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TEMPERATURE DEPENDENCE OF FREEDERICKSZ TRANSITION IN NEMATIC LIQUID CRYSTALS WITH QUANTUM DOTS

Emil PETRESCU[1], Stefan TEODORESCU[2], Emilian IUCIUC[2], Voicu ALEXANDRU[2]

Electric Freedericksz transition threshold was determined for 5CB with CdSe/ZnS quantum dots at different temperatures in nematic phase range. The results were compared with those obtained for 5CB only samples on the same temperature range. A discussion was made considering the possible molecular reorientation of 5CB at high temperature and the quantum dots self-assembling in the nematic matrix.

Keywords: nematic liquid crystals, quantum dots, Freedericksz transition.

1. Introduction

Nematic liquid crystals (NLC), widely used in many devices due to the low power consumption of LCD are more often used as a host medium for different kinds of nanoparticles such as carbon nanotubes [1, 2, 3] ferromagnetic nanoparticles [4, 5], ferroelectric nanoparticles [6] or recently discovered quantum dots [7, 8, 9]. Thus, the mechanic, electric, magnetic or optic properties of the nanoparticles can be studied, and new nanotechnologies can be developed.

Thermotropic nematic liquid crystals consist of rod like molecules presenting a crystalline order in liquid phase on a certain temperature range. They present dielectric anisotropy so, when an external electric field is applied the molecule's long axis changes its orientation. Due to elastic interactions between the molecules, this reorientation appears only if a critical value of the field is reached (Freedericksz transition threshold). This threshold field depends on LC's elastic properties but also on molecular orientation inside the cell [10] on the support surface [11]. Many papers studied the temperature dependence of the liquid crystal elastic constant using theoretical [12] or experimental analysis method: magnetic Freedericksz transition [13], acoustic analysis [14], optic or electric properties [15, 16]. They all report or suggest a decrease of the elastic constant of thermotropic liquid crystals when the temperature increases. This

[1] Prof., Dept. of Physics, University POLITEHNICA of Bucharest, Romania, e-mail: emilpd@yahoo.com

[2] Student, Faculty of Applied Sciences, University POLITEHNICA of Bucharest, Romania

means that the transition threshold, for planar aligned cells, should also decrease according to elastic continuum theory which leads to:

$$U_C = \pi \sqrt{\frac{K_{11}}{\varepsilon_0 \left(\varepsilon_{\parallel} - \varepsilon_{\perp}\right)}} \tag{1}$$

where U_C is the critical threshold value, K_{11} is the splay elastic constant, and $\varepsilon_{\parallel} - \varepsilon_{\perp}$ is the liquid crystal dielectric anisotropy. Experimental data obtained at different temperatures indicate a decrease of the critical voltage at low temperatures, $(T - T_{NI} < -6$ °C). After this temperature, all the samples, with or without quantum dots, present an increase of the critical threshold from 6 to 3 Celsius degrees below the nematic isotropic transition, followed by a decrease to isotropic phase limit.

2. Materials and Methods

Liquid crystal samples were prepared using 5CB nematic and CdSe/ZnS alloyed quantum dots (QD) in toluene with the florescence wavelength of 630 nm and an average size of 6 nm from Sigma Aldrich. The quantum dot solution was added into 5CB and sonicated for several hours. Then the mixture was placed in a vacuum room for several days until the whole toluene was evaporated. Finally, we obtained two mass concentrations of QD in nematic host: one of 0.8 % and one of 0.36 %. These mixtures were used to fill 15 micrometers thick planar aligned cells from Instec. The critical voltage was determined for each one at different temperatures in the nematic range using the experimental set-up presented in Fig. 1.

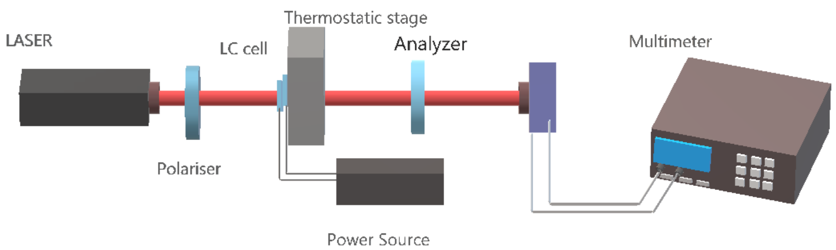

Fig. 1. Experimental set-up for determining the electrical Freedericksz transition.

Each cell was placed on a holder in the hot stage of the thermostat which stabilized the temperature with an accuracy of 0.1 °C. The holder terminals were connected to an alternate power source providing a step signal with the frequency of 10 kHz. A 632.8 nm laser beam was sent to the sample through the window holes of the thermostatic stage. Two crossed polarizers were placed on each side of the sample oriented at 45° from the laser polarization axis to obtain equal intensities for ordinary and extraordinary beams. The emergent beam was recorded using a ThorLab photovoltaic cell at different temperatures in the nematic range.

3. Results and Discussion

The intensity versus voltage plot was recorded for each sample by increasing the applied voltage with 0.1 V for each measurement. As it can be seen from the plot presented in Fig. 2, the emergent intensity is constant for low voltages and presents a succession of maxima and minima after the critical voltage (Freedericksz transition threshold) is reached. This dependence appears as a result of nematic liquid crystal refractive index variation due to the molecular reorientation under the action of the applied field. Thus, the transition threshold might be determined from the plot as the point where a significant change in the intensity is observed. In Fig.3 are presented the evaluations of the critical voltage for the three QD concentrations shown in Fig. 2.

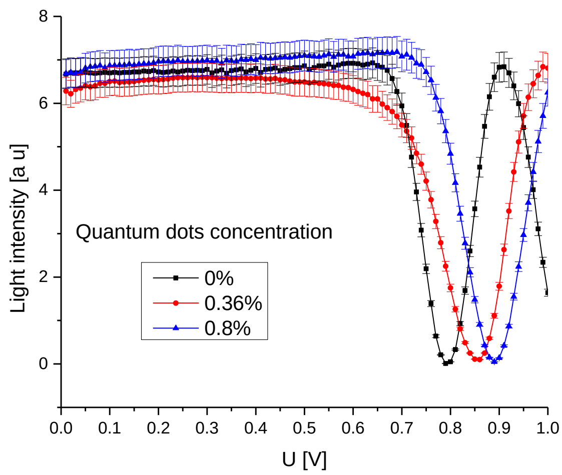

Fig.2. Intensity versus voltage plot for the 5CB planar aligned sample with different mass concentrations of quantum dots, at 3 °C below the nematic-isotropic transition.

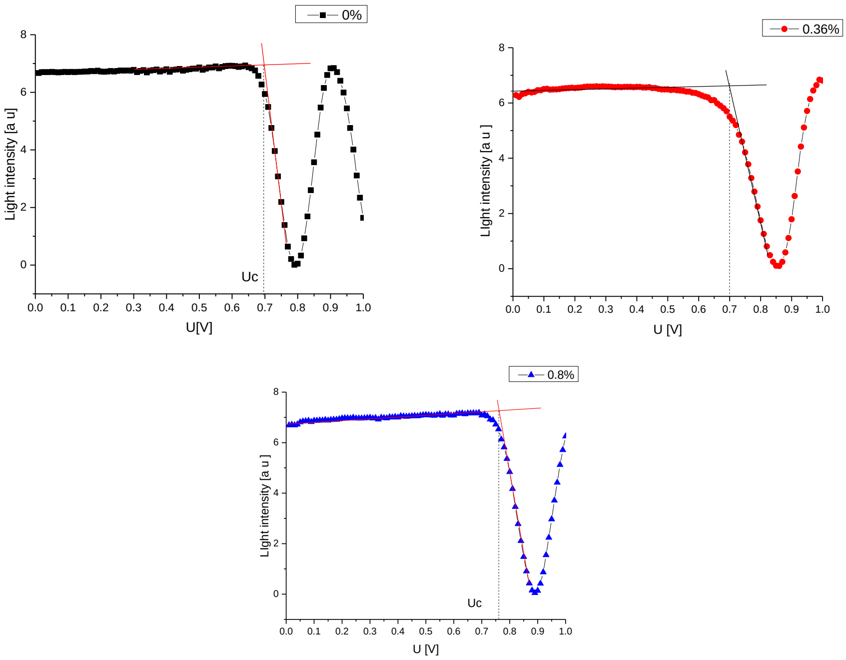

Fig. 3. Freedericksz transition threshold evaluation method using the intensity versus voltage plot for each concentration value, at 3 °C below the nematic-isotropic transition.

Similar plots were recorded for other temperatures in the nematic domain. Finally, a critical voltage versus temperature plot was obtained for the three analyzed samples (Fig. 4).

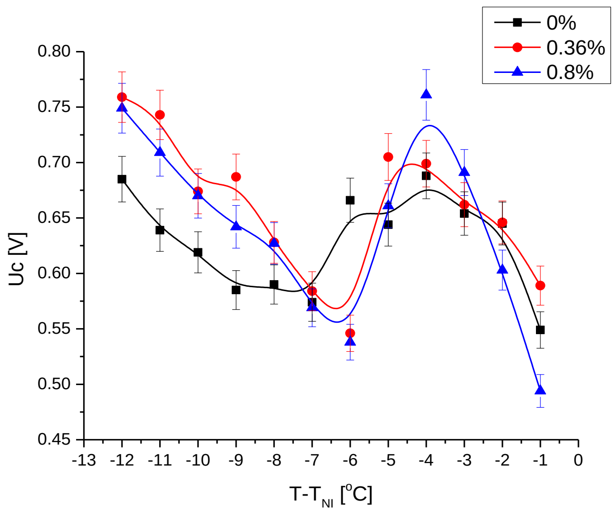

Fig. 4. Freedericksz transition threshold versus temperature of 5CB at different concentrations of quantum dots. Lines are guide to the eyes.

As it can be noticed, the critical threshold decreases with the increase of the temperature only for the first temperature in the range. When approaching to the nematic-isotropic transition limit, all the curves present a maximum followed by another decrease. Singh &Co [17] observed on a similar system a strong decrease of dielectric anisotropy which might compensate the elastic constant variation and explain the critical voltage increase between 6 °C and 3 °C below the nematic isotropic transition. On the other hand, when approaching to the isotropic phase, elastic constants also have strong decrease leading to smaller critical voltage [12], [15] which might explain the increase of the ratio between elastic constant and dielectric anisotropy.

Bogi and Faetti [15] studied the elastic and dielectric properties of 5CB versus temperature and their results were in good agreement with other results in the literature. Using their values for a simulation of critical voltages obtained from Eq.1, no maximum is observed near the nematic isotropic transition (Fig. 5). This means that there are some additional pre-transition phenomena, induced by temperature variations, that must be considered.

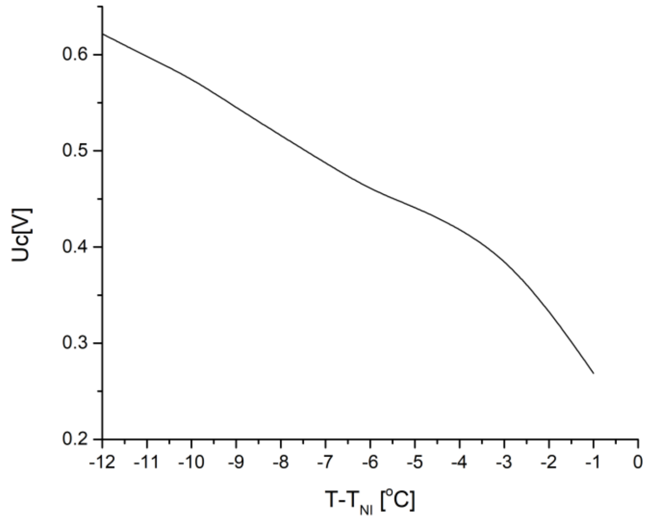

Fig. 5. Theoretical dependence of critical voltage on temperature.

Performing the same experiment, without an applied voltage, the intensity dependence versus temperature plot is similar to the one obtained for the Freedericksz transition threshold versus temperature (Fig. 6), confirming the temperature influence on molecular reorientation.

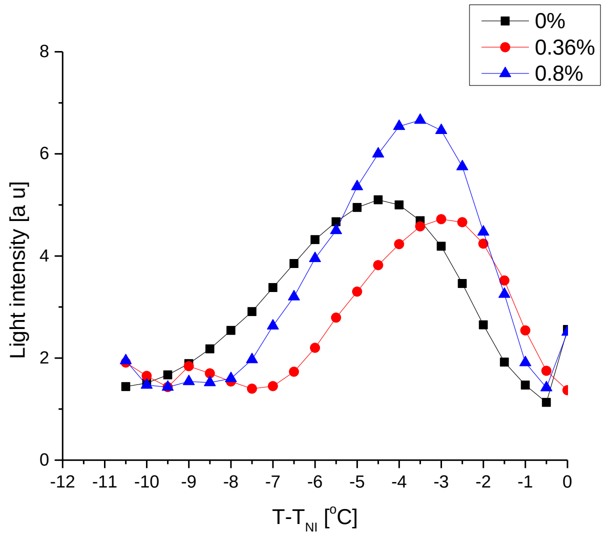

Fig.6. Emergent intensity through 5CB and 5CB+QD samples versus temperature without applied voltage.

From Fig. 4 it can also be observed an inhomogeneous dependence of the critical voltage on quantum dots concentration. From 12 °C to 7°C below the nematic isotropic transition, the doped samples with QD present higher critical voltages than the pure LC sample. This might be explained considering the quantum dots self-assembling in the liquid crystal matrix reported in [8] and [18] which suggest an increase of the transition threshold considering an analogy with the magnetic system presented in [19]. The smaller critical voltage obtained for the 0.8% concentration samples as compared to the 0.36%, one might be explained by the large size of quantum dots clusters. Thus, they pass from nanoparticles to microparticles range exhibiting completely different electric properties which affect the Freedericksz transition.

At higher temperatures, the nematic host's viscosity decreases so that the particles are easily dispersed in the sample. A different structure is obtained in the LC sample and a decrease of the critical voltage with the quantum dots concentration is observed. Koshina&Co [20] also reported a decrease of transition threshold when quantum dots were added. Other reports [7, 17] indicate a good dispersion of spherical quantum dots inside the nematic cell and a homeotropic alignment of LC molecules on quantum dot's surface.

A detailed theoretical discussion on the influence of quantum dots on Freedericksz transition threshold must also consider a particular alignment of molecular director on quantum dots surface as it is known there are many effects induced by the molecular director orientation and its distortions induced by laser field [21-22], by surface anchoring [23], or by LC viscosity [24]. Generally, we noticed a strong influence of nanoparticles doping on liquid crystal static properties [25 - 30].

6. Conclusions

Freedericksz transition threshold voltages were determined for thermotropic liquid crystal with or without 5CB at different temperatures in the nematic phase range. Experimental plot revealed the complexity of these mixtures due to the liquid crystal behavior at different temperatures and also due to the quantum dots self-assembling in certain conditions of temperature and concentration. A discussion of experimental results is made also considering previous research in this domain pointing some aspects that should be considered for future analysis of QD+LC systems.

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