OPTICS. QUANTUM ELECTRONICS. HOLOGRAPHY

PHOTOTUNING OF THE LASING SPECTRA OF DOPED CHOLESTERIC LIQUID CRYSTALS

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On the basis of induced cholesteric liquid crystals (CLCs), a new method for tuning the frequency of a laser with distributed feedback (DFB) has been proposed. The essence of the method consists in ultraviolet (UV) irradiation of the active media, which induces the phototransformation of chiral dopant molecules by changing their helical twisting power and a helical pitch. A principal capability to tune the lasing frequency of such a DFB laser smoothly and reversibly owing to the process of trans-cis isomerization of chiral molecules has been demonstrated experimentally.

The natural helical structure in CLCs allows one, when the CLCs are activated with lasing dyes, to create simple and compact lasers with DFB [1]. In an oriented CLC with the planar texture, the DFB emerges due to the Bragg scattering of light by an amplitude-phase grating which is formed by both the helical orientation of the CLC layers (the phase grating) and the absorption by a dye that is partially ordered in the CLC (the amplitude grating). In order to obtain the lasing, when exciting into the absorption band of the dopant dye making use of a pulsed laser (a solid or gas one), the fluorescence spectrum of the dye, which activates the CLC, should cover, as much as possible, the spectral range of Bragg diffraction by such a periodic structure. As for the lasing wavelength, it is determined by the period of the Bragg grating.

For the first time, such a laser has been realized in work [1]. Steroid CLCs activated by lasing dyes, which are characterized by a rather strong dependence of their helical pitch on temperature, were used as an active medium. Provided that the thickness of the CLC layer is about several tens of microns, which is necessary for the laser to operate, and the layer is oriented by rubbing followed by a shift of substrates with respect to each another, a weak coupling between such CLCs and the aligning substrates emerges. In this case, the variation of the helical pitch of the CLCs with temperature is smooth and monotonous, contrary to the variant of strong coupling, where the helix pitch has a jump-like behavior [2].

Since the lasers based on doped CLCs compose a unique class of lasers, the active medium of which can be implemented as a surface of any area and curvature and with no mirror resonators, they attract great interest in the domain of the development of displays with enhanced brightness or color laser projective screens [3]. Active studies of such lasers on the basis of new CLC materials, which are more technological than the viscous derivatives of cholesterol, have been started recently [4–7].

It is worth noting that, against the background of a permanently increasing interest in the researches of the lasing by doped CLCs as a class of one-dimensional photon crystals, some authors choose rather voluntarily the excitation pulse duration for pumping such lasers; they apply laser pulses with a rather long duration [4]. We consider it necessary to recall that the essential modifications of the optical characteristics of CLCs within a period of about 100 ns have been discovered in work [8], where the dynamics of the destruction of a CLC helical structure in the field of powerful nanosecond pulses was studied experimentally. Therefore, the application of laser pulses, whose duration is longer than 100 ns, is undesirable for the CLC excitation. It is the modification of thermo-optical characteristics of the CLC layer that can explain the

appearance of new modes in the lasing spectrum. The distance between them does not correspond to that between the modes of a Fabry—Perot interferometer which was observed in work [4] when pumping with 150-ns laser pulses. Instead of this interpretation, the authors of work [4] proposed a complicated and insufficiently argued hypothesis dealing with the peculiarity of the photon mode density at the edge of the opacity band of a photonic crystal. We notice that, in all the experimental works devoted to the study of the spectral lasing characteristics of doped CLCs, when the latter are excited by short nanosecond laser pulses (up to 30 ns) [1, 9–11], including those reported before work [4], the distance between the modes in the lasing spectra corresponded to that between the modes of the Fabry—Perot interferometer.

A lag in the temperature-induced variation of the lasing frequency and the necessity of thermal stabilization for the active substance complicate the wide application of DFB-lasers based on steroid CLCs. The employment of less inertial means to vary the helical pitch of CLCs — e.g., a controllable stretching/squeezing of aligned CLC layers [12], including polymeric CLC ones [6] — and, correspondingly, the lasing frequencies of lasers where those CLCs are used, is still problematic owing to the obvious technical difficulties of their application.

It is known that in some types of induced CLCs prepared on the basis of nematic liquid crystals (NLCs) with chiral dopants, UV irradiation stimulates a conformational molecular modification of the latter. CLCs of this type, including those prepared with the help of non-mesogen chiral dopants allow one to change their helical pitch by photoexciting certain stereo-isomeric forms of molecules owing to the fact that there are various photo-isomeric forms of molecules in them and their photo-isomerization proceeds easily [13, 14]. The chiral dopant that is in a trans- or a cis-form undergoes a conformational modification, the trans-cis isomerization, after having absorbed a quantum of UV radiation. The prevailing direction of the photoreaction is governed by the wavelength of the incident light, which corresponds to the maximal absorption of the trans- or the cis-form of the chiral dopant. The transition of a dopant molecule from the trans- to cis-conformation results in a modification of its chiral capability, which brings about, in its turn, the variation of the cholesteric helical pitch [13].

In its pure form, such an effect should manifest itself in mixtures "NLC–chiral dopant", whose helical pitch does not depend on temperature. The latter condition

is needed to exclude a shift of the helical pitch which may be induced by heating the liquid crystal with the activating UV radiation.

The variation of a helical pitch of CLCs under UV irradiation, which was studied in works [13, 14], was, in the main, irreversible and revealed itself through an increase in the maximum wavelength of the selective reflection (SR) band and its going beyond the visible range. The dependence of the SR band on irradiation has to be governed by the mechanism of phototransformation of chiral molecules. Such mechanisms were studied well enough for NLCs [15]. At the same time, we know only about early results of similar researches carried out for CLCs [13, 14]. However, those researches elucidated neither the mechanism which would provide the reversibility of the helical pitch nor the influence of the excitation selectivity, i.e. the excitation of only one of the photoisomeric forms, on the variation rate of the helical pitch.

Our work aimed at studying experimentally the dynamics of the helical pitch variation by analyzing the SR and lasing spectra. From the practical aspect, the purpose of the work was to study an opportunity for tuning the lasing frequency of doped CLCs under UV irradiation.

We studied liquid crystal specimens prepared on the basis of the mixtures of NLCs and chiral dopants of both the mesogen and non-mesogen types. The induced CLCs, being the mixtures of NLCs and chiral dopants, activated by a dye, were used as the active medium of a DFB-laser. In order to activate all types of the induced CLCs, the same F490 phenolenone dye was used. We used also commercial NLC mixtures.

For studying the influence of the chiral dopant type and the UV irradiation dose on the variation of the helical pitch, dopants of two types were used: a development of the Institute of Single Crystals, NASU, 2-(4′-phenylbenzylidene)-L-menthone (dopant 1) and a commercial product of the Merck firm ZLI 811 (dopant 2). They were introduced into nematics ZhK-440 (production of the NIIOPiK, Russia) and MJ 196180 (a commercial product of the Merck firm, respectively. The planar textures of CLCs, which were induced by those dopants, were fabricated according to the technique described in works [10, 11]. The thickness of induced CLC layers was controlled using Teflon spacers and was selected within the interval from 15 to 50 μm. The transmission spectra of the planar textures of both pure and doped CLCs were analyzed making use of an SF-20 spectrophotometer. For UV irradiation of CLCs, an
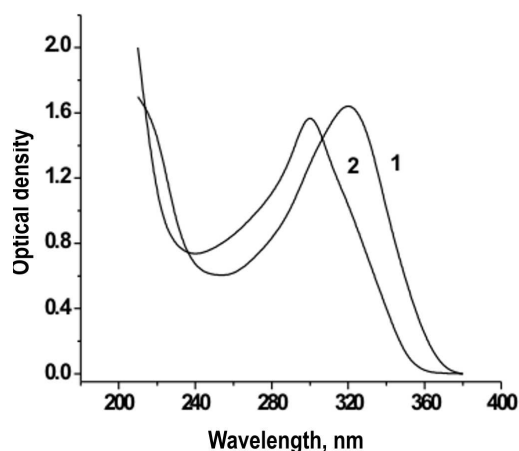
Fig. 1. Absorption spectra of a 0.01% solution of 2-(4′-phenylbenzylidene)-L-menthone in ethyl alcohol: before UV irradiation (1) and after 10-min UV irradiation (2)
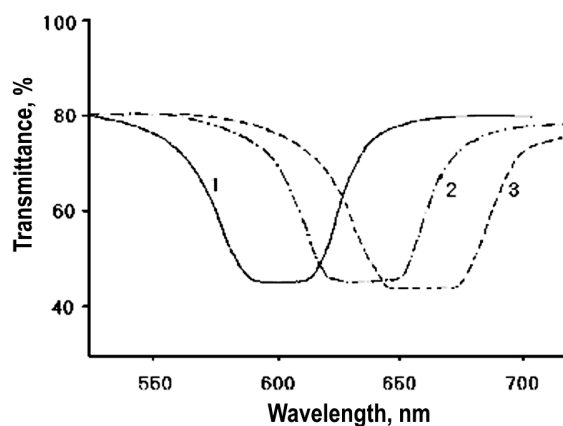

Fig. 2. Transmission spectra of the mixture ZhK—440 (88%) + 2-(4′-phenylbenzylidene)-L-menthone (12%) under UV irradiation: before irradiation (1), after 3-s irradiation (2), and 5-s irradiation (3)

OI-18 low-pressure mercury lamp with air-cooling, the radiation power of 38 mW/cm^{-2}, and the stabilized discharge current was used. A DFB-laser was excited by the emission of the second harmonic of another Nd^{3+}-glass laser ($\lambda = 530$ nm) with a passive Q-factor modulation, which operated in the mode of solitary nanosecond pulses ($\tau_i \approx 18$ ns). The lasing spectra of doped CLCs were registered on a spectrograph with a dispersion of 0.6 nm/mm.

Fig. 1 presents the absorption spectrum of the 0.01% solution of dopant 1 in ethyl alcohol (curve 1). The maximum of its long-wave absorption band is located at 325 nm. The absorption maxima of both stereo-isomeric forms are located close to each other and, practically, do not differ. After the 10-min irradiation of such a solution in a quartz cell with a mercury lamp with the radiation intensity indicated above, the absorption maximum shifts towards short waves by 20 nm (curve 2). If this dopant was introduced into ZhK-440 (the mixture composition was ZhK-440 (88%) and 2-(4′-phenylbenzylidene)-L-menthone (12%), the maximum of the SR band was observed at 605 nm.

The irradiation of a planar texture of a neat CLC of such content, located between quartz substrates, with the light of a mercury lamp leads to the modification of the transmission spectra, Fig. 2. We note that the edge of the absorption band of ZhK-440 is located at about 420 nm; therefore, in the visible range above 420 nm, both the NLC and the chiral dopant practically do not absorb. Hence, the modifications of the transmission spectrum, which emerge after the chiral dopant is introduced into the NLC, are governed by a SR from the helical periodic structure this dopant has created. The SR band began to shift after the 1-min irradiation. After the 3-min irradiation with a mercury lamp, the SR band became shifted towards the long-wave range by 40 nm (curve 2) and after the 5-min irradiation by 70 nm (curve 3) with respect to the SR spectrum of the non-irradiated specimen. After the 10-min irradiation, the red-shift of the SR band grew considerably and reached 150–200 nm. The shift of the SR band towards long waves evidences, in this case, for the conformational trans-cis transition of chiral dopant molecules. The growth of the concentration of non-complanar cis-form, which is characterized by lower chiral capability, results in the increase of the helical pitch.

An essential detail should be emphasized. As well as in works [13, 14], the change of the helical pitch under UV irradiation in our experiments was irreversible. Its reversing happened neither spontaneously, within several days, nor forcibly, as a result of heating the irradiated cell. Taking into account that the trans-form of an organic molecule is more stable, so that the cis-trans transition should happen, to a great extent, spontaneously [16], we believed that heating would initiate the reverse conformational cis-trans transformations of molecules. In our experiments, however, a reverse process for chiral dopant 1 was observed: the helical pitch of the CLC induced by this dopant grew monotonously at a rate of approximately
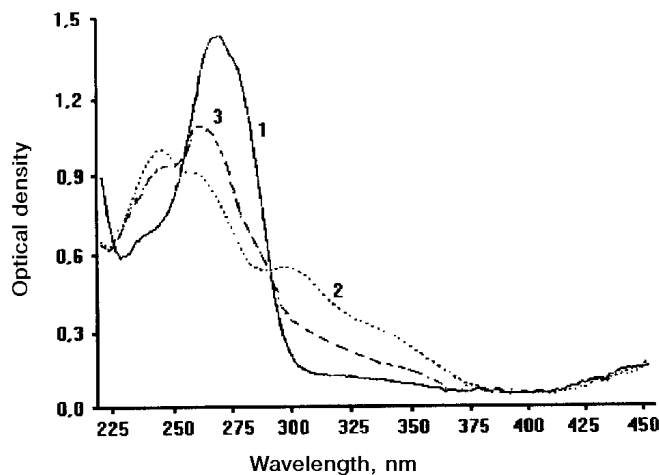
Fig. 3. Absorption spectra of a 0.01% solution of ZLI 811 in ethyl alcohol: before UV irradiation (*1*), after 10-min UV irradiation (*2*), and 15 h after UV irradiation (*3*)

Fig. 4. Transmission spectra of the CLC with the content LG—5 (77.54%) + ZLI 811 (22.46%): before UV irradiation (*B*), 40 s after UV irradiation (*C*), 50 s after UV irradiation (*D*), and 24 h after UV irradiation (*E*)

35—40 nm per month, even under condition of dark storage. In this case, the created cis-conformation of chiral dopant 1 can be considered rather stable and energy-beneficial.

Provided that the CLC induced by dopant 1 was activated with the F490 phenolenone dye, the lasing tunable within the limits of 45 nm under the action of UV irradiation with the intensity quoted above and the duration up to 2 s was obtained. The restriction of the frequency tuning interval is caused by the spectral position of the dye fluorescence band and the spectral range of amplification, within the limits of which the lasing was got [11]. The lasing spectrum was composed of three lines separated by a distance which, as well as in a Fabry—Perot interferometer, was defined by the thickness of the CLC active layer.

A trial of the chiral dopant of another type — ZLI811 — revealed that its twisting power is a half of the twisting power of chiral dopant 1. This dopant served as the basis for creating an induced CLC with the following content: MJ 196180 NLC (77.54%) + ZLI 811 chiral dopant (22.46%). The planar structure in such an induced CLC selectively reflected light in the orange range of the spectrum, with the SR band maximum being at 603 nm.

Fig. 3 presents the absorption spectrum of a 0.01% solution of ZLI 811 in ethyl alcohol (curve *B*). The maximum of the long-wave absorption band is at about 275 nm. After the 10-min UV irradiation of this solution in a quartz cell with the mercury lamp, the maximum of the absorption band shifts by 35 nm towards the
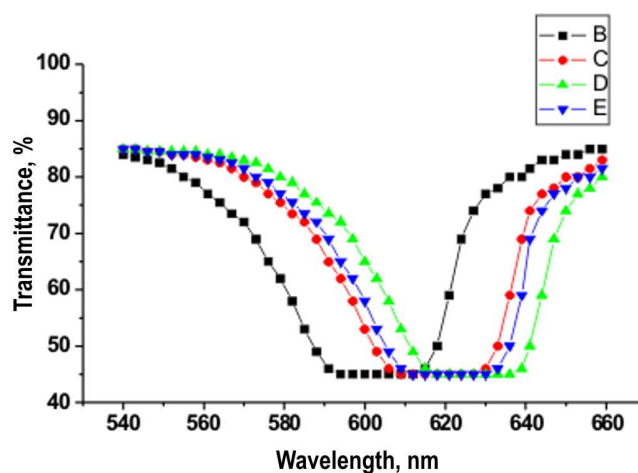
short-wave range, and the absorption spectrum becomes structured, which evidences for the availability of several stereo-isomeric forms in the solution (curve *2*). A practically full relaxation of the absorption spectrum (curve *3*) indicates that the photo-induced form is characterized by a finite lifetime. This testifies to that the energy barrier between two isomeric forms is lower in the case of chiral dopant 2 rather than in the case of chiral dopant 1.

The transmission spectra of a pure CLC formed by this dopant are depicted in Fig. 4 (curve *1*). In this case, neither the chiral dopant nor the NLC demonstrated absorption with the edge below 400 nm in the visible range. This means that the nature of the transmission spectrum of such an induced CLC are caused by selective reflection from the arising helical periodic structure. If the planar texture of the CLC located between quartz substrates is irradiated with UV light with the indicated intensity, the transmission spectrum shifts towards the long-wave range, as is shown in Fig. 4 (curves *C* and *D*). At a short irradiation (up to several minutes), the photo-induced variations partially relax (curve *E*), which is in a good correlation with the relaxation kinetics of photo-isomers presented in Fig. 3. At a longer irradiation, the relaxation of photo-isomers slows down, which manifests itself in a decrease of the interval of the short-wave shift after the UV irradiation being stopped. Within the 20-min irradiation duration with the mercury lamp possessing such an intensity, the linear dependence between the variation of the SR maximum position and
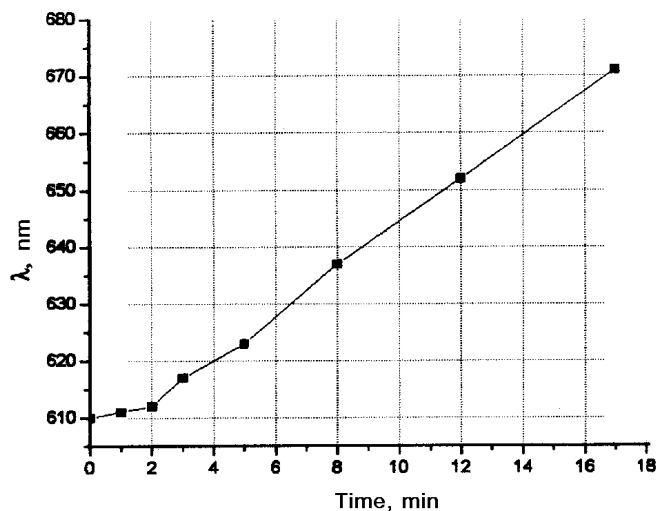
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Fig. 5. Dependence of the selective reflection maximum on the irradiation duration for a CLC induced by chiral dopant 2

Fig. 6. Photo-induced reconstruction of the lasing spectra of the CLC-based DFB-laser with the layer thickness of 50 μm: before UV irradiation (1), after 40-s UV irradiation (2), and after 90-s UV irradiation (3)

the irradiation duration is observed (Fig. 5). An important moment is that UV irradiation for more than 20 min almost does not induce the shift of the SR spectrum, which evidences for the saturation of the photo-isomerization process and the establishment of a stable balance between the trans- and cis-conformations of molecules of chiral dopant 2.

The lasing by such induced CLCs was obtained at their activation by neutral molecules of lasing dyes belonging to the phenolenone class F490. The lasing spectra are composed of a triplet, with a central more intense line and two lateral lines, the distance between which is defined, as in a Fabry–Perot interferometer, by the thickness of the specimen. Fig. 6 illustrates the reconstruction of the lasing spectrum in a specimen with quartz substrates under UV irradiation with a mercury vapor tube. After the 40-s irradiation, the lasing spectrum shifts towards the long-wave range by 3 nm. A repeated 50-s UV irradiation gives rise to an extra shift of the spectrum by 7 nm. The resulting shift after the integral irradiation within 90 s constitutes 10 nm.

One can see that the amplitude of the lasing spectrum displacement correlates with the UV-irradiation dose and has a linear character in the range of small doses. Such a linear displacement can be used for controlling the lasing spectrum of a CLC-based DFB-laser, provided that a method for the efficient reverse cis-trans conformational transformation of chiral dopant molecules in induced CLCs would be found. One of the ways to implement such a controllable monitoring can be the usage 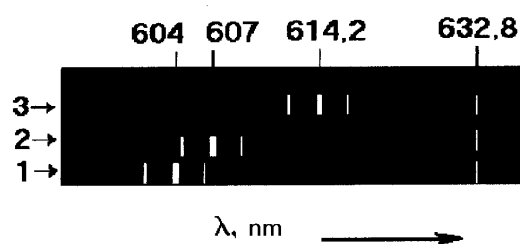of dopants possessing a larger difference between the absorption maxima of both photo-isomeric forms and the regulation of the ratio of photo-isomers in the active medium of a DFB-laser by their selective excitation.

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ФОТОПЕРЕСТРОЮВАННЯ СПЕКТРІВ ЛАЗЕРНОЇ ГЕНЕРАЦІЇ ДОМІШКОВИХ ХОЛЕСТЕРИЧНИХ РІДКИХ КРИСТАЛІВ

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Р е з ю м е

Запропоновано новий метод перестроювання частоти лазера з розподіленим зворотним зв'язком (РЗЗ) на основі індукованого холестеричного рідкого кристала. Цей метод пов'язаний із ультрафіолетовим опроміненням активного середовища, що спричиняє фототрансформацію молекул хіральних домішок, змінюючи закручуючу здатність домішки та крок спіралі. Експериментально показано принципову можливість плавного і реверсивного перестроювання частоти генерації такого РЗЗ-лазера за рахунок процесу *транс-цис*-ізомеризації хіральних молекул.