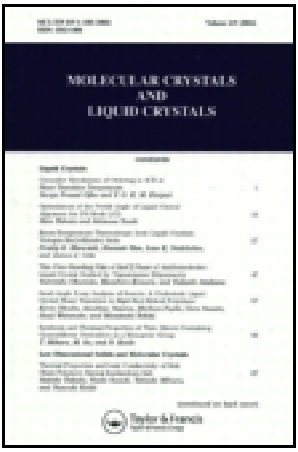

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UV-Radiation Controlled Tunable Cholesteric Dye Laser Based on an Azoxy Nematic Matrix

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For cholesteric liquid crystals (CLC) based on azoxy nematic ZhK-440 and cholesterol esters, variation of selective reflection band maximum with temperature and under irradiation by light of different wavelengths were studied. In these materials, lasing is hindered because fluorescence quantum yield of most lasing dyes falls sharply at concentrations 0.3–0.5 wt.%. We have shown that for some phenolenone and pyrromethene dyes the fluorescence quantum yield in such systems reaches 50% and more. Lasing has been obtained in CLC on the basis of azoxy nematic ZhK-440, with reversible phototuning by 30 nm towards shorter, and by 20 nm – towards longer wavelengths.

Keywords Dye-doped; fluorescence quantum yield; lasing spectra; nematic-cholesteric mixture; selective reflection

1. Introduction

It is known that in cholesteric liquid crystals (CLC) formed by nematic liquid crystal (NLC) matrices and chiral dopants, the molecular conformation of certain types of these dopants can be changed under UV irradiation. In such CLC, due to the presence of different photoisomeric forms of molecules and relative easiness of their photoisomerization, the helical pitch can be changed under photoexcitation [1].

The effect of variation of the helical twisting power of dopant molecules due to their transition from trans- to cis-conformation, which is accompanied by helical pitch changes, was earlier used for holographic recording [1], as well as for lasing frequency control of the CLC-based distributed feedback (DFB) lasers [2–4]. However, due to close location of the absorbance maxima of trans- and cis-conformation of the chiral dopant [4], this method of lasing frequency phototuning did not allow

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selective irradiation of specific conformations and control of their content in the irradiated area. Therefore, the tuning was a one-way process, with increasing concentration of cis-conformation under irradiation, lowering of the helical twisting power of the dopant, and slow shift of the lasing line towards the long-wave range. Reversal of the process, i.e., returning to the initial composition of stereoisomers, occurred spontaneously during 17–30 hours [4].

Recently, new ways have been proposed for realization of controlled reversible phototuning of the CLC helical pitch [5,6]. In these works, it was proposed to use azoxy nematics as photoisomerizable nematic hosts. The absorption bands of their stereoisomers are located in such a way that irradiation by wavelengths above 410 nm selectively affects only the cis-conformation. This allows selective excitation of the photoisomers and reversing the direction of lasing frequency variation.

However, it appeared that most of the known lasing dyes even at concentrations of less than 0.5 wt.% in azoxy solvents are subject to strong fluorescence quenching, and their quantum yield is lowered to several percent, which is not sufficient to achieve the lasing threshold [7,8]. This was a substantial hindrance for realization of lasing in such materials.

Therefore, our work was aimed at studies of spectroscopic characteristics of dyes of different chemical classes in CLC based on azoxy nematics with the objective of choosing appropriate dyes with sufficiently high fluorescence quantum yield, reaching the lasing threshold and obtaining reversible frequency tuning under irradiation by light of different wavelengths.

2. Samples and Experimental Set-Up

As a basic CLC material, we used a system containing ~75% of nematic ZhK-440 (2:1 mixture of 4-*n*-butyl-4′-methoxyazoxybenzene and 4-*n*-butyl-4′-heptanoylazoxybenzene, NIOPIK, Russia) and ~25% of chiral dopants of steroid nature (M5 – mixture of cholesterol esters: ~65% cholesteryl nonanoate, ~30% cholesteryl formate, 5% cholesteryl butyrate). This CLC was doped by fluorescent dyes of different types – benzanthrone, phenolenone (NIOPIK, Russia), pyrromethene (produced by the Exiton company) at weight concentration of 0.2 to 0.3%. The selective reflection (SR) band maximum was chosen to be superimposed with the fluorescence maximum of dyes (in the spectral region of about 600 nm). The absorption spectra were measured using a SF-20 spectrophotometer, the fluorescence spectra and quantum yield values were measured using a spectrometer MPF-4 "Hitachi".

The planar texture was produced by the known method of a surface roll formation by rubbing the cell substrates. We used quartz glasses with no UV-absorbing SnO_2 layers but covered with a polyimide layers rubbed in one direction. Optical pumping of the active CLC textures was carried out by the second harmonic (530 nm) of a Q-switched Nd^{3+} laser operating in a slow pulse repetition rate mode with the pulse duration ≅20 ns. The lasing spectra of the dye-doped CLC corresponding to each pumping pulse were optically imaged in a focal plane of a spectrograph with an inverse dispersion 0.6 nm/mm and then displayed by the web camera on a PC monitor.

3. Results and Discussion

Our basic CLC mixture (ZhK-440 + M5 mixture of the composition described above) was finely tuned by varying the M5 content within 1 to 3% to match the SR band to the fluorescence spectrum of each specific dye.

Figure 1 shows the wavelength of SR maximum of the CLC mixture as function of temperature before and after UV irradiation. It can be seen that irradiation by a hydrogen lamp during 10 min shifts the SR band maximum by ~60 nm towards shorter wavelengths. The inverse shift occurs under irradiation under the same exposure conditions by the same lamp with a ZhS-10 filter cutting off the wavelengths below ~410 nm.

As it is shown in Figure 1, irradiation during 50 min did largely reverse the SR band wavelengths (though not completely returning to the initial state).

A major problem was fluorescence quenching of the dyes in the azoxy-based LC matrix. The quantum yield was 5–10 times lower as compared with the same dyes in standard organic solvents. Since normal operation of a CLC-based DFB laser requires quantum yields of the dopant dye at the level of 50% and higher, we had to carry out a search, finding two classes of dyes apparently suitable for these purposes – phenolenone [7] and pyrromethene dyes. The latter are characterized by high quantum yield of fluorescence in nematic matrices [8]. The highest fluorescence quantum yield (60.9%) in CLC based on the 27.6% M5 + 72.4% ZnK-440 mixture was shown by the pyrromethene dye No 597, which was further used for our lasing experiments.

Spectral characteristics of this dye in the ZhK-440 + M5 mixture are shown in Figure 2. The transmission minimum in the 410 nm region (curve 1) corresponds to the absorption edge of ZhK-440, and the minimum at ~540 nm corresponds to the absorption maximum of the dopant dye. The shoulder at 570–590 nm corresponds to the CLC SR band. To broaden the frequency tuning range and to obtain lasing at the largest possible distance from the dye fluorescence maximum, we prepared a mixture of the following composition: 27.6% M5 + 72.4% ZhK-440. In this mixture, we succeeded in obtaining lasing at 598 nm, which corresponded to the long-wavelength edge of the CLC SR band.

The lasing spectra obtained are composed of one or two broad lines, with the distance between them corresponding to the distance between longitudinal modes

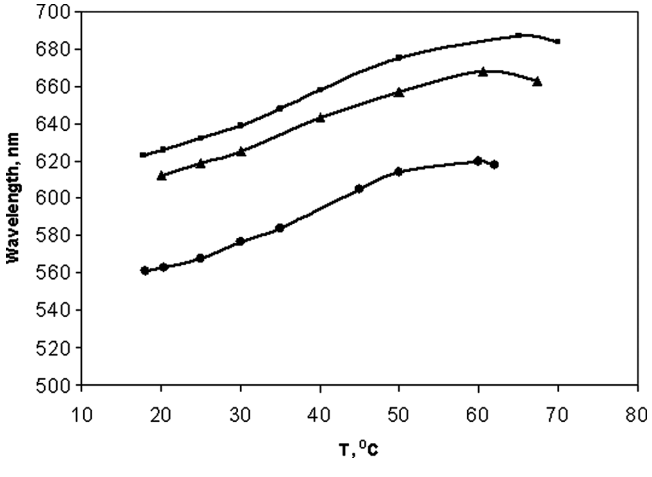

Figure 1. Maximum of SR band for CLC mixture 75% ZhK-440 + 25% M5 as function of temperature. Squares: initial mixture; circles – after irradiation by Hg lamp (~1.6 mW/cm^2) for 10 min; triangles – after irradiation by the same lamp with ZhS-10 filter for 50 min.

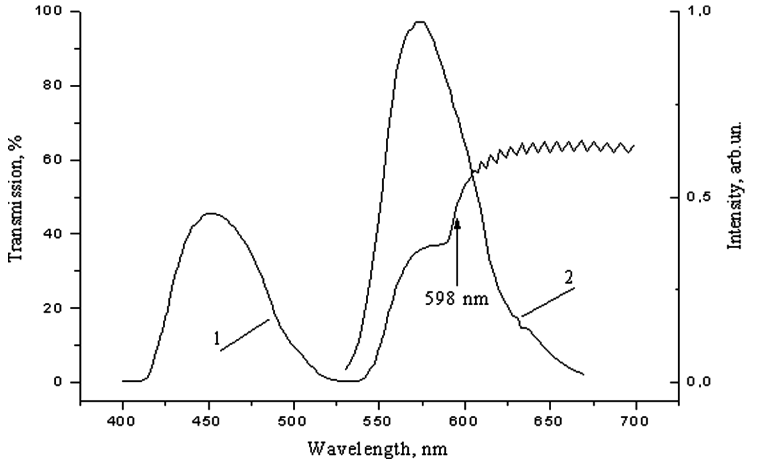

Figure 2. Transmission (1) and fluorescence (2) spectra of pyrromethene dye No. 597 in CLC based on azoxy nematics. Layer thickness is 15 μm. The arrow shows the lasing wavelength.

for 15 μm CLC layer thickness. Such shape of the spectrum is mainly due to non-perfect quality of the planar texture formed on substrates without SnO_2 layer, high scattering in the azoxy-based CLC material and rather high threshold excitation intensity.

The obtained lasing excitation thresholds at 15 micron CLC layer thickness were of the order of 600–800 kW/cm^2, i.e., noticeably higher than in DFB lasers based on purely steroid cholesterics [7], as well as in induced CLC of other types [4]. From the lasing threshold standpoint, our preparation method of the planar texture was not optimal. Our experiments on optimization of the lasing threshold have shown that, using polyimide-covered SnO_2 layers, the excitation threshold values could be

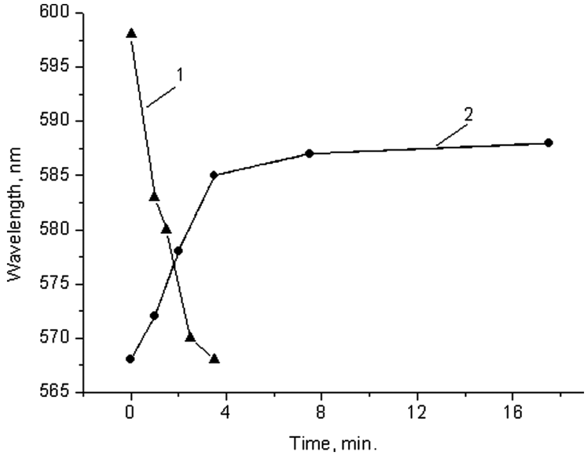

Figure 3. Lasing wavelength of pyrromethene dye No. 597 in mixture 27.6% + 72.4% ZhK-440: 1 – under irradiation by Hg lamp DRK-120, 120 W, distance 289 mm; 2 – irradiation in the same conditions with filter ZhS-10. CLC layer thickness –15 μm.

lowered by 10–15 times at the same layer thickness and with the same CLC material. However, UV absorption by the SnO_2 layer could adversely affect the speed and range of CLC helical pitch changes.

Figure 3 shows variation of the median line in the lasing spectrum of the pyrromethene dye in the CLC used under irradiation by the hydrogen lamp (curve 1). It can be seen that the achieved range of tuning towards shorter wavelengths is ~30 nm and is limited by amplification selectivity of the dye and high excitation intensity threshold. The reverse laser frequency tuning under irradiation through ZhS-10 filter is much slower and, like the SR band of the initial material (Fig. 1), its range is by ~10 nm narrower. Our studies have shown no noticeable spontaneous reversing of the lasing frequency during the measurement time (which was, together with irradiation and recording of the absorption spectrum, about 2–6 min). Check-up of the absorption spectrum after UV irradiation shows that the lasing spectrum is invariably located at the long-wave edge of the SR band.

4. Conclusions

The results of our studies have shown that pyrromethene dyes are promising for use as activators of azoxy nematics for DFB lasers on their base. Rather high fluorescence light yield of these dyes in azoxy nematics, provided more perfect CLC planar textures are used, allows obtaining low threshold excitation intensities in such DFB lasers, achieving also a broad range of lasing frequency tuning.

The frequency tuning time can be shortened by optimizing power and spectral range of the illumination. It should be also noted that, since the absorption band edge of the nematic is in the "blue" spectral region, for obtaining wider tuning ranges of such DFB lasers more promising could be dyes with fluorescence maximums in the "orange" and "red" regions.

A major task in further development of this method of DFB laser frequency tuning is creation of high-quality planar texture, with minimization of UV illumination losses at sufficiently high quantum yields of the dopant dyes.

Acknowledgment

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