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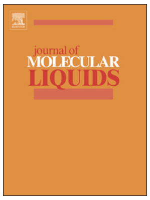

Analysis of physical parameters and collective dielectric relaxations in core/shell quantum dot ferroelectric liquid crystal composite

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ABSTRACT

The effect of doping of $Cd_{1-x}Zn_xS/ZnS$ core/shell quantum dots (QDs) on the physical parameters and dielectric relaxations of ferroelectric liquid crystal (FLC) with the variation of dopant concentration, temperature and frequency has been examined in the present study. Fourier transformed infrared spectroscopy reveals that the QDs interact with FLC molecules and affect their molecular dynamics. The UV absorbance of pure FLC material has diminished in the presence of QDs according to the dopant concentration in FLC. A substantial change has been observed in tilt angle, spontaneous polarization and relative permittivity with the addition of QDs. A faster optical response for FLC, when doped with 0.25 wt.% quantum dots, is one of the interesting finding of the present study. In the SmC* phase, a low frequency relaxation mode at 20 Hz along with the characteristic Goldstone mode has been observed. The occurrence of new low frequency relaxation mode is accredited to the ionization–recombination assisted diffusion of slow ions present in the FLC material. These results would certainly be helpful in the fabrication of low charge consumable and faster liquid crystal systems.

1. Introduction

Liquid crystals (LCs) exhibit a surfeit of distinctive and magnificent properties that can be efficiently tailored for various novel applications beyond the displays [1,2]. LCs are known to exist in several discrete mesophases with varying degrees of structural groups flanked by the extremes of an ordered crystal and a disordered liquid. The ferroelectric liquid crystals (FLCs) continue to be the center of demand due to their fast switching response, lower operational voltage, large optical contrast and memory effect, etc. [3]. On account of their tunable electrical, optical and chemical properties, nanomaterials have turned into requisite element of nanoscience and nanotechnology [4]. The reach of these materials is outstanding as they have broadly shared their significance in all branches of science, engineering and technology. The doping of nanoparticles (NPs) in LCs extensively helps in utilizing the striking traits of LCs without other chemical synthesis. Recently, the key significance of these composite has been verified in numerous studies [5–7]. The major endeavors of these investigations are the modification of electrical and optical properties of LCs by the doping of nanomaterials in different concentrations. The fabrication and utilization of optical and electro-optical devices based on nanocomposites are one of the primary outcomes. Nowadays in the field of LCs, the doping of nanomaterials (nanoparticles, nano-rods, quantum dots and carbon nanotubes) into FLCs is largely investigated [8–10].

The materialization of nanotechnology in the form of quantum dots (QDs) has fascinated a great deal of attention for scientific society. QDs were particularly attractive for tackling the problem of large size distribution. QDs have proved themselves as one of the crucial sectors of research in the past decade. Incomparable quantum confinement and variation of band gap of the QDs enforced promising utilization in budding areas of research such as optoelectronics, photovoltaic, lasers, light emitting diodes, biological fluorescent labels, drug delivery and solar cells [11–13]. The decrease of ionic contaminations by the ion capturing phenomenon along with the induction of new relaxation mode at higher frequency other than the Goldstone mode in FLC material with the addition of CdSe QDs has been recently reported by Singh et al. [14]. Hegmann et al. [15] have observed that the size, capping agent and concentration of CdSe and CdTe QDs play vital role in varying the electro-optical parameters of nematic LCs. The possibility of aggregation of the dopant producing adverse effect on the various properties of other FLC has also been studied [16]. A pronounced memory effect in FLC mixtures has been observed by Kumar et al. [17] by doping CdTe QDs. Many researchers have also focussed their investigation on different low frequency relaxations that are induced with the addition of varying nanoparticles including QDs. A number of other dielectric relaxation modes have also been examined in FLC materials. In the SmC*

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phase of KCFLC 7S, Biradar et al. [18] demonstrated the effect of gold nanoparticles on the low frequency dielectric relaxation. A low frequency dielectric measurement of the Felix 18/100 has been performed by Havriliak et al. [19]. Space charge accumulation at LC–polymer interface causing a very low frequency mode in a FLC material has been studied by Uehara et al. [20]. Novotna et al. [21] investigated the effect of thickness of the cell on the low frequency mode of the FLC material. The doping Ag NPs in chiral smectic mixtures results in sub hertz relaxation process as reported by Mandal et al. [22].

Here, the effect of $Cd_{1-x}Zn_xS/ZnS$ QDs on the physical parameters and dielectric relaxations of FLC SCE4 have been investigated. The present analysis is important for the better understanding of the molecular dynamics and applicability of these materials in devices. Fourier transform infrared spectroscopy (FTIR), UV–visible absorbance, tilt angle, spontaneous polarization, response time and relative permittivity have also been determined for the pure and composite system. In addition to this, the dielectric relaxations of pure and composite system in the frequency region of 5 Hz–1 MHz have been studied. A low frequency relaxation mode at 20 Hz along with Goldstone Mode at 100 Hz has been observed. The effect of adding QDs on the relaxation modes has also been discussed. The experimental results indicate the considerable changes in various properties of the composite system as compared to the pure FLC.

2. Experimental details

2.1. FLC material and quantum dots

The FLC material used in the present study was SCE4 (Clariant Chemicals Co. Ltd., Germany). The phase sequence of the FLC material is

$$\mathrm{SmC}^* \xrightarrow{57^0\mathrm{C}} \mathrm{SmA} \xrightarrow{88^0\mathrm{C}} \mathrm{N}^* \xrightarrow{122^0\mathrm{C}} \mathrm{Iso.}$$

$Cd_{1-x}Zn_xS/ZnS$ QDs have been used to dope in SCE4. These QDs were prepared by Gram-Scale One-Pot Synthesis method as illustrated by Bae et al. [23]. The diameter of core/shell QD was found to be 8.7 nm. In order to prepare FLC–QD composite, a suitable amount of the QDs (0.25 and 0.50 wt/wt.% termed as Mix.1 and Mix.2) were mixed into the pure SCE4 and then homogenized with an ultrasonic mixer for 1 h at 122 °C. The homogeneity of the composite was checked by the polarizing optical microscope under the crossed polarizer condition.

2.2. Preparation of sample cell

Planar aligned sample cells were used to study the dielectric and electro-optical properties of the pure and FLC–QD composite. The sample cells were prepared using the Indium tin oxide (ITO) coated glass plates. The conducting layer of ITO was treated with adhesion promoter and polymer nylon (6/6) to achieve the planar alignment. Following the drying of polymer layer, substrates were rubbed unidirectionally and then placed one over another to form a capacitor. A Mylar spacer (5 μm in our case) was placed between the two plates to maintain the thickness of the sample cell and then sealed with UV sealant. Analytical reagent grade benzene (C_6H_6) was used as standard reference to calibrate the empty sample cells. The assembled cells were filled with the pure FLC and FLC–QD composite by capillary action above the isotropic temperature of FLC.

2.3. Electro-optical measurement

The optical micrographs were taken using polarizing microscope (Radical instruments, RXLR-5) in crossed polarizer condition. The measurement of tilt angle at diverse voltage and at room temperature (35 °C) has been examined by applying a square wave of both polarities to the planar aligned sample cell. The sample was set for the two extinction positions to acquire the tilt angle. The tilt angle is half of the angle between the two extinction positions [24]. The spontaneous polarization of the pure and the composite has been measured via polarization reversal current method [25,26]. The detailed experimental array for this measurement has previously been reported by our group [16]. A 5 mW He–Ne laser of wavelength 633 nm has been used to apply signal to the sample cell along with a photo-detector (Instec, PD02-L1) to study the output response. The triangular and square wave pulses have been applied (20 Vpp and frequency 10 Hz) using a programmable function generator (Tektronix, AFG-3021B). The output was recorded on a digital storage oscilloscope (Tektronix, TDS-2024C). The rotational viscosity (γ_{GM}) for a cone motion in SmC* phase was calculated by the relation

$$\gamma_{GM} = \frac{P_S.\tau.E}{1.8} \tag{1}$$

where E is the applied switching field, P_s is spontaneous polarization and τ is the response time [27].

The FTIR spectra of the pure and FLC–QD composite were recorded at room temperature by the Fourier Transform Infrared Spectrophotometer (Shimadzu, IRAFFINITY-1) in the range 650–3500 cm^{-1}. The UV–visible absorption study was performed on the UV–visible Spectrophotometer (Elico, SL 210) for a wavelength interval of 300–400 nm at room temperature.

2.4. Dielectric measurement

A computer controlled Impedance/Gain Analyzer (Solartron SL1260) linked with a temperature controller has been used to study dielectric measurements in the frequency range 1 Hz to 10 MHz. The dielectric measurements as a function of frequency and temperature have been carried out by placing the sample holder on a computer controlled hot plate INSTEC (HCS-302) which has a temperature stability of ±0.1 °C. Owing to the overriding effect of finite resistance of ITO coated glass plates and lead inductance [28,29], the measurements in the higher frequency range have been edged to 10 MHz. Therefore, the measured data requires alteration in both low and high frequency range. On separating the real and imaginary part of Eq. (2) one may get

$$\varepsilon' = \varepsilon'(dc)f^{-n} + \varepsilon'(\infty) + \frac{\delta\varepsilon_{GM}\left[1 + (2\pi f\tau_{GM})^{(1-\alpha_{GM})}\sin(\alpha_{GM}\pi/2)\right]}{1 + (2\pi f\tau_{GM})^{2(1-\alpha_{GM})} + 2(2\pi f\tau_{GM})^{(1-\alpha_{GM})}\sin(\alpha_{GM}\pi/2)} \tag{2}$$

&

$$\varepsilon'' = \frac{\sigma(dc)}{\varepsilon_0 2\pi f^k} + \frac{\delta\varepsilon_{GM}(2\pi f\tau_{GM})^{(1-\alpha_{GM})}\cos(\alpha_{GM}\pi/2)}{1 + (2\pi f\tau_{GM})^{2(1-\alpha_{GM})} + 2(2\pi f\tau_{GM})^{(1-\alpha_{GM})}\sin(\alpha_{GM}\pi/2))} + Af^m \tag{3}$$

where $\delta\varepsilon_{GM}$ is the relaxation strength of the Goldstone mode, $\varepsilon'(\infty)$ is the high frequency limit of the dielectric permittivity, f is the frequency and τ_{GM} is the relaxation time. $\sigma(dc)$ is the dc ionic conductance, ε_o is the free space permittivity and f is the frequency whereas n, m and k are the fitting parameters. For the low frequency effect which occurs due to the electrode polarization capacitance and ionic conductance, terms $\varepsilon'(dc)f^{-n}$ and $\sigma(dc)/\varepsilon_o 2\pi f^k$ are added in Eqs. (2) & (3). The Af^m term is adjoined in Eq. (3) for high frequency effect as a consequence of the ITO resistance and lead inductance.

3. Results and discussion

The effect of doping $Cd_{1-x}Zn_xS/ZnS$ QDs into the pure SCE4 has been studied by recording the Polarizing Optical Microscope (POM)