

Synthesis of a solid-state dye mixture and its optical characteristics

Ju Yong Cho, Hyoungjin Kim and Won Kweon Jang*

Department of Aeronautic Electricity, Hanseo University, 46, Hanseo 1-ro, Seosan 31962, South Korea

Abstract: Dyes are fascinating laser mediums due to their high quantum efficiency. An energy transfer mechanism has improved their characteristics. In this paper, we synthesized a solid-state dye mixture that Coumarin-545(C-545) is co-doped with Rhodamine-6G(Rh-6G), and investigated its optical properties. Also, synthesis of the solid-state dye mixture is provided in detail. A donor (C-545) and an acceptor (Rh-6G) were excited, respectively. In the fluorescence when the acceptor alone was excited by a pump source, the peak wavenumber was $17,720\text{ cm}^{-1}$ and the spectrum width was 1387 cm^{-1} . When the acceptor was excited by absorbing the donor's fluorescence, the peak wavenumber was $17,963\text{ cm}^{-1}$, and the spectral width was 2081 cm^{-1} . These results demonstrate that the energy transfer mechanism allows solid-state dye mixture to extend the pumpable wavelength region even where an acceptor doesn't have absorption. Though the emission peak wavelength shifted to longer wavelength, but the bandwidth of fluorescence expanded.

1. Introduction

Dye lasers are widely applied as light sources especially in visible band, because they are useful for exciting dyes, and capable of high pulse energies and average powers [1,2]. Various dyes have been investigated to allow of a wide-wavelength from ultraviolet to near-infrared. The wavelength-selective components in the laser cavity make narrow-linewidth operation and tunability available [2].

Dye lasers have the potential in application fields of medicine, scientific research, and spectroscopy [1,2,3-5]. However, so far the toxicity and photodissociation still remains as to be overcome [6,7]. Triplet quenching, a main cause of photodissociation, has been treated by heat dissipation fluid system. The dye fluid circulation system is sophisticated, bulky [8,9], which has driven dye lasers out of many fields of application. Nevertheless, solid-state dye laser system is still attractive in the wavelength region, especially around $16,950\text{ cm}^{-1}$, of which the semiconductor laser systems cannot cover. Rh-6G has a large emission cross section around $16,950\text{ cm}^{-1}$, and easily pumpable with $18,868\text{ cm}^{-1}$ laser source of diode laser or second harmonic Nd:YAG laser. However, the second harmonic Nd:YAG laser is still sophisticated and expensive, and the diode laser at $18,868\text{ cm}^{-1}$ is not enough intense itself to use as a pumping light source. If we

* Corresponding author: E-mail: *jwk@hanseo.ac.kr

can have a gain medium that have an emission peak around $16,950\text{ cm}^{-1}$ and absorption band around shorter wavelength region than $18,868\text{ cm}^{-1}$, where a commercial diode laser is obtainable easily, it is possible to extend the application to $16,950\text{ cm}^{-1}$ region including medical therapy.

Polymerization of dye has been reported [9,10]. Since neither toxic solvent is necessary to build a dye laser system, nor fluid circulation is needed, a laser system is compact and low-cost. Many researches on the solid-state dye have been conducted with Rhodamin-6G(Rh-6G) due to its excellent optical characteristics [9,10]. In addition, it was a challenge to find a host material having exceptional properties such as high transparency in absorption and emission of dye, high solubility to dye, and damage resistance [9]. Polymethyl methacrylate(PMMA) has become a strong candidate. Though the solid-state dye has excellent characteristics, due to low thermal conductivity of PMMA, photodissociation is still a drawback to be solved.

Many dyes are investigated to enable dye lasers to cover a wide tunable range from ultra-violet to near-infrared. Many pump sources are also required to pump them, and it is not even easy to find a suitable source that has emission at an absorption wavelength of dye. Using energy transfer mechanism may be a solution. The energy transfer occurs when emission of a dye and the absorption of another dye are substantially superimposed. The dye emitting fluorescence is called a donor and the dye absorbing the fluorescence is called an acceptor. The donor absorbs light from a source, emitting fluorescence. Then the acceptor absorbs the donor's fluorescence, then emitting the fluorescence. With energy transfer mechanism, a broad band of emission is obtained, extending the tunable range of the dye lasers. Non-radiative energy transfer also occurs when molecules of the donor and acceptor are closed enough. Because dyes have exceptional characteristics in conversion efficiency and damage threshold, it is possible to improve them by mixing two different dyes [11].

For acquiring high pulse energies or average powers of dyes, the sources are crucial. In Rh-6G, high pulse energy is attainable, because high pulse energy at the absorption wavelength is obtained by the second harmonic Nd:YAG laser. In a continuous wave operation, since Rh-6G does not have suitable source for high average power, obtaining lasing action is difficult. In this paper, we synthesized solid-state dye mixture that Coumarin-545(C-545) is co-doped with Rh-6G, and evaluated its optical properties. Since the emission of C-545 significantly overlaps the absorption of Rh-6G, the energy transfer is effective. A semi-conductor technology makes the source with high average power available, allowing the strong fluorescence for C-545. In the mixture, Rh-6G absorbs C-545's fluorescence and then emits its fluorescence. Therefore, it allows the mixture to have the broader absorption band than that obtained by a source pumping Rh-6G alone. When Rh-6G was excited by absorbing C-545's fluorescence, the peak wavenumber and the spectral width were $17,963\text{ cm}^{-1}$ and 2081 cm^{-1} , respectively. This spectral width is broader by 649 cm^{-1} than that when the acceptor alone in the mixture was excited. The result shows that the energy transfer mechanism allows the mixture to have a wide fluorescence range. Therefore, a dye laser system has a wide tunable range.

Also this work is useful to develop the solid-state dye laser system into high average power.

2. Sample preparation

MMA of 20 ml was the host material. Molarity of 1 mM is ready for both Rh-6G and C-545. Since they have low solubilities to MMA, methanol was used for dissolving both Rh-6G and C-545. For polymerization, as an initiator, 1,12 -Azobis (cyclohexanecarbonitrile) was used. Mass fraction of the initiator was 1 wt% of MMA.

During the polymerization process, it is important to keep the temperature of the solution constant. 100 ml of a water tank was filled with water. Then, a dye solution container was sank into the water tank. The temperature of water stayed at 90 °C for 2 hrs. Then it dropped to 70 °C slowly for 5 hrs. To harden the sample, we kept it at 80 °C for 5 hrs, instead of using a convection oven.

3. Results and discussions

In order to evaluate the optical properties of the solid-state dye mixture, we employed an optical spectrum analyzer. Figure 1 shows the absorption spectrum of Rh-6G and the fluorescence spectrum of C-545. A peak wavenumber in the absorption was 18,867 cm^{-1} , and that in the fluorescence was 19,230 cm^{-1} . Though there was difference in the peaks, C-545's fluorescence greatly overlapped Rh-6G's absorption. It reveals that most of excited energy in C-545 is transferred to Rh-6G.

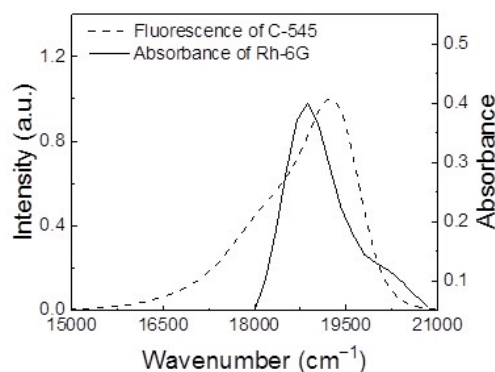


Fig. 1. Fluorescence spectrum of C-545, and absorption spectrum of Rh-6G.

Figure 2 shows the fluorescence spectrum of the mixture. A He-Ne laser with a central wavenumber of 18,416 cm^{-1} and a laser diode with a central wavenumber of 22,222 cm^{-1} were employed. The He-Ne laser directly excites the Rh-6G molecules in the mixture, and the laser diode excites the C-545 molecules, resulting in emission of its fluorescence. Then the Rh-6G molecules absorb the C-545's fluorescence, emitting Rh-6G's fluorescence. Though non-radiative energy transition occurred between C-545 and Rh-6G, it was negligibly small in this experiment. Figure 2 shows the fluorescence spectra when the mixture was pumped by the He-Ne laser and the laser diode, respectively. An optical power was set to 5 mW for both cases. The peak wavenumber and the spectral

width were $17,720\text{ cm}^{-1}$ and 1387 cm^{-1} , when the He-Ne laser was used. When A laser diode of $22,222\text{ cm}^{-1}$ was employed to excite the donor, its energy is transferred to the acceptor, resulting in the fluorescence of the mixture. The peak wavenumber was $17,963\text{ cm}^{-1}$, and the spectral width was 2081 cm^{-1} . Compared to the peak wavenumber in the fluorescence spectrum when the acceptor alone was directly pumped by the source, the peak wavenumber was slightly shifted by 243 cm^{-1} . But the spectral width is wider by 694 cm^{-1} . The energy transfer from the donor to the acceptor enables the wide fluorescence spectrum obtainable, allowing a wide tunable range.

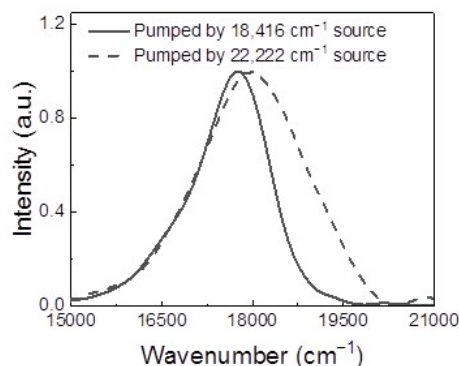


Fig. 2. A Fluorescence spectra of the mixture. The solid-state dye mixture pumped by a He-Ne laser of $18,416\text{ cm}^{-1}$ and a laser diode of $22,222\text{ cm}^{-1}$, respectively

Photodissociation is caused when the dye is pumped by the high power source. In this experiment, the photodissociation was observed when the optical power was over 100 mW. Figure 3 shows temperature variation and thermal profile on the solid-state dye. Figure 3(a) shows the maximum temperature changes on the solid-state dye as time goes on. As the pump source, the laser diode of $22,222\text{ cm}^{-1}$ was employed and its optical power was set to 100 mW. Initial temperature was $20\text{ }^{\circ}\text{C}$. And it heated up to $33\text{ }^{\circ}\text{C}$ in 30 s. After 180 s, the temperature reached $39\text{ }^{\circ}\text{C}$, and the irradiated spot is shown in Fig. 3(b). The black color indicates high temperature, and this black color region on the dye became translucent.

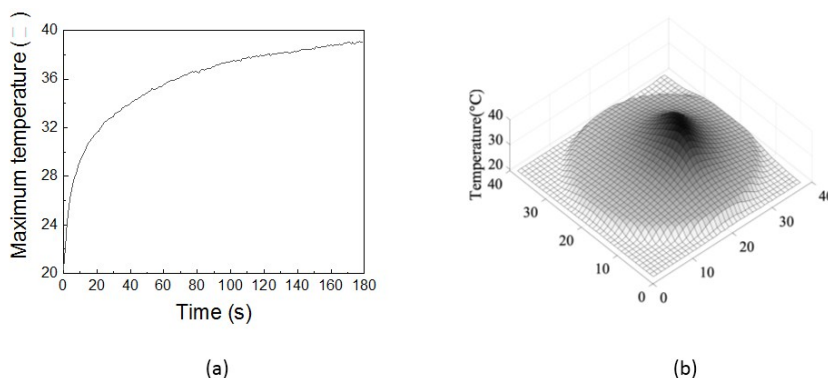


Fig. 3. Temperature variation and thermal profile on the dye. (a) Variation of maximum temperature on the solid-state dye as time goes on. (b) The irradiated spot in 180 s. The laser diode of $22,222\text{ cm}^{-1}$ is employed as a pump source. Its optical power is 100 mW.

We investigated the beam profiles after the pump beam passed the solid-state dye samples as shown in Fig. 4, because the thermal lens effect is not negligible in the high intensity focused operation. Figure 4(a) shows the initial beam profile after the pump beam passed through the solid-state dye sample. Figure 4(b) and 4(c) show the beam profiles after 30 s and 90 s, respectively. In Fig. 4(b), it was slightly blurred compared to Fig. 4(a). But, Fig. 4(c) shows an extremely blurred image, compared to other profiles. In Fig. 4(c), the maximum temperature at the spot was 37 °C.

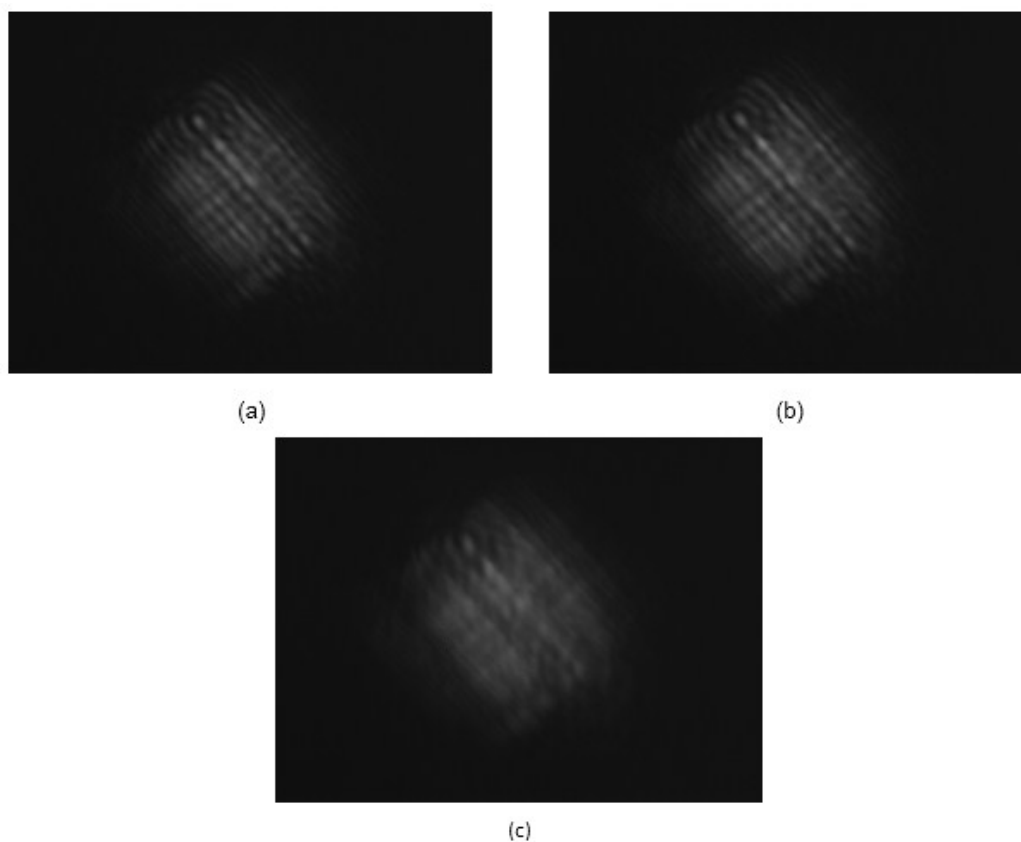


Fig. 4. The beam profile of the pump source. (a) The initial beam profile. The beam profile was recorded after (b) 30 s and (c) 90 s.

We also investigated the spectral change as shown in Fig. 5. Figure 5(a) shows the variation of the spectrum. Two spectral peaks were observed. The highest peak wavenumber was appeared at $18,976\text{ cm}^{-1}$ which was not changed until 30 s elapsed, and slightly shifted to $19,076\text{ cm}^{-1}$ after 90 s pumping. It was more shifted to $19,176\text{ cm}^{-1}$ after 180 s pumping. Compared to the spectrum shown in Fig. 1, this peak is related to the fluorescence of C-545. Another peak was appeared at $18,173\text{ cm}^{-1}$, which was from Rh-6G. Figure 5(b) shows the relative intensity of the fluorescence. The fluorescence is decreased in time. After 180 s pumping, the fluorescence intensity was decreased by 20% compared to the initial value.

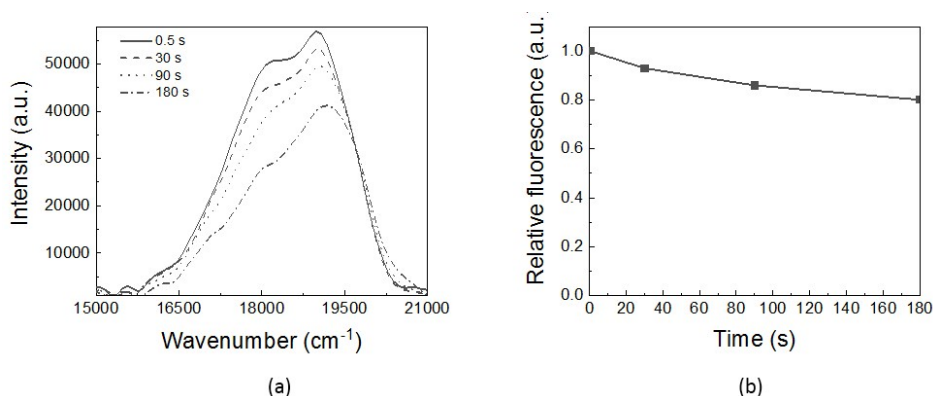


Fig. 5. Spectral change and relatively decreasing fluorescence with time. (a) Spectral change. (b) Relative decreasing fluorescence. The laser diode of 100 mW and 22,222 cm^{-1} was employed as a pump source.

4. Conclusion

The solid-state dye mixtures of Rh-6G and C-545 were synthesized, and its optical properties as well as thermal lens effect were investigated. Molarity was 1 mM for both Rh-6G and C-545. In the absorption spectrum of Rh-6G, the peak wavenumber was 18,867 cm^{-1} . In the fluorescence spectrum of C-545, the peak wavenumber was 19,230 cm^{-1} . The absorption spectrum widely overlaps the fluorescence spectrum. It is interpreted that most of energy is transferred from C-545 to Rh-6G. The fluorescence through the energy transfer mechanism revealed the peak wavenumber of 17,963 cm^{-1} . It was slightly shifted by 243 cm^{-1} , compared to 17,720 cm^{-1} from exciting Rh-6G alone in the mixture. The spectral width was 2081 cm^{-1} , which was wider by 649 cm^{-1} . In addition, thermal lensing effect and relatively decreasing fluorescence were observed when optical power of the pump source of 22,222 cm^{-1} is set to 100 mW. After 90 s was elapsed, the beam profile was extremely blurred, and after 180 s, the highest temperature in the irradiated spot was up to 39 °C and the fluorescence was decreased by 20%. These results show that the energy transfer mechanism allows the broad fluorescence of the solid-state dye mixture. Also it is expected that the high average power is obtained from the mixture if the source for pumping the donor is available in high average power. But the photodissociation remains as the problem to be solved.

Disclosures

The authors declare that there are no conflicts of interest related to this article.

Acknowledgements

We thank the anonymous referees for their useful suggestion.

References

1. F. J. Duarte, and A. Costela, Dye lasers; pp. 400-414, Elsevier, New York, 2004.

2. F. J. Duarte, *Solid-State Organic Dye Lasers from: Tunable Laser*; pp. 143-145, CRC Press, Florida, 2016.
3. A. Costela, L. Cerdà, and I. García-Moreno, "Solid state dye lasers with scattering feedback," *Progress in Quantum Electronics* 37, 348-382 (2013).
4. Yi Jiang, Yuan-Yuan Liu, Xu Liu, He Lin, Kun Gao, Wen-Yong Lai, and Wei Huang, "Organic solid-state lasers: a materials view and future development," *Chem. Soc. Rev.* 49, 5885-5944 (2020).
5. Y. G. Jiang, R. W. Fan, Y. Q. Xia, and D. Y. Chen, "Solid-State Dye Lasers Based on Polymethyl Methacrylate Modified with Methanol," *Laser Phys.* 21, 331-335 (2011).
6. R. Bornemann and U. Lemmer, "Continuous-wave solid-state dye laser," *Opt. Lett.* 31, 1669-1671 (2006).
7. Yuji Oki, Shotaro Miyawaki, Mitsuo Maeda, Masamitsu Tanaka, "Spectroscopic Application of Integrated Tunable Solid-State Dye Laser," *Optical review* 12, 301-306 (2005).
8. B. H. Soffer and B. B. McFarland, "Continuously tunable, narrow-band organic dye lasers," *Appl. Phys. Lett.* 40, 266-267 (1967).
9. A. Costela, I. G. Moreno, J. M Figuera, F. A. Guerri and R. Sastre, "Polymeric matrices for lasing dyes: Recent developments," *Laser Chem.* 18, 63-84 (1998).
10. A. Maslyukov, S. Sokolov, M. Kaivola, K. Nyholm, and S. Popov, "Solid-state dye laser with modified poly(methyl methacrylate)-doped active elements," *Appl. Opt.* 34, 1516-1518 (1995) .
11. G.V. Vijayaraghavan, and M. Basheer Ahamed, "Enhanced energy transfer between Co-dopants Pyronin-Y and Thionine incorporated into modified polymethyl methacrylate with addition of ZnO nanoparticles," *Spectrochim. Acta A* 158, 43-48 (2016).



This document was created with the Win2PDF "print to PDF" printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>