Structure and fluorescence of photonic colloidal crystals

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Light sources inside photonic crystals

5.1 Introduction

A study of light sources inside photonic crystals is pertinent in view of the primary aim of photonic crystals, i.e. modifying the radiative properties of such sources. Among the radiative properties of light sources inside photonic crystals, the emission spectrum is most readily accessible experimentally. Emission spectra of internal sources have been measured, and clear stop gaps in emission spectra have been observed. Apparently the photonic band structure strongly influences the emission spectrum. Important open questions remain, however. It appears that the observed stop gaps differ in several respects from the stop gaps encountered in conventional transmission spectra, e.g. the attenuation and the width of emission spectra are smaller than in transmission spectra. We will explain these observations with a simple model, outlined in Fig. 5.1. The essential ingredient is that the stop gaps do not cover all directions in the crystals, i.e. that light can propagate in directions outside the stop gaps. As a result, the spectrum from internal light sources includes light that is emitted in directions outside the stop gaps and subsequently scattered by defects close to the surface (Fig. 5.1a). In the presence of a photonic band gap, the scattered light is strongly attenuated because the stop gaps extend over $4\pi$ solid angle, trapping light in all directions (Fig. 5.1c). Thus the spectrum of sources inside photonic crystals reveals unambiguously whether a photonic band gap has been achieved.

5.2 Experiments

To experimentally realize light sources inside photonic crystals we used the dye-doped silica spheres $\mu$ESiUJ1-101 described in the previous chapter. The silica spheres (refractive index $n = 1.45$) are suspended in water ($n = 1.33$). The resulting colloidal suspensions are contained in long flat glass capillaries of 3 mm
Figure 5.1  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 band gap. The cross in the leftmost panel indicates a defect.

width and 0.3 mm internal path length. The samples form 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. The spacing of the crystal planes varies with height in the sample due to gravity. The spacing ranges from 206 to 221 nm, which corresponds to a density range of 53–65 vol%. Higher up in the samples, the less dense colloidal liquid phase coexists. The freezing density is 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, 0.5 mM NaCl was added to screen the charge on the spheres.

Fluorescence spectra were obtained by exciting the dye with an argon laser operating at a wavelength of 488 nm; the spectra were collected with a Carl-Leiss prism spectrometer, equipped with a photomultiplier. The spectrometer has a resolving power of 1 nm for the 0.1 mm slit settings used. It was calibrated using the spectral lines of a neon lamp. The samples were excited through the back surface, i.e. the side of the sample away from the detector. The detector is looking at the front surface. The capillaries were mounted on a rotation stage to orient the crystals with respect to the position 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.
5.3 Results and Discussion

We have obtained fluorescence spectra of dye in many different photonic crystals. A typical example is shown in Fig. 5.2 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 stop gap. The stop gap 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 stop gap depends on the density of spheres in the crystal. By changing the vertical position in a sample, we can vary the density and hence tune the stop gap wavelength. As an example, we have carefully tuned the stop gap on the dye emission spectrum in Fig. 5.2.

To obtain the transmission spectrum of the light emitted inside the crystal, we have taken the ratio of the fluorescence spectrum to the reference fluorescence spectrum of dye in a colloidal liquid in Fig. 5.2. In what follows, we will call the resulting relative fluorescence spectrum the “transfer function”. The transfer function has been normalized to 100% at long wavelengths; see Fig. 5.3. For comparison, we have also plotted a transmission spectrum of plane waves entering the crystal from outside. One can see that the stop gap in the transfer function has the same central wavelength of 580 nm as the stop gap in the conventional transmission spectrum. The stop gap in the transfer function, however, is narrower and the maximum attenuation of the transfer function is much less than that of the transmission of ex-

Figure 5.2 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 stop gap in the spectrum of the crystal.
We will now discuss the main features of the stop gaps in the transfer function.

We expect that the central wavelength of the stop gap is related to the lattice spacing of the crystal, the effective refractive index of the crystal, and the crystal's orientation. Transfer functions for various emission directions are presented in Fig. 5.4. Stop gaps are observed for all emission directions; away from the normal, the central wavelength of the stop gap goes to shorter wavelengths, qualitatively resembling Bragg reflection. The central wavelength of the stop gap as a function of angle is shown in Fig. 5.5, for stop gaps in the transfer function as well as for stop gaps in transmission spectra. The two stop gaps follow the same curve. The shift of the central wavelength is very well explained using Bragg's law $2d \sin \theta = \lambda/n_{\text{eff}}$ generalized to include an effective refractive index $n_{\text{eff}}$, if allowance is made for refraction at the sample interface using Snell's law. In diffraction experiments using external sources we have previously found that the effective refractive index of a photonic crystal is well described with the Maxwell-Garnett approximation. We note that Bragg's law with an effective Maxwell-Garnett refractive index yields results which closely correspond with dynamical diffraction theory. For comparison, it is shown that the experimental data in Fig. 5.5 are clearly in between Bragg's law with refraction of either water or silica. Without index matching bath, we found that refraction at the air-capillary interface introduces large systematic errors. In a previous experiment, Yamasaki and Tsutsui presented stop gaps in the transfer
Figure 5.4  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 stop gap shifts to shorter wavelengths if the crystal is rotated, in accordance with Bragg's law.

The data in Fig. 5.4 illustrate that for emission wavelengths that are equal to the Bragg wavelength at normal incidence, light can still propagate in oblique directions (see Fig. 5.1a). For shorter emission wavelengths, the light is Bragg reflected at a certain angle, but can propagate in other directions, such as the normal one (see Fig. 5.1b). The resulting variations in fluorescence intensity are familiar from x-ray fluorescence, where they are referred to as Kossel lines. In x-ray fluorescence, the term Kossel line is reserved for light which 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.  

The width of stop gaps in transmission is due mainly to photonic crystal effects, but also to disorder that occurs in any crystal. The latter includes strain, finite crystal size, crystal misorientations, and possibly even the lattice modes of the colloidal crystal. For a real photonic crystal, the observed width is thus equal to or larger than the intrinsic photonic width. An intrinsic width between 11.1 and 11.7 nm is predicted by dynamical diffraction and band structure theories. In Fig. 5.3, the stop gap in the transfer function is about 20 nm wide. The width of the stop gap in the transmission, however, is much larger. Apparently the course of
Figure 5.5  Central wavelength of the stop gap in the transfer function (∗) and in transmission spectra (+) as a function of rotation of the sample. The wavelengths are based on spectra taken using an index matching bath. The solid curve corresponds to Bragg's law with correction for refraction at the sample interface, using an effective refractive index of 1.39. The dotted curves are based on the refractive index of silica (upper curve) and water (lower curve).

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 stop gap is appreciable, even for small or imperfect crystals. This is also the case in Fig. 5.3. It is striking that for the same crystal the transfer function shows much less attenuation. To elucidate the origin of this difference, we have varied the position of the light source inside the sample as follows (cf. inset of Fig. 5.6): The light which 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 and at one edge and close to the back surface at the other edge of the sample. By imaging a specific part of the sample on 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 resulting transfer functions are shown in Fig. 5.6. The outermost curves correspond to regions that are 400 μm apart on the sample. Remarkably, the attenuation of the fluorescence stop gap 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. 5.3 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 ob-
servation that the stop gap is already present for sources close to the surface, we conclude that the stop gap takes only few crystal planes to build up. It is striking that the attenuation in the stop gap does not increase with further increasing depth of the source. Apparently the attenuation in the stop gap in the transfer function is mostly determined 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 a Bragg reflection. Due to reflection from the lattice planes, the laser beam penetrates only a short distance into the sample, and it predominantly bleaches the dye close to the surface. The bleaching did not deepen the stop gap, so we can exclude that the residual light comes from fluorescent dye close to the surface. The bleaching experiment also demonstrates that the residual light in the stop gap is not due to surface modes of the photonic crystal. We will explain below that the contribution of fluorescence generated in the surface layer to the residual light in the stop gap is indeed expected to be small.

Figure 5.6  Transfer functions (relative fluorescence intensities) for various distances from light source to sample surface, in a similar crystal as in Fig. 5.3. The depth of the light source varies with the depth of the light beam which excites the fluorescence (see schematic drawing). The upper curves have been offset by 0.5 and 1.0 respectively. Each curve corresponds to the position in the sample as indicated.
5.4 Propagation of light inside crystals

From a comparison between the transfer function and the transmission spectrum (Fig. 5.3), it is clear that a considerable amount of fluorescence light with wavelengths in a stop gap reaches the sample surface and then leaves the crystal in the direction of a stop gap. The explanation for this phenomenon is that defects near the surface of the crystal scatter in all directions, including the direction of the stop gap. The phenomenon can be understood as follows: Light emitted in the direction of a stop gap is attenuated, but the light can propagate perfectly well in other directions (Fig. 5.1a, Fig. 5.4). The light will be scattered by a small concentration of defects that always occur in any crystal. 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 stop gap, because the light traverses only a thin layer of photonic crystal. Thus, light appears in the direction of a stop gap. The intensity is determined solely by the defects that are close to the surface, defects that are deeper inside the sample do not contribute. The internal sources emit light in a large solid angle of nearly $2\pi$ to the front surface, hence an appreciable contribution is expected compared with the light that directly propagates into the 0.016$\pi$ solid angle of the detector. In contrast, in a plane wave transmission spectrum the contribution of diffuse scattering is hardly noticeable. The reason is that the beam that propagates to the detector is well collimated, whereas the randomly scattered light is spread over $4\pi$ solid angle. This elucidates why the stop gap in fluorescence is shallower than the deep stop gap in plane wave transmission spectra (cf. Fig. 5.3).

To give our explanation a quantitative basis, we now estimate the attenuation in the stop gap 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. 5.1a. Both contributions depend on the thickness of the surface layer and on the diffuse scattering of the blue or red light. The thickness of the surface layer was determined by comparing the fluorescence intensity of such a layer – excited by a blue beam at the Bragg condition – to 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 resulting fluorescence was detected outside the stop gap. Under Bragg excitation, we find a fluorescence intensity 6 times lower than found when illuminating the whole 300 $\mu$m sample thickness away from Bragg reflection. Apparently the surface layer is about 300 $\mu$m/6 = 50 $\mu$m thick.
Based on this layer thickness, one would expect a transmission in the stop gap of \( \exp(-6) = 0.3\% \). This estimate agrees very well with the measured transmission in the stop gap in Fig. 5.3. 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. 5.3), so at most 40\% of the incident light is scattered. Half of the scattered light reaches the front surface. We can now estimate the contribution (1) above: scattered blue light which excites the surface layer contributes \( (40\%/2)/6 = 3\% \) to the transfer function. Similar reasoning leads to an estimate of the contribution (2) of fluorescence light scattered in the surface layer, however the fluorescence is scattered more strongly because it is close to a stop gap. In a separate experiment, we have observed that scattering close to a stop gap can be a factor 3 to 4 stronger than far away from the stop gap. The contribution (2) is accordingly larger, i.e. \( \sim 10\% \). The resulting estimate for the relative intensity in stop gap of the transfer function is then \( \sim 3\% + 10\% \). This should be compared with the observed stop gaps in Fig. 5.3 of about 20\%. The estimated stop gap depth agrees well with observed attenuations in stop gaps, confirming the mechanism that we propose.

With the mechanism described above we can also explain the difference between the widths of the stop gaps in fluorescence and transmission. The fluorescence stop gap is caused by relatively few crystal planes that are well aligned close to the cell wall, therefore the measured stop gap width agrees well with the purely photonic width. A simple model calculation reveals that approximately 50 lattice planes (\( \sim 20 \mu m \) thickness) suffice to yield the width of 12 nm without finite size Scherrer broadening. The width of the fluorescence stop gap comes close to the width of the peak in reflection spectra, because both are caused by the outermost crystal planes. The stop gap 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 accounts not only for all of our experimental observations, it also explains previous uninterpreted data.

### 5.5 Conclusions

We have studied propagation of light generated inside high quality photonic crystals. Close to stop gaps, the propagation is determined by defects near the surface. The effect is confirmed by a quantitative analysis of the observed attenuations. Our result has an important bearing on the long awaited photonic band gap: 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 band gap, this diffuse contribution
to the transfer function vanishes over the full spectral width of the gap. It appears that a small number of defects that is unavoidable even in high quality crystals is an excellent probe for photonic band gap crystals. We conclude that the transport of light in photonic crystals consists of an intricate combination of propagation (away from stop gaps), and diffuse scattering (at the stop gaps) typical of random samples. For the latter, a large body of work already exists, which should facilitate detailed theoretical interpretation.16

References