Low power operation of ferroelectric liquid crystal system dispersed with zinc oxide nanoparticles

T. Joshi,[1] A. Kumar,[1] J. Prakash,[2] and A. M. Biradar[1,a]

[1]*Liquid Crystal Group, National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi 110012, India*
[2]*Instrument Design Development Center, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India*

We present the results based on electro-optical properties of zinc oxide nanoparticles (ZnO-NPs) doped ferroelectric liquid crystal (FLC). It is observed that ZnO-NPs-FLC system has low operating voltage and improved optical contrast. The lowering in operating voltage and improvement in optical contrast has been attributed to larger dipole moment of ZnO-NPs that enhances the anchoring of FLC molecules around ZnO-NPs. The effect of ZnO-NPs on the material parameters of FLC has also been observed. These studies will certainly provide a tool to understand the interaction of ZnO-NPs with FLC molecules that can be utilized to fabricate low threshold electro-optic devices. © *2010 American Institute of Physics.* [doi:10.1063/1.3455325]

The doping of nanostructure materials has resulted in the form of improved properties of various systems based on electronics, optics, and catalysis to biomedical sciences.[1,2] It is found that the doping of nanoparticles (NPs) has improved the electro-optical characteristics of various display devices.[3–5] Among all kinds of display devices, liquid crystal displays (LCDs) have attracted a great deal of interest of researchers around the world due to their promising and unique electro-optical features.[6,7] The addition of gold NPs in ferroelectric liquid crystals (FLCs) has been reported earlier in order to observe low threshold and nonvolatile memory effect.[8,9] Zhang *et al.*[10] observed the lowering of threshold voltage of CdS NPs doped 4-pentyl-4'-cyanobiphenyl (5CB) twisted nematic cells by 25%. The low power operation of vertically aligned LC by doping a minute amount of anatase TiO_2-NPs have been observed by Lee *et al.*[11]

Zinc oxide (ZnO) has been employed in a variety of devices such as gas sensors, solar cells, luminescent materials, and transparent conducting coatings due to its wide range of optical and electrical properties.[12–14] Huang *et al.*[15] explored the importance of addition of ZnO nanocrystals into the surface stabilized FLCs (SSFLCs) by probing the molecular binding of FLC molecules which surrounded the ZnO-NPs. Li *et al.*[16] proposed a model to show the interaction between ZnO-NPs and FLC molecules surrounding them.

In the present letter, we demonstrated the effect of ZnO-NPs on the electro-optical response of FLC material, namely, KCFLC 7S. The effect of ZnO-NPs on the physical parameters such as spontaneous polarization (P_S), rotational viscosity (η), and electro-optical response time (τ_R) has also been discussed.

The ZnO-NPs were synthesized in alcoholic medium using zinc acetate and lithium hydroxide at room temperature. For this study, homogeneously aligned cells (thickness 3 μm) have been prepared using rubbed polyimide technique. The pure as well as ZnO-NPs doped KCFLC 7S material were filled into the cell by means of capillary action. The phase sequence of the material used is as follows:

$$\text{cryst.} \overset{?}{\leftrightarrow} \text{SmC}^* \overset{73\,°C}{\leftrightarrow} \text{SmA}^* \overset{100.5\,°C}{\leftrightarrow} \text{N}^* \overset{114.5\,°C}{\leftrightarrow} \text{iso.}$$

The optical micrographs of the sample cells were taken with the help of polarizing optical microscope (Ax-40, Carl Zeiss, Germany) fitted with charge coupled device camera. Optical tilt angle measurements were taken with the cell mounted on a rotatable stage of the polarizing microscope on application of the bias field. The determination of P_S, η, and τ_R have been performed using an automatic liquid crystal tester (ALCT, Instec, U.S.A.). An impedance analyzer 6540 A (Wayne Kerr, U.K.) was used to obtain the behavior of relaxation frequency with temperature.

We have characterized the synthesized ZnO-NPs by taking its XRD pattern which is shown in Fig. 1. The typical size of ZnO-NPs is found to be around ~7 nm which is calculated using Debye–Scherrer formula.[17] The nature of alignments of pure and ZnO-NPs doped KCFLC 7S has been analyzed by observing their optical micrographs under crossed polarizers. Figure 2 shows the optical micrographs of bright and dark states of homogeneously aligned sample cells of pure and ZnO-NPs doped KCFLC 7S material. Figures 2(a) and 2(b) show the bright and dark states of pure KCFLC 7S material. It is clear from Figs. 2(a) and 2(b) that
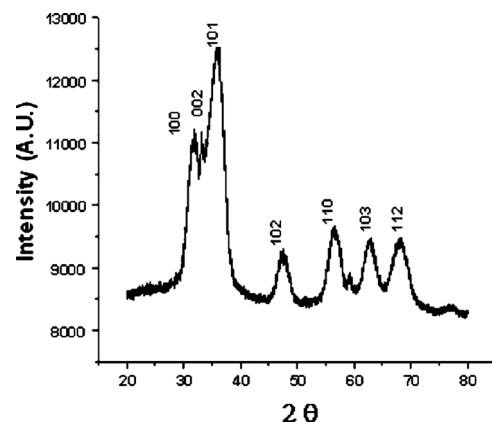

FIG. 1. XRD pattern of zinc oxide NPs.

a)Author to whom correspondence should be addressed. Electronic mail: abiradar@mail.nplindia.ernet.in.
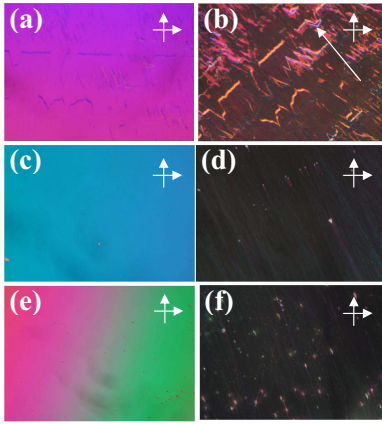
FIG. 2. (Color online) Polarizing optical micrographs of (a) bright, (b) dark state of pure KCFLC 7S material; (c) bright, (d) dark state of 1 wt % ZnO-NPs doped KCFLC 7S material; and (e) bright, (f) dark state of 2 wt % ZnO-NPs doped KCFLC 7S material. Crossed arrows show the crossed polarizers while as single arrow shows the rubbing direction.

FIG. 3. (Color online) Behavior of optical tilt (θ) of pure KCFLC 7S (squares) and ZnO-NPs doped KCFLC 7S (circles) with applied voltage at room temperature.

the homogeneous (HMG) alignment of pure KCFLC 7S is not uniform due to the presence of zigzag defects. In dark state of homogeneously aligned FLCs, there should be no light transmission. But the sharp edges of zigzag defects in the FLC materials allow the light leakage even in the dark state of the FLC cells. These defects degrade alignment and hence the optical contrast of the FLC cells. Figures 2(c) and 2(d) show the optical micrographs of bright and dark states of ∼1 wt % ZnO-NPs doped KCFLC 7S material. It can be seen clearly from figures that the addition of ZnO-NPs into the KCFLC 7S material has resulted almost defect free alignment. The number of light leakage centers has been increased on increasing the concentration of ZnO-NPs from 1 to 2 wt % [Figs. 2(e) and 2(f)]. The zigzag defects are almost absent in case of ZnO-NPs doped KCFLC 7S indicating the improvement in the optical contrast. It is worth to notice here that ZnO-NPs do not perturb the order of FLC molecules within a layer and only bind them along its direction of dipole moment through a coupling with the dipole moment present in the LC molecules. In case of FLCs, optical tilt is the primary order parameter which reveals most of the information about the switching behavior and molecular response to external electric field. The value of optical tilt increases with increasing applied voltage due to coupling of P_S with the applied field and attains a saturation value at certain value of applied voltage (which is called as saturation voltage). The saturation voltage is intrinsic property of the LC materials but it also depends on various factors such as anchoring energy, cell thickness, etc. Figure 3 shows the behavior of optical tilt angle of pure and ZnO-NPs doped KC-FLC 7S material, respectively, with applied bias at room temperature. One can clearly see from figure that optical tilt has been saturated at ∼2.5 V in case of ZnO-NPs doped KCFLC 7S material whereas for pure KCFLC 7S material saturation in tilt angle was achieved at ∼5 V. The doping of ZnO-NPs reduced the saturation voltage of KCFLC 7S material.

The doping of ZnO-NPs gave rise to long-range interparticle interactions of FLC molecules, surrounded the ZnO-NPs. This interaction is found to be dependent on the orientation and the local ordering of the FLC molecules with respect to the ZnO-NPs. It has been observed that a ZnO nanocrystal can interact with surrounding FLC dipolar mol-
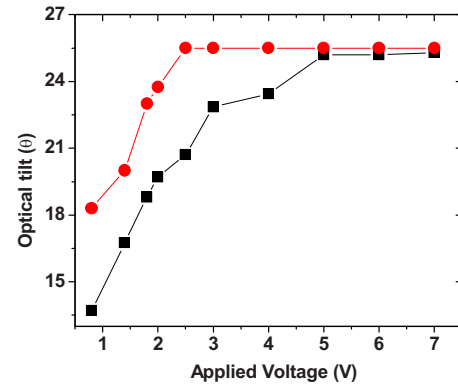
ecules and tie them together to respond to an external driving field in more unison.[16] The origin of permanent dipole moment is based on its structure to some extent. The *ideal* wurtzite structure never exists in which each tetrahedron has T_d symmetry, but, in a *real* wurtzite compound AB, a slight displacement of the A and B sublattices along the hexagonal c-axis occurs. The c/a ratio [which is defined as the ratio of magnitude of the third axis (c) to the axis lying in the basal plane (a); where a and c are the lattice parameters] should be 1.633 whereas in case of ZnO it is 1.6018.[18] Thus, the presence of a permanent dipole moment in real wurtzite, e.g., ZnO, can be attributed to C_{3v}-distortion of the elementary AB_4 tetrahedron. Shim and Guyot-Sionnest proposed that a major contribution for the possible origins of the large dipole moments includes internal bonding geometry, shape asymmetry, surface strain, and the surface localized charges.[19] The ZnO-NPs with diameter ∼7 nm possess dipole moment >100 D which is much larger than that of a LC molecule (∼1.5 D). This large value of dipole moment on ZnO-NPs interacts strongly with dipolar species present in the FLC mixture. This dipolar interaction enhances the anchoring and hence the ordering of FLC molecules which surround the ZnO-NPs. This enhanced ordering of FLC molecules has been resulted in the form of improved optical contrast of ZnO-NPs doped KCFLC 7S material. The magnitude of the electrical torque experienced by ZnO-NPs is larger due to their higher dipole moments and hence the FLC molecules coupled with these ZnO-NPs could be switched by the application of lower value of applied electric field.

Figure 4 shows the behavior of P_S, η, and τ_R of pure and ZnO-NPs doped KCFLC 7S material, respectively, with applied voltage at room temperature. It is clear from Fig. 4(a), that the value of P_S in case of ZnO-NPs doped KCFLC 7S is higher than that of pure one. The increment in the P_S is a consequence of increase in the effective polarization due to doping of ZnO-NPs. The dipole moments of all the ZnO-NPs get aligned in the field direction and add up with the FLC polarization to give larger value of P_S. The value of η of KCFLC 7S cell has been increased by doping ZnO-NPs into it [Fig. 4(b)]. The increase in the η has been resulted due to remarkable strength of dipolar interaction between ZnO-NPs and FLC molecules. The electro-optical response time can be calculated using the relation
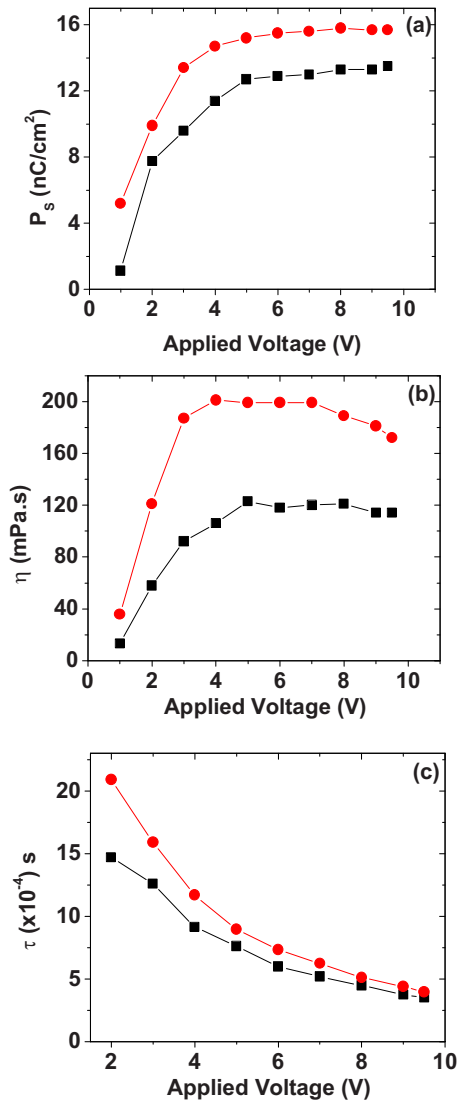
FIG. 4. (Color online) Behavior of (a) spontaneous polarization (P_S), (b) rotational viscosity (η), and (c) response time (τ_R) of pure KCFLC 7S (squares) and ZnO-NPs doped KCFLC 7S (circles) with applied voltage at room temperature.

$$\tau_R = \frac{\eta}{P_S E},$$

where τ_R and E denote response time and intensity of applied electric field, respectively. As both the value of P_S and η has been increased in case of ZnO-NPs doped KCFLC 7S material, the combined effect of increased value of these parameters has been resulted in the form of slightly slower response of the ZnO-NPs doped KCFLC 7S material [Fig. 4(c)].

Figure 5 shows the behavior of relaxation frequencies of pure and ZnO-NPs doped KCFLC 7S material with temperature. The transition from SmC* to SmA* phase has taken place at 70 °C for both, pure and ZnO-NPs doped KCFLC 7S material. The doping of ZnO-NPs has not affected transition temperature (T_C) which shows that ZnO-NPs do not perturb the ferroelectric ordering and it also ruled out the possibility of any chemical reactions or bonding of ZnO-NPs with FLC.
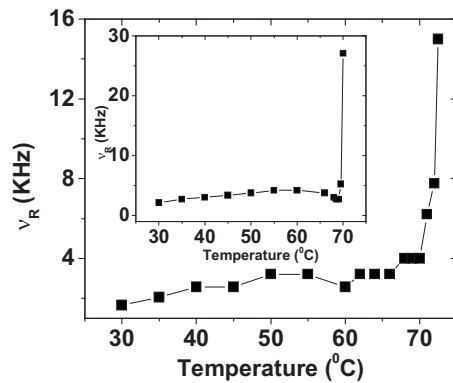

FIG. 5. Behavior of relaxation frequency (ν_R) of ZnO-NPs doped and pure (inset) KCFLC 7S material with temperature.

We observed that the dipolar interaction between ZnO-NPs and FLC molecules has been resulted in the form of low operating voltage and improved optical contrast of the ZnO-NPs doped FLC material. The lowering of the operating voltage and improvement in optical contrast have been attributed to the larger dipole moment of ZnO-NPs that enhances the anchoring of FLC molecules which surrounded the ZnO-NPs. These studies will certainly provide a tool to utilize the interaction of ZnO-NPs with FLC molecules in the form of good optical contrast and low threshold electro-optic devices.

[1] W. H. de Jong and P. J. A. Borm, Int. J. Nanomedicine **3**, 133 (2008).
[2] G. Reiss and A. Hutten, Nature Mater. **4**, 725 (2005).
[3] Q. Chen, M. R. Lin, J. E. Lee, Q. M. Zhang, and S. Yin, Appl. Phys. Lett. **89**, 141121 (2006).
[4] F. Aslam, J. Stevenson-Hill, D. J. Binks, S. Daniels, N. L. Pickett, and P. O' Brien, Chem. Phys. **334**, 45 (2007).
[5] J. H. Park and O. O. Park, Appl. Phys. Lett. **89**, 193101 (2006).
[6] D. K. Yang, J. L. West, L. C. Chien, and J. W. Doane, J. Appl. Phys. **76**, 1331 (1994).
[7] I. Dozov, M. Nobili, and G. Durand, Appl. Phys. Lett. **70**, 1179 (1997).
[8] S. Kaur, S. P. Singh, A. M. Biradar, A. Choudhary, and K. Sreenivas, Appl. Phys. Lett. **91**, 023120 (2007).
[9] J. Prakash, A. Choudhary, A. Kumar, D. S. Mehta, and A. M. Biradar, Appl. Phys. Lett. **93**, 112904 (2008).
[10] T. Zhang, C. Zhong, and J. Xu, Jpn. J. Appl. Phys. **48**, 055002 (2009).
[11] W.-K. Lee, J.-H. Choi, H.-J. Na, J.-H. Lim, J.-M. Han, J.-Y. Hwang, and D.-S. Seo, Opt. Lett. **34**, 3653 (2009).
[12] Q. Zhang, C. Xie, S. Zhang, A. Wang, B. Zhu, L. Wang, and Z. Yang, Sens. Actuators B **110**, 370 (2005).
[13] K. Matsubara, P. Fons, K. Iwata, A. Yamada, K. Sakurai, H. Tampo, and S. Nikki, Thin Solid Films **431–432**, 369 (2003).
[14] J. Zhang, W. Yu, and L. Zhang, Phys. Lett. A **299**, 276 (2002).
[15] J. Y. Huang, L. S. Li, and M. C. Chen, J. Phys. Chem. C **112**, 5410 (2008).
[16] L.-S. Li and J. Y. Huang, J. Phys. D: Appl. Phys. **42**, 125413 (2009).
[17] P. Scherrer, Gött Nachr **2**, 98 (1918).
[18] T. Nann and J. Schneider, Chem. Phys. Lett. **384**, 150 (2004).
[19] M. Shim and P. Guyot-Sionnest, J. Chem. Phys. **111**, 6955 (1999).