Observation of higher-order diffraction features in self-assembled photonic crystals

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The optical response of high quality three dimensionally (3D) ordered photonic crystals is analyzed in the high energy region. By tuning the reflectance with the angle of incidence of light, the peaks in the reflection spectrum that correspond to the first, second, and third order photonic stop bands and the van Hove singular point in the photon density of states are clearly distinguished. The high energy features have been observed for photonic crystals made from colloids of different diameters, having different index contrast and fabricated by two different self-assembly routes. The observation of van Hove singularity at near-normal incidence of light and its presence even in low index-contrast photonic crystals provide conclusive evidence that these high energy features are due to the perfect periodic ordering present in the photonic crystals with less defects and disorder.

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I. INTRODUCTION

Photonic crystals or photonic band gap materials are characterized by a dielectric constant (refractive index) which is spatially periodic in one, two, or three dimensions [1,2]. A complete photonic band gap results when the crystal forbids light propagation in a certain range of frequencies for all angles of incidence and polarization [3,4]. The challenge of fabricating photonic crystals with band gap region in the visible and near-IR wavelengths is enormous since the periodicity of the crystal is required to be of the order of wavelength of light in order to satisfy the modified Bragg’s law. When the Bragg’s law is satisfied only for certain directions, the light reflecting from the layers interferes constructively resulting in a high reflection or low transmission band of wavelengths called the pseudogap or the photonic stop band. Unlike the electronic band gap in semiconductors leading to absorption, the photonic band gap corresponds to the range of wavelengths that is not allowed to propagate through the structure resulting in reflection. A detailed review of the photonic crystals can be found in [5].

These materials have many potential applications in optoelectronics and optical communications [2,6–8]. When certain light emitting species embedded in photonic crystals are excited, the spontaneous emission from the species may get suppressed or enhanced. When the wavelength of the emitted light lies within the photonic stop band, the emission characteristics of the light get modified since there is no allowed level into which the photon can make a transition in the gap region (photon density of states is zero inside the complete photonic band gap and the local density of states is zero in a pseudogap region). When the emission wavelength of the source matches with the band edge wavelength, where the photon density of states is larger, light emission can be enhanced. The stimulated emission characteristics are also modified when the photonic stop band effect is present. Thus the study of light-emitting species embedded in a photonic crystal environment paves the way for low-threshold laser action in these exotic materials [2,9–11].

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The methods generally used for the fabrication of photonic crystals are derived from the conventional semiconductor device fabrication techniques. An alternative method, which is simple and inexpensive and generally called gravity sedimentation [12], is based on the self-assembly of monodispersed microparticles in a colloidal suspension for the fabrication of 3D ordered photonic crystals. This method suffers from the disadvantage of a large number of unwanted and uncontrolled defects present in the resulting crystals. A modified form of gravitational self assembly which is based on the capillary force to organize the colloids [13] gives samples of very high structural and optical quality.

Even though the photonic crystals fabricated using the self assembling method with standard colloids, such as polystyrene and silica, have less index contrast to open a complete photonic band gap [14], thus resulting in a pseudogap, these crystals provide the ideal platform to study the various optical properties. Self-assembly often leads to crystallization in fcc form with the (111) plane parallel to the substrate [15]. Hence the optical properties are usually probed from this plane of the crystal. Optical characterization requires the measurement of the reflection and transmission of the crystal at different wavelengths and at different angles of incidence to identify the presence of the photonic stop band [16–21]. Most of the studies are focused on the optical properties in the low energy region (corresponding to the first order gap).

Recently, the interest has shifted to the study of the optical response of these photonic crystals in the high energy region (around the second order photonic stop band) where many bands are involved in deciding the optical properties and therefore the situation is very complex [22–24]. Since the dispersion of the bands in the high energy region is much less (called flat bands), the group velocity is very low as compared to the low energy region [25]. Therefore, the interaction of electromagnetic (EM) waves with the crystal is very high leading to the enhancement of nonlinear effects at these band edges compared to the bands in the low energy region.

Li et al. [26] observed a surprising localization of light near the photonic stop band edge for a 2D photonic crystal waveguide instead of getting the strongest localization in the center of the photonic band gap. Later, Ibanescu et al. [27]
explained that the localization is not a surprising phenomenon, but it is due to the appearance of a van Hove singular point near the band edge in the photonic band structure where the density of states is higher. Therefore, phenomena which require high density of states will be enhanced at the band edges. Also it is predicted that phenomena like superprism and emission of active species embedded in a photonic crystal can be enhanced in these high energy regions [28,29]. Therefore, the analysis of optical properties of photonic crystals in the high energy region is very important both from the fundamental and application point of view. This is not an easy task, however, since the high energy region is well resolved only in crystals with a highly ordered structure.

In this paper, we analyze systematically the optical response of the photonic crystals in the high energy region and tune the spectral response with angle of incidence of light. We establish, by means of angle resolved reflection spectrum, the presence of a van Hove singular point and the implication that this singularity is only due to the periodic nature of the crystal. These high energy responses were analyzed for photonic crystals made using two important methods of fabrication from self-assembly, for crystals made of colloids of different diameters and for crystals having different index contrast. The observation of van Hove singularity at near-normal incidence of light in all the prepared samples and its presence even in low index-contrast photonic crystals emphasize the possibility of extremely good ordering in self-assembled photonic crystals.

This paper is organized as follows. In Sec. II, the experimental details will be presented. In Sec. III, results on the optical properties of the photonic crystal will be discussed with emphasis on the high energy features and tuning of the high energy response with angle of incidence of light. The existence of second and third order stop band and the presence of van Hove singular points in the samples will be emphasized. Section IV will give the conclusions.

II. EXPERIMENT

Polymers form an interesting class of materials having fairly high refractive index and low absorption in the visible and near-IR regions and are thus ideal for the fabrication of photonic crystals. Polymeric photonic crystals can be fabricated using the well known convective self-assembling or vertical deposition method (VDM) [13]. Recently, a very fast and efficient method for fabricating the 3D ordered photonic crystal was proposed. This is known as inward growing self-assembling or horizontal deposition method (HDM) [30]. We fabricated photonic crystals using the above two self-assembling methods for the present study, using the colloids of polystyrene (PS) and polymethyl methacrylate (PMMA). The structural characterization of the photonic crystals was done using optical microscope, scanning electron microscope (SEM), and atomic force microscope (AFM). The optical microscope image shows the crystal domains separated by cracks, of dimensions more than 100 μm × 100 μm indicating the quality of crystals fabricated. The SEM and AFM images show the (111) plane of the fcc lattice arranged parallel to the substrate [15]. All the samples analyzed in SEM were coated with a thin layer of gold to avoid any charging effects. AFM measurements are done in tapping mode. The optical spectra have been recorded using a Perkin-Elmer lambda-950 spectrophotometer. Details about the structural characterization of the photonic crystals used in this work can be found in [31,32].

The optical response of photonic crystals in the low energy region was measured from the (111) plane of fcc lattice at near-normal incidence (Γ−L direction in the reciprocal lattice). The spectrum presents a well defined reflectance peak at wavelengths corresponding to the diameter and the refractive index of the material of the sphere. Figure 1(a) shows the photonic stop band for crystals fabricated using VDM with PS spheres having diameter 280 nm clearly indicates the presence of photonic stop band around 610 nm. (b) Reflection spectra for a PS photonic crystal with sphere diameters 280 nm (thin line) and 488 nm (thick line) fabricated using VDM at an angle of incidence of 8°.
I(b). The first order photonic stop bands corresponding to 488 nm and 280 nm are around 1050 nm and 610 nm, respectively. The gap size, an important parameter that can be deduced from the experiment, is calculated and compared with the theoretical value [16] and found to be in good agreement. As seen in Fig. 1(b), the optical spectrum in the low energy region presents a high reflectance >50% in the first order photonic stop band for the crystals fabricated. Thus high quality photonic crystals can be prepared using the self-assembling method, which is essential for observing the optical response in the high energy region to be discussed in the next section. In the case of crystal with 280 nm colloids, the high energy features are observed in the wavelength range of 200–350 nm, while for the crystal with 488 nm colloids, the high energy region is between 250 to 600 nm.

III. OPTICAL SPECTRA IN THE HIGH ENERGY REGION

There is an increasing level of interest in understanding the optical spectra in the high energy region due to the possible enhancement of nonlinear optical and emission characteristics of the active species embedded in the photonic crystals. This is due to the presence of the flat or low dispersion characteristics of the active species embedded in the photonic crystals. It is established that these multiple peaks in reflection in the high energy region can be observed only in strongly modulated photonic crystals such as inverse photonic crystals, where the index contrast is larger, these spectral characteristics in the high energy region were later observed even in direct photonic crystals where the spheres are arranged in an air medium [22,23]. Very recently, the analysis of the optical response of these high energy regions has established that the peaks in reflection spectra do not lead to a photonic stop band (a decrease in the photon density of states) but they can be due to photonic modes which result when the incident light interacts with uncoupled bands [34]. This analysis led to the observation of van Hove singular point in the photon density of states and a correspondence between the calculated photon density of states with the observed reflection spectrum.

The main purpose of the paper is to identify the peaks in the experimentally observed angle-resolved reflection spectrum with those associated with the van Hove singular point and other higher order photonic stop bands. We compare our experimental results with the reported band structure and the calculated photon density of states for a 3D ordered photonic crystal structure given in Refs. [23,34]. It is established that the observation of the van Hove singular point is due to the perfect periodic ordering of the crystal just as in the case of electronic crystals [35] and not an accidental observation or due to any other structural disorder. The van Hove singular point is observed even at near-normal incidence in our work unlike its observation only at higher angles of incidence for bulk opal photonic crystals [34]. We will also present the tuning of the photonic stop band in the high energy region by varying the angle of incidence, analyze the effect of reducing the index contrast of the photonic crystals in the high energy response and confirm the observation of a van Hove singular point even for low index-contrast photonic crystals.

As compared to the photonic stop band in the low energy region (first order gap), the analysis of optical features in the high energy region is very complex as many bands are involved in the interaction. The folding of the bands into the first Brillouin zone will introduce the anticrossing of the bands, because of the translational symmetry of the crystal [36]. The high quality of the photonic crystal samples fabricated in this work enable us to clearly understand the optical response of photonic crystals in the high energy region.

Figure 2 shows the high energy response of the crystal made of PS spheres having diameters of 488 nm and 280 nm fabricated using VDM and HDM. The angle of incidence is 8°. It is clear that the optical spectrum is highly complex as theory predicts. The x axis is plotted in the reduced unit of $a/\lambda$ (corresponds to $a/\lambda/2\pi$), where “$a$” is the fcc lattice constant, in order to compare our experimental results with the photonic band structure given in Ref. [23] [Fig. 4 (left) in that work]. The first order Bragg peak appears at 0.6 $a/\lambda$ for PS with a reflectance of 55% (seen in Fig. 1; not shown in Fig. 2). The peak appearing at 1.16 $a/\lambda$ in Figs. 2(a) and 2(b) is also observed in the band structure given in Ref. [23]. This peak is observed in photonic crystals fabricated using two
different diameters and also by two different methods of fabrication. Detailed discussion about this peak will be given later. The peak appearing at 1.28 $a/\lambda$ corresponds to the second order Bragg diffraction from the (111) family of planes. This peak is also present in the band structure calculated in Ref. [23]. The reflection peak observed at 1.28 $a/\lambda$ in our work is fairly well resolved compared to many reports in the literature and this shows the quality of the crystals fabricated using both methods. The second order stop band in the case of samples made of diameter 488 nm and 280 nm shows a splitting as observed in Ref. [23], but in a less prominent manner.

There is a peak appearing at 1.63 $a/\lambda$ for the sample made with colloids of diameter 280 nm. This peak corresponds to the anticrossing of the bands, that is, between the bands which are folded back into the first Brillouin zone due to the translational periodicity and the $T-L$ bands [23]. There is another peak at 1.82 $a/\lambda$ for samples made with a colloidal diameter of 488 nm and it is present in samples prepared using both methods. This corresponds to the third order Bragg diffraction from the family of (111) planes. Unlike the first order photonic stop band, all these high energy bands consist of many flat bands indicating the complex interaction of light with the crystal [23]. The observation of first, second, and third order Bragg reflection from the sample shows the perfect ordering of the spheres and the efficiency of both the experimental techniques used for the fabrication of photonic crystals. The high energy response of the photonic crystal having a sphere diameter of 488 nm is shifted slightly to higher energy values compared to that of the photonic crystal fabricated using a sphere diameter of 280 nm; the reason for this will be discussed in the next paragraph. This trend is also observed for samples fabricated using HDM. This shows that these features are inherent optical properties of the photonic crystals and are not due to any other structural disorder or due to any scattering by the defects.

The vertical lines in Fig. 2 are drawn to show the correspondence between the positions of the peaks for the two crystals made from different diameters. In the reduced unit of $a/\lambda$, the positions should coincide. On the contrary, the high energy peaks for the crystal fabricated using spheres of larger diameter are shifted slightly to higher energy values as compared to the peaks associated with the crystal made from smaller diameter colloids for the two fabrication methods used in this study. The reason for this trend is the refractive index dispersion of polystyrene [37]. Bulk polystyrene shows normal dispersion. The wavelengths at which the photonic crystal characteristics appear are related to the colloidal sphere diameters used; the smaller the diameter, the lower the wavelengths. There is an increase in the effective refractive index of the crystals due to the increase in the refractive index of polystyrene in the short wavelength region. Therefore, the reflection peaks of photonic crystals made using smaller spheres will appear to be shifted to slightly higher wavelengths (lower frequency) than the peaks corresponding to photonic crystals made from larger diameter in the reduced unit of $a/\lambda$. This effect is more as one goes towards the higher energy side. This has been experimentally observed for polystyrene photonic crystals in an earlier work [23]. In addition to the refractive index dispersion, any variation in the sphere diameter (polydispersity) will also affect the positions of reflection peak in the high energy region, due to the scaling to “reduced unit.”

Now we compare our experimentally observed peak position with the calculated density of states for different crystal directions reported in Ref. [34] (Fig. 3 in Ref. [34]). The photon density of states shows a dip around 0.6 $a/\lambda$, which corresponds to the first order photonic stop band. The peak appearing around 1.1 $a/\lambda$ in the density of states at near normal incidence ($T-L$ direction in reciprocal lattice) moves toward the low energy region as the angle of incidence of light increases. They attributed this trend to the presence of saddle point van Hove singularities in the photon density of states. In our case, the reflection peak is clearly present around 1.1 $a/\lambda$ at near normal incidence as shown in Fig. 3 for samples fabricated using different diameters and fabrication methods. Therefore, we assign the reflection peak at 1.1 $a/\lambda$ at an angle of incidence of 8° to the van Hove singular point. Thus every peak in reflection does not correspond to a dip in the photon density of states. The superior quality of the photonic crystals fabricated in our work enables us to observe the van Hove singularity even at near-normal incidence of light. The entire set of observed reflection peaks in the high energy region has one-to-one correspondence in the spectrum between the two methods of fabrication. Hence the
new method, called HDM, is equally competent as the traditional method of fabrication of photonic crystals using VDM, but with additional advantages of lesser time and cost.

Figure 4 shows the variation of higher order stop band wavelength and van Hove singular points with increase in the angle of incidence of light. The closed symbols show the variation for a sample made with VDM and open symbols give the results for samples made using HDM. The peak positions of the first (shown as squares), second (shown as triangles), and third [shown as stars in Fig. 4(a)] order stop gap shift to shorter wavelength region (high energy region) with increase in angle of incidence of light. Also in Fig. 4(b), the variation of the reflection peak arising due to the anticrossing of the bands is shown as stars. This peak also shifts toward the high-energy side with increase in angle of incidence. But the peak corresponding to van Hove singular point [shown as circles in Figs. 4(a) and 4(b)] shifts toward the longer wavelength region (low energy region) as shown by the photon density of states calculations [34]. In Ref. [34], the density of states is calculated for different crystal directions. In that work, for light incident along LW and LK directions of the reciprocal lattice, the van Hove singular point moves towards the first order gap and at high angles of incidence the van Hove singular point merges with the photonic stop band. For light incident along the LU direction, the van Hove singular point is high in energy and is not merging with the photonic stop band. In our case, even at an angle of incidence of 68°, the van Hove singular point is well outside the gap indicating that the direction of propagation of light is along the LU direction.

It is clear from Figs. 4(a) and 4(b) that the van Hove singular point shifts towards the first order band edge with increase in angle of incidence of light. The presence of this singularity near the band edges is the reason for the observation of localization of light near the band edges as observed in Ref. [26]. This van Hove singularity or the saddle point marks the onset of diffraction in directions other than the incident and reflected direction and this onset of diffraction moves to lower energy (higher wavelength) as the angle of incidence increases [24,34]. In the present work, the experimentally measured onset of diffraction is at 1.17 $a/\lambda$ for an angle of incidence of 8°, at 1.08 $a/\lambda$ for an angle of incidence of 30°, and at 1.04 $a/\lambda$ for an angle of incidence of 60°. These values fairly match with the onset of diffraction values calculated in Ref. [34]. This van Hove singular point is observed for samples made using VDM and HDM with spheres having diameters of 488 nm and 280 nm. This feature is also observed for PS photonic crystal made using spheres of very low diameter of 165 nm (not shown here).

We also analyzed the optical spectra in the high energy region for a low index-contrast photonic crystal made using PMMA spheres (index contrast is 0.48 as against 0.59 for PS photonic crystal). The measured optical reflection spectrum at an incidence angle of 8° is shown in Fig. 5(a). The first order gap appears at 0.68 $a/\lambda$, along with other peaks in reflection, the prominent ones being the peak marked with a thick arrow at 1.22 $a/\lambda$ and the peak shown using a thin arrow at 1.36 $a/\lambda$. Figure 5(b) shows the optical spectrum in the high energy region at different angles of incidence of light. As observed for the case of PS photonic crystals, the peak due to second order diffraction from (111) plane shifts towards the high energy region, but the peak shown by the thick arrow in Fig. 5(a) shifts towards the low energy region. This latter peak is associated with the van Hove singular point. The onset of diffraction is now at 1.22 $a/\lambda$ at an incidence angle of 8° due to the reduction in index contrast [24]. The peak near 2.0 $a/\lambda$ at 15° is due to third-order diffraction, which also follows the modified Bragg’s law with incident angle variation. Thus the high energy response of a photonic crystal having less index contrast is also well resolved and the van Hove singular point is also observed in the low index-contrast photonic crystals. This is in contrast to the claim by authors in Ref. [33] that, for a bare photonic crystal, only a single second order Bragg peak can be observed in the high energy regions, while the multiple high energy features can be observed only in the case of strongly photonic crystals where index contrast is larger. With the present results, it is conclusively demonstrated that the optical properties associated with the high energy features can be observed irrespective of the index contrast and the sphere diameter, since
it is an inherent property of the photonic crystal requiring only the perfect periodic arrangement of the spheres.

IV. CONCLUSIONS

Self-assembled 3D ordered photonic crystals were fabricated using organic materials with the first-order photonic stop band in the visible and near-IR region using the well-known vertical self-assembling method and the recently reported inward growing self-assembling technique. The optical spectra showed the well resolved first order photonic stop band at the wavelength corresponding to the sphere diameter and refractive index of the materials used for the fabrication of photonic crystals. Optical responses of the photonic crystals were analyzed in the high energy region by means of angle-resolved reflection spectra for $a/\lambda > 0.8$. The appearance of second and third order diffraction indicates the perfect ordering present in the samples. The second and third order diffraction peaks followed the trend suggested by the modified Bragg’s law for angle-resolved reflectance while another peak in the reflectance spectrum showed the opposite trend.

This latter peak is attributed to the presence of saddle point van Hove singularity as in the case of electronic crystals. This trend is observed for photonic crystals having different diameters and index contrast. The observed optical features agree well with the theoretical predictions reported in the literature. The high quality of the photonic crystals fabricated in this work allows the observation of the van Hove singular point even at near-normal incidence of light.

The van Hove singular point and the other high energy features are reproduced for photonic crystals made using different materials and different self assembling fabrication techniques. The appearance of van Hove singularity and the high energy bands even in lower index contrast photonic crystals confirms that these features are the consequences of perfect periodic nature of the crystals and not due to any structural disorder. Experiments designed to study the nonlinear optical effects as well as emission characteristics of active species embedded in photonic crystals at wavelengths near the van Hove singular point, where the local density of states is larger similar to a localized state, are required for a thorough understanding of these properties.

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Observation of higher-order diffraction ...

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