SPECIAL TOPIC — Physical research in liquid crystal

Random lasing in dye-doped polymer dispersed liquid crystal film*

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A dye-doped polymer-dispersed liquid crystal film was designed and fabricated, and random lasing action was studied. A mixture of laser dye, nematic liquid crystal, chiral dopant, and PVA was used to prepare the dye-doped polymer-dispersed liquid crystal film by means of microcapsules. Scanning electron microscopy analysis showed that most liquid crystal droplets in the polymer matrix ranged from 30 μm to 40 μm, the size of the liquid crystal droplets was small. Under frequency doubled 532 nm Nd:YAG laser-pumped optical excitation, a plurality of discrete and sharp random laser radiation peaks could be measured in the range of 575–590 nm. The line-width of the lasing peak was 0.2 nm and the threshold of the random lasing was 9 mJ. Under heating, the emission peaks of random lasing disappeared. By detecting the emission light spot energy distribution, the mechanism of radiation was found to be random lasing. The random lasing radiation mechanism was then analyzed and discussed. Experimental results indicated that the size of the liquid crystal droplets is the decisive factor that influences the lasing mechanism. The surface anchor role can be ignored when the size of the liquid crystal droplets in the polymer matrix is small, which is beneficial to form multiple scattering. The transmission path of photons is similar to that in a ring cavity, providing feedback to obtain random lasing output.

Keywords: polymer dispersed liquid crystal film, random lasing, multiple scattering

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1. Introduction

The concept of polymer dispersed liquid crystal (PDLC) was originally introduced by the liquid crystal research group from University of Kent State.[1] PDLC is a novel functional liquid crystal (LC) composite material. LC droplets disperse in the polymer matrix of PDLC in nanometer or micrometer. A stereoscopic display with large area and wide viewing angle of high bright state and easily flexible can be realized. Therefore, it is widely applied in flat panel displays, switchable Bragg gratings,[2–4] and so on. The most versatile method to form PDLC structures are microcapsules of a homogenous mixture polymer and LC with strong stirring. The size of the LC droplets ranges from nanometer to micron by controlling the mechanical mixing speeds, curing degree, and so on. As usual, the refraction index of the polymer n_p is set to be equal to the ordinary refractive index of the LC n_o. The LC molecules randomly distribute in the droplets. There is an index difference at the interface between the LC droplets and the polymer matrix, which causes light scattering in the PDLC. The feedback for dye-doped chiral nematic LC is not provided by an external resonator, but is provided by multiple scattering. The multiple scattering is formed from the regular helical structures of LC. Therefore, it has the characteristics of compact cavity structure, lower threshold value, wide radiation wavelength, and so on.[5,6] PDLC has attracted much attention from many scientists and physicists.[7–13] There are currently many reports on lasing emission gained through dye-doped liquid crystal which is built on polymer and nano-particle. By controlling the size of the droplets during the PDLC process, two different mechanisms of lasing emission output can be achieved, one is random lasing and the other is photonic band gap lasing.[9] The introduction of Ag or ZnO nanoparticles to dye-doped PDLC will cause the low threshold random lasing emission output.[12] However, most of the studies focus on the emission characteristic and the energy threshold characteristic. There are fewer studies on the disorder scattering process and the temperature characteristics of PDLC.

In this study, a dye-doped PM597 PDLC film was fabricated by the microcapsule method, and a stable random laser action has been obtained. Furthermore, the threshold characteristics of random lasing, the energy distribution of light spot, and the temperature characteristic were analyzed. Lasing mechanisms of disorder scattering process within the dye-doped polymer dispersed LC film were investigated.

2. Experiment methods

The materials used to fabricate the dye-doped chiral liquid crystal consisted of 68.6 wt.% of nematic liquid crys-

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tal TEB30A ($n_e = 1.692$, $n_o = 1.522$, $\Delta n = 0.170$, $\varepsilon = 9.2$, $\Delta\varepsilon = 5.4$), 29.4 wt.% of the chiral dopant S-811, and 2 wt.% of laser dye pyrromethene-597 (PM597). To form the emulsions, the dye-doped chiral nematic LC lasing mixture was added at a concentration of 1.8 wt.% to the poly-vinyl alcohol (PVA) solution (14.78 wt.% in deionized water). The mixtures emulsified at 1000 rpm, using the FSH-2A homogerate machine. The dye-doped chiral nematic LC droplets uniform distributed in the PVA solution, and then dye-doped PDLC was obtained. The sizes of the LC droplets and the dye droplets in the emulsions were under the control of mechanical mixing speeds. The size of the droplets plays a decisive role on the lasing mechanism of the sample. The prepared dye-doped PDLC was immediately coated onto glass substrates. After drying treatment at room temperature, the sample preparation of the dye-doped PDLC film was finished. The thicknesses of the wet films obtained here was 0.2 mm and the thicknesses of the dry films was 80 μm. During the microcapsule method was used in the preparation process.

The experiment devices are shown in Fig. 1. The distribution of the LC droplets was observed by laser scanning confocal microscope LEXT OLS4100 (OLYMPUS). To measure the emission spectrum of lasing, the sample was photo-pumped by the second harmonic (532 nm) of a neodymium yttrium aluminium garnet (Nd:YAG) laser, which has a repetition rate of 5 Hz. The pump lasing was separated into two paths: one was used as the pump lasing and the other was monitored by an energy meter. The lasing spectrum of the sample was measured by a fiber spectrometer (Avaspec-2048-USB2, ARANTES), the fiber spectrometer was monitored real time by a computer. In order to lower the influence of the pump light on the detection results, the angle between the incident direction of the laser and the axial direction of the sample was kept at 45°. The energy threshold characteristic of the sample was examined by the energy meter and the fiber spectrometer. The specific means was recording the intensity of ransom lasing emission peaks with amplifying the energy of pump lasing.

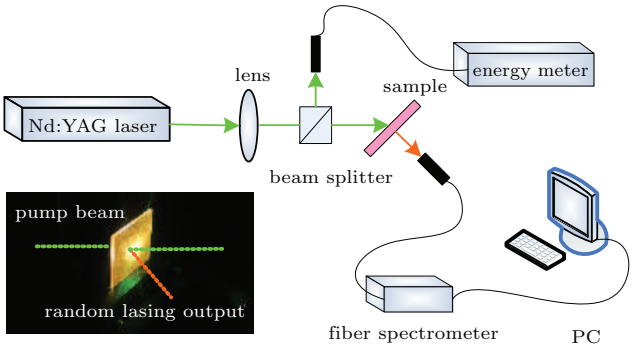


Fig. 1. (color online) Framework of experiment and detection devices.

3. Results and discussion

Figure 2 shows the polarized microscopy images of the dye-doped PDLC film. The degree of concavity and convexity of the sample is shown in Fig. 2(a), by which we can judge that due to the random distribution of the LC droplets, the thickness of the PDLC film becomes incongruity when dried. It can be seen from Fig. 2(b) that the LC droplets are more evenly distributed in the polymer matrix. The diameter of the LC droplets ranges from 30 μm to 40 μm. The size of the droplets is small. Therefore, the surface anchoring for LC can be ignored. So the helical axes arraying directions of the LC droplets are randomly distributed, as shown in Fig. 3. Determination of the affecting factors of LC alignments within the droplets is a very complicated problem. It depends on the surface arrangement of the film, the chiral twisting, the shape of the droplets, and the shrinkage degree of the film. During the drying process, the evaporation of water results in the change of the shape of the droplets from spherical to oblate. The reduction degree of volume depends on the composition proportion and the solvent content. The refractive index n_p of the PDLC polymer matrix is about 1.52–1.53. According to the formula[14] $n_{eff} = (2n_o + n_e)/3$, the effective refractive index, n_{eff}, of the LC droplets is about 1.579. By the date, we can see $n_{eff} > n_p$. The effective refractive index of the LC droplets and the refractive index of the PDLC polymer matrix are mismatch. So light can have multiple scattering in the dye-doped PDLC film.[15]

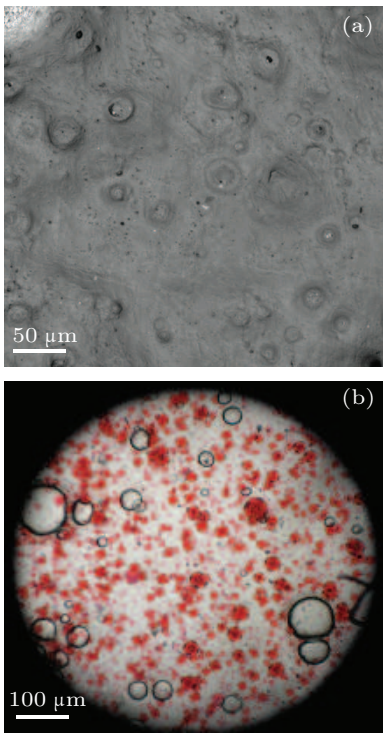


Fig. 2. (color online) Microscope images of the sample: (a) surface morphology, (b) distribution of LC.

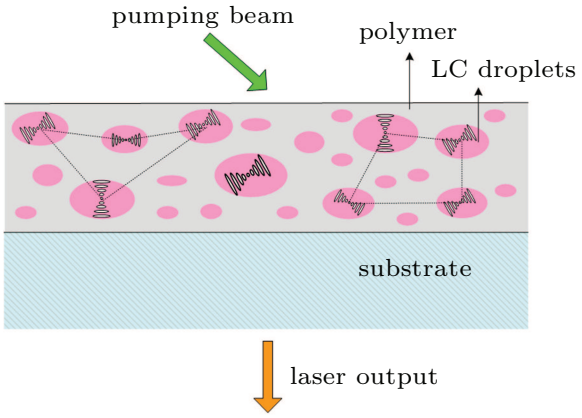


Fig. 3. (color online) Texture of the sample.

The emission spectrum of the random laser with various pumping energies that is shown in Fig. 4 occurs when the angle between the incident direction of the laser and the axial direction of the sample comes to 45°, It can be seen that the emission has an obvious energy threshold. At a low pumping energy, a broad spontaneous emission spectrum is observed. When the pumping energy increases to 9 mJ, the photon density is significantly increased. The scattering intensity increases sharply in the range of 575–590 nm. This leads to a narrower light scattering spectrum. A plurality of discrete and sharp random laser radiation peaks then appear. It is shown in Fig. 5 that when the incident pumping energy exceeds 15 mJ, the FWHMs of these emission peaks are about 0.2 nm. The FWHMs are almost unchanged with further increasing pumping energy. It is worth to mention that the experimental devices do not adopt an aperture system. The size of the light spot on the sample is larger than the size of the spectrometer detected light spot. Therefore, the pumping energy to the sample is smaller than the datum observed in the experiment. There are no effects on the observation of the threshold characteristics.

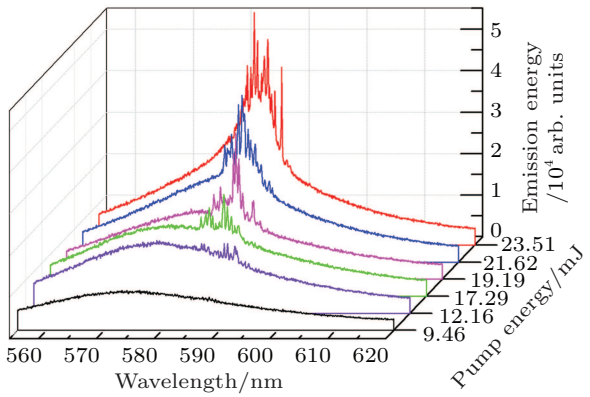


Fig. 4. (color online) Emission spectra with various pumping energies.

We draw a conclusion that the appearance of these discrete peaks results from light multiple scattering. With the increasing density of the LC droplets in the PDLC, the surface anchoring for LC can be ignored because the size of the droplets is small. The LC droplets are randomly distributed in the polymer matrix, so their own helical axes of chiral nematic LC distribute randomly. Namely, the arraying directions of the helical axes are different, which is beneficial for the multiple scattering of photons in the helical structure. A closed loop or micro cavity can be formed by multiple scattering, as the dashed line in Fig. 3 shows. These closed loops are similar to those in a ring resonator.[16] The gain for laser dye is obtained and the resonance is constantly formed by feedback amplification. Photons may localize in the micro cavity, lasing emission would be produced when the gain is more over the loss. The equation of the ring cavity theory is $L = \lambda^2/(n \times \Delta\lambda)$, where L is the length of the cavity, n is the refractive index of the medium, and $\Delta\lambda$ is the average wavelength spacing.[17] The cavity is formed by multiple scattering, and the length is 417–428 μm. The length of the cavity is much longer than the size of the LC droplets (30–40 μm). This proves that the emission in the experiment is due to random lasing mechanism formed by multiple scattering of LC. If the size of the LC droplets is larger, the arraying direction of the helical axis is not randomly distributed but along the normal direction of the surface when the PDLC film is dried. The stable band-edge lasing will be obtained.[9–11]

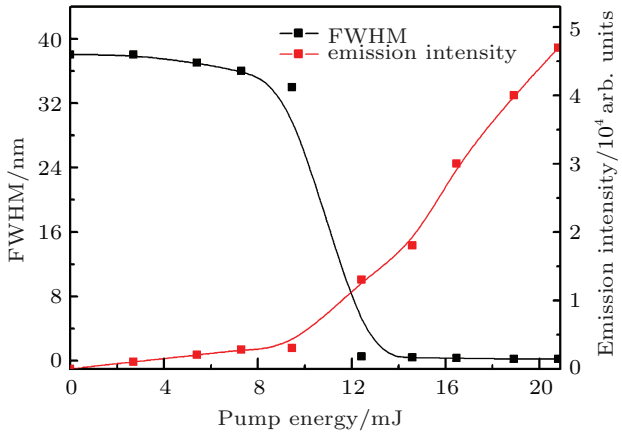


Fig. 5. (color online) Lasing threshold of the sample.

In order to prove that the emission mechanism of the dye-doped PDLC film in the experiment is random lasing and not band-edge lasing, the emission laser spot energy distribution is detected by a laser analyzer. Figure 6 shows the experiment results. The pumping energy is 19.19 mJ. The spatial characteristics of the laser spot can be directly seen. Figures 6(a) and 6(b) are the energy distribution of the lasing spot at the same position from different directions. We can see that there are many discrete emission peaks. This is intrinsically different from the band-edge lasing spot. The band-edge lasing presents a Gaussian distribution and the lasing emission changes with time. It is concluded that the emission obtained in the experiment is random lasing. A closed ring cavity will be formed

by multiple scattering, which determines the oscillation frequency. In addition, the frequency, the position, and the direction of luminescent are different for different ring cavities. The spectrum in the experiment results from some ring cavities. Because of the randomly distribution of the ring cavity, lasing output exists in all directions. However, the property of the lasing emission such as the line-width and spectral construction may change when changes take place in time and space.

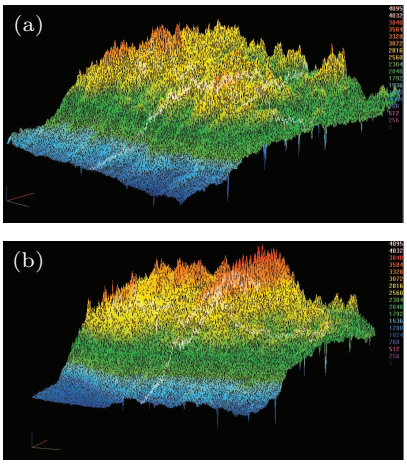


Fig. 6. (color online) The beam quality of random lasing observed from different directions.

The emission spectrum under heating is shown in Fig. 7. When the temperature of the sample is above the isotropic temperature, the emission peaks disappear. This happens because the liquid crystal, as the light scattering medium, has different phases at different temperatures. It also has different molecular orientations and different refractive index distributions. At room temperature, the liquid crystal presents a chiral nematic liquid crystal phase, the phenomenon of double refraction appears, and the light scattering becomes stronger. This is beneficial to the generation of random lasing. As the temperature rises, the liquid crystal is optically isotropic and the multiple scatting decreases obviously. The threshold of random lasing then increases and the emission peaks disappear.

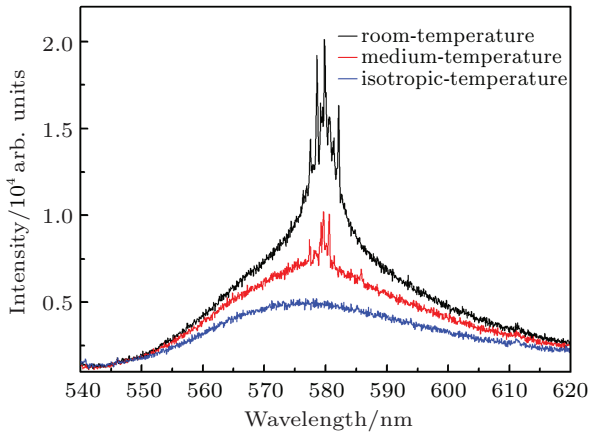


Fig. 7. (color online) The emissions at different temperatures.

4. Conclusion

In this paper, laser dye PM597, nematic liquid crystal TEB30A, and chiral dopant S-811 were used to prepare a dye-doped chiral nematic liquid crystal, which was then mixed with the polymer solution by the method of microcapsule. The size of the LC droplets in the polymer matrix is 30–40 μm. A 532 nm Nd:YAG pulsed laser was used to pump the sample. A plurality of discrete and sharp random lasing peaks appeared in the range of 575–590 nm. The line-width of these peaks is about 0.2 nm and the energy threshold is 9 mJ. The formation of random lasering is the result of multiple scatting. The size of the LC droplets is the decisive factor that influences the mechanism of lasing output, the mechanism is random lasing or band-edge lasing. Under heating, the emission peaks of random lasing disappear. This happens because the liquid crystal, as the light scattering medium, has different liquid crystal phases at different temperatures. As the temperature rises, the liquid crystal is optically isotropic and the multiple scatting decreases obviously. This is the fundamental cause of the random laser generation and disappearance.

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