New methods of highly efficient controlled generation of radiation by liquid crystal nanostructures in a wide spectral range

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Abstract. We report the recent results of research focused on a new kind of soft matter – the liquid-crystal nanocomposites with controllable mechanical and nonlinear optical properties. These are promising media for implementation of ultra-compact photonic devices and efficient sources of coherent radiation in a wide spectral range. We overview the technology of preparation of nematic-liquid-crystal media saturated with disclination defects. The defects were formed in different ways: by embedding nanoparticles and molecular objects, by exposure to alpha-particle flux. The defect locations were controlled by applying an electric field. We also present and discuss the recently discovered features of nematic-liquid-crystal media: a thermal orientation effect leading to the fifth-order optical nonlinearity, enormous second-order susceptibility revealed by measurements, and structural changes upon exposure to laser radiation. We report on efficient generation of harmonics, sum and difference optical frequencies in nematic-liquid-crystal media. In addition, transformation of laser radiation spectra to spectral supercontinua, and filamentation of laser beams were also observed in nematic-liquid-crystal media. We conclude that most nonlinear optical effects result from changes of the orientational order in the examined nematic liquid crystals. These changes lead to the symmetry breaking and disclination appearances.

1. Introduction
Nowadays a special kind of physical medium referred to as soft matter (or partially ordered media) is under intensive study in the physics of condensed state of matter [1]. Distinctive feature of soft matter is that the properties of such matter can undergo significant changes under relatively weak external action. The main focus of the mentioned study is exploration of intermolecular structures and forces, viscoelastic interactions, chemical bonds, and other features which govern mainly mechanical and linear optical properties of soft matter. Nonlinear optical properties of such matter are also varied. Their study may be both of scientific interest and leading to new practical applications.

Liquid crystals (LCs) are perhaps the most known and widely-used representatives of soft matter systems [2]. Besides nonlinear optical properties of LCs themselves, of particular interest are the properties manifested by LC-based composites with nanoparticles. Interest in LC-nanocomposites is aroused so far as creation of ordered defect structures [3] in such media opens up possibilities for design and implementation of a novel type of multidimensional photonic crystals with controllable nonlinear optical properties.

It is well known that, liquid crystals are viscous liquids with a structure determined by order and shape of constituent molecules [1,2]. Such liquids feature properties peculiar to crystals, in particular,
– anisotropy. Orientation vector of dipole molecules – director – determines the direction of an optical axis in LCs. The director is strongly affected by external factors, namely, electromagnetic fields (Freedericksz effect [1,2]), and thermal flows (thermal orientation effect [4]).

Orientation structure of LCs is not necessarily homogeneous. It may have singularities with ambiguous orientation of the director [3]. Orientation defects (in particular, disclinations) can be caused both by external actions and by internal factors. The volume form of a LC itself is one of the structuring factors. The defects can be produced also by particles embedded in LC structure. Of particular interest are nanoparticles, molecular particles, and alpha-particles that interact with LCs [5,6]. A foreign particle can make the center (singular point) of disclination the same as the volume form do. The state of LCs in the neighbourhood of singularities, the birth and interaction of disclinations, their impact on optical properties of LCs are not yet exhaustively studied and explained. However, it is precisely this fact that the mentioned particular state of LCs saturated with defects features extraordinary physical properties leading to a variety of effects useful for new practical applications. In what follows we study such effects and propose their application in photonics.

2. Nematic liquid crystals with particles-induced defect structures

In First, the effects given by insertion of nano-, molecular-, and alpha- particles into nematic liquid crystals (NLCs) subjected to an electrostatic field were studied experimentally and theoretically. Inserted particles form charged defects in the orientation structure of NLCs. The radius of these defects exceeds many times the size of the particles themselves. This phenomenon can be used as an efficient method to produce NLC orientation structures saturated with charged defects. The figure 1 shows the experimental setup used to observe modification of NLC orientation structures upon insertion of particles and application of electric field. The areas of complex optical anisotropy appear around singular points created by inserted particles. The resulting optical texture of the NLC orientation structure was visualized by means of polarizing microscope. The figure 2 and figure 3 show the images of the textures obtained with the use of NLCs doped by gold nanoparticles (~20 nm in diameter) and molecular particles (cromolyn), respectively. The textures appeared when an external spatially uniform electric field was applied. This electric field moves charged nanoparticles, initially situated on the substrates, into the volume of NLC. In this experiment the thickness of the NLC layers was ~ 100 microns. The concentration of the particles in the NLC layers was $10^4 \div 10^5$ mm$^{-2}$. The dc voltage applied to the electrodes was ~3 V.

Figure 1. Experimental setup used for observation of nanoparticle-induced singularities in the NLC orientation structure: 1 – light-emitting diode, 2 – condenser, 3 – polaroid, 4- NLC sample (5 – glass plates with electrodes formed by ITO-coating, 6 – spacing, 7 – NLC volume, 8 – electrodes formed by ITO-coating, 9 – leads of electrodes), 10 – polarizing microscope with a CCD – camera.
When NLC samples with nanoparticles were placed in a spatially periodic electrostatic field, we observed ordering optical textures, as shown in Figure 4. To produce such a regular array of nanoparticle-induced singularities we made use of glass substrates with special arrangement of electrodes formed by ITO-coatings (Figure 5). In these structures the spatial period (the lattice spacing) is fixed, but the refractive index and its gradient in the cells formed by singularities can be tuned by varying the strength of external electric field. Scaling down the dimensions of electrodes and applying independent voltage control to them, one can create a completely controllable phase grating. It is opens up opportunities for the development of a new class of photonic devices – 2-D and 3-D electronically controlled, variable photonic crystals.
A steady-state configuration of the director orientation in the vicinity of a nanoparticle-induced singular point, and the resulting optical pattern in light transmitted through crossed polarizers were also found theoretically [6]. Examples of the calculated graphs are depicted in figure 6 (a) and figure 6 (b). The calculations yielded almost all defect structures observed in the experiments with single nanoparticles (one nanoparticle in a large volume of NLC). Figure 6 (c) presents the microphotograph of an experimentally observed optical pattern of the defect arising from a single nanoparticle in NLC. The dense embedment of interacting nanoparticles in NLCs is not yet studied theoretically.
In addition we visualized the defect structures formed in NLCs by alpha-particles. To this effect the NLC sample was irradiated by alpha-particles from radioactive isotopes placed under the glass substrate. The particle energy was 4.5 MeV, the intensity of the particle flux was 10 decays\(\text{s}^{-1}\text{cm}^{-2}\). Because of non-transparency of the used radioactivity source we performed observation with incident light only. When a spatially uniform electric field was applied to the NLC sample being irradiated by alpha-particles, we observed (by means of a polarizing microscope) moving bright spots with irregular shapes (figure 7). The alpha-particles produce local dipole fields [5] which, being subjected to an external electric field, deform the NLC orientation structure and allow visualization of the particle-induced defects. The observed effect can be used for the development of a new type of sensitive alpha-particles detectors that will feature a visualization option (for the purpose of ionizing radiation characterization).

![Figure 7. A shot of a dynamic optical texture visualizing NLC orientation deformations induced by an alpha-particle flux.](image)

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3. Thermal orientation effect in NLCs
Thermal flow influence on the orientation structure of NLCs was detected experimentally. This effect was discovered in NLCs which are centrally symmetrical. Therefore it cannot be explained as the well-known thermo-mechanical effect attributed to cholesteric liquid crystals and deformed NLCs with broken symmetry [4]. A theoretical model was proposed for explanation. This model reveals existence of NLC’s orientation thermoelasticity governed by quadratic dependence on the temperature gradient [9]. The detected thermal orientation effect (unavoidable in the presence of radiation absorption) along with the well-known light-induced Fredericks effect [2] cause the central symmetry breakdown and formation of disclinations. Figure 8 demonstrates a calculated orientation structure and the photo of a corresponding optical texture in transmitted light which were obtained under impact of the both effects. In what follows we demonstrate experimentally that the complex impact of these effects on the NLC structure (first of all, central symmetry breaking) allows second-harmonic, difference-frequency, and supercontinuum generation in NLCs.
4. Laser frequency conversion in NLCs

Various transformations of laser radiation spectra in NLCs and accompanying modifications of the NLC orientation structure were studied experimentally. Thus, highly efficient difference frequency generation was obtained, for the first time, in a nematic liquid crystal excited by several visible lines from a cw argon laser with a total power of 0.08—1.5 W [7]. The maximum conversion efficiency was ≈1% and the measured quadratic susceptibility was ≈2×10⁻⁶ m/V. This value is about 6 orders of magnitude higher than the maximal known susceptibility attributed to an organic crystal NPP. The experimental data related to the parameters of generated difference-frequency radiation are depicted in figure 9. The observed laser frequency conversion in NLC has specific features compared to generation at difference frequencies in solid crystals. Therefore we conclude that approximation of quadratic nonlinearity in NLCs requires more precise definition.

Figure 9. The measured parameters of optical radiation obtained through difference frequency generation in NLC: (a) – indicatrix of the radiation, (b) – optical spectrum.

To study other types of laser radiation nonlinear transformation in NLCs, we made use of two fiber-coupled cw diode lasers with wavelengths of 980 nm and 1480 nm, respectively. The experiments were arranged in two different ways. In the first arrangement, the tip of an single-mode optical fiber delivering laser radiation was immersed in a narrow slot which was formed by glass plates and filled with NLC. The plate spacing was determined by the fiber tip diameter (125 microns).
Two induced orientation structures were observed in the NLC region being exposed to the laser radiation at 1480 nm: a 2-mm-long 10-µm-narrow beam with a divergence of less than 1° (depicted in figure 10), and nearly symmetric radial structures centered at the fiber tip (depicted in figure 11). These structures are attributed to the linear and point defects. As seen in figure 10, the self-confined beam in the NLC orientation structure has regular transversal dashes. This filamentation-like effect can be caused by combination of the thermal orientation effect due to absorption [4, 9] and the nonlinear orientation self-focusing due to light-induced Fredericks effect [2].

The radial structures (figure 11) appeared when a heat-spreading mirror-like plate was used in the above experimental arrangement instead of the bottom glass plate. In addition, an electrostatic field was applied to the NLC sample in that case. The voltage between electrodes was set about 4.5 V. The photos in figure 11 indicate that disclinations of different strengths can be obtained depending on the radiation intensity. Upon reaching a threshold intensity of the pump radiation we observed appearance of a visible irradiating spot (figure 11 (c)). This spot can be attributed, as we discovered later, to the complex laser frequency conversion in the NLC.

**Figure 10.** The particular orientation deformation induced by a laser beam in a homogeneous NLC structure, which features filamentation-like appearance. The image was obtained in transmitted light with the use of crossed polarizers and a microscope. The laser beam propagates from right (from an optical fiber tip) to left.

**Figure 11.** Radial orientation structures obtained in the NLC area around the optical fibre tip: (a) – disclination with a strength of 3/2, obtained under a pump power of 100 mW; (b) – disclination with a strength of 2, obtained under a pump power of 250 mW; (c) – the irradiating spot appearance, obtained under a pump power of 350 mW.
To examine the optical spectra of laser radiation transformed in NLC we used another experimental arrangement – a small drop of NLC was placed directly onto the tip of a radiation-delivery fiber. Examination of the optical spectra has revealed the following transformations. An octave spanning spectral supercontinuum with an apparent maximum forms in a spectral range from ~500 nm to ~1200 nm, when the NLC drop is pumped at 1480 nm (figure 12). The wavelength of the supercontinuum maximum and the supercontinuum width depend on the pump power. Narrow peaks of the second (~493 nm) and third (~740 nm) harmonics manifested themselves against the wide spectral profile of the supercontinuum. These spectral peaks appear in different points of the radiation indicatrix. Therefore it is hardly possible to register these harmonics simultaneously by a spectrometer. This phenomenon has a simple explanation – very different conditions of phase synchronisms. At a low level of pump power (30 to 100 mW) the generated radiation and the formed orientation structure have stationary properties. At a high pump power level (>250 mW) the intensity of the generated supercontinuum oscillates continuously, and the harmonics disappear (become indistinguishable against supercontinuum).

Figure 12. The spectral supercontinua generated in a drop of NLC pumped by a fibre-coupled diode laser at 1480 nm. The diversely coloured traces were acquired at different moments of time to illustrate the intensity oscillations. The spectrum traces (a) and the spectrum traces (b) were acquired from different points of the radiation indicatrix to manifest the contribution of the second and third harmonics, respectively.

When pumping was done at a wavelength of 980 nm, the third harmonic radiation belonged to the ultraviolet ($\lambda_{th}$~326 nm) as seen in figure 13 (a). The second harmonic (~490 nm) at the same point of the radiation indicatrix is much weaker and has a particular spectral profile shown in figure 13 (b). The observed spectral profiles underwent some stochastic transient changes upon switching the pump mode and adjusting the power level. Generation characteristics of the supercontinua and harmonics have threshold and hysteresis dependence on the pump power. It was noticed that when we used a multimode radiation-delivery fiber (pumping at 980 nm), the spectral profiles manifested much more irregularities as compared with the spectra obtained using a single-mode delivery fiber (pumping at 1480 nm). In both cases generation characteristics of the supercontinua and harmonics had threshold and hysteresis dependence on the pump power. It is also important to notice that exposure to the highest available radiation intensity of 400 kW/cm$^2$ did not lead to overheating of the NLC.
Figure 13. Optical spectrum of radiation generated in a drop of NLC pumped by a fibre-coupled diode laser at 980 nm: (a) – a full range spectral trace which manifests the dominating contribution of the third harmonic (~326 nm) in the selected point of the radiation indicatrix; (b) – magnification of the optical spectrum in the vicinity of the second harmonic (the diversely coloured traces were acquired at different moments of time to illustrate the intensity oscillations).

5. Conclusion
A concept of non-mechanical transportation of nanoparticles and their packaging into a regular lattice has been implemented using the possibility to control the orientation of NLC molecules by means of applied quasi-static electric field. These particles induce a set of spatially periodic singularities in the orientation structure of NLC, and thus yield an optical medium with a spatially periodic anisotropy – a photonic crystal. The key parameters of such a photonic crystal can be controlled by applied electric fields. It opens up possibility of development of new types of photonics devices for laser technology, telecommunications and optical computing. The demonstrated method of alpha-particles flux visualization by means of NLCs turned to be very sensitive, and, therefore, can be used for characterization of ionizing radiation beams in many practical applications. Enormous quadratic and cubic optical nonlinearities of NLCs subjected to thermal orientation effect along with light-induced Fredericks effect lead to efficient conversion of laser frequencies. Feasibility of laser radiation nonlinear transformation in a volume of NLC was demonstrated experimentally. The most effective transformations are the difference frequency generation in the mid-infrared and the spectral supercontinua generation in the visible and near-infrared ranges. The generation of the second and third harmonics was also achieved.

The obtained research results allow us to assume that nonlinear optical properties of NLCs make it possible to implement a new type of coherent radiation sources which can generate across the whole optical spectrum, from the ultraviolet to the far-infrared.

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