Spectral properties of opal-based photonic crystals having a SiO_2 matrix

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We study the transmission and reflection of electromagnetic waves propagating in bare opal photonic crystals. We find that the incomplete gap at the L point fully inhibits the transmission of waves propagating in the [111] direction for opal sample thicknesses that are easily obtainable. This property shows that bare opals could be good candidates for complete inhibition of transmission in the near-infrared and visible frequency range for given orientations. The dependence of the total reflectance on the angle of incidence has been calculated, and a good agreement has been found with available experimental data. We have also analyzed the modification of the transmission properties of bare opals induced by a sintering process. Our calculation predicts a linear decreasing of L-midgap frequency when the filling fraction decreases due to sintering, which is also in accordance with experiments. [S0163-1829(99)07239-2]

I. INTRODUCTION

Since the pioneering work of Yablonovitch[1] and John[2] it is now well acknowledged that three-dimensional periodic dielectric structures have the ability to control the propagation of electromagnetic waves.[3–5] Such systems, so-called photonic crystals, exhibit frequency ranges or photonic band gaps (PBG) where the electromagnetic waves cannot propagate. These gaps may exist over the whole Brillouin zone or only within a limited range of wave vectors, defining absolute or incomplete band gaps, respectively. At frequencies within absolute band gaps, the wave propagation is forbidden whatever the propagation direction, whereas for incomplete gaps only a limited domain of propagation directions are not allowed. In the microwave regime, photonic crystals with an absolute band gap can be easily fabricated by drilling holes in dielectric materials[6] or building the structure layer by layer.[7] Conversely, the construction of 3D photonic crystals with gaps in the visible or near-infrared frequency range requires engineering of complex microstructures, which are very difficult to realize by etching or microfabrication.[8] Consequently, many studies have been devoted to investigating self-ordered systems such as colloidal crystals[9] and materials made of three-dimensional arrays of dielectric spheres.[10] Among these, synthetic opals are very promising.[11,12] Synthetic bare opals are constituted by SiO_2 spheres that organize themselves by a sedimentation process in a face centered cubic (fcc) arrangement. Structures with a narrow distribution of diameters, lower than 5%, and perfect ordering (over ten microns) can now be synthesized. However, the refractive index contrast between silica and air is weak (1.5:1) and therefore bare opals exhibit no complete gaps even if the voids are partially in filled with semiconductor.[13–19] Progress in epitaxial techniques has shown that it is possible to use the bare opals as templates to realize materials called inverted opals.[20,21] For inverted opals the voids between the silica spheres are first filled with semiconductors of high-dielectric constant. Calculations of band structure of these inverted opals[22] show that a complete band gap appears between the eighth and ninth band provided that the two-component refractive index ratio is larger than 2.9 as long as the voids are fully in filled. In order to achieve the needed dielectric contrast, silica is then dissolved by chemical means so that the resulting material consists of air spheres separated by semiconductor veins. Resonant cavities can be designed to localize light of the corresponding range

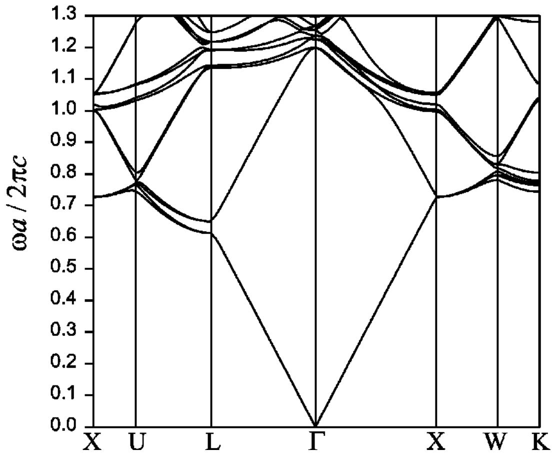

FIG. 1. Photonic band-gap structure along important symmetry lines in the Brillouin zone for bare opals, i.e., a close-packed fcc arrangement of silica spheres ($n = 1.5$) in air, which corresponds to a filling factor equal to 74%.

of frequencies. However, it is not a simple task to in-fill completely the voids in opals and many technical difficulties have to be overcome to achieve structures showing complete gaps. For devices other than cavities, it may be sufficient to take advantage of incomplete gaps that exist in bare opals that are more easy to fabricate. When the conditions of use for photonic crystals are well defined it is possible to orientate the crystal such that electromagnetic waves impinge on the entrance face at a well-defined angle of incidence. The existence of a band gap in this direction prevents the wave propagation. Therefore it is interesting to determine the characteristics of these gaps in order to attain their suitability for the control of light. Two parameters are important in this perspective: the width of the gaps, and the attenuation length, which measures the variation of the optical transmission and reflection when thickness of photonic crystal varies.

In this paper, we study the transmission and reflection properties of opal photonic crystals which consist of close-packed fcc arrangements of silica spheres in air. We are particularly interested in the incomplete band gaps appearing at low-frequency range for several propagation directions. We also study how these gaps are modified by the sintering process that is usually produced in order to increase the opal strength, prior to the in filling of the voids by a semiconductor. Several studies of the photonic band structure of fcc dielectric media have been carried out, mainly in relation with the opening of a gap at the W point.[23–26] More recently,[27–30] there is a renewed interest of these structures in connection with the photonic properties of inverted opals. However, up to date, little emphasis has been placed on the analysis of the reflection and transmission properties of bare and sintered synthetic opals.

II. TRANSMISSION ALONG [111] AND [100]

To facilitate the understanding of the reflection and transmission properties of bare opals, Fig. 1 shows the photonic band structure along the important symmetry lines of the Brillouin zone. We have considered a fcc close-packed structure of SiO_2 spheres with a refractive index $n_s = 1.5$ in air, the filling factor is 74%. The band structure was calculated using the plane wave method. To obtain good convergence over the considered energy range, 1067 plane waves of the reciprocal lattice are included in the calculation. Results are presented in terms of reduced frequencies $\omega a/2\pi c = a/\lambda$ where a is the lattice constant, c the speed of light in a vacuum, and the λ the vacuum wavelength. Since the refractive contrast is low (1.5:1), the band structure is nearly free-photon like. There are no complete gaps. First, consider the frequency distribution near the L point $[k_L = \pi/a\,(111)]$ that determines the transmission properties of the electromagnetic waves propagating along the [111] direction: a gap appears at reduced frequencies of 0.63, being its relative width, defined as the ratio between the gap width and the midgap frequency, 5.7%. At the X point $[k_X = 2\pi/a\,(100)]$, the band gap at 0.73 is virtually closed because the corresponding dielectric Fourier component is very small for close-packed configurations. Moreover, the energy of this gap is different from the lowest gap found at the L point due to the nonsphericity of the Brillouin zone.

We have calculated the transmission of bare opals for plane waves impinging at normal incidence on (111) and (100) surfaces using the transfer matrix method (TMM) introduced by Pendry and MacKinnon[31] to calculate the propagation of the electromagnetic waves through slabs of finite thickness. To study the (100) case we have employed the usual cubic cell of side a. In order to obtain good convergence we have used up to $26\times26\times26$ grid points inside the unit cell. With regards to the (111) case, we use a prismatic cell to simulate the opal oriented along this direction. Good accuracy is achieved using up to $7\times13\times18$ grid points.

Figures 2(a) and 2(b) show the transmission calculated for plane waves at normal incidence on (111) and (100) surfaces, respectively, for several slabs with a different number N of layers. Results are plotted in the frequency range around the lowest energy gap. Along the [111] direction, the distance between two identical planes of spheres is $a\sqrt{3}$. A minimum transmission appears at 0.63 due to the existence of a gap at the L point as predicted by the photonic band structure (see Fig. 1). As the thickness L of the slab increases, the transmission becomes weaker and reaches a level 10^{-4} for a slab of thickness $L = 50a$. Although the gap is incomplete the attenuation is rather large. Since samples with such thickness can be fabricated with the present processes of growth, this procedure could be used to build up reflective systems with good performances. Along the [100] direction, whose distance between two identical planes is a, the minimum of the transmission appears near the center of the X gap; i.e., at 0.73. This minimum also decreases as the number of layers increases. It is remarkable that at thickness $L = 64a$ one found just 50% transmission. This is a consequence of the small size of the gap at point X.

In Fig. 3 we have plotted in a logarithmic scale the behavior of the transmission minima observed in Figs. 2(a) and 2(b) as a function of the slab thickness L. The behavior is fully linear either for the minimum in the [111] direction (dotted line) as well as the one in the [100] direction (full line). From the slope of the lines, we obtain the corresponding attenuation lengths: $\Lambda_{111} = 3.44a$ and $\Lambda_{100} = 87.4a$. For comparison, we have also reported in Fig. 3 the transmission

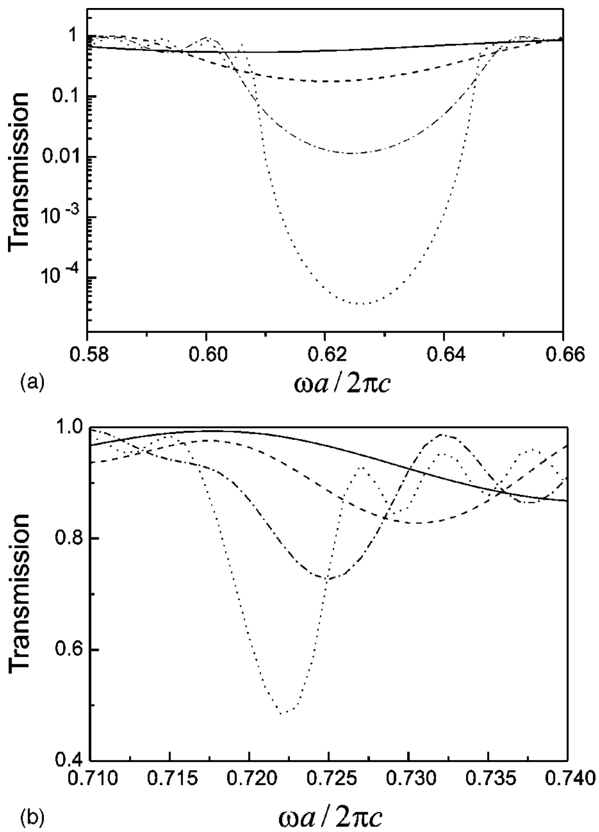

FIG. 2. (a) Transmission (in a logarithmic scale) of bare opals for normal incidence on the (111) surface for several slab thicknesses $L = Na\sqrt{3}$. Solid, dashed, dashed-dotted, and dotted correspond to $N = 4$, 8, 16, and 32, respectively. (b) The same for normal incidence on the (100) surface with $L = Na$. Solid, dashed, dashed-dotted, and dotted correspond to $N = 8$, 16, 32, and 64, respectively.

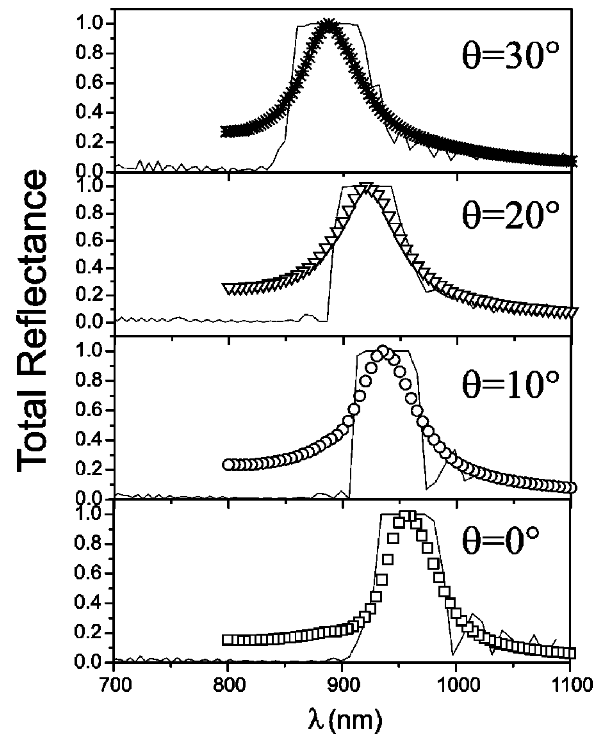

FIG. 4. Calculated (solid line) and experimental (symbols) total reflectance spectra of bare opals for several angles of incidence on (111) surface. The experimental data are normalized for a better comparison. The reflectance is calculated using the TMM with 128 monolayers.

of the same opal when the voids between the spheres are completely filled by a dielectric material with constant refractive index $n = 3$ (dashed line). Now, the decreasing is stronger due to the large value of the dielectric contrast (1.5:3) and the attenuation length $\Lambda_{111} = 1.9a$. To obtain with bare opals the same attenuation as for in-filled opals requires about twice more layers. It should be noted that the in filling by a material with a large refractive index lowers appreciably the gap frequency.

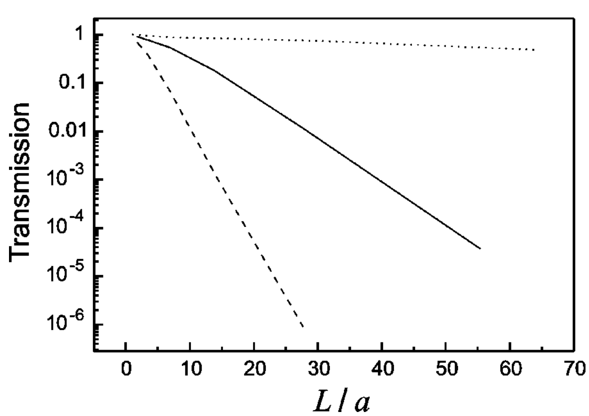

FIG. 3. Transmission at the center of the gap as a function of the slab thickness L. The solid line is for normal incidence on (111) surface of bare opal. The dotted line is for normal incidence on (100) surface of bare opal. Finally, the dashed line plots the results obtained for an opal fully in-filled with a dielectric material with constant refractive index $n = 3$.

III. ANGLE-RESOLVED REFLECTION AND COMPARISON WITH EXPERIMENTS

We have also analyzed the angular dependence of the total reflectance for the case of electromagnetic waves impinging the (111) surface, which is the surface of interest in the bare opal system. In Fig. 4 we plot, for several incident angles, the comparison between the reflectance peaks calculated using the TMM and the ones experimentally measured using absorption techniques.[32] The refraction index of silica spheres has been taken as $n_{SiO_2} = 1.45$ because they are slightly porous. The sphere diameter d has been fitted to obtain a perfect coincidence with the spectral position of the experimental peak maxima. Results showed in Fig. 4 has been obtained using 431-nm spheres in the calculations. It is noteworthy the overall good agreement at any angle of both the peak maxima positions and its shape. The reflectance peak maxima show a dependence with the impinging angle θ that follows the Bragg law

$$\lambda_{max} = 2d_{111}\sqrt{n_{eff}^2 - \sin^2\theta}, \tag{1}$$

where d_{111} is the separation between (111) planes, and n_{eff} is an effective refractive index. Since $d_{111} = 0.816d$, is known by fitting, one can use Eq. (1) to give n_{eff}.

This diameter size obtained from our calculation compared fairly well with the one given by the experimentalist, 440 nm. This size has been estimated by the fitting of the experimental peaks to a simple Bragg law using as input parameter the effective refractive index $n_{eff}=1.33$. This value corresponds to the average model $n_{eff}=n_{SiO_2}f+n_{air}(1-f)$, where f is the filling fraction of the spheres $(f=0.74)$. Since our calculation contains the full microstructure of the bare opal problem, we can conclude that the simple Bragg law produces a systematic overestimation of this diameter in around 2.5%. As regards the dependence on the azimuthal angle, we have found no dependence at low values of θ, as it is theoretically expected.

Therefore, we can conclude that the TMM is a useful tool to analyze the angular dependence of the reflectance in bare opal systems, and can be used to give accurately the diameter size of the silica spheres forming the opal.

IV. SINTERING EFFECTS

The fabrication of inverted opals requires that the structure formed by the filled voids be sufficiently robust. This property of robustness is unlikely to happen if the voids are interconnected just by the point contact between close-packed spheres. A sintering process of the opal produces the enlargement of the contact section between nearest-neighbors silica spheres. This process results in the formation of necks that can be used as channels of escape for the chemically dissolved silica.[32]

In this section, we analyze the effect of the sintering process on the reflectance properties of bare opals. The sintering consists of a shrinkage of the lattice constant produced by temperature when it increases above 950°.[32] Any given higher temperature shrinks the lattice constant to a value a' which is a fraction of the original one $a'=\eta a$ $(\eta\leqslant 1)$.

Theoretically, we have simulated this effect by allowing the overlapping between silica spheres. We have calculated the band gap at the L and X points by solving the Maxwell equations either by the plane-wave method and by a finite difference time domain method (FDTD).[33] Similar results were obtained with both methods. The main conclusion of this part is that the L pseudogap decreases for decreasing filling fraction. Figure 5(a) shows the sintering effects on the midgap energy as well as on the relative width $\Delta\omega/\omega_c$ (ratio between gap width and midgap frequency). For the sake of comparison we have also included the predictions made using the simple Bragg law on ω_c (full line); it coincides when the system is uniform and deviates when the void increases in size. Therefore, at a given lattice parameter, the very simple analytical model of Eq. (1) underestimates the energies at a given lattice parameter. This conclusion confirms the results of the later section: any fit of experiments performed using the Bragg law will overestimate the lattice constant. Regarding the relative width, it decreases continuously as a consequence of the band-gap closing.

The variation of the X pseudogap under sintering is rather different [see Fig. 5(b)]. As it is virtually closed when the spheres are just in contact, the gap opens up with decreasing filling fraction up to the voids are reduced to 5%. Then it progressively closes until the complete filling by silica. This

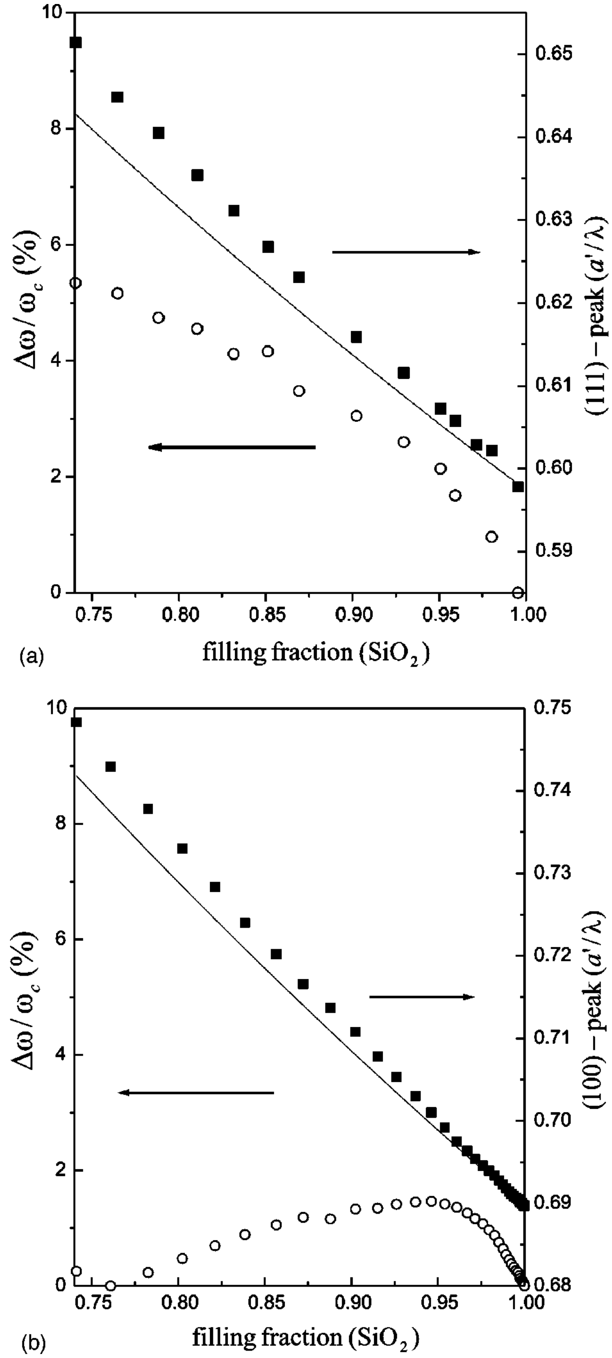

FIG. 5. (a) Behavior of the relative width and the midgap energy (in reduced units) of the pseudogap at the L point as a function of the filling fraction. $a'=\eta a$, where $\eta\leqslant 1$ is the shrinkage produced by the sintering on the initial lattice constant a. The full line calculates the same effect using the Bragg law, Eq. (1), using an effective dielectric function. (b) The same for the X point.

behavior stems from the Fourier transform of the dielectric constant which is zero for close-packed configuration then increases when the diameter of the spheres increases up to the uniform filling of the voids by silica cancels the gap.

V. CONCLUSION

We have reported spectral properties of photonic crystals based on artificial opals consisting of SiO_2 spheres stacked in a fcc structure. The state of the art in the different numerical techniques (transfer matrix, plane-wave, and finite difference time-domain methods) has been employed to fully characterize the incomplete band gaps at the L and X points of the fcc structure. The angle dependence of the reflectance shows a very good agreement with available experiments and let us conclude that the Bragg law used to determine the diameter of spheres in the opal overestimate its size. Also, we have studied the tunability of the gap produced by sintering. We conclude the feasibility of this structure to construct mirrors for near optical frequencies.

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