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Formation of periodic domains and change in physical properties of paramagnetic copper doped ZnO nanoparticle dispersed ferroelectric liquid crystal system

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article info abstract

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Copper doped paramagnetic ZnO nanoparticles (NPs) were dispersed in ferroelectric liquid crystal (FLC) matrix. The dielectric spectroscopy was performed by using the Cole–Cole equation. The experimental data was corrected for the low and high frequency limitations attributed to the ionic conductance and ITO resistance respectively. The presence of paramagnetic NPs reduces the net ferroelectricity of the pure FLC material which causes the lowering of relative permittivity for the NP dispersed FLC system as compared to pure FLC. NP assisted domains, having specific period and inclination, were also observed in the NP dispersed FLC system. These domains also contribute in the lowering of spontaneous polarization of the dispersed system. The domain formation also affects the response time and rotational viscosity of the pristine FLC material. The mobile ionic carriers, present in the FLC material, have been trapped on the surface of the NPs. The trapping of ionic carriers was verified by the a.c. conductivity measurement. The change in physical parameters of the pure FLC material due to the dispersion of NPs has been analyzed and explained in the present investigation.

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1. Introduction

Sustaining the properties of both the isotropic liquids and ordering like solids, the liquid crystals (LCs) are special class of soft condensed materials which have a broad range of applications [\[1](#page--1-0)–3]. The fascinating applications of LCs are due to their anisotropy, low viscosity, modulation of optical properties with light, tunable applied field dependent physical properties and many more [\[4,5\].](#page--1-0) A new class of LC material, known as ferroelectric liquid crystal (FLC) was introduced by Meyer et al. in 1975 [\[6\]](#page--1-0). The development of surface-stablished FLC by Clark and Lagerwall, in 1980, showed its interesting application in electrooptical devices having optical switching of submicron order [\[7\]](#page--1-0). FLCs have also proven their potential applicability in the tunable laser, diffraction grating, ionic impurity free memory devices, etc. [8–[10\]](#page--1-0).

The development of nanotechnology provides new dimensions to the experimental research by introducing the nanoparticles (NPs), carbon nanotubes (CNTs) and quantum dots (QDs) for the various fields of applied physics and technology. During the last decade, the tuning of physical properties of a host material with the addition of guest nanomaterial is the most convenient method. This multidisciplinary approach to enhance the practical applications of nanomaterial based composites has been widely used in various fields [\[11](#page--1-0)–13].

The composite system of FLCs with the variety of NPs has emerged as one of the perspective method for improving the performance of pristine FLC. The induction of dielectric relaxation mode and improved electro-optical properties of a FLC material due to nickel NPs, enhancement in the photoluminescence of the FLC with the addition of gold NPs, ionic impurity free memory applications of FLC with the help of zirconia NPs and induced photoluminescence in FLC due to Cu–ZnO NPs are few interesting applications of the NPs in the field of LC research [\[10,13](#page--1-0)–15]. During the last decade, the incorporation of various NPs in the FLC material, with different concentrations, is a noble approach for altering the properties of pristine FLC. In addition to this, NP driven vertical alignment by polymeric NPs and effect on the smectic ordering and phase transition temperature with the help of CdSe NPs has also been reported for the better understanding of the guest–host interaction in the NP-FLC composites [16–[18\].](#page--1-0) Dispersion of NPs in the FLC matrix perturbs the FLC geometry because of the larger size of NPs as compared to FLC molecular dimension. In this process, strong director deformations occur which breaks the continuous rotational symmetry of the system. The above mentioned factors are responsible for the modified properties of the pristine FLC due to the dispersion of NPs. The effect of the concentration of ZnO NPs in FLC has also been analyzed by Chaudhary et al. and the optimized dielectric and electro-optical parameters for the FLC-NP composite have been presented recently [\[19\]](#page--1-0).

In the present study, we report the dispersion of 8% Cu doped ZnO $(ZnO:Cu²⁺)$ NPs in a FLC material (FLC17/100). Our group has already reported the effects of these NPs in the nematic LC [\[20\]](#page--1-0).The electro-

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Fig. 1. Scanning electron microscopic (SEM) image of NP dispersed FLC at room temperature. The inset of the figure represents the SEM image of pristine $ZnO:Cu^{2+}$ nanoparticles (NPs) .

optical, electrical and dielectric studies have been carried out as a function of temperature and frequency in the SmC* phase. The experimental data has also been fitted by using the real and imaginary parts of the Cole–Cole equation to observe the low and high frequency problems attributed to the ionic conductance and electrode polarization capacitance or ITO resistance respectively. The experimental and corrected dielectric data have also been presented which show the importance of data fitting to avoid the superfluous contribution of impurity ions at lower frequencies. The formation of domain structure, due to the dispersion of NPs in FLC material, causes the alteration of electro-optical properties. The reduction of ferroelectricity of the pure FLC due to the dispersion of paramagnetic NPs has been analyzed and explained. The formation of stable domain structure, ion trapping phenomenon between NPs and ionic charge carriers in the FLC material along with the importance of corrections in experimental data are the main focus of the present investigation rather than our previously reported article on the FLC mixed with 10% Cu doped ZnO NPs [\[21\]](#page--1-0).

2. Experimental details

The investigated FLC material, used in the present study, is Felix 17/100 (commercial FLC mixture purchased from Clariant Chemicals Co. Ltd. Germany) and the phase sequence of the FLC mixture is Cr, SmC*, SmA, N*, Iso at −20 °C, 72 °C, 82 °C and 95 °C.

The rod shape Cu doped ZnO $(ZnO:Cu^{2+})$ NPs, used in the present study, were prepared by hydrothermal method. The content of copper in ZnO is 8 wt.%. The NPs are paramagnetic in nature,having diameters of 12–15 nm and length of 40–80 nm estimated by XRD spectra and Debye–Scherer equation i.e.d = 0.9λ /BCos θ , where d is the crystallite size, λ is the wavelength of radiation used, θ is the Bragg angle and B is the full width at half maxima (FWHM) on 2θ scale. The content of Cu in the ZnO determines the magnetic nature of NP. For lower content of Cu in ZnO (1–5 wt.%), the nature of NPs is ferromagnetic whereas the higher doping of Cu in ZnO ($>$ 5 wt.%) makes them paramagnetic in nature due to enhanced antiferromagnetic interactions between Cu–Cu ions. As the content of Cu in $ZnO:Cu^{2+}$ NPs used in the present study is 8%, therefore, they are paramagnetic in nature. Fig. 1 represents the scanning electron microscopic (SEM) image of the NP dispersed FLC material which shows almost uniform distribution of the NPs in the host FLC. The inset of Fig. 1 shows the SEM image of pristine ZnO: $Cu²⁺$ NPs. The detailed information about the synthesis and characterization of the $ZnO:Cu^{2+}$ NPs along with their magnetic properties have already been reported by Sharma et al. [\[22\]](#page--1-0). It is important to notice that the NPs of same composition but prepared by the different

Fig. 2. Experimental and corrected dielectric constant for (a) pure FLC 17/100 at 40 °C, (b) pure FLC 17/100 at 70 °C, (c) NP dispersed FLC at 40 °C and (d) NP dispersed FLC at 70 °C.

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