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TEMPORAL CHARACTERISTICS OF AFTERGLOW IN ARTIFICIAL OPAL

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We report the results of an experimental study of the temporal response of the artificial opal luminescence excited by UV pulses from a nitrogen laser at room temperature, liquid-nitrogen temperature, and in the intermediate range. While the response time does not exceed 15 ns at room temperature, the afterglow at liquid-nitrogen temperature was detected with a decay time of about 700 ms. We have revealed that the afterglow appears suddenly with just millisecond-range duration at a definite temperature of 130 ± 5 K. The temperature dependence of the afterglow is of importance for the explanation of surprising effects of the stimulated emission in a single nano-sized SiO_2 globule and the second harmonic generation in the material at liquid-nitrogen temperature.

K e y w o r d s: artificial opal, afterglow, nanocavity lasing.

1. Introduction

Artificial opal is a photonic metamaterial composed from spherical globules of amorphous silica (SiO_2) about 300 nm in diameter [1]. The globules are produced in a chemical reaction of hydrolysis of tetraethoxysilane $Si(OC_2H_5)_4$ in a water-ethanol solution [2]. The growth of globules (crystallization) continues until the necessary dimension is reached. The reaction is stopped, and the globules drop on the bottom of a vessel and self-pack in the solid matrix. Then dry opal samples are hardened by the hydrothermal treatment and annealing. A structure of artificial opal for perfect samples corresponds to face-centered cubic (FCC) lattice. However, real samples possess a noticeable number of defects. Figure 1, *a* gives an image of the ⟨111⟩ opal face with the nearly hexagonal packing of globules. Linear and nonlinear optical effects observed with artificial opals are of continuous interest in recent years [3]. While the theory was mostly developed in the past decades, the experimental treating demonstrates quite surprising features and unexpected results. Recently, we reported the origin of a narrow luminescence spectral peak (4 nm HWHM) and the generation of optical second and third harmonics in artificial opal under the excitation by a femtosecond pulse laser (800 nm wavelength) at liquid-nitrogen temperature. We note the material has no linear absorption in the near infrared region, but UV radiation owing to the third-harmonic generation can excite active centers with the following radiation from them in visible. Generally, the UV excitation generates a broad opal luminescence spectrum from 350 nm to 750 nm [4].

The high-power pulse excitation of artificial opal samples has revealed some surprising effects [5]. Figure 1, *b* presents the radiation spectrum of an opal sample cooled to liquid-nitrogen temperature under the excitation by 160-fs pulses from a Ti : Sapphire laser operating with the emission on the 800-nm central wavelength. The spectrum demonstrates definitely the presence of the second-harmonic peak and rather narrow emission contours at 408 nm. The position of the maximum correlates with a globule diameter of 295 nm, according to the Mie resonance condition [6]. The appearance of the maximum is a sign of the stimulated emission and gives a promise to achieve the nano-lasing in artificial opal. The effect of the second harmonic generation looks unusual for a non-crystalline amorphous material of SiO_2 glob-

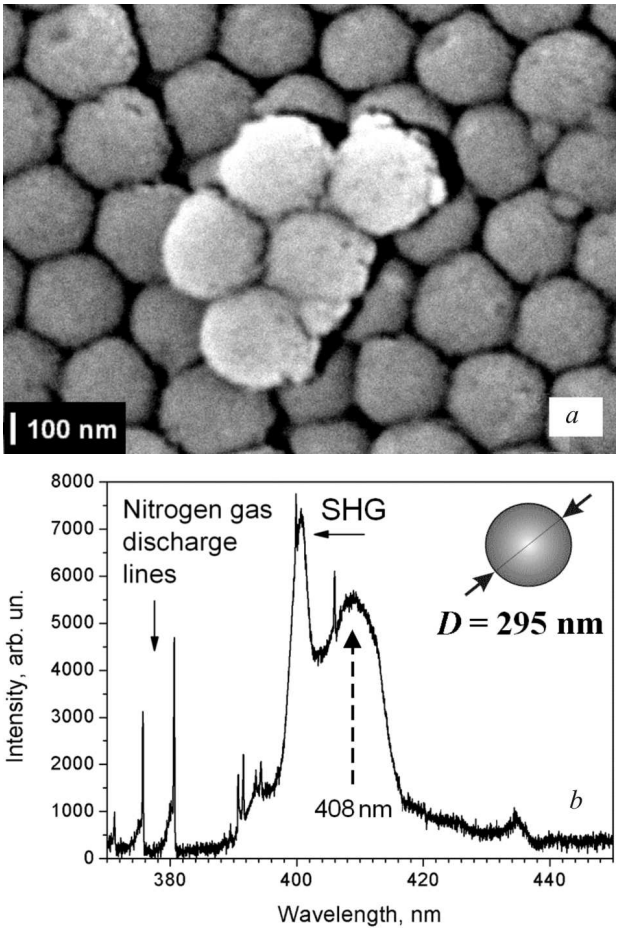

Fig. 1. Scanning electron microscope image of an artificial opal sample (⟨111⟩ face). The sample was treated with a globule diameter of 295 nm. Scale mark 100 nm is shown (*a*). Spectrum of light emission from a synthetic opal sample illuminated by the focused beam of a femtosecond-pulse laser (wavelength 800 nm). Dashed arrow shows the enhanced emission maximum corresponding to the Mie resonance for a spherical globule. Narrow spectral lines belong to radiation of nitrogen molecules excited in the laser spark (*b*)

ules. The reported observation of the effect is related to the situation of the opal matrix filled with immersion [7], and the mechanism is explained with account for the local breaking of the inversion symmetry at the surface of each spherical particle [8]. However, the nonlinear polarization at the second harmonic frequency can appear owing to the interference of an extremely high-power pulse with a seed radiation in the material [9]. Then the presence of some light in the artificial opal globules at the time moment of an exciting pulse coming is crucial. The specific feature of the detected effects of the second-harmonic generation and the enhanced emission around the Mie resonance wavelength is that they are observed only at low temperatures (close to liquid-nitrogen temperature). Probably, this issue gives a key for the explanation of the origination of effects. In this view, the determination of the decay time of the excitation induced in a SiO_2 nanosphere by a short-pulse laser radiation is of importance [10].

2. Experimental

In this report, we present the results of measurements of the time characteristics for the optical luminescence of artificial opal. In the experiment, we used a pulsed N_2-laser with a pulse duration of 9 ns and the operation wavelength $\lambda_{ex} = 337$ nm. This choice allows us to observe the material response to the UV radiation excitation by a single pulse or a pulse train by ordinary methods. With a repetition rate of 25–100 Hz, the interval 40–10 ms between the pulses is large enough to measure the temporal response in the microsecond range. A pump pulse power amounted about 1.5 kW. With this level of excitation, we cannot expect any nonlinear optical effects and detect only the linear response. This experiment models the situation that occurs under the periodic pulse excitation by a femtosecond laser with the 1-kHz repetition rate in the sense of temporal events. A laser beam was focused on the artificial opal sample, and the illuminated point was projected by a glass lens to a photomultiplier. A glass filter was used to cut off the pumping UV light. The signal from a detector was directed to a digital oscilloscope. An example of the luminescence response to a train of exciting pulses at room temperature is shown in Fig. 2.

To resolve the single-pulse response of artificial opal at room temperature, we used another high-speed detector. The result is presented in Fig. 3. The room-temperature experiment with the single pulse detection has shown that the time response τ of opal does not exceed 15 nanoseconds.

Similar measurements were performed at liquid-nitrogen temperature (LNT). The sample was placed on a copper plate plunged in a cavity filled with liquid nitrogen. The temperature was measured with the K-type thermocouple. The material luminescence signal was enhanced in the magnitude and substan-

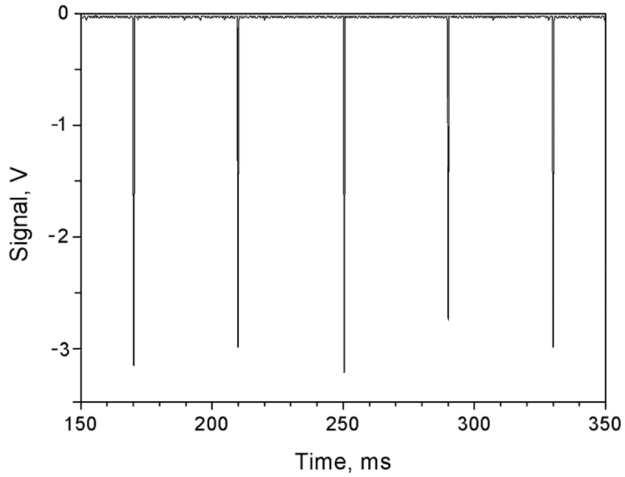

Fig. 2. Luminescence response of an artificial opal sample to a train of exciting UV pulses (λ_{ex} = 337 nm) from an N_2 laser. (Note the negative voltage signal). A repetition rate is 25 Hz, and the pulse duration is not resolved on the time scale used. Luminescence signal neither is seen between the pump pulses nor after the train

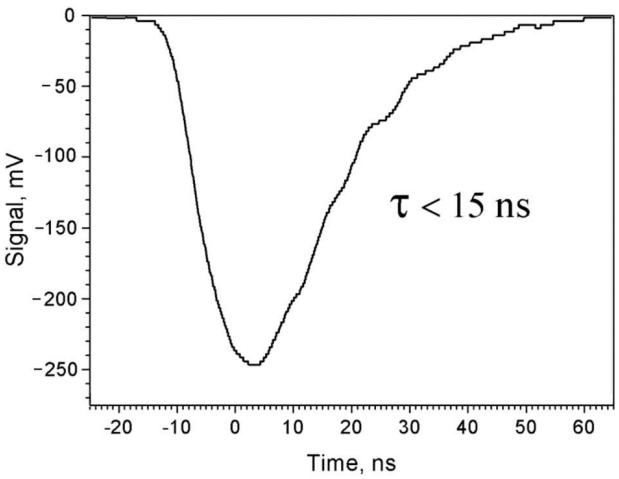

Fig. 3. Time-resolved luminescence response to a single UV exciting pulse at room temperature

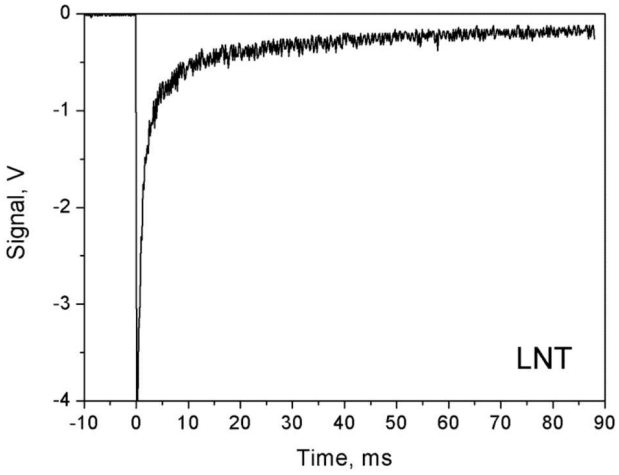

Fig. 4. Time-resolved luminescence response to a single UV exciting pulse at liquid-nitrogen temperature. The afterglow appears after the fast-response peak

tially in the response time duration. The corresponding oscillogram is presented in Fig. 4. There is a sharp direct-response peak, which continues the same time as in the room-temperature experiment, but additionally the afterglow decay appears with the duration about 100 ms. To determine the afterglow decay time, we approximated linearly the logarithm of the signal modulus. The linear dependence ensures an exponential dependence with the decay time $\tau \approx 75$ ms. However, in general, the decay is not single-exponential.

With the pulse-periodic pump, the steady state luminescence level is a result of the consolidated impact of pulses in a train. Figure 5 demonstrates the signal rise excited by a train of 22 pulses following with a rate of 100 Hz and the relaxation after the switching-off of the pump. The measured afterglow decay time amounts about 700 ms, noticeably higher than the single-pulse measurement result (Fig. 4). Actually, the afterglow with a duration about 1 s is exactly seen by eye. Now, instead of the single exponential decay process, we see the relatively fast decay with the "short" time τ_s (75 ms) and "long" time τ_l (700 ms).

Then we selected three spectral ranges: one in a violet part of the luminescence spectrum (380–450 nm), the second in the interval 450–560 nm (green), and the third in the orange-red part above 580 nm. Practically most of radiation is concentrated in the central part of the luminescent spectrum. The comparison has shown no noticeable difference between the "green" and "orange" parts. However, in the violet range, we detected a slight difference in the decay times. The comparison is shown in Fig. 6 for the natural logarithms of corresponding signals (taken as absolute values).

Finally, we have examined the origin of the afterglow. Even at room temperature, the detailed inspection revealed the weak time-delayed "tail" with a duration of 1.3 τ_s not seen in Fig. 3 (the 1 τ_s afterglow existence was also noted in [11]). Thus, in the

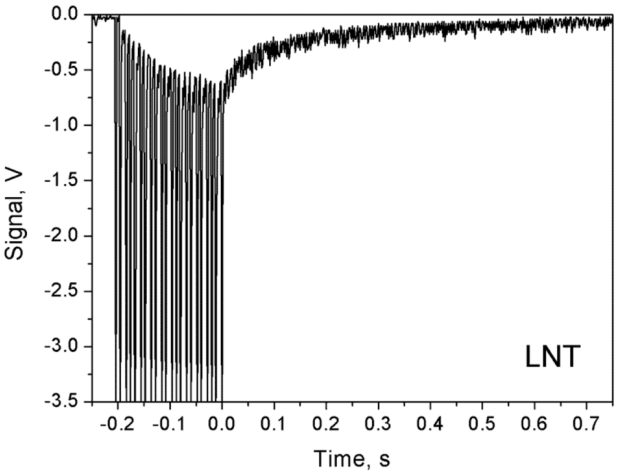

Fig. 5. Luminescence response of an artificial opal sample to a UV-pump (22-pulse train) from an N_2 laser at liquid-nitrogen temperature. The sharp peaks are direct response spikes same as in Fig. 4. Long-time afterglow signal is seen. The characteristic decay time amounts to about 0.7 s

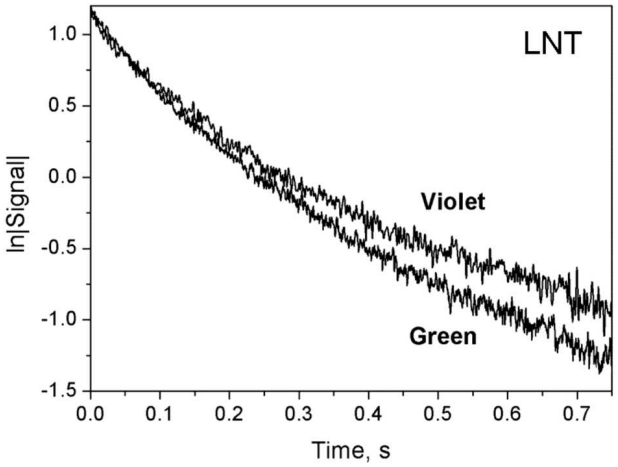

Fig. 6. Comparison of the measured afterglow decay processes for spectral windows 380–450 nm (Violet) and 450–560 nm (Green) excited in artificial opal by a UV pulse train at liquid nitrogen temperature

temperature interval from 300 K to 80 K, the afterglow duration increased by 10^4 times. Moreover, this fascinating transformation occurs just in a very short temperature interval from 140 K to 130 K. With thermocouple-based temperature monitoring, we detected the afterglow appearance in this interval, first as a short-time tail (millisecond range) following an individual pulse, and then the accumulation of the signal to the long-range (∼1 s) afterglow. This means

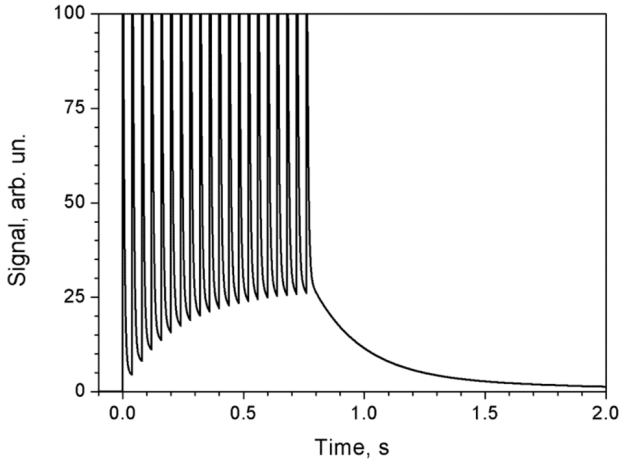

Fig. 7. Calculation of the luminescence response to a pulse-periodic pump (20-pulse train). The parameters used are: pulse-response duration 1 ms, repetition rate 25 Hz, train duration 800 ms, "short" time $\tau_s = 100$ ms, "long" time $\tau_l = 1$ s

that the response time rises gradually from the microsecond range to the millisecond range in the interval from room temperature to about 135 K and then suddenly to the 1-second range duration.

3. Discussion and Conclusions

In the set of experiments, we succeeded to find the existence of the temperature threshold for the artificial opal afterglow to appear suddenly with millisecond-range duration at the temperature 135 ± 5 K. The peculiarity of the luminescence response is the "short" decay time after a single pump pulse and a "long" afterglow after a train of pulses. In this sense, the origin of the temperature threshold finds the explanation as the destination of single-pulse afterglow duration to the interval between neighbor pulses. This moment corresponds to the overlapping of the exciting pulse with the just excited states, and probably to the excitation from these states, which results finally in the population of long-living metastable levels. To model the pulse-periodic situation, we have calculate the luminescence signal from a system possessing two different decay times, one 100 ms and another 1 s, and direct pulse-response duration 1 ms (this choice allows us to display the sharp peaks, as well as the long decay). The results are shown in Fig. 7 in good qualitative agreement with the experimental dependence (Fig. 5).

The behavior of the artificial opal luminescence at LNT gives the evidence to the favor of the explanation of the nonlinear effects detected with the high-power excitation: strong femtosecond-range pulse radiation can interfere with the light excited in the opal nano-spheres by the preceding pulse. While the light fields differ strongly in wavelengths, and their phases are not matched, the short pulse duration favors the coherent interaction and a nonlinear frequency transformation (second harmonic generation). On the other hand, a substantial increase of the material luminescence is necessary to overcome a lasing threshold. Probably, liquid-nitrogen temperature is not required for these nonlinear effects. The measured "short" time of the afterglow at LNT ($\tau_s \approx 75$ ms) ensures the overlapping of the periodically coming pulses (25 Hz repetition rate) with the afterglow light originated from the material excitation by preceding ones. Thus, the afterglow duration at liquid-nitrogen temperature seems to be more than enough to satisfy the condition for the temporal overlapping with a repetition rate of 1 kHz of the femtosecond-pulse laser used in [5], and the requirement of the sample cooling to LNT is therefore overbalanced. We expect a moderate cooling to the level of the afterglow appearance, whose duration of about 1 ms will be enough for the registration of the second-harmonic generation and starting the pre-lasing effect. In summary, the direct measurements of the response time of the afterglow from artificial opal excited by UV short pulses are carried out. The stimulated-emission effects related to a possibility of nanocavity lasing under conditions of the Mie resonance in a dielectric sphere are discussed.

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ЧАСОВІ ХАРАКТЕРИСТИКИ ПІСЛЯСВІТІННЯ У ШТУЧНОМУ ОПАЛІ

Р е з ю м е

Подано результати експериментального вивчення часового відгуку штучного опалу, збудженого ультрафіолетовими імпульсами від азотного лазера, при кімнатній температурі та температурі рідкого азоту. Якщо при кімнатній температурі час відгуку люмінесценції не перевищує 15 нс, при температурі рідкого азоту спостережено появу післясвітіння з часом спадання приблизно 75 мс від одного імпульсу та 700 мс від цуга імпульсів. Ми знайшли, що післясвітіння з мілісекундною тривалістю виникає раптово при визначеній температурі 130 ± 5 K. Температурна залежність відгуку важлива для пояснення несподіваних ефектів стимульованої емісії в окремій нанорозмірній глобулі SiO_2 та генерації другої гармоніки у матеріалі при температурі рідкого азоту.