Birefringence studies in ferroelectric liquid crystal doped with titanium dioxide nanoparticles

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Abstract—The following research work determines experimentally the birefringence of the ferroelectric liquid crystal (FLC) W212 doped with titanium dioxide nanoparticles (TiO_2 NPs) of low concentration in the FLC matrix. For this reason, the method based on transmittance measurements through the investigated sample in the polariscope setup is applied. Optical microscopy observations indicated good alignment quality of the FLC-NP mixtures in planar glass cells. The birefringence measurements clearly indicate that TiO_2 NPs reduce the birefringence of the W212 FLC for wavelengths in the measured range between 500 nm and 700 nm. The results can be valuable, especially in the context of modeling and designing a new class of FLC-based optical elements both in planar cells and photonic liquid crystal fibers.

Ferroelectric liquid crystal (FLC) is the common name for chiral smectic C* liquid crystals (SmC*) formed of elongated molecules aligned in a helicoidal structure. They have been extensively studied for their significance in the development of optoelectronics and modern photonics, resulting in various applications [1]. A recent review of the state of the art of FLCs in photonic technology was published elsewhere [2].

The FLCs possess inherent ferroelectricity within the helical molecular structure, providing even faster electro-optical response times than commonly used nematic liquid crystals. For the first time, the ferroelectricity in SmC* was observed by Meyer in 1975 [3]. To meet the requirements for FLC-based photonic devices, the materials must satisfy many crucial parameters, such as the temperature range of the SmC* phase, spontaneous polarisation, birefringence, rotational viscosity, elastic constant, and dielectric anisotropy. The behavior of these parameters also strongly depends on external physical factors like temperature or electric and magnetic fields. The FLC's response time is defined as the relation between rotational viscosity γ_φ and spontaneous polarisation P_s and applied electric field intensity E according to the formula:

$$\tau = \frac{\gamma_\varphi}{P_S E} . \qquad (1)$$

Short switching times in the FLCs are possible when rotational viscosity is low and spontaneous polarisation is high. However, large values of the spontaneous polarisation can also increase the rotational viscosity of the FLC material. Another critical factor in the context of photonic applications of the FLCs is their molecular alignment and order parameters. Some difficulties in proper alignment in the SmC* phase may occur due to the influence of the temperature. By decreasing the temperature, the FLC layer tends to lower its thickness. As a result, the alignment of the FLC molecules can change from a homogeneous bookshelf structure into a chevron structure with local defects [4]. To avoid disturbed alignment of the FLC molecules, thermo-aligning and photo-aligning techniques can be utilized [5−6]. Recently, there have also been successful attempts to enhance the FLC parameters by doping the FLC with different kinds of nanoparticles (NPs), such as gold [7]. In recent years, titanium dioxide (TiO_2) NPs have exhibited significant potential for doping FLC materials. The TiO_2 NPs allow the suppression of free ionic charges that are usually present in the FLC and have a negative influence on the FLC parameters.

As reported by Gupta [8], the TiO_2 NPs, when dispersed in FLCs, cause a reduction of the D.C. conductivity and increase the FLC-NP spontaneous polarization. Some of the positive impacts of the TiO_2 NPs on enhancement of the FLC parameters were reported in [8–10].

The following research investigates the birefringence behavior in FLCs doped with TiO_2 NPs as a potential candidate for tuneable FLC-based polarising devices. In the previous work [11], the influence of TiO_2 NPs on spontaneous polarisation and response time in the photonic liquid crystal fibers was reported. It is believed that the presence of the TiO_2 NPs in the FLC can control the birefringence of the mixture.

To determine the birefringence of the FLCs, different methods have been reported, such as the modified method of the Abbe refractometer [12], the laser transmission technique [13], or the Fabry-Perot interference approach [14]. However, the most convenient method is based on the measurement of the white light transmittance through the homogeneously aligned FLC sample placed between two crossed or parallel polarisers under 45 degrees with respect to the polariser axis according to the formula [15]:

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$$\Delta n = \frac{\lambda}{\pi d} arctan\left(\sqrt{\frac{T_{cross}(\lambda)}{T_{par}(\lambda)}}\right), \qquad (2)$$

where $T_{cross}(\lambda)$ is the normalized transmittance through the sample between crossed polarisers and $T_{par}(\lambda)$ is the normalized transmittance through the sample between two parallel polarizers. The typical values for the FLCs birefringence are between 0.15 to 0.25. However, lower birefringence values are also desired in the photonic applications [12]. It should be noted that the FLC's birefringence can be influenced by an external electric field applied to the sample. In this case, the effective birefringence of the FLC should be defined as [16]:

$$\Delta n_{eff}(\lambda) = \Delta n\left[1 - \frac{3}{2}sin^2(\theta) + \frac{sin^2(2\theta)}{1-\frac{3}{2}sin^2(\theta)}\left(\frac{\varepsilon_0\chi_G}{P_s}\right)E^2\right], \qquad (3)$$

where: θ is the tilt angle, P_s is the spontaneous polarization, and the χ_G is the dielectric susceptibility of the FLC's helical structure, also known as the Goldstone mode.

The explored FLC material W212 (synthesized at the Military University of Technology, Poland) exhibits the following phase transition temperatures upon heating: Cr→ 10ºC→ SmC*→ 99.8 ºC→ SmA*→ 126.6ºC→ Iso. The helical pitch p=7 µm, spontaneous polarisation P_s=100 nC/cm^2, and tilt angle θ=40º were measured at room temperature and reported in [17–19].
The TiO_2 NPs selected for preparing samples were in an anatase form and were fabricated according to the method presented in [9–10]. The mean size of the TiO_2 NPs was 25-35 nm. In the first stage of the FLC-NP nanocomposite preparation, the TiO_2 NPs were dispersed in toluene and subjected to the ultrasonication procedure for 2 hours to ensure a uniform distribution of the TiO_2 NPs in the solution. After leaving the sample for one day undisturbed, the colloid homogeneity was tested optically. Next, the TiO_2 NP solution was mixed with the proper amounts of W212 FLC to obtain 0.2% wt./wt. and 0.5% wt./wt. NPs concentrations.

Low concentrations of TiO_2 NPs were selected to avoid uncontrolled aggregations of the NPs due to non-zero dipole moments and to provide undistorted molecular order of the FLC in smectic layers [20]. The final step of FLC-NP nanocomposite preparation involved ultrasonication for the next 2 hours and evaporating redundant toluene at 70ºC. Sandwich-type planar empty cells with a thickness of 3 µm (HG3.0 from Military University of Technology) and with unidirectional rubbing were used in the experiments. The cells were infiltrated with a W212-TiO_2 mixture through capillary action at the temperature of 140ºC, at which the W212 FLC remains in the isotropic phase. After that, the infiltrated cells were cooled slowly from the isotropic phase to room temperature at 1ºC/min. Moreover, a square-shaped signal of amplitude 20 V_{pp} and frequency of 15 Hz was applied to the cell. A slow cooling procedure and simultaneous application of a low-frequency electric field promote a better alignment of the FLC-NP mixture in the cell's volume. To confirm the quality of the W212-TiO_2 mixture alignment, the samples were observed under the polarizing optical microscope (Keyence VHX-5000) and presented in Fig. 1.

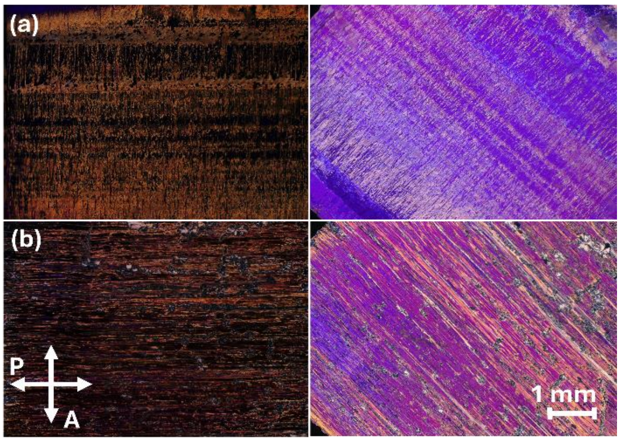

Fig. 1. Optical microscopic textures of W212 FLC doped with TiO2 NPs in (a) 0.2% wt./wt. and (b) 0.5% wt./wt. concentrations observed in the 3µm-thick glass cell. The textures are for azimuths 0 and 45 degrees with respect to the polarizer.

The optical observations indicate that both cells infiltrated W212-TiO_2 are aligned uniformly. However, for the concentration of 0.5% wt./wt. of the TiO_2 NPs, some distortions in the alignment (Fig. 1b) can be observed. It can result from local aggregations of the TiO_2 NPs in the volume.
A schematic diagram of the experimental setup used for performing the birefringence measurements in the W212-TiO_2 mixture is shown in Fig. 2.

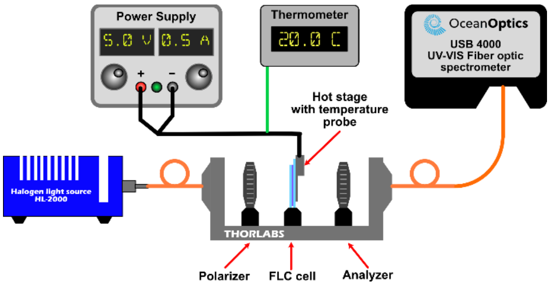

Fig. 2. Schematic diagram of the electro-optical setup for determining the FLC cell's birefringence in function of temperature.

The halogen light source (Mikropack HL-2000) was used to perform the measurements. The light from the input multimode fiber was collimated by the lens and next polarised by the linear polariser with a polarisation axis aligned at the azimuth of 0°. Next, the light beam passes through the investigated FLC-NP cell with its optical axis aligned at 45° with respect to the polariser axis. For thermal measurements, the examined cell infiltrated with the W212-TiO_2 mixture is placed on the custom-made hot stage with a digital temperature sensor of the resolution 0.1°C. The transmitted light beam then passes through the analyzer aligned orthogonally or parallelly to the polariser. Both the polarizer and analyzer are thin-film sodium-silicate polarizers designed for 500–720 nm (Thorlabs, FBR-LPVIS). The optical signal was collected by the fiber optic spectrometer operating in the range of 350–1000 nm (Ocean Optics, USB4000). By analyzing the transmittance of the signal at room temperature (20°C), the birefringence was calculated according to Eq. (2).

The measurements were performed in a spectral range between 500 nm and 700 nm at 20°C. The variation of the normalized transmittance for the undoped W212 FLC sample and doped with the TiO_2 admixture is presented in Fig. 3.

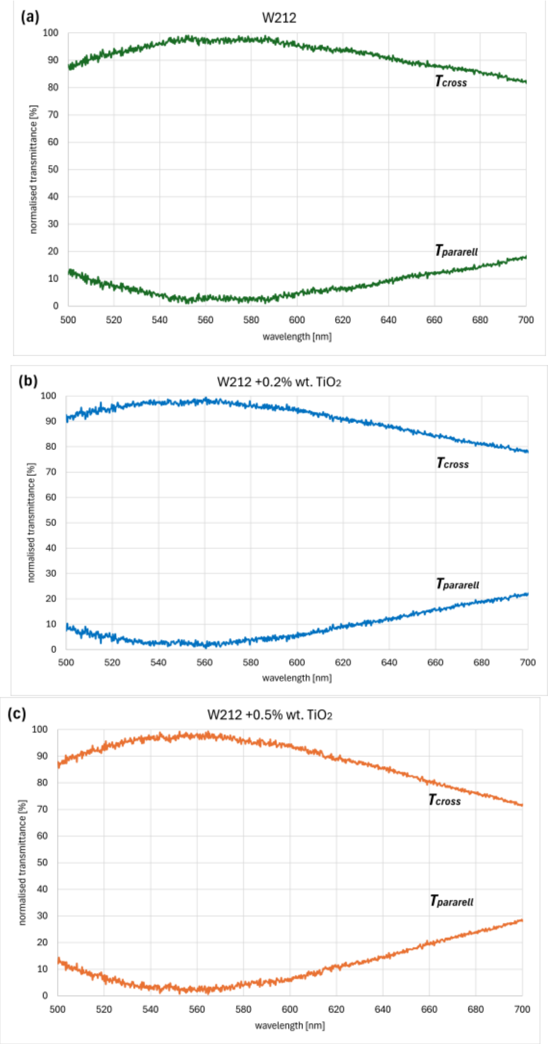

Fig. 3. Normalised light transmittance with crossed and parallel polarisers for (a) undoped W212 FLC sample and doped with TiO_2 NP's admixture in concentrations of (b) 0.2% wt. and (c) 0.5% wt. The layer thickness of each sample was 3μm.

As shown in Fig. 3 the presence of TiO_2 NPs in the W212 FLC caused a change in the transmittance spectra. The results of birefringence measurements are presented in Fig. 4.

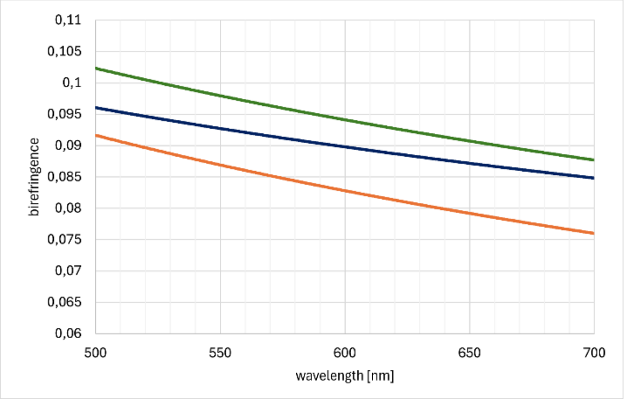

Fig. 4. Dispersion of the birefringence of the examined FLC-NP mixtures measured at room temperature 20°C.

It can be observed that the higher concentrations of TiO_2 NPs as a dopant cause the decrease of the W212 birefringence in the whole measured spectrum. This behavior can be attributed to local disturbances of the order parameter that lead to an overall reduction in the birefringence of the W212-TiO_2 mixture. Moreover, it should be noted that higher concentrations of the TiO_2 dopant may also lead to deterioration of the FLC order parameter and its birefringence.

The influence of temperature on birefringence was also investigated. As mentioned, the investigated cell doped with W212-TiO_2 mixture was heated by a custom-made hot stage controlled by the programmable power supply. A wavelength of 633 nm was selected to estimate the thermal dependence of the birefringence.

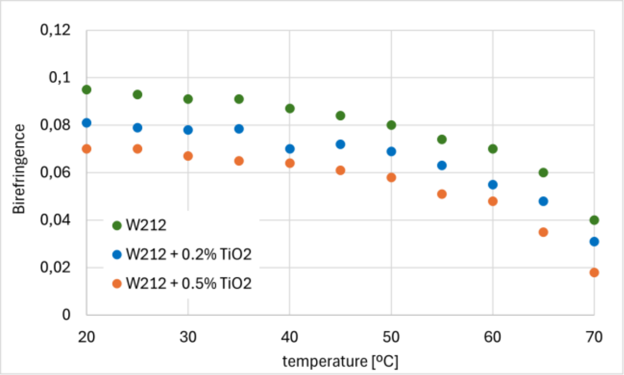

Fig. 5. Temperature variation of the birefringence at the wavelength 633 nm.

The thermal measurements were performed from 20°C to 70°C, in which the investigated samples remained in the SmC* phase. The measurements for higher temperatures were not possible due to the limitations of the heating unit. Nevertheless, as shown in Fig. 5, birefringence from the investigated samples exhibits apparent variations as a function of temperature, which is the expected behavior in FLCs and other liquid crystal materials.

To conclude, it was shown that TiO_2 NPs as a dopant to FLC material influence birefringence. The results indicate that the presence of the TiO_2 NPs can decrease birefringence of the W212 FLC. The measurements were performed for TiO_2 NPs dopants up to 0.5% wt. because higher concentrations of the NPs could lead to deterioration of the FLC order parameter.

The studies that were presented on the determination of W212-TiO_2 birefringence may be valuable, especially in the context of modeling and designing a new class of FLC-based optical elements for photonics. Even though the studies were performed in sandwich-type planar cells, the results can also help develop the photonic liquid crystal fibers infiltrated with a W212-TiO_2 mixture.

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