Light generation at the anomalous dispersion high energy range of a nonlinear opal film

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Abstract: We study experimentally and theoretically light propagation and generation at the high energy range of a close-packed fcc photonic crystal of polystyrene spheres coated with a nonlinear material. We observe an enhancement of the second harmonic generation of light that may be explained on the basis of amplification effects arising from propagation at anomalous group velocities. Theoretical calculations are performed to support this assumption. The vector KKR method we use allows us to determine, from the linear response of the crystal, the behavior of the group velocity in our finite photonic structures when losses introduced by absorption or scattering by defects are taken into account assuming a nonzero imaginary part for the dielectric constant. In such structures, we predict large variations of the group velocity for wavelengths on the order or smaller than the lattice constant of the structure, where an anomalous group velocity behavior is associated with the flat bands of the photonic band structure. We find that a direct relation may be established between the group velocity reduction and the enhancement of a light generation processes such as the second harmonic generation we consider. However, frequencies for which the enhancement is found, in the finite photonic crystals we use, do not necessarily coincide with the frequencies of flat high energy bands.

OCIS codes: (050.5298) Photonic crystals; (160.5293) Photonic bandgap materials; (190.0190) Nonlinear optics; (190.4400) Nonlinear optics, materials

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1. Introduction

In the band structure of photonic crystals (PC) an anomalous behavior for the group velocity is seen to appear in the high energy region, when the wavelength of the light is on the same order or smaller than the lattice constant [1]. In that region of extremely flat bands, the group velocity would be almost zero for a broad spectrum of wavevectors within the PC. Interesting applications as spontaneous emission enhancement or photoluminescence tuning that take advantage of such anomalous group velocity have already been proposed [1–3]. However, a better understanding of the physics behind this anomalous behavior is still needed. Indeed, the experimentally observed transmittance and reflectance spectra of high quality opal slabs at that region where the flat bands appear do not seem to match the theoretical band structure of a perfect structure [4,5]. In the same frequency region an unexplained dependence of the group velocity respect to the thickness of the opal has also been reported [6]. Recently, an analysis of the optical response of finite crystals based on the calculation code reported by Stefanou et al. [7,8] developed from the vector Korringa-Kohn-Rostoker (KKR) method [9,10] showed that, when absorption is taken into account, the predicted transmission or reflection spectrum matches very well any experimentally measured transmission or reflection spectrum, respectively [11,12]. Besides, slow light phenomena are currently the subject of extensive research since a reduced group velocity may be exploited to achieve tunable delays or to enhance various optical nonlinearities [1,13,14].

In the present paper, we used the same type of vector KKR calculation method to extract the group velocity for the transmitted and the reflected fields as a function of the wave frequency. The KKR method allows us to determine the phase change of the specularly reflected and forwardly transmitted beams that emerge from the structure when an incident light beam impinges normally to the surface of the crystal slab. From there, it is straightforward to obtain the group velocity as a function of the inverse wavelength of the incident field.

We report also an experimental observation of second harmonic generation (SHG) at the high-energy region of a face-centered-cubic (fcc) lattice of microspheres. The opal-like films are made by depositing polystyrene spheres coated with a nonlinear (NL) material onto a flat substrate. We find that a solid PC film made of a few packed sphere layers is able to enhance SHG when the fundamental wavelength is on the order of the

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lattice constant. The wavelength dependence of second harmonic generation in that region is analyzed using the vector KKR calculation method to extract the group velocity for the transmitted and the reflected electric fields as a function of the wave frequency for a PC of polystyrene spheres.

2. Nonlinear opal preparation and characterization

To analyze the effect that the anomalous group velocity behavior may have on the generation of light, we prepared a NL artificial opal to be able to measure SHG at the high energy range. The versatility as well as the high quality of synthetic opals makes them perfect candidates to study the optical response of these structures at such high frequencies [15,16]. We modified monodisperse 380 nm diameter carboxyl/sulfate latex spheres, by chemically binding to their surface a NL chromophore. The dye molecule used was Crystal Violet (CV) which was modified to have a hydroxyl binding group. Such hydroxyl group was covalently linked to the functional carboxylic acid groups present at the surface of the spheres [17]. The chemically modified spheres present a high coverage of their surface, estimated to be on the order of 70% [17,18]. After the reaction the sulfate groups remain unaltered preventing coagulation and also helping to maintain stability during the crystallization process of the opal. Once the NL latex colloid was obtained we took advantage of the natural tendency of charged spheres to self assemble in an fcc configuration and grew a close-packing crystalline film. To obtain a high quality sample, we used a crystallization method based on the spin coating of a concentrated suspension of spherical colloids using a mixture of volatile solvents as dispersion media [15]. This technique allows us the control of thickness as well as the orientation of the sub-micrometer-size spherical colloids. The opal we fabricated was made of 10 [111] oriented layers of the modified NL polystyrene spheres deposited on a glass substrate.

We characterized the crystal performing measurements of the reflection and transmission spectra in the ΓL direction using UV/Vis/NIR spectrophotometer with a 0.2 nm spectral resolution. The spectral reflectance and transmittance in the ΓL direction of the NL opal is shown in Fig. 1. A maxima around 810 nm which corresponds to the [111] pseudogap is clearly visible. Note that transmission measurement is affected, at particularly short wavelengths, by an effective optical extinction caused by an incoherent diffuse scattering due to the presence of lattice defects.

We used the vector KKR method to characterize the linear response of the fabricated crystal. In this model, the 3D crystal slab is first divided into layers parallel to a given crystallographic plane, each 2D layer containing periodically arrayed identical spheres. Next, the multipole expansion in spherical waves is used to account for the multiple scattering processes inside each layer. Finally, a series expansion in a plane wave basis is used to describe the electromagnetic interactions between layers and to compute the far-field power flux in either side of the crystal slab [8]. To properly account for losses introduced by defects or disorder in the lattice and CV absorption, the dielectric constant of the spheres is kept fully complex (ε_s = 2.5 + 0.14i), where the imaginary part is determined by fitting the first order Bragg reflection band. For simplicity, we have considered the CV absorbance contribution to such imaginary part as constant in wavelength. The dielectric constant of the surrounding medium (air) is ε = 1, while the dielectric constant for supporting glass substrate for the opal structure is ε_{glass} = 2.34. For convergence reasons, the values of the code parameter, LMAX, that controls the cutoff value of the angular momentum in the spherical-wave expansion of the electric fields is taken as LMAX = 9. The code parameter, RMAX, of the plane wave expansion of the electric field, is taken as RMAX = 26, meaning that the first 41 reciprocal-lattice vectors are taken into account [8]. A comparison of the calculated R and T with the experimentally measured ones is shown in Fig. 1. An excellent agreement is found at short wavelengths, where the numerical calculation reproduces the main features at the high energy range.

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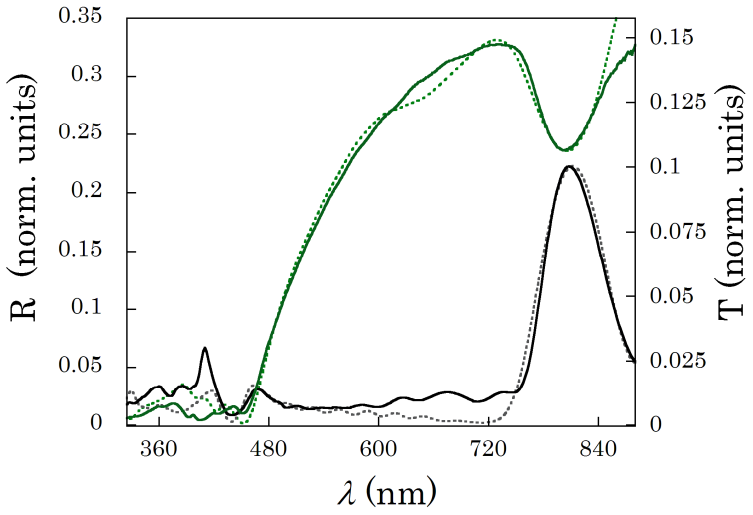

Fig. 1. Experimental spectral reflectance (black solid curve), calculated specularly reflected intensity (grey dotted curve), experimental transmittance (green solid curve), and calculated transmitted intensity (green dotted curve) as a function of wavelength, λ, in vacuum. As the structure is slightly distorted we have used a smaller lattice parameter at the lower energy spectral range.

3. Observation of second harmonic generation from a nonlinear opal

We performed SHG measurements pumping the NL opal using an amplified Ti:Sapphire laser emitting 150 fs pulses with an average energy per pulse of 1 mJ. The laser beam was focused down to a spot of 2 mm in diameter on the crystal which was placed in a rotating mount with the rotating axis perpendicular to the plane of incidence. The Amplified Ti:Sapphire we used was tunable in a range limited to about 80 nm around 800 nm. Upon incidence of the fundamental p-polarized wave propagating close to [111] direction of the crystal, we measured the corresponding total second harmonic (SH) forward-generated transmitted light. Such SHG light was filtered using a monochromator and measured using a photomultiplier tube. Note that the NL interaction takes place at the sphere surface where the inversion symmetry is locally broken [19]. Besides, since the thickness of the opal -around 3,5μm- is much shorter than the coherent length for the nonlinear interaction, the phase-matching condition imposed by the momentum conservation law is not a requirement. Under this scope, a weak SH signal is expected to be generated by the NL opal.

The measured SH signal while we tuned the wavelength of the fundamental field is shown in Fig. 2 as a function of the SH wavelength. We observe that as we increase the frequency of the incoming photons, in the range of the amplified laser tunability, SHG becomes more efficient. Indeed when the incoming laser was tuned at 768 nm, SHG generation was enhanced by a factor larger than 15 times with respect to the efficiency when the incoming laser was tuned at 840 nm. At 760 nm the amplified laser was at its emission edge, where the pulse broadens and losses intensity, and at this wavelength and beyond no reliable measurements could be performed. When the angle of the incident beam with respect to the perpendicular to the [111] planes, inside the crystal, was scanned over the range from 0 to 12 deg., we observed no significant changes in the SHG measurements indicating that SHG is non phase-matched.

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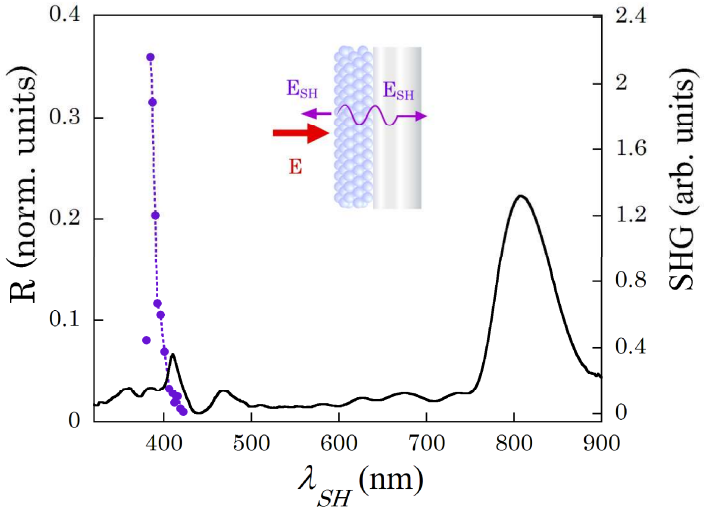

Fig. 2. Spectral reflectance as a function of wavelength (black solid curve) and SHG intensity as a function of the generated SH wavelength, (violet solid dots). The dotted line is only a guide for the eye. The inset: Schematic drawing of the opal sample used in the experiments.

4. Group velocity and second harmonic generation

When we consider light generation or to be more specific SHG at the high frequency range, an important parameter, in the case of a thin NL crystal, is the wavelength dependent group velocity [1]. We may numerically determine such group velocity by evaluating the phase delay introduced by the crystal to the reflected and transmitted electric fields. From such phase delays, we found the group velocity associated to the transmitted field v_g^T and the one associated to the reflected field v_g^R, using: $v_g^{T,R} = L(\partial\omega/\partial\theta^{T,R})$, where L is the crystal length, ω the frequency, θ the phase delay, and the superscripts R and T indicate reflected and transmitted, respectively. In the frequency region where we have experimentally measured SH generation we observe that, both, v_g^T and v_g^R exhibit a strong wavelength dependence. Indeed, as seen in Fig. 3 in the interval where a/λ changes from 0.8 to 1.6, both group velocities can either be superluminal, positive or negative, or even approach zero. It is interesting to note that we observe a strong dependence of the group velocity on the number of crystalline layers that we will analyze in more detail elsewhere [20]. The group velocities of the numerical calculation shown in Fig. 3 correspond to the case when the number of crystalline planes normal to the light propagation direction is the same as the one for the opal used in the experiment. At the interval of the SHG experiment where a/λ ranges from approximately 1.2 to 1.35, we observe that on average both group velocities decrease. Such decrease corresponds to an increase in the SHG efficiency. In other words, a reduction in the group velocity implies an increase in the interaction time, which results in a more efficient generation. Note that, irrespective of the fact that we measure a transmitted SH signal, SHG is affected by both, v_g^T and v_g^R, given that in the frequency region where we measure the nonlinear interaction, forward and backward propagating waves are expected to exchange energy very efficiently [21]. Indeed, an enhancement on the nonlinear interaction is only observed when both group velocities are below the group velocity of the effective average homogenous medium. Such group velocity was determined to be approximately 0.7 times the speed of light in vacuum (cf. Figure 3). On the contrary, the least efficient generation is observed when both, v_g^T and v_g^R, or only one of these two group velocities takes a value above the group velocity of the effective average homogenous medium. When SH occurs close to the high energy region of 3D photonic crystals exhibiting a very short coherence length, it has been shown that material

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dispersion can be compensated by a structural effective index correction for the fundamental wave [22], However, in the present case, from our numerical evaluation of the phase delays, we extracted the phase velocities corresponding to the fundamental and SH waves, and showed that a significant mismatch persists at all wavelengths of the limited frequency range where SH was observed. Other effects, such as resonance enhancement, typically found in 1-D structures, are not visible here either, due to the absorption and structural defects, which result in a nonvanishing imaginary part for the index of refraction.

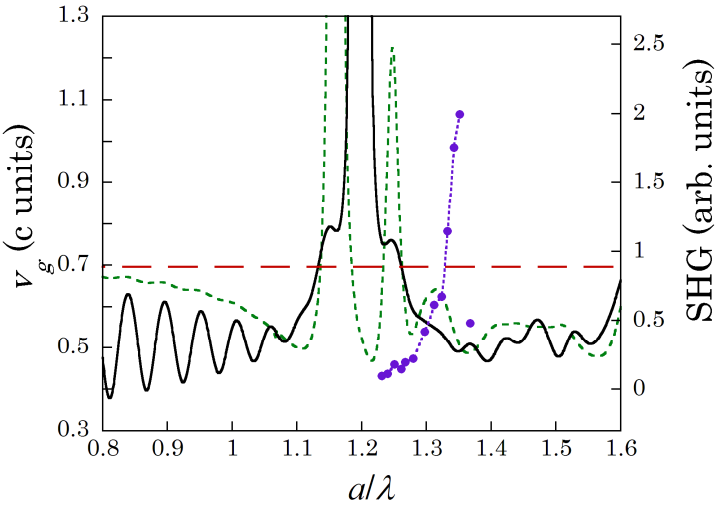

Fig. 3. Reflected wave group velocity (black solid curve), transmitted wave group velocity (green dotted curve) and measured SHG intensity (violet dotted points) for a 10 [111] planes opal made of polystyrene spheres in air on a semi-infinite glass substrate. All plotted as a function of frequency in reduced a/λ units where a is the lattice parameter. The dashed line in violet is only a guide for the eye. The red horizontal line corresponds to a constant average group velocity for the fcc close-packed structure: $v_g = (0.74 * \sqrt{2.5} + 0.26)^{-1}$. Group velocities are expressed in c units, where c is the speed of light in vacuum.

5. Conclusions

In conclusion, we have observed an enhancement of SHG at the high energy region in a NL opal film, in which wavelengths become comparable to the lattice constant of the crystal. Applying the vector KKR method we have been able to theoretically determine the group velocity behavior from 3D finite photonic structures that include extinction. In the high energy region of a 3D opal slab, strong reductions as well as fluctuations of the group velocity are obtained in the frequency range $1.1<a/\lambda<1.3$. For $a/\lambda>1.26$ the phase delays of the specularly reflected and forwardly transmitted electric fields give a significant reduction of the group velocity with respect to its average value. Precisely, at the spectral range where we observe that SHG increases. As expected, NL light generation enhancement is effective when the group velocity is reduced enabling a longer interaction time. In other words, we have shown that is the group velocity slowing-down which provides an enhancement mechanism for the NL process. However, a direct identification between the above calculated anomalous group velocities for a thin opal film with extinction, and the predicted high energy flat bands of the photonic band structure for an ideal infinite periodic structure seems difficult to establish. Indeed, frequencies for which the enhancement is found, in the finite PCs we use, do not necessarily coincide with the frequencies of those flat bands. The results we obtained may be rather useful in applications of 3D PCs where the anomalous group velocity dispersion is intended to be used. In addition, the surface quadratic NL process we observe could be used as an alternative way to explore the optical response of ordered periodic structures at

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high energies, where the wavelength is on the order or shorter than the characteristic lattice constant.

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