REVERSIBLE PHOTOTUNING OF LASING FREQUENCY IN A DYE-DOPED CHOLESTERIC LIQUID CRYSTAL

I.P. ILCHISHIN,[1] L.M. LYSETSKIY,[2] T.V. MYKYTIUK,[1] M.I. SERBINA[2]

[1]**Institute of Physics, Nat. Acad. of Sci. of Ukraine**
(46, Nauky Ave., Kyiv 03680, Ukraine; e-mail: lclas@iop.kiev.ua)

[2]**Institute for Scintillation Materials STC "Institute for Single Crystals",**
Nat. Acad. of Sci. of Ukraine
(60, Lenin Ave., Kharkiv 61001, Ukraine)

We have implemented a new method of phototuning of the lasing frequency of dye-doped cholesteric liquid crystals (CLCs) fabricated on the basis of mixtures of the azoxy nematic ZhK-440 and cholesterol derivatives. The essence of the method consists in changing the helix pitch at the irradiation of a CLC with light of different wavelengths. For the majority of lasing dyes, the quantum yield of the fluorescence in such materials is found to sharply decrease at weight concentrations of 0.3–0.5%, which interferes with lasing in them. A dye of the pyrromethene class which provides a quantum yield of the fluorescence of more than 50% at the indicated concentrations is discovered. The lasing in an CLC on the basis of azoxy nematic ZhK-440 has been obtained, and the reversible phototuning by 30 nm toward shorter and by 20 nm toward longer wavelengths has been carried out.

1. Introduction

Cholesteric liquid crystals with a helical periodic structure are capable to dissolve laser organic dyes, forming an active medium for frequency-tuned lasers. A combination of CLCs and organic dyes in the same medium allows distributed feedback (DFB) microlasers to be created in such structures [1, 2]. The feedback in such a medium is realized owing to the Bragg scattering and the amplification of radiation emission by the dye at the helical periodic structure. This feature makes DFB lasers on the basis of dye-doped CLCs promising for the creation of display information systems with high brightness, because the absence of a mirror resonator allows the active medium of such a laser to be produced in the form of a surface of any area and curvature.

The prospects of applications of such lasers in novel information display systems stimulated the start of their active researches at many scientific centers. The researches are mainly carried on making use of new CLC-materials, which are technologically more feasible than the viscous derivatives of cholesterol, for which the lasing was obtained for the first time [3–6].

The major method of lasing frequency tuning in CLC-based DFB-lasers remains the temperature-induced variation of a helix pitch [1, 2]. The tuning inertia and the necessity of the CLC thermostabilization make a wide application of such a laser difficult in practice. Therefore, searching for new, more operative ways of the lasing frequency tuning in liquid-crystal lasers is a challenging problem.

It is known that, in a number of CLC types obtained on the basis of nematic liquid crystals (NLCs) with twisting chiral admixtures, the molecules of those admixtures change their conformations and, respectively, their twisting ability under the action of ultra-violet radiation. The CLCs of such a type – including those obtained with the help of nonmesogenic chiral admixtures – owing to the fact that they contain various photoisomeric forms of molecules, which can be easily photoreisomerized [7, 8], allow the helix pitch to be changed, when definite stereoisomeric molecular forms are photoexcited.

Earlier, the effect of the twisting ability change of admixture molecules at their transition from *trans* to *cis* conformation, which is accompanied by the helix pitch variation, was used for the holographic recording [8], as well as to control the frequency of a CLC-based DFB-laser [9–12]. Since the proximity of absorption maxima in *trans* and *cis* conformations of an applied chiral admixture was high [11, 12], this method of frequency phototuning did not allow one to apply a selective light irradiation of separate molecular conformations and to regulate their content in the irradiation zone. Therefore, the tuning process was unidirectional, with the increase of the content of *cis* conformation at irradiation, a reduction of the admixture twisting ability, and a smooth shift of the lasing line toward long waves. Reversing, i.e. coming back to the initial content of stereoisomers, occurred spontaneously within 17–20 h and practically did not depend on external factors (temperature, electric field, and so forth) [12].

Recently, new ways were proposed to implement a controllable reversible phototuning of the helix pitch in CLCs [13, 14]. For this purpose, the authors of works [13, 14] suggested to use nematics on the basis of azoxy compounds (azoxy nematics), in which the absorption bands of stereoisomers are arranged in such a manner that only one *cis* conformation is selectively irradiated, if light with a wavelength that exceeds 410 nm is used. Such an arrangement of the absorption bands gives an opportunity of their selective excitation and the reversing of the lasing frequency tuning direction.

However, it turned out that generating dyes in azoxy – nematics at concentrations at the level of several tenths of one percent demonstrate the strong concentration quenching of fluorescence, so that their quantum yield diminishes to a few percent, which is not enough for the threshold of laser generation to be attained [2]. At the beginning of our work, there was no information in the literature concerning the laser generation in such materials. Therefore, our work aimed at studying the spectroscopic characteristics of dyes belonging to various classes in CLCs (the available azoxy nematic ZhK-440 served as a basis), selecting dyes with a high enough quantum yield of fluorescence, achieving the laser generation threshold, and implementing the reversible tuning of its frequency by irradiating CLCs with light characterized by different wavelengths.

2. Experimental Part

A research of the frequency tuning in a DFB-laser on the basis of induced CLCs by UV irradiation – which could be realized owing to the *trans–cis* isomerization of a twisting admixture in a nematic liquid crystal (NLC) – showed that the lasing spectral shift correlates with the dose of UV irradiation, demonstrating a linear character in the range of small doses [9, 11, 12]. Such a linear shift could be used to control the lasing spectrum of such a DFB-laser, provided that a way would be found for the effective reverse *cis–trans* transformation of twisting admixture molecules in the induced CLCs. An application of admixtures with a large difference between the absorption maxima in both photoisomeric forms and the regulation of the ratio of photoisomers in the active substance of a DFB-laser by their selective excitation can be one of the ways to implement such a control.

To realize the reversible phototuning, we used CLC mixtures consisting of about 75% of nematic ZhK-440 and about 25% of mesogenic chiral admixture of the M5 type (a mixture of cholesterol ethers: 30% of cholesteryl formiate, 5% of cholesteryl butyrate, and 65% of cholesteryl pelargonate). The CLCs were activated by dyes of various types (benzanthrone, phenolenone, pyrromethene) at their weight concentrations of 0.2–0.3%. The maximum of a selective reflection (SR) band was chosen near the dye fluorescence maximum (in the spectral range near 600 nm). The mixture of ZhK-440 and M5 with the composition indicated above was the base one at studying the temperature and spectral characteristics, as well as lasing. If the position of the SR band within the dye fluorescence contour had to be changed, the content of M5 was also varied within 1–3%. The absorption (transmission) spectra of planar structures – both pure and doped CLCs – were studied on SF-20 and Hitachi-330 spectrophotometers. The fluorescence spectra and their quantum yield were studied with an MPF-4 Hitachi spectrophotometer.

The planar textures of induced CLCs were prepared following the technique of rubbing the substrate surfaces, which form the ordered layer of a liquid crystal. To study the transmittance and the lasing in the visible spectral range, we used quartz substrates without an SnO_2 layer, which absorbs UV radiation, but covered with a layer of polyimide varnish rubbed unidirectionally. When studying the CLC absorption spectra in the UV range, leucosapphire substrates were used. The planar texture was formed at depositing a layer of polyvinyl alcohol onto the substrate by immersing the latter into a 0.1% polyvinyl alcohol aqueous solution, drying it, and rubbing with a soft tissue in one direction.

The layer thicknesses of induced CLCs were fixed within the interval from 3 to 30 μm by using fluoroplastic spacers. For UV irradiation of CLCs, a low-pressure mercury lamp with air cooling of the DRK-120 type, with a radiation power of 120 W, and a stabilized discharge current was used. The DFB-laser on the basis of induced CLCs was excited by the second laser harmonic of an Nd^{3+}:glass laser ($\lambda = 530$ nm) with passive Q-switching operating in the mode of separate 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 and displayed on a computer monitor with the help of a web-camera.

The influence of UV irradiation on azoxy-nematic-based CLCs was studied first by analyzing their optical absorption spectra. In Fig. 1, the absorption spectra of a thin (3 μm) CLC layer in the liquid crystal phase at a temperature of 28 °C are presented. At UV irradiation with an intensity of 20 mW/cm^2 for 10 min, the intensity of the absorption band of ZhK-440 with a maximum at about 360 nm (curve *2*) decreases in comparison with the intensity of the same band before irradiation (curve *1*),
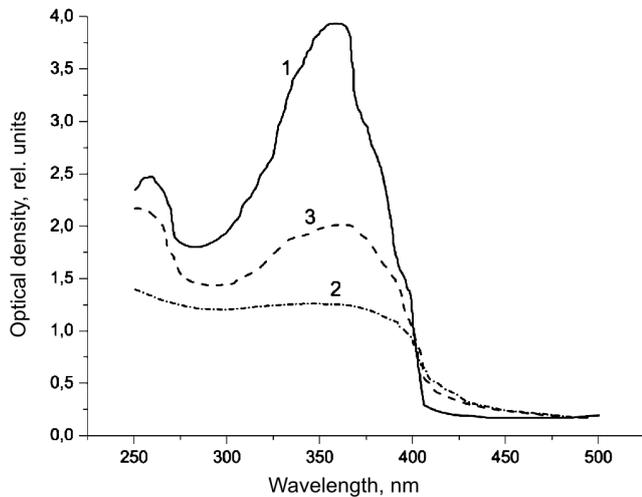
Fig. 1. Transformation of the absorption spectrum of the LC mixture 27.6% M5 + 72.4% ZhK-440 (*1*) at room temperature ($T = 28$ °C), (*2*) after UV irradiation, and (*3*) after UV irradiation through a ZhS-10 filter ($\lambda > 410$ nm). The layer thickness is 3 μm

Fig. 2. Absorption of the LC mixture 27.6% M5 + 72.4% ZhK-440 in the isotropic phase ($T = 73$ °C): (*1*) before UV irradiation, (*2*) after UV irradiation, and (*3*) after UV irradiation through a ZhS-10 filter. The layer thickness is 3 μm

which evidences the transition from the *trans* into the *cis* isomeric form. At UV irradiation for 25 min through a ZhS-10 filter, which cuts off light with the wavelength $\lambda < 410$ nm, a reversal of 360- nm band absorption takes place (curve *3*) owing to the partial reverse transition of the azoxy compound from the *cis* into the *trans* form.

Figure 2 demonstrates (curves *1* and *2*) that a similar process of transition from the *trans* into the *cis* form of LC molecules takes place in the isotropic phase of the same CLC, but no reversal process is observed after UV irradiation through a ZhS-10 filter for 25 min (curve *3*). No reversal process was also observed in standard organic solvents. It is the main feature of the photoisomerization process in azoxy-nematic LCs.

An interesting peculiarity of absorption spectra obtained for the system concerned in the isotropic phase is the fact that the measured values of optical density D for the same specimen under identical measurement conditions are much larger than those in the cholesteric phase. It can be connected with the absorption dichroism of azoxy compounds (in a planar structure, the actually obtained value is close to $D_\perp$, the absorption optical density in the direction normal to the director in the quasinematic layer, whereas, at temperatures higher than the isotropic transition one, T_f, when the orientational ordering disappears, a much larger quantity $D_\parallel$, the absorption optical density in the direction along the director in the quasinematic layer, starts to contribute [15]). An analogous phenomenon, a drastic increase of
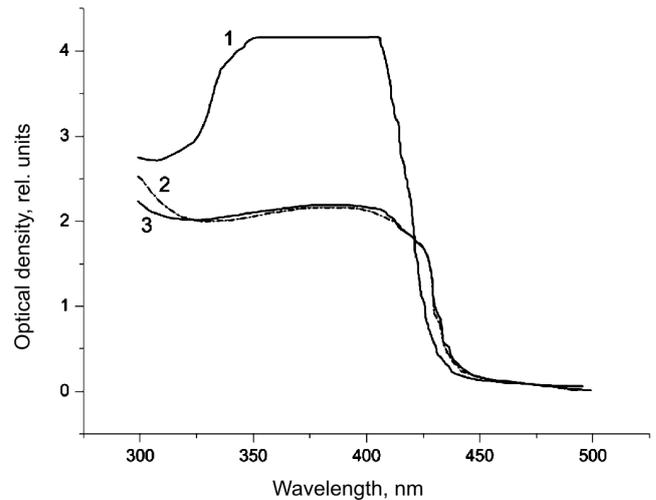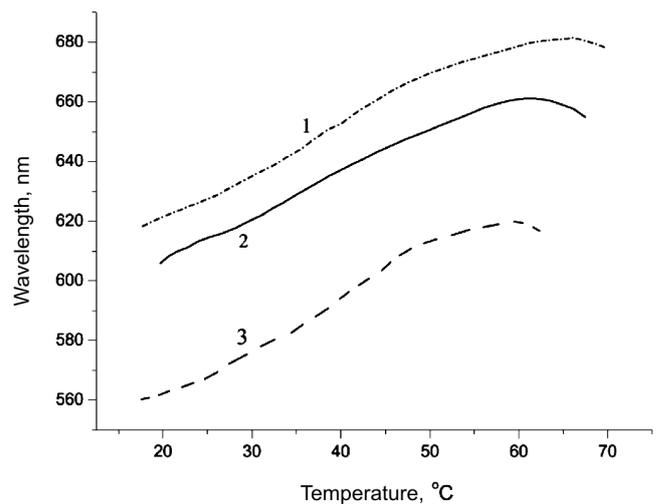

Fig. 3. Temperature dependences of the selective reflection maximum for the LC mixture 25% M5 + 75% ZhK-440: (*1*) before UV irradiation, (*3*) after 10-min UV irradiation, and (*2*) after subsequent 20-min irradiation through a ZhS-10 filter. The layer thickness is 15 μm

the measured optical density at the nematic–isotropic phase transition, was marked by us earlier [16].

In Fig. 3, the temperature dependences of the SR band maximum for the base mixture after its UV irradiation are depicted. At irradiation with a mercury lamp for 10 min, the SR band center shifted by 60 nm toward the short-wave range. The reverse process of *cis-trans* isomerization occurred at irradiation with the same lamp (provided that the exposition conditions were the same)
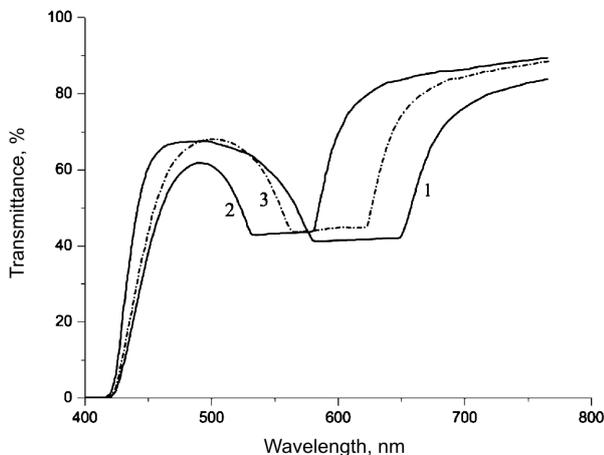
Fig. 4. Transmission spectra of the LC mixture 25% M5 + 75% ZhK-440 irradiated with light with various wavelengths: (*1*) before irradiation, (*2*) after 10-min UV irradiation with a DRK-120 lamp, and (*3*) after 10-min UV irradiation with a DRK-120 lamp through a ZhS-10 filter. The layer thickness is 30 μm

Fig. 5. (*1*) Transmission and (*2*) fluorescence spectra of pyrromethene dye PM-597 in the LC mixture 27.6% M5 + 72.4% ZhK-440. The layer thickness is 15 μm. The arrow indicates the initial lasing wavelength

through a ZhS-10 filter. Irradiation during 20 min resulted in that the positions of SR band maxima became restored, although not completely.

The formation of *cis* isomers, the molecules of which have a considerably lower geometrical anisomery, also manifested itself in a decrease of the temperature of the phase transition from the liquid crystal into the isotropic phase T_f. The partial *cis-trans* isomerization at irradiation through a ZhS-10 filter gave rise to the corresponding growth of T_f (Fig. 3).

Together with a change of the position of the azoxynematic SR band, the process of *trans-cis* isomerization also resulted in the variation of other optical characteristics.

In Fig. 4, the SR bands for the base mixture of the azoxy nematic LC and the twisting admixture M5 obtained before (curve *1*) and after (curve *2*) UV irradiation are depicted, as well as the reversing of the SR band in the course of the *cis-trans* isomerization occurring when the illumination through a ZhS-10 filter was carried on (curve *3*). One can see that the birefringence was substantially lower in the *cis* form of the LC, which resulted in a reduction of the SR band half-width. In turn, this gave rise to the growth of the lasing threshold for a DFB-laser, because the Q-factor of such LC structure depends on the refractive index modulation depth, i.e. on the birefringence. This fact, together with the selectivity of dye amplification, has to be taken into account, when optimizing the parameters of such a DFB-laser and expanding the range of its frequency reversible phototuning.
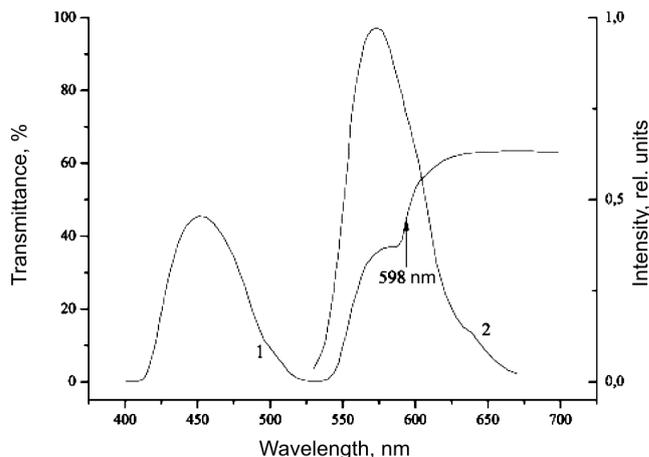
In the course of researches dealing with the spectroscopic characteristics of dyes in CLCs on the basis of azoxy nematics, the quenching of dye fluorescence turned out to be the main problem. The quantum yield for the majority of dyes with effective fluorescence fell down by a factor of 5 to 10 in comparison with standard solutions, where it has the maximal value. A quantum yield of the doping dye fluorescence of about 50% and higher is needed for a CLC-based DFB-laser to operate normally [2]. Therefore, in the course of our searches, we found two classes of dyes that are suitable for this purpose: these were phenolenone (NIIOPiK, Dolgoprudnyi, Russia) and pyrromethene (Eksiton) dyes. They are distinguished by their high quantum yield of fluorescence and the high efficiency of laser generation in isotropic solutions and polymers [17]. Among those, pyrromethene dye No. 597 had the highest quantum yield (60.9%) in CLCs on the basis of the mixture 27.6% M5 + 72.4% ZhK-440; therefore, it was used for the laser generation.

In Fig. 5, the spectral characteristics of this dye in a CLC on the basis of the mixture ZhK-440 + M5 are shown. An absorption maximum (curve *1*) at about 410 nm is the edge of the absorption band of nematic ZhK-440, a peak at 540 nm is an absorption maximum of the doping dye, and a shoulder in the interval 590–570 nm corresponds to the SR band of the CLC. In order to extend the range of frequency tuning and obtain the lasing at a maximal possible distance from the dye fluorescence maximum, we chose the mixture 27.6% M5 + 72.4% ZhK-440. It allowed us to obtain the lasing at a wavelength of 598 nm, which corresponds to the longwave edge of the SR band produced by the CLC matrix.

Lasing spectra consist of two lines (or one wide line), the distance between which corresponds to that between the longitudinal modes at a layer thickness of 15 μm. Such a spectral shape is mainly governed by a low quality of the planar texture formed on substrates free of an SnO$_2$ layer, a higher scattering in CLCs on the basis of azoxy nematics, and rather a high threshold intensity of excitation.

The threshold intensities of lasing excitation amounted to 600–800 kW/cm^2 at a layer thickness of 15 μm, being considerably higher than those for DFB-lasers on the basis of steroid CLCs, as well as induced CLCs of other types [12]. In terms of the lasing threshold magnitude, the technique selected by us to form a CLC planar texture was not optimal. Our experiments on the lasing threshold optimization demonstrated that the usage of an SnO$_2$ layer with polyimide varnish allows the threshold intensity of excitation to be reduced by a factor of 12 to 15, provided the same thickness of the layer and the same CLC material. However, the absorption of UV light by the SnO$_2$ layer can also affect the rate of CLC helix pitch variation and the range of this variation.

In Fig. 6, the dependence of the medium line position in the lasing spectra of pyrromethene dye in the used CLC on the duration of irradiation with a mercury lamp is exhibited (curve 3). One can see that the attained tuning range toward the short-wave side amounts to 30 nm, being limited by the amplification selectivity in the dye and a high threshold intensity of excitation. The reversal tuning of the lasing frequency (reversing) at illumination with a mercury lamp through a ZhS-10 filter takes a much longer time interval, and, as it was in the CLC-substance without the dye (curve 2 in Fig. 3), the corresponding interval is by almost 10 nm narrower. The researches of the lasing frequency tuning dynamics showed that there was no appreciable spontaneous reversing of the frequency within the time interval of the lasing spectrum registration, which, together with the time of the specimen irradiation and the time of the transmission spectrum record, amounted to 2 to 6 min. The test of the transmission spectrum after UV irradiation showed that the lasing spectrum was permanently located at the long-wave edge of the SR band.

3. Conclusions

Our researches showed that pyrromethene dyes are promising substances to be used as activators of azoxy nematic LCs applied in DFB-lasers on their basis. A
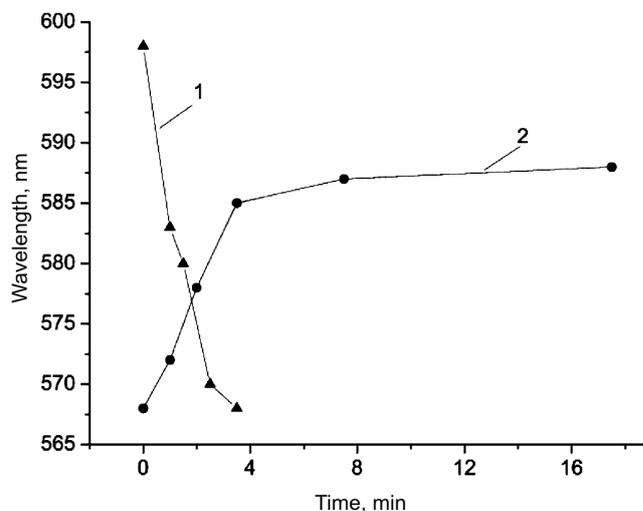

Fig. 6. (1) Medium wavelength tuning in the lasing spectrum of dye PM-597 in the induced CLC on the basis of nematic ZhK-440 as a function of the UV irradiation duration; (2) reversible phototuning at UV irradiation through a ZhS-10 filter, provided that all other irradiation conditions are the same. The layer thickness is 15 μm

high enough quantum yield of the fluorescence of such dyes in azoxy nematics, provided that more perfect planar textures are used, will allow the threshold intensities of the excitation in such a DFB-laser to be considerably reduced and, correspondingly, the range of the lasing frequency tuning to be expanded. The time interval of the frequency tuning can be made shorter by optimizing the power and spectral range of illumination. Note that, since the absorption band of a nematic has an edge in the blue spectral range, dyes with maxima of fluorescence bands in the orange and red spectral ranges are more advantageous for their use in such DFB-lasers from the viewpoint of the tuning range expansion. A task of creating a high-quality planar texture and minimizing the radiation losses of UV illumination at a high enough quantum yield of the doping dye fluorescence can be regarded as a main issue for this technique of frequency tuning.

1. I.P. Ilchishin, E.A. Tikhonov, V.G. Tishchenko, and M.T. Shpak, JETP Lett. **32**, 27 (1980).

2. I.P. Ilchishin, A.G. Kleopov, E.A. Tikhonov, and M.T. Shpak, Bull. Acad. Sci. USSR. Phys. Ser. **45**, 13 (1981).

3. I. Kopp, B. Fan, H.K.M. Vthana, and A.Z. Genack, Opt. Lett. **23**, 1707 (1998).

4. B. Taheri, A.F. Munoz, P. Palffy-Muhoray, and R. Twieg, Mol. Cryst. Liq. Cryst. **358**, 73 (2001).

5. H. Finkelmann, S.T. Kim. A.F. Munoz, P. Palffy-Muhoray, and B. Taheri, Adv. Mater. **17**, 1069 (2001).

6. M. Kasano, M. Ozaki, K. Yoshino, D. Ganzke, and W. Haase, Appl. Phys. Lett. **82**, 4026 (2003).

7. V.B. Vinogradov, L.A. Kutulya, Yu.A. Reznikov, V.Yu. Reshetnyak, and A.I. Khizhniak, Techn. Phys. Lett. **15**, 23 (1989).

8. V.B. Vinogradov, L.A. Kutulya, Yu.A. Reznikov, V.Yu. Reshetnyak, and A.I. Khizhniak, Mol. Cryst. Liq. Cryst. **192**, 272 (1990).

9. S.V. Gryschenko, I.P. Ilchishin, and O.V. Yaroshchuk, in *Technical Program of the 10th Conference on Laser Optics (St. Petersburg, Russia, 2000),* p. 71.

10. A. Chanishvili, G. Chilaya, G. Petriashvili, R. Barberi, R. Bartolino, G. Cipparrone, A. Mazzulla, and L. Oriol, Appl. Phys. Lett. **83**, 5353 (2003).

11. I. Ilchishin, O. Yaroshchuk, S. Gryshchenko, and Eu. Shaydiuk, Proc. SPIE **5507**, 229 (2004).

12. I.P. Ilchishin, O.V. Yaroshchuk, E.O. Shaidiuk, V.V. Shaplavskyi, and Yu.V. Sharavara, Ukr. Fiz. Zh. **50**, 1231 (2005).

13. G. Chilaya, A. Chanishvili, G. Petriashvili, R. Barberi, R. Bartolino, M.P. De Santo, M.A. Matranga, and P. Collins, Mol. Cryst. Liq. Cryst. **453**, 123 (2006).

14. S.V. Serak, N.V. Tabiryan, G. Chilaya, A. Chanishvili, and G. Petriashvili, Mol. Cryst. Liq. Cryst. **488**, 42 (2008).

15. L.M. Blinov, *Electrooptical and Magnetooptical Properties of Liquid Crystals* (Wiley, New York, 1983).

16. O.V. Korzovskaya, L.N. Lisetskii, and V.D. Panikarskaya, Visn. Kharkiv. Univ. N 422, Biofiz. Visn. N 2, 85 (1998).

17. M.V. Bondar and O.V. Przhonskaya, Kvant. Elektron. **25**, 775 (1998).

РЕВЕРСИВНЕ ФОТОПЕРЕСТРОЮВАННЯ ЧАСТОТИ ЛАЗЕРНОЇ ГЕНЕРАЦІЇ В ДОМІШКОВОМУ ХОЛЕСТЕРИЧНОМУ РІДКОМУ КРИСТАЛІ

І.П. Ільчишин, Л.М. Лисецький, Т.В. Микитюк, М.І. Сербіна

Р е з ю м е

Реалізовано новий метод фотоперестроювання частоти генерації домішкових холестеричних рідких кристалів (ХРК), утворених на основі сумішей азокси-нематика ЖК-440 і похідних холестерину, шляхом зміни їх кроку спіралі при опроміненні світлом різної довжини хвилі. Встановлено, що для більшості генеруючих барвників у таких матеріалах різко падає квантовий вихід флуоресценції при вагових концентраціях 0,3–0,5%, що перешкоджає отриманню в них лазерної генерації. Віднайдено барвник пірометенового класу, в якого при вищенаведених концентраціях квантовий вихід флуоресценції становить більше 50%. Отримано лазерну генерацію в ХРК на основі азокси-нематика ЖК-440 і реалізовано реверсивне фотоперестроювання на 30 нм в короткохвильовий бік і на 20 нм – у довгохвильовий.