Luminescence spectrum thermal properties of Rhodamine 6G doped polymethyl metacrylate film sandwiched between cholesteric liquid crystal layers

R B Alaverdyan¹, T K Dadalyan¹, A S Karapetyan¹ and N S Torosyan¹
Yerevan State University, Alex Manoogyan 1, 0025 Yerevan, Armenia
E-mail: tigranxf@gmail.com

Abstract. We experimentally investigate fluorescence spectrum properties of multilayer system consisting of Rhodamine 6G doped polymethyl metacrylate thin film sandwiched between two right handed cholesteric liquid crystal layers at various temperatures and pumping powers. We observe fluorescence intensity enhancement while increasing sample temperature from 16 to 22°C when pumping sample with constant power laser irradiation. At constant temperature fluorescence intensity also increases with increasing pumping power.

1. Introduction

Development of compact and tunable optical elements that provide control of light radiation and parameters is a very important problem of contemporary science. Thanks to their optical properties Photonic Crystals (PC)-s have attracted a great deal of interest. In the recent years a considerable number of studies are devoted to investigation of Photonic Band Gap materials (PBG). These are structures with periodic modulation of refractive index and prohibit the propagation of light within certain frequency band [1].

Studies of PBG materials have started with the works of Bykov [2], Yablonovich [3] and John [4] where existence of PBG-s in media with periodic modulation of refractive index were predicted and since that PBG materials have found many practical applications. The ability of PC-s to inhibit spontaneous emission within band gap may be used to create low threshold lasers [5].

Much attention is paid to studies of PC-s that assume control of their properties by external influence. This enables one to control characteristics of propagating light. This can be easily met with both liquid crystals and their dye-doped polymeric film containing structures.

Cholesteric Liquid Crystals have self organized helical structure, with periodical modulation of refractive index and are reflecting circularly polarized light with the same handedness as CLC helix (selective reflection of the light); this allows us to consider CLC-s as 1D photonic crystals[6,7]. For normal incident light with wavelength within n_oλ ≤ λ ≤ n_eλ region, and circularly polarization with the same handedness of helix reflection coefficient is 1, whereas reflection coefficient for light with opposite handedness propagates without reflection. Here n_o and n_e are ordinary and extraordinary refractive indices of CLC and p is the pitch of the CLC helix [22]. In addition to selective reflection property the sensitivity of CLC pitch to external factors such as temperature, electric field is making them very interesting object of intensive studies and predicts many interesting practical applications, such as optical diodes, filters and optical windows and other compact optical components[8-10,15].

In combination with laser dyes CLC-s have found one of their very interesting applications. Unique properties of CLC-s enabled one to create low threshold and mirrorless tunable dye lasers [11-14]. CLC PBG sensitivity to the external factors provides tunability of the wavelength of lasing from these systems. The CLC-s in these systems could be used as dielectric mirrors or distributed feedback gratings [25]. In the case, when CLC is used as dielectric mirror, the active medium is separated from CLC; this could be implemented with various types of polymers [16-19], which are good alternative for gain medium of liquid state dye lasers. These types of solid state dye lasers have several advantages of small size of active medium and use of inflammable and safe for environment materials.
There are several studies devoted to improvement of lasing characteristics of these systems [20, 21]. The spectral peculiarities of systems containing isotropic defect layer sandwiched between two CLC layers are widely investigated theoretically [26-30].

Because of easy processability and other physical properties polymethyl metacrylate provides great opportunity to conduct experiments on multilayer systems consisting of Liquid Crystalline materials and polymer films.

During experiments we have used Rhodamine 6G laser dye, which is efficient laser dye and covers the wavelength region from 500 to 700 nm. It is very popular dye for experiments and applications. It has remarkable photostability and solubility in the most known solvents [24]. Usually Rhodamine 6G gain medium is pumped by the 2-nd harmonic of Nd: YAG laser (532 nm).

In the present work we study spectral properties of the system consisting of Rhodamine 6G doped polymethyl metacrylate thin films sandwiched between two right handed CLC layers. We experimentally investigate thermal peculiarities of the system fluorescence, excited with the laser irradiation with 532 nm wavelength at various pumping powers.

2. Experimental setup and materials

For obtaining solid state matrix for Rhodamine 6G we have used polymethyl Metacrylate (PMMA), which could be solved in chloroform or dichlorehane.

The CLC used in experiment was a mixture of 18 wt. % cholesteryl oleate (5-Cholesten-3b-ol 3-Olate), 35 wt. % of cholesteryl pelargonate and 47 wt. % of commercial Nematic Liquid Crystal E7.

The sample consists of glass substrates, R6G doped PMMA thin film sandwiched between CLC layers (Figure 1). The thickness of R6G doped PMMA layer is 25 µm, concentration of R6G is 4*10⁻² mol/liter. The distance of dye doped PMMA layer from glass substrates was given by means of spacers with thickness of 10 µm. The dimensions of PMMA layer were 10*10 mm². For avoiding PMMA layer deformations and non-uniformities, the film was partially covered by spacers, so 5*5 mm² sized central area of R6G doped PMMA was used for measurements.

For obtaining CLC uniform aligning the glass substrates were coated with polymer, and rubbed in anti-parallel directions. The CLC mixture was heated into the isotropic phase and droplet filled into the cell, containing R6G doped PMMA film on spacers. Then it was left for two days in the room temperature. The right handed helical CLC structure formed. Then four sides of the cell were glued.

Figure 1 The sketch of the CLC-R6G-CLC multilayer system, g-glass substrate, s-spacers, which kept the thickness of CLC layers (c) 10 µm, f-R6G doped PMMA film with the 25 µm thickness

The R6G doped PMMA film was obtained by adding R6G into the PMMA dichlorehane solution and spin coated on polyethylene film. After volatilization of dichlorehane the PMMA film formed and then was separated from polyethylene film.

The temperature of the cell was adjusted by a temperature controller which is tuning the temperature of Peltier thermoelectric module. The temperature of controller was set with accuracy of 0.5⁰ C. Temperature of the sample was measured by means of thermocouple, which was placed adjacent to the sample.

For fluorescence spectrum study, the Rhodamine 6G doped film was pumped with various powers of cw laser, with the wavelength of the second harmonic of Nd: YAG laser emission (532nm). For sample pumping the oblique angle geometry of pumping beam incidence was used. The angle between pumping beam and the cell normal was 54⁰, the pumping laser spot had 2 mm diameter. We have
measured fluorescence of the system at 15, 12 and 8 mW pumping powers. The experimental setup is shown on Figure 2.

**Figure 2.** Experiment geometry. Pump beam is incident to the cell normal at \( \phi = 54^\circ \), the fluorescence is collected by means of lens with 6 cm focal length.

Fluorescence spectrum was registered by homemade apparatus, consisting of monochromator ISP 51; the spectrum was registered using CCD camera. The measurements were carried out with image processing special program working in Lab View environment, which measures the values of the grayscale image pixels along given line. The optical resolution of the spectrophotometer was less than 1 nm.

### 3. Results and discussions

During experiments we have measured fluorescence form R6G doped PMMA 25 \( \mu \)m thin film which was sandwiched between two right handed CLC layers at various temperatures and pumping powers. Particularly the measurements were carried out within 16-22\(^\circ\)C temperature region. Pumping powers were 15, 12 and 8 mW of cw laser irradiation with 532 nm wavelength.

The luminescence spectrum of the multilayer system under various pumping powers is depicted on Figure 3. Three curves correspond to the 15, 12 and 8mW pumping powers. The temperature of the system is 22\(^\circ\)C. From the chart it could be seen that fluorescence of Rhodamine 6G covers wavelength region 535-640 nm. With increase of pumping power luminescence increases.

**Figure 3.** Fluorescence from CLC-R6G-CLC system increases with the pumping power. Temperature is 22\(^\circ\)C; the pumping powers are given on the curves.

In figure 4 the CLC-R6G doped PMMA film-CLC system fluorescence spectrum thermal dependences are represented. In this graph we have combined fluorescence from multilayer system at the same pumping power, but different temperatures of the sample.

From figure 4 it could be noticed that fluorescence of the system is increasing with increase of temperature.
Figure 4. The temperature dependence of fluorescence spectrum. The pumping power is 15mW

This result most likely could be explained by temperature shift of selective reflection band which causes reflection of pumping laser irradiation. As it was mentioned CLC could be interpreted as distributed feedback grating, with period sensitive to external temperature. In our mixture the raise of temperature leads to decrease in the helical pitch of CLC. The central wavelength of selective reflection band is proportional to helical pitch and is given with $\lambda_c \sim p(T)$ where $p$ is helical pitch of CLC and $T$ is temperature of the system. So the central wavelength of selective reflection band shifts with change of temperature. In our experiment we used oblique incident pumping beam so at 16°C the selective reflection takes place and a part of pumping laser energy is reflected and R6G is excited with less pumping power. The further increase of temperature shifts selective reflection band toward short wavelength region and at 22°C pumping light is out of selective reflection band and pumping beam passes through the system without any reflection and this causes the increase of fluorescence intensity. Because of non-uniformities of the CLC pitch the selective reflection band edges could be not sharp, so this might be the reason that reflection changes not dramatically as expected.

The Transmission spectrum measurement of the system is complicated because of the strong absorption of R6G in visible wavelength region [23].

4. Conclusions
In this study we’ve investigated fluorescence spectrum of CLC – R6G doped PMMA thin film – CLC multilayer system, which was excited by 532 nm wavelength cw laser irradiation with various powers at different temperatures of the sample. The pumping powers were 15, 12 and 8mW. We observe increase of fluorescence intensity corresponding to pumping power increase when temperature is constant. The fluorescence spectrum intensity at constant pumping power and increasing temperature also increases. Increasing fluorescence intensity at constant pumping power and various system temperatures could be caused by temperature shift of selective region band. However this interpretation of obtained results must be confirmed by additional experiments which are in progress. Obtained results are demonstrating easy tunability of the system which makes the system promising for further investigation.

Acknowledgments
This work was supported by State Committee of Science Republic of Armenia, grant 11-1c194.

REFERENCES
[1] Sibilia C, Benson T M, Marciniak M, Szoplik T 2008 Photonic Crystals: Physics and Technology Springer-Verlag Italia
[2] Bykov V P 1972 Spontaneous emission in a periodic structure Sov. Phys. JETP 35 269
[3] Yablonovitch E 1987 Inhibited spontaneous emission in solid state physics and electronics Phys. Rev. Lett 58 2059-2062
[4] John S 1987 Strong localization of photons in certain disordered dielectric superlattices Phys.Rev. Lett 58 2486-2489
[5] Ozaki M Kasano M Kitasho T Ganzke D Haase 2003 W Electro-Tunable Liquid Crystal Laser Adv. Matter. 15 974-977
[6] de Gennes P E 1974 The physics of Liquid Crystals Oxford
[7] Khoo Iam-Choon 2007 Liquid Crystals 2-nd edition John Wiley & Sons New Jersey,()
[8] Song M H Park B Takanishi Y 2006 Simple electro-tunable optical diode using photonic and anisotropic liquid crystal films Thin Solid Films 509 49 – 52
[9] Song M H Park B 2006 Electrotunable Non-reciprocal laser emission from a liquid crystal photonic device Adv. Funct. Mater. 16 1793–1798
[10] Hwang J., Song M. H., et.al., “Electro-tunable optical diode based on photonic band gap liquid-crystal heterojunctions nature materials”, nature materials 4, (2005)
[11] Coles H Morris H 2010 Liquid Crystal lasers Nature Photonics 4 676-685
[12] Takanishi Y Youko O 2010 Low threshold lasing from dye-doped cholesteric liquid crystal multi-layered structures Optics Express 18 12909-12914
[13] Wang Chun-Ta Lin Tsung-Hsien 2008 Multi wavelength laser emission in dye-doped photonic liquid crystals Optics Express 16 18334-18339
[14] Palto S P 2006 Lasing in LC thin films JETP 103 472
[15] Lukishova S G Belyaev S V 1996 Behavior of nonlinear liquid crystal mirrors, made of a nonabsorbing cholesteric, in the cavity of an Nd:YAG laser operating in the cw regime and at a high pulse repetition frequency Quantum Electron 26 796-798
[16] Shaposhnikov A A Kuznetsova R T 2004 Absorption, luminescent and lasing properties of laser dyes in silica gel matrices and thin gel films Quantum Electron 34 715-721
[17] Bezrodni V I Derevyanko N A 2001 Dye laser on base of polyurethane matrix JTP 71
[18] Korobkin Yu V Sidorov O 1996 Gain media of lasers on dye doped epoxides and other thirosin containing materials JTP 67
[19] Takahashi Y Maeda A Kojima K Uchida K 2000 Luminescence of dyes doped in a sol-gel coating film”, Journal of Luminescence 87 - 89 767-769
[20] Shirvani-Mahdavi H Fardad Sh Mohajerani E Wu Shin-Tson 2010 High efficiency cholesteric liquid crystal lasers with an external stable resonator Optics Express 18 13593-13599
[21] Chilaya G Chanishvili A Petriashvili G 2006 Enhancing cholesteric liquid crystal laser stability by cell rotation Optics Express 14 9939- 9943
[22] Belyakov V A Sonin A S 1982 Optics of Cholesteric Liquid Crystals Nauka Publ Moscow
[23] Alaverdyan R Dadalyan T Hayrapetyan N 2011 Proc of SPIE 8114 Liquid Crystals XV(San Diego)
[24] Shankarling G S Jarag K J 2010 Laser dyes Resonance 804-818
[25] Chilaya G Chanishvili A et. al. 2011 Materials Sciences and Applications 2 116-129
[26] Belyakov V A 2006 Mol. Cryst. Liq. Cryst.43 453
[27] Gevorgyan A H Harutyunyan M Z 2007 Chiral photonic crystals with anisotropic defect layer Phys. Rev. E 76 031701
[28] Gevorgyan A H Harutyunyan M Z 2009 Tuning of Lasing wavelength in Chiral Photonic Crystals with an anisotropic defect layer J. Mod. Opt. 56 1163-1173
[29] Gevorgyan A H Oganesyan K B 2011 Defect modes of Chiral Photonic Crystals with an anisotropic defect Opt. Spectrosc. 110 952-960
[30] Gevorgyan A H Oganesyan K B Harutyunyan E M Arutyunyan S O 2010 Opt. Commun. 283 3707-3713