Physica Scripta. Vol. T66, 146–150, 1996

Photonic Band Gap Materials: The "Semiconductors" of the Future?

C. M. Soukoulis

Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, IA 50011 U.S.A.

Received April 22, 1996; accepted April 24, 1996

Abstract

An overview of the theoretical and experimental efforts in obtaining a photonic band gap, a frequency band in three-dimensional dielectric structures in which electromagnetic waves are forbidden, is presented.

1. Introduction and history

Electron waves traveling in the periodic potential of a crystal are arranged into energy bands separated by gaps in which propagating states are prohibited [1]. It is interesting to see if analogous band gaps exist when electromagnetic (EM) waves propagate in a periodic dielectric structure (e.g., a periodic lattice of dielectric spheres of dielectric constant ϵ_a embedded in a uniform dielectric background ϵ_b). If such a band gap or frequency gap exists, EM waves with frequencies inside the gap cannot propagate in any direction inside the material. These frequency gaps are referred to as "photonic band gaps".

Photonic band gaps can have a profound impact on many areas in pure and applied physics [2, 3]. Due to the absence of optical modes in the gap, spontaneous emission is suppressed for photons with frequencies in the forbidden region [4, 5]. It has been suggested that, by tuning the photonic band gap to overlap with the electronic band edge, the electron-hole recombination process can be controlled in a photonic band gap material, leading to enhanced efficiency and reduced noise in the operation of semiconductor lasers and other solid state devices [3, 5]. The suppression of spontaneous emission can also be used to prolong the lifetime of selected chemical species in catalytic processes [6]. Photonic band gap materials can also find applications in frequency-selective mirrors, band-pass filters, and resonators. Besides technical applications in various areas, scientists are interested in the possibility of observing the localization of EM waves by the introduction of defects and disorder in a photonic band gap material [7–9]. This will be an ideal realization of the phenomenon of localization uncomplicated by many-body effects present in the case of electron localization. Another interesting effect is that, zero-point fluctuations, which are present even in vacuum, are absent for frequencies inside a photonic gap. Electromagnetic interaction governs many properties of atoms, molecules, and solids. The absence of EM modes and zero point fluctuations inside the photonic gap can lead to unusual physical phenomena [7–12]. For example, atoms or molecules embedded in such a material can be locked in excited states if the photons emitted to release the excess energy have frequency within the forbidden gap. All the aforementioned ideas [3] about new physics and new technology hinge upon the assumption of the existence of material with photonic gaps.

To search for the appropriate structures, scientists at Bellcore employed a "cut-and-try" approach in which various periodic dielectric structures were fabricated in the microwave regime and the dispersion of EM waves were measured to see if a frequency gap existed [13]. The process was time consuming and not very successful. After attempting dozens of structures over a period of two years, Yablonovitch and Gmitter identified [13] only one structure with a photonic band gap. This structure consists of a periodic array of overlapping spherical holes inside a dielectric block. The centers of the holes are arranged in a face-centered-cubic (fcc) lattice and the holes occupy 86% of the volume of the block.

Stimulated by the experimental work, theorists became interested in the solution of the photonic band problem and in the search for structures with photonic band gaps. Early work in this area employed the "scalar wave approximation" which assumed the two polarizations of the EM waves can be treated separately, thus decoupling the problem into the solution of two scalar wave equations. When we first became involved with the photon band problem, calculations had already been completed for the experimental structure in the scalar wave approximation [14, 15]. The results showed the existence of a gap but the position and size of the gap were not in quantitative agreement with the experiment, indicating the need for a full vector wave treatment. It turned out from subsequent calculations that the errors made in neglecting the vector nature of the EM wave were more serious than initially anticipated, and the scalar wave calculations actually gave qualitatively wrong results.

The vector wave solution of Maxwell's equations for a periodic dielectric system was carried out independently by several groups shortly after the appearance of the scalar wave results [16–18]. All of the methods employ a plane wave expansion of the electromagnetic fields and use Bloch's theorem to reduce the problem to the solution of a set of linear equations.

When the photon band structure for the experimental fcc structure [13] of 86% air spheres in a dielectric matrix, was calculated [18], it showed that the experimental fcc structure does not have a complete photonic band gap for the lowest-lying bands. A very large depletion of DOS is found, called a "pseudo-gap". Actually, this result was also obtained earlier by two other groups [16, 17], although at that time we were not aware of their results. At this point, the existence of photonic gap materials was seriously doubted [19]. However, since we found that the plane wave

expansion method [16–18] can solve the photon band problem efficiently and much faster than the experimental "cut-and-try" method, we used it to investigate whether other structures could succeed where the fcc air sphere structure failed.

1.1. *Photonic band gap structures with the diamond lattice symmetry*

Ho, Chan, and Soukoulis were the first to give a prescription for a periodic dielectric structure [18] that possesses a full photonic band gap rather than a pseudogap. This proposed structure is a periodic arrangement of dielectric spheres in a diamond-like structure. A systematic examination [18] of the photonic band structures for dielectric spheres and air spheres on a diamond lattice, as a function of the refractive index contrasts and filling ratios, was made. It was found that photonic band gaps exist over a wide region of filling ratios for both dielectric spheres and air spheres for refractive-index contracts as low as 2. However, this diamond dielectric structure is not easy to fabricate, especially in the micron and submicron length scales for infrared or optical devices. However, after we communicated our findings about the diamond structure, Yablonovitch very quickly devised [20] an ingenious way of constructing a diamond lattice. He noted that the diamond lattice is a very open structure characterized by open channels along the [110] directions. Thus, by drilling cylindrical holes through a dielectric block, a structure with the symmetry of the diamond structure can be created. Since there are 6 sets of equivalent [110] directions in the lattice, there are 6 sets of holes drilled. If the crystal is oriented such that the [111] surface is exposed, then three sets of these holes will be slanted at angles of 35.26° with respect to the normal [111] direction. The remaining three sets of holes have their axes parallel to the [111] surface and are harder to make on a thin film oriented in the [111] direction. Thus, in the end, the experimentalists decided to abandon the second three sets of holes and construct a structure with only the first three sets of holes (see Fig. 15, in the article by Yablonovitch in Ref. [3]) which became the first experimental structure that demonstrates the existence of a photonic band gap, in agreement with the predictions [21] of the theoretical calculations. This is a successful example where the theory was used to design dielectric structures with desired properties.

We repeated our calculations for several variations on the diamond lattice [21]. One calculation uses the diamond lattice generated by 6 sets of air cylinders or dielectric cylinders in the six [110] directions. The other calculation uses a diamond rod lattice in which, instead of putting spheres at the lattice sites, we joined them together by nearest-neighbor rods. We also tested the effects on the photon band gap when 3 sets of cylinders are omitted in the 6-cylinder diamond structure. All of these structures exhibit photonic band gaps, with the best performance coming from a diamond rod lattice, which achieves a maximum gap of 30% for a refractive index contrast of 3.6.

Very narrow photonic band gaps (PBG) have also been found [22] in a simple cubic geometry. For 2D systems [23–25], theoretical studies have shown [23, 24] that a triangular lattice of air columns in a dielectric background is the best overall 2D structure, which gives the largest photonic gap with the smallest refractive index contrast. In addition, it was demonstrated [26–29] that lattice imperfections in a 2D and/or 3D periodic arrays of a dielectric material can give rise to fully localized EM wave functions. Experimental investigations of the photonic band gaps in either 2D or 3D have been mostly done [20, 26, 28, 29] at microwave frequencies because of the difficulty in fabricating ordered dielectric structures at optical length scales. In fact, the main challenge in the photonic band gap field is the discovery of a 3D dielectric structure that exhibits a photonic gap but, in addition, can be built by microfabrication techniques on the scale of optical wavelengths.

2. Layer-by-layer photonic band gap structures

The search for simplifying the structure and reducing the dimensionality of the structural building blocks continued. The Iowa State group has designed [30] a novel three-dimensional layer-by-layer structure that has a full three-dimensional photonic band gap over a wide range of structural parameters. The new structure (Fig. 1) consists of layers of one-dimensional rods with a stacking sequence that repeats every fourth layer with a repeat distance of c. Within each layer the rods are arranged in a simple one-dimensional pattern and are separated by a distance a, a significant simplification from the two-dimensional grid found earlier. The rods in the next layer are rotated by an angle θ which has the value of 90° but in general could vary from 90° to 60° but still have a full three-dimensional photonic band gap. The rods in the second neighbor plane are shifted by half the spacing, a, relative to rods in the first plane in a direction perpendicular to the rods. The rods in every alternate layer are parallel (Fig. 1). This structure has the symmetry of a face centered tetragonal (fct) lattice. For the special case of $c/a = \sqrt{2}$, the lattice can be derived from a fcc unit cell with a basis of two rods. This layered structure can be derived from diamond by replacing the 110 chains of atoms with the rods.

This structure was first fabricated [31] in the microwave regime by stacking alumina cylinders and demonstrated to have a full three-dimensional photonic band gap at microwave frequencies (12–14 GHz). A similar structure was also fabricated with alumina rods that had a band gap between 18 and 24 GHz. We have also fabricated [32–34] the layer-by-layer structure with rectangular rods of silicon by micro-

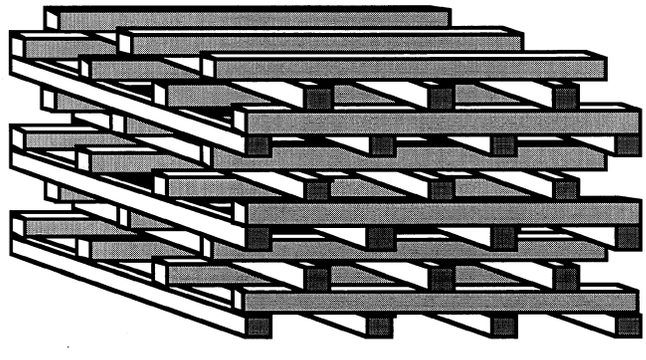

Fig. 1. The new layer-by-layer structure producing full three-dimensional photonic band gaps. The structure is constructed by an orderly stacking of dielectric rods, with a simple one-dimensional pattern of rods in each layer. Although rods of rectangular cross-section are shown here, the rods may also have cylindrical or elliptical cross sections.

machining silicon [110] wafers, using anisotropic etching properties of silicons and an orderly stacking procedure. The structure with rectangular Si-rods have been fabricated for three different length scales producing midgap frequencies of 95 GHz, 140 GHz, and 450 GHz using progressively thinner silicon wafers. In all three cases the band edge frequencies are in excellent agreement with the calculated values. The structure with midgap at 94 GHz has also been fabricated by laser machining alumina wafers, illustrating the usefulness of our layer-by-layer structure. This performance puts the new structure in the frequency range where a number of millimeter and submillimeter wave applications have been proposed, including efficient mm wave antennas, filters, sources, and waveguides. However, most of these applications are based on the presence of defect or cavity modes, which are obtained by locally disturbing the periodicity of the photonic crystal. The frequency of these modes lie within the forbidden band gap of the pure crystal, and the associated fields are localized around the defect. We have demonstrated [35, 36], the existence of such cavity structures built around the layer-by-layer PBG crystal. The defects are formed by either adding or removing dielectric material to or from the crystal. We have observed [35, 36] localized defect modes with peak and high Q values. The measurements are in good agreement with theoretical calculations.

An interesting class of photonic crystals is the A7-family of structures [37]. These structures have rhombohedral symmetry and can be generated by connecting lattice points of the A7 structure by cylinders. The A7 class of structures can be described a two structural parameters – an internal displacement u and a shear angle α- that can be varied to optimize the gap. For special values of the parameters the structure reduces to simple cubic, diamond, and the Yablonovitch 3-cylinder structure. Gaps as large as 50% are found [37] in the A7 class of structures for well optimized values of the structural parameters and fabrication of these structures would be most interesting. It is worth noting that the fcc structure does have [38, 39] a true photonic band gap between the eight and the ninth bands (see Fig. 2). The fcc lattice does not have [16–18] a PBG between the lowest bands (bands 2 and 3).

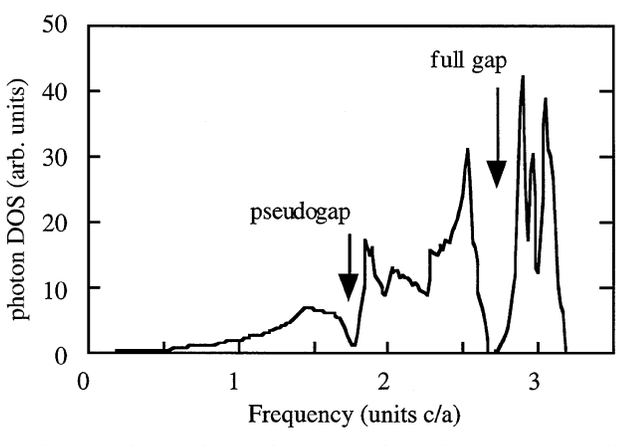

Fig. 2. Density of states for the fcc system of low dielectric spheres (filling ratio 0.74) in a high dielectric background, with a refractive index contrast of 3.1, displaying the full gap between the 8 and 9 bands and the weaker pseudogap between bands 2 and 3. Frequencies are in dimensionless units where c is the speed of light (in the dielectric background) and a the lattice constant.

An alternative layer-by-layer structure has been recently proposed by Fan *et al.* [40] to fabricate PBGs at optical frequencies. This consists of a layered structure of two dielectric materials in which a series of air columns is drilled into the top surface. The structural parameters have been optimized to yield 3D photonic gap to midgap ratios of 14% using Si, SiO_2 and air, to 23% using Si and air (i.e., the SiO_2 layers are replaced by air). Both the design introduced by Fan *et al.* [40], and the "three-cylinder" PBG introduced by Yablonovitch and Scherer [41], as well [30–36] as our layer-by-layer structure have difficulties in creating PBGs at optical frequencies.

3. Theoretical techniques and transfer matrix results

All of the theoretical results discussed above were obtained with the plane-wave expansion technique [16–18], which is now very well developed. However, most of the theoretical techniques concentrate on the calculation of the dispersion of the photon bands in the infinite periodic structure, while experimental investigations focus mainly on the transmission of EM waves through a finite slab of the photonic band gap patterned in the required periodic structure. Even with the knowledge of the photon band structure, it is still a nontrivial task to obtain the transmission coefficient for comparison with experiment. Another important quantity for the photonic band gap experiments and devices is the attenuation length for incident EM waves inside the photonic band gap. Another topic of interest is the behavior of impurity modes associated with the introduction of defects into the photonic band gap structure. While this problem can be tackled within a plane wave approach using the supercell method [26, 27] in which a simple defect is placed within each supercell of an artificially periodic system, the calculations require a lot of computer time and memory. Recently, Pendry and MacKinnon [42] introduced a complimentary technique for studying photonic band gap structures which is called the transfer-matrix method. In the transfer matrix method (TMM), the total volume of the system is divided into small cells and the fields in each cell are coupled to those in the neighboring cells. Then the transfer matrix is defined by relating the incident fields on one side of the PBG structure with the outgoing fields on the other side. Using the TMM, the band structure of an infinite periodic system can be calculated. The main advantage of this method is the calculation of the transmission and reflection coefficients for EM waves of various frequencies incident on a finite thickness slab of the PBG material. In this case, the material is assumed to be periodic in the directions parallel to the interfaces.

We want to stress that this technique can also be applied to cases where the plane-wave method fails or becomes too time consuming. For example, when the dielectric constant is frequency dependent, or has a non-zero imaginary part, and when defects are present in an otherwise periodic system, this technique works well. The TMM has previously been applied in studies of defects in 2D PBG structures [43], of PBG materials in which the dielectric constants are complex and frequency dependent [44], of 3D layer-by-layer PBG materials [32], of 2D metallic PBG structures [45, 46] and 3D metallic structures [46]. In all these examples, the

agreement between theoretical predictions and experimental measurements is very good, as can be seen in Fig. 3.

In particular, for 2D systems consisting of metallic cylinders [46], there is considerable difference between the two polarizations. For p-polarized waves, the results are qualitatively similar to the dielectric PBG systems. Propagating modes are interrupted by band gaps appearing close to the edges of the Brillouin zone. On the other hand, for s-polarized waves, there is a cut-off frequency v_c. There are no propagating modes for frequencies between zero and v_c, so the transmission has a very sharp drop in this frequency range. Above v_c, there is the usual behavior of bands interrupted by gaps.

For 3D metallic PBG structures [46], the results are very sensitive on the topology of the structure. Systems with isolated metallic scatterers (cermet topology) exhibit similar behavior to the dielectric PBG materials. But, for metallic scatterers forming a continuous network (network topology), there are no propagating modes for frequencies smaller than a cut-off frequency for both polarizations and for any incident angle. Note that for dielectric PBG materials, there is no cut-off frequency for both types of the topology. We have shown this behavior, in both 2D and 3D cases, can be explained using a simple waveguide model where the v_c is predicted with good accuracy. This cut-off frequency is well below the plasma frequency and is related to the structure of the system.

In all the periodic cases studied, the absorption can be largely neglected for metallic PBG structures with lattice constants, a, less than about 100 μm which correspond to frequencies below about 1 THz. Therefore, for frequencies less than about 1 THz, wide stop-band filters constructed from periodic metallic PBG materials can be used as alternatives to similar filters constructed from dielectric PBG.

By breaking the connections in the 3D metallic networks, defect states appear below the cut-off frequency, resulting in a peak in the transmission. The smaller the volume of the removed metal, the smaller the frequency where the defect peak appears. This is a very interesting feature of the metallic PBG which, in connection with the fact that the filling ratio of the metal can be less than 0.01, can be used in the construction of narrow band-pass filters smaller in size than those constructed from dielectric PBG. By increasing the lattice constant, the Q factor and the transmission at the defect peak increase by order of magnitudes, while the dimensionless defect frequency remains almost constant. The absorption at the frequency where the defect peak appears increases as the lattice constant increases, an effect which may create problems in some of the possible applications. An important advantage of metallic PBG structures is they could be smaller in size and lighter than the corresponding dielectric PBG materials.

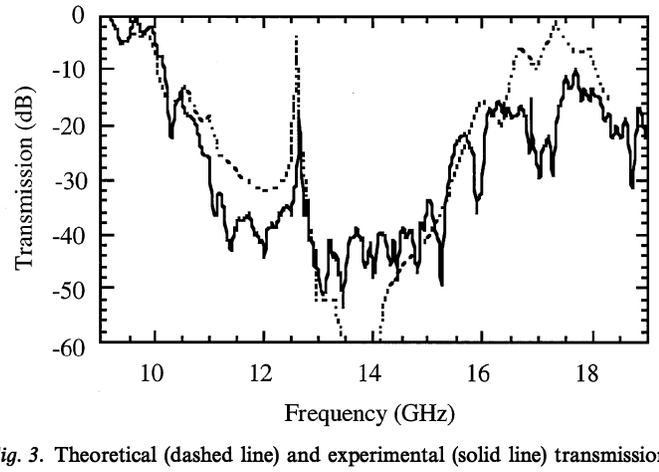

Fig. 3. Theoretical (dashed line) and experimental (solid line) transmission characteristics of a defect structure.

4. Conclusions

In summary, we have reviewed the theoretical and experimental efforts in obtaining 2D and 3D dielectric structures that possess a full photonic band gap. The plane-wave method results of Ho, Chan, and Soukoulis suggested the first structure to exhibit a true photonic band gap, and the Yablonovitch "3-cylinder" structure of diamond symmetry was the first experimental structure with a photonic band gap. We have demonstrated that a systematic search for the structures that possess optimal photonic gaps can be conducted via theoretical calculations. We find that the photonic band gap depends crucially on (i) the local connectivity or geometry, (ii) the refractive index contrast and (iii) the filling ratio of a structure. Multiply-connected geometries produce larger gaps than simply connected structures.

We have designed a new layer-by-layer structure that has a full three-dimensional photonic band gap. Each layer consists of a set of one-dimensional pattern of parallel dielectric rods. The rods were rotated by 90° between neighboring layers and shifted by half the distance a between second neighbor layers. This stacking procedure led to a unit cell of four layers. This structure has been fabricated by stacking alumina rods producing full 3-dimensional photonic band gaps between 12 and 14 GHz. The structure has been fabricated by micromachining silicon wafers and stacking the wafers in an orderly fashion producing millimeter wave photonic band gap structures at progressively smaller length scales. We have achieved these photonic band gap structures with midgap frequencies of 100 and 500 GHz. A number of applications of the microwave and millimeter wave PBG crystals may be realized with the structures we have already fabricated. This layer-by-layer structure is very promising for the extension of photonic band crystals into the infrared and optical regimes an area that will surely lead to new areas in basic physics together with novel applications. We are excited about the future applications of photonic band gaps and the prospects of using our calculational techniques to design and help the fabrication of these photonic band gap materials.

Acknowledgements

The theoretical work was done in collaboration K. M. Ho, C. T. Chan, M. Sigalas and R. Biswas. Ames Laboratory is operated by the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences and Advanced Energy Projects and by NATO Grant No. 940647.

References

1. Kittel, C., "Introduction of Solid State Physics" (5th Edition, Wiley, 1976) Ch. 7.

2. Proceedings of the NATO ARW, "Photonic Band Gaps and Localization" (Edited by C. M. Soukoulis) (Plenum, N.Y. 1993); "Photonic Band Gap Materials" (Edited by C. M. Soukoulis) NATO ASI, Series E, vol. 315 (1996)
3. For a recent review see the special issue of J. Opt. Soc. Am. **B10**, 280–408 (1993) on the Development of Applications of Materials Exhibiting Photonic Band Gaps; and Joannopoulos, J. D., Mead, R. D. and Winn, J. N., "Photonic Crystals" (Princeton, 1995).
4. Purcell, E. M., Phys. Rev. **69**, 681 (1946).
5. Yablonovitch, E., Phys. Rev. Lett. **58**, 2059 (1987).
6. Lawandy, N., in: "Photonic Band Gaps and Localization" (Edited by C. M. Soukoulis) (Plenum Publ., N.Y. 1993), p. 355.
7. John, S., Phys. Rev. Lett. **58**, 2486 (1987); John, S., Comments, Cond. Matt. Phys. **14**, 193 (1988); John, S., Physics Today **32**, 33 (1991).
8. "Scattering and Localization of Classical Waves in Random Media" (Edited by P. Sheng) (World Scientific, Singapore 1990).
9. Drake, J. M. and Genack, A. Z., Phys. Rev. Lett. **63**, 259 (1989).
10. Condat, C. A. and Kirkpatrick, T. R., Phys. Rev. **B36**, 6783 (1987).
11. Martorell, J. and Lawandy, N. M., Phys. Rev. Lett. **65**, 1877 (1990).
12. Kurizki, G. and Genack, A. Z., Phys. Rev. Lett. **66**, 1850 (1991).
13. Yablonovitch, E. and Gmitter, T. J., Phys. Rev. Lett. **63**, 1950 (1989).
14. Satpathy, S., Zhang, Z. and Salehpour, M. R., Phys. Rev. Lett. **64**, 1239 (1990).
15. Leung, K. M. and Liu, Y. F, Phys. Rev. **B41**, 10188 (1990).
16. Leung, K. M. and Liu, Y. F., Phys. Rev. Lett. **65**, 2646 (1990).
17. Zhang, Z., and Satpathy, S., Phys. Rev. Lett. **65**, 2650 (1990).
18. Ho, K. M., Chan, C. T. and Soukoulis, C. M., Phys. Rev. Lett. **65**, 3152 (1990).
19. Maddox, J., Nature **348**, 481 (1990).
20. Yablonovitch, E., Gmitter, T. J. and Leung, K. M., Phys. Rev. Lett. **67**, 2295 (1991); Yablonovitch, E. and Leung, K. M. Nature **351**, 278 (1991).
21. Chan, C. T., Ho, K. M. and Soukoulis, C. M., Europhys. Lett. **16**, 563 (1991).
22. Sözuer, H. S. and Haus, J. W., J. Opt. Soc. Am. **B10**, 296 (1993) and references therein.
23. Villeneuve, P. R. and Piche, M., Phys. Rev. **B46**, 4964 (1992); ibid **46**, 4973 (1992).
24. Meade, R. D., Brommer, K. D., Rappe, A. M. and Joannopoulos, J. D., Appl. Phys. Lett. **61**, 495 (1992).
25. Plihal, M., Shambrook, A., Maradudin, A. A. and Sheng, P., Opt. Commun, **80**, 199 (1991); M. Plihal and A. A. Maradudin, Phys. Rev. **B44**, 8565 (1991).
26. Yablonovitch, E. *et al.*, Phys. Rev. Lett. **67**, 3380 (1991).
27. Meade, R. D., Brommer, K. D., Rappe, A. M. and Joannopoulos, J. D., Phys. Rev. **B44**, 13772 (1991).
28. McCall, S. L., Platzman, P. M., Dalichaouch, R., Smith, D. and Schultz, S., Phys. Rev. Lett. **67**, 2017 (1991).
29. Robertson, W. *et al.*, Phys. Rev. Lett. **68**, 2023 (1992).
30. Ho, K. M., Chan, C. T., Soukoulis, C. M., Biswas, R. and Sigalas, M., Solid State Comm. **89**, 413 (1994).
31. Ozbay, E. *et al.*, Phys. Rev. **B50**, 1945 (1994).
32. Ozbay, E., Tuttle, G., Biswas, R., Sigalas, M. and Ho, K. M., Appl. Phys. Lett. **64**, 2059 (1994).
33. Ozbay, E. *et al.*, Optics Lett. **19**, 1155 (1994).
34. Ozbay, E. *et al.*, Appl. Phys. Lett. **65**, 1617 (1994).
35. Ozbay, E. *et al.*, Appl. Phys. Lett. **67**, 1969 (1995).
36. Ozbay, E., Tuttle, G., Sigalas, M., Soukoulis, C. M. and Ho, K. M., Phys. Rev. **B51**, 13961 (1995).
37. Chan, C. T., Datta, S., Ho, K. M. and Soukoulis, C. M., Phys. Rev. **B49**, 1988 (1994).
38. Sozuer, H. S., Haus, J. W. and Inguva, R., Phys. Rev. **B45**, 13962 (1992).
39. Suzuki, T. and Yu, P., J. Opt. Soc. of Am. **B12**, 571 (1995).
40. Fan, S., Villeneuve, P., Meade, P. and Joannopoulos, J., Appl. Phys. Lett. **65**, 1466 (1994).
41. Cheng, C. and Scherer, A., J. Vac. Sci. Tech. **B13**, 2696 (1995).
42. Pendry, J. B. and MacKinnon, A., Phys. Rev. Lett. **69**, 2772 (1992).
43. Sigalas, M. M., Soukoulis, C. M., Economou, E. N., Chan, C. T. and Ho, K. M., Phys. Rev. **B48**, 14121 (1993).
44. Sigalas, M. M., Soukoulis, C. M., Chan, C. T. and Ho, K. M., Phys. Rev. **B49**, 11080 (1994).
45. Smith, D. R., Shnetz, S., Kroll, N., Sigalas, M. M., Ho, K. M. and Soukoulis, C. M., Appl. Phys. Lett. **65**, 645 (1994).
46. Sigalas, M. M., Chan, C. T., Ho, K. M. and Soukoulis, C. M., Phys. Rev. **B52**, 11744 (1995).