Magnetically tunable random lasing from polymer dispersed liquid crystal doped ferromagnetic nanoparticles in capillary

Cite as: AIP Advances 9, 115015 (2019); https://doi.org/10.1063/1.5120438
Submitted: 18 July 2019 . Accepted: 21 October 2019 . Published Online: 18 November 2019

H. T. Dai, M. N. Gao, Y. X. Xue, A. X. Xiao, A. Ahmad, Z. Mohamed, C. L. Liu, Q. Lu, and S. Z. Feng
Magnetically tunable random lasing from polymer dispersed liquid crystal doped ferromagnetic nanoparticles in capillary

Cite as: AIP Advances 9, 115015 (2019); doi: 10.1063/1.5120438
Submitted: 18 July 2019 • Accepted: 21 October 2019 • Published Online: 18 November 2019

H. T. Dai, M. N. Gao, Y. X. Xue, A. X. Xiao, Z. Mohamed, C. L. Liu, Q. Lu, and S. Z. Feng

AFFILIATIONS
1 Tianjin Key Laboratory of Low Dimensional Materials Physics and Preparing Technology, School of Science, Tianjin University, Tianjin 300072, China
2 School of Precision Instrument and Optoelectronics Engineering, Tianjin University, Tianjin 300072, China
3 Key Laboratory of Opto-electronics Information Technology, Ministry of Education, Tianjin 300072, China
4 AnHui Zhongyi New Materials Technology Company, AnHui 239500, China

AUTHOR TO WHOM CORRESPONDENCE SHOULD BE ADDRESSED: qienil@tju.edu.cn

ABSTRACT
In this paper, magnetically tunable random lasing from a polymer dispersed liquid crystal (PDLC) in a capillary was achieved by means of doping with magnetic nanoparticles (MNP). We experimentally explored the effects of the concentration of MNP and the amplitude and direction of the magnetic field on the emission properties of random lasing, such as threshold, envelope of the emission spectrum, and intensities. The related mechanism was also investigated theoretically. Experimental results also showed that weakly tuned effects appeared from the sample with a polymer or pure liquid crystal (LC) doped with MNP in comparison with PDLCs. Our research would provide an additional way to achieve tunable compact LC-based lasers.

I. INTRODUCTION

In 1994, Lawandy et al. first verified the phenomenon that stimulated radiation amplification can be achieved in disordered gain media through experiments, namely random lasing. At present, the applications of random lasing have far reaching impacts on other disciplines, for example, photonics and biology, and scholars have conducted multiple studies in this regard.1–4 Generally, random lasing is generated in several ways, for example, from laser crystal powder, laser dye doped in a particle suspension, or a powdered semiconductor, such as ZnO, TiO2, Fe3O4, etc.5 With the advance in materials, the random lasing behavior has also been found in liquid crystal (LC) systems or LC-based systems.6–11 Thanks to the reorientation of liquid crystal molecules under external excitation, such as force,12 temperature,13 electric and magnetic field,14 and light,15–17 laser radiation based on liquid crystal systems can be easily influenced and modulated by external excitation. Electric stimuli are the most commonly used due to their high precision for tunable LC devices. However, in some special circumstances such as optical fiber or microtubules, the preparation of electrodes is difficult, and high voltage is required. Additionally, temperature can also be used to tune the properties of liquid crystals. However, the temperature field changes slowly, and the region cannot be easily defined precisely, which limits the widespread application of this method. The photocontrollable method is also a promising way to achieve tunable LC devices, which work with photoisomerization of azo-dyes.

In recent times, significant attention has been paid to study the magnetic effect of LCs or LCs doped with ferromagnetic materials. Intrinsically, LC molecules would respond to an external magnetic field. On the other hand, the guest-host effect can be utilized to tune the orientation of LC molecules by...
doping with ferromagnetic nanorods or particles. Ye et al. studied the electromagnetic and thermal modulation of random lasing in dye-doped liquid crystal systems.\textsuperscript{11} In 2017, Mur et al. studied magnetic field tuning and whispering cavity mode lasing emission of a ferromagnetic nematic liquid crystal microdroplet structure.\textsuperscript{15}

So far, multiple studies related to liquid crystal lasers have focused on planar liquid crystal cell structures or cuvettes. In recent years, LC-based lasers have been prepared in optical fibers or two-dimensional capillary structures for various application scenarios. As reported, LC lasing devices prepared in fibers or capillaries were anticipated for more compactness or integration.\textsuperscript{16,17}

In this paper, LC-based lasers in capillaries with a polymer dispersed liquid crystal (PDLC) (cap-PDLC) doped with ferromagnetic MNPs were prepared, and the random lasing properties of the prepared samples were explored experimentally. Experimental results showed that the envelope center of random lasing has a blue-shift, and the threshold of the samples increases with the increase of the concentration. The larger blue-shift of the envelope center of the random lasing spectrum with a parallel magnetic field is shown in comparison with that of the perpendicular magnetic field. Meanwhile, the intensity of lasing with the magnetic field in the parallel direction is stronger than that of the perpendicular magnetic field in the vertical direction.

II. EXPERIMENT

The prepolymer of PDLCs is prepared by mixing dipentaerythritol pentaacrylate (DPPHA, 29 wt.%), co-polymer cross linking agent N-vinyl-2-pyrrolidone (NVP, 10 wt.%), co-initiator N-phenylglycine (NPG, 0.8 wt.%), photo initiator rose bengal (RB, 0.1 wt.%), laser dye 4-(dicyanomethylene)-2-methyl-6-(4-dimethylamino-styryl)-4H-pyran (DCM, 0.1 wt.%), and nematic liquid crystal (E7, \( n_o = 1.521, n_e = 1.746, 31 \text{ wt.} % \)) provided by Merck, and phthalate diglycol diacrylate (PDDA, 29 wt.%). The syrups were mixed uniformly by ultrasonication for 2 h at 40°C in a dark environment. Then, the MNPs modified with oleic acid (inner diameter of 10 nm, solvent cyclohexane) supplied by Dona Company were dispersed into the syrups. Figure 1(b) shows the picture of ferromagnetic nanoparticles under a scanning electron microscope. Next, the capillary was inserted into the solution to fill the prepolymer by capillarity and exposed to UV for 15 min at 25°C. The prepared sample is shown in Fig. 1(a). Figure 1(c) shows the schematic of the PDLC doped with MNPs after curing. The LC droplets are dispersed in the polymer matrix.

The configuration’s pumping and spectrum collection of random lasing emission are the same as those in Ref. 16. An AvaSpec-ULS 2048L/3648TEC spectrometer was used to collect the emission spectrum of random lasing in experiment. 532 nm laser pulses (10 ns at 10 Hz) were focused onto the samples with a cylindrical lens (\( f = 20 \text{ cm} \)). The external magnetic field was applied with a cylindrical NdFeB magnet. The intensity of the magnetic field was tuned by varying the distance between the magnet and the capillary. The directions of the magnetic field could be applied along the axial direction of the sample (\( B || \)) or perpendicular to the axial direction of the sample (\( B _\perp \)) as shown in Fig. 1(c).

III. RESULTS ANALYSIS

A. The effect of doped Fe\(_3\)O\(_4\) concentration on random lasing stimulation

Figures 2(a)–2(d) show the random lasing spectrum for four samples with a doping concentration of 0 wt.%, 0.01 wt.%, 0.02 wt.%, and 0.03 wt.% MNPs in the PDLC at various pump energies. From Figs. 2(a)–2(d), it is evident that the random lasing emission from samples doped with MNPs is weaker than the random lasing from the samples without MNP doping, which can be ascribed to the absorption of MNPs in samples. The thresholds in Fig. 2 are 9.5 \( \mu J \), 11.5 \( \mu J \), 12.3 \( \mu J \), and 18.5 \( \mu J \), respectively. It can be seen that the lasing...
FIG. 2. The spectra of random lasing from samples with MNP doping concentration of 0 wt. % (a), 0.01 wt. % (b), 0.02 wt. % (c), and 0.03 wt. % (d) in the PDLC with various pump energies.

threshold increased with increasing concentration of MNP doping. This effect also resulted from the higher absorption of MNPs with larger concentration.

Meanwhile, the envelope center of random lasing has a blue-shift with the increase of the concentration of MNPs in the PDLC as shown in Fig. 3. As we all know, the emission peak would be affected by the resonator cavity parameters. With this knowledge, the blue-shift in Fig. 3 could be explained by the shortened resonator cavity induced by the decrease in the mean free path (MFP) with increasing concentration of MNPs. However, with the increase of the concentration of MNPs, the dye molecules drifted apart from the gain volume, which resulted in the reduction of the dye concentration. Consequently, the gain length (GL) of the sample is increased. In addition, the decrease in the dye concentration can also reduce self-absorption, which can lead to the blue-shift of the envelope center of the laser spectrum as well.

To verify the above analysis, we have examined the transport mean free path (TMFP) and gain length of the system quantitatively. It is known that the transport mean free path (TMFP) $l_t$ is the same scale as $l_s$, where $l_s$ is the scattering mean free path (SMFP). Considering a dilute system with scattering particles, the scattering mean free path is determined by $^{19,22}$

$$l_t = l_s \frac{1}{1 - \langle \cos \theta \rangle},$$

where $ho$ is the number density of MNPs, which is $1.106 \times 10^{18}/m^3$, and $\sigma$ is the scattering cross section. The TMFP $l_t$ is related to $l_s$, $^{19,21}$

$$l_t = \frac{l_s}{1 - \langle \cos \theta \rangle},$$

where $\langle \cdot \rangle$ is the average operation. For our situation, $\langle \cos \theta \rangle = 0.5$ or $l_t = 2l_s$.

The scattering cross sections (SCSs) can be determined by $^{21}$

$$\sigma = \frac{3}{8} \pi x^2 \left(\frac{\rho^2 - 1}{\rho^2 + 2}\right) \sigma_g,$$

where $x = \frac{2\pi}{\lambda}$, with $r$ being the radius of the scattering particle and $\lambda$ being the wavelength, and $n$ is the refractive index of particles. The scattering geometrical cross section is defined as $\sigma_g = \pi r^2 = 7.8 \times 10^{-17} m^2$. For MNPs, $x = 0.059$, $n = 2.42$, and $r = 5$ nm. As a result, the scattering cross section of MNPs is $2.2139 \times 10^{-22} m^2$.

FIG. 3. The collection spectra of random lasing of four samples doped with MNPs at different concentrations at an energy of 17.5 $\mu$J.

AIP Advances 9, 115015 (2019); doi: 10.1063/1.5120438
© Author(s) 2019
The gain length (GL) at the onset of lasing is given by

$$L_g = \frac{V^2}{l_t}, \quad (4)$$

where $V$ is the excitation volume. The excitation volume and the gain length can be calculated theoretically. From Eqs. (1) and (2), the TMFP is inversely proportional to the number density of nanoparticles. The shorter the TMFP, the shorter will be the length of the resonant cavity. Therefore, the blue shift of the emission wavelength would be observed. At the same time, according to Eq. (4), the shortening of the TMFP would result in a shorter gain length. The threshold, therefore, would be increased and the emission intensity would be decreased with higher density of nanoparticles. The experimental results coincide with theoretical analysis.

### B. The effect of the external magnetic field on the emission properties of random lasing from PDLCs in a capillary

The figure of merit of MNP doping is due to the sensitive magnetic response of LC molecules originating from the guest-host effect, i.e., the variation of the guest molecule (MNPs) leads to reorientation of the host molecules (LC molecules). Figs. 4(a) and 4(b) show the effects of the applied magnetic field on the random lasing properties of the PDLC for parallel and perpendicular magnetic directions, respectively. It can be seen that the parallel magnetic field would induce a larger blue-shift of the envelope center of the random lasing spectrum than that of the perpendicular magnetic field. Meanwhile, the intensity of lasing with the magnetic field in the parallel direction is stronger than that of the magnetic field in the vertical direction. However, the blue-shift of random lasing would be saturated when the magnetic field intensity reaches 6 mT. This was perhaps due to the MNPs in the LC being aligned completely.

As we all know, both LC molecules and MNPs can respond to the external magnetic field. Figures 4(c) and 4(d) show the emission spectrum of random lasing from the PDLC without and with MNP (0.02 wt. %) doping by applying various magnetic fields, respectively. According to Fig. 4(c), the external magnetic field can tune the emission properties of the PDLC without MNP doping; however, the amount of shift of the envelope center is very small in...
FIG. 6. (a) Spectra of random lasing with an applied parallel magnetic field in the pure liquid crystal doped with MNPs. (b) The emission properties of random lasing with varying magnetic field in the sample with pure polymer dispersed with MNPs.

comparison with the sample of PDLC doped with MNPs, as shown in Fig. 4(d). Therefore, the guest-host effect of MNPs in LCs would dominate the properties of random lasing from the PDLC doped with MNPs which makes it a promising candidate for magnetically tunable LC-based lasers.

Considering the guest-host effect between MNPs and LC molecules, the motion or rotation of MNPs under an external magnetic field would lead to reorientation of LC molecules. The relaxation of samples doped with MNPs would disappear when the external magnetic field is applied, suggesting that it depends on the reorientation of LC molecules and not on that of the MNPs. The modulation results of random lasing, therefore, would be different between the increasing and decreasing magnetic fields.

Figure 5 shows the variation in the threshold of lasing from the samples with and without MNPs by means of the magnetic field. Simultaneously, it demonstrates the error of the data. Experimental results have shown that a higher energy required to achieve random lasing in samples doped with MNPs in comparison with the samples without MNP doping. On the one hand, the high light absorption of MNPs leads to this higher lasing threshold. On the other hand, the movement of Fe₃O₄ molecules leads to the reorientation of liquid crystal molecules, which reduces the effective refractive index and increases the threshold of laser stimulation.

In sample without MNPs, when the external magnetic field applied, the more regular orientation of liquid crystal molecules would be anticipated, which reduces the scattering intensity and results in a large threshold which ranges from 8 to 10 μJ/pulse.

To explore the role of the liquid crystal in the MNP doped samples, we also explored the random lasing properties of the samples prepared with the pure liquid crystal or polymer doped with MNPs. Figures 6(a) and 6(b) demonstrate the spectra of random lasing with the applied parallel magnetic field in the pure liquid crystal doped with MNPs and the polymer doped with MNPs, respectively. It can be seen that there was only a tiny shift of the envelope center of random lasing for both samples. In the polymer sample, MNPs are fixed internally by the polymer matrix. Therefore, the MNPs cannot be driven by an external magnetic field to achieve the tunable lasing effect. For the pure LC sample, random lasing is induced by the cavity formed by the nonuniform orientation of LC molecules, and the doped MNPs did not dominate the random distribution of LC molecules. Subsequently, the movement of MNPs in the LC cannot affect the random lasing behavior dramatically.

Finally, we considered the sample with the PDLC. The LC was enclosed as random distributed droplets by the polymer matrix in the PDLC. The random lasing from the PDLC is due to the cavity formed by the scattering of LC droplets. Hence, the effective index of LC droplets would be sensitive to local variation of LC molecules. When the magnetic field was applied, the movement of MNPs would disturb the orientation of LC molecules in the droplets locally. This disturbance would change the effective index of the LC droplets dramatically and result in an apparent spectral shift.

IV. CONCLUSION

In conclusion, a magnetically tunable random laser from a PDLC doped with MNPs in a capillary was demonstrated. Experimental results showed that the envelope center of the random lasing presented a blue-shift with increasing MNP concentration. Magnetically tuned effects were also explored. When the applied external magnetic field increases, a blue-shift of the emission spectra was observed experimentally. Furthermore, the spectral shift and emission intensity are related to the direction of the external magnetic field. The sample is more sensitive to the applied magnetic field along the axial direction of the capillary. Additionally, we also explored the magnetically tuned effects of the emission properties of random lasing from both PDLC samples without MNP doping and the pure polymer doped with MNPs. The results showed that guest-host effects between MNPs and LCs play a dominant role in magnetically tuned mechanisms. Thus, the guest-host effect provides an instant way to manipulate the random lasing.

ACKNOWLEDGMENTS

The authors acknowledge the National Natural Science Foundation of China (Grant No. 61975148), the Natural Science Foundation of Guangdong Province (Grant No. 2017A030313034), the Science, Technology and Innovation Commission of Shenzhen Municipality (Grant Nos. JCYJ20170817111349280 and KQTD2016030111203005), and Guangdong Innovative and Entrepreneurial Research Team Program (Grant No. 2017ZT07C071).
REFERENCES

1. N. M. Lawandy, R. M. Balacgandran, A. S. L. Gomes, and E. Sauvain, *Nature* **368**, 436 (1994).
2. H. Cao, Y. G. Zhao, S. T. Ho, E. W. Seelig, Q. H. Wang, and R. P. H. Chang, *Phys. Rev. Lett.* **82**, 2278 (1999).
3. R. C. Polson and Z. V. Vardeny, *Appl. Phys. Lett.* **85**, 1289 (2004).
4. D. S. Wiersma, *Nat. Phys.* **4**, 359 (2008).
5. S. Gottardo, S. Cavalieri, O. Yaroshchuk, and S. W. Diederik, *Phys. Rev. Lett.* **93**, 263901 (2004).
6. T. Gotoh and H. Murai, *Appl. Phys. Lett.* **60**, 392 (1992).
7. Y. H. Wu, Y. H. Liu, Y. Q. Lu, H. W. Ren, Y. H. Fan, J. Wu, and S. T. Wu, *Opt. Express* **12**, 6382 (2004).
8. D. Cupelli, F. P. Nicoletta, G. D. Filpo, P. Formoso, and G. Chidichimo, *J. Polym. Sci., Part B: Polym. Phys.* **49**, 257 (2010).
9. L. H. Ye, C. Hou, C. G. Lv, C. Zhao, Z. L. Yin, Y. P. Cui, and Y. Q. Lu, *Appl. Phys. B* **115**, 303 (2014).
10. L. H. Ye, Z. L. Yin, C. Zhao, C. Hou, Y. Wang, Y. P. Cui, and Y. Q. Lu, *J. Mod. Opt.* **60**, 1607 (2013).
11. L. H. Ye, B. Liu, C. Zhao, Y. Wang, Y. P. Cui, and Y. Q. Lu, *J. Appl. Phys.* **116**, 053103 (2014).
12. Z. G. Zheng, Y. N. Li, H. K. Bisoyi, L. Wang, T. J. Bunning, and Q. Li, *Nature* **531**, 352 (2016).
13. L. Wang, S. J. Ge, W. Hu, M. Nakajima, and Y. Q. Lu, *Opt. Mater. Express* **7**, 2023 (2017).
14. L. Wang, X. W. Lin, W. Hu, G. H. Shao, P. Chen, L. J. Liang, B. B. Jin, P. H. Wu, H. Qian, Y. N. Lu, X. Liang, Z. G. Zheng, and Y. Q. Lu, *Light: Sci. Appl.* **4**, e253 (2015).
15. M. Mur, J. A. Sofi, I. Kvasic, A. Mertelj, D. Lisjak, V. Niranjan, I. Musevic, and S. Dhara, *Opt. Express* **25**, 1073 (2017).
16. M. Z. Chen, H. T. Dai, D. S. Wang, Y. Yang, D. Luo, X. D. Zhang, and C. L. Liu, *Journal of Applied Physics* **123**, 10 (2018).
17. J. Zhang, H. T. Dai, C. Yan, D. G. Xu, Y. J. Liu, D. Luo, and X. W. Sun, *Opt. Mater. Express* **6**, 1367 (2016).
18. C. Y. Tsai, Y. M. Liao, W. C. Liao, W. J. Lin, P. Perumal, H. H. Hu, S. Y. Lin, C. H. Chang, S. Y. Cai, T. M. Sun, H. I. Lin, G. Haider, and Y. F. Chen, *Adv. Mater. Technol.* **2**, 1700170 (2017).
19. H. Cao, *J. Phys. A: Math. Gen.* **38**, 10497 (2005).
20. F. M. Zehentbauer, C. Moretto, R. Stephen, T. Thevar, J. R. Gilchrist, D. Pokrajac, K. L. Richard, and I. Kiefer, *Spectrochim. Acta, Part A* **121**, 147 (2014).
21. X. H. Wu, A. Yamilov, H. Noh, H. Cao, E. W. Seelig, and R. P. Chang, *J. Opt. Soc. Am. B* **21**, 159 (2004).
22. X. Wu, W. Fang, A. Yamilov, A. A. Chabanov, A. A. Asatryan, L. C. Botten, and H. Cao, *Phys. Rev. A* **74**, 053812 (2006).
23. D. S. Wiersma and A. Lagendijk, *Phys. Rev. E* **54**, 4256 (1996).