

Guest–host interaction in ferroelectric liquid crystal–nanoparticle composite system

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Abstract. The present paper deals with the characterization of a ferroelectric liquid crystal–nanoparticle (FLC–NP) composite system. The dielectric, electrical and polarization property of the FLC–NP composite system have been studied as a function of temperature and frequency. Ferroelectric Cu-doped ZnO (Cu–ZnO) nanoparticles have been added to the pure ferroelectric liquid crystal (FLC) Felix 17/100. The nanoparticles are bigger in size as compared to FLC molecules; therefore, they distort the existing geometry of FLC matrix and set up an antiparallel correlation with the dipole moments of the host FLC molecules. This antiparallel correlation of guest–host geometry reduces the net ferroelectricity of the composite system and modifies all the physical properties of the pure FLC. The change in properties has been analysed and explained in the light of guest–host interaction.

Keywords. Ferroelectricity; nanoparticle; dielectric property; electro-optical property.

1. Introduction

The chiral smectic C (SmC*) liquid crystalline phase, has a helical stack of layers in which molecules are uniformly tilted. The tilt of the molecules is coupled to the layer thickness producing local biaxiality in the medium. Due to the chirality of the molecules, the mirror symmetry in the system leads to the possibility of sustaining an electric polarization (P), along the local twofold axis, spiraling uniformly about the twist axis of the helical structure. The ferroelectric properties in liquid crystals (LCs), discovered by Meyer *et al* (1975), are in a way lying hidden in its helicoidal structure. This helix can be unwound by either application of electric field or by surface interactions, which make them proper ferroelectrics having a net spontaneous polarization. Electro-optic effect in SmC* phase, discovered by Clark and Lagerwall (1980) makes it important from application point of view and alienate this phase from other class of LCs. Therefore, technologically this phase is very useful and commonly used in device applications due to its threshold behaviour, fast response time, etc. (Lagerwall 2000).

Scenario of the experimental research, in the field of liquid crystal materials, has changed with the development of nanoscience. The nanoparticles and carbon nano-

tubes are getting importance due to their potential applications. Different types of nanoparticles and carbon nanotubes have been used as dopant to improve the various physical properties of the nematic and ferroelectric liquid crystalline materials (Kaur *et al* 2007; Prakash *et al* 2008; Arora *et al* 2009; Manohar *et al* 2009; Li and Huang 2009). The use of nanoparticles and carbon nanotubes, to improve the physical and electro-optical properties of LCs, is a novel method to change the LC parameters without synthesizing new LC material according to the requirement. Therefore, the field of study of guest–host effect in LCs (Srivastava *et al* 2008) became much wider in the past few years from the research and application point of view.

The ZnO nanoparticle has attracted interest of researchers due to its semiconducting property and a wider bandgap of order 3.37 eV. In addition to these properties, they have also shown their importance in the fabrication of piezoelectric transducers, photonic crystals, photo detectors, photodiodes, etc. The surface defect in ZnO leads to some important and useful features also. The effect of Cu²⁺ doping as a luminescence activator and as a compensator of n -type material is of great importance for II–VI semiconductors. ZnO:Cu²⁺ nanoparticle has shown the green luminescence property with the variation of doping concentration of Cu (Sharma *et al* 2011).

The present work is an attempt to explain the interactions between ferroelectric liquid crystal (FLC) molecules and Cu–ZnO nanoparticles (NP). The change in FLC

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geometry, due to the addition of NPs, has also been explained in the present paper. The behaviour of the conductivity of the doped FLC is driven by the semiconducting nature of the Cu–ZnO NPs. The orientational configuration of the pure ferroelectric liquid crystal matrix is also found to be changed with the mixing of NPs. The dielectric, electrical and polarization properties have been well studied for a definite temperature and frequency range for both pure and doped FLC.

2. Experimental

2.1 FLC and nanomaterial

The ferroelectric liquid crystal (FLC) material used in the present study is Felix 17/100 (Clariant Chemicals Co. Ltd.) and the phase sequence of the sample is Cr, SmC*, SmA*, N*, Iso at –20, 72, 82 and 95 °C. The nanoparticle-doped sample of Felix 017/100 was prepared by the dispersion of nanoparticles (NPs) in 2% wt/wt concentration in the pure FLC and termed as doped-FLC. The NPs, used for present study, are ZnO-doped with 10% of Cu. These NPs are prepared by solvothermal method using ethanol as solvent. The whole preparation reaction is carried out in a high pressure autoclave. The average crystallite size of NPs using Debye–Scherrer's equation was found to be ~ 10 nm. The scanning electron microscope (SEM) analysis of NPs provide the information about their rod shape structures and its diameter is about 12–15 nm and length is about 40–80 nm (Sharma *et al* 2011). To prepare the NPs, doped-FLC sample, an appropriate amount (in the weight ratio) of NPs (2% in the present case) were mixed into the pure FLC and then homogenized with an ultrasonic mixer at 90 °C for one hour and uniform dispersion of NPs was ensured. The uniform distribution of the NPs in FLC matrix has been analysed by polarizing optical microscope (POM) textures and scanning electron microscopy (SEM).

2.2 Preparation for sample cell

The dielectric study of NP-doped FLC were conducted on planar geometry. The sand-witched type (capacitor) cells were made using two optically flat glass substrates coated with indium tin oxide (ITO) layers. To obtain planar alignment, the conducting layer were treated with the adhesion promoter and coated with polymer nylon (6/6). After drying the polymer layer, substrates were rubbed unidirectionally. The substrates were then placed one over another to form a capacitor. The cell thickness was fixed by placing a Mylar spacer (6 µm in the present study) in between the plates and then sealed with UV sealant. The empty sample cells were calibrated using analytical reagent (AR) grade CCl₄ (carbon tetrachloride) and C₆H₆ (benzene) as standard references for dielectric

study. The LC nanoparticle suspension was prepared by mixing the weight ratio i.e. 2% wt/wt concentration of NPs in the pure FLC. The assembled cells were filled with the pure and doped FLC at a temperature slightly higher than the isotropic temperature by means of capillary method and then cooled gradually up to room temperature under the small a.c. electric field. This ensures the uniform distribution of NPs in FLC. The alignment of the sample was checked by the polarizing microscope under the crossed polarizer–analyser arrangement.

2.3 Dielectric and electro-optical measurement

The dielectric measurements have been performed by a computer-controlled impedance/gain analyser (HP 4194 A) attached with a temperature controller in the frequency range of 100 Hz–10 MHz. The dielectric measurements have been carried out as a function of temperature by placing the sample on a computer-controlled hot plate INSTEC (HCS-302). The temperature stability was better than ± 0.1 °C. Measurements in the higher frequency range have been limited to 10 MHz because of the dominating effect of finite resistance of ITO coated on glass plates and lead inductance (Manohar *et al* 2007, 2011; Srivastava *et al* 2007).

The dielectric relaxation phenomenon of the pure and doped FLC have been analysed using Cole–Cole relation:

$$\varepsilon^* = \varepsilon(\infty) + \frac{\delta\varepsilon}{1 + (i2\pi f\tau)^{1-\alpha}} \quad (1)$$

where $\delta\varepsilon$ is the relaxation strength of the relaxation mode and $\varepsilon(\infty)$ the high frequency limit of the relative permittivity data, f the frequency, τ the relaxation time and α the distribution parameter. As liquid crystals are improper dielectrics therefore, the experimental data suffers from the two basic problems. The low and high frequency deviation in dielectric data and exceedingly require correction for low and high frequency values. On separating the real and imaginary part of (1), one may get:

$$\varepsilon' = \varepsilon'(dc)f^{-n} + \varepsilon'(\infty) + \frac{\delta\varepsilon'[1 + (2\pi f\tau)^{(1-\alpha)} \sin(\alpha\pi/2)]}{1 + (2\pi f\tau)^{2(1-\alpha)} + 2(2\pi f\tau)^{(1-\alpha)} \sin(\alpha\pi/2)}, \quad (2)$$

and

$$\varepsilon'' = \frac{\sigma(dc)}{\varepsilon_0 2\pi f^k} + \frac{\delta\varepsilon'(2\pi f\tau)^{(1-\alpha)} \cos(\alpha\pi/2)}{1 + (2\pi f\tau)^{2(1-\alpha)} + 2(2\pi f\tau)^{(1-\alpha)} \sin(\alpha\pi/2)} + Af^m. \quad (3)$$

Here $\sigma(dc)$ is the d.c. ionic conductance, ϵ_0 the free space permittivity and f the frequency while n , m and k are the fitting parameters. The terms $\epsilon'(dc)f^{-n}$ and $\sigma(dc)/\epsilon_0 2\pi f^k$ are added in (2) and (3) for correcting the low frequency effect due to the electrode polarization capacitance and ionic conductance. The Af^m term is added in (3) for correcting the high frequency effect due to the ITO resistance and lead inductance (Srivastava 2008; Gouda 1992). The other abbreviations are same as given (1). The experimental data have been fitted in these equations and corrected for low and high frequency values (Singh *et al* 2012).

The spontaneous polarization of the pure and the doped system was determined by polarization reversal current method (Gouda 1992; Kondo *et al* 2000; Misra *et al* 2008; Srivastava 2008). The detailed experimental arrangement for this measurement has already been reported by our group (Misra *et al* 2008).

3. Results and discussion

The variation of relative permittivity and dielectric loss on the frequency scale at 36 °C has been plotted in figure 1(a, b), respectively. The usual trend of relative permittivity and dielectric loss on the frequency scale has been recorded for both pure and doped FLC. The magnitude of relative permittivity and dielectric loss for the doped FLC is lowered as compared to the pure FLC. This lowering in the value of relative permittivity and dielectric loss is due to the antiparallel correlation between the dipole moments of the guest nanoparticle and the host FLC (Ghosh *et al* 2011). When we add nanoparticles (NPs) in the FLC sample, the dipole moments of both the materials interacts with each other. The parallel interaction between the dipole moments enhances the net dipole moment of the doped system whereas the anti parallel interaction reduces the net dipole moment. If net dipole moment of the doped system is greater than that of the host material, the parameters like relative permittivity increases and vice versa. In the present investigation, the relative permittivity and dielectric loss of the NPs-doped FLC sample is lesser than the pure FLC sample which indicates that the dipole moment of NPs interacts anti parallel with that of the pure FLC molecules. In addition to this, the dielectric loss for the doped FLC is lowered as compared to the pure FLC. This proves that the NPs provide a more ordered FLC system in which loss factor reduces due to the presence of the NPs. It is clear from figure 1(b) that only Goldstone mode (GM) of relaxation (GM appears due to the phase angle fluctuations of FLC molecules) was observed for both pure and doped FLC.

Figure 2(a) depicts the temperature dependence of the inverse of relative permittivity (IRP) for both the pure and the doped FLC at 133 Hz. The nature of IRP on the

temperature scale for both the pure and the doped FLC is nonmonotonic. For a certain temperature, the IRP possess its least value on the temperature scales. The value of IRP on both sides of this certain temperature increases. This least value of IRP is analogous to the maximum relative permittivity of the undoped and doped FLC system which is related with the maximum charge containing capacity of both the FLC systems. The certain temperature at which FLC systems show maximum charge containing capacity (or strength of the FLC system) is 51 and 57.5 °C for pure and doped-FLC system, respectively. This result also suggests that the NPs-doped FLC system can be used as low charge consumption device for a wider temperature range as compared to the pure FLC system.

In addition to this, the variation of the inverse of the relative permittivity for the doped FLC is steeper than that of the pure FLC. The steeper nature of the inverse relative permittivity temperature curve is due to the presence of the NPs. The presence of NPs causes a rapid change in the liquid crystalline phase near the SmC*–SmA phase transition temperature. It was also observed

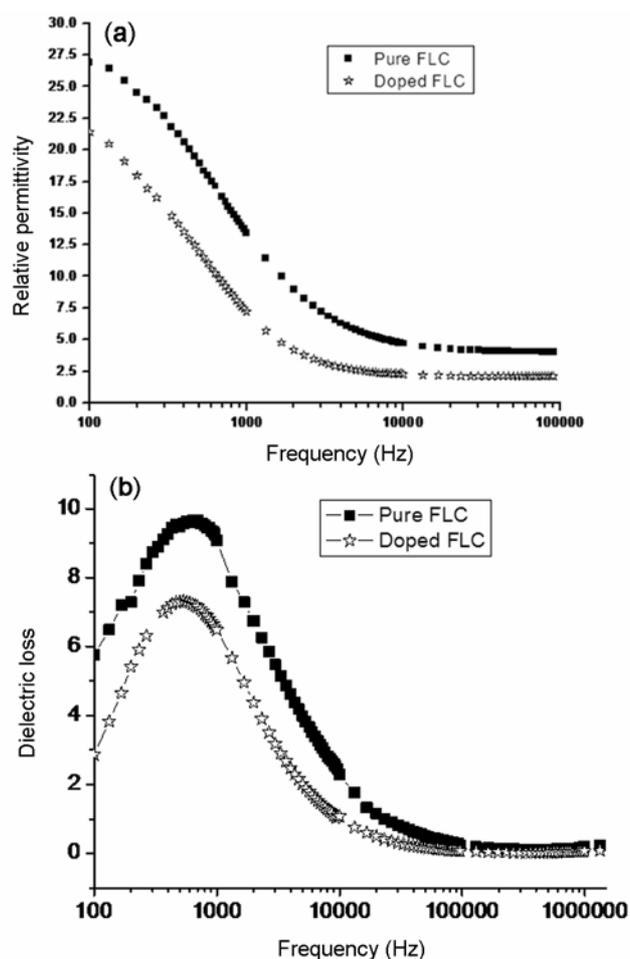


Figure 1. (a) Change in relative permittivity with variation of frequency for pure and doped FLC sample and (b) variation of dielectric loss on frequency scale at 36 °C.

that the value of the relative permittivity for the doped FLC is less than that of the pure FLC. The reduced value of the relative permittivity for the doped FLC is due to the antiparallel correlation between the dipole moments of the guest NPs and host FLCs. This correlation is possible if NPs are ferroelectric in nature. The ferromagnetic nature of these NPs has already been reported by Sharma *et al* (2009). We checked the ferroelectric nature of the NPs by plotting the polarization-electric field hysteresis. The pure NPs do not possess proper ferroelectric hysteresis behaviour. A non-switching ferroelectric hysteresis (Herng *et al* 2011) has been observed for the Cu-ZnO NPs shown in figure 2(b). As NPs are bulky in nature, therefore they required a strong electric field to switch. In the present case, the electric field applied to the NPs was

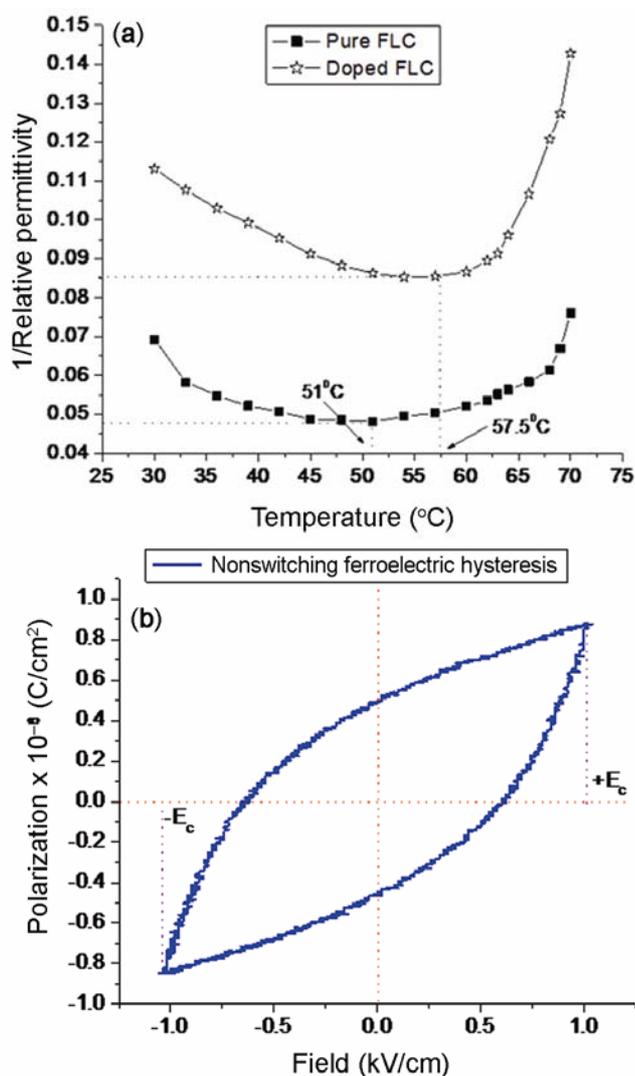


Figure 2. (a) Temperature dependent nature of inverse of relative permittivity for pure and doped-FLC sample at 133 Hz and (b) non-switching polarization-electric field hysteresis of pristine NPs to show ferroelectric nature of NPs.

not sufficient for complete switching which results non-switching ferroelectric hysteresis behaviour of the NPs. We assumed that the antiparallel correlation of the dipole moments holds between the guest NPs and the host FLC due to the ferroelectric nature of the NPs and FLC molecules which results a reduced ferroelectricity in the composite system. Due to this effect, a lowered relative permittivity of the doped FLC has been observed. We can also understand the lowering of relative permittivity for the doped FLC on the basis of the size of NPs in the FLC matrix. As the size of NPs is bigger than that of the FLC molecular dimension, therefore, they perturb the FLC geometry and create hindrance in the motion of FLC molecules. NPs also produce the lateral stress on the FLC molecules which alter the smectic layer separation. This effect degrades the helical structure of FLC molecules in the presence of NPs. Pratibha *et al* (2010) has reported the distortion of smectic layer due to the presence of gold nanoparticle which supports our present assumption. This causes a lowering in the value of the relative permittivity.

The relaxation frequency (f_R) has been plotted against the temperature in figure 3 for both pure and doped FLC sample. This nature of relaxation frequency for the pure FLC sample has already been reported by our group (Misra *et al* 2008). It is found that the variation of relaxation frequency on the temperature scale for the doped FLC is little bit changed as compared to the pure FLC. It increases slightly with the increase in the temperature and achieves its maximum value at 42 °C temperature as compared to the pure FLC and further increment in the temperature causes a decrease in the value of f_R (Kundu *et al* 2004). For the entire SmC* phase (from 30 to 72 °C), the value of relaxation frequency for the NPs doped FLC is lesser than the pure FLC. This decrement in the value of relaxation frequency

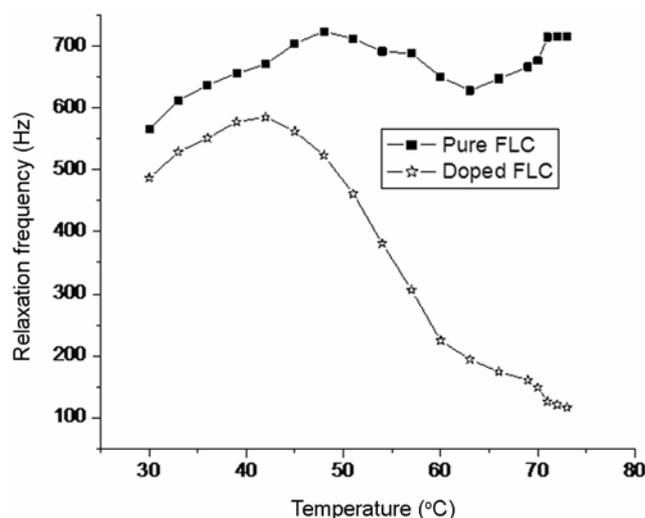


Figure 3. Variation of relaxation frequency with change in temperature for pure and doped FLC sample.

for the doped FLC sample can be explained by the following relation

$$f_R = \frac{K_2 q^2}{2\pi\gamma} \quad (4)$$

where K_2 is twist elastic constant, q the wave vector of helix and γ the rotational viscosity.

With the addition of Cu–ZnO NPs in pure FLC geometry, the wave vector of helix is altered. In addition to this, K_2 and γ are also responsible to produce a change in relaxation frequency. The temperature dependence of the K_2 in the present case is small; therefore, we considered that the effect produced by the twist elastic constant is negligible. The wave vector of helix and rotational viscosity are two main factors by which relaxation frequency gets affected. As the size of NPs is bigger than the FLC molecule, therefore, these NP penetrates few adjacent smectic layers of FLC geometry which results a distortion in the helical structure of FLC molecules. The rotational viscosity of the pure FLC system has been enhanced with the addition of NPs which results a decrease in the value of relaxation frequency. The effect of NP doping on the tilt angle and rotational viscosity of the pure FLC will be discussed later in the paper. In the present case, we are not able to calculate the activation energy with the help of the Arrhenius plot (a plot of log of relaxation frequency vs $1000/T$) because the Arrhenius plot is not monotonic for the entire range of the SmC* phase. The relaxation frequency for the pure and the doped sample is inferior from 30 to 72 °C (the entire range of SmC* phase).

In figure 4, nature of the relaxation strength on the temperature scale is plotted for pure and doped FLC

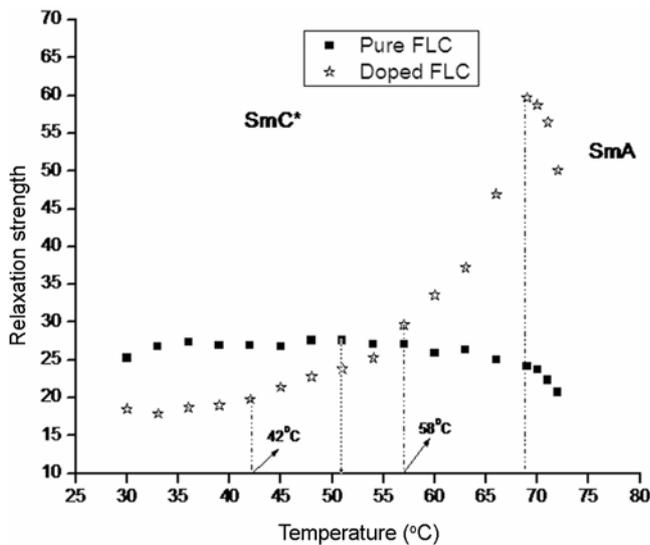


Figure 4. Variation of relaxation strength on temperature scale for pure and doped FLC sample.

samples. For the pure FLC sample, relaxation strength is almost temperature independent and falls at the vicinity of SmC*–SmA* phase transition temperature. A continuous and nonlinear increase of the relaxation strength on the temperature scale has been observed for the doped FLC system in the entire SmC* phase. At the SmC*–SmA* phase transition temperature, relaxation strength shows its maximum value and falls sharply when SmC* phase changes into SmA* phase. This is due to the change in geometry of the phase as it approaches from SmC* to SmA* phase. For the initial temperature interval (30–55 °C), the value of relaxation strength is lowered than that of the pure FLC sample whereas it overcome the relaxation strength value of pure FLC at 58 °C. This dual nature of relaxation strength in SmC* phase for doped FLC system may be explained by the semiconducting property of Cu–ZnO NPs. ZnO is a semiconducting material well known for its wide bandgap and high exciton bonding energy at room temperature. The doping of Cu metal in ZnO changes the orbital of ZnO NPs in such a way that the character of ZnO and Cu–ZnO remains same (Wang *et al* 2011). The breakdown produced by the NPs near 50 °C causes a sharp increase in the relaxation strength value for the doped FLC system.

The change in conductivity (Kremer 2003) on the temperature scale for both pure and doped FLC is depicted in figure 5. The variation of conductivity with temperature for the doped system shows an agreement with the relaxation strength. The conductivity of the pure FLC is almost constant in the SmC* phase and decreases slightly in the vicinity of the SmC*–SmA* phase transition temperature. The behavior of the conductivity of doped FLC is not similar to that of the pure FLC. The conductivity of the doped FLC increases with the

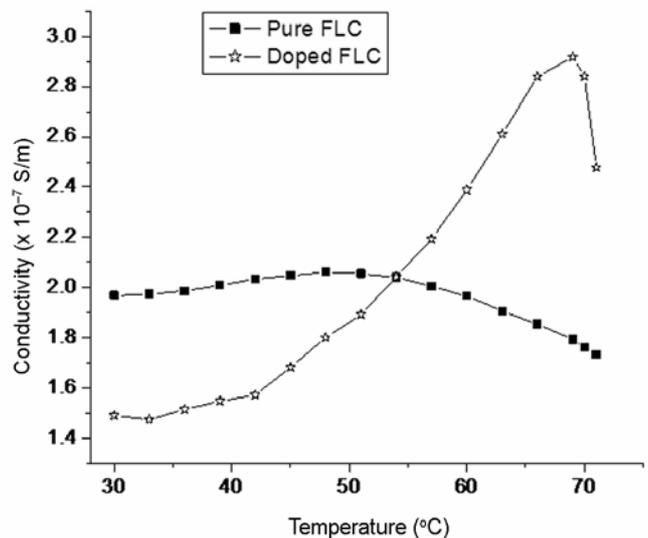


Figure 5. Change in conductivity with temperature for pure and doped-FLC.

increase in temperature and achieve its maximum value near the $\text{SmC}^*-\text{SmA}^*$ phase transition temperature. The value of conductivity of doped FLC sharply decreases at the $\text{SmC}^*-\text{SmA}^*$ phase transition temperature. For the initial temperature interval (30–50 °C), the value of conductivity is lower than that of the pure FLC and becomes equivalent at 55 °C. For higher temperature interval (i.e. 60–72 °C), the conductivity of doped FLC overcomes to that of the pure FLC. This behaviour of conductivity again suggests that the semiconducting nature of Cu–ZnO NPs affects the nature of the doped FLC and conductivity of the doped system follows the semiconducting characteristics. The additional CuO phase, present in NPs, traps the ionic carriers (reduced value of the conductivity in the temperature interval of 30–50 °C) which make an easier path for the noise free and heat resistive electronic devices based on the guest–host type composite system.

Figure 6 shows the variation of macroscopic polarization (P) as a function of the applied bias voltage for both the pure and the doped FLC sample. The linear increase of P with bias field corresponds to the field induced distortion (partial unwinding) of the helix. The spontaneous polarization is the saturation value of the curves in the figure 6. A remarkable change in the value of spontaneous polarization for doped FLC sample has been observed. For the doped FLC system, the value of spontaneous polarization is 2.4 times lesser (see table 1) than that of the pure FLC sample. This decrease in the value of spontaneous polarization is due to the reduction of ferroelectricity in the composite system. The ferroelectric nature of NPs and antiparallel correlation of dipole moments between the guest NPs and host FLC molecules are responsible for the decrement in the net ferroelectricity of

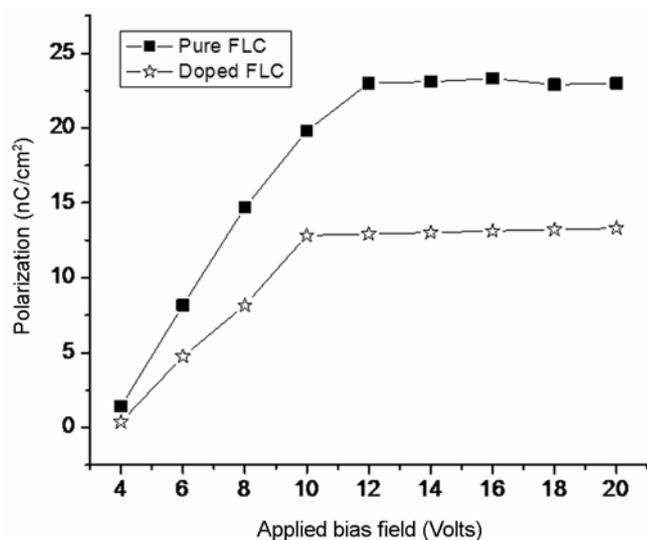


Figure 6. Change in macroscopic polarization (P) as a function of applied bias voltage at room temperature.

the composite system. The presence of NPs in FLC sample also causes the distortion in the layer structure of the FLC molecules. This distortion in the layer structure of the FLC sample may also be a factor for the reduction

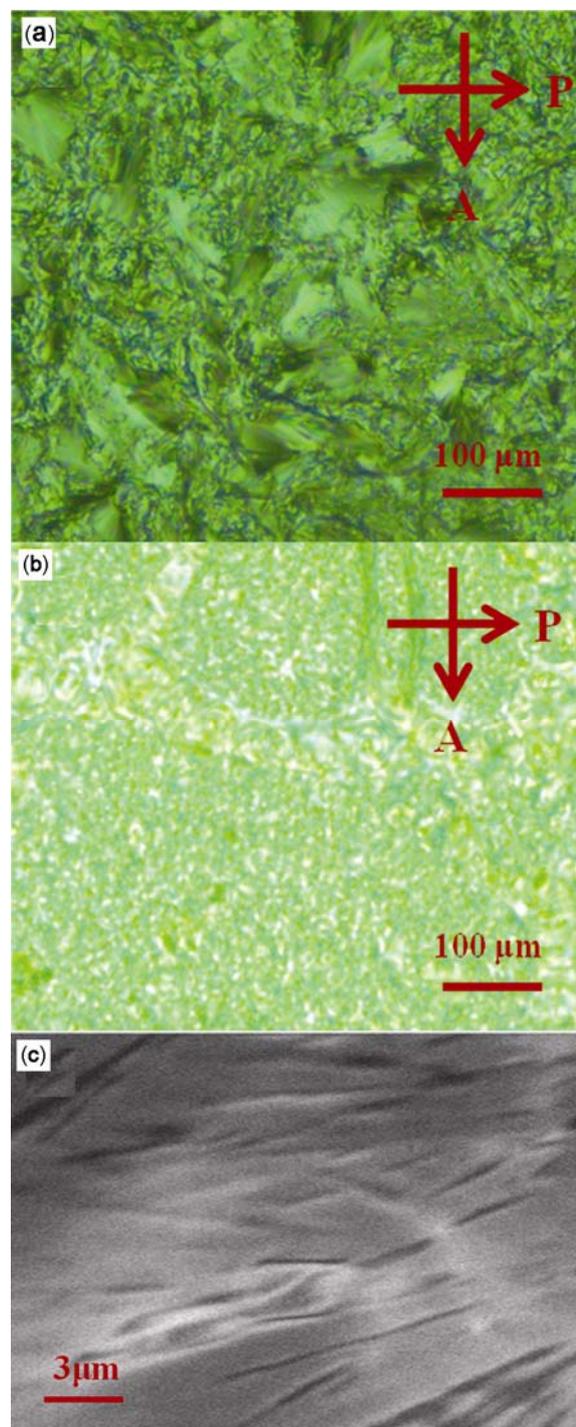


Figure 7. Polarizing optical micrographs (optical texture) under crossed polarizer–analyser condition at room temperature for (a) pure FLC, (b) doped-FLC without using any preferred alignment layer and (c) scanning electron microscopic image (SEM image) of NPs doped-FLC sample.

Table 1. Change in electro-optical parameters of pure FLC and doped-FLC at 36 °C.

E–O parameters	Temperature (°C)	Pure FLC	Doped FLC
Rotational viscosity (m Pa s)	36	45.82	54.99
Spontaneous polarization (P_s) (nC/cm ²)	36	34.01	13.90
Tilt angle (θ) (in degree)	36	27	26.5
P_s/θ	36	1.25	0.52

of the effective polarization of the NPs doped FLC sample. It is also clear from figure that the value of P saturates early on the applied bias field scale for the doped FLC system as compared to the pure FLC. Due to the effective dipole moment of the doped system, the FLC molecules coupled with Cu–ZnO NPs could be switched by the application of lower value of applied bias field; therefore, we found a lowering of the threshold voltage for the doped FLC system.

A detailed comparative study of rotational viscosity, tilt angle and spontaneous polarization at 36 °C for both pure and doped FLC system is shown in table 1. The value of spontaneous polarization and tilt angle for the doped FLC system were found to decrease after the doping of Cu–ZnO NPs while the value of rotational viscosity was increased for the doped FLC system as compared to the pure FLC. This increased value of rotational viscosity for the doped system is mainly responsible for the lowered value of relaxation frequency. The spontaneous polarization-tilt angle ratio for the doped FLC has also been reduced by almost half as compared to the pure FLC which shows that the tilting of the FLC molecules also changes when they interact with the NPs. Figures 7(a and b) shows polarizing optical micrographs of pure and doped FLC sample at room temperature under crossed polarizer–analyser condition without any preferred alignment, whereas the figure 7(c) is SEM image of the NPs doped FLC sample. It is clear from the SEM image that the NPs disperse almost uniformly in the FLC sample. The change in optical texture clearly indicates the change in optical tilt of the FLC molecules due to the dispersion of NPs. In addition to this, the presence of NPs also perturbs the helical structure of the FLC molecules. The presence of NPs also changes the intensity of transmitted light through the doped FLC sample as compared with the pure FLC which is analogous to the change in contrast of the doped FLC sample. The change in the helical structure and thus change in pitch is responsible for the change in colour of the optical texture of the doped FLC sample as compared with the pure FLC sample. When NPs are dispersed in FLC sample, it may cause the aggregation of NPs which affects the performance of the FLC sample; therefore, the dispersion of nanoparticles in the FLC matrix is a difficult task for its application in devices. Thus, any device fabrication based on NP–FLC composite needs a high degree of alignment and dispersion quality.

4. Conclusions

The results of guest–host interaction can be summarized in the following points.

(I) Almost all the physical parameters of ferroelectric liquid crystal material have been altered with the dispersion of Cu–ZnO NPs. As the size of NPs is bigger than the FLC molecules, therefore, it perturbs the FLC geometry as well as hinders the FLC molecular dynamics which results the modification in electrical, polarization and dielectric parameters.

(II) The reduced value of relative permittivity indicates towards the reduction of ferroelectricity in the doped FLC sample which may be due to the antiparallel correlation between the dipole moments of the guest NPs and host FLC. The distortion in the helical structure of the FLC molecules as well as the change in orientational order may be another probable reason for the reduction in the relative permittivity. The result of reduced relative permittivity for the doped-FLC gives a new idea about the LC-based low charge consumption devices under a wider temperature range.

(III) Nonlinear increasing trend of relaxation strength in the entire SmC* phase for doped FLC sample is explained by semiconducting nature of NPs. Semiconducting breakdown and electronegative character of the additional CuO phase exist in the NPs plays an important role to determine the present function of the doped FLC. The behaviour of conductivity of the doped-FLC system is also influenced by the semiconducting nature of the NPs.

(IV) Mixing of Cu–ZnO NPs in pure FLC sample for a definite concentration shows a reduced value of spontaneous polarization which is the result of ferroelectric nature of NPs and antiparallel correlation of dipole moments of FLC molecules and NPs. The distortion in the helical structure of the FLC system and change in orientational order are other factors by which the value of polarization gets affected. The lowering of threshold voltage in case of the doped FLC system is also a meaningful feature of the present study.

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