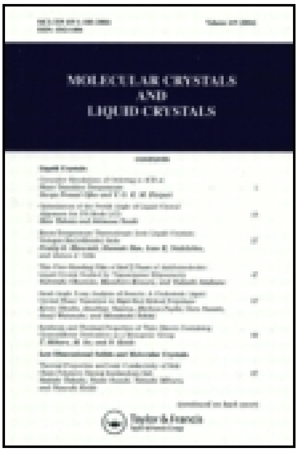

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Effect of CdS Nano-Crystal Dispersion on Dielectric Properties of Ferroelectric Liquid Crystal

Surjya Sarathi Bhattacharyya [a] [b] , A. Mukherjee [b] , S. L. Wu [c] , Seung Hee Lee [a] & B. K. Chaudhuri [b]

[a] Department of BIN Fusion Technology and Department of Polymer Nano-Science and Technology, Chonbuk National University, Jeonju, Jeonbuk, Korea

[b] Department of Solid State Physics, Indian Association for the Cultivation of Science, Kolkata, India

[c] Department of Chemical Engineering, Tatung University, Taipei, Taiwan, R.O.C.

Version of record first published: 30 Jun 2011

To cite this article: Surjya Sarathi Bhattacharyya, A. Mukherjee, S. L. Wu, Seung Hee Lee & B. K. Chaudhuri (2011): Effect of CdS Nano-Crystal Dispersion on Dielectric Properties of Ferroelectric Liquid Crystal, Molecular Crystals and Liquid Crystals, 541:1, 270/[508]-275/[513]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.569255

Mol. Cryst. Liq. Cryst., Vol. 541: pp. 270/[508]–275/[513], 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.569255

Effect of CdS Nano-Crystal Dispersion on Dielectric Properties of Ferroelectric Liquid Crystal

SURJYA SARATHI BHATTACHARYYA,[1,2]
A. MUKHERJEE,[2] S. L. WU,[3] SEUNG HEE LEE,[1] AND
B. K. CHAUDHURI[2]

[1]Department of BIN Fusion Technology and Department of Polymer Nano-Science and Technology, Chonbuk National University, Jeonju, Jeonbuk, Korea
[2]Department of Solid State Physics, Indian Association for the Cultivation of Science, Kolkata, India
[3]Department of Chemical Engineering, Tatung University, Taipei, Taiwan, R.O.C.

Photosensitivity in ferroelectric liquid crystal (FLC) material has been developed by dispersing Cadmium Sulfide (CdS) nano-particles in FLC (CdS-FLC) host. The nematic (N^*) – ferroelectric (SmC^*) phase transition temperature for the CdS-FLC sample in absence and presence of white light excitation decreases by 6 and 14°C, respectively, compared to host material due to enhanced disorder. The anomalous behaviour in temperature dependent dielectric permittivity of CdS-FLC sample in presence of white light excitation in N^* as well as SmC^* phase has been explained on the basis of enhanced free charged density and self assembly of CdS-LC in the phases.

Keywords Dielectric permittivity; ferroelectric liquid crystals; nanocrystals; photosensitivity

1. Introduction

Dispersion effects of colloidal nano particles in liquid crystal (LC) matrix is a topic of intense interest in present day research concerning the fundamental importance as well as applications in various LC devices. Although, many works has been done on nano particle dispersed nematic liquid crystalline system, so far very little research interest has been shown to study nanoparticle dispersed non-nematic (viz. smetic) LC host materials. In this context, we can distinguish; Matsui and Yasuda who used amorphous TiO_2 nanoparticles (~17 nm in diameter) randomly dispersed in

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Address correspondence to Surjya Sarathi Bhattacharyya, Department of BIN Fusion Technology and Department of Polymer Nano-Science and Technology, Chonbuk National University, Jeonju, Jeonbuk, Korea. Tel.: +91-33-24734971; Fax: +91-33-24732805; E-mail: sspbkc@rediffmail.com; sspbkc@iacs.res.in

ferroelectric liquid crystal (FLC) mixture, and demonstrated the effectiveness of such mixtures for video rate gray-scale FLC devices [1]. More recently, Kaur *et al.* reported gold nanoparticle doped FLC, where the presence of gold colloids generated higher tilt angles, memory effects, and lower threshold voltages [2]. Ferroelectric nano particle dispersion effects in nematic host become significant in this context, has been studied mostly by collaborative effort of Prof. West and Prof. Reznikov and their group [3,4]. Concerning present day material research, several pure photo responsive nano particles (CdS, CdTe etc.) were broadly studied and showed immense prospective in the field of electroluminescence, photovoltaic device and in photo detection [5]. However, they have hardly ever been studied as dopants, dispersed in LC host substance. The distribution of dissolved ions in LC's, confined between two charged surfaces, has also been a subject of continued interest in recent years [6]. Thus, we intend to study the consequence of distributed free charges on the dielectric properties of FLCs. Hence, our aim in this paper is to develop photo sensitivity in FLC material by dispersing a spare amount of Cadmium Sulphide (CdS) nano material and to investigate the effect of additional charge distribution as a result of photo sensitive nano-dispersion over the temperature dependent dielectric properties of the FLC sample.

2. Experimental Methods

For our present investigation, the semiconducting CdS nano-crystals are prepared by the microwave irradiation technique following the method proposed by S. Karan *et al.* [7]. The synthesized CdS nano-powder was characterized by high resolution TEM imaging showing CdS nano particles of average size ~2.5 nm (Fig. not shown). The ferroelectric liquid crystal viz. FELIX R3206 (Merck) having the phase sequence: Iso. $-107.0°C-N^* - 78.4°C–SmC^*–12°C–(-6)$ Cr (spontaneous polarization ~18.3 nc/cm^2) was chosen as the host material for dispersing the CdS nanoparticles. CdS nanoparticles (0.5 wt%) are dispersed in FLC (here after referred to as CdS-FLC) which was dissolved in chloroform, using ultrasonication for several hours sequentially for preparing a homogeneous mixture. After very slow evaporation of the solvent viz. chloroform, the mixture thus formed was kept for two days undisturbed. The upper layer of the sample is used for the experiment to avoid any precipitation of nano particles.

Figure 1 shows the room temperature UV Visible absorption spectra measured by absorption spectrophotometer (Shimadzu UV-vis 2101PC) for the pure FLC and CdS-FLC nano composite samples used in present investigation. Both the samples show distinct absorption peak at about same wavelength (~285 nm) in the UV range, assuring the absorption due to FLC host. Interestingly, pure FLC doesn't show any absorption peak in the visible regime, however, the CdS dispersed FLC shows distinct absorption peak (~408 nm) in the visible range. Hence, it is evident that CdS nanocrystals have induced photo sensitivity in the said sample. The spectral character of the white light source used for exciting the CdS-FLC system has also been checked. The intensity of the light source is found to be negligible in UV wave length regime compared to visible region. It has also been noted that the intensity of the light source is perfectly zero at ~285 nm, whereas it is intense in the visible, ~400 nm wavelength regime.

The pure as well as CdS-FLC samples were filled in self devised cells of thickness ~10 μm with active area ~16 mm^2 by means of capillary action technique in the

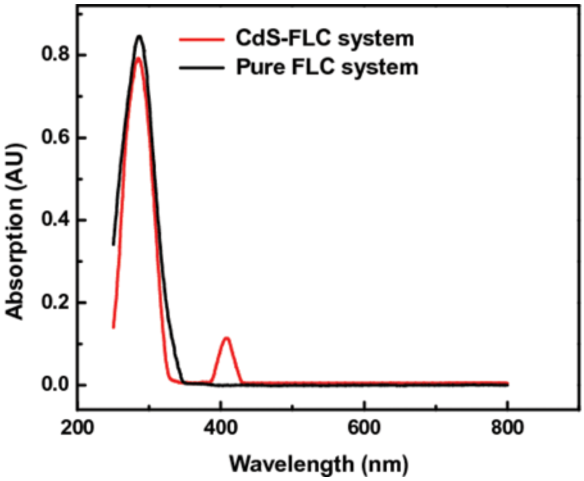

Figure 1. The room temperature absorption spectra of pure FLC (black line) and CdS-FLC sample (red line).

isotropic phase of the liquid crystal similar to our earlier work [8,9]. Indium tin oxide (ITO) coated transparent glass substrates were used as electrodes of the cells. Substrates were prepared by coating the glass plates with polyvinyl alcohol (PVA) and baking at 140°C for 2 hrs. Homogeneously aligned samples were obtained by rubbing the substrate in one direction. Each cell was previously calibrated by using air and toluene as the standard references. The sample under investigation was slowly cooled from isotropic phase for better alignment. The measuring temperature was controlled by the Mettler FP82 hot stage along with Mettler FP90 controller with an accuracy of ±0.1°C. A computer controlled HP-4192A impedance analyzer is used for dielectric measurements. The nano dispersed sample was also investigated under a polarization microscope (Debro-PM1) (Fig. not shown) showing no signature of cluster formation which assured a homogeneous distribution of CdS nano-crystals within the FLC matrix. We did not find any signature of occurrence of chemical reaction or degradation of the sample during the experimental tenure of few days. The results shown in subsequent discussion found consistently with repeated experiments with freshly prepared samples. However, aging investigation of these samples can be interesting to the community.

3. Results and Discussion

Figure 2 represents the temperature dependent real (ε') and imaginary (ε'') part of dielectric permittivity of the pure FLC as well as CdS-FLC material films in low (~0.2 kHz) and high (~100 kHz) frequency regime. The said investigation has been carried out both in presence (WL (with light) condition) and in absence of shining white light (WOL (without light) condition) of intensity ~1.8 kLux. This worth mentioning here that the low frequency relaxation process (Goldstone mode) commonly observed in FLC materials due to phase fluctuation of the azimuthal orientation of the director is found to be suppressed in CdS-FLC systems both in WL as well as WOL conditions. Also the composite system did not show the other collective mode

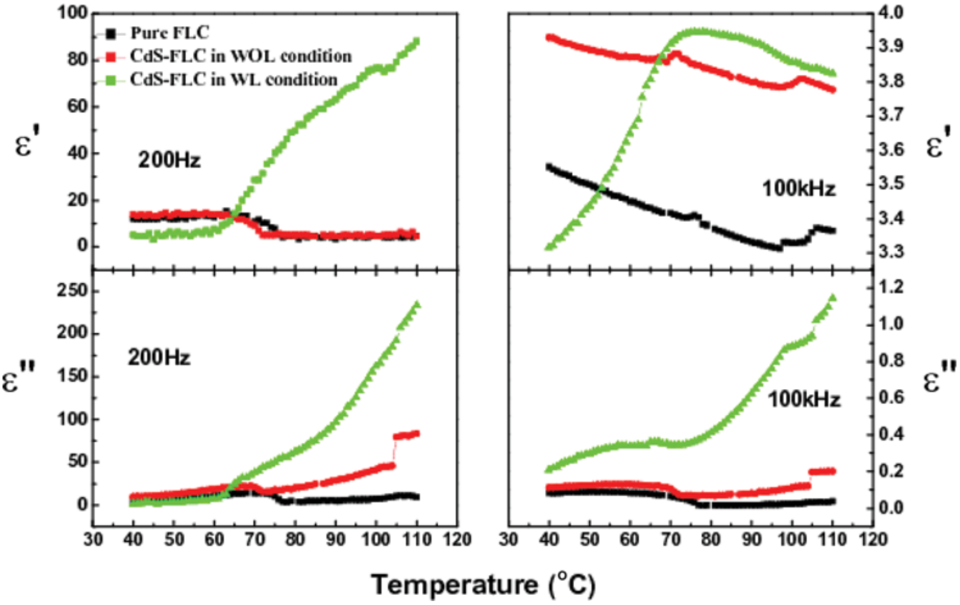

Figure 2. Real ($\varepsilon'(\omega)$) and imaginary part ($\varepsilon''(\omega)$) of dielectric permittivity at 200 Hz (a) and 100 kHz (b) of three samples: Pure FLC, CdS-FLC in absence of light (WOL condition), CdS-FLC in presence of light (WL condition).

obtained in pure FLC due to amplitude fluctuation of LC director. The detailed relaxation investigation is interesting, but beyond the scope of present investigation, would be discussed elsewhere. The ε' and ε'' values for the CdS-FLC sample under WL condition both in N* as well as I phases are found to be significantly higher than the corresponding values of the pure FLC and CdS-FLC systems measured in WOL condition. All the measurements of pure FLC have been done in WL condition. This is to ensure that the experimentally observed effects are exclusively induced by CdS nano-crystals. The ε' at low frequency exhibits a dip and shows a small hump at high frequency ~78°C as a signature of N*-SmC* transition in pure FLC sample. Similar trend has also been observed in the temperature dependent ε'' curve. But for CdS-FLC both in WL and WOL conditions similar nature of ε'-T plot have been observed at different lower temperatures 64 and 72°C, respectively. Clearly this observation suggests that the N*-SmC* transition temperature in CdS-FLC is lowered by 6°C in WOL and by 14°C in WL conditions compared to those observed for pure FLC. This is to be noted here that, the differential scanning calorimetric study of the CdS-FLC sample in WOL condition at 2°C/minute scanning rate have shown 4°C reduction in N*-SmC* transition temperature (Figure not shown), and the difference is attributed to the difference heating and cooling rate in the mentioned investigation.

The observed phenomenon may be explained, considering the self assembled molecular ordering in various liquid crystal phases and its interaction with the dispersed nano-crystals. Moreover, the energy band structure of both the LC host and the guest nano-crystals are also playing important roles. In presence of visible light, the CdS nanocrystals in the CdS-FLC sample generate large number of exciton. The variation of charge density in between charged electrodes for various liquid crystal phases has been theoretically demonstrated by Roy *et al.* [6]. The periodic structure of liquid crystals in smectic phases generates large oscillations in the charge densities especially close to charged plates, whereas the charge density within the nematic as well as in the isotropic phases of LC shows continuous variation, having maximum potentials at the charged boundaries. Since nanocrystals band gap is smaller than host liquid crystal (evident from UV-Vis absorption spectra of the samples shown in Fig. 1), the possible routes for exciton and charge transfer in CdS-FLC composite sample may be as follows: (a) Absorption in the liquid crystal, followed by electron transfer onto the nano-crystal, (b) Absorption in the liquid crystal, followed by exciton transfer onto the nano-crystal, followed by hole transfer onto the liquid crystal, (c) Absorption in the nano-crystal, followed by hole transfer onto the liquid crystal. Here it is noteworthy to mention that the π-π^* electronic transition occurs in the UV wavelength regime for liquid crystals and responsible for UV absorption in liquid crystal showing respective band gap [10].

As the intensity of the white light source in the UV regime is found to be negligible compared to the visible regime, hence the process (c) as mentioned above might be dominating over processes (a) and (b). As a result, hole transferred from CdS nano-crystal to LC should make the matrix electrically positive leaving the nano-crystalline CdS to negative. Again, the CdS nanocrystals provide a very high active surface area, which enhances the charge carrier percolation across the liquid crystal matrix. During the dielectric measurement, the required oscillating field ($\sim$0.1 V/μm) supplies the required energy to separate a significant amount of charges, in the sample. As the light kept shining during the entire measurement, we may assume natural generation and recombination process of electron-hole pairs keeping the electron-hole pair concentration fixed within the sample. Again in the N^* and I phases, the ionic distribution is continuous within the cell. However the presence of discrete molecular layers in smectics causes the charges to distribute in discrete layers according to Roy *et al.* [6]. Even in absence of light, the dispersion of CdS nano-crystals enhances dielectric permittivity of LC material. Therefore, it can be inferred that spare amount of CdS nano-crystals also significantly contributing to the dielectric properties of LC in the dispersed sample. However, in presence of light irradiation, additional contribution of charges comes into play following previous description. Hence, the contribution of charges in addition of CdS nano-crystals, is responsible for the increment in ε' of CdS-FLC material in WL condition compared to those of the pure and CdS-FLC sample in WOL condition in N^* and I phases.

Interestingly, as shown in Figures 2(a) and (b), the ε' values of CdS-FLC in WL condition, after exhibiting minor anomaly at the boundary of N^*-SmC* phase shows a decreasing trend. It is found to become even lower than those of pure FLC and CdS-FLC in the WOL state, deep inside the SmC* phase. In addition, the crossover temperature for ε' of CdS-FLC in WL condition with respect to the other samples is found to be frequency dependent. The layered molecular ordering and tilt induced polarizations are the additional specialty of the SmC* phase, in comparison with the N^* phase. Hence, the polar CdS nanocrystals might have a tendency to arrange within the smectic layers in such a manner which cancels the dipolar contribution of FLC. With reduction of temperature, the increment of viscosity of the SmC* phase might also assist their localization process. As a result, the net dipole moment and dielectric permittivity of CdS-FLC in WL condition decreases deep inside the SmC* phase.

4. Conclusion

Nano-crystal (viz. CdS) induced photosensitivity has been demonstrated in liquid crystal material. The N*-SmC* phase transition temperature have been found to be reduced by 6 and 14°C compared to host material in absence and presence of visible light excitation. This change is due to nano-crystal induced enhanced disorder in the CdS-FLC system. The CdS-FLC sample shows significant increment in dielectric permittivity (ε') in N* phase compared to pure FLC, due to enhanced free charge density in those systems. Interestingly, in the SmC* phase, ε' value for CdS-FLC decreases in presence of white light compared to pure FLC and CdS-FLC in dark state; due to cancellation of the dipolar contribution of FLC by typical self assembly of ionized CdS nanocrystals.

Acknowledgment

The authors are grateful to Council of Scientific and Industrial Research, Govt. of India and WCU program through MEST (R31-2008-000-20029-0) for financial support.

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