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Modified spontaneous emission spectra of laser dye in inverse opal photonic crystals

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We have observed strongly modified spontaneous-emission spectra from laser dye in photonic crystals made of inverse opals in titania (TiO$_2$). We identify stop bands with large relative widths of 15%, comparable to the dyes’ emission spectrum, and 75% attenuation of the emission strength. For a wide range of angles, two stop bands are simultaneously manifested; their angle-dependent frequencies display an avoided crossing that is corroborated by reflectivity experiments. The edges of the stop bands agree well with band-structure calculations, but differ from simple Bragg diffraction as a result of multiple wave coupling. The strongly reduced dispersion of the Bloch modes likely causes a significant change in the density of states.

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Photonic crystals are receiving intense scrutiny, not only as regards the novel physics they embody [1,2], but also as the underlying architecture for all-optical microchips [3]. Widely pursued to control the atom’s spontaneous-emission rate [1,4], photonic crystals are periodic dielectric composites that control light propagation by Bragg diffraction [7], since the periodicity of the refractive-index variations is on the order of the wavelength of light [5,6]. The achievement of a full photonic band gap, a range of frequencies for which the Bragg diffractions simultaneously inhibit light propagation for all directions and polarizations, is the raison d’être for three-dimensional photonic crystals. Photonic band-gap crystals will not only influence emission spectra but, as the density of states vanishes inside such gaps, also emission rates; intricate dynamics are expected [8]. Even in the absence of photonic band gaps, important advances in the control of emission have already been made in two-dimensional structures, producing, for example, efficient miniature lasers [9].

Previous studies of embedded dyes [10,11] and semiconductors [12] in three-dimensional weakly photonic crystals have revealed modified emission spectra. The luminescence was inhibited in particular directions, forming stop gaps whose frequencies depend on angle, in accordance with Bragg diffraction by a single set of lattice planes. No significantly altered emission lifetimes have been observed, however, because the densities of states are hardly modified [13,14]. The observed minor changes in lifetime agree well with the few percent reduction in total solid angle for light propagation due to Bragg diffraction [11], as a result of the low dielectric contrasts involved and the crystals’ weak interaction with light.

Recently, novel photonic crystals have been developed from materials with high dielectric constants [15,16]. These so-called air-sphere crystals, or inverse opals, interact so strongly with light that the propagation of light is inhibited for more than 55% of all directions [17]. Here, we investigate spontaneous emission of laser dye inside such crystals and identify a mechanism by which the directional properties of the spectrum are modified. For emission in directions nearly normal to the (111) lattice planes, we observe single Bragg stop bands. For emission directions between 25° and 55°, however, dual stop bands are observed in the emission spectra, with unprecedented large widths of 15%. The angular dependence of the central frequencies of these stop bands display an avoided crossing, characteristic of coupled modes. This behavior agrees with complementary reflectivity results [18] and with theoretically calculated dispersion curves. It appears that the emission spectra are strongly modified by simultaneous diffraction from (111) and (200) crystal planes. The avoided crossing is a manifestation of three-dimensional confinement, since the first Brillouin zone of an fcc crystal is fully enclosed by the (111) and (200) Bragg planes and their symmetry-related equivalents. Multiple diffraction results in Bloch modes with little dispersion, which is the basis for the formation of photonic band gaps. Such modes likely cause significant changes in the density of states, thus paving the way to novel quantum optical effects [8].

The photonic crystals studied here are fcc crystals of air spheres in titania (see Fig. 1), with lattice parameters varying between $a = 480$ and 510 nm, and a dielectric contrast ranging from 6.25 to 6.5; for a detailed description and characterization, see Ref. [16]. The samples have overall dimensions on the order of millimeters and are composed of a number of high-quality crystal domains with diameters as large as 50 μm. To incorporate the dye, the air-sphere crystals were immersed in a dilute solution of Nile Blue [19] in ethanol ($\sim 70$ μmol/l) for 24 h to promote the adsorption of dye molecules at the TiO$_2$-air interfaces of the voids (see Fig. 1), and then rinsed and dried. To ensure emission from solely internal sources, the dye adsorbed near the external sample surface was first selectively bleached by illuminating the photonic crystal with an intense laser beam (wavelength $\lambda = 514$ nm) at the Bragg angle; see Ref. [11].

The optical setup used to measure emission spectra is shown in Fig. 1. The dye inside the crystals was excited with a $p$-polarized laser beam incident at angles away from the Bragg angle (for $\lambda = 514$ nm), and focused to $\sim 30$ μm in

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spectra recovered; and the frequency range of suppressed emission moves toward high frequencies, as expected for photonic crystal stop bands due to a single Bragg diffraction. It was demonstrated that the line shape was independent of the pump intensity, and that the emitted intensity was linear with the pump power; hence lasing or amplified spontaneous emission effects can be excluded. By discretely traversing the pump power, lasing or amplified spontaneous emission was demonstrated that the line shape was independent of the detection angle, with angular resolution of 5°. Due to the very low concentration of adsorbed dye (estimated at $10^2$ molecules per air sphere), and concomitant low fluorescence, several spectra were averaged and smoothed, yielding an effective spectral resolution of $100 \text{ cm}^{-1}$. Detector dark count and stray light background have been subtracted. The measured intensities of all spectra recorded at the various angles have been adjusted to overlay their low- or high-frequency ranges, where no crystal effects are observed, to correct for the angle-dependent variation in detection efficiency. Techniques for measuring reflectivity are described in Refs. [17, 18, 20].

The emission spectra at select detection angles for a crystal with $a = 501$ nm are presented in Fig. 2(A). For emission directions in excess of 60° [Fig. 2(A) magenta curve], appreciable modification of the spectral line shape ceased, and the high-frequency edge of the emission spectrum has the same characteristic spectral shape as seen at low detection angles, between 0° and 25°. This implies that the $a = 60°$ stop band of the crystal does not overlap the emission spectrum of the dye. In comparison, at $a = 0°$ [Fig. 2(A) red curve], the photonic crystal greatly suppresses emission over a wide spectral range, from 14000 to 16500 cm$^{-1}$. With increasing emission angle, the low-frequency components of the emission spectra recover, and the frequency range of suppressed emission moves toward high frequencies, as expected for photonic crystal stop bands due to a single Bragg diffraction. It was demonstrated that the line shape was independent of the pump intensity, and that the emitted intensity was linear with the pump power; hence lasing or amplified spontaneous emission effects can be excluded. By discretely traversing the pump power, lasing or amplified spontaneous emission was demonstrated that the line shape was independent of the detection angle, with angular resolution of 5°. Due to the very low concentration of adsorbed dye (estimated at $10^2$ molecules per air sphere), and concomitant low fluorescence, several spectra were averaged and smoothed, yielding an effective spectral resolution of $100 \text{ cm}^{-1}$. Detector dark count and stray light background have been subtracted. The measured intensities of all spectra recorded at the various angles have been adjusted to overlay their low- or high-frequency ranges, where no crystal effects are observed, to correct for the angle-dependent variation in detection efficiency. Techniques for measuring reflectivity are described in Refs. [17, 18, 20].

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the low- and high-frequency edges are extracted separately by dividing $\alpha_1$ spectra by $\alpha_2$ spectra ($\alpha_1 < \alpha_2$) until the edge ratios converge. The low-frequency edge of the $\alpha_1$ stop band is obtained by dividing the $\alpha_1$ spectrum by emission spectra for increasing $\alpha_2$; the line shape of the ratio will converge as the difference between $\alpha_1$ and $\alpha_2$ increases. Similarly, the high-frequency edge at $\alpha_2$ is obtained by noting the convergence of the inverse ratio as $\alpha_1$ is decreased. While we noted weakly sample-dependent emission line shapes (due to differences in doping conditions), the line-shape ratios are sample independent, hence the stop bands are unambiguously determined. Figure 2(B) clearly demonstrates that the photonic periodicity imposes a strong attenuation on the transfer of radiant energy to free space.

Naively, one would expect the emission to completely vanish at the center of a stop band. We observe, however, an attenuation up to 75% near the center of the gap at $\alpha = 0^\circ$. Limited attenuation has been seen previously [10–12], and was attributed to diffuse scattering by intrinsic defects near the external crystal-air interface [11]. The pertinent mechanism in the present case is related: since the mean-free path $l \sim 15 \mu m$ [21] is much smaller than the $\sim 200 \mu m$ sample thickness, light propagates diffusively in the bulk of the samples. Diffuse light emanating from a depth $z < l$ from the crystal-air interface propagates ballistically to the interface, but may be redirected to the detector by scattering from intrinsic defects. Since $l$ is larger than the attenuation length for Bragg diffraction $l_B$ (typically $l_B \sim l \times 0.2$ to 0.5 [21]), light scattered at $z < l_B$ is hardly Bragg attenuated, while light scattered at $l_B < z < l$ reveals a stop band. This simple model predicts a total attenuation in the stop band of about 50% to 80%, in agreement with our observations.

At low emission angles [e.g., at $\alpha = 0^\circ$, Fig. 2(B), red curve], single broad stop bands are revealed. Interestingly, at higher angles there appears to be a transition to a double stop band: the first clear evidence of this is for $\alpha = 25^\circ$ at $\sim 18 000 \text{ cm}^{-1}$ [Fig. 2(B), green arrows]. We denote the lower-frequency stop bands by $S_1$, and the higher-frequency stop bands by $S_2$. With increasing angle, this second stop band becomes more apparent while $S_1$ decreases in amplitude. The intensity ratio for $\alpha = 45^\circ$ [Fig. 2(B), blue arrows] shows evidence of an $S_1$ feature at $17 000 \text{ cm}^{-1}$ and a strong $S_2$ feature at $18 700 \text{ cm}^{-1}$. By $\alpha = 60^\circ$, the $S_1$ band has vanished and the low-frequency edge of $S_2$ has moved beyond $18 500 \text{ cm}^{-1}$ (black arrow), leaving the spectrum essentially unsuppressed. It is clear that the observed phenomena cannot be explained by simple Bragg diffraction [7], but are likely a coupled wave phenomenon.

To further investigate whether the light emitted by internal sources indeed probes the photonic band structure, we have performed reflectivity experiments on the same sample using externally incident plane waves, since this technique readily identifies the central frequencies and widths of stop bands [17,18]. To facilitate direct comparison, we represent the reflectivity data $R$ as $1 - \beta R$, where $\beta$ is a scaling constant accounting for differences in probe geometries and physical properties. The maximum reflectivity at normal incidence was limited to 20%, due to the use of a large probe beam (500 $\mu m$) that samples grain boundaries between

![FIG. 3. Angular dependence of the stop band edges, determined from spectra as in Fig. 2(B). The squares and circles are the lower and upper edges, respectively, of the $S_1$ stop band; the triangles and inverted triangles are the lower and upper edges, respectively, of the $S_2$ stop band. The dashed curves are frequencies calculated from the photonic band structures using the plane-wave expansion method, and the dotted curve is the center frequency assuming single (111) Bragg diffraction.](image)
lating as a function of wave vector, with the latter converted to angle using momentum conservation parallel to the sample surface; the dashed curves in Fig. 3 show the results. The two curves that start at \( \alpha = 0^\circ \) are the mixed (000) and (111) modes that bound the (111) Bragg diffraction stop gap. It is clear that the calculated modes agree very well with the edges of the emission stop band \( S_1 \). The intermediate and highest frequency modes agree well with the edges of the \( S_2 \) stop band. The observed avoided crossing behavior is due to the (200) Bloch mode (which decreases in frequency) that mixes with the (000) and (111) modes. This has also recently been observed in reflectivity \cite{18}. It is clear that in the range of the avoided crossing, the intermediate mode is repelled by the outer two ones and becomes nearly dispersionless. This is expected to lead to a modification of the density of states in this particular frequency range.

A photonic band gap in strongly interacting photonic crystals can be regarded as fully dispersionless modes for all directions simultaneously (i.e., all angles in Fig. 3). Recently, complex reflectivity features have been observed in the frequency range where fcc crystals will develop a photonic band gap \cite{20,22}, which has been interpreted as a complex multiple Bragg diffraction phenomenon \cite{20}. The identification of relevant spectral features by us is thus an important step towards the understanding of emission spectra in the frequency range of a photonic band gap.

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