Photonic Materials Based on Mixtures of Cholesteric Liquid Crystals with Polymers

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Cholesteric liquid crystals (CLC), polymer stabilized cholesteric liquid crystals (PSCLC), and polymer dispersed cholesteric liquid crystals (PDCLC) are promising dye-doped optically pumped lasing materials with an inherent photonic band gap structure. At low polymer concentrations, lasing from PSCLC occurs in modes near the edge of the selective reflection band. Electric field applied to the samples sandwiched between conducting glasses enhances PSCLC lasing emission. Lasing behavior changes dramatically at higher polymer concentrations in PDCLCs: numerous lasing peaks appear on the top of the emission band. New effects are explained in terms of lasing in photonic defect modes and photonic band gap modes.

Introduction

Photonic band gap (PBG) materials have recently attracted considerable attention because of their potential applications in display technology, telecommunications, and fiber optics.[1,2] CLCs and polymer CLCs are PBG materials with unique polarization properties and ability to self-organize. The selective reflection band of CLCs for the light circularly polarized in the direction of structural anisotropy is produced by coherent multiple scattering on periodic helical structure.[3] Ideal cholesteric structure does not impede the transmission of light of the opposite circular polarization. The lack of propagating modes for a given polarization suggests that the density of states for such a light vanishes within the band gap. Because stimulated emission from dye molecules doping CLC is proportional to the density of states, CLC dopes show weak emission within the band gap, but at the band edge, a series of closely spaced narrow modes appear. Light residence time within CLCs is greatly increased at the band-edge modes thus enhancing the probability for stimulated emission and lowering the lasing threshold.[4,5] Low lasing thresholds also occur in photonic defect modes within the selective reflection band if certain local defects disturb the periodic cholesteric structure. Photonic defect modes produced by separation of cholesteric layers were predicted by Yang[6] but have not yet been reported; those produced by rotating one part of the sample around its helical axis without separating the two parts were suggested by Hodgkinson and authors.[7–9] No lasing in photonic defect modes have been revealed by lasing studies on chiral thermotropic liquid crystals,[4,5,10] liquid crystalline elastomers,[11] or networks.[12] Lasing in lyotropic liquid crystals was hypothesized to be introduced by disorder.[13]

Below we report lasing in polymer dispersed cholesteric liquid crystals (PDCLC) and polymer stabilized cholesteric liquid crystals (PSCLC) which have never been studied before for lasing potential. PSCLCs, in which polymer concentrations do not exceed several percents, have been studied as promising display materials.[14,15] PDCLCs have polymer concentrations of

up to 60% or more.[14] PSCLCs are produced by mixing chiral liquid crystal with a polymer into a polymer-stabilized focal conic polydomain structure. Light is scattered on cholesteric domains. The electric field makes the liquid crystals align with the field, and the material becomes transparent.

PDCLCs consist of chiral liquid crystal droplets dispersed in a solid polymer matrix. Changing liquid crystal orientation by applying an electric field allows us to control the intensity of the transmitted light.[14,16] In both PDCLCs and PSCLCs, the cholesteric domain disorder increases with polymer concentration.

PDCLC/PSCLCs films were prepared using polymer-induced phase separation that occurs during polymerization of the liquid crystal–monomer mixture when liquid crystalline molecules form domains or droplets of various sizes. At lower polymer concentration, the domains tend to be larger.

Both PDCLC and PSCLC systems are promising lasing materials because their properties may be controlled by an electric field and the selective reflection band lies within the visible spectrum. Moreover, low-threshold random lasing and lasing in photonic defect modes may occur. Details of switching in PDCLC/PSCLCs are beyond the scope of this study. In fact, the transition from the opaque to transparent state can hardly be obtained in PDCLCs with chiral domains, because refractive indices may not exactly match between the chiral droplet and matrix.[17] Our goal was to study the effects of polymer concentration and PSCLC/PDCLC multidomain structure on lasing.

The concept of random lasing, first introduced by Letokhov,[18] suggests that multiple scattering makes photons linger in the medium. Such a phenomenon was revealed in a number of systems including powdered rare-earth crystallites and solutions of colloidal microparticles.[19] Random lasing with a coherent feedback is seen as a series of narrow peaks whose width decreases as pump power grows.[20–22]

Confined CLCs is a scattering system whose domains show a PBG structure. This paper reports the results of the first study of such systems at low and high polymer concentrations and shows that dramatic changes in lasing spectra at higher polymer concentrations should be attributed to photonic defect modes and PBG structure of cholesteric droplets.

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Experimental Section

Nematic liquid crystal ZLI 4788 (Merck Co.) and chiral dopants cholesteryl pelargonate and cholesteryl oleate (Aldrich Chemical Co.) were used as received. Chiral nematic was a mixture of 17% cholesteryl oleate + 32% cholesteryl pelargonate + 51% ZLI 4788 with negatively anisotropic dielectric susceptibility and refractive index of about 1.536. The selective reflection band was centered at 580 nm. Norland Optical Adhesives 71 and 65 (NOA 65, trimethylopropane diallyl ether, trimethylopropane tristhiol, and isophorone diisocyanate ester) were used as UV-curable monomers; pyrromethane 597 (Exciton Inc.) was used as laser dye. Refractive indices of cured NOA 71 and NOA 65 are 1.56 and 1.54, respectively. Norland monomers are commonly used in preparing polymer dispersed liquid crystals (PDLCs) because they polymerize well, are transparent, and produce droplets[23,24] over a broad monomer concentration range (20−60%). Pyrromethane 597 is highly miscible with cholesteric materials; however, to avoid aggregation of dye molecules and absorption of the pumping beam, only low dye concentrations were used. In toluene solutions, the dye's absorption and emission peaks were at 526 and 575 nm, respectively. A Nd:YAG laser (Photonics Industries, Inc.) was used to excite the dye near its absorption maximum. The emission was focused on the monochromator's entrance slit. The pump pulse duration was ca. 45 ns. The dye emission band overlapped the selective reflection band of the cholesteric material.

The CLC−polymer mixture was placed between two conducting ITO-coated plates covered with rubbed polyimide and irradiated by UV light. ITO coating allowed us to apply electric fields. Sample thicknesses were controlled by two plastic strip spacers in the range 10−35 μm.

Results and Discussion

Lasing in a neat CLC with nearly planar orientation always occurs at the edges of the selective reflection band close to the maximum of dye emission band. Figure 1 shows typical transmission and emission spectra of a pure cholesteric at two film thicknesses. In the thinner (15 μm) monodomain sample, the lasing peak matches the first band-edge mode, whereas in thicker (35 μm) films, where modes are not so distinct, the peak is close to the selective reflection band edge.

The fine band-edge structure depends on film thickness and planar orientation. The thicker the film is, the closer the modes are. Thin samples with broad first mode are poor resonators. As sample thickness increases, the first mode gets narrower, indicating longer photon dwell times. In 25−35 μm thick samples, the first mode becomes too narrow to observe as selective reflection band edge gets eroded by small fluctuations in pitch and director orientation. Such samples have Grandjean texture with the cholesteric helical axis perpendicular to the substrate and domain size (the distance between oily streak defects) of several millimeters on average. The lasing threshold is the lowest in samples 25−35 μm thick but increases again in much thicker samples with their imperfect planar structure and fluctuating pitch. In much thicker samples, the fine band-edge structure is washed out.[25]

Applying DC voltage (up to 10^4 V/cm) has no effect on the lasing (lasing intensity or peak position) of the neat cholesteric mixture: in pure thin cholesteric samples, the domain planar orientation is so perfect that electric field neither improves it nor affects lasing behavior. A further voltage increase causes the opaque state due to dynamic scattering.[3]
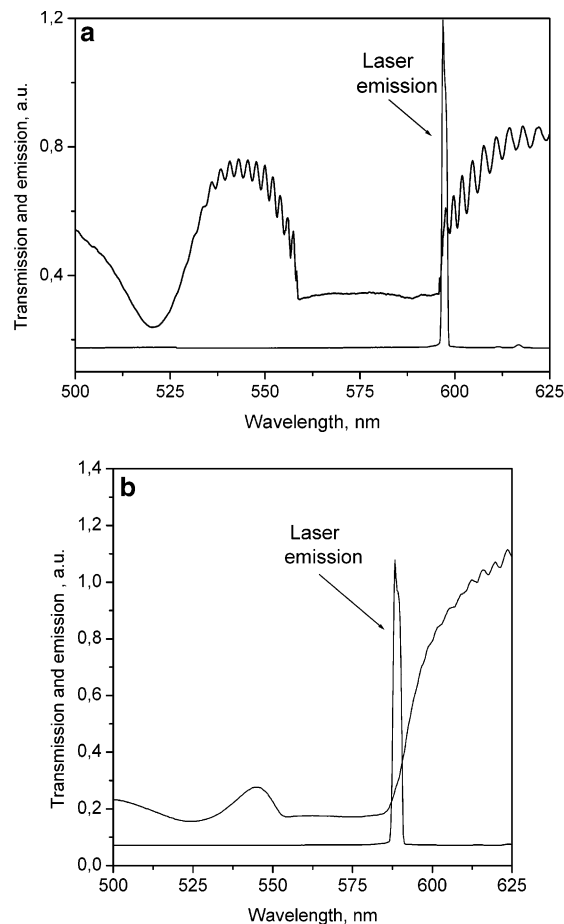

Figure 1. Transmission and emission spectra of CLCs. (a) Thin (15 μm) monodomain neat sample; (b) thick (35 μm) neat sample.
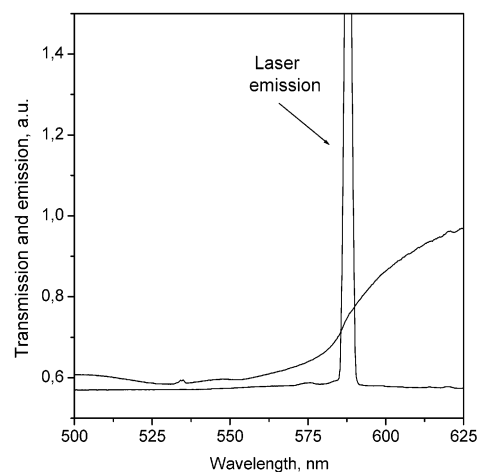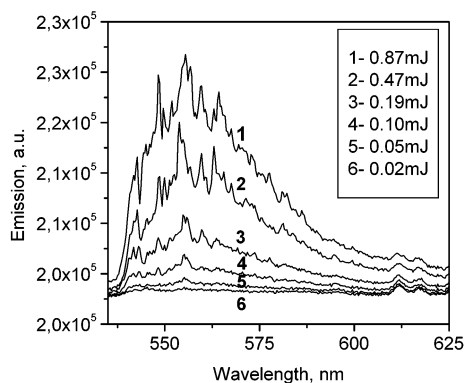

**Figure 2.** Transmission and emission spectra of the PSCLC sample (35 μm).

In PSCLC, at higher polymer concentrations of 5−10%, new cholesteric domains appear causing changes in selective reflection. The selective reflection band edges become smoother, and the band broadens (Figure 2). The domain size (estimated using optical microscopy) is hundreds of microns on average. The film texture is close to focal conic with a rather planar domain orientation. The lasing threshold is typically about 20% higher than in a pure cholesteric film of the same thickness. The electric field increases lasing intensity until it saturates. Figure 3 shows the effect of applied voltage on lasing intensity at ca. 0.2 mJ pumping energy. The electric field seems to improve the domains' planar orientation. A further voltage increase reduces

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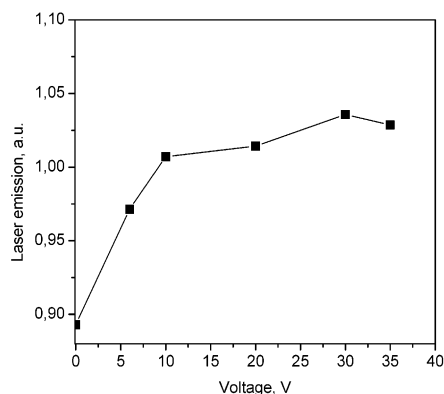
**Figure 3.** Dependence of lasing emission from the PSCLC sample on electrical field.

Figure 4. Emission spectrum of the chiral PDCLC sample with 30% polymer concentration.
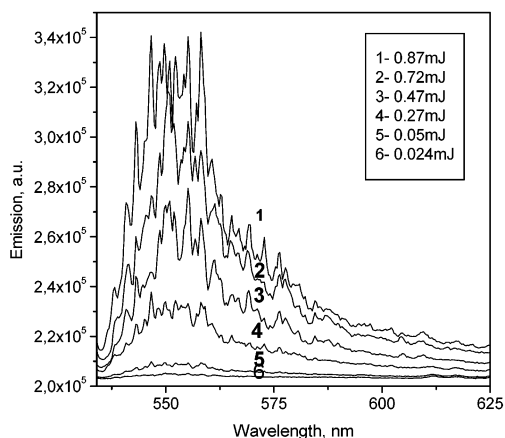
Figure 5. Emission spectrum of the chiral PDCLC sample with 60% polymer concentration.

the selective reflection band sharpness and depth and depresses lasing, which is also attributable to dynamic scattering.[3]

At a polymer concentration as high as 30%, the selective reflection band becomes fuzzy and lasing changes dramatically: peaks appear on the top of the emission band over a broad wavelength range (Figure 4). The electric field does not increase lasing intensity but some peaks become sharper and change position. At 60% polymer concentration, the lasing spectra are similar to those at 30% (Figure 5). Increasing the pump energy makes peaks sharper and higher. Here again, the electric field has rather little effect on lasing intensity. Narrow lines appearing on the top of the emission band and intensifying at higher pumping energies are characteristic of coherent random lasing.[20−22] The random lasing may be caused by local changes in refractive indices of the domain−matrix interface. At this
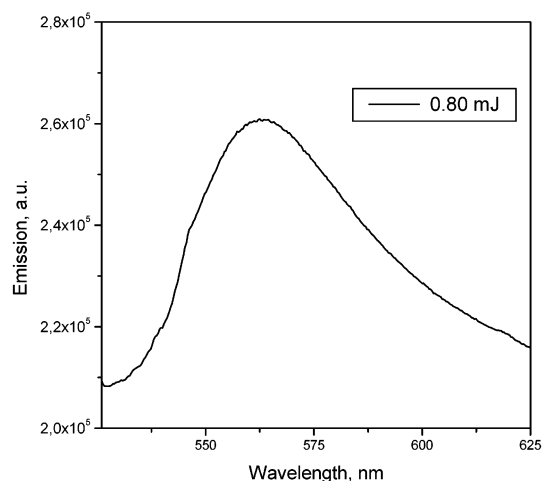
Figure 6. Emission spectrum of the nonchiral PDLC sample with 60% polymer concentration.

concentration, the size of the cholesteric droplets dispersed in the matrix is reduced to 20−40 μm, which is still larger than cholesteric helix pitch. The optical microscopy shows the droplets to be quite irregular, often with internal defects and touching each other. All of this is necessary to produce various chiral defects.[7−9] In our experiments, the exact position of the lasing peaks was found to depend on the position of pumping beam spot on the PDCLC sample, i.e., on the sample's local structure. Note that major lasing peaks retain their spectral position within the same spot at different pumping energies (Figures 4 and 5). A similar behavior was reported for random lasing materials.[20−22]

To better understand whether random lasing contributes to the observed spectral changes in PDCLC, new nonchiral PDLC samples were prepared with 30−60% polymer concentrations (NOA 71) using pure nematic liquid crystal ZLI 4788 instead of the cholesteric mixture. The experimental setup and conditions were the same as those producing similar PDLC film textures. Figure 6 shows typical emission spectra of nonchiral samples with no sharp peaks on the top of the emission band even at the highest pump beam intensity.

We suggest the following explanation of the effects observed in PSCLC/PDCLCs.

In neat CLCs, lasing occurs at the band edge of the monodomain samples and is caused by higher photon dwell times at the edge of the material's PBG structure (Figure 1a). The authors have described these phenomena in detail elsewhere.[4,5]

In CLCs with low polymer concentrations (PSCLC), lasing occurs in the band-edge modes of several slightly disoriented domains, with each domain's lasing directed perpendicularly to its cholesteric plane. Because of domain disorientation and size disparity, lasing (still perpendicular to the cholesteric planes) occurs at slightly different wavelengths and directions. The electric field tends to align the domains within the plane thus improving sample planarity and producing lasing almost perpendicular to the sample and, therefore, of high intensity (Figure 2).

In PDCLCs, at 30−60%, polymer concentrations domains become more smaller and numerous, which also gives more polymer-separated domains, more domains with defects, and adjacent domains of different orientation. This produces photonic defect modes within the selective reflection band.[6−9] The position of lasing peaks in these modes depends on the distance between domains, domain orientation, and the refractive index

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of the domain−matrix interface. Light scattering, both domain−domain and domain−matrix, is especially intense at higher polymer concentrations. It mainly occurs at the droplet−matrix interface and makes the domain-emitted light deflect (in the direction perpendicular to domain planes) toward monochromator slit. As a result, on the top of the emission band, the lasing peaks appear emitted at both the selective reflection band edges and photonic defect modes in the domains of different pitch and orientation. The electric field has no major effect on PDCLC lasing intensity: domains are too disoriented to adopt a uniform planar orientation.

Conclusions

Lasing in PSCLCs and PDCLCs was studied for the first time and shown to depend on the PBG structure of cholesteric samples. In PSCLCs at low polymer concentrations, lasing occurs at the selective reflection band edge. The electric field somewhat increases the lasing intensity in PSCLCs by improving the planar domain orientation. In PDCLCs, lasing behavior changes dramatically at high polymer concentrations showing numerous peaks to appear on the top of the broad emission band rather than lasing within a well-defined narrow range. The peaks become sharper and more intense as pumping energy increases, which suggests the lasing occurs at both the selective reflection band edge and photonic defect modes within the selective reflection bands of cholesteric domains dispersed in the matrix.

The discovered phenomena suggest PSCLC/PDCLCs' potential use as electrically controllable PBG materials. Tuning domain size and distribution in polymer matrix may significantly improve PSCLC/PDCLCs electrical and optical properties. Our experiments on PDCLCs call for further study of light emission and random lasing in materials with active PBG structures.

References and Notes

(1) Joannopoulos, J. D.; Meade, R. D.; Winn, J. N. *Photonic Crystals*; Princeton University Press: Princeton, NJ, 1995.

(2) Sakoda, K. *Optical properties of Photonic Crystals*; Springer-Verlag: Berlin, 2001.

(3) Chandrasekhar, S. *Liquid Crystals*, 2nd ed.; Cambridge University Press: New York, 1992.

(4) Kopp, V. I.; Fan, B.; Vithana, H. K. M.; Genack, A. Z. *Opt. Lett.* **1998**, *23*, 1707.

(5) Kopp, V. I.; Zhang, Z. Q.; Genack, A. Z. *Phys. Rev. Lett.* **2001**, *86*, 1753.

(6) Yang, Y. C.; Kee, C. S.; Kim, J.-E.; Park, H. Y. *Phys. Rev. E* **1999**, *60*, 6852.

(7) Hodgkinson, I. J.; Wu, H.; Thorn, K. E.; Lakhtakia, A.; McCall, M. W. *Opt. Commun.* **2000**, *184*, 57.

(8) Kopp, V. I.; Shibaev, P. V.; Bose, R.; Genack, A. Z. *Proc. SPIE* **2002**, *4655*, 141.

(9) Kopp, V. I.; Genack, A. Z. *Phys. Rev. Lett.* **2002**, *88*, 033901.

(10) Munoz, A.; Palffy-Muhoray, P.; Taheri, B. *Opt. Lett.* **2001**, *26*, 11.

(11) Finkelmann, H.; Kim, S. T.; Munoz, A.; Palffy-Muhoray, P.; Taheri, B. *Adv. Mater.* **2001**, *13*, 1069.

(12) Schmidtke, J.; Stille, W.; Finkelmann, H.; Kim, S. T. *Adv. Mater.* **2002**, *14*, 746.

(13) Shibaev, P. V.; Tang, K.; Genack, A. Z.; Kopp, V. I.; Green, M. M. *Macromolecules* **2002**, *35*, 3022.

(14) *Liquid Crystals in Complex Geometries*; Crawford, G. P., Zumer, S., Eds.; Taylor & Francis: London, 1996.

(15) Guillard, H.; Sixon, P. *Liq. Cryst.* **2001**, *28*, 933.

(16) Crooker, P. P.; Yang, D. K. *Appl. Phys. Lett.* **1990**, *57*, 2529.

(17) Crawford, G. P.; Whitehead, J. B.; Zumer, S. Optical Properties of Dispersed Liquid Crystals. In *The Optics of Thermotropic Liquid Crystals*; Elston, S., Sambles, R., Eds.; Taylor & Francis: London, 1998; p 233.

(18) Letokhov, V. S. *Sov. Phys. JETP* **1968**, 26, 835.

(19) Wiersma, D. S.; van Albada, M. P.; Lagendijk, A. *Nature* **1995**, *373*, 103.

(20) Burin, A. L.; Ratner, M. A.; Cao, H.; Chang, R. P. H. *Phys. Rev. Lett.* **2001**, *87*, 5503.

(21) Cao, H.; Zhao, Y. G.; Ho, S. T.; Seelig, E. W.; Wang, H.; Chang, R. P. H. *Phys. Rev. Lett.* **1999**, *82*, 2278.

(22) Cao, H.; Xu, J. Y.; Zhang, D. Z.; Chang, S.-H.; Ho, S. T.; Seelig, E. W.; Liu, X.; Chang, R. P. H. *Phys. Rev. Lett.* **2000**, *84*, 5584.

(23) Nephew, J. B.; Nihei, T. C.; Carter, S. A. *Phys. Rev. Lett.* **1998**, *80*, 3276.

(24) Cairns, D. R.; Genin, G. M.; Wagoner, A. J.; Briant C. L.; Crawford, G. P. *Appl. Phys. Lett.* **1999**, *75*, 1872.

(25) St. John, W. D.; Fritz, W. J.; Lu, Z. J.; Yang, D.-K. *Phys. Rev. E* **1995**, *51*, 1191.