Titanium nanoparticles doping of 5CB infiltrated microstructured optical fibers

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Abstract—Optical properties 5CB liquid crystal (LC) cells and 5CB infiltrated microstructured optical fibers doped with 1 wt.% titanium nanoparticles (NPs) of the size ~100nm, have been studied. NPs were found to modify properties of both LC cells and LC-infiltrated fibers. Preliminary thermo-optic properties of photonic liquid crystal fiber with Ti-doped 5CB were researched. Additionally, preliminary electro-optic characteristics of the nanoparticles doped LC cell have been obtained.

Liquid crystals (LCs) are still materials of unceasing interest, because of their unique properties as, for instance: electric field-induced director axis reorientation or a relatively wide range of thermally tunable optical anisotropies. All these properties made LCs to be widely used in various electro-optical applications such as, e.g. LC display, spatial light modulators, tunable filters, polarizers and switches. However, these devices still need a significant improvement of their electro-optical response times, which are relatively slow in comparison to electroluminescent devices. Over the last years, a lot of research efforts have been made to improve the properties of LCs by doping them with different materials like polymers, dyes, or carbon nanotubes [1-2].

Recently, there has been a growing interest in dispersing nanopatricles (NPs) in LCs. Metallic NPs can adopt a vast number of structural geometries with an electronic structure. Even a small amount of metallic NPs should be sufficient to influence the dielectric anisotropy and threshold voltage of LCs [3-5]. The most common dopants are gold and silver NPs [6-9]. Both materials have been shown to improve electro-optical properties (such as reducing switching voltage and Fredericks transition) and increasing ionic conductivity, dielectric anisotropy as well as thermal stability of LC. In addition to this, gold nanoparticles are reported to stabilize the nematic phase of an LC host. However, using NPs with an LC is not always flawless. One of the main disadvantages is the aggregation of NPs inside an LC, which affects its properties. Because of that, it is required to stir the mixture before every use to have again a uniform structure. Related to this is the reproducibility of the results. For example, there is no guarantee that every time the stirring process allowed to obtain the same uniform structure without any sediment and due to that the experiment results may slightly differ.

Combining the ease of LC physical properties tuning and structure of a photonic crystal fiber (PCF), a new type of fiber, i.e. photonic liquid crystal fiber (PLCF) was proposed more than 10 years ago [10]. PLCFs are characterized by improved control of spectral, polarization, and guiding properties. It appeared that the use of LCs as an infiltrating material greatly improved previously mentioned optical properties of PCFs. Also, first attempts have been undertaken to infiltrate a PCF with LCs doped with barium titanate NPs [11].

In this paper we report the application of pure titanium (Ti) NPs as a doping material. Titanium is a paramagnetic material with relatively low conductivity. The presence of Ti NPs in a nematic LC should increase the influence of an electric field on LC molecules by trapping charged ionic impurities and by suppressing the screen effect. To our best knowledge, there has been only one paper [12] reporting the use of these NPs. In the mentioned paper, it has been also demonstrated that the electro-optic properties of nematic LCs doped with titanium NPs changed according to Ti nanoparticle doping concentration. However, pure Ti is a highly flammable substance that cannot be used in the presence of air. For that reason, NP doping of the LC was realized in an argon atmosphere within the facilities of the Faculty of Chemistry, Warsaw University of Technology. After NP doping, the LC was mixed with ultrasounds for ~5minutes. Mixing with an LC reduced the flammable properties of an NP material and so it could be used outside an argon atmosphere. In our work we used 1 wt.% concentration of titanium NPs (~100nm) mixed with a 5CB nematic LC, where used NPs were commercially available from Sigma Aldrich, Poland.

Initially, the research involved comparing properties of a pure (undoped) 5CB LC and an LC doped with Ti NPs by placing both materials between two glass plates and observing them under the crossed polarizers of a polarizing microscope. Different molecules orientations were observed. It appeared that the sample with an undoped 5CB had a predominant planar molecules alignment (Fig.1), where the Ti-doped 5CB was

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characterized by a strong self-induced (without any aligning layers on glass plates) homeotropic alignment (Fig.2).

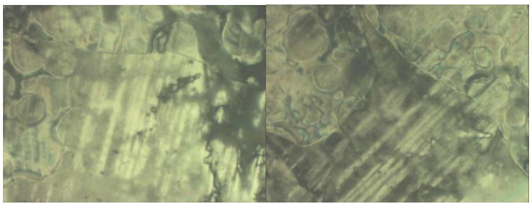


Fig. 1. LC cell with undoped 5CB under crossed polarizers (sample at 0° (left) and 90° (right) relative to polarizers).

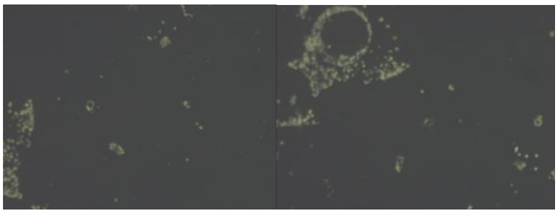


Fig. 2. LC cell doped with Ti nanoparticles right after ultrasonication (sample at 0° (left) and 90° (right) relative to polarizers).

Also there have been observed differences in the alignment quality between LC mixtures with NPs right after (Fig.2) and one day after ultrasonication (Fig.3). We expect that a sort of sedimentation process occurs and, as a consequence, NPs are not any more uniformly distributed within a container and, as a result, the Ti-doped 5CB mixture acts similarly to the undoped sample.

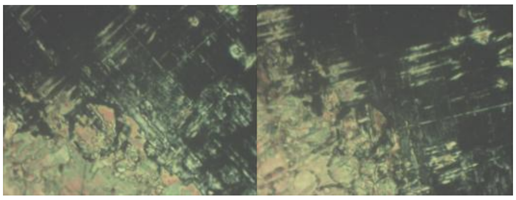
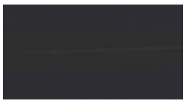


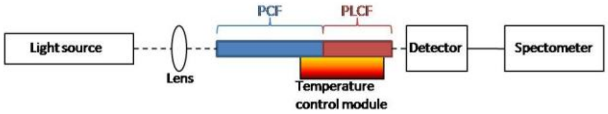
Fig. 3. LC cell with doped with Ti nanoparticels one day after ultrasonication [sample at 0° (left) and 90° (right) relative to polarizers].

Afterwards we put both mixtures inside microcapillaries to check if the results obtained in the LC cells could be repeated in a different geometry. We used silica-based microcapillaries with an inner diameter of 60μm and an outer diameter of 125μm. The samples were filled by capillary forces and observed under a polarizing microscope (crossed polarizers). The results are shown in Fig.4. We can see that in the sample with undoped 5CB, molecules we had a planar alignment at the inner surface of the capillary. However, in the sample with Ti-doped 5CB molecules responded differently, because the presence of NPs might influence the orientation of LC molecules, which resulted in the reduction of an LC order parameter (Tab.1).

Tab.1 Comparison of an LC molecules alignment in microcapillaries infiltrated with a doped and undoped 5CB.

	0° relative to polarizers	45° relative to polarizers	90° relative to polarizers
Sample with undoped 5CB			
Sample with Ti-doped 5CB			

The next step was to put both doped and undoped LC mixtures inside a PCF to obtain PLCFs. A halogen lamp was used as a light source and as a host PCF we used a silica-based fiber with a 125μm diameter and 6 rows of 4.1μm-wide micro-holes. Both PCF samples were 15cm long with 2-3cm PLCF sections infiltrated with the mixtures (Schem.1).



Schem.1. Experimental setup for measuring changes of propagation spectrum in PLCF.

In both cases, a photonic band gap (PGB) effect was observed and there has been a noticeable difference between both spectra of undoped PLCF and PLCF doped with NPs (Fig.4). This phenomenon was related with an investigation of the LC cells under a polarizing microscope. The change of propagation properties in Ti-doped PLCF is due to a change in the refractive indices of an LC in the photonic structure of a PLCF. The spectrum shift characterizing the Ti-doped PLCF could be attributed to NPs distorting LC molecules orientation around them, similarly to what was observed in LC cells (previous part of the experiment).

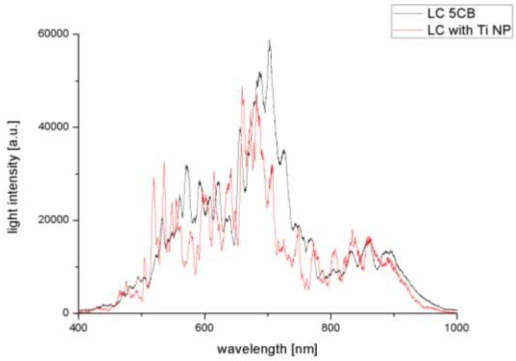


Fig. 4. Propagation spectrum for PCF filled with pure LC and with LC with NP.

We have also investigated temperature dependence of photonic bandgaps in the PLCF filled with NPs. In the experiment, the section of the PCF infiltrated with Ti-doped 5CB, was heated by using the Peltier module and the output spectrum was collected by using an Ocean Optics USB4000 spectrometer with a 0.2nm optical resolution. The thermal shift of photonic band gaps is a common phenomenon in PLCFs [13]. As expected, after heating, temperature tuning of photonic band gaps for the range of 26.6°C to 55.3°C was observed, see Fig.5. It is evident that with increased temperature the PBG become blue shifted. Also a narrowing effect of photonic bandgaps can be observed.

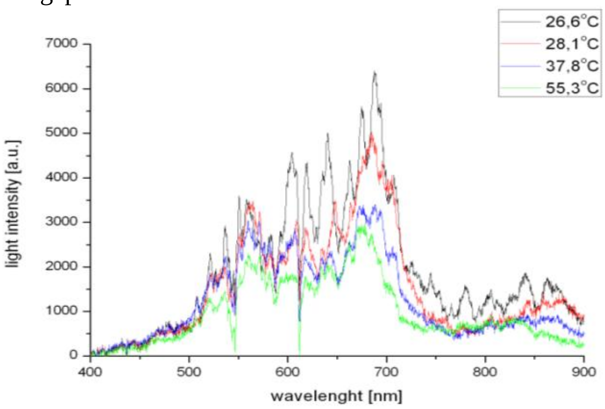


Fig. 5. Thermal tuning of photonic bandgaps in the PLCF infiltrated with Ti-doped 5CB.

Additionally, the influence of an external electric field on both undoped and doped 5CB was investigated. Here, both mixtures were introduced into LC cells with ITO layers with proper surface treatment to induce planar (homogenous) orientation. Preliminary results showed that there are comparable long switching times (10-20ms), independent from the presence of NP (Fig. 6). The comparison of achieved times is presented in Table 2. The fact that in both cases the switching times are comparable may be connected with some of the parameters of the used nematic LC (such as dielectric anisotropy or refractive indices).

Tab. 2. Comparison of switching times in an LC cell with undoped and doped 5CB.

	Rise time [ms]	Fall time [ms]
LC cell with 5CB	24,8	24,8
LC cell with Ti-doped 5CB	24,0	20,0

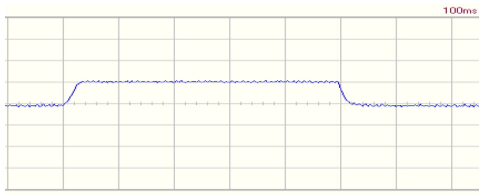


Fig.6 Comparison of switching times for LC cells with undoped 5CB (top) and Ti-doped 5CB (bottom).

In conclusion, there is a noticeable difference both in molecules orientation and in propagation spectra of PLCFs based either on the Ti-doped or the undoped 5CB. Preliminary results indicate that the observed photonic bandgaps can be tuned with temperature towards lower wavelengths. However, this blue shift is not always clearly visible and especially during cooling, the LC molecules need a double period of time to return to their original state. The slow reaction of molecules could corresponds to unstable boundary conditions, due to the lack of appropriate orienting layers. We assume that the bandgap shift, as well as relatively long switching times could be improved by changing the concentration of NPs inside the LC. Further experiments are still in progress.

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