Dramatic Enhancement of Third-Harmonic Generation in Three-Dimensional Photonic Crystals

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We have observed a dramatic enhancement of third-harmonic generation in 3D polystyrene-air photonic crystals pumped by a near infrared laser beam. As the pump wavelength is tuned, the peak of the enhancement occurs when the third-harmonic wavelength approaches the short-wavelength edge of the band gap. We show that the origin of the enhancement is phase matching provided by the periodic structure of the photonic crystals.

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Photonic crystals possess optical properties not present in any naturally occurring material; these properties can be precisely tailored for specific applications [1]. Of particular interest is the study of the nonlinear optical properties of photonic crystals [2]. A standard application of nonlinear optics is the frequency conversion of optical radiation and, in particular, the generation of frequency harmonics. Third-harmonic generation (THG) is a very useful technique that can convert the coherent output of infrared lasers to shorter wavelengths in the visible and near ultraviolet. However, the smallness of the third-order optical susceptibility and the strong natural dispersion of the refractive index of most materials have prevented the practical utilization of one-step third-harmonic generation. Therefore, in practice, one employs a cascaded two-step process to produce the third harmonic with high conversion efficiency [3–5]. However, it would be more convenient as well as conceptually simpler to find the right conditions for the implementation of direct one-step third-harmonic generation. In this Letter, we report a dramatic enhancement in the efficiency of third-harmonic generation using a three-dimensional (3D) polystyrene photonic crystal medium.

Having perfect phase matching of the pump and generated signal is essential for efficient nonlinear frequency conversion. One way to achieve this condition for the case of third-harmonic generation is to use an anomalous dispersion region where the refractive index of the medium decreases with the optical frequency. In bulk media, anomalous dispersion is typically accompanied by extremely high absorption which prevents the useful implementation of this idea. However, in a photonic crystal anomalous dispersion created by the periodic structure need not be accompanied by loss and strong third-harmonic generation can be obtained. While phase matching for third-harmonic generation could also be achieved in 1D multilayer structures, a demonstration of this effect in 3D photonic crystals is of much higher technological importance, as the 3D photonic crystals have the potential for becoming the basis for the next generation of integrated photonic devices by providing features not present in periodic 1D structures. For instance, greater localization of the field is possible by confining light in three dimensions, leading to smaller sizes of optical elements on the chip [6]. In addition, complex defect waveguide structures can be achieved in 3D photonic crystals.

The crystals used in our experiments are fabricated by close packing of colloidal polystyrene microspheres. Even though polystyrene possesses only a weak third-order nonlinear susceptibility, we observe a strong third-harmonic generated beam. These circumstances suggest that even stronger generation could be achieved in photonic crystals fabricated of highly nonlinear constituents.

Third-harmonic generation in 1D periodic and Fibonacci superlattices has been demonstrated previously [7,8]. However, methods used in these experiments have relied on the second-order nonlinear susceptibility of the materials and two parametric processes, second-harmonic generation and sum-frequency generation, to generate the third-harmonic signal. Also, third-harmonic generation from a defect created in a one-dimensional photonic crystal has been observed experimentally [9]. In contrast to this work, here we report on one-step phase-matched THG in a 3D photonic crystal without defects.

Some work on the nonlinear optical properties of 3D polystyrene-air photonic crystals has been done in the last couple of years. Colloidal nanoassemblies of polystyrene microspheres with a layer of strongly nonlinear molecules adsorbed onto the surface have been reported to provide the phase-matching conditions for second-harmonic generation [10]. Recently, we have reported the enhancement of two-photon-excited up-converted emission in dye doped polystyrene photonic crystals [11]. In that case,

and in contrast to the work reported here, the maximum enhancement of up-converted emission appears in transmission on both sides of the photonic band gap.

Here we demonstrate that when an ultrashort laser pulse with the proper wavelength passes through a 3D polystyrene-air photonic crystal, a dramatic enhancement of single-step third-harmonic generation is observed at the short-wavelength edge of the photonic band gap. To prepare photonic crystals for this experiment, a new and very efficient method called the vertical deposition technique was used. The method provides crystals with a very low concentration of defects and with long-range particle order [12,13]. Moreover, it is particularly suitable for fabrication of thin photonic crystals using polystyrene nanoparticles. Two photonic crystals consisting of polystyrene spheres formed into a face-centered cubic (fcc) crystal structure were used in our experiments. One crystal, which we call the blue crystal, was formed of 198 nm diameter spheres; the other crystal (the green crystal) was formed of 228 nm diameter spheres.

A high-peak-power excitation beam produced by an optical parametric generator (OPG) was focused into the photonic crystal and the third-harmonic light generated inside the crystal was collected by a Nikon Plan 10× objective with a numerical aperture of 0.25. The wavelength of the pump was tunable from 1.1 to 1.6 μm. The OPG was pumped by a mode-locked Ti:sapphire oscillator-amplifier laser system operating at a 1 kHz repetition rate and producing 160 fs pulses at a wavelength of 790 nm with a spectral width of 8 nm. In our experiments, the intensity at the focus was kept below 500 GW/cm^2, so that continuum generation from polystyrene would not interfere with the THG measurements.

When the blue and green crystals were illuminated by focused laser beams in the [111] crystallographic direction at wavelengths of 1.36 and 1.56 μm, respectively, a bright beam at the third-harmonic wavelength was observed in both transmission and reflection. Figure 1 shows the wavelength dependence of the intensity of the third-harmonic light generated in the blue (squares) and green (triangles) polystyrene photonic crystals. The linear transmittance of the crystals in the [111] crystallographic direction is also shown in Fig. 1. For both crystals, the maximum generation occurs when the third-harmonic wavelength is tuned to the short-wavelength edge of the band gap. This fact is crucial for understanding the origin of the enhancement of THG. If the condition for maximum generation depended on the wavelength of the fundamental radiation coinciding with the stop-gap edge, one would infer that the nature of the increased response was the local field enhancement of the incident field. Instead, in the present case, the origin of the dramatic ($\sim 25\times$) enhancement seems to be pure phase matching.

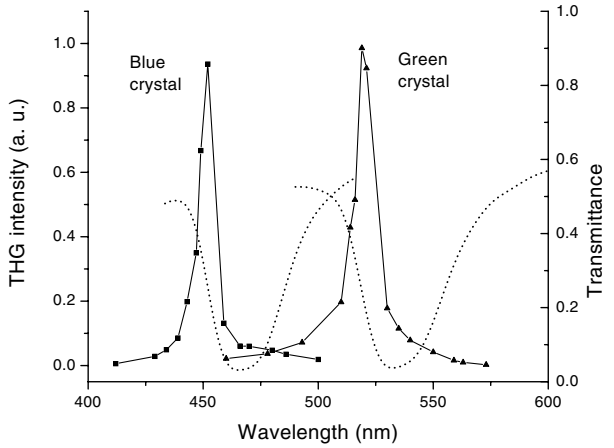

FIG. 1. Intensity of the generated third-harmonic signal plotted as a function of wavelength for the blue (squares) and green (triangles) crystals. The dotted lines represent linear transmittance of the photonic crystal samples in the vicinity of their band gaps.

To explain how phasematching occurs in periodic structures of our crystal, let us analyze the photon dispersion relation for an fcc photonic crystal in terms of the effective refractive index, $n_{\mathrm{eff}}(\omega) \equiv k(\omega) \times c/\omega$, where $k(\omega)$ is the real part of the wave vector of light propagating in the medium, ω is its optical frequency, and c is the speed of light in vacuum. We calculate the effective refractive index of an infinite fcc polystyrene crystal as a function of the normalized frequency, $f \equiv a/\lambda = a\omega/2\pi c$, where a is the lattice constant of the crystal and λ is the wavelength of incident light in vacuum, as shown in Fig. 2 (inset) for the green crystal. Both the material dispersion of polystyrene and the photonic

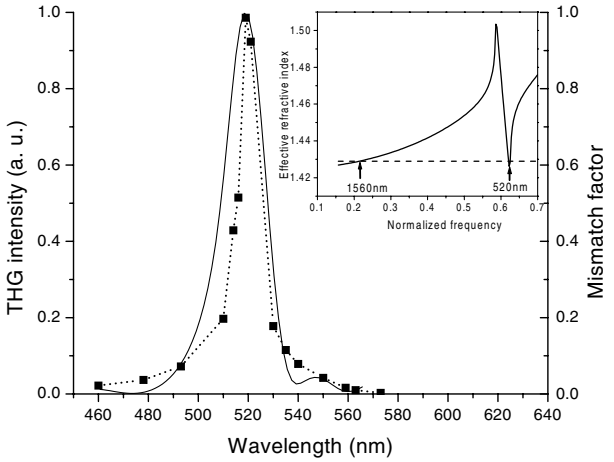

FIG. 2. The phase mismatch factor for the third-harmonic generation process (solid line) and the measured intensity of THG in the green crystal (solid squares) plotted as functions of the THG wavelength. The inset shows how the fundamental and the third-harmonic waves are phase matched in the green crystal in terms of the effective refractive index.

crystal dispersion are accounted for in this calculation. Our samples consist of approximately 50 layers of polystyrene microspheres in the direction of light propagation. The infinite crystal approximation works sufficiently well for such a number of layers [14]. At low frequency, the effective refractive index depends only on the material dispersion because the wavelength is much longer than the spatial periodicity of the structure. As the frequency is tuned towards the band gap, the effective index deviates strongly from the natural refractive index of polystyrene leading to poor phase matching. However, phase matching could be restored at some point in the anomalous dispersion region of the band gap, so that when light at this frequency propagates in the forward direction in the crystal its wave vector is phase matched with that of the low-frequency pump [15]. Thus a strong third-harmonic generation could be observed. In our experiments, the thickness of the crystal was only 10 μm and the THG was observed in transmission as well as in reflection due to multiple Bragg reflections of the third-harmonic signal inside the crystal.

The wave vector mismatch for THG, $\Delta k(\omega) = 3(\omega/c)(n_{\text{eff}}(\omega) - n_{\text{eff}}(3\omega))$, has a zero (corresponding to perfect phase matching) at a normalized frequency of 0.621 inside the gap and the corresponding fundamental frequency of 0.207 as shown in Fig. 2 (inset). To find the spectral dependence of the intensity of the THG, one needs to examine the phase-mismatch factor, $F(\omega) = \text{sinc}^2[\Delta k(\omega)L/2]$, where L is the interaction length, which we assume to be equal to the thickness of our sample. The intensity of the third-harmonic generation is proportional to the phase-mismatch factor [16] $F(\omega)$. In Fig. 2, we plot the phase-mismatch factor $F(\omega)$ superimposed on the actual data points for the intensity of the third harmonic generated from the green crystal. Note the good overall fit and the fact that our model predicts the location of the peak of THG exactly, without any free parameters. The phase-matching model also explains the weak background THG far away from the band gap. Thin layers of photonic crystal media used in our experiment generate the third-harmonic light even when the pump is detuned from the optimal wavelength and natural dispersion is not compensated by the anomalous dispersion induced by the periodic structure. This background radiation is approximately 25 times less intense than the perfectly phase-matched THG at the peak.

Assuming perfect phase matching, the conversion efficiency for third-harmonic generation from a sample of length L can be estimated as $\eta = (3\omega)^2 \frac{(2\pi)^4}{(nc)^4} I^2 L^2 \chi^{(3)2}$, where ω is the fundamental frequency, I is the intensity of the fundamental field, n is the refractive index of the medium, and $\chi^{(3)}$ is the cubic nonlinear susceptibility of the sample [5,16]. Under the conditions of our experiment, we calculate the conversion efficiency to be 9.3×10^{-5}, which is just slightly larger than the total measured conversion efficiency of 6.0×10^{-5} in reflection and transmission. This comparison shows that, although the absolute value of the conversion efficiency is small, we are close to the limit set by the physical dimensions and nonlinear susceptibility of our sample. To verify that the observed signal is generated by a $\chi^{(3)}$ nonlinear process, we have also experimentally demonstrated the cubic dependence of the third-harmonic generation on the pump pulse energy as shown in Fig. 3.

On the basis of these results — that is, the dramatic enhancement of the third-harmonic intensity when the third-harmonic wavelength approaches the short-wavelength edge of the band gap and high directionality of this signal — we conclude that the observed enhancement of the third-harmonic generation in a 3D photonic crystal is due to the phase-matching phenomenon. A photonic crystal composed of a conjugated polymer, which possesses a much larger third-order nonlinearity [17], could produce more efficient frequency conversion, because strong nonlinear material properties and phase-matching conditions can be provided separately. Even thin layers of such a photonic crystal medium could be used to fabricate infrared visualizing cards that operate at a practically important wavelength of 1.5 μm. Once the technology of fabrication is developed to produce photonic crystals of high optical quality and of appreciable thickness (a few millimeters), highly efficient frequency conversion of coherent infrared light sources to the short-wavelength range of visible light and the ultraviolet will be possible. The ability to provide phase-matching conditions for third-order nonlinear processes in 3D photonic crystals structures is also important for optical signal processing in integrated devices based on photonic crystal waveguides and photonic crystal active elements. Integration of third-harmonic upconversion with other functions that can be performed by photonic band gap devices, such as microcavity effect,

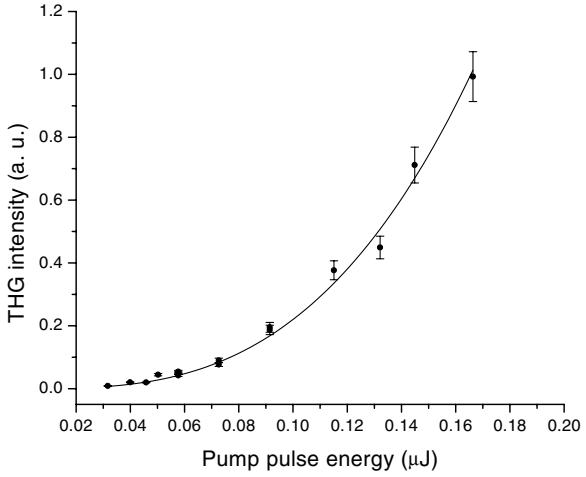

FIG. 3. Pump power dependence of the third-harmonic signal. Circles: experimental points; solid line: cubic fit.

photonic crystal waveguide, etc., may provide a useful pathway for novel methods of signal processing.

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