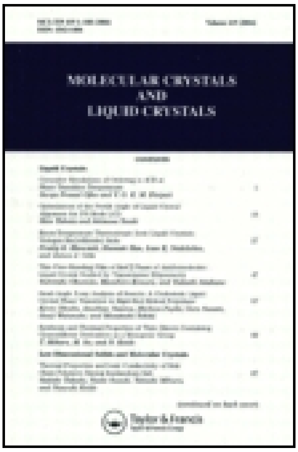

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Always Cholesterics…but Sometimes Chiral Smectic C, TGB and Blue Phases

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To cite this article: Guram Chilaya (2012): Always Cholesterics…but Sometimes Chiral Smectic C, TGB and Blue Phases, Molecular Crystals and Liquid Crystals, 561:1, 8-35

To link to this article: http://dx.doi.org/10.1080/15421406.2012.686692

Mol. Cryst. Liq. Cryst., Vol. 561: pp. 8–35, 2012
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.686692

Always Cholesterics . . . but Sometimes Chiral Smectic C, TGB and Blue Phases

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Cholesteric liquid crystals Chiral Smectic C and pretransitional twist grain boundary and blue phases, owing the self-organized periodical structure, sensitive to external fields, have provide several possibilities for construction new photonic and optoelectronic devices. In the optically controlled condensed matter systems department of the Institute of Cybernetics of Georgia the extensive investigation of chiral liquid crystals are carried out since 1972. In the present report, results obtained by Georgian group and also in collaboration with scientists Germany, France, Italy, Russia, Spain, Ukraine, USA will be reviewed, paying a special attention to electrooptics and photoptics of this chiral liquidcrystalline phases and practical application for creation image converters, UV sensors, displays and compact broadband tunable lasers.

Introduction

Liquid crystals (LCs) are liquids in which molecules have a specific ordered orientation and, consequently, possess anisotropy of the physical properties [1, 2]. The liquidcrystalline (mesomorphic) state is observed for molecules with a specific shape in a particular temperature range (thermotropic LCs) or at particular concentrations in a solvent (lyotropic LCs). LCs can be formed by monomer and polymer molecules. If LCs formed by elongated molecules, they called as a calamatic one and for disk like molecules as discotic LCs, accordingly. LCs possesses polymorphism: they exhibit two major classes nematics (N) and smectics (Sm). NLC characterized by only long range orientational order and smectics by an additional translational order. Among different types smectic LCs, smectic A (SmA) and smectic C (SmC) LCs have the simplest structures. Long molecular axes are perpendicular to the smectic layers planes in SmA and are tilted with respect to the layers in SmC, accordingly. The following phase sequence is observed in thermotropic calamatic LCs with increasing of temperature: crystal- SmA - SmC – NLC-isotropic fluid.

Chirality, or handedness, is a property of objects and molecules that are not symmetrical. In NLC and SmC LCs with chiral molecules and in mixtures of achiral nematics and C-smectics with chiral molecules, the supramolecular helical structures are formed, i.e., the so-called cholesteric (chiral nematics) and chiral C smectics (SmC*) with the spatially modulated period P (where P is the helix pitch) [3]. Transition of cholesterics to isotropic

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This article is dedicated to the memory of my wife Stella Chilaya.

*Address correspondence to Guram Chilaya, V. Chavchanidze Institute of Cybernetics of Georgian Technical University, Tbilisi, Georgia. E-mail: gchilaya@gmail.com and smectic phases are accompanied by formation of specific structures. These are frustrated twist grain boundary (TGB) and blue phases (BP) formed in the phase transitions via formation of systems of exotic complex defects.

Due to the effect of helix divergence near the cholesteric smectic A phase transition, the pitch have to be increased with decreasing temperature. This effect theoretically was considered by de Gennes as an analogy between superconductors and smectic A [4]. In spirit of de Gennes theory, near the phase transition from the cholesteric to smectic phase, an intermediate phase, called TGB phase, was predicted in [5]. BPs are observed in chiral liquid crystals usually characterized by small helix pitch in the transitions from the cholesteric to the isotropic phases. The theory of the structure and symmetry properties of BP was developed within the framework of the Landau phase transitions theory and predicted the existence the intermediate phases [6].

1. Optical Properties of Cholesterics

Locally, a CLC is very similar to a NLC. However, in CLC the direction of the preferable orientation of the molecules **n** (director) varies periodically in space. The spatial period of CLC is equal to one-half of pitch (because unpolarity of the cholesteric structure). The helix may be right-handed or left-handed, depending on absolute configuration of the molecules. According to the chemical nature of the constituent molecules CLC can be subdivided in the following ways: (1) steroids, mainly cholesterol esters and their mixtures with each other, from which takes the name CLC. As indicated in [7, 8] derivatives of cholesterol are the first examples of thermotropic liquid crystals described in the literature [9–12]; (2) non-steroidal cholesterics (so-called chiral nematics); (3) induced cholesteric systems comprising a nematic matrix and a liquidcryastalline or non- liquidcryastalline optically active dopant (OAD) [13, 14]. Small amount of a chiral compound, dissolved in nematic LC, transforms it into a cholesteric phase [15].

The ability of a dopant to torque a nematic phase is called “helical twisting power” (HTP). For small concentrations of chiral dopant the linear dependence between reciprocal value of pitch (1/P) and concentration of chiral dopant (c) and HTP expressed as $\mathrm{HTP} = (\mathrm{P} \cdot \mathrm{c})^{-1}$. Typical inverse pitch vs. concentration dependences in the nematic-cholesteric mixtures is shown in Fig. 1 [7]. As shown in this figure in some mixtures a helix sign inversion is observed when the concentration of the components is changed. The cholesteric phase is thermodynamically equivalent to the nematic phase. The simple equation for orientational order parameter S for nematics was first introduced by Tsvetkov [16]:

$$\mathrm{S} = (1/2)\langle 3\cos 2\vartheta - 1\rangle,$$

θ is the angle between the long molecular axis and local director **n**.

The order parameter of NLC can be derived from the refractive indices n_o and n_e and the general Lorentz–Lorenz equation results for liquids of anisotropic molecules [17]

$$S \cdot \Delta\alpha/\bar{\alpha} = \mathrm{n}_\mathrm{e}^2 - {\mathrm{n}_\mathrm{o}}^2/\bar{\mathrm{n}}^2 - 1$$

where the mean refractive index of a nematic $\bar{n} = ({\mathrm{n}_\mathrm{e}}^2 + 2{\mathrm{n}_0}^2)/3$, the mean polarizability $\bar{\alpha} = (\mathrm{a}_\parallel + 2\mathrm{a}_\perp)/3$ and $\Delta \mathrm{a} = \mathrm{a}_\parallel - \mathrm{a}_\perp$

The optical anisotropy in CLC is negative, i.e. $\mathrm{n}_\mathrm{oh} > \mathrm{n}_\mathrm{eh}$, where $\mathrm{n}_\mathrm{eh} \equiv \mathrm{n} \| \mathrm{h}$ and $\mathrm{n}_\mathrm{oh} \equiv \mathrm{n} \perp \mathrm{h}$ are the refractive indices for the extraordinary and the ordinary beams, respectively. If

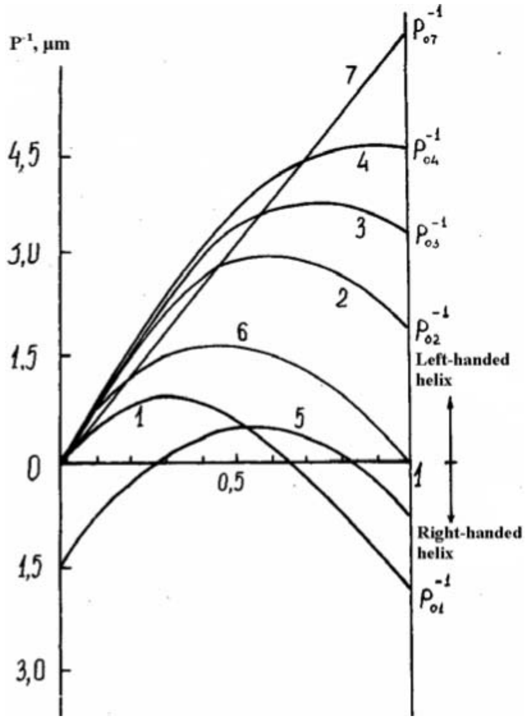


Figure 1. Inverse pitch $(P)^{-1}$ vs. concentration dependences in the nematic-cholesteric mixtures: 1—4—nematics + cholesterol derivatives with different intrinsic pitches P_o, 5—chiral nematic + cholesterol derivative, 6—nematic + compensated mixture of cholesterol derivatives, 7—nematic + chiral nematic of the similar structure.

the local nematic refractive indices are given by n'_e and n'_o, the average refractive indices with respect to the helix axis h can be written as: $n_{eh} = n'_o$, $n_{oh} = (n'^2_e + n'^2_o)\ \frac{1}{2}$. The index **h** indicates that the macroscopic optical axis corresponds to the direction of the pitch axis.

Precise measurements of the refractive indices of racemic (nematic) and the optically active (cholesteric) form of the *p-methoxybenzilidene - (p′ - isopentacil) amyl* show, that the refractive indices fulfill this theoretical expectation within experimental error (±.0005). Figure 2 [13]. The optical anisotropy of the LC phase is determined by the anisotropy of the polarizability of the molecules and by the degree of their order which is described by the order parameter S. The obtained results indicate that the orientational order parameter S in a layer of a CLC is the essentially the same as in the nematic phase occurring in the corresponding racemic mixture.

The CLCs with long pitch ($P \gg \lambda$, where λ is the wavelength of visible light) was studied for the first time by C. Mauguin [18]. This type of configuration can be obtained by mechanical twist of nematics and is used in conventional twisted nematic displays [19]. In this case the light propagating parallel to the helical axis may be described by a superposition of two eigenwaves having electric field vectors parallel and perpendicular to the director and the structure behaves as a polarizing waveguide: the plane of polarization of linearly polarized modes follows the twist.

For short pitch when λ and P are comparable, the eigen waves become elliptical, and in the limiting case circular. In this limiting case, selective reflection occurs due to Bragg diffraction. The diffraction in CLC is responsible for remarkable optical properties [20]. The wavelength of the maximum of selective reflection band (SRB) or the middle of SRB, depending on the shape -λ_0 (λ_B) and the spectral width $\Delta\lambda$ are equal m $\lambda_B = P\ n \cos\theta$ and $\Delta\lambda = P\ \Delta n$, accordingly. Here m is the diffraction order, θ is the angle of light incidence, n is the refractive index and Δn is the birefringence of the medium.

In the case of light propagating along the axis of the helix only the first–order Bragg reflection is observed. The reflected and transmitted light are circularly polarized and their signs depend on the sign of rotation of the CLC helix. Thus, a CLC layer splits a nonpolarize light into two circularly polarized ones with opposite sign of rotation. The indication of signs of rotation depends on approaches for definition of handedness of rotation. We examine the definition of handedness of rotation in detail.

Substances that rotate the plane of polarization of light beam propagating through them are called optically active (chiral). Circular polarization (CP) could be characterized by handedness and helicity. Handedness is associated with space alone, while helicity is with space and time. Helicity is associated with the sign of angular momentum projected onto the propagation direction. Light has both handedness and helicity; the cholesteric structure only handedness.

There are two approaches for definition of handedness of rotation [21].

1. In quantum ("modern") physics the definition is based on the sign of a photon angular momentum along the direction of propagation. The right-hand circularly polarization (RHC) of the beam of light corresponds to a clockwise rotation of the electric field vector in the perpendicular plane of the light propagating direction and left-hand polarization to counter clockwise rotation of the electric field in vector in this perpendicular plane. RHC polarized beam of light propagating along the direction of the right-hand thumb, the electric field revolves in time along the direction of fingers. The RHC polarized light propagating along

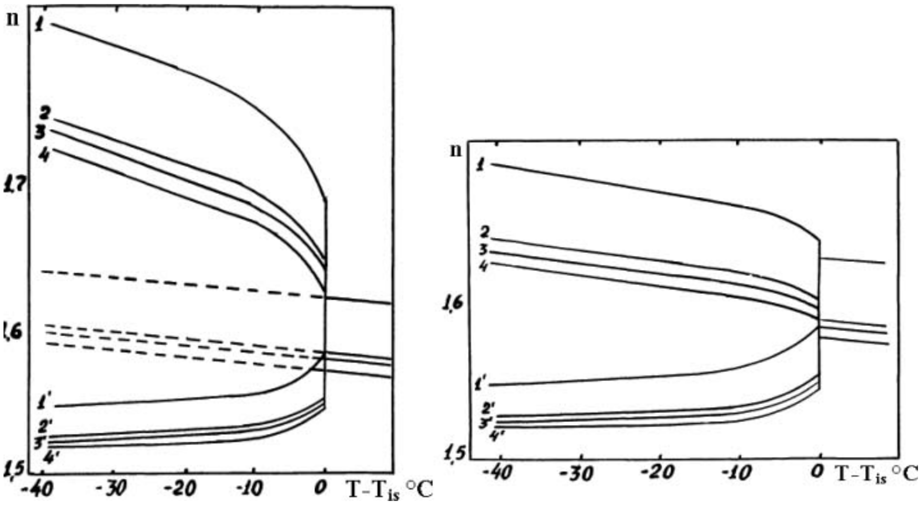


Figure 2. Left—Indices of refraction of NLC : 1—n_e and 1′—n_0 for 436 nm; 2—n_e and 2′—n_0 for 546 nm; 3—n_e and 3′—n_0 for 577 nm; 4—n_e and 4′—n_0 for 690 nm; Right—Indices of refraction of CLC : 1—n_{eh} and 1′—n_{0h} for 436 nm; 2—n_{eh} and 2′—n_{0h} for 546 nm; 3—n_{eh} and 3′—n_{0h} for 577 nm; 4—n_{eh} and 4′—n_{0h} for 690 nm;

R CLC don't "feels" ("see") the periodicity of the helicoidal structure, "goes easily" and does not diffract and transmitted. Conversely, LHC polarized light due to Bragg diffraction-reflected.

2. In Optical physics ('Classical"- traditional) the definition of circular polarization is used, where its sign is determined from the sense of the field vector rotation for an observer toward whom the photon moves. It is the nature of all screws and helices that it does not matter which direction you point your thumb when determining its handedness. As an example we propose to consider the nut as a cholesteric cell when CP light revolves in time along the direction of screw of bolt. The advantage of this convention is that the handedness of the space helix is independent of the direction of viewing.

In the case of classical convention the instantaneous spatial electric field pattern has an opposite handedness then CP light coming.

Thus, comparing these two methods is indicated that, for the RHC polarized light defined by first method, the instantaneous spatial electric field pattern is a left-handed helical structure.

According to the modern conceptions the CLCs can be treated as a medium with a photonic band gap [22, 23]. The ability to shift the selective reflection wavelength by changing the external factors (electric, magnetic, acoustic fields, temperature, light irradiation, local order . . .) make the CLCs attractive for many applications [24].

The property of cholesteric liquid crystals to change the reflected color with temperature (due to the temperature dependence of the pitch) is known for a long time [25] and CLC are successfully used as a thermochromic material [26].

In Fig. 3 the wide possibilities for control the temperature dependence of pitch are shown. Three component mixtures of induced chiral systems were used. Two chiral compounds were added to a nematic of which one (b) induced a cholesteric with a temperature independent helix pitch, whereas the other (a), induced a cholesteric with the temperature-dependent inversion of the helix sign [27]. As shown in Fig. 3 this three component mixture provides smooth control of the dp/dT value. The whole visible-light spectrum can be observed within the temperature range equal to 0.02°C for mixture of smectogenic 4—n-hexyloxyphenyl 4-n′-octyloxybenzoate (HOPOOB) with nonmesogenic optically active dopant tigogenin caprate (T C) (Fig. 4) [28].

In some polar nematic mixtures the nematic phase occurs in at higher as well as at lower temperature relative to the smectic A phase [29]. The lower temperature nematic phase designated as a reentrant phase (N_{re}). Reentrant phase was also observed in induced cholesteric mixtures [30]. The following phase sequence was observed: crystal 62°C$\rightarrow N_{re}$ 75°C$\leftrightarrow$SmA 153°C $\leftrightarrow$ N173°C $\leftrightarrow$isotropic liquid. In Fig. 5 the temperature dependence of the pitch for the mixtures with different concentrations of optically active dopant is shown.

2. Electrooptics of Cholesteric Liquid Crystals

The investigations of LCs usually were performed in "sandwich" type cells, consisting of two glass or quartz plates and spacers there between to provide a necessary thickness of layer (5–100 μm). Several types of electrooptic effects have been observed in cholesteric liquid crystals, depending on the surface treatment (boundary conditions), the helical pitch P, the thickness-to-pitch ratio d/P, the dielectric anisotropy $\Delta\varepsilon$ and the frequency of the applied field [31]. Some of these electrooptic effects are caused by texture changes. In Fig. 6 textures of CLC are shown. Planar (Grandjean) texture is observed when helical axis is normal to the surface. This texture is realized in the case of the parallel boundary

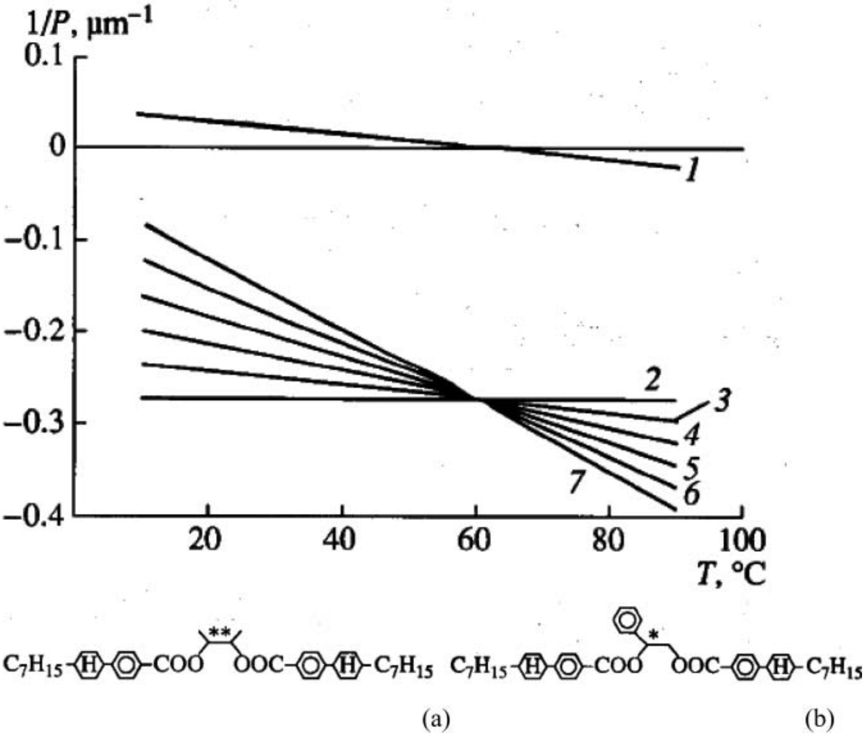


Figure 3. Temperature dependences of (1/P) for the mixture of NLC (RO-TN 404) + chiral (a) and chiral (b). (1)—NLC+(a) (1 wt%); (2)— NLC+ (b) (1 wt%); (3–7) — [NLC+ (b) (1 wt%)] + (a) : (3) (1 wt%), (4) (2 wt%), (5) (3 wt%), (6) (4 wt%), (7) (5 wt%), accordingly.

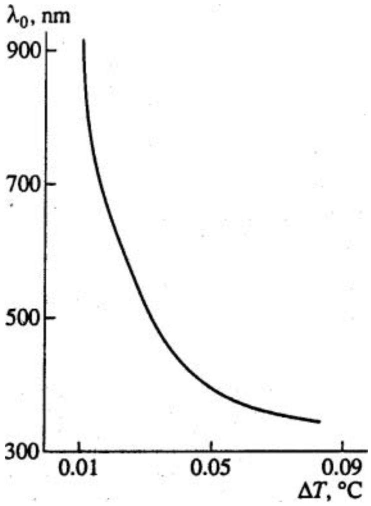


Figure 4. Temperature dependence of the wavelength of the selective-reflection maxima for the mixture HOPOOB (72 wt%) +T C (28 wt%). The first point of the temperature interval T = 0.0l°C corresponds to the temperature of 69.5°C.

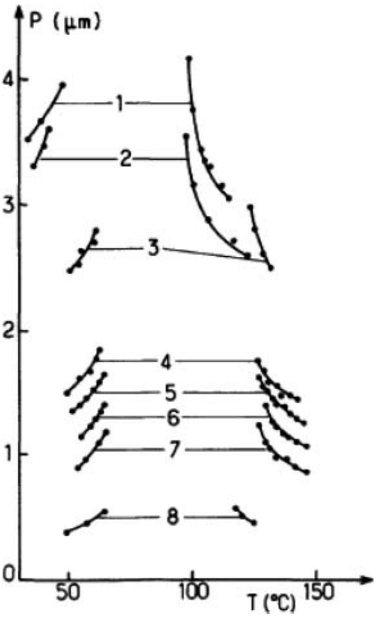
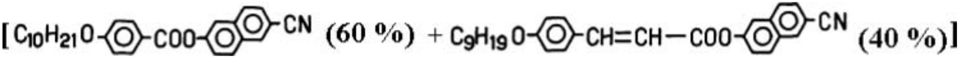


Figure 5. Temperature dependence of the pitch for the mixture NLC



with different concentrations of nonmesogenic optically active dopant TC (numbers correspond to TC concentration).

conditions. In the "fingerprint" texture, due to normal boundary conditions, helical axes oriented parallel of surfaces. Focal conic texture is a no oriented, destroyed texture.

In cholesteric LCs with negative dielectric anisotropy - $\Delta\varepsilon < 0$, the dynamic scattering mode effect was observed for applied low frequency electric fields [32]. The electric field induces hydrodynamic instabilities which cause a diffuse scattering appearance. The scattering state is maintained after removal of the field, thereby providing an optical memory effect ("storage mode"). Effect is connected with the transition planar texture (transparent field-off state) → confocal texture [33]. The stored scattering state can be erased by the application of a high frequency electric field which reorganizes the planar structure. Experimentally was shown that erasure frequency is in proportion of the reverse of the dielectric relaxation time [34].

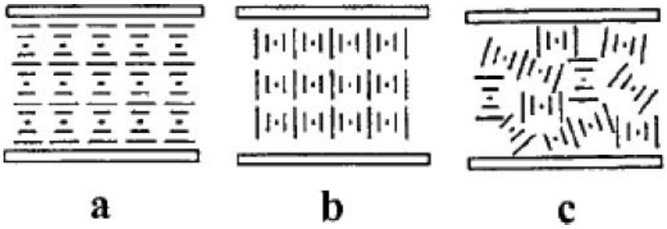


Figure 6. Textures of CLC (a) planar, (b) "fingerprint", (c) focal conic.

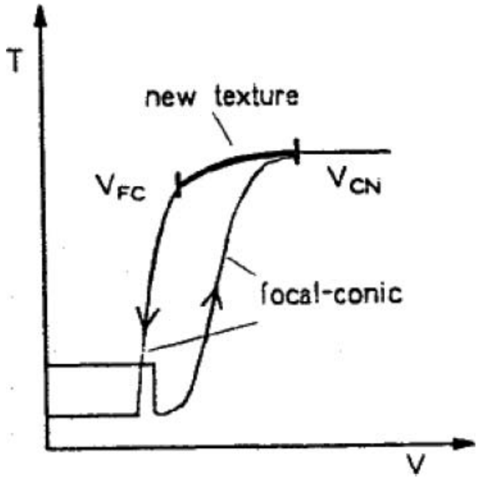


Figure 7. General transmission change in CLC for increasing and decreasing applied voltage.

In CLC with positive dielectric anisotropy, the cholesteric-nematic phase transition was theoretically predicted [35, 36] and experimentally observed in electric fields [37, 38]. If the electric field E is applied perpendicular to the helix axis h of a cholesteric LC, the helix unwinds at the field strength $E = E_{CN}$ and the homeotropic nematic structure is established. If the electric field is applied parallel to the helix, the situation is more complicated. Here, distortions of the helix and the formation of regular patterns can be observed. For short pitch, a shift of the reflection peak to shorter wavelengths (blue shift) was observed [39–41]. It was assumed that above a threshold field a conical deformation of the planar texture leads to a distortion of helix (inclined planar structure-quasiplanar) or pitch contraction and in both cases λ_B is shifted to shorter wavelengths [42, 43]. In higher fields the structure becomes focal conical, and at $E = E_{CN}$ the structure is transformed also into the homeotropic nematic one. For homeotropic orientation hysteresis (bistability) and storage effect was observed for normal surface orientation [44]. The possibility for a bistability was shown in all cases of surface treatment (including nontreated cells) of cholesteric samples whose cell thickness d is comparable to the helical pitch P [45, 46]. Various pitch-thickness ratios and influence of of homeotropic and planar boundary conditions have been investigated [47–50].

The detail study of of electrooptic effects in cholesteric LCs with positive $\Delta\varepsilon$ and initial planar structure was made in [51–53]. For increasing and decreasing voltage, as shown in Figure 7, a sequence of structures (planar - confocal - homeotropic- confocal- planar) was observed. At the strong electric field E_{CN} the helix unwinds. After switching the field off, during the transition from homeotropic nematic state into a planar cholesteric one an electric field induced texture with unusual properties was observed [51]. The angular and electric-field dependence of spectral characteristics indicate that this state possesses diffractive grating properties. When white light is incident onto that structure iridescent colors are observed. Was noted that “the electric- field controlled cholesteric texture with diffractive grating properties is hence a result of the specific balance between the influence of the electric field and the twisting forces in the cholesteric structure” [51]. This texture named as a “new texture”. The initial (undisturbed) values of helical pitch of the investigated mixtures varied from 0.5 to 3μm, but more attention was paid to a CLC with a pitch $P \geq 0.8\ \mu$m for observing the voltage-controlled color effect and also to a voltage controlled variation of the

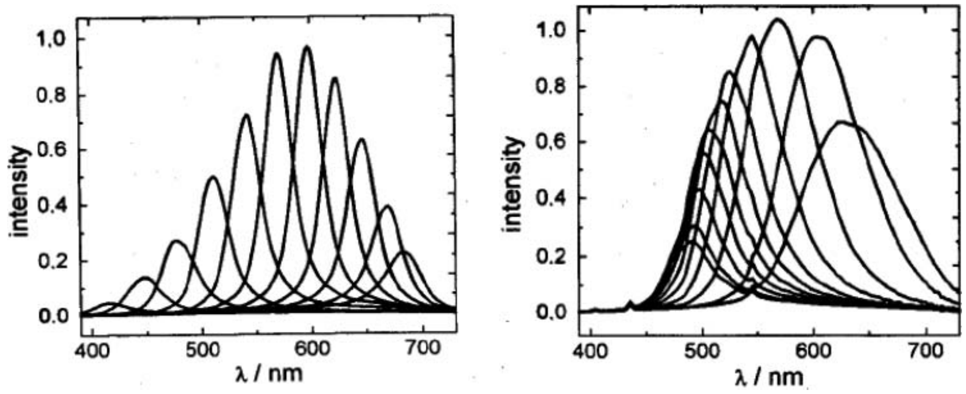


Figure 8. Dependence of the color on the observation angle and the applied voltage; mixture MLC 6023/S811, $P_0 = 0.8\ \mu$m, $d = 5\ \mu$m, $\phi = 40^o$; left part: θ is 15^o for the left curve and is increased in 5^o steps, V = 15 V; right part: V is 20 V for the right curve and is decreased in steps of 2 V, $\theta = 40^o$.

laser beam deflection. In Fig. 8 the dependence of the color on the observation angle and the applied voltage is shown. This color change effect was observed also in polymer-dispersed cholesteric films [51] and gels [54]. The electric- field controlled cholesteric gratings was studied for small pitch and analyzed experimentally and theoretically in detail in [55, 56] and corresponding textures named as M state.

A low control voltage cholesteric-nematic transition can be obtained for a large spiral pitch. The Mauguin region is approached on increasing P. In this case is CLC could be considered with a medium pitch (chirality). Close to the Bragg wavelength λ_B, a CLC behaves "pure" optically active, i. e. it shows no linear birefringence. In [57] electrooptics of "amorphous" cholesterics with medium chirality was investigated. For obtain "amorphous" cholesteric structure with random orientation of liquid crystal molecules and a helical axis oriented normal to the surfaces CLC cells coated with polyamide (without rubbing). All parts of the amorphous cholesteric structure with medium chirality rotate the polarization plane by the same angle. The whole structure can be considered as optically active. In this case, the angle of rotation is independent of the direction of the polarization plane of the incident light. This is the basic property used for electrooptic application of the amorphous cholesteric structure with medium chirality. The experiments are performed in the polarized light (crossed polaroids). Characteristic features of this effect are: (1) low demands on the surface conditions (non-rubbed cell), (2) an ability to function in any position between crossed polarizers, (3) wide and uniform viewing angle, (4) rise times less than 10 ms and the decay times of 12- 20 ms. The electrooptic effect was also studied in polymer dispersed liquid crystal (PDLC) films [58].

Mostly in publications was shown various possibilities in employing CLCs for smoothly tuning of the pitch in planar oriented cells under the action of applied external forces. However, as discussed in last years, the continuous change of the pitch, initiated by a smooth variation of the temperature, electric field or light intensity in thin planar oriented CLC cells, turns out to be unrealizable. Depending on the pitch and cell thickness values, surface anchoring conditions one can observe pitch jump, helix distortion accompanied by creation of defects. In planar structure when the director anchored on the top and the bottom of surfaces the helix could be considered as a total number of half pitches in the direction normal to the surfaces and the change of pitch is possible only with the help of so-called "pitch jumping" effect. Theoretically the pitch jump process explained by the phenomena of thermal hysteresis [59]. Experimentally pitch jumps and thermal hysteresis in the samples were investigated in [60]. Despite the fact that field unwinding of the cholesteric helix is thermodynamically profitable, the continuous change of the pitch with electric field predicted in [34] is impossible without creation of defects which leads of helix distortion due to a strong topological limitation on the unwinding process [61]. On the other hand basically in many experiments was realized the smooth change and thus the smooth controlling of the pitch.

2. Light – Controlled Effects in Cholesteric Liquid Crystals

It is known that the optical characteristics of liquid crystals substantially change under exposure to light. This is predominantly associated with the strong optical anisotropy of liquid crystals and the cooperative response of their molecules. There are at least three possible mechanisms for the change of the LC parameters under the light illumination: thermal, orientational (reorientation torque caused by dielectric coupling of the electric field of the light with the medium) and conformational [62]. Light-induced effects have been investigated in different liquid crystals. However, cholesteric liquid crystals are of special interest because "no other macroscopic parameter seems to be so sensitive to smallest changes in molecular structure and composition as the helical pitch" [7].

We will consider the photo transformation effects in cholesterics. In these mixtures, either a chiral component or a nematic component, or both components, can be photosensitive. Special photosensitive (chiral or achiral) compounds can be added to photoinsensitive chiral nematic mixtures. The phototransformation of molecules results in different, frequently interdependent, and sometimes opposite effects in cholesteric liquid-crystals [3, 20, 63]. These effects involve change in the orientational order, lowering of the phase transition temperature to the isotropic phase, and change of the the refractive indices, on the one hand, and changes in the concentration and shape of the molecules responsible for the formation of a helical structure, on the other hand. In cholesteric LC the photo-transformation of molecules can cause a change of the pitch, and thus a shift of the wavelength of selective reflection.

A large number of papers for pitch controlling in CLC mixtures have been devoted to systems consisting of conformationally active molecules, which are capable of light-induced *trans-cis* isomerization. Usually the amount of photoactive material in these systems is small. Even more recently, CLC mixtures with a photoisomerizable nematic component typically comprising 60–80 wt.% of the sample, with the rest of the sample being a photoinactive chiral compound [64–66]. Nematic liquid crystals with conformationally active azo-and azoxy-compounds were utilized.

The trans form of azo- and azoxy-compounds absorbs in UV-violet region of spectrum up to about 400 nm, and the cholesteric pitch decreases with exposure to UV irradiation and accordingly the blue shift of the color of cholesteric film is observed. This effect is reversible: the pitch returns to its initial state when the irradiating light has a wavelength greater than 400 nm. In CLC mixture based on azoxy nematic ZhK-440 (NIOPIK, the mixture of 2/3 p-n-butyl-p-methoxyazoxybenzene and of 1/3 p-n-butyl-p-heptonoiloxyazoxybenzene) reversible light control of the selective reflection band with shifts as large as 210 nm was observed as shown in Fig. 9. In this mixture non-photosensitive - nematic MLC-6815(Merck) and optically active dopant ZLI-2011 (Merck), transparent in UV range are doped to ZhK-440.

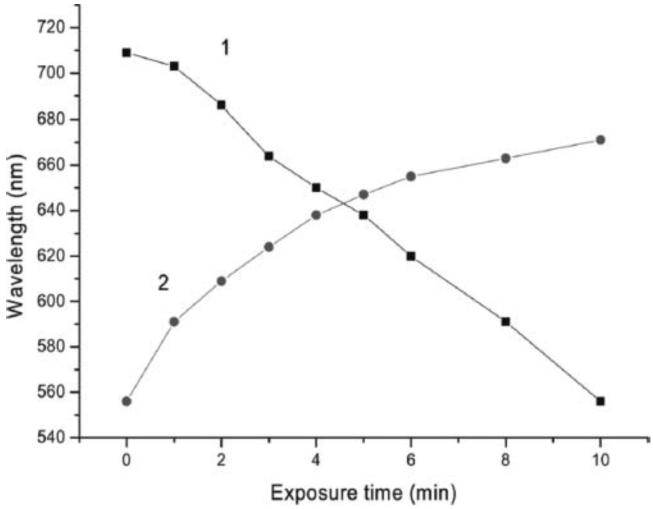
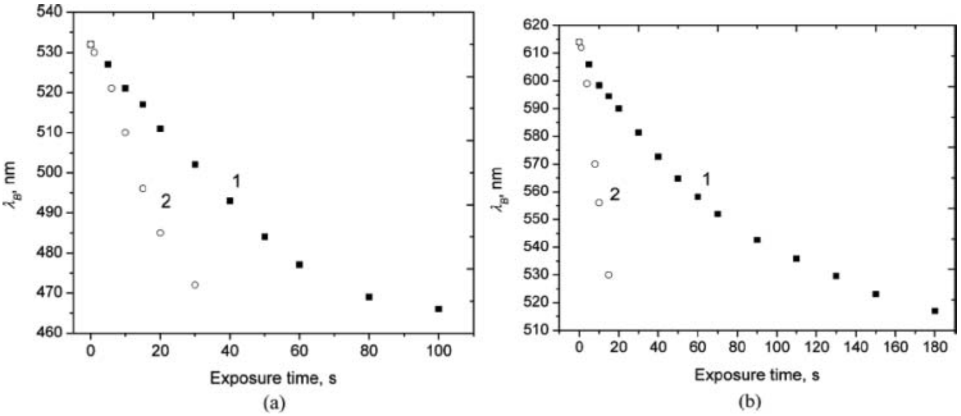


Figure 9. Selective reflection wavelength of mixture 75 wt% (75 wt% ZhK-440 + 25 wt% MLC-6215) + 25 wt% ZLI-2011 as a function of time when exposed to the mercury lamp with band pass filters, 240–390 nm (1) and 410–500 nm (2).

Phototuning of SRB to shorter wavelengths was induced with a green (532 nm) laser (Nd: YAG, Crystal Laser Co) beam in CLC based on highly sensitive azobenzene nematic BEAM 1005 (BEAM Co.) and UV transparent non-photoisomerizable optically active dopant MLC-6248 (R-2011) (Merck) [67]. The shift of the photoinduced reflection band is accompanied with several phenomena such as formation of 2D periodic structures. Nonlinear optical switching due to changes of transmission and reflection was studied. Phototuning from green to blue and from red to green wavelengths in two mixtures: 1005(69.4%)/6248(30.6%) (mixture 1) and 1005(74%)/6248(26%) (mixture 2) observed at exposure of the materials with green laser is shown in Fig. 10. For comparison, phototuning upon illumination with a UV light at 365 nm is shown as well.



(a) (b)

Figure 10. SRB wavelength for mixtures 1 (a) and 2 (b) as a function of the exposure time to (1) a green laser beam (I = 14 mW/cm^2) and (2) to a UV radiation (I = 10 mW/cm^2).

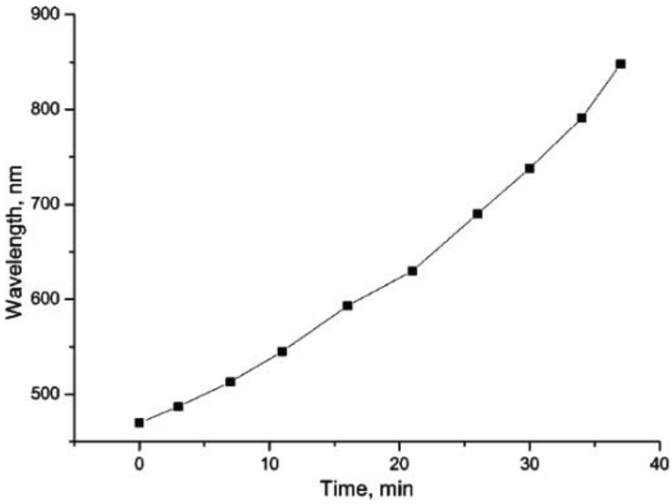


Figure 11. Dependence of the maximum of the selective reflection peak on the exposure time for the mixture in weight 72% (50% ZLI-1184 + 50% ZLI-1185) + 28% ZLI-811.

The high light sensitivity of azo and azoxy compounds made it possible to use light emitting diodes (LED) instead of mercury lamp in order to control P of CLC A shift of SRB more than 400 nm was observed in CLC mixture with azobenzene nematic LCs (1205, BEAM Co.) [68]. The reversible control over the helical pitch was obtained in CLC mixtures of nematic azo- and azoxy- compounds hosts with the use of two LEDs 405 nm and 466 nm [69].

In [70, 71] experimentally has been observed that in a CLC mixture of the transparent nematic component with the frequently used optically active dopant ZLI-811 (Merck), the exposure to ultraviolet light with a wavelength shorter than 290 nm results in an long-wavelength shift of the selective reflection peak by more than 400 nm. This effect is stable in time and irreversible. Considering the chemical formula of ZLI-811 the photosensitivity was explained by photo-Fries rearrangement, typical of aromatic esters. The dependence of the selective transmission on the irradiation time is shown in Fig. 11.

Recently, photo tuning of more than 2000 nm has been distinguished in CLC mixture by the use in CLC mixture with a chiral bis (azo) dopant. [72], Moreover, using the high HTP bis_azo-_chiral dopants, by exposure of UV light bandwidth of SRB ~100 nm was broadened to as much as 1700 nm [73].

3. Chiral Smectic C and Pretransitional from Cholesteric TGB and Blue Phases

Chiral smectic C phases exhibit analogous optical properties to cholesterics but the period is equal to full pitch P [74, 75]. Using oblique incident light both second-order and first-order Bragg reflections was observed: $m\lambda_B = 2\ P\ n\ \cos\varphi$, where m—is the diffraction order, φ—is the angle of incidence, n—is the mean refractive index of medium

Experimental measurements of second and first order diffraction for oblique incidence light allowed calculating an extremely small value of pitch of 0.145 μm [76]. The two component mixture which consists of the achiral liquid crystal 4,4′-diheptyloxyazoxybenzene (HOAB) and the optically active dopant 2,5-bis-[4-(2-chloropentanoyloxy)-phenyl] —

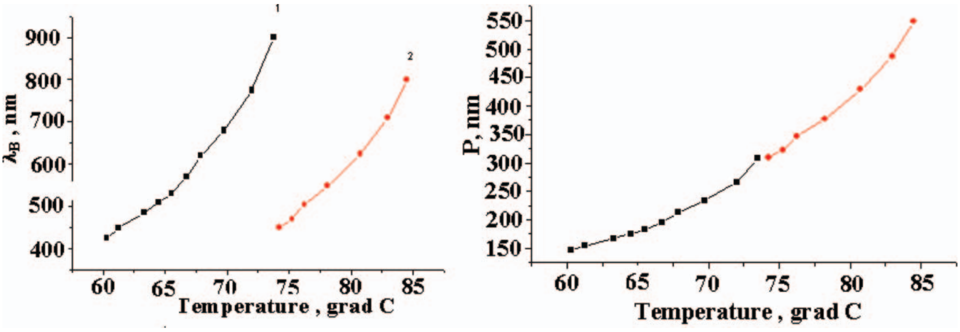


Figure 12. The temperature dependence of wavelength (λ_B) of first (1) and second (2) order diffraction (left) and P (right) for mixture of 40% HOAB for inclined angle $\varphi = 20^o$.

pyrimidine was studied. In Fig. 12 the dependence of wavelength (λ_B) of first and second order diffraction and helix pitch P on temperature for mixture of 40% HOAB for inclined angle $\varphi = 20^o$ is shown. P was calculated from data of λ_B of the both diffraction order, taking for n the value equal to 1.55.

As indicated in Introduction in mixture of smectogenic nematic with chiral dopant, near the phase transition from the cholesteric to smectic A phase, an intermediate phase is formed, called "Twist Grain Boundary" (TGB). This complex "defect" phase represents the frustrated phase derived from chiral molecules and stabilized by screw dislocation [77]. The pretransitional phase with anomalous selective reflection properties was observed in three component chiral systems, consisted of two nematogenic liquid crystals with different phase sequences (one with smectic A phase and another with smectic C phase) and optically active nonmesomorphic dopant (Fig. 13) [78–80].

In the cholesteric phase the output intensity of nonpolirized light of SRB (λ_B) is equal approximately to 50% the input intensity. But in the temperature interval corresponding to intermediate phase λ_B ceases changing with temperature and unusually low intensity of transmitted light (~20%) have been observed [78]. Calorimetric investigations gave evidence that the intermediate state is a separated twisted mesophase. X-ray investigations pointed that this phase has a layered structure. The layer spacing of 33 Å corresponds to that in the Smectic A phase [79]. These results allowed identifying this pretransitional phase as the TGB phase. However, besides of anomalous selective reflection, the texture, pitch dependence on temperature and behavior in electric field in this pretransitional phase differed with those in conventional TGB phase. We do not exclude that the intermediate phase could be similar to the structural composition used in [81], where a nematic layer, owning phase retarder properties, is arranged between two cholesteric layers with the same handedness. In our case, instead of nematic layers, smectic A layers oriented normal to the cell surfaces, and thus with director parallel to surfaces, could exist [82]. In Fig. 14 this layered structure is shown. Another possibility is that a smectic A layer is sandwiched between two TGB layers.

Blue phases (BPs) are observed in CLCs with short pitch in the transition to isotropic phase. The BP is characterized by a polymorphism: in order of increasing temperature formed to three main distinct blue phases BP1, BPII and BPIII [83]. A fourth blue phase BPS has been observed transforming from the supercooled BPI [84, 85]. Electro-optical effects in room temperature BP with positive dielectric anisotropy have been studied [86]. The following mixture of the chiral CB15 (Merck) component – 4-cyano-4′-(2-methylbutyl)

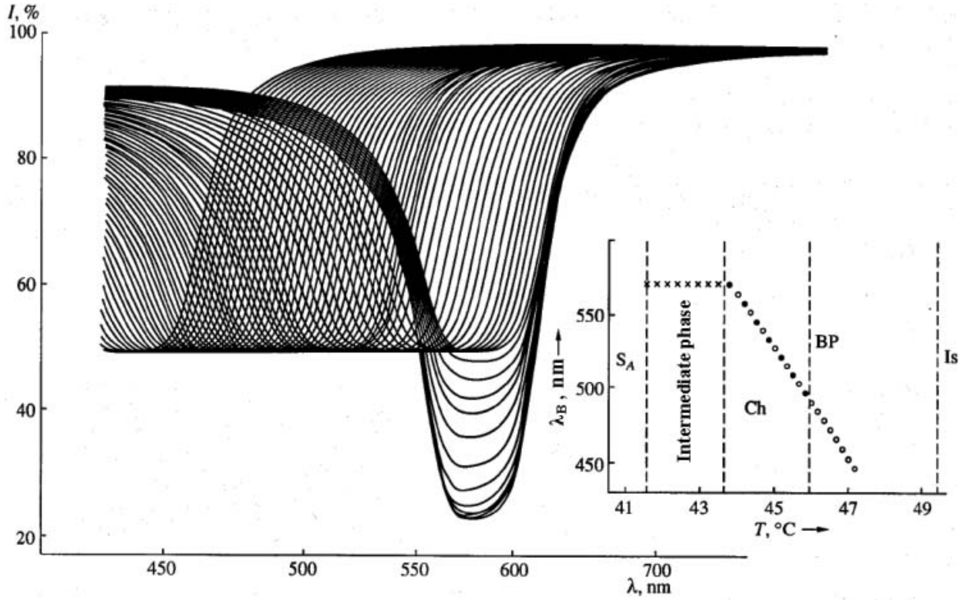


Figure 13. Transmission spectrum of the mixture: 82 wt% [80 wt% 8CB + 20 wt% HOPOOB] + 18 wt% TC obtained during lowering of the temperature. In the inset: the schematic phase diagram and the temperature dependence of the λ_B. Open circles correspond to cholesteric heating, filled ones, to cholesteric cooling.

biphenyl, and nematic ZhK-807 (NIOPIK)—a six-component mixture of alkyl and alkoxy-cyano biphenyls was employed.

As shown in Fig. 15 the maximum wavelength of the Bragg reflection (λ_0) of blue phases, BP II and BP I, shifts to longer wavelength with increasing electric field. The electric field influences more strongly on BP II: a reversible shift of λ_0 up to 80 nm was observed. The red shift of the wavelengths observed for the BPI and the BP II is associated with

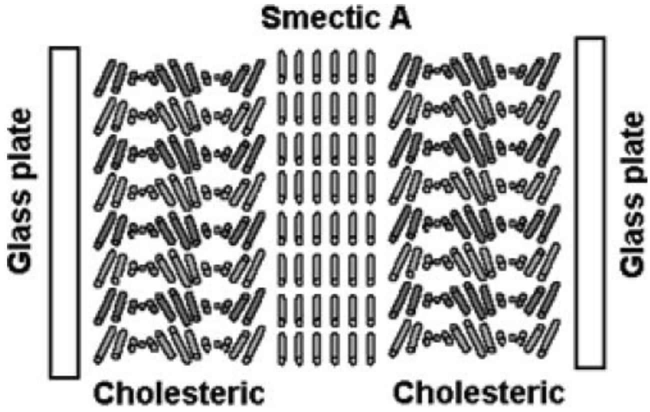


Figure 14. The model of layered structure.

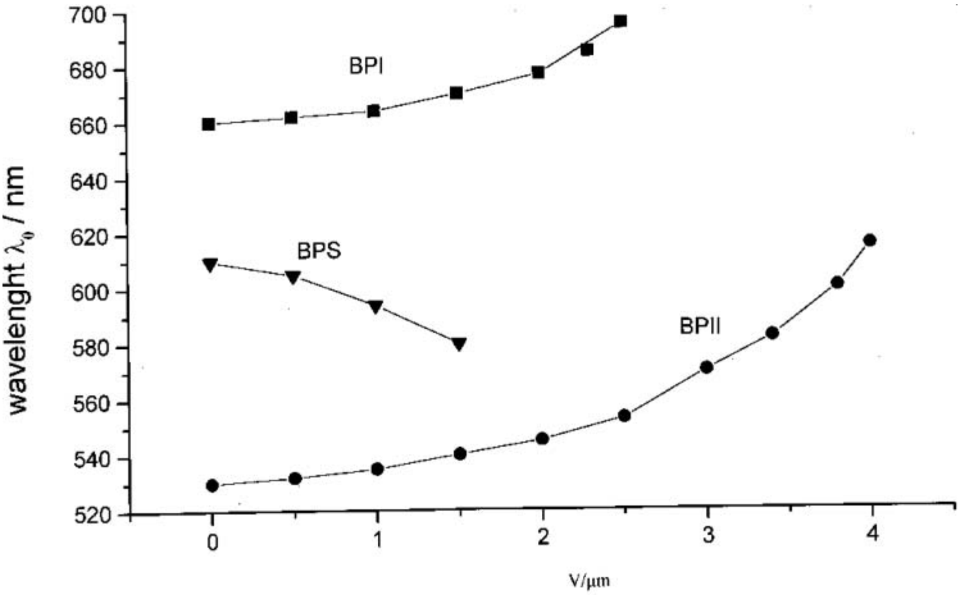


Figure 15. Wavelength λ_0 *versus* E (V/μm) for the mixture containing 50 wt% of CB15 and 50 wt% of ZhK-807. Notation: (▼) BP S at 17.80°C; (●) - BP II at 19.40°C; (■) – BP I at 18.80°C.

the helix unwinding in the electric field in e mixtures of the positive dielectric anisotropy. however, the shift for the BP S is directed toward shorter wavelengths.

In Fig. 16 e transmission spectra is shown for the BP II in applied electric field for the mixture with CB15 concentration equal to 50.5 wt.% at the temperature 19.85°C. The reversible BP II → BP I phase transition at electric field strength E = 2 V /μm and at E>4 V/μm, the reversible BP II → nematic phase transition were observed.

Together with electrooptics the photooptic properties of BPs also have been studied. In [87] or the first time the change of Bragg wavelengths in blue phases and creation of blue

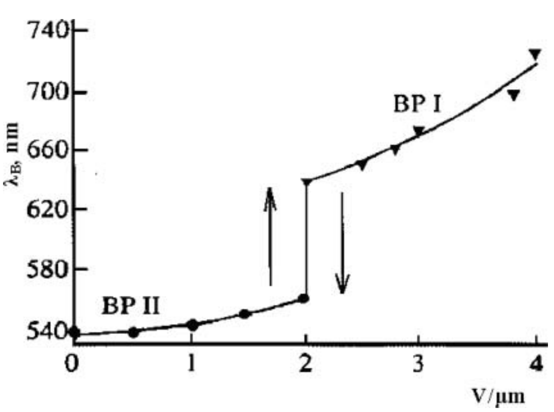


Figure 16. Wavelength λ_0 *versus* E (V/μm) for the mixture containing 49.5 wt% of CB15 and 50.5 wt% of ZhK-807 taken at 19.85°C in BP II range.

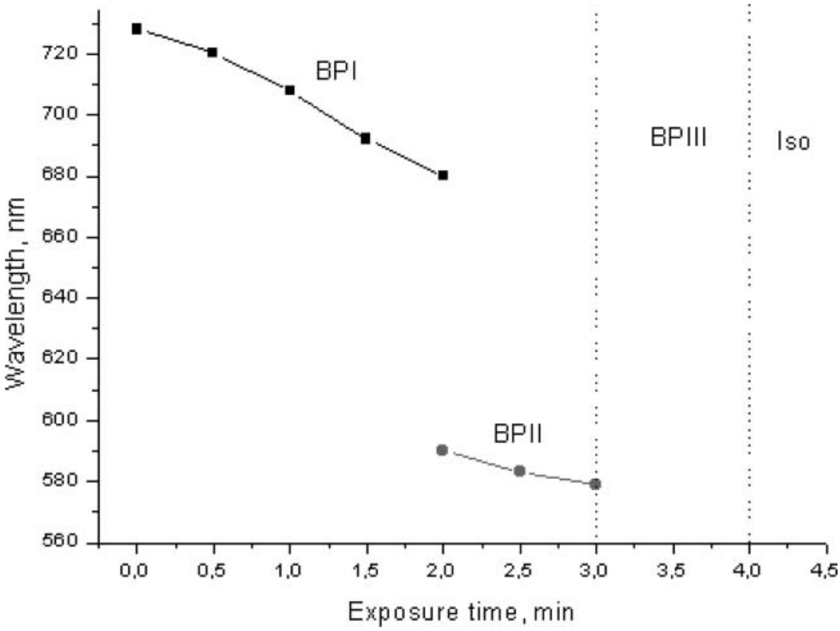


Figure 17. The exposure time dependence of the selective reflection wavelength at 29°C when exposed to UV light from themercury lamp and 365 nm filter.

phases due to light irradiation were investigated. As nematic host in this case ZhK-440 was employed which at UV irradiation undergoes to *trans-cis* summarization. For the mixture 52% ZhK-440 and 48% CB-15 (by weight) in the case of BPI we fixed the temperature (29°C), when $d\lambda_B/dT = 0$. As shown in Fig. 17 for BPI under UV irradiation λ_B decreases with increase of exposure time, and after 2 min irradiation the transition to BPII was observed. After 3 min of irra diation the transition into BPIII was observed. During 4 min of irradiation the transition from BPI into isotropic phase takes place. Under UV irradiation in the case of BPS, λ_B increases with increasing of exposure time as shown in Fig. 18. The effect is reversible: under irradiation by visible light (436 nm) the decrease of λ_B was observed.

Thus blue phases may be considered as examples of tunable photonic crystals with many potential applications

4. Application of Cholesterics

The following proposals of practical application of CLCs will be considered:

4.1. Image converters

The image converter (IC) based on the combination of semiconductor-dielectric (SD) structure and CLC (Fig. 19) owing to its functional possibilities and easy technologies have prospects in optical data processing systems [88, 89]. The advantages of a real-time near IR-to-visible IC in the combination of a narrow band semiconductor (Si) — dielectric

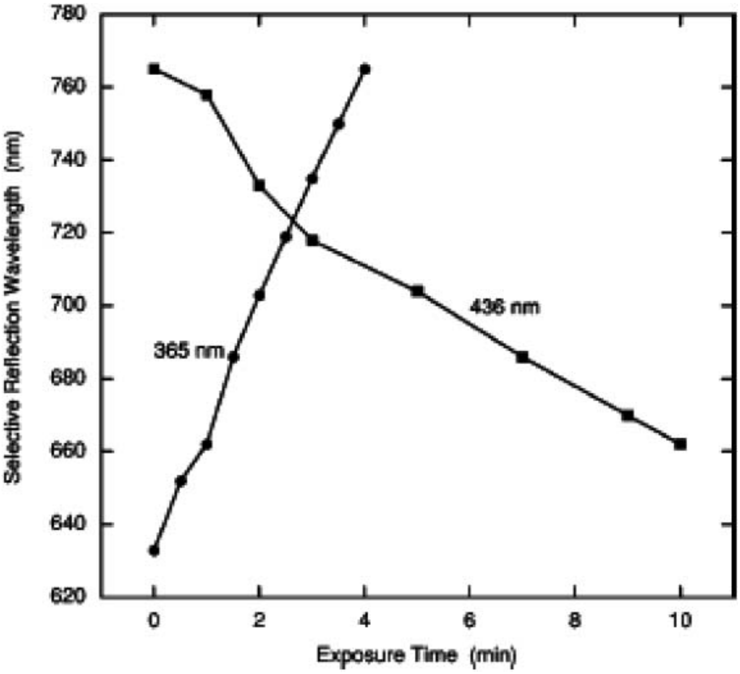


Figure 18. Selective reflection wavelength of mixture II in BPS as a function of time when exposed to the UV lamp first with a 365 nm filter and then with a 436 nm filter.

structure and CLC using cholesteric-nematic phase transition are: broad bandwidth, high resolution, incoherent- coherent image conversion, wavelength conversion capability, possibility translate image picture into positive to negative, considerable decrease of image exposition time, which is not limited by inertia of LC.

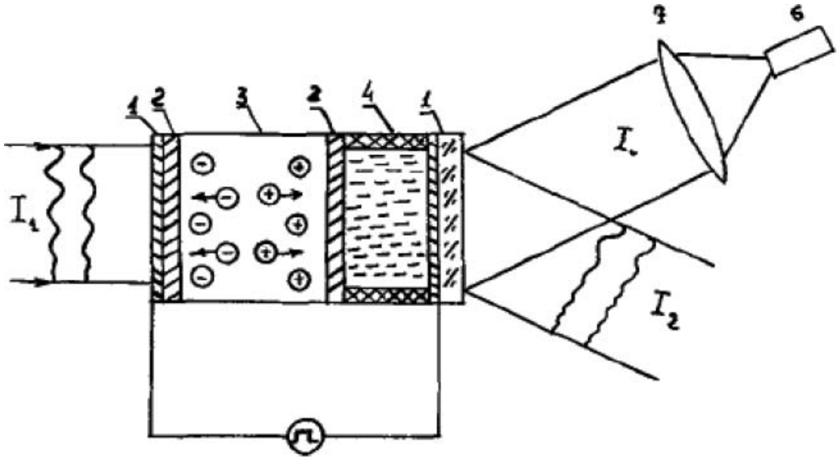


Figure 19. Configuration of IC: 1 – elctrodes, 2 – dielectric layers, 3 – semiconductor, 4 – CLC, 5 – pulse voltage, 6 – laser, 7 – collimator, I_1 input image, I_2 – read-out image.

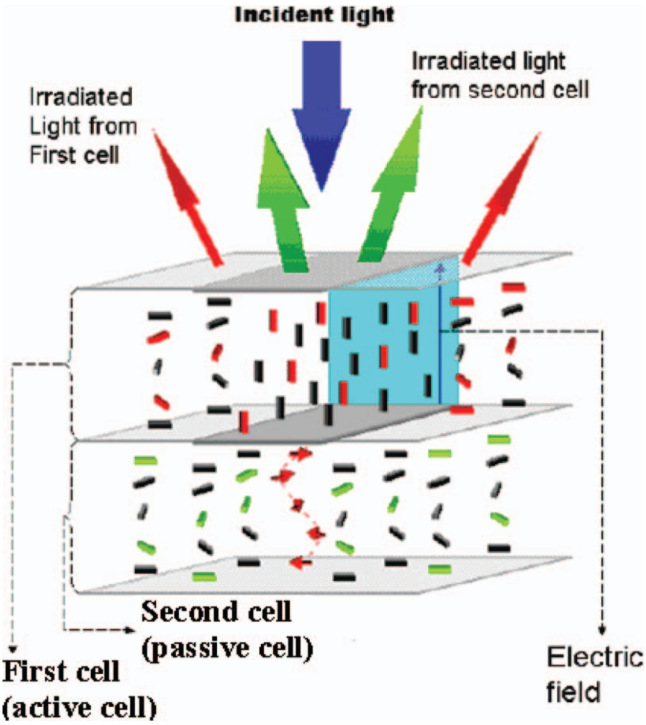


Figure 20. The illustration of two layered cell.

4.2. Luminescent LC Displays.

LCDs based on a luminescent dichroic-dye-doped CLC with positive dielectric anisotropy are proposed [90]. In the initial state, the orientation of the dye molecules provides effective light absorption and irradiation. By applying an electric field to the cell, the absorption and thus the luminescence is absent. A two-color luminescence could be achieved by sandwiching two cells: the upper cell consists of a cholesteric LC with two dyes (sensitizer and emitter) and is used with an applied voltage (active cell); the lower cell consists of a cholesteric LC doped with one dye and works without applying a voltage (passive cell). In Figs. 20 and 21 the illustration of two layered cell and the luminescence spectrum of two dyes are shown accordingly.

4.3 UV sensors.

Photooptic effect in CLC was successfully used for creation of UV detectors. UV radiation can be divided into three main categories UVA (320–400 nm), UVB (280–320 nm) and UVC (100–280 nm). The human skin is well known to be affected by solar Ultraviolet –UV-B radiation. The Erythemal Response Spectrum demonstrates erythemal skin sensitivity for every UV wavelength. Hence development of a new materials based on photosensitivity of cholesterics to definite ranges solar irradiation has nowadays a relevant practical interest. In [91] was shown that the CLC mixture based on azoxy ZhK-440 nematic host can be used as a sensor material of solar UV A radiation and a mixture consisting of non-photoisomerizable nematic and a photosensitive chiral dopant. ZLI-811 as a UV C part of solar irradiation

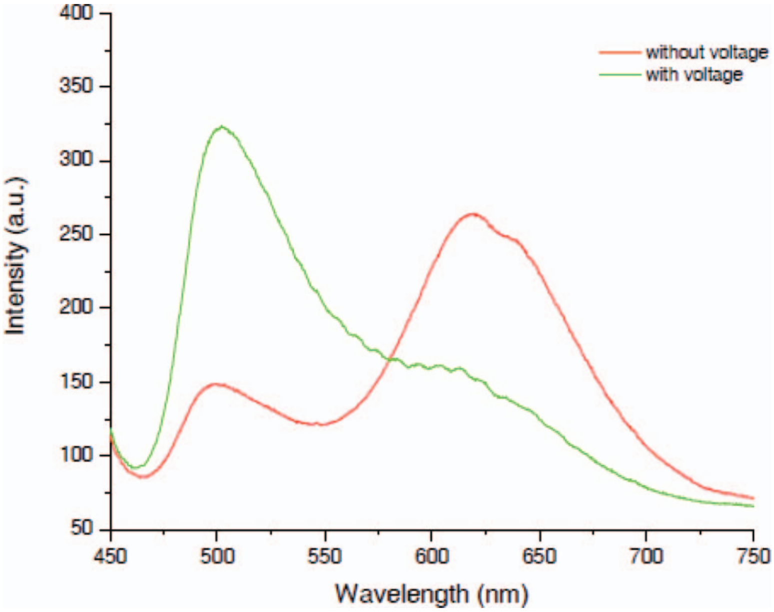


Figure 21. Luminescence spectrum of cholesteric LC in double-layer combination. The lower cell consists of a cholesteric LC doped with green dye and used without an applied voltage. The upper cell consists of a cholesteric LC with two dyes [one green (sensitizer) and one red (emitter)] and used in the off-state (red line) or on-state (green line).

accordingly were used (absorption wavelength range of ZhK 440 is 320–400 nm and the ZLI-811 absorbs at wavelengths shorter than 290 nm).

Was considered 2 ways for the realization of creation cholesteric mixtures sensitive to solar UVB irradiation. The first mixture is based on a cholesteric system (nematic + optically active dopant) doped with ergosterol (provitamin D_2) [92, 93]. Was shown a possibility of UVB radiation (280–315 nm) detection by monitoring the helical pitch changes caused by the photo induced transformation of provitamin D_2 to vitamin D_2, having opposite signs of their helical twisting power in the cholesteric matrix (Fig. 22).

The second mixture is based on a photosensitive nematic component in CLC mixture-a derivative of cinnamate (CH=CH-COO) - ZhK-537, which has an absorption spectrum very close to the spectrum of human skin sensitivity to sunburn (UV-B range: 290–320 nm) and thus is able to precisely measure UV in accordance with the Erythemal Response Spectrum - erythemal skin sensitivity- for every UV wavelength (Fig. 23). The photograph of a LC sample in Fig. 24 shows the change of colors caused by the shift of the selective reflection peak in a sample exposed to direct sunlight. The photograph demonstrates that this color change feature can be practically used in UV-meters.

4.4. *Wide range tunable compact CLC lasers.*

In Dye lasers CLC could be used: as a resonator mirror and as a distributed feedback medium in dye doped (DD) distributed feedback (DFB) CLC laser.

If a small amount of dye with linear dichroic absorption is dissolved in a CLC the helical structure transforms the linear dichroism into circular dichroism. However, the absorption is

Figure 22. Change of colours for mixture 92% (73% ZLI-1695 + 27% ZLI-811R) + 8% ProD$_2$ (Dark blue – before irradiation, blue – after 15 min UV irradiation and green – after 40 min UV irradiation.

suppressed when the wavelengths of absorption and selective reflection coincide. (Bormann effect) [2, 83], as experimentally observed in [93, 94]. Accordingly, the structure of a CLC doped with a luminescent dichroic dye acquires the property of polarized luminescence. When the wavelengths of both the selective reflection and luminescence coincide, one circularly polarized component of the luminescent light is suppressed [95].

The idea of tunable lasing in cholesteric liquid crystals was put forward in [96] and the theoretical analysis performed in [97]. For the first time lasing with distributed feedback in a DD CLC was observed in a ternary mixture of cholesterol derivatives (steroids) and a benzanthrone dye, where tunability of lasing was achieved varying the temperature [98].

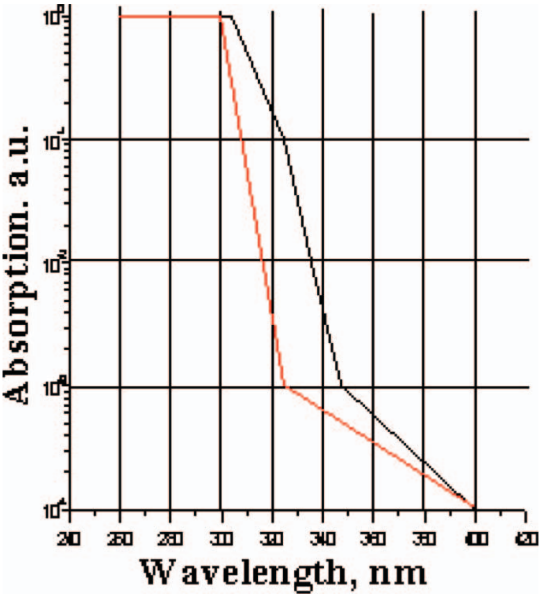


Figure 23. The Erythemal Response Spectrum and absorption of the UV sensitive cholesteric mixture ZLI 1695+1% ZhK-537 (black line).

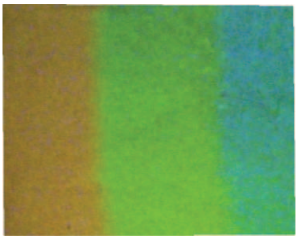


Figure 24. Three-color square. Change of colour under direct sun irradiation. Gold – no UV exposure. Green – 4 min direct sun irradiation. Blue – 8 min in the mixture 76.5% (50% ZLI 1695+50% Zhk-537)+ 23.5% ZLI 6248.

The lasing was observed in the center of SRB. Recently were investigated lasing thresholds and lasing spectra as a function of the planar texture perfection in steroid CLC [99]. The location of the lasing spectrum at the SRB center was explained by the coupled wave model [100]. Other side in analogy with the electronic band gap in semiconductors CLC could be as a medium with a photonic band gap [101]. In DD CLC the fluorescent emission is suppressed inside the reflection band and enhanced at the band edges. This approach

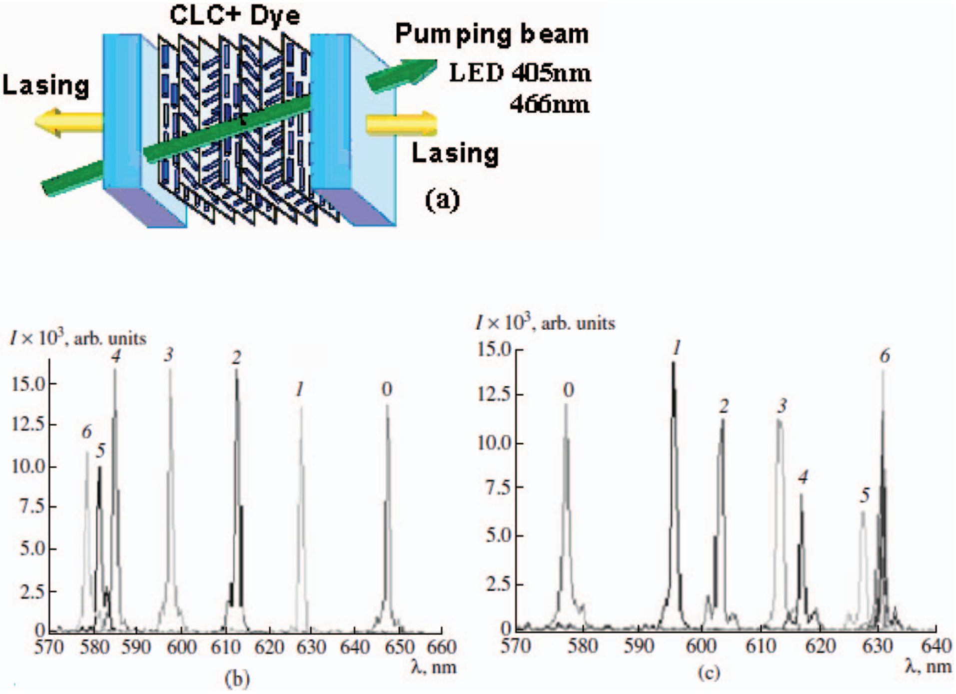


Figure 25. (a) Experimental scheme. (b) Lasing spectrum of the cell containing mixture 99.5% (71%ZhK-440 + 29% MLC-6247) + 0.5%DCM before (0) and after irradiation with 405 nm LED for 1 min (1), 2 min (2), 4 min (3), 6 min (4), 8 min (5) and 10 min (6). (c) Backward shift of the lasing wavelength when 405 nm LED is switched off (0) and 466 nm LED is switched on for increasing exposure times: (1) 30 sec (1), 1 min (2), 1min and 30 sec (3), 2 min (4), 3 min (5), from 4 to 10 min (6).

allowed explaining the observed laser emission at the edge of the selective reflection band in DD CLC [102].

The lasing wavelength in DD CLCs can be tuned by varying the chiral-dopant concentration or the temperature, under mechanical tension, and with the use of an applied electric field [98, 102, 103]. In [70] was proposed the tuning of the lasing wavelength by light. Since the publication of this pioneering work, there have appeared a number of papers concerning the phototunable cholesteric liquid-crystal lasers [104–108].

Recently LED-controlled reversible smooth tuning of lasing in DD CLC was studied [69]. As shown in Fig. 25 the reversible tuning of the lasing wavelength in CLCs containing nematic ZhK-440 (azoxy- photo-sensitive component) was accomplished by varying the time of irradiation of samples with two LEDs. The LED emitting at 405 nm controlled the blue shift of lasing wavelength and the LED emitting at 466 nm caused the reverse shift. The second harmonic of a Q-switched Nd:YAG laser was used as a light source for pumping the CLC laser. The pulse wavelength, width, and repetition rate were 532 nm, 4 ns, and 1 Hz, respectively.

An alternative approach to the laser generation tuning over a wide range of wavelengths was proposed in [71]. In this work a DD CLC cell with an induced gradient of the helical pitch was employed. The tuning range of laser radiation was limited by the width of the dye emission band. Then, the range of laser wavelengths was considerably extended using a specially designed DD CLC cell: the gradient of chiral dopant concentration was supplemented with spatial distribution of different dyes [110]. The cholesteric liquid-crystal mixture contained six dyes. The total luminescence band of these dyes covered the range from 373 to 684 nm. The cell was filled in such a way that the concentration gradient of the chiral dopant ensured the specific helical pitch necessary for dye lasing. In some regions of the cell, two dyes operating in the Förster regime were involved in the lasing. The lasing spectra obtained by the displacement of the described cell are depicted in Fig. 26. A Nitrogen laser (337 nm, 7 ns, 1–10 Hz) was used as a pump source. Thus the tuning of a DD CLC mirror-less laser in the UV-NIR wavelength range was obtained using a single device based on a CLC as a resonator and several laser dyes [111].

One of the main drawbacks of DD CLC lasers, limiting their technological application is their low stability. Several attempts were made to optimize lasing conditions and

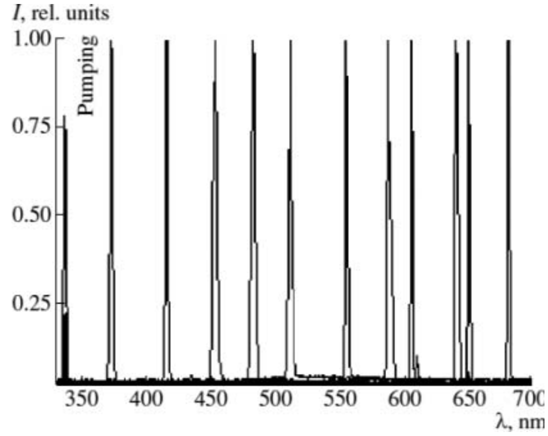


Figure 26. Lasing spectra of the cell with a pitch gradient and six dyes.

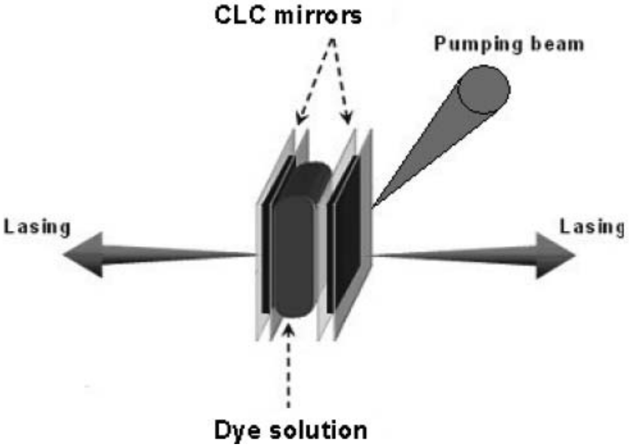


Figure 27. Scheme of dye laser with CLC mirrors.

performance characteristics in order to improve their technological appeal. A rotating cell was suggested to avoid deformation of the CLC texture and bleaching of the dye due to the high energy of the pumping beam [112]. It was demonstrated that the addition of chiral luminescent compounds allows a fine tuning of the laser emission [113]. An enhancement of lasing efficiency was also observed using a CLC as a reflector in a DD CLC laser [114]. Another way to enhance the lasing property of DD CLC systems is the defect mode lasing. The introduction of a defect in the CLC structure can be achieved in two ways: by replacing a part of the host medium with a material that has a different dielectric constant e.g. two layers of CLC sandwiching a layer of an isotropic medium [115] or by introducing a phase jump inside the CLC cell [116, 117]. The use of a CLC layer as a resonator-mirror in conventional lasers was carried out long time ago [118–123]. The lasing in three layers cell where a dye solution is sandwiched between two CLCs can be considered as the defect mode type. Different dye solutions were investigated: in three layered structures where between two CLC layers with the same pitch and handedness a dye doped nematic LC [124] or a dye doped CLC [125] was sandwiched. Also the defect mode type lasing was studied when between dielectric multilayer a dye doped CLC [126] or a dye doped nematic LC [127] was sandwiched. It should be noted that the lasing threshold observed with the three-layered helical CLC is lower than for conventional DD CLC lasers [126, 128–130]. A frequency-tunable dye laser in which one of the resonator mirrors was an oriented layer of a cholesteric liquid crystal was proposed long time ago.

Recently a novel defect mode type lasing in a three layer system, where a cell containing a dye solution was sandwiched between two CLC films was investigated [131–134] (Fig. 27). The separation of the CLC and the active medium allows: (1) to avoid the degradation of the CLC structure caused by the absorption of the pumping energy, (2) to use dyes not soluble in LCs and (3) to use the optimal thickness both for the CLC layer and for the dye solution layer (thicker dye layer and thinner CLC layer). For obtaining the wide range tunable laser emission two approaches were exploited: spatially tunable and temperature tunable systems.

In the spatially tunable system one of the CLC cells contained a wide band gap material while the second one represented a cell with a spatially modulated pitch. For the cell preparation the concentration gradient method was used. Three mixtures with different

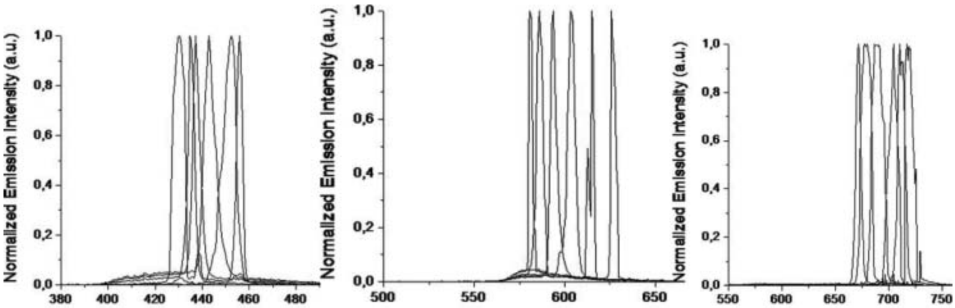


Figure 28. Laser emission and tuning from three different cells filled with solution of glycerol +luminophore OF(mb) (ICMA, Universidad de Zaragoza-CSIC, Spain) (a), Rhodamine 6G (Sigma Aldrich), (b) and LDS698 (Exciton) (c).

concentration of the optically active dopant were prepared. The cell was partially filled, by capillarity, with one of the three mixtures; the filling was then completed using in sequence the other two mixtures. The threshold of laser generation was estimated to be 0.75 μJ/pulse. The tuning of the laser emission, from UV to near IR, was observed in different cells using different luminescent dyes (Fig. 28).In this chapter were presented various possibilities in employing CLCs in application.

Summary

To summarize, our aim was to show that CLCs are very important electro- and photo- optical material due to high sensitivity of macromolecular parameter - helix pitch to insignificant changes in applied external fields and in the molecular structure.

This paper presents an overview of the results obtained by a large collaboration of scientists from Georgia, France, Germany, Italy, Russia, Spain, Ukraine and USA and I shoud like to express my grateful thanks to co-authors and colleagues for this cooperation.

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