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Disorder-correlated enhancement of second-harmonic generation in strongly photonic porous gallium phosphide

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ABSTRACT We report an order of magnitude enhancement of second-harmonic generation (SHG) from porous gallium phosphide relative to SHG in crystalline gallium phosphide. Optical heterodyning measurements of photon free-path length reveal a correlation between SHG enhancement and disorder of the porous material.

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1 Introduction

Interference phenomena and localization of light in photonic crystals and disordered, strongly scattering photonic media modify the structure of photonic bands, giving rise to new interesting regimes of nonlinear-optical interactions [1]. Photonic crystals have been shown to substantially enhance harmonic-generation and wave-mixing processes due to properly engineered phase matching [2, 3] and Fabry–Perot-type resonances in the density of modes [4–6]. Nanoporous structures, on the other hand, can phase match nonlinear-optical interactions due to the formation of birefringence [7–9] and through mesoscopic effects, manifested in the sensitivity of the nonlinear response to the sizes of pores and nanoclusters [10].

Local-field effects typically start to play an important role in the nonlinear optics of disordered media when the size of inhomogeneities becomes comparable with the wavelengths of optical fields. Multiple scattering of photons in such random media can result in an optical analog of Anderson localization [11], leading to a phase-transition-type change in the transport of light [12]. The criterion of localization is $kl \sim 1$, where $k = 2\pi n/\lambda$ is the wave vector, n is the refractive index, λ is the wavelength, and l is the mean photon free-path length. The regime of strong localization when kl approaches 1 is of great interest for various applications, including enhancement of nonlinear-optical interactions. Note that optical harmonic generation in disordered media has not been studied completely yet; the theory is developed mainly for the case of weak localization of light [13].

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In this paper, we focus on second-harmonic generation (SHG) in porous gallium phosphide (por-GaP). Crystalline gallium phosphide (c-GaP) is transparent in the visible (red) region and characterized by a high refractive index (3.1 at 1200 nm, 3.46 at 600 nm [14]); besides, it has one of the highest values of quadratic dipole susceptibility among inorganic crystals [15]). Electrochemically etched pores and GaP nanocrystals are usually hundreds of nanometers in diameter [16]. These factors make por-GaP a very promising material for the investigation of light localization and its role in nonlinear optics. On the other hand, harmonic-generation enhancement can be one of the indicators of light localization. Indeed, a more than an order of magnitude rise of second-harmonic intensity in por-GaP in comparison with the crystalline one was reported [17–19]. Moreover, the SHG efficiency rises with a decrease in the ratio of the wavelength to the scatterer size. Thus, it seems to be very interesting to examine the correlation between the photon free-path length, which gives a measure of disorder in the medium, and SHG efficiency. In the paper, we report the results of such a study.

2 Experimental

2.1 *Samples*

Films of por-GaP were formed by means of electrochemical etching of crystalline n-type GaP:S (6×10^{17} cm^{-3}) in ethanoic HF (2 M) solutions. The surface orientation of the substrate was (111). To control disordering, samples of different porosities were prepared. The porosity of the samples was controlled by varying the applied voltage (see Table 1). Porosities were estimated through charge-transport measurement. Atomic-force microscopy measurements show that for the por-GaP films the sizes of the pores and nanocrystals range from 250 to 500 nm [18, 19]. These sizes of inhomogeneity suggest strong light scattering and the obtained por-GaP samples are indeed characterized by efficient scattering, which is rather Mie scattering than the Rayleigh one [19].

2.2 *Experimental setup*

To study the SHG efficiency versus the results of photon free-path length measurements we employed

No.	Voltage	Porosity	Thickness	Effective refractive index	Diffusion coefficient	Free-path length	kl
1	17 V	12%	28 µm	3.11	139 µm/ps	4.3 µm	67.2
2	20 V	22%	28 µm	2.87	111 µm/ps	3.1 µm	44.7
3	23 V	55%	16 µm	2.08	31 µm/ps	0.6 µm	6.3

TABLE 1 The etching regimes, porosities, and properties of por-GaP

a femtosecond Cr:forsterite laser (radiation wavelength is 1.250 µm, the repetition rate is 80 MHz, the pulse duration is 60 fs, and the mean radiation power is 200 mW). The laser beam was mechanically chopped. The second-harmonic signal was collected by a telescope, detected with a silicon photodiode, and analyzed by a SRS 830 lock-in voltmeter. SHG experiments were carried out in reflection geometry; the angle of incidence was 45°. To obtain the orientation dependences of the second-harmonic signal, the fundamental laser radiation polarization was rotated by a half-wave plate. A Glan–Taylor prism was used to analyze the second-harmonic polarization. The orientation dependences were measured for parallel and perpendicular polarizations of the fundamental radiation and the second harmonic (see Fig. 1a).

A photon diffusion study was carried out by means of optical femtosecond heterodyning [20]. We measured the cross-correlation function for incident, A, and scattered by the sample, S, waves,

$$C(\tau) = \int_{-T/2}^{T/2} A(t-\tau)S(t)\,\mathrm{d}t , \qquad (1)$$

with the help of a Michelson interferometer. Here, T is the vibration period of the movable mirror used to introduce time delay. The vibration amplitude was 1 mm; the mirror velocity was 12 cm/s. The signal was detected by an InGaAs photodiode (Fig. 1b).

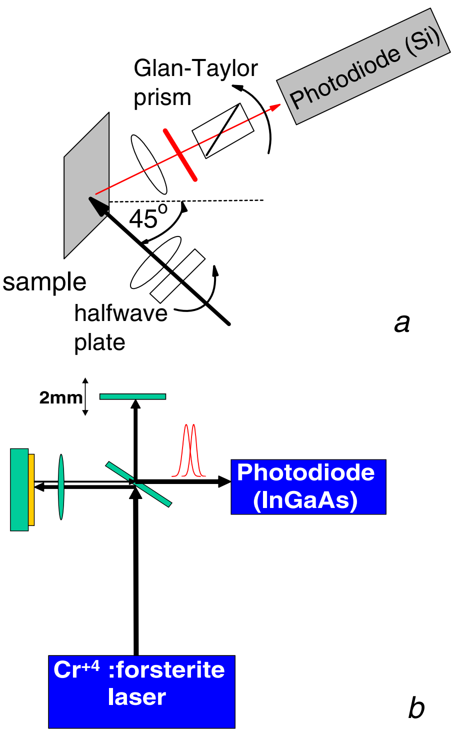

FIGURE 1 Sketches of experimental arrangements for SHG (**a**) and femtosecond heterodyning (**b**)

3 Results and discussion

3.1 *Photon diffusion measurements*

The results of the cross-correlation function measurements are shown in Fig. 2. With the help of Fourier transformation we extracted the signal at the frequency of the movable mirror vibration $\nu = 2v_{\mathrm{m}}/\lambda$, where v_{m} is the mirror velocity and λ is the laser wavelength. The dependence of the power at this frequency on the time delay $P_\nu(t)$ [20] was analyzed (see Fig. 3). The dependences demonstrate periodic fall and rise of the power with the period of mirror vibration.

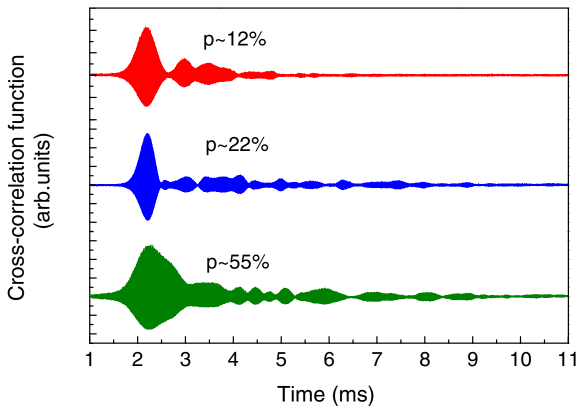

FIGURE 2 Experimentally measured cross-correlation functions for the samples of different porosities

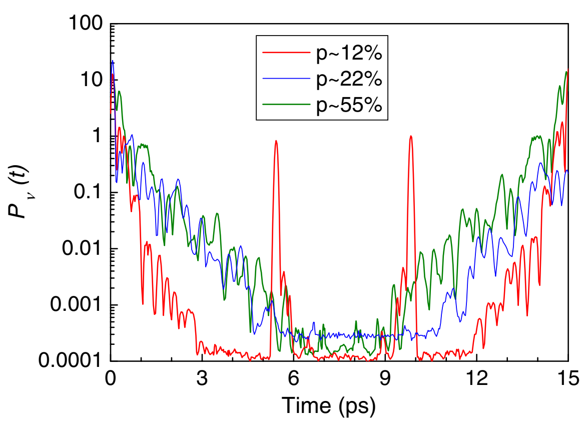

FIGURE 3 Dependence of the power of the signal at the frequency of the movable mirror vibration P_ν on the time for por-GaP samples of different porosities

For the sample of lower porosity, the peaks corresponding to the reflection from the back crystalline/porous GaP interface are easily seen, whereas for samples with a stronger scattering these peaks are absent. Small-amplitude frequent peaks in the $P(t)$ dependence are speckles. In the medium without absorption the power decrease is satisfactorily approximated with an exponential function

$$P(t) \propto \exp\left(-\frac{\pi^2}{L^2}Dt\right), \tag{2}$$

where L is the thickness of the sample and D is the photon diffusion coefficient. Thus found D values allow us to estimate the mean free-path length l [12]:

$$l = \frac{3D}{v} \approx \frac{3Dn_{\text{eff}}}{c}. \tag{3}$$

Here, in order to estimate the rate of energy transfer v, we used phase velocity c/n_{eff}, where n_{eff} is the effective refractive index calculated in the effective-medium model and c is the speed of light. An increase of the porosity results in a decrease of the free-path length (see Table 1).

3.2 *SHG measurements*

The experiment on SHG demonstrates a rise of efficiency of the process with the porosity increasing and the free-path length decreasing. Figure 4 presents orientation dependences of SHG efficiency for the samples of different porosities as well as for the initial sample. In contrast to c-GaP, por-GaP has isotropic orientation dependences. The anisotropy of the orientation dependences as well as the difference in SHG efficiencies for parallel and perpendicular polarizations are related to anisotropy of Fresnel factors. This fact indicates an effective multiple scattering of the second harmonic in por-GaP. As one can see, a rise of the porosity and the corresponding shortening of the mean free-path length result in an enhancement of SHG (see Fig. 5); namely, for both parallel and perpendicular orientations of the fundamental and second-harmonic polarizations a seven-fold decrease of the mean free-path length leads to an increase in the SHG efficiency by a factor of almost two.

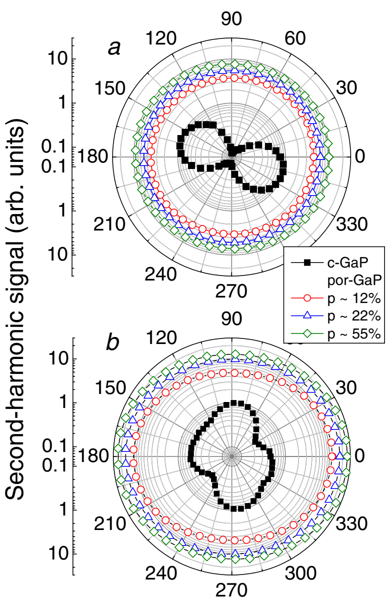

FIGURE 4 Orientation dependence of the SHG efficiency for por-GaP samples of different porosities and initial crystalline GaP. Second-harmonic polarization is perpendicular (**a**) and parallel (**b**) to the polarization of the fundamental radiation

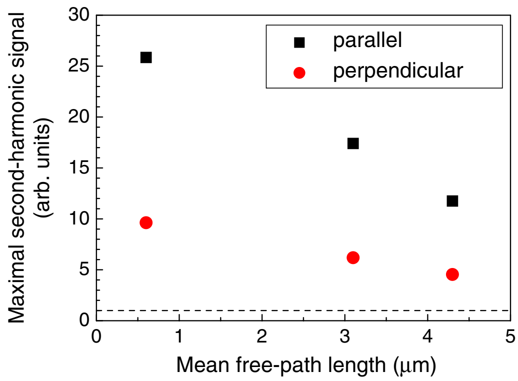

FIGURE 5 Dependence of the SHG efficiency on the mean free-path length for parallel and perpendicular geometries. The *dotted line* shows the level of the second-harmonic signal for crystalline GaP

Estimated kl values (see Table 1) show that the implemented regime is far from the phase-transition region from diffuse scattering to Anderson localization. Obviously, smaller free-path lengths correspond to smaller volumes of radiation field localization and, therefore, to a higher field intensity. As a result, the local field enhancement leads to a higher average square of the field and, consequently, to a higher efficiency of SHG.

4 Conclusion

Thus, we demonstrated that strongly photonic por-GaP allows substantial SHG enhancement. For multiply scattering porous GaP films, the SHG efficiency is shown to increase by an order of magnitude with a decrease in the free-path length. Optical heterodyning measurements of the photon free-path length reveal a correlation between SHG enhancement and disorder of the porous material.

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REFERENCES

1 C.M. Bowden, A.M. Zheltikov (eds.), Nonlinear optics of photonic crystals. Spec. Issue J. Opt. Soc. Am. B **19**(9) (2002)
2 N. Bloembergen, A.J. Sievers, Appl. Phys. Lett. **17**, 483 (1970)
3 J.P. van der Ziel, M. Illegems, Appl. Phys. Lett. **28**, 437 (1976)
4 M. Centini, C. Sibilia, M. Scalora, G. D'Aguanno, M. Bertolotti, M.J. Bloemer, C.M. Bowden, I. Nefedov, Phys. Rev. E **40**, 4891 (1999)
5 G. D'Aguanno, M. Centini, M. Scalora, C. Sibilia, Y. Dumeige, P. Vidakovic, A. Levenson, M.J. Bloemer, C.M. Bowden, J.W. Haus, M. Bertollotti, Phys. Rev. E **64**, 16 609 (2001)
6 M. Centini, G. D'Aguanno, L. Sciscione, C. Sibilia, M. Bertolotti, M. Scalora, M.J. Bloemer, Opt. Lett. **29**, 1924 (2004)
7 L.A. Golovan, V.Yu. Timoshenko, A.B. Fedotov, L.P. Kuznetsova, D.A. Sidorov-Biryukov, P.K. Kashkarov, A.M. Zheltikov, D. Kovalev, N. Künzner, E. Gross, J. Diener, G. Polisski, F. Koch, Appl. Phys. B **73**, 31 (2001)

8 P.K. Kashkarov, L.A. Golovan, A.B. Fedotov, A.I. Efimova, L.P. Kuznetsova, V.Yu. Timoshenko, D.A. Sidorov-Biryukov, A.M. Zheltikov, J.W. Haus, J. Opt. Soc. Am. B **19**, 2273 (2002)
9 S.V. Zabotnov, S.O. Konorov, L.A. Golovan, A.B. Fedotov, A.M. Zheltikov, V.Yu. Timoshenko, P.K. Kashkarov, H. Zhang, JETP **99**, 28 (2004)
10 L.A. Golovan, L.P. Kuznetsova, A.B. Fedotov, S.O. Konorov, D.A. Sidorov-Biryukov, V.Yu. Timoshenko, A.M. Zheltikov, P.K. Kashkarov, Appl. Phys. B **76**, 429 (2003)
11 P.W. Anderson, Phys. Rev. **109**, 1492 (1958)
12 A. Lagendijk, J. Gómez Rivas, A. Imhof, F.J.P. Schuurmans, R. Sprik, in *Photonic Crystals and Light Localization in the 21st Century*, ed. by C.M. Soukoulis (Kluwer, Dordrecht, 2001), p. 447
13 V.E. Kravtsov, V.M. Agranovich, K.I. Grigorishin, Phys. Rev. B **44**, 4931 (1991)
14 B.O. Seraphin, H.E. Bennett, R.W. Willardson, A.C. Beer (eds.), *Optical Properties of III-V Compounds* (Academic, New York, 1967)
15 R. Sutherland, *Handbook on Nonlinear Optics* (Marcel Dekker, New York, 1996)
16 F.J.P. Schuurmans, D. Vanmaekelbergh, J. van de Lagemaat, A. Lagendijk, Science **284**, 141 (1999)
17 I.M. Tiginyanu, I.V. Kravetsky, J. Monecke, W. Cordts, G. Marowsky, H.L. Hartnagel, Appl. Phys. Lett. **77**, 2415 (2000)
18 L.A. Golovan, V.A. Mel'nikov, S.O. Konorov, A.B. Fedotov, S.A. Gavrilov, A.M. Zheltikov, P.K. Kashkarov, V.Yu. Timoshenko, G.I. Petrov, L. Li, V.V. Yakovlev, JETP Lett. **78**, 193 (2003)
19 V.A. Mel'nikov, L.A. Golovan, S.O. Konorov, D.A. Muzychenko, A.B. Fedotov, A.M. Zheltikov, V.Yu. Timoshenko, P.K. Kashkarov, Appl. Phys. B **79**, 225 (2004)
20 K.P. Bestem'yanov, V.M. Gordienko, A.A. Ivanov, A.N. Konovalov, A.A. Podshivalov, Quantum Electron. **34**, 666 (2004)