

Dielectric, electro-optical and spectroscopic properties of silver doped zinc oxide-ferroelectric liquid crystal composite system

Kaushlendra Agrahari^{1*}, Sanjeev Kumar Trivedi¹, Ram Raseele Awasthi¹, Vivek Kumar Nautiyal², Rakesh Kumar Sonker³, Rajiv Manohar⁴

¹Faculty of Engineering and Technology, Khwaja Moinuddin Chisthi Language University, Lucknow, India.

²Department of Physics, Chaudhary Charan Singh University, Meerut, India.

³Department of Physics, Acharya Narendra Dev College, University of Delhi, Delhi, India.

⁴Department of Physics, University of Lucknow, Lucknow, India.

*Corresponding author: agr.kaushal@gmail.com

Received 1 February 2023; Accepted 20 April 2023; Published online 26 April 2023

Abstract:

In the present study, silver doped zinc oxide nanoparticles (NPs) have been added in the pristine ferroelectric liquid crystal (FLC). The dielectric, electro-optical and spectroscopic properties were investigated of the pristine FLC and FLC-NPs composite system. The dispersion of NPs into the pristine FLC material strongly influences the various properties of the composite system. Due to dispersion of NPs, a rapid increment in the dielectric permittivity and faster switching was observed for the FLC-NPs composite system. Absorbance of the UV light got diminished in the presence of silver doped zinc oxide NPs. Photoluminescence emission of the pristine FLC material has been quenched after the addition of NPs and a red shift was also detected. The possible applications of this investigation have been suggested in the letter.

Keywords: Composite system; Dielectric permittivity; Absorbance; Photoluminescence

1. Introduction

Liquid Crystals (LCs) are partially ordered, anisotropic fluids, which are thermodynamically located between the crystalline solid and isotropic liquid. They exhibit orientational or low dimensional positional order of their long molecular axis which results into anisotropic physical properties, such as refractive index, dielectric permittivity, elastic constant, or electric conductivity. One of the major applications of LCs is displays and photonic devices. Their operation is based on electro-optical effects in LCs, with which their dielectric and conductive properties are closely coupled [1–3]. Among the LC materials, Ferroelectric LCs (FLCs) have gained intense attention of researchers in recent years due to their remarkable properties i.e. fast switching, low threshold voltage, improved optical contrast, memory effect, wide viewing angle characteristics, etc. [4–6]. FLC materials exhibit the ferroelectric properties due to the low symmetry of chiral smectic C (SmC*) phases [7].

At the same time, ground-breaking developments have been made in the fields of nanotechnology and nanoscience, which led to the birth of a series of novel nanomaterials [8–11]. These nanostructured materials, have achieved remarkable academic and industrial attention due to their size-dependent electronic, optical, magnetic, and chemical properties and have been widely used in almost every field of science from energy, optics, computing, biosciences and medical sciences [12–14]. With the continuous advancement of technology, enrichment in the basic properties of available LCs is exceedingly required. Dispersion of LC compounds with different nanoparticles (NPs) is the most popular approach adopted to improve the physical and electro-optical properties of LC devices. Certainly, when the nanomaterials encounter liquid crystals, a highly interesting and unique synergy will be observed, leading to an abundance of exclusively new and potential applications [15–19]. Various different types of NPs such as organic, semiconducting, ferromagnetic, metallic, and insulating are being

used to produce technologically improved electro-optic devices [20–24]. As a dopant for LCs, metal oxide NPs are interesting materials with intriguing properties and have received immense interest in the scientific community owing to their exclusive physical and chemical properties resulting from their limited size and a high density of edge surface sites [25–27]. Singh et al. have found the occurrence of photoluminescence in FLC by doping it with Cu-ZnO NPs [28]. Sharma et al. have reported an increase in the contrast ratio, birefringence and band gap after the dispersion of ZnO NPs in NLCs [29]. Incorporation of Au/SnO₂ Nanocrystals (NCs) enhances the optical tilt angle, PL intensity and reduces saturation voltage of a FLC mixture as observed by Doke et al. [30]. This modification in electrical and optical properties was attributed to change in dynamics of FLC molecules in presence of the NCs. Ayeb et al. have found that doping of pure and copper-incorporated TiO₂ NPs in NLC 5CB decreases the dielectric anisotropy, response time and splay elastic constant [31].

Zinc oxide (ZnO) is a wide and direct bandgap (about 3.37 eV at room temperature) semiconductor with high exciton binding energy (60 meV at room temperature), and unique optical and luminescence properties [32–34]. Doping in ZnO with selective metals could amend its luminescent characteristics and accelerate the course of their practical applications [35–37]. The diffusion of copper or silver into ZnO can induce variations in its lattice structure and correspondingly, in the interrelated physical properties. Therefore, in this letter, we report the dielectric, electro-optical and spectroscopic properties of pristine FLC and silver doped zinc oxide nanoparticles-FLC composite system.

2. Experimental Details

The host FLC material used in the present study is Felix 16/100 (Clariant Chemicals Co. Ltd.) and the phase transition of the sample is Cr, SmC*, SmA, N*, and Iso at -20°C, 72°C, 82°C, and 90-94°C. The nanocrystalline powder of Ag-doped ZnO was synthesized by chemical

co-precipitation method [38]. For making the composite, first we dissolve the optimized concentration (0.5 wt.%) of NPs into the Chloroform and then take the desired amount of solution to disperse in the host FLC material. After the dispersion, composite was homogenized with an ultrasonic mixer for 5 h at 100 °C temperature. The fabrication of LC cells has already been described in our previous work [24]. The pristine FLC and composite was filled in the assembled cells by capillary method at a temperature higher than the isotropic temperature of the FLC material.

3. Results and discussion

The frequency dependence of the dielectric permittivity for the pristine FLC and FLC-NPs composite system at room temperature has been shown in figure 1. The addition of silver doped zinc oxide NPs in the pristine FLC causes an increase in the value of dielectric permittivity which is related to the strength of the helical geometry of the FLC molecules. The enhancement in effective dipole moment (increase in net polarization) of the composite system on the addition of NPs increases the dielectric permittivity. Notably NPs prepared by hydrothermal method have more uniform size and possess only some surface defects. The higher interaction of the FLC molecules with surface defects increases the net dielectric permittivity of FLC-NPs composite system.

Fast switching time is one of the basic requirements for display applications and was determined using polarization reversal technique by applying a square wave of appropriate frequency. The voltage dependence of response time (τ) for pristine FLC and FLC-NPs composite system indicates that τ decreases with an increase in voltage as shown in figure 2. It is evident from the figure that the switching time of FLC molecules gets faster in the presence of NPs. The probable reason for the faster switching process is the lower value of rotational viscosity which offers a decreased viscous torque. Therefore, the faster response of composite system is attributed to the reduced viscous torque.

Figure 3 represents the absorbance in arbitrary unit on the

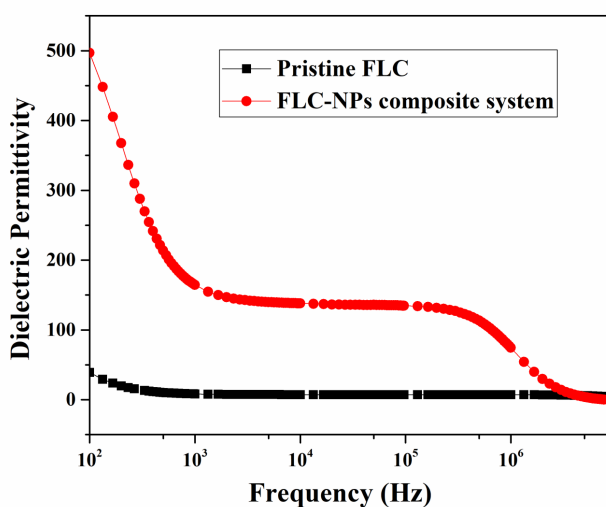


Figure 1. Variation of dielectric permittivity with frequency for pristine FLC and FLC-NPs composite system.

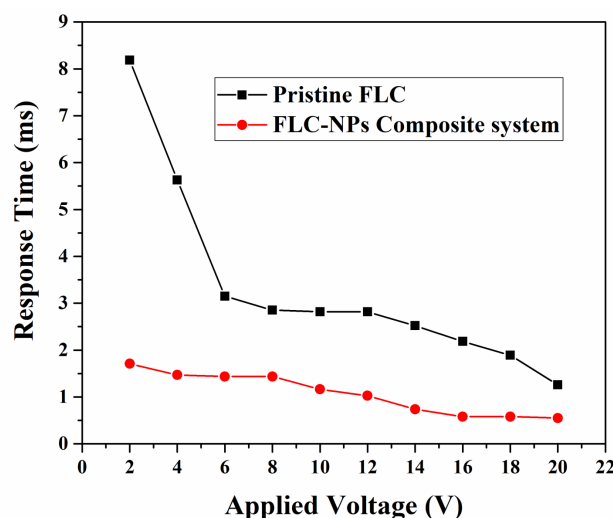


Figure 2. Variation of response time with applied voltage for pristine FLC and FLC-NPs composite system.

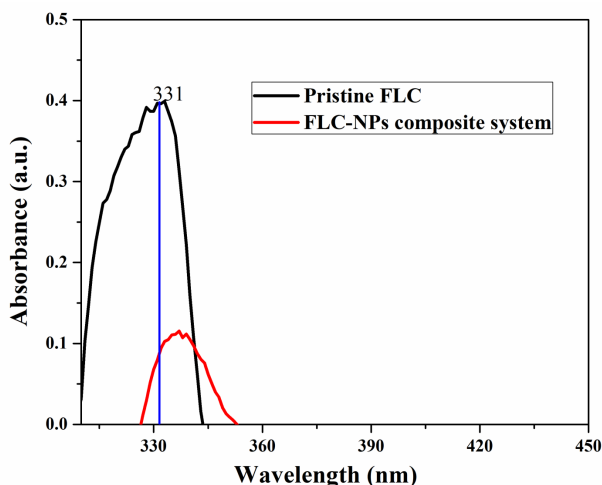


Figure 3. Variation of absorbance with wavelength for pristine FLC and FLC-NPs composite system.

wavelength scale (nm) for the pristine FLC and FLC-NPs composite system. The UV-visible absorption study was performed at room temperature to examine the absorbance of white light by the pristine FLC and FLC-NPs composite. It is noted from the graph that pristine FLC and FLC-NPs composite absorb a broad regime of UV light between 310 and 360 nm. The absorbance of the FLC-NPs composite is lower than the pristine FLC and a major absorbance peak was found at 331 nm for the pristine FLC. This absorption peak may be attributed to the $\pi - \pi^*$ transitions which are usually observed in all the thermotropic LCs. The perturbation in the geometry of the FLC molecules by the dopant nanoparticles is accountable for the reduction in the absorbance of FLC-NPs composite. Another reason behind the decrease in the absorbance might be due to the scattering centers formed in the presence of NPs.

The variation of photoluminescence (PL) intensity at wavelength scale for the pure FLC and composite system has been depicted in figure 4. The absorbance wavelength was

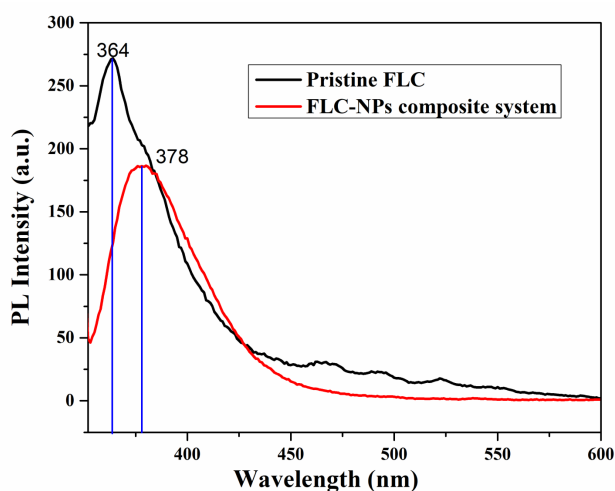


Figure 4. Variation of PL intensity with wavelength for pristine FLC and FLC-NPs composite system.

selected as excitation wavelength for the PL measurements. From the figure, it is obvious that the PL intensity of the pristine FLC material has been decreased after the addition of NPs which may be due to absorption of major portion of PL emission of the FLC material by the NPs. Besides the reduction in PL intensity, a slight red shift has also been observed in the PL emission because NPs are acting as PL quencher in the pristine FLC. The PL emission peak was centered at 364 nm and 378 nm for the pristine FLC and FLC-NPs composite system, respectively.

4. Conclusions

In summary, Ag-doped ZnO nanoparticles were dispersed in the pristine FLC Felix 16/100 and the dielectric, optical and electro-optical properties were investigated for the composite system. Due to the alignment capability of NPs, the optical micrograph of composite system was found to be altered. The relative permittivity of composite system was found to be increased as the dipole moment of NPs supported the dipole moment of pristine FLC and effective dipole moment was increased. The switching time gets faster for the composite system owing to reduced viscous torque and rotational viscosity. Absorbance and photoluminescence have been found to be decreased for the composite system. The observed outcome of the present study may be applied to faster switching displays and charge storing devices.

Conflict of interest statement:

The authors declare that they have no conflict of interest.

References

- [1] D. Demus, J. W. Goodby, G. W. Gray, and H. W. Spiess. *Handbook of Liquid Crystals Set*. John Wiley, 1 edition.
- [2] T. Kato, N. Mizoshita, and K. Kishimoto. "Functional Liquid-Crystalline Assemblies: Self-Organized Soft Materials". *Angew. Chem. Int. Ed.*, **45**:38, 2005.
- [3] J. P. F. Lagerwall and G. Scalia. "A new era for liquid crystal research: Applications of liquid crystals in soft matter nano-, bio- and microtechnology". *Current Appl. Phys.*, **12**:1387, 2012.
- [4] F. Castles, S. M. Morris, D. J. Gardiner, Q. M. Malik, and H. J. Coles. "Ultra-fast-switching flexoelectric liquid-crystal display with high contrast". *J. Soc. Inf. Disp.*, **18**:128, 2010.
- [5] A. Andreev, T. Andreeva, I. Kompanets, and N. Zalyapin. "Helix-free ferroelectric liquid crystals: electro optics and possible applications". *Appl. Sci.*, **8**:2429, 2018.
- [6] Q. Guo, K. Yan, V. Chigrino, H. Zhao, and M. Tribelsky. "Ferroelectric Liquid Crystals: Physics and Applications". *Cryst.*, **9**:470, 2019.
- [7] R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller. "Ferroelectric liquid crystals". *J. Phys. Lett.*, **36**:69, 1975.

- [8] T. Hegmann, H. Qi, V. M. Marx, and J. Inorg. “Nanoparticles in liquid crystals: synthesis, self-assembly, defect formation and potential applications”. *Organomet. Polym. Mater.*, **17**:483, 2007.
- [9] A. Mnyusiwalla, A. S. Daar, and P. A. Singer. “Mind the gap: science and ethics in nanotechnology”. *Nanotech.*, **14**:R9, 2003.
- [10] C. Burda, X. Chen, R. Narayanan, and M. A. El-Sayed. “Chemistry and properties of nanocrystals of different shapes”. *Chem. Rev.*, **105**:1025, 2005.
- [11] J. Liu, H. He, D. Xiao, S. Yin, W. Ji, S. Jiang, D. Luo, B. Wang, and Y. Liu. “Recent advances of plasmonic nanoparticles and their applications”. *Mater.*, **11**:1833, 2018.
- [12] M. W. Chik, Z. Hussain, M. Zulkefeli, M. Tripathy, S. Kumar, A. B. A. Majeed, and K. Byrappa. “Polymer-wrapped single-walled carbon nanotubes: a transformation toward better applications in healthcare”. *Drug Deliv. Trans. Res.*, **9**:578, 2019.
- [13] O. C. Farokhzad and R. Langer. “Impact of nanotechnology on drug delivery”. *ACS Nano*, **3**:16, 2009.
- [14] F. S. Kim, G. Ren, and S. A. Jenekhe. “One-dimensional nanostructures of π -conjugated molecular systems: assembly, properties, and applications from photovoltaics, sensors, and nanophotonics to nanoelectronics”. *Chem. Mater.*, **23**:682, 2011.
- [15] J. W. Goodby, I. M. Saez, S. J. Cowling, V. Görtz, M. Draper, A. W. Hall, S. Sia, G. Cosquer, S. E. Lee, and E. P. Raynes. “Transmission and amplification of information and properties in nanostructured liquid crystals”. *Angew. Chem. Int. Ed.*, **47**:2754, 2008.
- [16] H. Qi and T. Hegmann. “Impact of nanoscale particles and carbon nanotubes on current and future generations of liquid crystal displays”. *J. Mater. Chem.*, **18**:3288, 2008.
- [17] C. Blanc, D. Coursault, and E. Lacaze. “Ordering nano and microparticles assemblies with liquid crystals”. *Liq. Cryst. Rev.*, **1**:83, 2013.
- [18] U. Shivakumar, J. Mirzaei, X. Feng, A. Sharma, P. Moreira, and T. Hegmann. “Nanoparticles: complex and multifaceted additives for liquid crystals”. *Liq. Cryst.*, **38**:1495, 2011.
- [19] I. Dierking. “Nanomaterials in liquid crystals”. *Nanomat.*, **8**:453, 2018.
- [20] P. Selvaraj, K. Subramani, B. Srinivasan, C. J. Hsu, and C. Y. Huang. “Electro-optical effects of organic N-benzyl-2-methyl-4-nitroaniline dispersion in nematic liquid crystals”. *Sci. Reports*, **10**:14273, 2020.
- [21] K. Agrahari, G. Pathak, R. Katiyar, G. Yadav, T. Vimal, S. Pandey, D. P. Singh, S. K. Gupta, and R. Manohar. “response and relaxation behaviour of ferroelectric liquid crystal”. *Mol. Cryst. Liq. Cryst.*, **652**:195, 2017.
- [22] T. Vimal, S. Pandey, S. K. Gupta, D. P. Singh, K. Agrahari, G. Pathak, S. Kumar, P. K. Tripathi, and R. Manohar. “Manifestation of strong magnetoelectric dipolar coupling in ferromagnetic nanoparticles FLC composite: evaluation of time dependent memory effect”. *Liq. Cryst.*, **45**:687, 2018.
- [23] S. K. Prasad, M. V. Kumar, T. Shilpa, and C. V. Yelamagad. “Enhancement of electrical conductivity, dielectric anisotropy and director relaxation frequency in composites of gold nanoparticle and a weakly polar nematic liquid crystal”. *RSC Adv.*, **4**:4453, 2014.
- [24] K. Agrahari, G. Pathak, T. Vimal, K. Kurp, A. Srivastava, and R. Manohar. “Dielectric and spectroscopic study of nano-sized diamond dispersed ferroelectric liquid crystal”. *J. Mol. Liq.*, **264**:510, 2018.
- [25] H.H. Kung. *Transition Metal Oxides*, volume 45. Elsevier, Amsterdam.
- [26] V.E. Henrich and P.A. Cox. *The Surface Science of Metal Oxides*. Cambridge University Press, 1 edition.
- [27] J. A. Rodriguez and M. F. Garcia. *Synthesis, Properties, and Applications of Oxide Nanomaterials*. John Wiley, 1 edition.
- [28] D. P. Singh, S. K. Gupta, A. Srivastava, and R. Manohar. “The phenomenon of induced photoluminescence in ferroelectric mesophase”. *J. Lumin.*, **139**:60, 2013.
- [29] A. Sharma, P. Malik, R. Dhar, and P. Kumar. “Improvement in electrooptical and dielectric characteristics of ZnO nanoparticles dispersed in a nematic liquid crystal mixture”. *Bull. Mater. Sci.*, **42**:215, 2019.
- [30] S. Doke, P. Ganguly, and S. Mahamuni. “Dielectric and electrooptical studies of Au-SnO₂ core/shell nanocrystals incorporated ferroelectric liquid crystal”. *Liq. Cryst.*, **47**:2305, 2020.
- [31] H. Ayeb, S. Alaya, M. Derbali, L. Samet, J. Bennaceur, F. Jomni, and T. Soltani. “Electrooptical and textural studies of 5CB nematic liquid crystal doped with TiO₂ and Cu-TiO₂ nanoparticle”. *Liq. Cryst.*, **48**:223, 2021.
- [32] I. A. Ezenwa. “Synthesis and optical characterization of zinc oxide thin film”. *Res. J. Chem. Sci.*, **2**:26, 2012.
- [33] Z. L. Wang. “Zinc oxide nanostructures: growth, properties and applications”. *J. Phys. Condens. Matter.*, **16**:R829, 2004.
- [34] M. Suche, S. Christoulakis, K. Moschovis, N. Katsarakis, and G. Kiriakidis. “ZnO transparent thin films for gas sensor applications”. *Thin Sol. Films*, **515**:551, 2006.
- [35] M. Ghosh and A. K. Raychaudhuri. “Structural and optical properties of Zn1MgO nanocrystals obtained by low temperature method”. *J. Appl. Phys.*, **100**:034315, 2006.

- [36] X. B. Wang, C. Song, K. W. Geng, F. Zeng, and F. Pan. "Photoluminescence and Raman scattering of Cu-doped ZnO films prepared by magnetron sputtering". *Appl. Surf. Sci.*, **253**:6905, 2007.
- [37] B. P. Zhang, N. T. Binh, Y. Segawa, and K. Wakatsuki. "Optical properties of ZnO rods formed by metalorganic chemical vapor deposition". *Appl. Phys. Lett.*, **83**:1635, 2003.
- [38] R. Singh, D.P. Singh, P. Gupta, P. Jain, Sanchita, T. Mishra, A. Kumar, S.S. Dhawan, and P.A. Shirke. "Nanoparticles alter the withanolide biosynthesis and carbohydrate metabolism in *Withania somnifera* (Dunal)". *Indus. Crops Prod.*, **127**:94, 2019.