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Luminescence response of synthetic opal under femtosecond laser pumping

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ABSTRACT

Synthetic opal is an artificial photonic metamaterial composed from spherical globules of amorphous silica (SiO_2) about 300 nm in diameter. We report, for the first time to our knowledge, the origin of a narrow luminescence spectral peak (4 nm HWHM) and optical second and third harmonic generation in synthetic opal samples under femtosecond laser excitation (800 nm) at liquid-nitrogen temperature. Stimulated-emission effects are discussed related to the possibility of nanocavity lasing at the condition of the first Mie resonance in a dielectric sphere.

1. Introduction

Photonic crystals are periodic solid structures with a lattice period Λ close to an electromagnetic wavelength λ (usually in visible light range) [1]. Currently much attention is paid to the investigation of optical properties of photonic crystals in a view of various applications in photonics and quantum electronics [2]. Light wave in photonic crystal is affected by Bragg diffraction. That means, propagation in definite directions is accompanied with strong interaction between forward and backward running coupled waves [3]. Nearly 100% reflection occurs when the Bragg condition is satisfied, and therefore light cannot propagate in the medium. In this way stop-zones, or photonic bandgaps originate in the transmission spectrum.

Oppositely, if a light source (e.g. excited ion) radiates within a periodically modulated medium, the light emission will possess some features related to the existence of the photonic bandgap and the luminescence spectrum will be modified. With the presence of a gain in the medium the lasing effect in such distributed-feedback structure can be achieved in so-called “edge modes” at both sides of a bandgap [4]. In general, the physics of light interaction with photonic crystals both in the frame of linear and nonlinear optics is quite rich of surprising effects like Anderson localization [5], Fano resonance [6], quantum optics phenomena [7,8] and nanoparticle plasmons [9]. Despite the main features related to the bandgaps in photonic crystals there are also specific moments originating from the structure of the constituent elements which build the photonic crystal. Actually, this is the subject of the present article.

We performed a set of experiments with synthetic opal (3D photonic crystal) samples using femtosecond laser pumping. To explain the observed spectrum transformation we put forward the idea of a lasing precursor caused by a feedback in a spherical nanocavity.

2. Methods and materials

In this study we used synthetic opal which is composed from spherical globules of amorphous silica (SiO_2). The globules are assembled in a face-centered cubic lattice of the Synthetic Opal Matrix (SOM) [10–12]. Fig. 1 gives a scanning electron microscope image of a SOM ordered lattice <111> face. Globules dimension (diameter) D is close to 300 nm.

Synthetic opal is a sort of artificial metamaterial with specific properties. Its crystalline periodic structure is responsible for the appearance of stop-zones for the propagating light [12]. (The “pseudogap” zone existence is fairly seen when a SOM sample is immersed with a liquid of nearly-matching refractive index [13].)

While the material itself is transparent, some actinic centers cause luminescence in the visible range under ultraviolet (UV)

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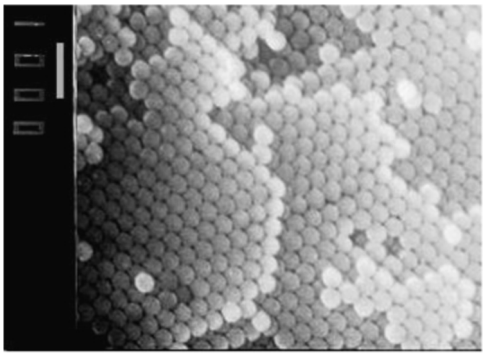

Fig. 1. Scanning electron microscope image of a surface fragment of a SOM sample. Assembling of globules in <111> crystal plane produces hexagonal pattern. Scale mark at the left indicates 1000 nm.

radiation excitation. The luminescence response occurs in a broad spectrum 450–700 nm and demonstrates quite surprising long-time decay at the low-temperature conditions [14]. The spectrum shape depends on the observation angle and the presence of a photonic bandgap was found to occur [15–17].

The initial goal of this study was an attempt to observe the influence of the photonic bandgap on a SOM luminescence. The evaluation of the bandgap location with respect to <111> crystal axis (normal to the top face of a sample) on the basis of Bragg law $\lambda_B = 2\Lambda n_{ef}$ taking into account the periodicity parameter $\Lambda = D\sqrt{2/3}$ and the effective (average) refractive index of SOM $n_{ef} \approx 1.27$ [10] gives the value for the Bragg wavelength $\lambda_B \approx 622$ nm. Calculation for the $<1\bar{1}0>$ results in 660 nm Bragg wavelength.

The idea of the experiment was to use infrared (IR) optical pumping with the wavelength far enough from the spectral region corresponding to the bandgap. This radiation is able to penetrate to the depth of a sample and stimulate material luminescence in the visible range. The mechanism of up-conversion is not defined to date and probably consists in the effect of two- and three-photon absorptions. (Alternatively, third optical harmonic generation can be involved.) According to our expectations, we recorded the luminescence in the visible range. Surprisingly, unexpected narrow-band emission was detected at about 400 nm as well as second and third harmonics of the pump radiation.

3. Experiments with SOM excitation by femtosecond laser pulses at liquid-nitrogen temperature

The central wavelength λ_{ex} of the pump spectrum (Ti:Sapphire 160 femtosecond pulse laser operating with an amplifier at the repetition rate 1 kHz) amounted to 800 nm (near IR range). The optical breakdown in the air (laser spark) was observed at the waist of the focused beam. With the measured average power up to 150 mW the pulse power can be calculated to amount to 1 GW.

The SOM sample with dimensions about $3 \times 4 \times 5$ mm^3 and globule diameter 295 nm was placed on a copper plate plunged in a cavity filled with liquid nitrogen. No additional covers or air evacuation were provided. Therefore the actual temperature of the sample differs from the liquid nitrogen temperature (LNT) and was in the range of about 90–110 K (measured with the aid of an iron-constantan thermocouple). Below we shall refer to this temperature as LNT, keeping in mind the difference.

The sample was illuminated in the direction normal to the <111> axis with 140 mm and 100 mm focal distance lenses. The luminescence was observed only at the laser pulse intensity exceeding about 10^3 GW/cm^2 threshold. To measure the

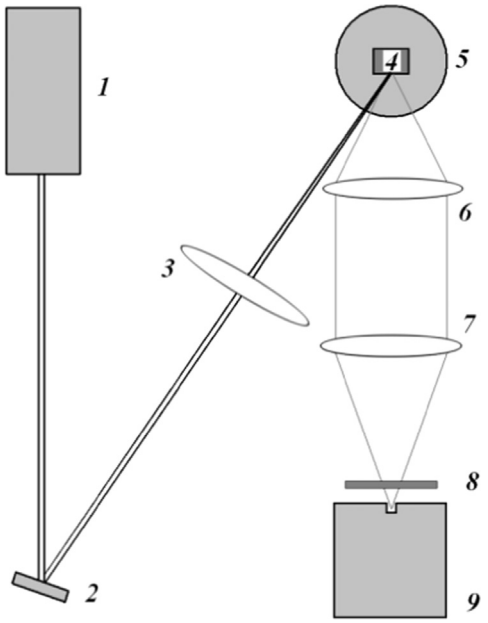

Fig. 2. Principal scheme of the experiment: (1) femtosecond pulse laser (excitation source), (2) a mirror, (3) the focusing lens, (4) the SOM sample placed on a cryostat (5). The optical system is formed from quartz lenses (6, 7) and color glass filter (8) for illumination of the entrance slit of the spectrophotometer (9).

luminescence spectrum, the light emission from the illuminated point on SOM sample was collected by a quartz lens optical system and directed to the spectrophotometer Acton Spectra Pro 2500i. The scattered IR pump radiation was blocked by a glass filter, as shown in Fig. 2.

Under the threshold there was no detectable light from the sample. Above the threshold the sample luminescence becomes visible to eye in the dark laboratory room. The recorded spectra are shown in Fig. 3(a and b). With the pump beam focusing by 140 mm focal distance lens the luminescence maximum appeared in visible range at about 570 nm, and short-wavelength emission was also detected at 330–420 nm. Probably the dip at 675 nm is a consequence of the photonic bandgap existence preventing light emission. A presence of the second-harmonic radiation is seen as a peak at about 400 nm (Fig. 3(a)). The spectrum fragment with the definite second harmonic peak is shown in Fig. 3(b) with better resolution.

With tighter focusing (100 mm focal distance lens) the SOM luminescence spectrum has radically changed. A narrow luminescence contour (4 nm HWHM) appeared at 408 nm overlapped with the peak at $\lambda = 400$ nm corresponding to the second optical harmonic of the pump frequency (Fig. 3(c)). (Narrow spectral lines are assigned to belong to the emission from nitrogen excited in the laser spark.) The halfwidth of the peak at 408 nm (HWHM) amounts to 4 nm. The relative intensities of the peak and the second-harmonic peak varied noticeably.

Then, in the UV spectral region from 260 to 330 nm a peak of the third harmonic of the pump frequency was detected at 267 nm without any other observable sample luminescence. The whole UV and visible range of the recorded SOM luminescence spectrum is shown in Fig. 4. Surprisingly, luminescence maximum at 560 nm has disappeared at all.

The revealed transformation of the luminescence spectrum with the increase of the pump intensity is a sign of the presence of a gain and a feedback in the medium. There is an important question why namely the maximum at 408 nm wave length appears “from nothing” and becomes dominant in the luminescence spectrum (Fig. 4). We can seek the answer in the