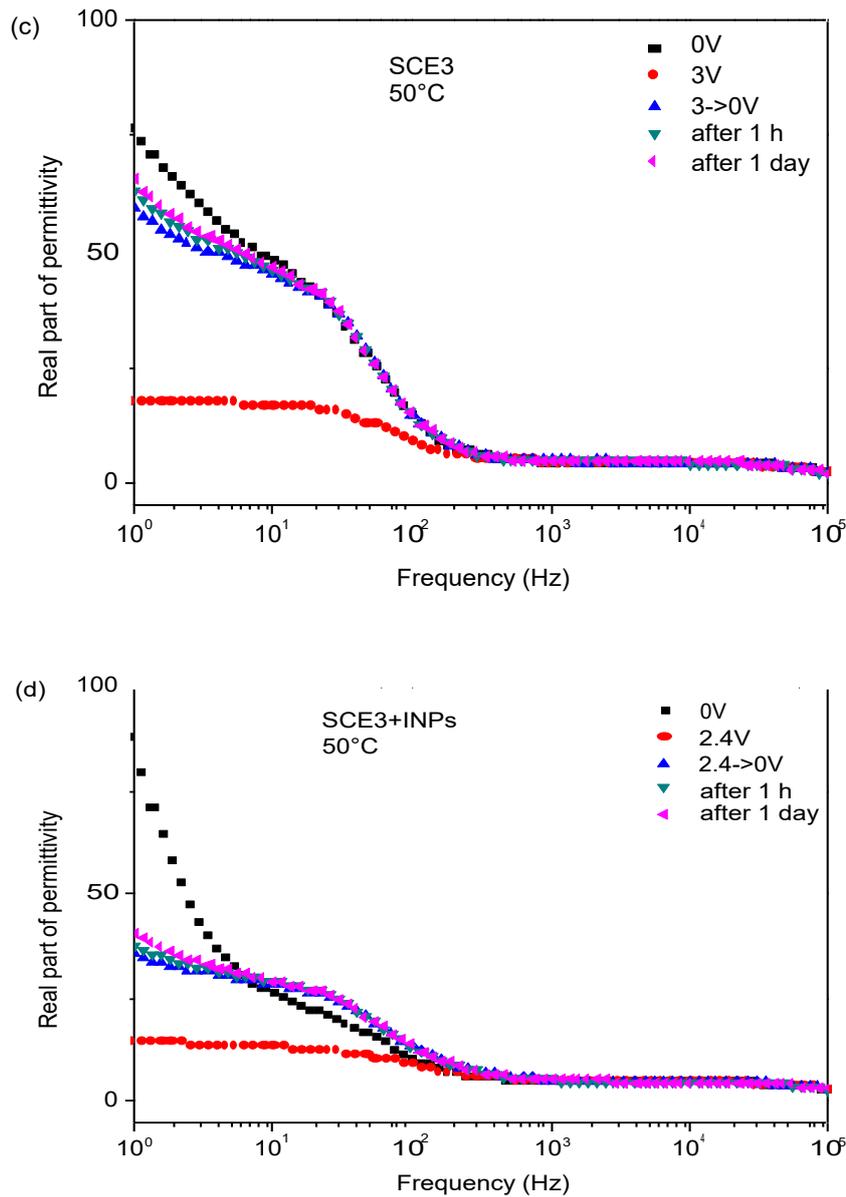
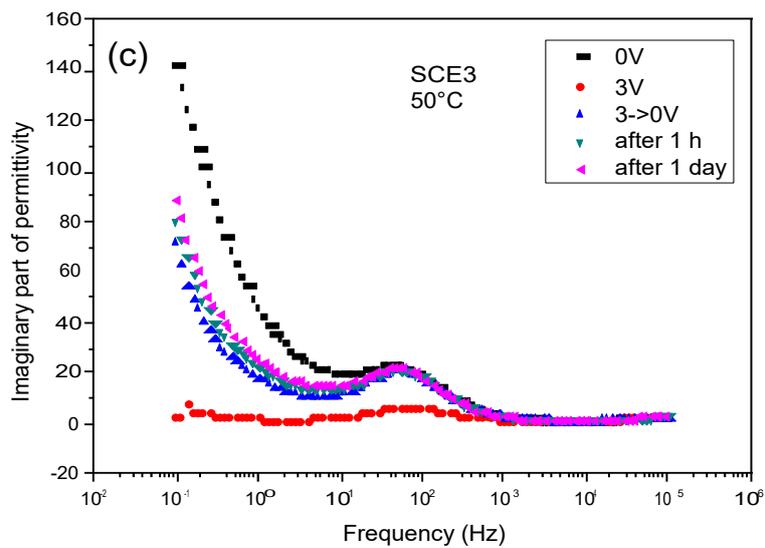
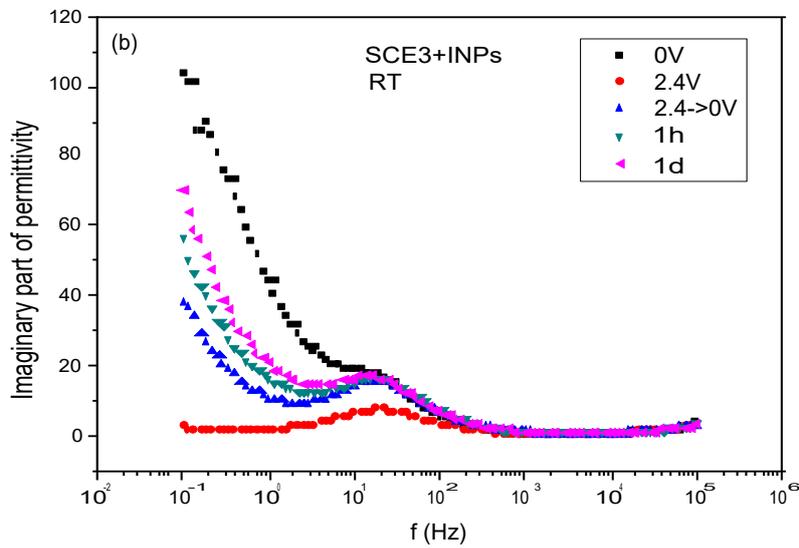
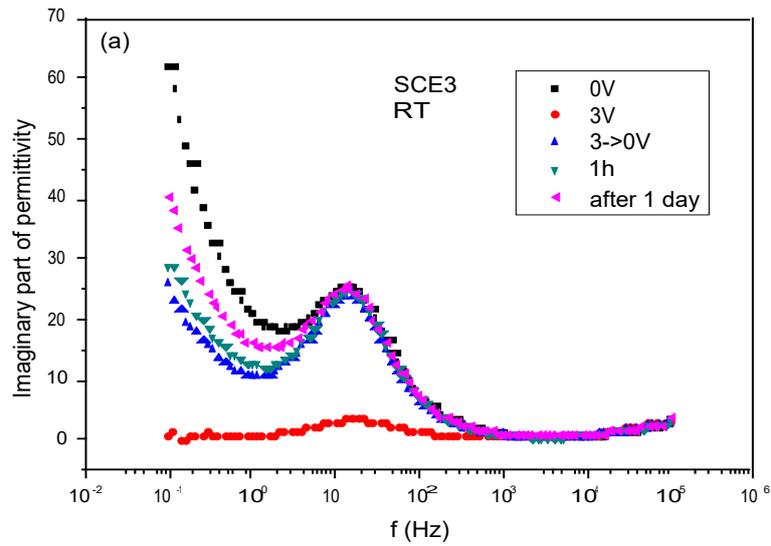


Fig. 3 Memory effects in pure liquid crystal at room temperature (a), in doped liquid crystal at room temperature (b), in pure liquid crystal at 50°C (c), in doped liquid crystal at 50°C (d).

From the analysis of the Imaginary parts of permittivity related to the previous measurements, it is possible to deduce the mechanism underlying the improved memory effect observed in the doped samples. In fig. 4(a) and 4(c) it is clear that the Goldstone mode result quite pronounced both before and after the application of a bias voltage for both room temperature and 50C. This means that the SCE3 recovers a smectic-C phase almost unchanged respect to the initial one after the removal of the bias. On the contrary, as showed in fig. 4(b) and 4(d), the SCE3+NPs sample initially does not show a well defined Goldstone mode for the reasons above mentioned, nevertheless it is restored after the removal of the bias voltage which indicates that the doped sample tend to rearrange in the smectic-C phase once the bias is turned out. As showed in fig.4(b) and 4(d), the restored smectic-C phase tend to persist over time enhancing the memory effect with respect to the pure SCE3.



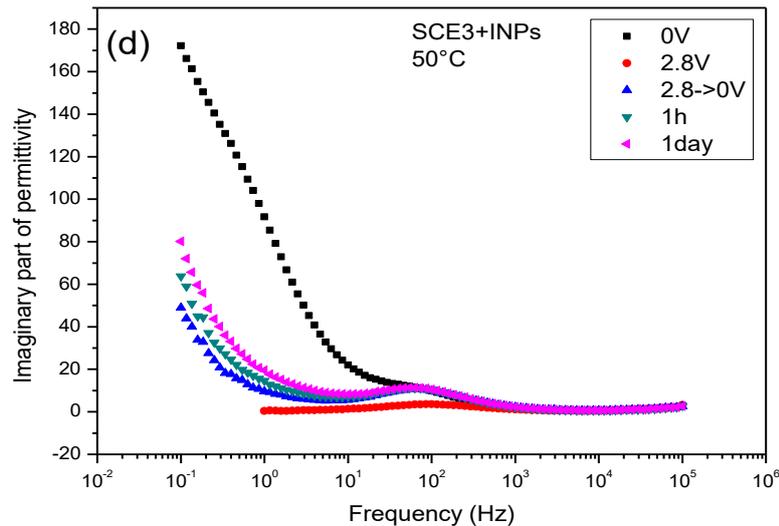


Figure 4. Memory effects in pure liquid crystal at room temperature (a), in doped liquid crystal at room temperature (b), in pure liquid crystal at 50°C (c), in doped liquid crystal at 50°C (d). Imaginary parts.

IV. CONCLUSIONS

LCs nanocomposites are becoming an increasingly important area of research, thanks to the unique combination of liquid crystals and nanoparticles that can be controlled by electric fields and temperature, thus resulting useful for technological applications, like displays, flat-panels, new kind of sensors and digital non-volatile memory devices. The dielectric spectroscopy technique has been used to study non-volatile memory effects in a commercial ferroelectric smectic liquid crystal doped with iron nanopowder with hydrophilic carbon shell. The electrical partially reversible bistable behavior revealed by dielectric spectroscopy could be a first step towards the achievement of permanent non-volatile memory devices as required by the electronics industries.

In summary, the effect of dispersion of the iron nanopowder on the dielectric and non-volatile memory of FLCs SCE3 has been analyzed and explained. Our study does not show appreciable memory effects in commercial ferroelectric liquid crystals while they are present in the doped one. The memory effect remains for days before it returns to initial conditions. From our data, it would seem that this memory effect is due to a sort of switch between an initial phase, strongly distorted because the presence of the iron nanoparticles, to a restored smectic-C phase which take place by the application of a bias voltage. The restored smectic-C phase remain stable in time giving rise to the observed non-volatile memory effect. We have hypothesized that the initial strongly distorted phase could be ascribed to the interaction between the polar group -COOH and -OH of the carbon shells covering the nanoparticles with the polar ends of the FLCs.

Further investigations are underway using different types of ferromagnetic nanoparticles.

REFERENCES

- [1] Tom Coughlin, Roger Hoyt, and Jim Handy, *Digital Storage and Memory Technology (Part 1)*, IEEE discussing developments in digital storage technology, November 2017
- [2] Torsten Hegmann, Hao Qi, and Vanessa M. Marx. *Journal of Inorganic and Organometallic Polymers and Materials*, Vol. 17, No. 3, September 2007
- [3] Chigrinov, V.G.; *Liquid Crystal Devices: Physics and Applications*; Artech House: Boston, 1999.
- [4] Crawford, G.P.; Eakin, J.N.; Radcliffe, M.D.; Jones, A.C.; Pelcovits, R.A. *J. Appl. Phys.*, 2005, 98, 123102. DOI: 10.1063/1.2146075
- [5] Lagerwall, S.T.; *Ferroelectrics and Antiferroelectric Liquid Crystals*; Willy-VCH, New York, 1999.
- [6] Meyer, R.B.; Liebert, L.; Strzelecki, L.; Keller, P.; *J. Phys. Lett.* 1975, 36, 69. DOI:10.1051/jphyslet:0197500360306900
- [7] Joshi, T.; Kumar, A.; Prakash, J.; Biradar, A.M.; *Appl. Phys. Lett.*, 2010, 96, 253109. DOI: 10.1063/1.3455325
- [8] Chen, Q.; Lin, M. R.; Lee, J. E.; Zhang, Q. M.; Yin, S.; *Appl. Phys. Lett.*, 2006, 89,141121. DOI: 10.1063/1.2360183
- [9] Zhang, T.; Zhong, C.; Xu, J.; *Jpn J. Appl. Phys.*, 2009,48, 055002.DOI: 10.1143/JJAP.48.055002
- [10] S. E. Braslavsky, *Pure Appl. Chem.*, Vol. 79, No. 3, pp. 293–465, 2007
- [11] Prakash, J.; Choudhary, A.; Kumar, A.; Mehta, D. S.; Biradar A. M., *Appl. Phys. Lett.* 2008; 93: 112904.
- [12] Marino, L.; Marino, S.; Wang, D.; Bruno, E.; Scaramuzza, N. *Soft Matter*. 2014; 10: 3842.
- [13] Marino, L.; Koduru, H. K.; Marino, S.; Facal, P. M.; Wang, D; Dabrowski, R.; Scaramuzza, N. *Nanosci Technol.* 2017; 4(1): 1-10.
- [14] Goel, P.; Arora, M.; Biradar, A. M. *Journal of Applied Physics* 2014; 115, 124905.
- [15] Pradeep Kumar, Avinash Kishore, Aloka Sinha, *Adv. Mater. Lett.* 2016, 7(2), 104-110.
- [16] Y. Garbovskiy and I. Glushchenko. *Crystals*, vol. 5, no. 4, pp. 501–533, 2015
- [17] Kumar, P.; Kishore, A.; Sinha, A.; *Adv. Mater. Lett.* 2016, 7(2), 104-110.
- [18] Kumar, M.; Kumar T.; Avasthi, D. K. *Scripta Materialia*, 2015, 105,46. DOI: 10.1016/j.scriptamat.2015.04.030
- [19] Enachi, M.; Lupan, O.; Braniste, T.; Sarua, A.; Chow,L.; Mishra, Y.K.; Gedamu, D.; Adelung, R.; Tiginyanu I. *Phys. status solidi. RRL*, 2015, 1. DOI: 10.1002/pssr.201409562
- [20] Chen, P.S.; Huang, C.C.; Liu, Y.W.; Chao, C.Y. *Mol. Cryst. Liquid Cryst.*, 2009, 507, 202. DOI: 10.1080/15421400903051374

- [21] Chou, T.R.; Hsieh, J.; Chen, W.T.; Chao, C.Y. *Jpn. J. Appl. Phys.*, 2014, 53, 071701. DOI: 10.7567/JJAP.53.071701
- [22] Chandran, A.; Prakash, J.; Ganguly, P.; Biradar.; A.M. *RSC. Adv.*, 2013, 3, 17166. DOI: 10.1039/C3RA41964A
- [23] Tang, C.Y.; Huang, S.M.; Lee, W. *J. Phys. D.*; 2011, 44, 355102. DOI: 10.1088/0022-3727/44/35/355102
- [24] Urbanski, M.; Lagerwall J. P. F. *J. Mater. Chem. C*, 2016, 4, 3485
- [25] Tomylko, S.; Yaroshchuk, O. ; Kovalchuk, O.; Maschke U. ; Yamaguchi, R. *Ukr. J. Phys.*, 2012, 57, 239–243.
- [26] Ha, Y. S.; Kim, H. J.; Park, H.G.; Seo, D. S. *Opt. Express*, 2012, 20, 6448–6455.
- [27] García-García, A.; Vergaz, R.; Algorri, J. F.; Geday, M. A. ; Oto'n, J. M. *J. Phys. D: Appl. Phys.*, 2015, 48, 375302.
- [28] MacGregor, A. R. A. *J. Mod. Optics*, 1990, 37, 919-935.
- [29] Stewart, I. W.; *The Static and Dynamic Continuum Theory of Liquid Crystals*; Taylor & Francis, London and New York, 2004.
- [30] F. Gouda, K. Sarp, and S. T. Lagerwall. *Ferroelectrics*, 1991, Vol. 113, pp. 165-206
- [31] B. Rozic, M. Jagodic, S. Gyergyek, M. Drofenik, S. Kralj, G. Cordoyiannis, and Z. Kutnjak. *Mol. Cryst. Liq. Cryst*, Vol. 545: pp. 99, 1323–104, 1328, 2011.
- [32] Dharmendra Pratap Singh, Tripti Vimal, Yatin J. Mange, Mahesh C. Varia, Thomas Nann, K. K. Pandey, Rajiv Manohar, and Redouane Douali. *Journal of Applied Physics*, 123, 034101, 2018.