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Electrical and polarization behaviour of titania nanoparticles doped ferroelectric liquid crystal

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ABSTRACT

The present study focuses on the effect of anatase TiO_2 (titania) nanoparticles (NPs) on conductivity and polarization in a ferroelectric liquid crystal (FLC). Different dielectric and electro-optical measurements have been conducted to explore the charge transportation and polarization mechanism in titania NPs doped FLC system. Doping of titania NPs show reduced dc conductivity of doped LC system attributed to the trapping of free charges by titania NPs at its surface. Polarization has been found to increase at low fields indicating reduction of field screening effect in doped FLC system. Optical response of the doped FLC system has been improved due to decreased intervention of ionic charges particularly at small electric fields. The present study will be helpful in minimizing the slow response problems and the grey level shift in liquid crystal devices which arise due to ionic effects. Copyright © 2015 VBRI Press.

Keywords: Ferroelectric liquid crystals; nanoparticles; conductivity.

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Introduction

Liquid crystal materials are widely used in liquid crystal displays as low power consumption displays. Ferroelectric liquid crystals (FLCs) are most exciting class of liquid crystals due to its bistable behavior and fast response and wide viewing angle **[1-5]**. FLCs show high switching speed at low voltage due to spontaneous polarization (Ps) owing to molecular chirality **[5, 6]**. In the age of modern technology the low power and fast response liquid crystal devices are of great interest of research. Therefore FLCs have great scope in spatial light modulators (SLMs), digital holograms and telecommunication devices due to its very fast switching behaviour **[5]**.

FLCs suffer from the field-induced deformation of molecular helix in deformed-helix FLCs and domain nucleation in surface-stabilized FLCs. Therefore FLCs have some drawbacks as compared to nematic liquid crystals to utilize in liquid crystal displays. The performance of LC devices can be improved by doping of nanoparticles (NPs), quantum dots (QDs) and other nanomaterials as reported by different research groups **[7-13]**. The main motive to dope these materials is to improve the E-O properties of LCs, which have shown some encouraging results such as high Ps, fast response and low-power operation. Mikulko et al. have observed that $BaTiO_3$ NPs significantly improved the response time of FLC mixture besides reducing the spontaneous polarization (Ps) **[14]**. Joshi et al. have reported that the semiconducting ZnO NPs can be used to reduce the threshold voltage of FLCs **[15]**.

In the recent years insulating NPs have also shown a great scope as dopant in the liquid crystals **[16, 17]**. These insulating NPs do not actually interact/weakly interact with LC molecules as in the case of metallic or semiconducting NPs **[14, 15]**. In LC devices, the impurity ions create major problem particularly at low frequencies and high temperature. The presence of these impurities degrade the performance of LC displays such as reduced contrast ratio, grey level shift, high threshold and lead to slower response. Joshi et al. have reported that insulating alumina NPs can reduce the ionic effect in FLCs caused by impurity charges **[17]**. Tang el al. observed the reduction in the ionic concentration in nematic LC by doping anatase TiO_2 (titania) NPs which improve the voltage holding ratio (VHR) of LC system **[18]**.

Most of the work on titania doped LC has been carried out on uniaxial nematic LCs by different research groups. In the present article we report doping of the titania NPs in rather complex LC with biaxiality i.e. FLC, to study its effect on conductivity and polarization of FLC system. The motive of the present work is to reduce the ionic effects in FLC without disturbing its intrinsic properties i.e. spontaneous polarization (Ps) and rotational viscosity. Spontaneous polarization and response time measurement has been done to understand the effect of titania doping on FLC performance. Dielectric measurement has also been carried out to understand the charge storage and charge transportation in pure and doped FLC system which effects the polarization of FLC system.

Experimental

Materials

The FLC material used in the present study is Felix17/100 (Clariant Chemicals Co. Ltd., Germany) with phase sequence Cr–SmC*–SmA–N*–Iso at -20 °C, 72 °C, 82 °C and 95 °C respectively. Anatase TiO_2 NPs (Sigma Aldrich, UK) (20-24nm) have been doped in concentration of 1.0% wt/wt in Felix17/100. FLC and nanoparticles have been used as purchased without any further purification. The composite has been prepared by mixing the titania NPs with Felix 17/100 and homogenized with an ultrasonic mixer to get uniform dispersion.

Preparation of sample holder

We have prepared 5µm thick planar aligned cells of ITO coated glass plate by polyimide rubbing method. The sandwiched 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 was treated with the adhesion promoter and coated with polymer nylon (6/6). After drying the polymer layer, substrates were rubbed unidirectional the antiparallel way. The cell thickness was fixed by placing a mylar spacer (10µm in our case) in between and then sealed with UV sealant. The pure and doped FLC samples have been filled in these cells at isotropic temperature of FLC by mean of capillary action.

Dielectric study

An Impedance analyzer HP4194A has been used to obtain the dielectric behavior of pure and titania NPs doped FLC samples. Dielectric relaxation phenomenon of the pure and doped FLC system has been analyzed using following equation **[19]**.

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

and,

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

Where $\delta\varepsilon'_{GM}$ is the relaxation strength for the Goldstone mode and $\varepsilon'(\infty)$ is high frequency limit of the dielectric permittivity, f is frequency and τ is the relaxation time. Here $\sigma(dc)$ is the dc ionic conductance, ε_o is free space permittivity and f is the frequency while n, m and k are the fitting parameters. The terms $\varepsilon'(dc)f^{-n}$ and $\sigma(dc)/\varepsilon_o 2\pi f^k$ are added in (1) & (2) for correcting the low frequency effect due to the electrode polarization capacitance and ionic conductance. The Af^m term is added in (2) for correcting the high frequency effect due to the ITO resistance and lead inductance. The experimental data have been fitted in these equations and it has been corrected for low and high frequency values.

Electro-optical study

Spontaneous polarization (Ps) measurement has been carried out by the polarization current reversal method at fixed temperature **[1]**. The optical response of the FLC has been studied by square wave method using a 5mW diode laser of wavelength 633nm. The optical response has been taken using photo detector (Instec PD02-L1). The triangular and square wave pulses have been applied using a function generator (Tektronix AFG-3021B). The electrical response of the samples was taken by an oscilloscope (Tektronix TDS-2024C). All the experiments have been carried out in heating cycle using a computer controlled hot stage (Instec HCS-302) with an accuracy of 0.1 ^{0}C.

Results and discussion

The behaviour of relative permittivity and dielectric loss of pure and titania doped FLC system with change in frequency at different temperatures has been illustrated in **Fig. 1**. It can be seen that the value of relative permittivity and dielectric loss has decreased after doping of titania NPs in FLC system. The decrease in the value of dielectric parameters is more prominent at lower frequencies where free ionic charges play an important role in the dielectric medium. It indicate that the doping of titania NPs are reducing the effect of free ionic charges in FLC system. The decrease in dielectric values has also been observed for goldstone mode of titania doped FLC system. This suggest that ionic impurities also affect the phase fluctuation of FLC molecules causing high dielectric values in pure FLC system which get decreased after doping titania NPs. Both of these results indicate the alteration of polarization and charge transportation behaviour in FLC medium after doping titania NPs.

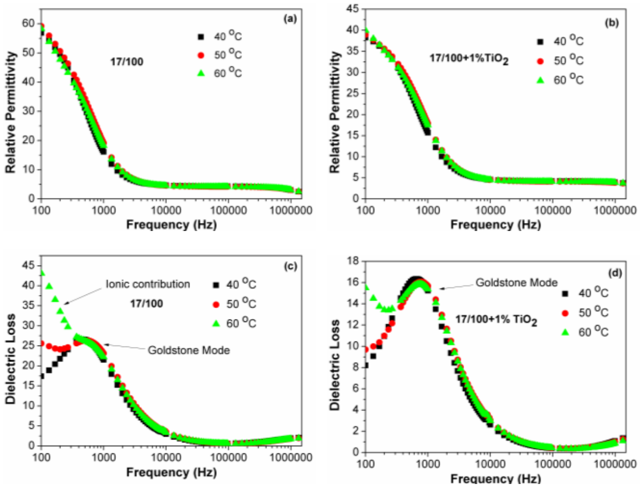

Fig. 1. Measured (a and b) relative permittivity and (c and d) dielectric loss for 17/100 and titania NPs doped FLC respectively with variation of frequency at different temperatures.

To explore the effect of titania NPs on charge transportation behaviour of FLC system, we have calculated the dc conductivity of the pure and doped FLC systems using equation 2 and plotted in **Fig. 2**. DC conductivity is caused by the movement of free ionic charges present in LC medium under applied electric field.

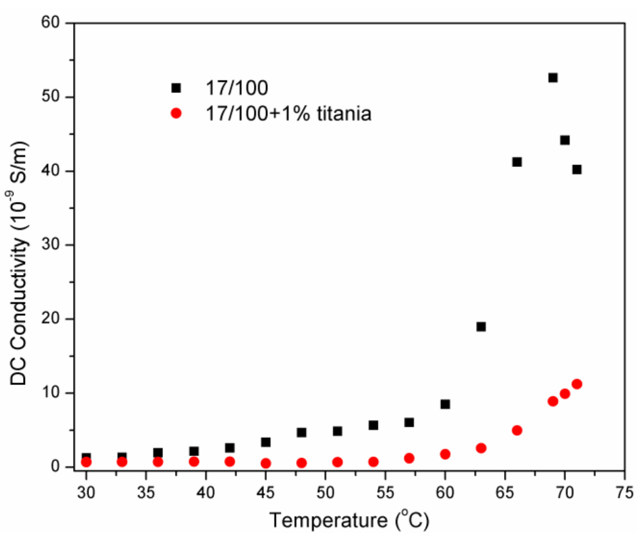

Fig. 2. DC conductivity of pure and titania NPs doped FLC as a function of temperature.

Fig. 2 shows that conductivity has significantly decreased for the doped FLC system as compared to pure FLC. This decrease is more prominent at high temperatures where ionic charges have sufficient energy to move between electrodes. This indicates that the titania NPs are restricting the migration of impurity charge carriers in LC medium. Anatase titania NPs are insulating in nature and do not contribute to the conductivity of the doped FLC system. In the presence of electric field applied across the doped LC cell, the titania NPs get polarized with opposite charges on both sides of NPs. In the presence of electric field the free charge carriers transporting between electrodes get trapped by these opposite charges on NPs. After trapping, the effective transported ion concentration reduces at lower frequencies and results in decrease in the conductivity for the doped FLC system **[16]**. Hence a decrease in dielectric values have been observed due to its strong dependence on transported ion concentration at low frequencies.

In the pure FLC system, the free ions get easily adsorb at both the alignment layers and create an undesired field-screening effect at the electrode surface. This screening effect allows the LC molecules to experience a relatively low voltage within the cell as compared to applied voltage. Therefore the presence of these impurity ionic charges reduces the polarization of FLC molecules due to the screening of electric field. **Fig. 3** shows the variation of spontaneous polarization (Ps) with change in applied electric field at 10 Hz frequency at 36 ^{o}C for pure and titania doped FLC system. It is observed that the value of Ps has been increased for the titania doped FLC system. This increase in Ps value is clearly noticeable at low electric field which becomes insignificant after a critical field value. The high value of Ps in doped FLC system indicates that titania NPs are suppressing the screening effect by trapping of free charges as discussed above. Hence the polarization component of FLC molecules can align more preferably along the field direction resulting in high Ps value. However the change in Ps saturation value is not much effective which confirms that the change in Ps value observed is only due to reduction of screening effect which has no effect on Ps saturation value. It also verify that the titania NPs are interacting weakly with FLC molecules causing slight change in Ps saturation value.

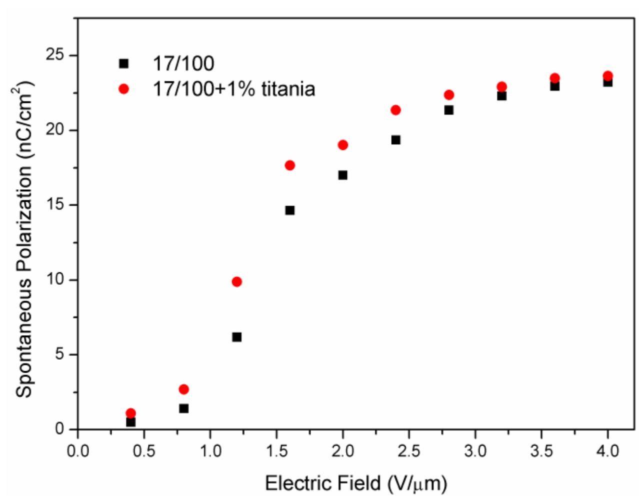

Fig. 3. Variation of spontaneous polarization of pure and titania NPs doped FLC as a function of applied electric field at 36 °C.

Fig. 4 illustrates the variation of response time with the change in applied electric field at 10 Hz at 36 ^{o}C. It can be observed that the response time for doped FLC has been improved by 4ms at low voltage. However a slight improvement in response time is observed at high voltage. This trend of response time with electric field is directly related to the behaviour of spontaneous polarization of doped FLC system. The high Ps values at low field makes the doped FLC system faster as compared to pure FLC system. After saturation the improvement in response time become very small due to slight change in Ps value. Therefore the doping of titania leads the small deviation of response time of FLC system with change in voltage particularly at low voltages. This suggests that titania NPs are excellent constituent to improve the switching behaviour of LC devices at low voltages.

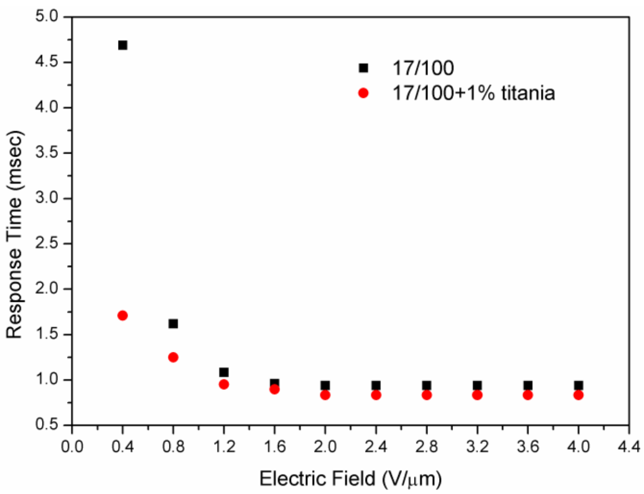

Fig. 4. Change in response time of pure and titania NPs doped FLC as a function of applied electric field at 36 ^{o}C.

Fig. 5 shows the behaviour of rotational viscosity (γ_d) with change in electric field for pure and doped FLC system at 36 ^{o}C.

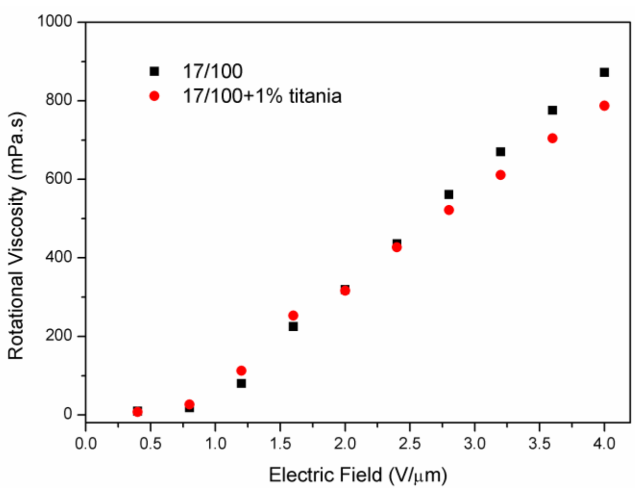

Fig. 5. Behaviour of rotational viscosity of pure and titania NPs doped FLC as a function of applied electric field at 36 ^{o}C.

The rotational viscosity of the pure and doped FLC system has been calculated using following equation **[13]**.

$$\gamma_d = \tau . P_S . E \qquad (3)$$

Here τ is response time and E is the applied electric field. The rotational viscosity has not been changed significantly for titania doped FLC system at low fields and therefore the improvement observed in response time is only due to the increase of Ps values. The small deviation of rotational viscosity of doped system from its value for pure FLC system indicated that titania NPs are well dispersed in FLC matrix and is not disturbing the FLC movement under external electric field. The slight decrease in rotational viscosity at high field values for titania doped FLC system suggest the reduced ionic interference in movement of polarized FLC molecules. Hence a slight improvement is observed in response time at higher electric field values.

Conclusion

The present study report the effect of titania NPs on the dielectric and electro-optical properties of ferroelectric liquid crystal. The study shows that the conductivity of doped FLC system has been decreased due to the reduction in the effective transported ion concentration attributed to trapping of free charges by polarized titania NPs at its surface. This trapping causes the less adsorption of free charges at electrode surface and therefore results as suppression of the field screening effect. Hence increase in polarization values has been observed at low field values which get saturated at high fields as in pristine FLC. The response time study with applied electric field shows that the titania NPs have reduced the response time to very low values at small electric fields. Since the change in saturation polarization and rotational viscosity is very small for titania doped FLC system, the present studied system can be useful for development in LC devices with faster response of different grayscale at small voltages without disturbing the intrinsic properties of pure FLC system.

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Reference

1. Lagerwall S.T. *Ferroelectric and antiferroelectric liquid crystals* New York, Wiley-VCH, **1999**.
2. Clark, N.A.; Lagerwall, S.T. *Appl. Phys. Lett.* **1980**, *36*, 899. **DOI:** 10.1063/1.91359
3. Prakash, J.; Mehta, D.S.; Choudhary, A.; Kaur, S.; Rathore, V.; Biradar, A.M. *J. Appl. Phys.* **2008**, *103*, 044103. **DOI:** 10.1063/1.2838488
4. Akaogi, J.; Koizumi, Y.; Ono, M.; Furue, H. *Mol. Cryst. Liq. Cryst.* **2014**, *596*, 106. **DOI:** 10.1080/15421406.2014.918333
5. Srivastava, A.K.; Pozhidaev, E.P.; Chigrinov, V.G.; Manohar, R. *Appl. Phys. Lett.* **2011,** *99*, 201106. **DOI:** 10.1063/1.3661170
6. Datta, T.; Kundu, S.; Nayek, P.; Majumder, T.P.; Roy, S.K.; Haase, W. *Cur. Appl. Phys.* **2009**, *9*, 605. **DOI:** 10.1016/j.cap.2008.05.009
7. Singh, D.P.; Gupta, S.K.; Pandey, K.K.; Yadav, S.P.; Varia, M.C.; Manohar, R. *J. Non Cryst. Solids* **2013**, *363*, 178. **DOI:** 10.1016/j.jnoncrysol.2012.12.029
8. Singh, D.P.; Gupta, S.K.; Pandey, A.C.; Manohar, R *Adv. Mat Lett.* **2013**, *4*, 556. **DOI:** 10.5185/amlett.2012.11463
9. Gupta, S.K.; Singh, D.P.; Tripathi, P.K.; Manohar, R.; Varia, M.C.; Sagar, L.K.; Kumar, S. *Liq. Cryst.* **2013**, *40*, 528. **DOI:** 10.1080/02678292.2012.761735
10. Kaur, S.; Singh, S.P.; Biradar, A.M.; Choudhary, A; Sreenivas, K. *Appl. Phys. Lett.* **2007**, *91*, 023120. **DOI:** 10.1063/1.2756136
11. Reznikov, Y.; Buchnev, O.; Tereshchenko, O.; Reshetnyak, V.; Glushchenko, A.; West, J. *Appl. Phys. Lett.* **2003**, *82*, 1917. **DOI:** 10.1063/1.1560871

12. Gupta, S.K.; Kumar, A.; Srivastava, A.K.; Manohar, R. *J. Non Cryst. Solids* **2011**, *357*, 1822.
DOI: 10.1016/j.jnoncrysol.2011.01.034
13. Gupta, S.K.; Singh, D.P.; Manohar, R. *Curr. Appl. Phys.* **2013**, *13*, 684.
DOI: 10.1016/j.cap.2012.11.006
14. Mikulko, A.; Arora, P.; Glushchenko, A.; Lapanik, A.; Haase, W. *Euro Phys. Lett.* **2009**, *87*, 27009.
DOI: 10.1209/0295-5075/87/27009
15. Joshi, T.; Kumar, A.; Prakash, J.; Biradar, A.M.; Hasse, W. *Appl. Phys. Lett.* **2009**, *96*, 253109.
DOI: 10.1063/1.3455325
16. Chen, W.T.; Chen, P.S.; Chao, C.Y. *Jap. J. Appl. Phys.* **2009**, *48*, 015006.
DOI: 10.1143/JJAP.48.015006
17. Joshi, T.; Prakash, J.; Kumar, A.; Gangwar, J.; Srivastava, A.K.; Singh, S.; Biradar, A.M. *J. Phys. D: Appl. Phys.* **2011**, *44*, 315404.
DOI: 10.1088/0022-3727/44/31/315404
18. Tang, C.Y.; Huang, S.M.; Lee, W. *J Phys D: Appl. Phys.* **2011**, *44*, 355102.
DOI: 10.1088/0022-3727/44/35/355102
19. Cole, K.S.; Cole, R.H. *J. Chem. and Phys.* **1941**, *9*, 341.
DOI: 10.1063/1.1750906