Light sources inside photonic crystals

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We have measured the optical fluorescence spectra of dye incorporated in high-quality photonic crystals made from colloids. The spectra reveal a stopgap that is due to Bragg reflection with strikingly reduced attenuation compared with plane-wave transmission. The modified attenuation is independent of the position of the sources in the sample and is brought about by diffuse scattering from defects near the surface. In the presence of a photonic bandgap, the diffuse component would disappear. Thus we have found a simple, unambiguous probe for the presence of photonic bandgaps. © 1999 Optical Society of America
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1. INTRODUCTION

Photonic crystals are three-dimensional periodic dielectric composites in which the refractive index varies on length scales of the order of optical wavelengths. The propagation of light in such photonic materials is analogous to the well-known wavelike propagation of electrons in a crystalline structure.[1] The periodic structure gives rise to Bragg diffraction, which is associated with stopgaps for propagation in certain directions. If the light is strongly coupled to the crystal, a photonic bandgap, i.e., a frequency band in which no light can propagate through the crystal in any direction, is expected to be present. One of the most important consequences of the presence of a photonic bandgap is that spontaneous emission of excited atoms with a transition frequency in the gap is inhibited,[2] a condition that may serve as the basis for lasers without threshold.[3]

In this paper we experimentally investigate modification of the spectra of light sources inside photonic crystals. Emission spectra of internal sources have been measured before, and stopgaps in emission spectra have been observed.[4–9] Important open questions remain, however. It appears that the stopgaps that have been observed differ in several respects from the stopgaps that are encountered in conventional transmission spectra; e.g., the attenuation and the width of emission spectra are smaller than in transmission spectra. To determine the origin of these differences we studied the dependence of the spectra on direction of emission, depth in the crystal, and lattice parameter. We observed that the spectrum of internally generated radiation, similarly to that of external radiation, experiences stopgaps but with strikingly reduced attenuation. The spectrum from internal light sources includes light that is emitted in directions outside the stopgaps and is subsequently scattered by defects close to the surface [see Figs. 1(a) and 1(b)]. In the presence of a photonic bandgap, the scattered light is strongly attenuated because the stopgaps extend over a 4π solid angle, trapping light in all directions [Fig. 1(c)]. Thus the spectrum of sources inside photonic crystals reveals unambiguously whether a photonic bandgap has been achieved.

2. EXPERIMENTS

To realize light sources experimentally inside photonic crystals, we doped colloidal crystals[10] with fluorescent dye.[11] We synthesized spheres[11] of 121-nm radius and a size variation of only 1.5%. The dye is homogeneously distributed inside the spheres. The density of Rhodamine Isothiocyanate dye molecules in the spheres was intentionally kept below 0.5 mmol/L to avoid reabsorption and nonradiative transfer. The dye molecules were covalently bonded to the silica in the spheres and covered by a 50-nm thick layer of silica to prevent washing out by the suspending liquid. This arrangement prevents unwanted chemical interactions of the dye with the liquid and particle surfaces.[12] The silica spheres (refractive index $n = 1.45$) were suspended in water ($n = 1.33$). The resultant colloidal suspensions were contained in long, flat glass capillaries of 3-mm width and 0.3-mm internal path length. The samples formed large, highly ordered *fcc* crystals with the (111) planes parallel to the walls of the capillaries, as revealed by our synchrotron small-angle x-ray diffraction studies.[13–15] The spacing of the crystal planes varied with height in the sample as a result of gravity. The spacing ranged from 206 to 221 nm, which corresponds to a density range of 53–65 vol. %. Higher up in the samples there was a less dense colloidal liquid phase. The freezing density was close to the freezing density of hard spheres of 54 vol. %, consistent with the screened Coulomb interactions that occur in these systems. In our samples, we added 0.5 mM of NaCl to screen the charge on the spheres.

We obtained fluorescence spectra by exciting the dye with an argon laser operating at a wavelength of 488 nm; the spectra were collected with a prism spectrometer equipped with a photomultiplier. The samples were excited through the back surface, i.e., the side of the sample away from the detector. The detector was looking at the front surface. We mounted the capillaries upon a rotation stage to orient the crystals with respect to the posi-

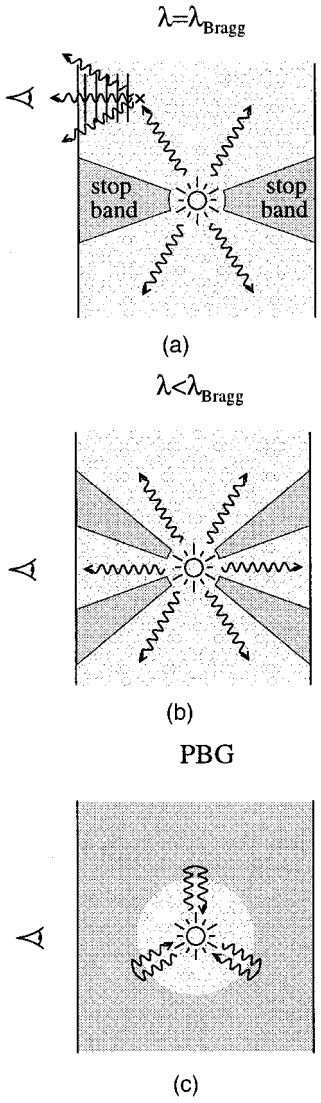

Fig. 1. Schematic drawing of the trajectory of light emitted by a point source inside a photonic crystal (a) when the light is just Bragg reflected from the crystal planes indicated, (b) for Bragg reflection at shorter wavelength, when the reflection is inclined to the lattice planes, and (c) in a crystal with a photonic bandgap. The cross in the top panel indicates a defect.

tion of the detector. Optical transmission spectra were measured with a collimated halogen lamp. Spectra were taken directly or by use of a cylindrical index-matching bath filled with dimethylformamide to suppress refraction at the surface of the sample capillary.

3. RESULTS AND DISCUSSION

We obtained fluorescence spectra of dye in many different photonic crystals. A typical example is shown in Fig. 2 and compared with the spectrum of dye in a colloidal liquid. The crystal changes the fluorescence spectrum of the dye considerably: The spectrum acquires a pronounced stopgap. The stopgap is caused by the (111) crystal planes. The crystal planes act as Bragg mirrors for the fluorescence, preventing part of the light from leaving the crystal. We observed that the central wavelength of the stopgap depends on the density of spheres in the crystal. By changing the vertical position in a sample, we could vary the density and hence tune the stopgap's wavelength. As an example, we carefully tuned the stop gap on the dye emission spectrum in Fig. 2.

To obtain the transmission spectrum of the light emitted inside the crystal, we took the ratio of the fluorescence spectrum to the reference fluorescence spectrum of dye in a colloidal liquid as shown in Fig. 2. In what follows, we call the resultant relative fluorescence spectrum the transfer function. The transfer function was normalized to 100% at long wavelengths; see Fig. 3. For comparison, we also plotted a transmission spectrum of plane waves entering the crystal from outside. One can see that the stopgap in the transfer function has the same central wavelength of 580 nm as the stopgap in the conventional transmission spectrum. The stopgap in the transfer function, however, is narrower, and the maximum attenuation of the transfer function is much less than that of the transmission of external plane waves. We now discuss the main features of the stopgaps in the transfer function.

We expect that the central wavelength of the stopgap is related to the lattice spacing of the crystal, the effective refractive index of the crystal, and the crystal's orientation.[16] Transfer functions for various emission directions are presented in Fig. 4.

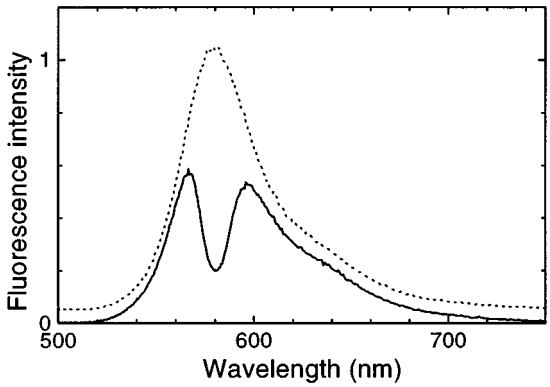

Fig. 2. Fluorescence spectrum of dye in a photonic colloidal crystal (solid curve) and in a colloidal liquid of spheres (dotted curve, offset by 0.05). Bragg reflection causes a stopgap in the spectrum of the crystal.

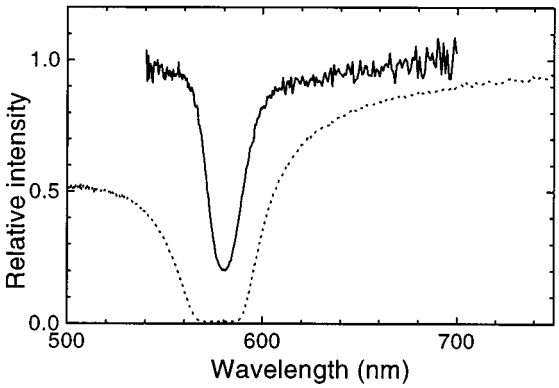

Fig. 3. Transfer function of a light source inside a crystal (solid curve, relative fluorescence intensity) and of a light source outside the crystal, far away (dotted curve, transmission of a plane wave). Both spectra were taken perpendicular to the (111) crystal planes.

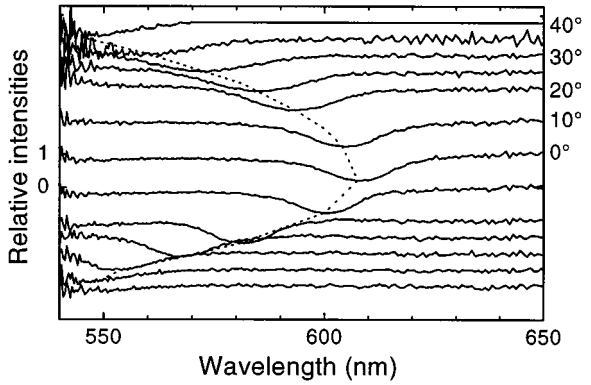

Fig. 4. Transfer function for sample rotations of 0°–40° in two directions. The spectra have been divided by a reference spectrum and normalized at long wavelength. For positive rotations the curves have been offset upward; for negative rotations, downward. The stopgap shifts to shorter wavelengths if the crystal is rotated, in accordance with Bragg's law.

Stopgaps are observed for all emission directions; away from the normal, the central wavelength of the stopgap becomes shorter, qualitatively resembling Bragg reflection. The central wavelength of the stopgap as a function of angle is shown in Fig. 5 for stopgaps in the transfer function as well as for stopgaps in transmission spectra. The two stopgaps follow the same curve.

The shift of the central wavelength is well explained by use of Bragg's law $2d \sin \theta = \lambda/n_{\text{eff}}$ generalized to include an effective refractive index n_{eff}, if one uses Snell's law to allow for refraction at the sample interface. In diffraction experiments with external sources it was previously found that the effective refractive index of a photonic crystal is well described by the Maxwell–Garnett approximation.[16,17] We note that Bragg's law with an effective Maxwell–Garnett refractive index yields results that closely correspond to those expected from dynamic diffraction theory.[18] For comparison, we show that the experimental data lie clearly between Bragg's law with refractive indices for water and silica. We found that, when an index-matching bath was not used, refraction at the air–capillary interface introduced large systematic errors.

The data in Fig. 4 illustrate that, for emission wavelengths that are equal to the Bragg wavelength at normal incidence, light can still propagate in oblique directions [see Fig. 1(a)]. For shorter emission wavelengths, the light is Bragg reflected at a certain angle but can propagate in other directions, such as the normal direction [see Fig. 1(b)]. The resultant variations in fluorescence intensity are familiar from x-ray fluorescence, in which case they are referred to as Kossel lines. In x-ray fluorescence the term Kossel line is reserved for light that originates inside a crystal. The variations in fluorescence that we have measured here correspond to true Kossel lines; the patterns of lines that occur in elastically scattered light are, strictly speaking, Seemann diagrams.[18]

The widths of stopgaps in transmission are due mainly to photonic crystal effects but also to disorder that occurs in any crystal.[19] The latter includes strain, finite crystal size,[18] crystal misorientations, and possibly even the lattice modes of the colloidal crystal.[20] For an actual photonic crystal the observed width is thus equal to or larger than the photonic width. A width of 11.1–11.7 nm is predicted by theories of dynamic diffraction and band structure.[18,21] In Fig. 3 the stopgap in the transfer function is ~20 nm wide. The width of the stopgap in the transmission, however, is much greater. Apparently the course of plane waves through the sample is qualitatively different from that of light coming from inside.

In transmission experiments the attenuation at the center of a stopgap is appreciable, even for small or imperfect crystals.[22,23] This is also the case for Fig. 3. It is striking that for the same crystal the transfer function shows much less attenuation. To elucidate the origin of this difference, we varied the position of the light source inside the sample as follows (cf. the inset of Fig. 6): The light that excites the dye is sent through the sample at a glancing angle of 30° with the surface. Thus the beam is close to the front surface at one edge and close to the back surface at the other edge of the sample. By imaging a

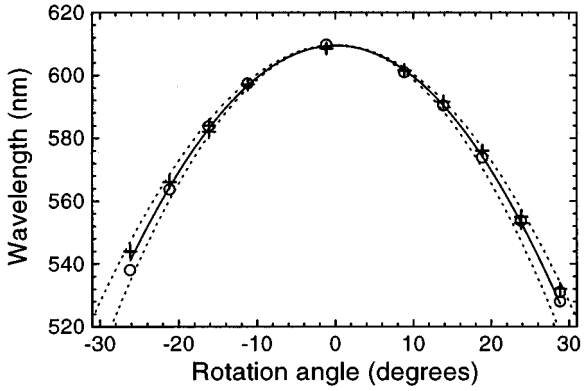

Fig. 5. Central wavelength of the stopgap in the transfer function (open circles) and in transmission spectra (crosses) as a function of rotation of the sample. The solid curve corresponds to Bragg's law with a correction for refraction at the sample interface, with an effective refractive index of 1.39. The dotted curves are based on the refractive indices of silica (upper curve) and water (lower curve).

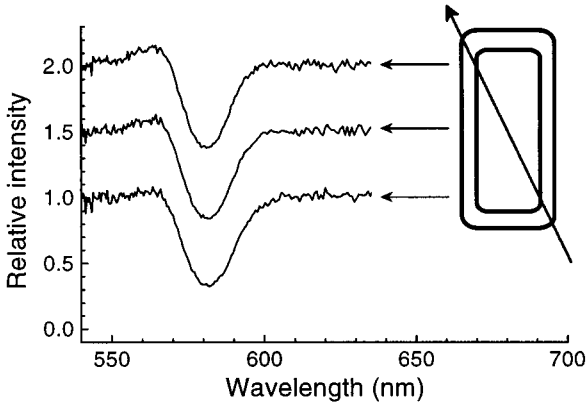

Fig. 6. Transfer functions (relative fluorescence intensities) for various distances from the light source to the sample surface, in a crystal similar to that in Fig. 3. The depth of the light source varies with the depth of the light beam that excites the fluorescence as indicated schematically on the right. The upper and middle curves have been offset by 0.5 and 1.0, respectively. Each curve corresponds to the position in the sample as indicated.

specific part of the sample onto the detector we select the depth of the emitting sources. The beam waist at the sample measures only 20-μm full width at half-maximum, and the width of the imaged area is 50 μm, both much less than the 300-μm sample thickness. The resultant transfer functions are shown in Fig. 6. The outermost curves correspond to regions that are 400 μm apart on the sample. Remarkably, the attenuation of the fluorescence stopgap does not depend on the depth of the sources. We can exclude the possibility that the depth dependence is washed out by a diffuse excitation beam: Fig. 3 shows that there is a large transmission of light at the excitation wavelength. Indeed, we observed a well-defined blue beam behind the sample. From the observation that the stopgap is already present for sources close to the surface, we conclude that the stopgap can build up after only few crystal planes. It is striking that the attenuation in the stopgap does not increase with further increase in the depth of the source. Apparently the attenuation in the stopgap in the transfer function is determined primarily close to the surface but not by the bulk of the crystal.

We verified that the fluorescence originates in the bulk of the sample by photochemically bleaching the dye close to the surface with an intense laser beam tuned to Bragg reflection. Because of reflection from the lattice planes, the laser beam penetrates only a short distance into the sample, and it bleaches the dye predominantly close to the surface. The bleaching did not deepen the stopgap, so we can exclude the possibility that the residual light comes from fluorescent dye close to the surface. The bleaching experiment also demonstrates that the residual light in the stopgap is not due to surface modes of the photonic crystal. As we explain below, the contribution of fluorescence generated in the surface layer to the residual light in the stopgap is indeed expected to be small.

4. PROPAGATION OF LIGHT INSIDE CRYSTALS

From a comparison between the transfer function and the transmission spectrum (Fig. 3) it is clear that a considerable amount of fluorescent light with wavelengths in a stopgap reaches the sample surface and then leaves the crystal in the direction of a stopgap. The explanation for this phenomenon is that defects near the surface of the crystal scatter in all directions, including the direction of the stopgap. The phenomenon can be understood as follows: Light emitted in the direction of a stopgap is attenuated, but the light can propagate perfectly well in other directions [see Figs. 1(a) and 4]. The light will be scattered by a small concentration of defects that always occur in any crystal.[19] Radiation scattered by defects deep inside the crystal will experience an attenuation similar to that in a plane-wave experiment. If light is scattered by defects close to the surface of the crystal, this radiation will appear unattenuated outside, even in the direction of a stopgap, because the light traverses only a thin layer of photonic crystal. Thus, light appears in the direction of a stopgap. The intensity is determined solely by the defects that are close to the surface; defects that are deeper inside the sample do not contribute to intensity. The internal sources emit light in a large solid angle of nearly 2π to the front surface; hence that light is expected to make an appreciable contribution to the intensity compared with the light that directly propagates into the 0.016π solid angle of the detector. In contrast, in a plane-wave transmission spectrum the contribution of diffuse scattering is hardly noticeable. The reason for this is that the beam that propagates to the detector is well collimated, whereas the randomly scattered light is spread over a 4π solid angle. This explanation elucidates the reason why the stopgap in fluorescence is shallower than the deep stopgap in plane-wave transmission spectra (see Fig. 3).

To give our explanation a quantitative basis, we now estimate the attenuation in the stopgap of the transfer function, which is determined by fluorescent light emanating from a surface layer. We distinguish two main contributions to this fluorescence intensity: (1) fluorescence generated in the surface layer itself by scattered blue light from the excitation beam and (2) scattering in the surface layer of red fluorescence light generated deeper inside the sample [see Fig. 1(a)]. Both contributions depend on the thickness of the surface layer and on the diffuse scattering of the blue or red light.

We determined the thickness of the surface layer by comparing the fluorescence intensity of such a layer—excited by a blue beam at the Bragg condition—with the fluorescence intensity produced by an incident beam that illuminates the whole sample thickness. The excitation beam was Bragg reflected at the back surface of the sample, and the resultant fluorescence was detected outside the stopgap. Under Bragg excitation of the incident beam we found a fluorescence intensity six times lower than what we found when we illuminated the whole 300-μm sample thickness away from Bragg reflection. Apparently the surface layer is $\sim 300\,\mu\text{m}/6 = 50\,\mu\text{m}$ thick. Based on this layer thickness, one would expect a transmission in the stopgap of $\exp(-6) = 0.3\%$. This estimate agrees very well with the measured transmission in the stopgap in Fig. 3.

The amount of diffuse scattering in the sample can be estimated from the transmission. For the blue excitation beam the transmission is $\sim$60% (see Fig. 3), so at most 40% of the incident light is scattered. Half of the scattered light reaches the front surface.

We can now estimate contribution (1) above: scattered blue light that excites the surface layer contributes $(40\%/2)/6 = 3\%$ to the transfer function. Similar reasoning leads to an estimate of contribution (2) of fluorescence light scattered in the surface layer; however, the fluorescence is scattered more strongly because it is close to a stopgap.[20] In a separate experiment, we observed that scattering close to a stopgap can be a factor of 3–4 stronger than scattering far away from the stopgap. Contribution (2) is accordingly larger, i.e., $\sim$10%. The resultant estimate for the relative intensity in the stopgap of the transfer function is then $\sim 3\% + 10\%$, which should be compared with the observed stopgaps in Fig. 3 of $\sim$20%. The estimated stopgap depth agrees well with observed attenuations in stopgaps, confirming the mechanism that we propose.

With the mechanism described above we can also ex-

plain the difference between the widths of the stopgaps in fluorescence and transmission. The fluorescence stopgap is caused by relatively few crystal planes that are well aligned close to the cell wall; therefore the measured stopgap width agrees well with the purely photonic width. A simple model calculation reveals that approximately 50 lattice planes (~20-μm thickness) suffice to yield the width of 12 nm without Scherrer broadening[18] caused by finite crystal size. The width of the fluorescence stopgap comes close to the width of the peak in reflection spectra,[24] because both are caused by the outermost crystal planes. The stopgap in transmission, on the other hand, samples the complete thickness of the sample (more than a thousand lattice planes), including planes far from the capillary wall, which may be less well aligned. Thus the diffuse scattering mechanism not only accounts for all our experimental observations but also explains previous uninterpreted data.[4–9]

5. CONCLUSIONS

We have studied propagation of light generated inside high-quality photonic crystals. Close to stopgaps, the propagation is determined by defects near the surface. The effect was confirmed by a quantitative analysis of the observed attenuations. Our result has an important bearing on the long-awaited photonic bandgap: In that case a source inside a crystal cannot emit in any direction; hence the source of diffuse light is shut off. In a material with a photonic bandgap, this diffuse contribution to the transfer function vanishes over the full spectral width of the gap. It appears that a small number of defects, which are unavoidable even in high-quality crystals, is an excellent indicator for the presence of photonic bandgaps in crystals. We conclude that the transport of light in photonic crystals consists of an intricate combination of propagation (away from stopgaps) and the diffuse scattering (at the stopgaps) that is typical of random samples. For the latter, a large number of studies already have been made, which should facilitate detailed theoretical interpretation.[25]

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