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Quantum Dot Doped Ferroelectric Liquid Crystal System: Investigation of Electro-Optical Parameters and Relaxation Behavior

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The effect of QDs on the dielectric and electro-optical (E-O) properties of different ferroelectric liquid crystal matrices has been studied in the SmC phase. A substantial change in the different parameters like tilt angle, spontaneous polarization and relative permittivity has been observed for the doped system. For the better understanding of the effect of QDs on FLC relaxation process another quantum dot CdSe has been dispersed in two other FLC systems 16/100 and DOBAMBC. The effect of QDs on the three FLC systems on relaxation behavior attributes to the alteration of tilt angle in different way in different doped system. This difference in relaxation behavior is observed due to the dissimilar composition and structure of FLC mixture and FLC molecule.*

Keywords Ferroelectric liquid crystal; quantum dots; relaxation behavior

1. Introduction

Over the last two decades the advancement in the field of nanoscience has had tremendous impact on science and technology. Materials having physical dimensions of the order of 1 to 100 nanometers (nm) known as Nanomaterial's, exhibiting unique optical and materialistic properties. Size dependent properties of nanomaterials has proved them to be very promising aspirant for observing various important phenomena [1– 3]. Significant research interest has been developed in recent year for low dimensional nanostructures such as zero-dimensional nanoparticles (NPs), one-dimensional nanorods and nanowires due to their unique properties and functionalities that can be finely controlled by quantum confinement phenomenon. The 3-dimensional quantum confinement effect is basically the strong confinement of electrons and holes in the case where the radius of a particle is below the exciton Bohr radius of the material. Among all of the nanostructure, QD has emerged as the finest nano additive. Semiconductors QD are made from the combination

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of group II and VI elements (e.g., CdSe,ZnO), group III and V elements (e.g., InP and InAs), and group IV–VI elements (e.g., PbS) having diameter in the range of 2 to 10 nm [4, 5]. Their quantum confinement property leads to the distinctive electrical and optical properties [6].

Liquid crystal materials are well known for their anisotropic dielectric and electro – optical properties [7]. With great success now a day, liquid crystals have also been studied for their application in other technologies beyond the liquid crystal display. Use of nano additives in liquid crystalline material has shown a new direction for study over the last few years. To understand the interactions of nano additives in a liquid crystal solvent various experiments has been done so far.

Till now various aspects of the combination of liquid crystal material and nano additives has been studied by different research groups all over the words. This field has been explored exclusively and still has lots of new dimensions to explore. QD affects the physical parameter of liquid crystal considerably. The dielectric properties are strongly affected by the presence of QDs. It has been reported by Shivani et al. that the doping of QDs lead to the almost two times faster response time behaviour of composite system [8]. The doping of QDs in the liquid crystal causes a strong interaction between them leading to the different phenomenon to occur such as enhanced diffraction efficiency of the composite has been reported by Anczykowska et al., due to the reinforcement of light/matrix interaction [9]. The charge storage capability of QDs has led to a new concept: "QD memory." It is also found that the charge carriers stored by QDs can retain over time scales exceeding seconds or even hours [10].

As our object in this research work, is to study the interactions occurring between the quantum dots and liquid crystal molecules when being bring together in a measured way. In the study of composite system of FLC and QDs the size of the quantum dot plays an important role. QDs interacts with different FLC material in different ways leading to substantial change in the different parameters like tilt angle, spontaneous polarization and relative permittivity of the doped system. The effect of QDs on FLC relaxation process has been studied for 17/000, 16/100 and DOBAMBC. The effect of QDs on the three FLC systems on relaxation behavior has been discussed with the help in the change in tilt angle of doped system.

2. Experimental Details

2.1 FLC Material and Quantum Dots

The investigated FLC materials used in the present study were Felix 17/000, 16/100 and DOBAMBC (Clariant Chemicals Co. Ltd., Germany and Frintron Lab, USA).

$Cd_{1-x}Zn_xS/ZnS$ QDs have been used to disperse in Felix 17/000. $Cd_{1-x}Zn_xS/ZnS$ QDs (termed as QD1) were prepared by Gram-Scale One-Pot Synthesis method as described by Bae et. al [11]. The diameter of core/shell QD was found to be 8.7 nm. CdSe QD (termed as QD2) has been used to disperse in 16/100 and DOBAMBC. The diameter of CdSe QD was found to be 3.5 nm [12]. The doped system was prepared by mixing an appropriate amount of the QDs (1% wt/wt) in FLC systems and then homogenized with an ultrasonic mixer for 1 h at 117°C. The homogeneity of the doped was checked by the polarizing optical microscope under the crossed polarizer-analyzer condition.

2.2 Preparation of Sample Cell

The dielectric and electro-optical study of the pure and QD doped FLC system has been conducted on the planar geometry. The sample cells for the present study were prepared using the Indium tin oxide coated glass plates. The planar alignment was obtained by treating the conducting layer with adhesion promoter and polymer nylon (6/6). After drying the polymer layer, substrates were rubbed unidirectionally. The substrates were then placed one over another to form a capacitor. The cell thickness was fixed by placing a Mylar spacer (5 μm in our case) in between and then sealed with UV sealant. The empty sample cells were calibrated using analytical reagent (AR) grade benzene (C_6H_6) as standard reference for the dielectric study. The assembled cells were filled with sample by capillary action above the isotropic temperature of FLC.

2.3 Electro-Optical Measurement

The tilt angle measurement at different voltage has been studied at room temperature (35°C) by applying (10^4 Vcm^{-1}) square wave of both polarities at 0.2 Hz to the planar aligned sample cell. The tilt angle was obtained by setting the two extinction position of the sample. The tilt angle is half of the angle between the two extinction positions [13]. To measure the spontaneous polarization of the pure and the doped system, polarization reversal current method has been used [14–16]. The detailed experimental arrangement for this measurement has already been reported by our group [17].

2.4 Dielectric Measurement

The Dielectric measurements have been carried out by a computer controlled Impedance/Gain Phase Analyzer (HP 4194 A) attached with a temperature controller in the frequency range 100 Hz to 10 MHz. The dielectric measurements as a function of temperature have been carried out by placing the sample holder on a computer controlled hot plate INSTEC (HCS-302) having temperature stability of $\pm$0.1°C. The measurements in the higher frequency range have been limited to 10 MHz because of the dominating effect of finite resistance of ITO coated on glass plates and lead inductance [18].

3. Results and Discussion

The variation of tilt angle (θ) with temperature for the pure Felix 17/000 and QDs doped FLC system in the SmC* phase at 35°C is shown in figure 1. It is clear from the figure that the tilt angle decreases with increase in temperature and vanishes at SmC*-SmA transition. The value of θ decreases with the doping of QDs. For the pure sample, the only interaction is between FLC molecules. The interaction between FLC molecules and QDs does not have much effect on the decrement of tilt angle as the QDs lying near to the FLC molecule produce similar effect on it from all the sides which in turn cancel out. Therefore, the QD-QD interaction dominates over the FLC-QD interaction. It has been estimated that FLC molecules around the QDs get less tilted on account of the favorable attraction between the two nearby QDs which represses the conical geometry of the FLC molecules. Consequently, the tilt angle for the doped system decreases. A similar trend of variation has been observed in another study showing decrease in tilt angle with QD doping [12].

The variation of spontaneous polarization (P_s) for pure Felix 17/000 and the QDs doped FLC system with temperature for 20Vpp triangular wave is shown in figure 2. It is found that the P_s for QDs doped FLC system has decreased. The change in the P_s value of

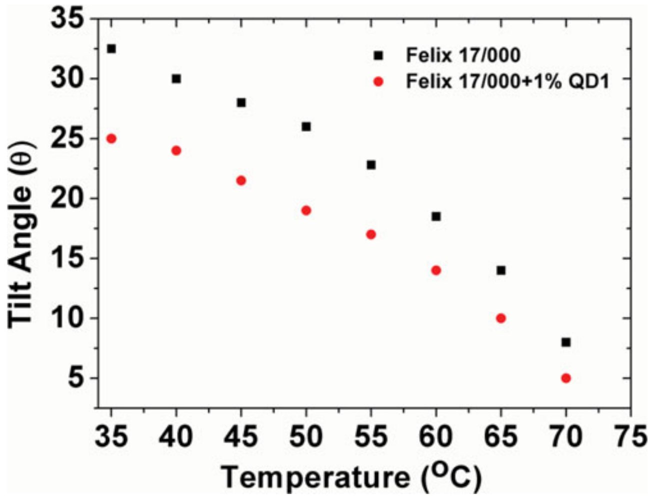

Figure 1. The variation of tilt angle (θ) with temperature for the Felix 17/000 and 1% $Cd_{1-x}Zn_xS/ZnS$ QDs dispersed Felix 17/000.

FLC material following the dispersion of QDs could be understood by taking into account the two reasons. First, the value of P_s is directly coupled with that of the tilt angle of the FLC molecule. It is clear from figure 1 that the value of tilt angle has been decreased for the doped system; therefore, the decrease in the value of P_s value can be accredited to the reduction of tilt angle. Second, the effective dipole moment of the doped system decreases on addition of QDs. Thus, the value of P_s for the doped system reduces. Biradar et al. [19] has also reported the decrease in the value of P_s for other FLC material by doping CdTe QDs.

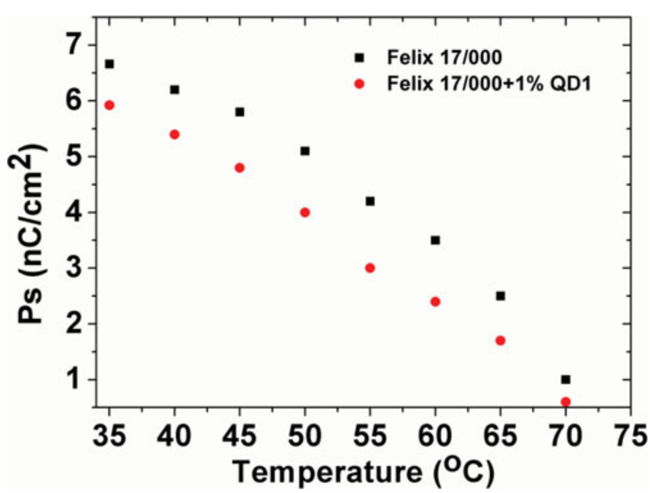

Figure 2. The variation of spontaneous polarization with temperature for the Felix 17/000 and 1% $Cd_{1-x}Zn_xS/ZnS$ QDs dispersed Felix 17/000.

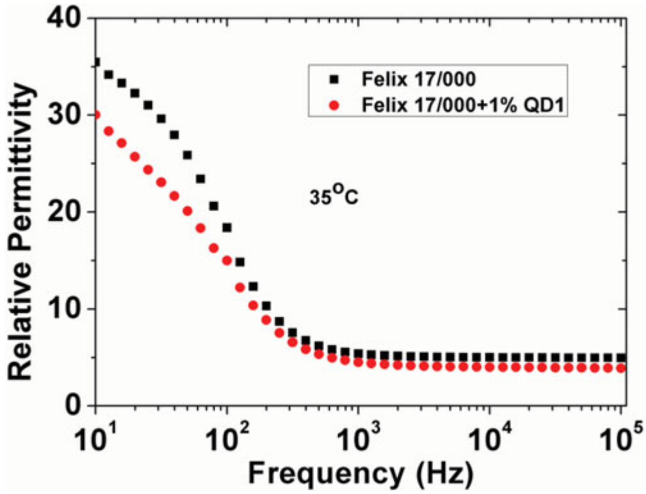

Figure 3. The variation of relative permittivity with frequency for the pure and 1% $Cd_{1\text{-}x}Zn_xS/ZnS$ QDs dispersed Felix 17/000 measured at 35°C.

The relative permittivity of the pure Felix 17/000 and doped system with variation of frequency at room temperature is shown in figure 3. It can be seen that the relative permittivity has been decreased for QD doped FLC system as compared to pure FLC system. The evident reason behind the decrease in the value of relative permittivity for the QD doped FLC system is linked with the decrease in the effective dipole moment of the FLC after adding QDs. This decrease in the effective dipole moment of the doped system also leads to the decreased value of P_s for the doped system. An additional cause for the decrement in the value of relative permittivity may be ascribed to the decrease in charge storage capacity of the doped system. It is known that $\varepsilon_r = C/C_0$, the addition of QDs into the pure FLC system disturbs the FLC geometry. This perturbed FLC geometry change the capacity of FLC system and therefore reduces the charge storage capacity of the doped system [8]. The decreased capacity of the doped system results in diminishing the value of relative permittivity. Thus, the observed decrement in the relative permittivity can be attributed to the decreased value of spontaneous polarization and charge storage capacity of the FLC with the doping of QDs.

Figure 4 shows the variation of Tanδ for pure and QDs doped FLC system with change in frequency at 35°C. It can be seen that the shift in relaxation peak of Goldstone mode for QD doped FLC system is small but span a high frequency range. This implies that the distribution of relaxation increasing with the doping of QDs. It suggests that the change in tilt angle due to doping of QDs in FLC is influencing the goldstone mode of pure FLC system. For the better understanding of the effect of QDs on FLC relaxation process another quantum dot i.e. CdSe QDs have been used to dope in two different FLCs (16/100 and DOBAMBC) with same concentration (1% wt/wt) of CdSe QDs as $Cd_{1\text{-}x}Zn_xS/ZnS$ QDs.

Figure 5 shows the variation of Tanδ for Felix 16/100 and 1% CdSe QD doped FLC system with change in frequency at 35°C. A clear goldstone mode has been observed for both the FLC system with slight shifting of relaxation peak for the doped system. In addition to this a new relaxation peak is also observed for the doped system at higher frequency side of Goldstone mode. It indicates that the doping of QDs is not only disturbing the Goldstone

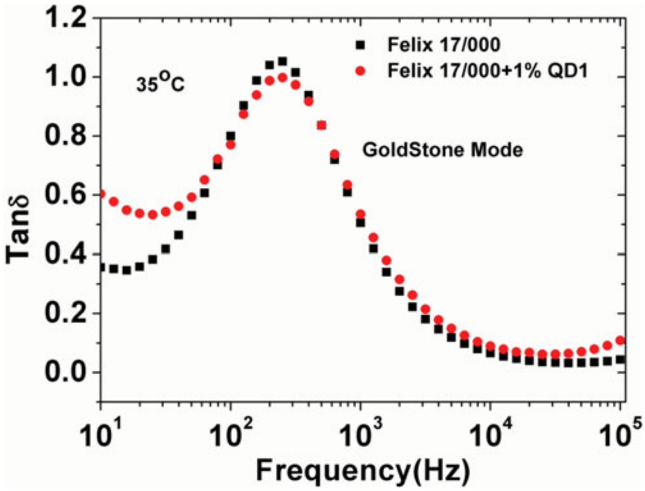

Figure 4. The variation of Tanδ for pure and 1% $Cd_{1-x}Zn_xS/ZnS$ QDs dispersed Felix 17/000 with change in frequency at 35°C.

mode but also causes a new relaxation mode to occur. This suggests that the QDs greatly influence the tilt angle of FLC system in a way to produce a new relaxation mode due to tilt fluctuation. Felix 17/000 and Felix 16/100 are two different FLC mixtures; therefore QDs influences the tilt angle differently due to unlike strength of interactions between QDs and FLC molecules.

It will be interesting to observe the effect of QDs on FLC system if a high relaxation mode similar to the new mode as observed in 16-000 is already present in the FLC system. To understand the effect of change in tilt angle due to doping of QDs in such FLC system,

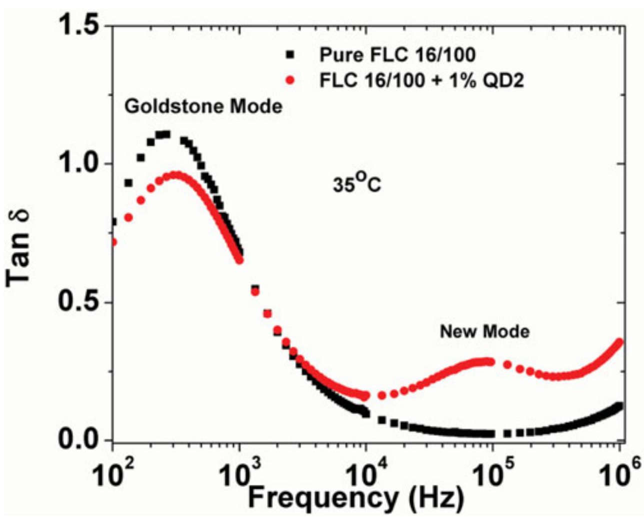

Figure 5. The variation of Tanδ for pure and 1% CdSe QDs dispersed Felix 16/100 with change in frequency at 35°C.

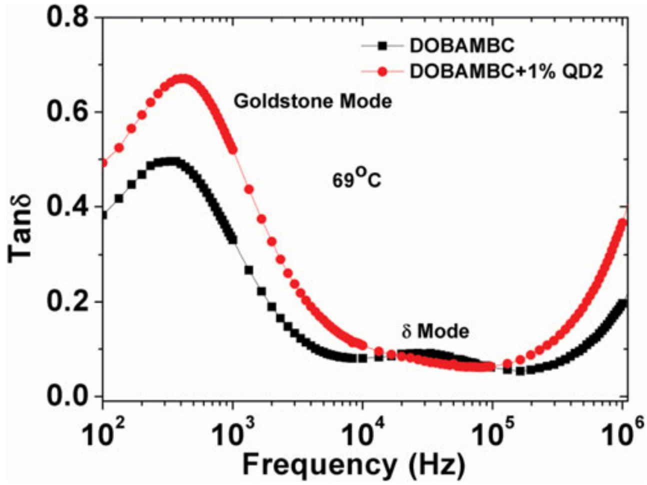

Figure 6. The variation of Tanδ dispersion curve for pure and 1% CdSe QDs dispersed DOBAMBC with change in frequency at 69°C.

1% CdSe QDs have been dispersed in DOBAMBC. Figure 6 shows the Tanδ dispersion curve for pure and 1% CdSe QDs dispersed DOBAMBC at 69°C. A Goldstone mode and δ mode is clearly observed for the pure FLC system. The δ mode is observed due to the small fluctuation of —C = O group in DOBAMBC molecule. In QD2 doped FLC system no such mode is observed however the Goldstone mode is clearly observed with high distribution of relaxation as compared to that of pure FLC.

The effect of QD1 and QD2 on the three FLC systems on relaxation behavior attributes to the alteration of tilt angle in different way in different doped system. This difference in relaxation behavior is observed due to the dissimilar composition and structure of FLC mixture and FLC molecule. Therefore, the QDs induce unlike changes in tilt angle in different FLC system. However, the complete study reveals that the QDs interactions with FLC system give rise to a pretilt to FLC molecules causing change in relaxation behavior due to molecular motion.

4. Conclusions

In shortness, the effect of QDs on the physical parameters of FLC materials has been examined in the present study. The doping of QDs into pure FLC provides a capable way of altering the dielectric and electro-optical properties of the FLC 17/000. The result of the present investigation provide a better understanding of the influence of the semiconductor QDs doping on various properties of FLC. The reduction in the value of various parameters like θ, P_s, and relative permittivity of the doped system has been clarified on the basis of molecular interactions among QDs and FLC material. For the better understanding of the effect of QDs on FLC relaxation process CdSe QDs have been used to dope in two different FLCs (16/100 and DOBAMBC) with same concentration (1% wt/wt) of QDs as that of $Cd_{1-x}Zn_xS/ZnS$ QDs. Thus, the doping of $Cd_{1-x}Zn_xS/ZnS$ QDs into the pure FLC provides possibilities for improvement of different parameters and less energy consumption for the display technology.

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