23.3: Cholesteric Colloid of Ferroelectric Nano-particles

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Abstract

In this paper, we report on the influence of sub-micron ferroelectric particles on optical, dielectric and electro-optical properties of cholesteric host. An ultra-small fraction of ferroelectric nanoparticles in a cholesteric liquid crystal greatly increases the birefringence of the latter and its dielectric anisotropy that results in a broadening of the reflection band, decreasing of the driving voltage of the switching between bistable textures and in an increasing of its steepness.

1. Introduction

A supramolecular helical structure of chiral nematic liquid crystals (cholesterics) brings a lot of fascinating properties. If the helical pitch is comparable to the wavelength of light a distributed optical feedback results in selective light reflection and giant optical activity. Effective control of helical pitch value and chiral structures of cholesterics by external field and temperature makes cholesterics extremely promising for uses in photonic and electro-optic devices, such as photonic crystals, light shutters and switches, adaptive laser-optics and lasing.

Effect of electric-field-driven texture transition between planar and focal conic textures makes a base of operation of bistable cholesteric displays [1], future of which looks incredible due to fascinating possibility to make flexible polymer bistable LCD's by roll-to-roll technology [2]. Despite substantial advantages, a wide use of cholesteric LCD's is still restrained by high driving voltages and rather low contrast of the devices. Therefore, development of new cholesteric materials is a crucial task for a widespread application of cholesteric LCD's.

Recently a new class of LC systems has been proposed – diluted colloids of ferroelectric nanoparticles in nematic matrixes [3-4]. These systems macroscopically appear identical to a pure nematics providing, however, strongly enhanced optical and electro-optical properties. In particular, ferroelectric nanoparticles strongly increase dielectric anisotropy and birefringence of the nematic host. Our preliminary studies also showed advanced characteristics of cholesterics doped with ferroelectric nanoparticles. Introducing the particles leads to the decrease of driving voltages, increase of the both reflection contrast and the steepness of the transition [5].

2. Experimental

Nanoparticles of submicron size were fabricated by a long-lasting milling of (1÷10) μm micro-crystals of ferroelectric material thiohypodiphosphate ($Sn_2P_2S_6$) together with an oleic acid working as a surfactant. The micro-crystals were ultrasonically dispersed and grounded in a vibration micro-mill for 120 h. The upper size limit of the particles 0.2 μm was estimated with scanning electron microscopy. The nanoparticles–surfactant mixture was dispersed in a cholesteric matrix by an ultra-sonic mixer, making the cholesteric colloid with a volume fraction of the particles, $c_v \approx 0.2\%$. The cholesteric mixture (CLC) that consisted of nematic matrix ZLI 4801-000 doped with 35 wt.% of a chiral agent R-811 (both from Merck). Clearing temperature of the cholesteric mixture appeared to be $T_c = 69\ ^oC$. We also studied the colloid of ferroelectric particles of the same concentration in the only nematic matrix ZLI 4801-000 (NLC), which exhibited nematic – isotropic phase transition at $T_c = 97\ ^oC$. Both colloids were stable during at least several months. To estimate the influence of the employed surfactant its mixtures with the both chiral nematic and pure nematic LC's were made

The colloids were studied in the cells comprised of two ITO coated glass substrates each covered with rubbed polyimide polymer layers and separated with rod-like polymer spacers. The cells' gaps were in the range $d = 4.5 \div 20$ μm. For the studies of the electrically driven texture transition, the bared ITO-coated substrates were used. The filling of the cells was made at elevated temperature, $T > T_c$.

3. Results and discussion

3.1 Properties of Chiral Nematic Systems

Introduction of an ultra-small fraction of ferroelectric nanoparticles into a cholesteric LC resulted in well-profound changes of basic optical and electro-optical characteristics of the cholesteric matrix. The maximum of the Brag selective reflection band at 40 ^oC has been shifted towards shorter wavelengths ($\delta\lambda^{max} \approx 27\,nm$), and the halfwidth of the Brag band has been increased ($\Delta\lambda_{LC} \approx 36\,nm$, $\Delta\lambda_{col} \approx 39\,nm$), as is seen in Figure 1.

Direct measurements of the cholesteric pitch by measuring the distance between Grandjean-Cano disclination lines in a wedge cell showed also a decrease of the chiral pitch value in the colloid: from $P_{LC} = 332\,nm$ to $P_{col} = 302\,nm$. Since the halfwidth of the Brag band, the pitch and the birefringence of the cholesteric matrix are related as:

$$\Delta\lambda_{LC} = P \cdot n_a ,$$

these data allowed us to estimate the relative changes of the birefringence of the CLC nano-colloid with respect to the pure cholesteric mixture: $n_{a,col} / n_{a,LC} \approx 1.19$.

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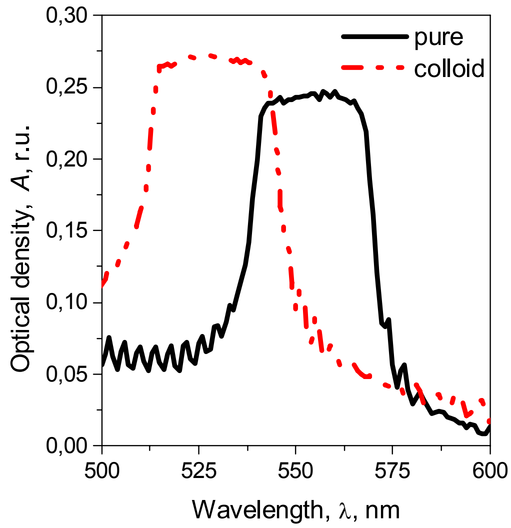

Figure 1. Selective reflection from planar CLC layer: solid line – pure CLC, dashed line – ferroelectric CLC colloid

In the agreement to our tentative results [5], we found that the ferroelectric particles changed the bistable electro-optical response of the cholesteric. The measuring setup corresponds to the conventional driving scheme [1]. First, a resetting voltage V_{reset} (1 kHz, 60 = V) during 100 ms was applied to switch the material to the homeotropic stage and reset to the planar texture afterwards. After a 1 s delay the addressing pulse was applied during 100 ms, and the reflectance of the cell at the 35^o-incidence was measured (Figure 2).

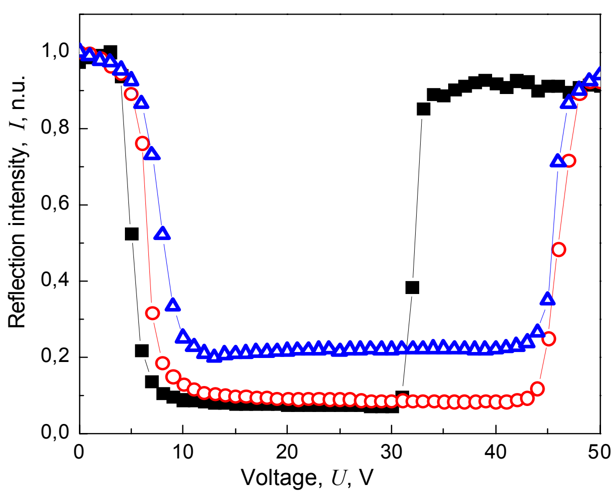

Figure 2. Voltage-contrast characteristics of texture transition: open circles – pure CLC, solid squares – ferroelectric CLC colloid, open triangles – CLC-surfactant mixture.

The dependence of the cell reflectance on the addressing pulse voltage for the cholesterics and colloid is shown in Figure 2. One can see a substantial decrease of the threshold voltage of transition from the planar texture to the homeotropic one: $U_{LC}^{p-h} \approx 48\,V$; $U_{col}^{p-h} \approx 33\,V$.

The threshold voltage of the planar-homeotropic transition can be estimated according [1] as:

$$U^{p-h} \approx \frac{\pi^2}{P}\sqrt{K_{22}/\varepsilon_0\varepsilon_a} \; .$$

Assuming that the Frank constant K_{22} is not affected by the particles one can estimate the relative change of dielectric anisotropy, ε_a, in the colloid: $\varepsilon_{a,col}/\varepsilon_{a,LC} \approx 2.6$.

3.2 NLC Nano-Particle Colloid

Thus, the described results denote that the changes of the optical properties and electro-optical response of cholesteric LC are determined by substantial increase of the both birefringence and dielectric anisotropy of the matrix due to the presence of the particles. To check this idea, were measured the dielectric constants perpendicular and parallel to the director, $\varepsilon_{\|}, \varepsilon_{\perp}$, and birefringence, n_a , of the pure LC and nano-colloid, made solely with the nematic constituent. To determine a possible contribution of the surfactant to the changes of the properties of the nematic matrix, the NLC doped with 2 wt.% of the oleic acid was also studied. This volume fraction of the surfactant was certainly larger than that in the nano-colloid. The measurements of the capacity of LC cells with planar and homeotropic alignment were performed by a standard bridge technique. The results of the measurements together with the values of the clearing temperatures are shown in the Table 1.

Table 1. Values of dielectric constants, dielectric anisotropy and clearing temperature of NLC ZLI-4801-000, its nano-particle colloid and its mixture with surfactant.

	Nematic matrix	Nematic-nano-particle colloid	Nematic doped with surfactant
$\varepsilon_{\perp}$	2.8	4.0	2.9
T_{N-I}	6.2	12.6	6.2
ε_a	+3.4	+8.6	+3.3
T_c , ^{o}C	96	94.5	91.5

It is seen that while the values $\varepsilon_{\|}, \varepsilon_{\perp}$, remain almost unchanged for the NLC-surfactant mixture, a remarkable increase of the both components as well as of the dielectric anisotropy has been observed for the NLC-nano-particle colloid. These results are supported by observations of the significant drop of the Freedericksz transition voltage in planar cells filled with the colloid (Fig.3).

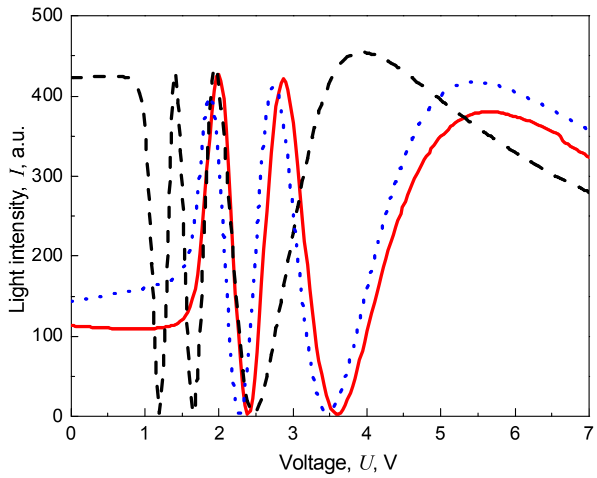

Figure 3. Investigations of Freedericksz transition: solid line – pure NLC, dashed line – NLC-nano-particle colloid, dotted line – NLC-surfactant mixture.

It is clearly seen that the Freedericksz threshold voltage in the colloid is substantially shifted towards smaller voltages than that of the both pure NLC and its mixture with the surfactant. From the expression for the Freedericksz threshold voltage [6]:

$$V_{Fr} = \pi \sqrt{\frac{K}{\varepsilon_0 \tilde{\varepsilon}_a}}$$

it is possible to estimate the changes of the effective dielectric anisotropy of the colloid with respect to the pure NLC given that the Frank elastic constants remain unchanged. Indeed, on the one hand, a very small shift of the clearing temperature have clearly pointed out the order parameter in the colloid [7] remained unchanged. On the other hand, we have performed measurements of the times characteristic of the relaxation of director from the Freedericksz transition after the field removal for the all of the NLC systems, which have also supported the assumption of the elastic constants stability.

Thus, the estimated by the independent methods increase of the effective dielectric anisotropy of NLC nano-colloid $\varepsilon_{a,col} / \varepsilon_{a,LC} \approx 2.6 \pm 0.1$ coincides surprisingly well with that obtained from the measurements in the cholesteric colloid ($\varepsilon_{a,col} / \varepsilon_{a,LC} \approx 2.6$).

3.3 Increase of Birefringence

In addition, the estimations of phase retardation values were made from the Freedericksz transition experiments, which have also shown a remarkable increase of the birefringence in the nano-colloid: $n_{a,col} = 0.106$ with respect to the pure NLC (0.091). The value of the ratio $n_{a,col} / n_{a,LC} = 1.16$ appeared to be rather close to the value obtained for the cholesteric colloid (1.19). Alongside with the dielectric constants, there was also no any notable influence of the surfactant on the birefringence of NLC.

The dependences of the birefringence n_a of the pure nematic LC, the nematic doped with the surfactant and of the colloid on the reduced temperature T/T_c are presented in Figure 4.

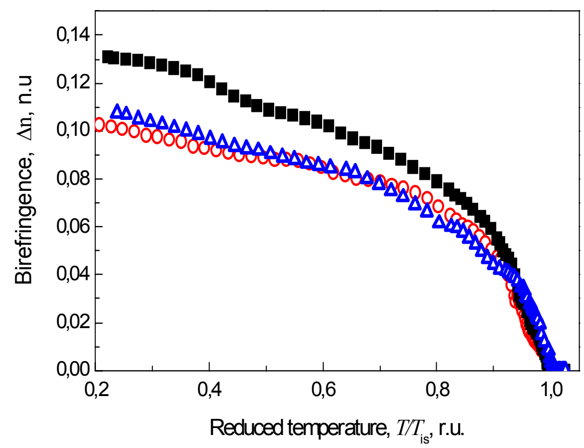

Figure 4. Temperature dependences of phase retardation: open circles – pure NLC, solid squares – ferroelectric NLC nano-colloid, open triangles – NLC-surfactant mixture.

One can see that the dependences $n_a(T/T_c)$ for the pure and doped nematics practically coincide. It corresponds to the general consequence of Mayer-Zaupe theory about universality of the dependence of nematic order parameter on reduced temperature [8] and points at dispersion interaction between the surfactant and nematic matrix in our case. Insertion of the ferroelectric particles, however, results in the evident shift of the dependence $n_a(T/T_c)$. It allows us to suggest that the increase of the refractive index in the colloid is caused by a strong dipole – dipole interaction between the particles and LC molecules. High anisotropy of polarizability of the particles, which might be another cause of the birefringence increasing, was, however, ruled out by an additional comparison of refractive indices of the isotropic phases of NLC nano-colloid and pure NLC, the difference in which appeared to be less than 1%.

4. Conclusions

Introduction of ferroelectric nanoparticles into cholesteric matrix has been shown as a promising method of improvement of electro-optical characteristics of different LC cells by a non-chemical way. A low fraction of the ferroelectric particles led to the broadening of the reflection band, essential decreasing of the driving voltage for switching between bistable textures and increasing the steepness of the switching. These changes are the result of the strong effect of the ferroelectric particles on the optics and dielectric properties of the nematic matrix. The observed increase of the birefringence and dielectric anisotropy of the nematic matrix by the particles is caused by a giant dipole moment of ferroparticles that change the intermolecular interaction in the LC matrix and give a direct contribution to the value of the effective dielectric constants of the matrix. The obtained results seem to be very important in view of improvement of the working characteristics of the materials utilized in bistable cholesteric LCD's.

6. Acknowledgements

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