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Higher order Bragg diffraction by strongly photonic *fcc* crystals: onset of a photonic bandgap

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Abstract

We have measured angle-resolved reflectivity of *fcc* photonic crystals made of air spheres in titania (TiO_2), with lattice constants between 830 and 860 nm, that strongly interact with light. At normal incidence, we observe three new Bragg peaks at frequencies of 14800, 16700 and 18100 cm^{-1} in the range of 2nd order diffraction. The peak frequencies have negligible dispersion over more than 30° angular range, unlike usual Bragg diffraction. The number, center frequencies and angular range of the peaks agree well with stop gaps in photonic bandstructures, computed for a model wherein the TiO_2 is distributed in shells about close-packed and interconnected air spheres. It appears that higher-order Bragg diffraction in strongly photonic crystals is caused by a complex coupling of many Bloch waves that results in dispersionless bands. The computed stop gaps persist for stronger photonic crystals with larger filling fraction or increased dielectric contrast. The 16700 cm^{-1} peak is the precursor of a complete photonic band gap. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Photonic crystals are three-dimensional composites of dielectric materials with a periodicity of the order of the wavelength of light [1–4]. Due to the periodic variation of the dielectric constant, the crystals possess photonic band structures, analogous to electronic band structures in solid state physics [5]. Incident waves that satisfy the Bragg condition for a set of lattice planes are diffracted for a range of frequencies, a stop band [6]. The widths of stop bands gauge the interaction strength between light and a crystal, and increase with the dielectric contrast [7,8]. For weakly photonic crystals, the edge frequencies of a stop gap increase with angles of incidence away from the normal, following the well-known Bragg law [6,7]. With increasing photonic interaction and increasing frequency, light can diffract from more than one set of lattice planes simultaneously. Such multiple Bragg diffraction results in band repulsions between Bloch states, causing the frequencies of the edges of the stop gaps to become independent of angle of incidence [9]. In the limit of strong photonic interaction, many Bloch states interact so strongly that the edges of the stop gaps hardly vary for all propagation directions. This results in a common gap for *all* directions and all

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polarizations: a photonic band gap. Photonic band gaps are eagerly pursued in order to completely control emission from light sources or to localize photons [1–4].

Many groups are presently making strongly photonic crystals using process engineering [10,11]) or self-assembly [12,13] methods. A complete photonic band gap has yet to be identified for various material reasons, ranging from finite size effects to insufficient dielectric contrast. On the diagnostic side, one may wonder what experimental features are characteristic of a photonic band gap or even the onset of such? In prior work in the microwave regime, photonic band gaps have been identified as the range of frequencies for which transmission stop bands overlap for many directions of incidence [14,15]. A difficulty with this method is that apparent stop bands can also be caused by ''uncoupled'' modes, with a symmetry that impedes coupling to (plane) waves outside the crystal [16,17], or by modes whose peculiar (k,ω)-dispersion hampers the impedance matching to waves outside the crystal. Therefore, complementary band structure calculations are usually necessary to confirm the presence of a band gap [14,15]. For self-assembled systems that usually form face-centered cubic (*fcc*) crystals, the question is even more appropriate: for dielectric contrasts larger than 7.84 a band gap is predicted between the 8th and 9th Bloch bands [18,19]. This is the frequency range of (222) Bragg diffraction, also referred to as 2nd order diffraction [5]. In this range, the dispersion relations are strongly modified by multiple Bragg-wave coupling [9]. Surprisingly, there have been no studies of photonic crystals in the frequency range beyond 1st order Bragg diffraction to date.

Here, we present angle-resolved reflectivity measurements on carefully grown, strongly photonic *fcc* crystals of air spheres in titania. At normal incidence, we observe three new Bragg peaks at frequencies of 14800, 16700 and 18100 cm^{-1}, beyond the (111) 1st order Bragg diffraction at 8700 cm^{-1}. With increasing reflection angle, the highest frequency reflection band remains at the same frequency to within its bandwidth, unlike the usual Bragg behavior. The lower frequency bands also have weak dispersion but they disappear near 30°. We identify the new peaks with stop gaps in photonic band structures, computed for a model wherein the TiO_2 is distributed in shells on close-packed and interconnected air spheres. The existence and characteristics of the higher-order stop gaps are very sensitive to the dielectric topology in the crystal compared to the 1st order stop gaps. The new stop gaps occur in the frequency region where 2nd order (222) Bragg diffraction would occur in a weakly photonic crystal, and where a complete photonic band gap is expected in a strongly photonic crystal. In strongly photonic crystals, the usual higher-order Bragg diffraction has changed to a complex coupling of many Bloch waves, that causes reflection bands to display little dispersion. The 16700 cm^{-1} peak is the precursor of the photonic band gap, although the dielectric contrast of our samples is just below that needed to achieve such a gap. As a corollary, we note that the observation of dispersionless reflectivity or transmission bands is not unambiguous evidence of a complete photonic band gap.

2. Experimental

We have recently reported a novel method for the creation of strongly photonic crystals consisting of an *fcc* arrangement of air spheres in a titania (TiO_2) backbone [13]. Improved growth techniques have led to large crystal domains of high quality: synchrotron small angle X-ray scattering (SAXS) experiments reveal single crystal diffraction patterns for X-ray beam diameters as large as 500 μm [20]. The X-ray patterns show Bragg peaks with Miller indices as a high as $hkl = 880$, indicating excellent crystalline order with mean square displacements of the air spheres less than a few percent of the lattice parameter. Scanning electron microscopy and SAXS indicate that the air spheres are close-packed, and are connected by windows or channels (cf. Fig. 2b of [13]). We have studied samples with lattice parameters $830 < a < 860$ nm and a TiO_2 volume fraction of $0.06 < \varphi < 0.12$ [20]. From the (111) Bragg reflection frequency (8700 cm^{-1}) and the values of a and φ, we derive that the dielectric constant of the TiO_2 in the crystals is equal to the bulk value of about 6.25 at that frequency [21]. This result contrasts with structures of porous, lower-index TiO_2 that has been obtained elsewhere by other means [22]. Our samples have lateral dimensions of several mm and thicknesses of ~ 200 μm. Under white light illumination, the samples reveal red, orange, and greenish opalescence. Suitable spots on the samples were selected by visual inspection of the reflection of a red He–Ne laser beam that co-propagates with the broad band beam of the reflectivity setup. Spectra for the specular component of the reflected light from [111] faces were obtained as a function of angle of incidence α with the same setup as used previously [9]. The diffraction vector is in the plane spanned by the [111] and $[11\bar{2}]$ axes, i.e., the plane through the Γ, U, L, K points of the *fcc* Brillouin zone of reciprocal space [5]. Reflectivity was calibrated by rationing to spectra taken off a fresh silver mirror. The angular resolution in the experiments is $\pm 5°$.

3. Results

Fig. 1 shows the optical reflection spectrum taken at normal incidence for a crystal with $a = 860$ nm. The strong peak at 8700 cm^{-1} is the previously observed $hkl = 111$, 1st order Bragg diffraction peak (cf. Ref. [8,9]), whose broad width (fwhm) of 13% of the center frequency confirms the strong interaction between light and the crystal. We observe *three* strong new peaks with reflectivities up to 30%, at frequencies of 14830, 16760, and 18070 cm^{-1}, in

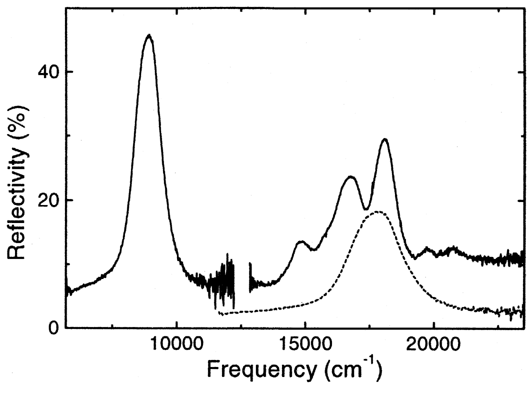

Fig. 1. Reflection spectra for titania air-sphere crystals at normal incidence as a function of frequency $(\omega/2\pi c)$ in wave numbers (solid curves). The peak at 8700 cm^{-1} is the *fcc* (111) 1st order Bragg reflection. The three peaks at 14830, 16760, and 18070 cm^{-1} are in the range of 2nd order diffraction. For comparison, the dashed peak at 17600 cm^{-1} is the (111) peak plotted at double the frequency (and reduced in reflectivity) as an estimate of a (222) 2nd order Bragg peak in the weak photonic limit.

agreement with the visually observed colors. There is tentative evidence of weak features at 19800 and 20600 cm^{-1}, but we will not consider these further. For comparison, in Fig. 1, we plot the (111) 1st order peak at twice its frequency to simulate a (222) 2nd order peak that may be expected on the basis of simple Bragg diffraction from weakly photonic crystals [5,6]. The comparison shows that the new bands occur in the range of 2nd order Bragg diffraction, although they clearly differ from usual 2nd order diffraction. Experiments on crystals with $a = 830$ nm reveal similar peaks, systematically shifted to higher frequencies by ~ 1000 cm^{-1}. This agrees with an inverse relation between frequency and a and confirms that the new peaks are Bragg diffraction-like. We exclude that the three new peaks are the result of sample imperfections:

1) If each of the new peaks were caused by crystal domains with discretely different lattice parameters, there should be a corresponding set of 1st order diffraction peaks. Clearly, this is not the case.

2) If the overall reflection band from 14000 to 18500 cm^{-1} were the result of crystal strain effects, a strain distribution with a width of $\sim 4500/16250 = 25\%$ would be implied. Such a huge strain can not be sustained by a crystal, since strains in excess of 5 to 10 % already result in amorphization or phase separation [23,24]. The hypothesis is also at variance with the observation of strong reflection peaks, and with the highly ordered structures evidenced by electron microscopy and X-ray scattering [8,13,20]. A large strain distributed over length scales much longer than a unit cell is excluded in the previous point.

3) Reflection experiments on weakly photonic colloidal crystals, that are the parent structures of air-sphere crystals, reveal a single 2nd order peak at twice the frequency of the 1st order diffraction peak (not shown here), in agreement with simple Bragg diffraction [6].

The observation of He–Ne laser reflection with little speckle indicates that the samples have good surface quality. The less than 100% reflectivity observed is possibly due to the white-light beam averaging a 10 times larger area than the He–Ne beam, or to residual crystal disorder, both of which are not expected to influence the shape of the spectra.

Fig. 2 displays the high frequency component of the spectra at 0°, 15°, 30°, and 45°. Compared to

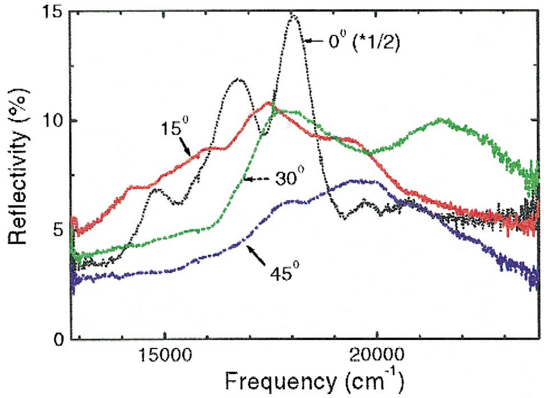

Fig. 2. (color) Reflection spectra of titania air-sphere crystals for angles of incidence of 0° (dotted curve, multiplied by 0.5), 15° (red solid curve), 30° (green dashed curve), and 45° (blue dash-dotted curve).

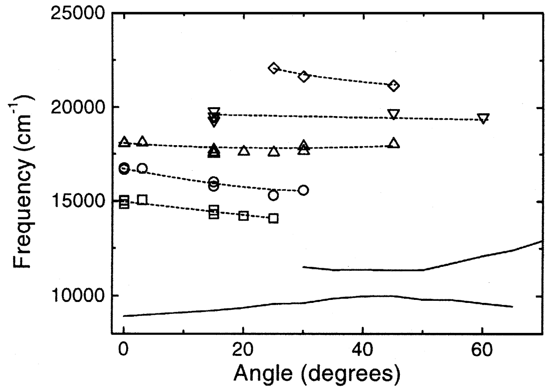

Fig. 3. Frequencies of the higher order reflection bands as a function of reflection angle α. Symbols are experimental data, dashed curves are guides to the eye. Drawn curves are the 1st order diffraction peaks, that show an avoided crossing due to multiple diffraction, see Ref. [9].

normal incidence, the peaks in the 15° spectrum have broadened and shifted down by ~ 500 cm^{-1}, the reflectivity is reduced, and a new component has appeared at 19200 cm^{-1}. At 30°, the overall spectrum has shifted to the blue, in qualitative agreement with Bragg behavior. The 14800 cm^{-1} and the 16000 cm^{-1} bands have disappeared, and there is a broad band centered at 17800 cm^{-1}. At 45°, there are bands at 18000, 19800, and 21000 cm^{-1}. The decrease in reflectivity amplitude with angle may be due to surface boundary conditions or multiple Bragg diffraction and grating modes that take light into non-specular directions.

Fig. 3 shows the peak frequencies of the dominant reflection bands as a function of angle, to within our ability to define center frequencies of the broad features. The band at 14800 cm^{-1} (squares) and the band at 16800 cm^{-1} (circles) shift to slightly lower frequencies with increasing angle, before vanishing near 30°. The band at 18100 cm^{-1} (upward triangles) shifts less than 500 cm^{-1} in the range 0–45°. At about 15°, a band appears at 19800 cm^{-1} (downward triangles) and remains to 60°. At 30°, a band appears at 22000 cm^{-1} that shifts down to ~ 21000 cm^{-1} at 45°. Between 25 and 45°, a band occurs near 22000 cm^{-1}. It is striking that the reflection peaks hardly shift over the angular range in which they exist. A shift on the order of $1/(\cos\alpha)$, often observed for 1st order Bragg diffraction, would be anticipated on the basis of simple Bragg diffraction. For example, the 18100 cm^{-1}-band could be expected to shift to 20900 cm^{-1} at 30°. This indicates that a simple Bragg diffraction model is not appropriate at high frequencies. A small dispersion is typical of strongly coupled Bloch modes associated with multiple Bragg diffraction [9].

4. Model calculations and discussion

To obtain insight into our observations, we have computed the photonic band structures for our air-

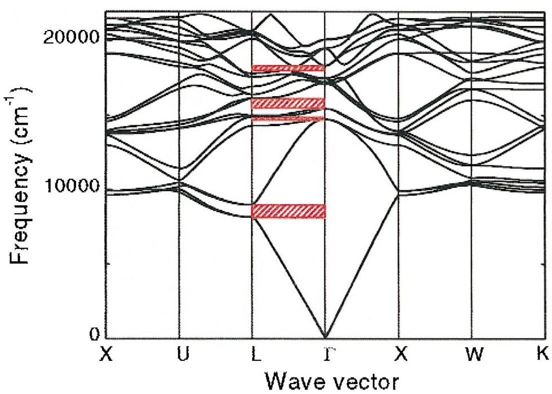

Fig. 4. (color) Photonic band structures for our titania air-sphere crystals, between common high-symmetry points in the Brillouin zone [5]. The results are computed with a model of dielectric shells with inner radius 1.0, outer radius 1.09, and connecting windows between the air spheres with radius 0.4. The dielectric constant of the TiO_2 is $\varepsilon = 6.5$, the lattice parameter is 860 nm, and 339 plane waves have been used. Stop gaps in the $\Gamma - L$ direction are indicated by hatched boxes.

sphere crystals by the well-known plane-wave expansion method for vector waves [3,4]. Each of the eigenmodes for frequency ω and wave vector $\mathbf{k}$ is represented as

$$E_{\mathbf{k}}^{\omega}(r,t) = \exp(-\mathrm{i}\,\omega t)\sum E_{\mathbf{k},\mathbf{G}}^{\omega}\exp[\mathrm{i}(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}],$$

where the sum extends over all reciprocal lattice vectors $\mathbf{G}$ [5]. We have used a spatially dependent dielectric function $\varepsilon(\mathbf{r})$ that corresponds closely to the detailed structure obtained from SAXS and scanning electron microscopy experiments [13,20]. the *fcc* crystals are well described by overlapping shells of dielectric material (titania), with inner radius 1.0 (touching close-packed air spheres) and outer radius 1.09 in units of the radius of close-packed spheres. This leaves the characteristic octagonal air voids seen e.g. in Fig. 2b of Ref. [13]. The air spheres inside the shells are connected to their twelve nearest neighbors by cylindrical windows with radius 0.4. The resulting TiO_2 filling fraction is $\varphi = 0.10$, the average for the samples considered. The dielectric constant of titania is taken as $\varepsilon = 6.5$, the isotropically averaged value for visible light [21]. Bandstructures were calculated using up to 339 plane waves, although for the first 20 bands discussed here the frequencies are defined to better than 1% for as few as 120 plane waves. As a check of earlier results [9] we note that the frequency (8700 cm^{-1}) and width (1100 cm^{-1}) of the (111) stop-gap at normal incidence are well reproduced.

Fig. 4 shows the bandstructure for our crystals along high symmetry directions in the *fcc* Brillouin zone, calculated for a lattice parameter $a = 860$ nm. We find three high frequency stop gaps beyond the 1st order stop gap (8700 cm^{-1}) between the Γ and L-points. These gaps can be directly compared to the reflectivity peaks at normal incidence, even though the peaks are somewhat asymmetrical: the gap between the 5th and the 6th bands centered at 14800 cm^{-1} coincides well with the reflection peak at 14830 cm^{-1}, the gap between the 8th and the 9th bands centered at 15800 cm^{-1} coincides reasonably with the reflectivity peak at 16760 cm^{-1}, and the gap between the 16th and 17th bands centered at 18100 cm^{-1} coincides very well with the reflection peak at 18070 cm^{-1}. The notion that the new high frequency peaks are unlike simple ($hkl = 222$) 2nd order Bragg diffraction is confirmed by the computations: the 14800 and 15800-stop gaps are very well reproduced by considering modes with $\mathbf{G} = (000), (111), (200)$, and symmetry related components. In contrast, usual (222) diffraction entails a combination of only two modes, namely (000) and (222) [6]. The results confirm theoretically that the observed phenomena are caused by many strongly coupled Bloch modes, associated with multiple Bragg diffraction [9].

Considering that we have not incorporated adjustable parameters or the natural dispersion of the dielectric constant in the model, the agreement with experimental results is gratifying. Additional computations indicate how sensitive the high frequency gaps are to details of the topology of the model, i.e., the details of $\varepsilon(\mathbf{r})$. If we eliminate the connecting windows altogether, while increasing the outer radius of the titania shells to ~ 1.1 to keep φ constant, no high frequency stop-gaps occur. If we increase φ to its maximum value (0.26) in a close-packed *fcc* crystal of air spheres and increase ε of the backbone to 7.84, all three gaps survive but only the one between the 8th and 9th bands develops into a complete photonic gap, in agreement with earlier work [18,19]. These results indicate that the reflectivity peak at 16700 cm^{-1} is the precursor of the photonic band gap.

Calculations of the band structure along directions at an angle θ with respect to the Γ–L direction, toward the U-point, indicate that the lowest stop-gap collapses for $\theta \sim 10°$ while the two higher gaps collapse for $\theta \sim 15°$. Although the theoretical gaps collapse in the same angular sequence and range as the experimentally observed decrease of the reflectivity peaks at 14830, 16760, and 18070 cm^{-1}, a quantitative comparison with experiment is a challenge, and the interpretation of the features at 19800 and 22000 cm^{-1} remains open. Since plane wave band structure calculations assume infinitely large crystals, effects caused by coupling of the light from outside to inside a crystal are neglected. Experimentally, wave vector projection effects are well understood in the range of 1st order diffraction (see Refs. [8,14,15]), but these effects are compounded at higher frequencies, e.g., by grating modes (see below). This makes it difficult to directly compare external (α) and internal (θ) angles of propagation. Interpretation of the complex reflection patterns at high frequencies where the photonic band gap is expected, call for real-space calculations, such as finite difference time domain or transfer matrix techniques.

In experiments on 2D photonic crystals, Labilloy et al. have found that surface grating modes can play an important role in the study of the optical properties of photonic crystals [25]. In our case, the longest surface grating period is $d = \sqrt{(3/8)}\, a_{fcc} = 526$ nm. At normal incidence, the 1st order grating mode propagates in air with a maximum wavelength of 526 nm, or a minimum frequency of 19000 cm^{-1}, which is not relevant, see Fig. 1. For oblique incidence, however, the cut-off frequency shifts down, e.g. to 12700 cm^{-1} at $\alpha = 30°$, hence the grating modes may become relevant and reduce the apparent reflectivity of the higher order Bragg diffraction.

If considerations of conserved momentum parallel to the crystal surface [8,14,15] are assumed in the frequency range of the newly observed peaks, the next Brillouin zone is reached at angles of about 30°. Hence the observed bands would be dispersionless over the whole face of the relevant Brillouin zone [5], a characteristic that might be expected for a crystal possessing a complete band-gap. On the other hand, the band structures in Fig. 4 do not reveal a photonic band gap for the *fcc* titania crystals. These facts taken together warrant a note of caution in using reflectivity (or transmission) data to define a complete gap. On the other hand, two experimental probes of photonic band gaps have recently been proposed: Megens et al. predict that a band gap can be identified by a stop band with an attenuation close to a hundred percent in the emission spectrum of light sources inside a photonic crystal [26]. Imhof et al. [27] have observed that edges of photonic gaps appear as divergences of the group velocity dispersion, while the dispersion is zero inside gaps. This method applied for all directions of propagation thus also identifies a photonic band gap.

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