From Single to Multi Mode Lasing: The role of materials revealed in optical simulations

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ABSTRACT

The comparative study of thin film Cholesteric Liquid Crystal (CLC) lasers made from different materials and optically pumped by an external solid state laser reveals a striking dependence of lasing behaviour (ranging from single mode at the edge of the selective reflection band to multimode lasing) on the morphology and microstructure of CLC films. The materials studied belong to two groups: low molar mass liquid crystals and polymers. It is shown that the orientation of individual chiral domains and fluctuations in helical pitch contribute significantly to the type of lasing displayed by the material. Different ways of preparing CLC cells that lead to predominantly one type of lasing are discussed. The importance of variations of the helical pitch and domain orientation in producing single and multimode lasing is justified by optical simulations (4x4 matrix method) of lasing in multilayered samples.

Introduction

Light scattering in the periodic helical structure of CLC produces a stop band (selective reflection band – SRB) for the light with the same sense of polarisation as the helicity of the CLC, which can be considered as a structure of twisted planar nematic planes with ordinary and extraordinary indices of refraction contributing to the birefringence $\Delta n = n_e - n_o$ [1]. In the case of planar orientation of cholesteric planes and probing light beam directed along the helical axis, the spectral position of the centre of the SRB is defined by the wavelength

$$\lambda = \frac{P(n_0 + n_e)}{2}$$

where $P$ is a helical pitch of the chiral CLC structure.

Dye-doped and optically pumped CLCs have attracted the interest of the scientific community for a long time [2,3], but the spectral attribution of lasing in CLCs to the band edge modes near the SRB was made only twenty years later [4]. This sparked renewed research interest in the band edge lasing in different types of CLCs [5–14], including thermotropic and lyotropic liquid CLCs confined between two flat glass substrates [6], responsive polymer CLCs of different nature [7] and compositions of CLC with polymers [8,9]. The accounts of the research were reviewed in Refs [10–14].

Depending on the physical state of active media, the microlasers based on CLCs will be referred in this article as liquid and polymer lasers. Liquid and polymer CLC lasers based on almost ideal planar structures were shown to display lasing at one or a few modes near the

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band edge. The slope efficiency of these lasers is relatively high [11]. The birefringence of twisted nematic planes and their planarity determine the efficiency of the planar chiral resonator [12,13]. Low threshold lasing from chiral droplets and colloids was also reported in Ref [14].

CLCs as one-dimensional photonic bandgap materials for circularly polarised light may also exhibit localised modes inside the bandgap if the periodicity of the helical structure is somehow disrupted. The possible use of this property for achieving low threshold lasing gave an additional boost to research in the area of solid CLCs, with defects specifically designed and prepared either by photopolymerisation of monodomain liquid CLC samples or by utilising polymer networks with randomly distributed defects [15,16]. Lasing at especially created defects in otherwise planar cholesteric structures is often referred to as lasing at localised or ‘defect modes’ [16,17]. However, it is important to underscore that vitrification of melted CLC [15] as well as polymerisation of CLC samples often results in the appearance of additional inhomogeneities (not necessarily ‘desirable’), for example, pitch variations across the sample. The extra defects can also be introduced in polymer-stabilised CLCs or polymer-dispersed liquid crystals in which the droplets of CLC are embedded in the polymer matrix or domains of CLCs are separated by the elements of polymer networks [18]. Lasing modes can be excited not only at the spectral edge of the SRB band but also inside it [19–21]. The defects and inhomogeneities can be created in the CLC matrix by different means, for example, by adding nanoparticles [19] and large polymer molecules [20] or by fast temperature changes of CLCs, leading to the appearance of disorientsed domains [21]. This type of lasing is referred to as a random lasing [22], the type of lasing with emitted light forming a closed path due to multiple light scattering at optical inhomogeneities. Random lasing in many aspects is related to a light localisation problem [23,24].

Interestingly, in most papers published on lasing, only one type of lasing (single-mode lasing, lasing from defects or random lasing) is considered. It makes understanding transitions between different types of lasing in non-ideal planar samples made from different materials difficult.

The purpose of this paper is to fill this knowledge gap by considering experimental techniques of creating mono- and multidomain samples with different types of disorder resulting in different types of lasing. We also present a computational model describing the transition between different lasing modes and show that lasing from the samples with different types of defects leads to multimode lasing either at the edge of the SRB or inside it.

**Experimental**

Some chemical structures of the monomer compound used to produce multidomain samples are shown in Figure 1. Merck mixture E63 was used together with the chiral dopant CB15 in order to produce monodomain CLC with the SRB centred at 590 nm with a spectral bandwidth of about 60 nm. The mixture is characterised by low viscosity and, therefore, it forms unstable defect structures. They are referred in the text as liquid CLCs.

Wacker monomers (Figure 1) were used in order to synthesise polymer samples with different numbers of defects and to study the effects related to multimode lasing.

The monomers are bulky cyclic siloxanes with liquid crystalline pendant groups, derivatives of cholesterol and 4-(6-acryloxy)phenyl 4-(propyl)benzoate. These monomers melt and form CLC at c.a. 70°C and they

![Figure 1. Chemical structure of the monomer.](image-url)
are much more viscous than liquid CLC samples (the estimation of viscosity by the two-plates method [8] indicates at least three orders of magnitude difference). Thus, the oil streak and other defects appearing in the sample are more persistent and need more time to quench. These compounds are precursors for polymer CLCs and are referred to in the text as viscous CLCs. They were initially dissolved in toluene with the addition of 2% of benzophenone, then dried, melted and polymerised under UV irradiation in the CLC state.

Pyrromethane 597 was used as a lasing dye in both compositions in a mass concentration of c.a. 0.2%. This dye has high quantum efficiency and a relatively large spectral distance between absorption and emission bands. The liquid and viscous CLC compositions were optimised in order to get the high-frequency edge of the SRB close to the maximum of the dye emission peak positioned at c.a. 580 nm. The position of the SRB could only be tuned by changing the temperature (or the addition of small amounts of dopants). It was found that the optimal temperature in terms of sample viscosity, quality and handling is about 70° C. The spectral position of the SRB centre at this temperature was at c.a. 630 nm.

The following technique allowed the creation of high-quality monodomain and multidomain samples. Two glass plates with surface flatness of about one tenth of the green light wavelength (λ = 550 nm) were kept in a holder with a precise and controllable adjustment of the gap between the glass plates. This was achieved by three high-precision screws with a rotation corresponding to a 0.1-micron shift along the z-axis of the setup (Figure 2). The additional screw H on the upper plate allowed for a horizontal motion of the upper plate in order to create inhomogeneous defects inside the sample. The parallelism of the two glass plates was maintained visually by following the interference pattern between the glasses. In order to create planar orientation, the glasses were treated with polyimide following the standard annealing and rubbing procedure. The monodomains of different thicknesses are formed by injection of liquid CLC between the plates with a subsequent increase in the distance between the plates whilst maintaining their parallelism. Large monodomains were formed when the distance between the plates was about 10 microns. With the increasing thickness of the sample, the size of the monodomain decreased as defects appeared inside the sample due to the addition of CLC. For a sample with a thickness of 40 microns, the typical monodomain size of liquid CLC was about 10 mm (as determined by the distance between two oil streaks).

The same setup was used to create polymer samples from viscous CLCs. The size of the monodomains viewed from the above was typically smaller, about hundreds of microns. The whole system was heated to the appropriate temperature above 70° C and UV light was shined from both sides on the sample in order to induce polymerisation and reduce the effect of helical pitch variation across the sample. Highly

![Figure 2](image-url) (Color online) Setup for creating planar liquid and polymer CLC samples.
inhomogeneous samples could also be created by the aforementioned setup if one of the plates moved horizontally during sample preparation.

The lasing experiments were performed as follows. The pulse from the YAG laser (New Wave Research Inc) hits the sample at an angle of 20–30 degrees. The beam is focused on CLC by a long focal length lens allowing the formation of a narrow and lengthy ‘neck’. The spectra were recorded using an Ocean Optics spectrometer collecting light in a relatively narrow cone of 5–10 degrees. It is important to note that quantifying lasing threshold in absolute values lied out of the scope of this study and the focus of this research was on the comparative study of the spectral positions of lasing peaks in ordered and disordered samples.

**Results and discussion**

**Monodomain samples**

The typical transmission and emission spectra of liquid monodomain CLC samples are shown in Figure 3(a). The oscillations of transmission near the band edge are clearly visible. In a stable monodomain sample, lasing occurs at the first mode near the band edge. Often, when few lasing pulses hit the same spot of the sample, a few more lasing modes can be excited (thermal effects lead to local reorganisation of the CLC structure, changes in the helical pitch and planarity). The relative lasing threshold decreases with the increasing thickness of the sample up to 35 microns and then stabilises. The value of lasing threshold in polymer samples compared to the one in liquid samples is normally higher by a factor of 2–5 (this study concentrates only on the comparison of the number and spectral position of lasing modes with respect to the SRB in liquid and polymer CLC samples, not on quantifying lasing thresholds in samples with different types of disorder).

The transmission spectrum of polymer samples with a moderate thickness is less featured with smaller and less distinctive band edge oscillations (Figure 3(b)) than liquid CLC samples of the same thickness. The relative lasing threshold in polymer samples is often higher and starts to saturate at a thickness of about 25 microns. Polymer samples prepared by irradiation of just one side of the sample display slight variation of reflected colour from two sides of the sample with a blue colour shift on the side of the sample placed closer to the UV light source (the shrinkage of the polymer during polymerisation results in a shorter helical pitch). In thicker samples, this effect is more pronounced.

![Figure 3](#) (Color online) Transmission and lasing from monodomain liquid and polymer samples: a) liquid CLC and b) polymer CLC.

Thus, polymerisation of thin samples (with a thickness of about 10 microns) results in monodomain CLCs with relatively uniform pitch distribution and distinctive band edge oscillations. However, polymerisation of thick samples often introduces a helical pitch gradient and variations in domain orientations across the sample.

**Multidomain samples**

Multidomain liquid samples can be easily created either by quick addition of liquid CLC (or CLC mixed with nanoparticles) or by the quick shift of the upper plate with respect to the lower glass (Figure 2). Examination of the samples under the microscope revealed that both methods resulted in the appearance of numerous oil streak defects in liquid samples and small penetrating domains with an average size of less than hundreds of
microns. In pure CLC samples, the oil streak defects slowly disappeared, whilst in viscous CLC samples, oil streak defects were stable for hours. The domains positioned close to the glass substrates retained their planarity, whilst domains positioned further from the glass substrate seemed to have slightly different colours. Lasing from the areas with oil streaks was suppressed due to the intense light scattering from individual oil streaks or their aggregates. Interestingly, the small horizontal disturbance leading to deformation of liquid CLC without creating stable oil streak resulted in lasing appearing at higher modes and increased lasing threshold. Further deformation led to the disappearance of narrow lasing lines replaced with broader amplified emissions from the sample. Transmission spectra of areas with oil streaks are broad with the transmission of incident light less than 50%, which indicates higher light scattering.

Polymer multidomain samples, however, had a different morphology. The oil streaks were still present, but the structure of their conglomerates was washed out. The domains reflected different colours due to the variations in the helical pitch and orientation of the individual domains. Transmission spectra are also broad with the sloping band edge. Lasing from these samples often displays several peaks inside the SRB with a higher threshold than lasing in monodomain samples (Figure 4). The increasing intensities of the emission peaks correspond to increasing energies of the pumping pulses (parameter E in Figure 4). The interesting feature of the lasing spectrum is that sharp peaks appear on the top of the otherwise broad emission spectrum and their position is maintained within the spectrum. The latter is often considered as a characteristic of random lasing when light scattering from randomly distributed scatterers creates a closed loop for light, thus playing a role of a resonator in classical lasing [20–23]. Random lasing was observed in cholesteric liquid crystals doped with nanoparticles [19]. It was also observed in polymer-dispersed CLCs [18], where the lasing was attributed to numerous scattering events in the disordered material and lasing from highly disoriented droplets.

In order to understand whether the observed lasing behaviour (see Figures 3,4) can be interpreted in the framework of the multidomain model with a distribution of different types of defects (disoriented domains in the case of liquid samples and domains with a helical pitch change in the case of polymer samples), the optical modelling of lasing was conducted.

![Figure 4](image_url) (Color online) Transmission and lasing from a multidomain polymer sample, parameter E corresponds to a linear change in the energy of the pumping pulses.

**Optical modelling**

Optical calculations were performed in the framework of the Berreman 4x4 matrix method [25] in order to clarify the nature of the transition from mono- to multimode lasing occurring in monodomain and multidomain liquid and polymer samples. The following model was employed in order to study lasing from monodomain samples and samples without the light scatterers. The planar CLC slabs with a thickness of about 5–10 helical pitches each were separated by thin isotropic layers with the average refractive index equal to the average refractive index of the slab (in order to avoid effects related to the Fresnel reflection and appearance of localised modes originating from the disruption in the refractive index). The calculations were performed for a set of seven CLC slabs (Figure 5), four of which were fixed and three internal ones were allowed to disorient by angle α simulating the disorientation in inner domains in liquid and polymer samples with respect to the CLC surface. In the framework of the Berreman model, the disorientation essentially leads to a variation of the angle of incident light. The helical pitch was allowed to change in all slabs. In the case of polymer models, the helical pitch of two outer slabs was shorter in order to account for the spectral blue shift of outer CLC layers occurring during polymerisation.

The simulation of lasing was performed by introducing a gain (imaginary part γ of the refractive index, \( \varepsilon = \varepsilon_0 + i\gamma \)) for the spectral interval corresponding to the emission of real dye. Increasing gain corresponds to
higher pump energy in real experiments. However, no quantitative correspondence can be established between the two. The major subject of this study was to study the relationship between the position of lasing peaks with respect to the SRB and the type of sample disorder. The shape of the dye emission band was approximated by a Lorentzian. The maximum of emission was at c.a. 580 nm and the width of the emission band was 60 nm.

The validity of this model was checked by reproducing the transmission optical spectrum of a perfectly planar monodomain sample discussed at the beginning of the experimental section and lasing from this sample (Figure 6). All CLC slabs of this sample were planar and parallel to each other. The indexes of refraction were $n_\alpha = 1.72$ and $n_\beta = 1.54$ and the helical pitch $P = 400$ nm. It can be seen that the correspondence between the experimental transmission spectrum and the calculated one is very good. The simulation of lasing also shows the appearance of the peak at the first higher frequency mode ($\gamma = 0.002$). It is important to underscore that in the framework of the Berreman transfer matrix approach, the lasing threshold is defined as a divergence of reflection and transmission. Therefore, the modelling of active media with a small positive gain produces the emission from active media and calculated intensities of emission peaks do not fully describe the non-linearity of lasing above the threshold. However, the spectral positions of lasing peaks are reproduced correctly, reflecting the optical structure of the bandgap.

Polymer samples can also be characterised by variations in the helical pitch in individual domains. The birefringence of the Wacker polymer (Wacker company’s data) was $\Delta n = n_\alpha - n_\beta = 0.1$. The position and shape of the SRB allow estimating the average helical pitch of the sample $P = 400$ nm, assuming the average refractive index $n_{av} = 1.55$. These data were used in calculations in order to simulate the light transmission and lasing from these samples. The experimental transmission spectrum of thick samples is very broad due to the fluctuations in the helical pitch, order parameters and domain orientations. So, the purpose of the modelling was not to reproduce the whole spectrum but rather to examine the role of disorder, namely the changes in the helical pitch and domain orientation occurring in polymer samples.

First, the ideal sample with cholesteric pitch $P = 400$ nm and $\delta n = n_\alpha - n_\beta = 0.1$ was simulated as a reference for simulations of disorder. The results of optical property calculations performed for the ideal CLC sample (lasing angles were averaged over the cone of 8 degrees as in real experiments) are shown in Figure 7 (curves 1 and 2). The lasing peak was near the band edge; increasing the gain resulted in higher lasing intensity at the first mode near the SRB.

Second, the samples with varying helical pitches were studied. The internal slabs of the sample were assigned a longer helical pitch. Outer slabs were assigned a shorter helical pitch that changed from 380 nm and increased to a maximum of 415 nm in the centre of the sample. These numbers were chosen in accordance with experimental data showing the fluctuations in the spectral position of the SRB at different points of the sample. About forty transmission spectra were simulated for different incident angles and some of them showed sharp changes in transmission spectra over the spectral area of the SRB. Averaging over all these angles produced broad and featureless transmission spectra. The results of averaging over eight spectra are presented in Figure 7 (curves 3 and 4) and they still contain peaks in
transmission at 590 nm and 610 nm. The lasing also occurred at 590 nm and 610 nm. This simulation is closer to the experimental spectrum shown in Figure 4, curves 1–2, with a bandgap between c.a. 600 and c.a. 660 nm and lasing peaks at c.a. 610 nm. It is important to underscore again that under increasing pump energy, the exact positions of lasing modes may change even within one sample but still be within a certain spectral range and for the polymer samples, the positions are always within but close to the edge of the SRB band.

The results of optical calculations of samples with a larger degree of disorder (varying helical pitches and slab orientations) are shown in Figure 7 (curves 5 and 6). The angles α between internal domains (see Figure 5) were changing between 0 and 20 degrees. The helical pitch was changing between 370 and 420 nm. The transmission spectra and lasing peaks were also averaged inside the cone of lasing (over eight degrees). This model produced four lasing peaks lying at the different wavelengths, but well inside the SRB at c.a. 560 nm, 580 nm, 605 nm and 630 nm.

Finally, based on the parameters used for calculating transmission and lasing spectra shown in Figure 7, curves 3 and 4 (these spectra resemble the experimental polymer spectra), our model was used to reproduce more closely the experimental spectrum shown in Figure 4. The helical pitches for seven slabs were increasing from 379 nm (for the outer slabs) by a step of 8 nm and reached a maximum at 403 nm for the central slab.

The thicknesses of all slabs except the central one corresponded to five helical pitches and the thickness of the central slab corresponded to seven helical pitches. The three central slabs were also allowed to rotate within 10 degrees as it is illustrated in Figure 5. The averaged transmission and lasing spectra are shown in Figure 8. Taking into account the inherent disorder in the experimental sample, the calculated transmission and emission (curves 1 and 2) spectra compare well with experimental data presented in Figure 4, with emission peaks in the range of 600–615 nm positioned inside the SRB (curve 1). Interestingly, the increase of gain results in redistribution of lasing intensities in lasing spectra (compare curve 1 corresponding to γ = 0.0025 and curve 2 corresponding to γ = 0.008 in Figure 8, in the latter case, the amplitude of the emission makes the transmission invisible), whilst the spectral positions of lasing peaks remain the same. This underscores (as we indicated before) that these are the spectral positions of lasing peaks (not their amplitudes) that determine the structure of the optical bandgap.

It is important to note that in the studied model, the light propagates along the straight line and the results are averaged over different paths as it happens in real experiments. The model considers scattering effects only along straight paths. In spite of such a restriction, the multiple lasing peaks are still produced in highly disordered samples within the SRB, but this phenomenon does not represent classical random lasing [21,22] that requires a formation of closed two- or three-dimensional loops of scattered light within the active media.

Figure 7. (Color online) Results of optical calculations of three different structures: curves 1 and 2—ideal planar structure with P = 400 nm, curves 3 and 4—planar structure with different helical pitches P (within 380 nm < P < 420 nm) and curves 5 and 6—structure with varying helical pitches and orientations of slabs (within 20 degrees).

Figure 8. (Color online) Calculation of transmission and emission in the fine-tuned model for the disordered polymer sample (curve 1 corresponds to γ = 0.0025 and curve 2 corresponds to γ = 0.008) and experimental spectra are shown in Figure 4.
Conclusions

Mono- and multidomain samples of cholesteric liquid crystals were synthesised and their optical properties including optically pumped lasing were studied. Large liquid monodomain CLCs can be prepared as very thick samples (about 120 microns). Large and uniform polymer monodomain samples are difficult to prepare due to the shrinkage of the monomer during polymerisation as well as the appearance of inhomogeneities and defects. Single-mode lasing occurred in monodomain samples and multimode lasing occurred in multidomain samples with disoriented domains and the presence of oil-streak defects. Optical simulations show that multimode lasing can be explained by introducing inhomogeneities (out-of-plane deviations from planar orientation and helical pitch variations). The more inhomogeneous the samples, the more lasing peaks appear inside the SRB.

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