Applied Physics Letters

Raman mode random lasing in ZnS-β-carotene random gain media

Jayachandra Bingi, Anita R. Warrier, and C. Vijayan

Citation: Appl. Phys. Lett. **102**, 221105 (2013); doi: 10.1063/1.4807668
View online: http://dx.doi.org/10.1063/1.4807668
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v102/i22
Published by the AIP Publishing LLC.

APPLIED PHYSICS LETTERS **102**, 221105 (2013)

Raman mode random lasing in ZnS-β-carotene random gain media

Jayachandra Bingi, Anita R. Warrier, and C. Vijayan[a)]
Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India

(Received 21 March 2013; accepted 8 May 2013; published online 3 June 2013)

Raman mode random lasing is demonstrated in ZnS-β-carotene random gain media at room temperature. A self assembled random medium is prepared with ZnS sub micron spheres synthesized by homogeneous precipitation method. β-Carotene extracted from pale green leaves is embedded in this random medium. The emission band of ZnS random medium (on excitation at 488 nm) overlaps considerably with that of β-carotene, which functions as a gain medium. Here, random medium works as a cavity, leading to Raman mode lasing at 517 nm and 527 nm triggered by stimulated resonance Raman scattering. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4807668]

Random media consisting of monodispersed or polydispersed sub-micron particles have been shown to be capable of localizing light.[1,2] Multiple scattering in such media causes photons to form closed localized loops which in turn may contribute to enhance the quantum efficiency of a gain medium[3] and trigger stimulated emission and random lasing in the medium. Emission from a random laser is much similar to that from conventional lasers except that it is multidirectional and can be achieved at low thresholds.[4] Random lasing has been reported in many random media such as organic and polymer thin films,[5] semiconductor powders,[6] suspensions,[7] and human tissues.[8] Random lasing has potential for applications in a wide range of fields such as biomedical imaging, remote sensing and display technology.[9–11] The possibility of broad angular emission modes, ease of large scale fabrication, and cost effectiveness makes random lasing attractive for technological advancements. One of the main challenges in developing random lasers is the inability to achieve predictable lasing modes.[12] Since light follows a random path in random media, it is difficult to establish a particular lasing mode. These modes tend to shift randomly due to the fact that the random paths taken by subsequent pulses within the medium would be different. Thus a large number of modes coexist and compete for the available gain so that no specific frequency can dominate and the random laser can have different spectral features each time it is excited. Thus, controlling the lasing mode has been a challenge throughout.[13] However, the principle of random lasing suggests that if an effective control of mode is achieved, the lasing wavelengths can be tuned by varying the refractive index and the particle size of the dispersed particles.[4] A few groups have attempted to achieve tuning and control of modes in random lasing in different ways such as temperature tuning of random lasing,[14] resonance driven random lasing,[15] variation of effective lifetime of the cavity,[16] and choice of different pump beam profiles.[17] Tuning of lasing peaks from UV to blue spectral region has been achieved by changing the temperature in the case of a random medium made up of ZnO nanoneedles.[18] Random lasing wavelengths of ZnO/Al_2O_3 nanopowder were controlled by varying the weight fraction of Al_2O_3.[19]

In this letter, we report on the design and fabrication of a random medium with monodispersed ZnS sub-micron spheres embedded with β-carotene molecules and the observation of Raman mode random lasing in this medium. The significance of the work is that mode control is achieved in this case as the lasing mode corresponds to the Raman mode of the carotene molecule. Most of the drawbacks of random lasing from media in physical forms of powder and colloidal suspension are avoided in the present case where the medium is in the form of a self assembled film of sub-micron spheres. The wavelengths which undergo strong scattering in the random media depend on the sphere size and refractive index of the material.[20] Hence the emission modes of the random laser could be tuned by varying the particle diameter. Here, we study multiple scattering in the ZnS random medium and its effect on molecular vibrational modes of carotene biomolecule leading to predictable lasing modes. It was reported recently that Raman modes of the fluorescent materials get enhanced by embedding them in random media.[21] Such a possibility can also lead to design of Raman lasers with tunable modes with specific advantages for applications.[22]

ZnS is a wide band gap, fluorescent material with a high refractive index (2.35) in visible region[23] making it an ideal candidate material for fabrication of random media. β-Carotene molecules are chosen for incorporation into the ZnS random medium in the present work as its fluorescence emission peak matches well with the laser (488 nm) induced emission peak of ZnS random medium. ZnS (cubic crystalline structure) sub-micron spheres are synthesized by the homogeneous precipitation method.[24] The sub-micron spheres are nearly monodisperse with a mean diameter of 215 nm. These nanospheres are coated over microglass slides (2×1 cm^2) by solvent evaporation method and the resulting random arrangement can be seen in Figure 1. The randomness can be improved by proper choice of the pH of the ZnS colloidal solution.[25] β-Carotene molecules extracted from pale green leaves using acetone as the solvent are incorporated into ZnS random media by the solvent evaporation technique. Laser fluorescence studies are done using HORIBA HR800UV Laser Raman spectrometer, with Argon ion laser of excitation wavelength 488 nm, focused using a 100× objective lens at normal incidence to the sample surface.

The experiment is performed at different laser power in the range of 1 μW to 30 μW. In all cases, a broad emission

[a)]Author to whom correspondence should be addressed. Electronic mail: cvijayan@physics.iitm.ac.in

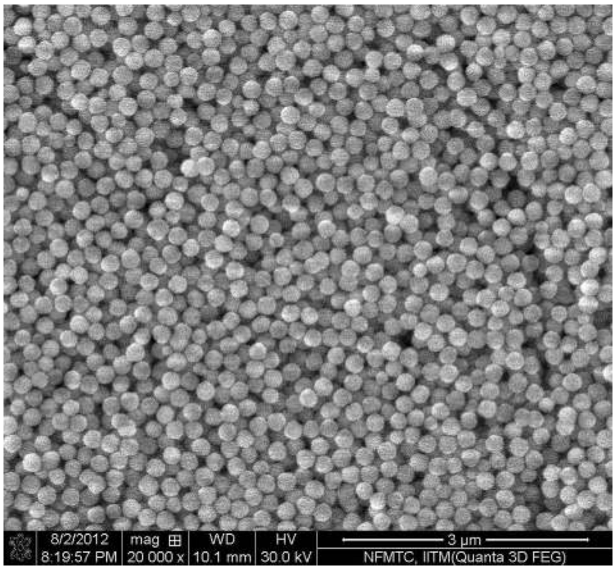

FIG. 1. FESEM image shows the randomly arranged ZnS sub-micron spheres coated over microglass slide.

band is observed with peak at 560 nm. There is a peak narrowing as the power is increased and threshold behaviour is also seen around an excitation power of 11 μW, shown in inset of Figure 2. Thus this emission appears to be a case of amplified spontaneous emission (ASE) from the ZnS random medium as shown in Figure 2. The emission spectra of ZnS random medium, β-carotene (shown in the inset of Figure 3), and the composite medium are shown in Figure 3. The emission bands of ZnS random medium and β-carotene overlap considerably. The Raman modes can be seen as tiny kinks in the emission profile of β-carotene at 513 m, 517 nm, and 527 nm.

The emission spectrum from the composite medium clearly shows considerable enhancement of the Raman modes of β-carotene, at three specific wavelengths 513 nm, 517 nm, and 527 nm, in sharp contrast to the broad spectra obtained for pure ZnS random media and pure β-carotene. These peaks appear over the incoherent ASE background due to the random medium.

On repeating the experiment at different excitation powers, it is observed (Figure 4) that the mode intensity of

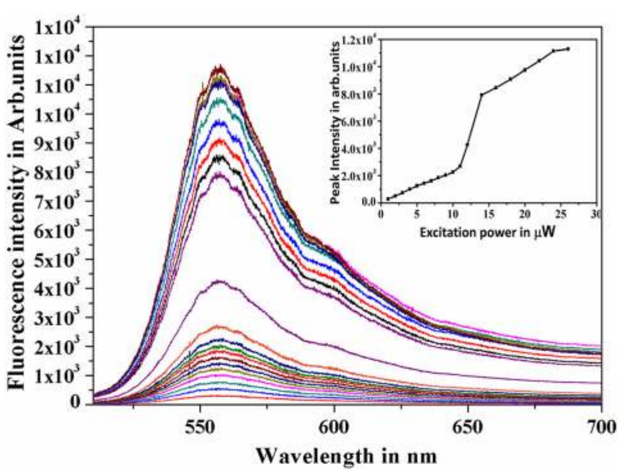

FIG. 2. Emission spectra of ZnS random media exhibiting ASE.

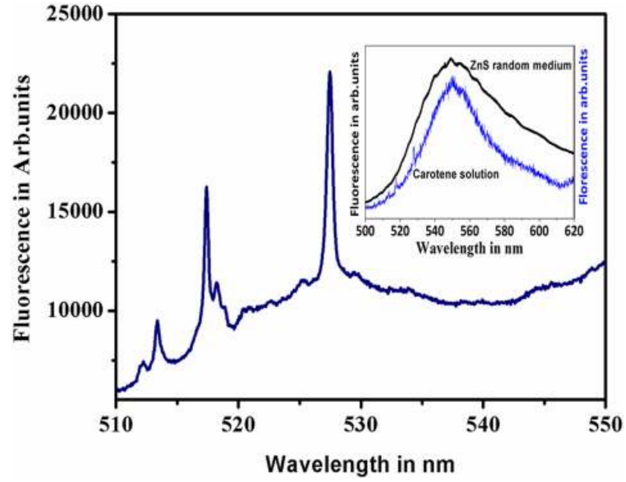

FIG. 3. Emission spectra of ZnS-β-carotene random media and the individual emission spectra of ZnS random media and β-carotene molecule.

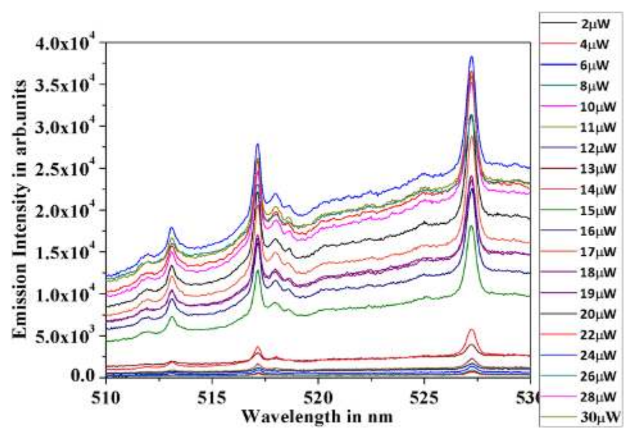

FIG. 4. Emission spectra of ZnS-β-carotene composite random media with Raman lasing at 513 nm, 517 nm, and 527 nm.

emission at 527 nm increase with increase in excitation power and clearly exhibit a threshold behaviour (at $\sim$14 μW), as shown in Figure 5, where the emission intensity at 527 nm is plotted against the excitation power. The emission intensity remains almost constant when the power is increased beyond 20 μW. So the composite system thus

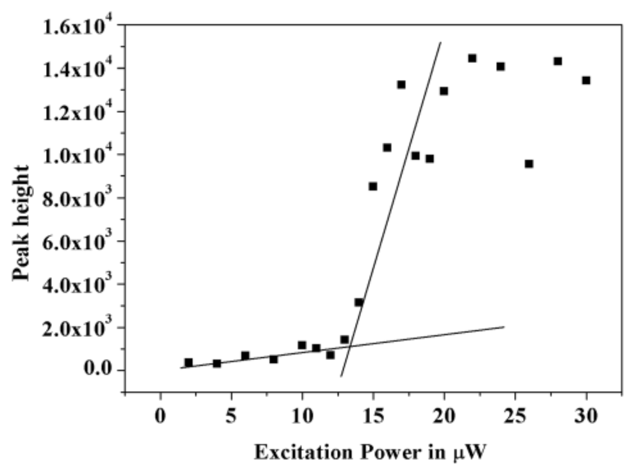

FIG. 5. The threshold behaviour in emission at 527 nm from ZnS-β-carotene random media.

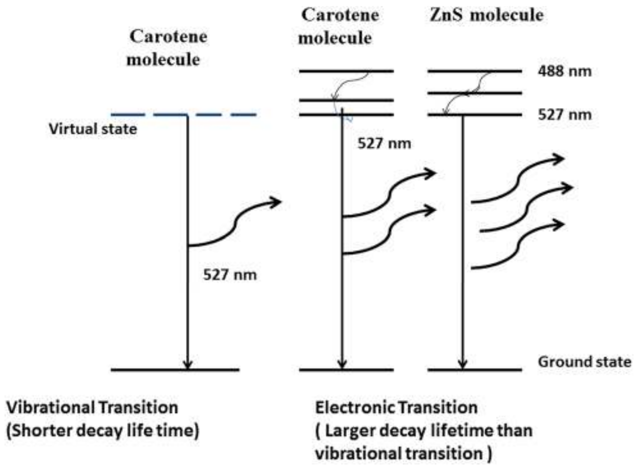

FIG. 6. Energy level diagram indicating the possible vibrational and electronic transitions responsible for random lasing Raman lasing in ZnS-β-carotene composite random media.

fabricated exhibits predictable lasing modes. Random lasing at the Raman modes of β-carotene is triggered by stimulated resonance Raman scattering (SRRS) assisted by the ZnS random medium in view of the spectral overlap of the emission bands.[26]

The possible mechanism for random lasing at 527 nm can be understood on the basis of SRRS in the following manner. Figure 6 shows the energy level diagram and the possible vibrational and electronic transitions in the composite media. The vibrational Stokes transition at 527 nm occurs well within the emission bands of both ZnS and β-carotene. As the lifetime corresponding to the vibrational transition is shorter than that of the electronic transitions, "Stokes photons" are present in the system before electronic transitions occur. These pre-existing photons at 527 nm undergo multiple scattering in the random media and trigger stimulated emission from the excited states of both ZnS and β-carotene molecules. Thus composite random medium works effectively as a laser cavity for the wavelengths corresponding to the Raman modes of the gain medium.

It is also clear from Figure 4 that the modes at 517 nm and 527 nm do not shift or fluctuate with different excitation powers and remain stable for any number of repeated excitations. Hence, predictable and stable emission modes can be obtained from such a random composite system. The use of a random medium (ZnS), whose fluorescence matches with that of a gain medium (β-carotene) thus leads to lasing at predictable Raman modes of the gain medium. As lasing occurs at Raman modes, this system has the potential to be used as a Raman laser whose wavelength can be tuned by varying the wavelength of excitation over a certain range. Lasing can be achieved at desired wavelengths by a proper choice of the gain and the random media with spectral overlap of the absorption and emission bands. The present study highlights the scope of designing low threshold random laser media with predictable modes and indicates the possibility designing Raman lasers.

[1] M. Storzer, P. Gross, C. M. Aegerter, and G. Maret, Phys. Rev. Lett. **96**, 063904 (2006).
[2] D. S. Wiersma, P. Bartolini, Ad. Lagendijk, and R. Righini, Nature **390**, 671 (1997).
[3] P. D. Garcia, R. Sapienza, A. Blanco, and C. Lopez, Adv. Mater. **19**, 2597 (2007).
[4] D. S. Wiersma, Nat. Phys. **4**, 359 (2008).
[5] S. K. Cohen, P. N. Stavrinou, D. D. C. Bradely, and S. A. Maier, Appl. Phys. Lett. **99**, 041114 (2011).
[6] 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).
[7] K. Firduas, T. Nakamura, and S. Adachi, Appl. Phys. Lett. **100**, 171101 (2012).
[8] R. C. Polson and Z. V. Vardeny, Appl. Phys. Lett. **85**, 1289 (2004).
[9] B. Redding, M. M. Choma, and H. Cao, Nat. Photonics **6**, 355 (2012).
[10] Z. N. Wang, Y. J. Rao, H. Wu, P. Y. Li, Y. Jiang, X. H. Jia, and W. L. Zhang, Opt. Express **20**, 17695 (2012).
[11] G. R. Williams, B. Bayram, S. C. Rand, T. Hinklin, and R. M. Laine, Phys. Rev. A **65**, 013807 (2001).
[12] H. K. Liang, S. F. Yu, and H. Y. Yang, Appl. Phys. Lett. **96**, 101116 (2010).
[13] M. Sakai, Y. Inose, K. Ema, T. Ohtsuki, H. Sekiguchi, A. Kikuchi, and K. Kishino, Appl. Phys. Lett. **97**, 151109 (2010).
[14] A. G. Ardakani, M. Hosseini, A. R. Bahrampour, and S. M. Mahdavi, J. Appl. Phys. **112**, 043111 (2012).
[15] S. Gottardo, R. Sapienza, P. D. Garcia, A. Blanco, D. S. Weirsma, and C. Lopez, Nat, Photonics **2**, 429 (2008).
[16] R. G. S. El-Dardiry and A. Lagendijk, Appl. Phys. Lett. **98**, 161106 (2011).
[17] N. Bachelard, J. Andreasen, S. Gigan, and P. Sebbah, Phys. Rev. Lett. **109**, 033903 (2012).
[18] H. Y. Yang, S. P. Lau, S. F. Yu, A. P. Abiyussa, M. Tanemura, T. Okita, and H. Hatano, Appl. Phys. Lett. **89**, 011103 (2006).
[19] T. Nakamura, B. P. Tiwari, and S. Adachi, Appl. Phys. Lett. **99**, 231105 (2011).
[20] H. Cao, Waves Random Media **13**, R1 (2003).
[21] V. P. Yashchuk, E. A. Tikhonov, A. O. Bukatar', O. A. Prigodiuk, and A. P. Smaliuk, Quantum Electron. **41**(10), 875 (2011).
[22] A. Z. Grasyuk, Sov. J. Quantum Electron. **4**, 269 (1974).
[23] *Hand Book of Optics*, 3rd ed., edited by M. Bass (McGraw Hill Publications, New York, 2010).
[24] Y. D. Kim, K. Sonezaki, H. Maeda, and A. Kato, J. Mater. Sci. **32**, 5101 (1997).
[25] F. Piret and B. L. Su, Chem. Phys. Lett. **457**, 376 (2008).
[26] S. Varghese, S. J. Yoon, E. M. Calzado, S. Casado, P. G. Boj, M. A. D. García, R. Resel, R. Fischer, B. M. Medina, R. Wannemacher *et al.*, Adv. Mater. **24**, 6473 (2012).