Stimulated Light Emission in Dense Fog Confined inside a Porous Glass Matrix

E. Gross, D. Kovalev, N. Künzner, J. Diener, and F. Koch
Physik-Department E16, Technische Universität München, D-85747 Garching, Germany

M. Fujii
Department of Electrical and Electronics Engineering, Faculty of Engineering, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan

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We report on light amplification through stimulated emission in a dielectrically disordered medium. Liquid fragments confined in the solid matrix of porous quartz layers result in a random fluctuation of the dielectric function, and dye molecules embedded in the voids yield optical gain. The level of opacity is tunable by the ambient vapor pressure of the dielectric substance. In the multiple scattering regime, a strong intensity enhancement of the dye emission accompanied by significant spectral narrowing is observed above the threshold for a layer being in the opalescence state.

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A spatial modulation of the dielectric function in a medium strongly modifies the propagation of light waves. A periodic sequence of dielectric layers having alternating high and low refractive index prevents the straight propagation of incident light waves with wavelength comparable to the optical thickness of a dielectric layer. Instead, this structure (dielectric Bragg mirror) reflects photons in a certain wavelength range. Further spectral selectivity can be achieved by combining two mirrors to form a resonator, exhibiting certain modes with well defined wavelengths. Photons in these modes are coupled back to the resonator and, therefore, provide a coherent feedback mechanism. By inserting an active medium in the resonator, the basic scheme of a conventional laser is realized.

In general, losses, e.g., absorption and scattering, diminish the efficiency of a conventional laser. Theoretical predictions of light amplification in a medium having both strong light scattering and optical gain properties [1] were therefore in apparent contradiction to experimental observations. Scattering of light occurs in an inhomogeneous medium exhibiting a fluctuation of the dielectric function and results in deflection of photons out of the collimated light beam. The strength of the effect is largest for light having wavelength comparable to the size and spatial separation of the randomly distributed scatterers and increases with the dielectric contrast [2]. For a quantitative description the scattering length l_{sc} is introduced which allows one to distinguish three regimes based on the relevant length scales [3]. Considering the case of weak scattering $l_{sc} > L$ (L: characteristic sample size) for a conventional laser, photons are removed from the active region by scattering events. Reduction of l_{sc} in a system with gain leads to the strong scattering regime, characterized by $\lambda_{emission} < l_{sc} < L$, with $\lambda_{emission}$ denoting the wavelength of the fluorescence light. Emitted photons are multiple scattered and cannot leave the active region. Therefore, scattering does not contribute to losses but serves as an incoherent feedback mechanism. This enhances the optical path length and light is amplified by stimulated emission. Via further increase of the scattering efficiency, the regime of light localization ($l_{sc} \approx \lambda_{emission}$) is achieved. In this scenario, coherent feedback is present and is strong enough for a photon to be scattered back to its initial point during the random walk in the medium. These closed loop paths can serve as a cavity having certain modes similar to an ordinary laser. In that sense, scattering in a dielectrically disordered medium is similar to the reflection from mirrors in ordinary lasers. However, in the localization regime the efficiency of light amplification is limited since the penetration length of pumping light in the active medium may also be very small.

In recent years, these considerations have been experimentally verified. For strong light scattering systems exhibiting gain, e.g., grinded laser crystals [3], semiconductor powders [4], and colloidal suspensions [5], incoherent and coherent feedback has been demonstrated. However, for studying light amplification in random media, a system is desired where the scattering length is controlled externally while keeping the other optical properties of the sample, particularly the optical absorption constant. Therefore, ordered [6] and disordered [7] dielectric structures infiltrated with liquid crystals have been proposed. The strength of scattering can be varied by an applied external electric field [8] or by temperature [9,10].

We report in this Letter on stimulated light emission of an optically excited, random medium with tunable scattering properties. As a dielectrically disordered, active medium we employed dye-infiltrated porous quartz layers whose pores are partially filled by a dielectric substance. The condensate is nonuniformly distributed over the whole layer and liquid fragments (droplets) serve as scattering objects. Since efficient light scattering is achieved if the spacing between droplets is comparable with their sizes, our system can be regarded as dense fog confined in a porous matrix. Varying the vapor pressure allows us to control the amount of liquid condensed in the voids of the

porous layer and, therefore, to adjust the length scale of the dielectric fluctuations. This results in a tunable l_{sc} in the range from 500 μm, which exceeds the sample thickness, down to 3.7 μm. At the same time, the optical absorption of the layer is not influenced by the condensate as verified by optical transmission measurements. For layers being in a strongly scattering, i.e., opalescence, state, above a certain pump intensity threshold we observed a strong increase in dye fluorescence, accompanied by a significant spectral narrowing of the dye emission band. This clearly indicates amplified spontaneous emission in the multiple scattering regime.

To obtain porous quartz, porous silicon layers have been prepared by electrochemical etching of (110) oriented, p-doped bulk silicon wafers with a resistivity of 50 mΩ cm in a 1:1 by volume mixture of hydrofluoric acid (50 wt% in water) and ethanol [11]. The current density and etching time was 40 mA/cm^2 and 20 min, respectively. The porous layers were detached from the substrate by an electropolishing step resulting in free-standing porous silicon layers with a thickness of 54 μm, a porosity of 60%, and a mean pore size of 10 nm [12]. To minimize absorption of the porous matrix in the visible range, the samples were transformed to optically transparent porous quartz layers by annealing at 1000 °C for 2 h in oxygen ambient. A gain substance is introduced into the pores by immersing the porous layer in a 3×10^{-3} M solution of dye molecules (DCM) dissolved in acetone with subsequent evaporation. The sample is mounted in an optical cryostat, and filling and draining of the pores by a dielectric liquid is achieved by regulating the vapor pressure inside the chamber. As a dielectric substance acetone (bulk saturation vapor pressure is 260 mbar at 293 K) was used and all experiments were carried out at room temperature. In the photoluminescence experiments dye molecules imbedded in the pores of the layers are excited from the front side at normal incidence by a pulsed, frequency-doubled Nd-YAG laser (excitation wavelength: 532 nm, repetition rate: 10 Hz, pulse duration: 8 ns, spot size: 3 mm). Emitted light is collected and measured with a monochromator equipped with a charge-coupled device.

For the characterization of the scattering efficiency of a medium, l_{sc} is a suitable length scale. It is determined from the ballistic portion of the intensity of a transmitted light beam using the simple relation $I(L) = I_0 \exp(-L/l_{sc})$ [13]. However, evaluation of this fundamental value is not straightforward if the strength of absorption and scattering change simultaneously [14]. It is difficult to separate the different contributions of scattering and absorption to the reduced flux of ballistically propagating photons [15,16]. On the contrary, the optical transmission measurement of our layer shown in Fig. 1 proves a constant absorption if liquid is condensed in the pores, whereas the opacity is tunable. Therefore, we can directly evaluate l_{sc} from the extinction of the incident light intensity. In Fig. 1 we monitor the intensity of a

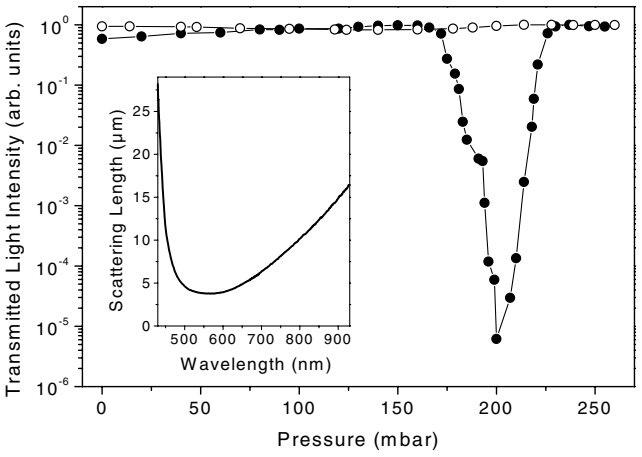

FIG. 1. Intensity of the collimated beam of a He-Ne laser (632.8 nm) transmitted through a 54 μm thick, dye-infiltrated (DCM) porous quartz layer during isothermal adsorption (open circles) and desorption (solid circles) of acetone. Inset: Spectral dependence of the scattering length of photons in the state of strongest opacity ($P = 200$ mbar).

collimated light beam of a He-Ne laser (632.8 nm) transmitted through a 54 μm thick, dye-infiltrated (DCM) layer of porous quartz during filling (open circles) and draining (solid circles) the pores with acetone. On the adsorption branch the transmittance of the layer is constant while during desorption a strong decrease of the transmitted light intensity is observed in a narrow pressure range. The porous quartz matrix itself can be considered as an optically homogeneous medium since the structural sizes are significantly smaller than the wavelength of visible light. While the increase of the vapor pressure results in successive filling of the pores via adding shells of adsorbed molecules to the walls of the pores, on the desorption branch molecules are removed from the meniscus [17]. From the point of view of optics, these two scenarios are quite different, especially for systems having an interconnected pore network and exhibiting in addition a pore size distribution. Macroscopically, spatially uniform filling of the pores results in a continuous increase of the mean dielectric function of the layer. The removal of the condensed liquid first starts in big pores and requires continuous percolation paths through the layer. Those are influenced by smaller pores which play a role of bottleneck because they can be emptied only at lower vapor pressure [18]. Therefore, in a certain pressure range during desorption the continuous liquid network is separated in fragments of liquid in the porous matrix [12]. This breakdown of the dielectric homogeneity results in a spatial variation of the dielectric constant of the layers on a macroscopic length scale, thus affecting their scattering properties. Further reduction of the pressure leads to a fast draining of the remaining liquid and the transmittance properties of the layer recover completely. The spectral dependence of the scattering length of the layers is determined by optical transmission measurements. A parallel beam of white light having normal

incidence is used as illumination and the spectrally resolved intensity of the collimated beam transmitted through the layer is measured with a monochromator equipped with a charge-coupled device. By dividing the spectrum of the transmitted light intensity on the desorption branch (I_{des}) to that one measured at the same pressure on the adsorption branch (I_{ads}), the absorption due to the porous matrix and the incorporated dye molecules cancels. l_{sc} is determined according to the relation $l_{sc} = L/\ln(I_{ads}/I_{des})$, with L being the thickness of the layer. The inset in Fig. 1 shows the spectral dependence of l_{sc} for a porous quartz layer being in the strongest opalescence state (vapor pressure: 200 mbar). A well pronounced minimum indicates a resonant, Mie-type of scattering [19]. The spectral position of the minimum allows us to estimate roughly the size of the dielectric perturbations to be 300 nm. This size is similar to the particle size of solid scatterers in other systems [4,5]. The shortest scattering length of 3.7 μm is found at 565 nm, whereas for pump ($\lambda = 532$ nm) and fluorescence ($\lambda = 640$ nm) photons the scattering length turns out to be 3.8 and 4.6 μm, respectively. These scattering lengths are much shorter than the measured absorption length of the sample, being 114 μm at 532 nm and 400 μm at 640 nm. This verifies that the attenuation of the transmitted light beam results from scattering and not from absorption. The condition $\lambda < l_{sc} < L$ is fulfilled in the opalescent state and the optical path is enhanced for both pump and fluorescence photons. This allows us to realize two distinct regimes of dye emission for a porous quartz layer being in the strongest opalescence state.

Figure 2(a) shows the photoluminescence (PL) spectrum of a porous quartz layer infiltrated with dye molecules (DCM) in the ambience of acetone at bulk saturation pressure (dotted line) for pulsed excitation by a frequency-doubled Nd-YAG laser at low excitation intensity. By reducing the pressure we observed a monotonic rise of the PL intensity with increasing scattering strength of the sample reaching a maximum in the strongest opalescence state [Fig. 2(a), solid line]. No change of the line shape of the dye emission band is observed and the enhancement of the PL intensity is purely related to the pump light: in the opalescence state pump photons are multiple scattered in the medium and the probability of absorption by dye molecules increases. Similar PL experiments performed under high excitation intensities reveal a different behavior [Fig. 2(b)]. When the optical properties of the layer change from transparent to opaque, the initially broad emission band (dotted line) narrows drastically and the peak emission intensity increases by 1 order of magnitude (solid line). The observed behavior is governed by two effects that cannot be separated. Like in the weak excitation regime, trapping of pumping light results in an overall rise of the PL intensity. Additionally, the high occupation number of emitted photons is further increased in the opalescent state, since scattering prolongs the traveling time of photons in the

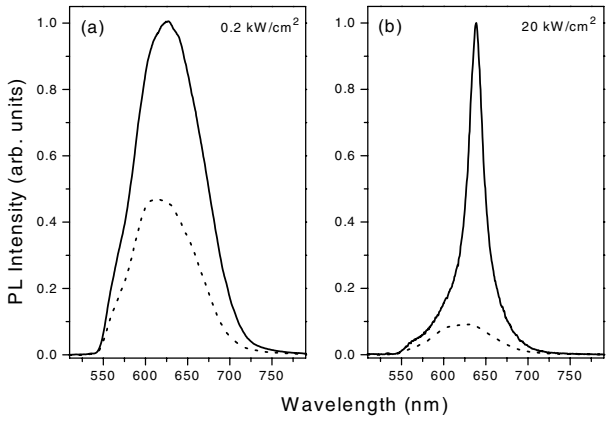

FIG. 2. PL spectra of dye molecules (DCM) incorporated into the pores of a porous quartz layer at low (a) and high (b) excitation intensities. Dotted lines correspond to completely filled pores of the layer by acetone, solid lines to the layer being in the strongest scattering state.

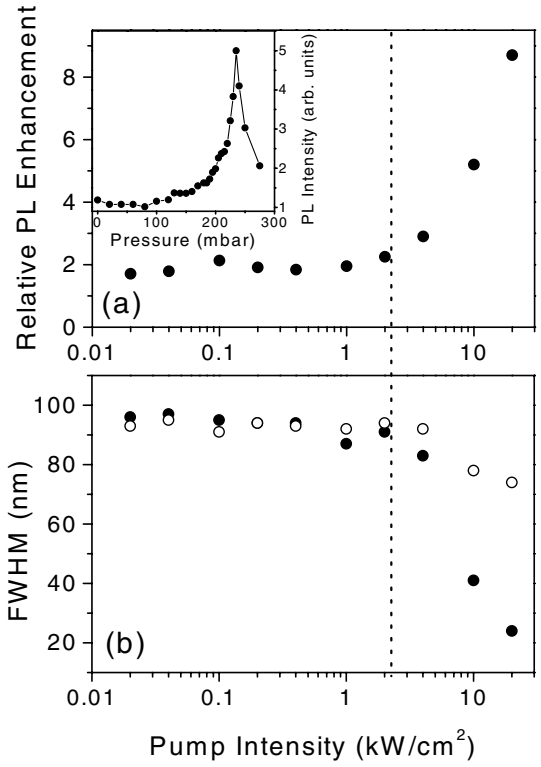

FIG. 3. (a) Relative PL intensity enhancement of a dye-infiltrated porous quartz layer when transforming the layer from the transparent to the scattering state as a function of pump intensity. (b) Full width at half maximum (FWHM) of the emission band of a dye-infiltrated porous quartz layer with completely filled pores by acetone (open circles) and being in the strongest scattering state (solid circles) as a function of pump intensity. Gain threshold is indicated by the vertical dotted line. Inset: Dependence of the PL peak intensity of a dye-infiltrated porous quartz layer on the ambient vapor pressure of acetone. Excitation intensity is 10 kW/cm^2.

sample. Thus, stimulated emission dominates and gain narrowing occurs. Because the scattering length is still much larger than the wavelength of the emitted light, coherent feedback is not realized and single laser modes due to closed loop paths are not observed.

A definite proof of stimulated light emission is the presence of a threshold in activating net gain in the system. Therefore, we measured the dependence of dye emission on the pump intensity for a porous quartz layer being in the strongest scattering state (Fig. 3). Since stimulated emission above a certain pumping light intensity occurs even for completely filled pores, the relative intensity enhancement is plotted in Fig. 3(a). This quantity is defined as the ratio of the PL peak intensity determined for the layer being in the strongest opalescence state and being transparent, i.e., having completely filled pores. The corresponding bandwidth of the dye emission is shown in Fig. 3(b) for the sample in the strongest scattering (solid circles) and nonscattering (open circles) state. This presentation allows one to clearly identify the effect of opalescence on the emission characteristics. Above the threshold, indicated by the vertical dotted line, multiple light scattering results in an increase of the PL intensity and simultaneously spectral narrowing occurs. Adjusting the optical scattering length of a single layer enables us to study its influence on the process of light amplification at a fixed excitation intensity of 10 kW/cm^2 (see inset in Fig. 3). Desorption of acetone from the pores results in light scattering in a narrow pressure range (see Fig. 1) and is accompanied by a rise of the PL peak intensity.

Similar experiments have been performed on porous quartz layers with incorporated dye molecules having a maximum emission at 821 nm (LDS 821 dye). From the spectral dependence of the scattering length we deduce $l_{sc} = 11.3\ \mu m$ in this spectral range and we observed a relative intensity enhancement of only 20% without line narrowing even at highest pumping intensities. Comparison of Fig. 1 and the inset in Fig. 3 reveals an interesting property concerning the pressure at which our layers are transformed from the transparent to the opaque state. At high intensities of the incident light the illuminated region of the sample is heated locally due to absorption. The liquid is partially evaporated from the pores and scattering appears at a significantly higher pressure. Therefore, opalescence can be induced by the incident light itself, and weakly absorbing porous quartz layers with liquid confined in the pores can be employed as an optical switch for blocking intense light beams.

To summarize, we demonstrate a novel approach in realizing a strongly scattering medium that exhibits stimulated emission of light. In fact, the system can be considered as an inverse colloid: liquid fragments of macroscopical size are embedded in the solid matrix of porous quartz, whereas dye molecules are incorporated into the pores. Draining of an interconnected pore network filled by liquid results in a breakdown of the dielectric homogeneity of the liquid network. The size of the droplets and their spatial separation, i.e., the length scale of the dielectric perturbation, is adjustable and is defined by the ambient vapor pressure. An additional degree of freedom in controlling the strength of scattering is given by the dielectric contrast which can be varied by a proper choice of the liquid and the porosity of the layer. In the regime of multiple scattering, the dwell time of pump and fluorescence light in the active region is increased and this affects the dye emission. At low pumping energies, spontaneous emission is enhanced. Above the threshold, the bandwidth of the emission spectrum narrows while the intensity is rising. This evidences stimulated emission due to incoherent feedback of emitted photons in the scattering regime. The presented system is a promising candidate to study light amplification in random media, because the relevant parameters can be varied independently.

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[1] V. S. Letokhov, Sov. Phys. JETP **26**, 835 (1968).
[2] S. John, Phys. Rev. Lett. **53**, 2169 (1984).
[3] D. S. Wiersma and A. Lagendijk, Phys. Rev. E **54**, 4256 (1996).
[4] H. Cao *et al.*, Phys. Rev. Lett. **82**, 2278 (1999).
[5] N. M. Lawandy *et al.*, Nature (London) **368**, 436 (1994).
[6] K. Busch and S. John, Phys. Rev. Lett. **83**, 967 (1999).
[7] D. S. Wiersma *et al.*, Phys. Rev. B **64**, 144208 (2001).
[8] D. Kang *et al.*, Phys. Rev. Lett. **86**, 4052 (2001).
[9] D. S. Wiersma and S. Cavalieri, Nature (London) **414**, 708 (2001).
[10] S. W. Leonard *et al.*, Phys. Rev. B **61**, R2389 (2000).
[11] A. G. Cullis, L. T. Canham, and P. D. J. Calcott, J. Appl. Phys. **82**, 909 (1997).
[12] D. Kovalev *et al.*, J. Appl. Phys. **91**, 4131 (2002).
[13] H. P. Schriemer *et al.*, Phys. Rev. Lett. **79**, 3166 (1997).
[14] X. Zhang and Z. Q. Zhang, Phys. Rev. B **65**, 155208 (2002).
[15] F. Scheffold *et al.*, Nature (London) **398**, 206 (1999).
[16] A. Z. Genack, Phys. Rev. Lett. **58**, 2043 (1987).
[17] G. J. Sidney and K. S. Sing, *Adsorption, Surface Area and Porosity* (Academic, London, 1967).
[18] J. H. Page *et al.*, Phys. Rev. Lett. **71**, 1216 (1993).
[19] M. Born and E. Wolf, *Principles of Optics* (Cambridge University, Cambridge, 1997), 6th ed.