Directed UV and X-ray generation in nanomaterials at the optical excitation

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Abstract. Efficient electromagnetic emission of radiation in the spectral range with wavelengths shorter than exciting light wavelength was observed at the nanomaterials excitation by laser pulses. Emission was registered in a visible (blue-green) range, in vacuum UV and in soft X-ray. Luminescence was registered both in the air and in the vacuum chamber. Synthetic opal matrices and nanocomposites on their base (matrices infiltrated with different liquids) were used as samples. Luminescence was excited with the help of different lasers: ruby laser, second harmonic of Nd:YAG laser and copper vapor laser. In the visible range two regimes of luminescence were observed: fast (few μs) and slow (up to 12 s). Slow luminescence was registered at temperatures lower than 110 K. Spectra of X-ray emission were registered. The connection of this emission with the triboluminescence effect is considered.

1. Introduction
Interaction of electromagnetic fields with nanostructured materials has specific characteristics compared to the interaction with bulk substance. It is caused by nanomaterials morphology, leading to the electromagnetic field increasing near the surface and to the appearance of band-gaps. Many nonlinear effects have in nanomaterials higher efficiency and lower threshold. It was shown in [1] that stimulated Raman scattering (SRS) in liquids, infiltrated into pores of synthetic opal matrix has a lower threshold than in corresponding bulk substance and can be excited in a small amount of liquid. In [2] correlation of the SRS high conversion efficiency and band-gap for such nanocomposites was demonstrated.

The other characteristic feature of the electromagnetic fields interaction with nanomaterials is the appearance of new nonlinear effects, for instance, low-frequency Raman scattering (LFRS), caused by
light interaction with acoustic vibrations of nanoparticles or nanosized structure elements [3]. Stimulated analog of this scattering – stimulated low-frequency Raman scattering (SLFRS) [4] was registered in many different nanomaterials: metal, dielectric, semiconductors - both high-ordered and random materials [5]. Frequency shifts of SLFRS are situated in gigahertz or terahertz range. SLFRS high conversion efficiency is evidence of very strong excitation of such vibrations, which can lead to other nonlinear phenomena. One of such effects is long light emission under excitation of nanomaterials with short laser pulses. We observed this effect in different nanomaterials under 20 ns pulses of the ruby laser at the liquid nitrogen temperature [7]. The emission spectrum was observed in the blue-green range, which is anti-Stokes compare to the excitation wavelength, so we can call it anti-Stokes luminescence [8]. One of the reasons for this effect is triboluminescence – light emission under the mechanical impact. This well-known effect recently attracted the attention of researchers due to the possibility of its using for monitoring of engineering constructions damages and for the creation of sensors of mechanical impact on solid surfaces, mainly in astronautics [9]. Practical applications led to the need for the theoretical understanding of the triboluminescence effect nature. The most part of the works (both experimental and theoretical) on triboluminescence and fractoluminescence (light emission, caused by material destruction) dealt with the mechanical impact on bulk solids [9, 10], in particular, on crystalline quartz or on quartz glass [11]. It was shown that light emission is a result of small cracks arising and siloxane bonds breaking in this process. The energy in a visible spectral range is emitted at the transitions from excited to the ground electronic states of radicals. Triboluminescence in nanomaterials on the base of SiO2 was studied in [12]. It was shown that this effect is different in nanoscale and bulk materials.

In the present work we show that not only visible light is emitted under laser pulses impact on nanomaterials, but also higher energy electromagnetic radiation: UV and X-ray.

2. Experimental samples, setup and results

2.1. Samples

Synthetic opal matrices and nanocomposites on their base were used as samples. These nanomaterials are widely used in nanophotonics, nonlinear optics and many areas of nanotechnologies. Opal matrices are three-dimensional structures formed from close-packed SiO2 globules arranged into a face-centered cubic lattice and connected with strong siloxane bonds. Opal matrices have no full bandgap, but due to the submicron size of the spheres, these structures have stop zones in the visible spectral range for various modes propagating in certain directions. The position of the center of such a stop zone is \( \Lambda_{\text{phg}} = 2D (2/3) 0.5 n_{\text{eff}} \cos \theta \), where \( n_{\text{eff}} \) is the effective refractive index of the matrix. By filling the voids between spheres with liquids having different refractive indices, it is possible to control the parameters of the stop zone and increase the efficiency of nonlinear processes due to the changes in the photon states density near the bandgap edge. In the present work, we used opal matrices with globules diameters 220 and 250 nm. Voids between globules were infiltrated with the following liquids: ethanol, acetone, glycerol, water.

2.2. Experimental setup.

Different lasers have been used for anti-Stokes emission excitation. The most part of the experiments have been made with the help of ruby laser with wavelength 694.3 nm, single pulses with 20 ns duration and maximal energy 0.3 J. We also used copper vapor laser, operating in a frequency mode with 10 kHz frequency at wavelengths 510 nm and 578 nm with 15 ns pulse duration and mean power 3 W and Nd:YAG laser 2nd harmonic with following parameters: wavelength 532 nm, pulse duration 20 ns, repetition rate 10 Hz, mean power 50 W.

Laser light was focused on the sample by lenses with different focal lengths. Experiments have been performed at different temperatures (from room temperature to the liquid nitrogen temperature) both in the air and in a vacuum. We created for this aim a vacuum cryogenic chamber made from stainless steel with quartz glass windows. In his chamber vacuum could be reached up to \( 10^{-5} \) mm Hg with the help of
two vacuum pumps: for vacuum and turbomolecular. Graduated thermocouple registered the temperature of the sample.

The principal scheme of the experimental setup is presented in figure 1.

![Figure 1. Setup for the study of electromagnetic emission in the wavelength range shorter than exciting light.](image)

The high-speed optical camera based on the AM1X5 sensor registered spatial distribution of the luminescence and its dynamics. It captured 1024x1024x8 images at a speed of 5000 frames/sec with the possibility of the proportional increase in the shooting rate while reducing the resolution.

Luminescence spectra in a visible range have been registered with the help of mini-spectrometer with fiber input.

Spatial distribution of radiation excited by the laser pulses in the samples studied in the X-ray and ultraviolet range was registered using a radiographic image recorder. It gave the possibility to obtain images for the medium and hard X-ray range and vacuum ultraviolet (from ~ 10 eV to ~ 300 keV) with the image output to the computer in real time. It was also possible to take pictures of the radiation spatial distribution with exposure from 3 s to 5 ns.

The temporal characteristics of the emission have been studied with the help of high-speed photodiodes, connected with an oscilloscope. Synchronization of the system was carried out from a two-channel generator of delayed pulses.

The UniSpec 503 gamma-ray spectrometer of Canberra was used to record X-rays spectra. It could not register spectra of single nanosecond pulses, therefore for spectral measurements, synthetic opals were excited by a copper vapor laser, operating in a frequency mode. In this case, the X-ray radiation was recorded in the accumulation mode.

2.3. Experimental results.

In the visible range with the help of speed camera, we registered bright anti-Stokes luminescence both in the opal matrices without infiltration and samples infiltrated with different liquids. Light emission duration was essentially different at room and low temperatures. At room temperature light emission was fast; its duration was few μs. At the temperature of liquid nitrogen, we registered slow luminescence with a duration up to 12 s, while the exciting pulse duration was 20 ns. The luminescence of studied samples in the visible range was approximately the same in the vacuum camera and without it. The luminescence of the opal matrix infiltrated with ethanol, registered at the beginning of light emission, is presented in figure 2.
Figure 2. The moment of ruby laser pulse focusing on the sample and beginning of the sample luminescence for opal matrix infiltrated with ethanol (in the vacuum).

Luminescence of the samples infiltrated with different liquids at 1, 2 and 3 seconds after excitation is presented in figure 3.

Figure 3. Luminescence of the samples infiltrated with a) ethanol, b) glycerol at the liquid nitrogen temperature.

We studied the temperature dependence of light emission and found out that the slow dependence had a temperature threshold, which was the same for opal matrices without infiltration and samples infiltrated with liquids. Its value was 110 K. More detailed investigations of the emission temporal dependence showed that the first part of it was different in different experiments. In the most part of experiments, a gap on the curve of temporal dependence was registered after 400-500 ms after an exciting pulse. Typical curves of temporal dependence for temperatures lower and higher temperature threshold are shown in figure 4.

Figure 4. Temporal dependence of anti-Stokes luminescence in synthetic opal matrix infiltrated with ethanol: a – temperature above 110 K; b – temperature below 110 K.
In some experiments we registered in the first part of the temporal dependence (approximately 50 – 100 μs) bright flashes with an interval of 6-7 μs. After this first part, the temporal dependence curves had character near to the exponential. It is possible to approximate it by one or (more exact) two exponents. Similar results were obtained in [13] for luminescence of pressured SiO₂ nanoparticles at low temperature.

We also observed in synthetic opal matrices and nanocomposites on their base radiation emission in the high-energy range: ultraviolet (UV) and soft X-ray. UV emission was registered under excitation by ruby laser with the help of a radiographic recorder. The wavelength of the emission was approximately 100 nm; its spatial distribution was symmetrical. At the receiver of the recorder we observed round spot with diameter 3 mm. In these experiments the samples were placed in the vacuum chamber, the distance from the sample to receiving plane of the radiographic recorder was 100 mm. The UV emission, registered on the recorder, is shown in figure 5.

![Figure 5. Emission in the vacuum UV range on the receiving plane of the radiographic recorder.](image)

X-ray emission from samples investigated was observed both in opal matrices without infiltration and samples infiltrated with liquids (ethanol or acetone). We registered X-ray emission under excitation with different lasers: single pulses of the ruby laser, second harmonic pulses of Nd:YAG laser and copper vapor laser operating in frequency mode. In all cases, X-ray emission was registered on the X-ray film in special cassettes as bright spots. A typical picture of such emission is presented in figure 6.

![Figure 6. X-ray emission in the opal matrix under laser pulses excitation registered with X-ray film.](image)

In the case of excitation by ruby laser pulses, we also registered X-ray emission with the help of a radiographic recorder. To divide X-ray from UV emission we used a filter from Teflon film with cut-off 4 keV. The emission registered on the receiver of the recorder had a view of small spots with almost Gaussian distribution.

![Figure 7.](image)
3. Discussion

Two regimes of luminescence (fast and slow) were observed in bulk quartz under mechanical impact [11] and in pressed SiO$_2$ nanoparticles under UV radiation (Xe lamp or laser radiation higher harmonics) excitation [13]. In our case light emission is observed at the laser light excitation in the spectral range shorter than the exciting light wavelength. One of the main processes leading to such anti-Stokes light emission is triboluminescence. High-energy emission in nanomaterials under strong mechanical or electromagnetic impact is also connected with the triboluminescence process. The initial reason for both processes is the breaking of molecular bonds, dividing of electrical charges and charged radicals formation. It leads to the defects appearance and luminescence arising due to the transitions from excited levels to the ground states of radicals. This process was studied in quartz and quartz glass [11]. Under mechanical impact, microcracks appear in bulk material and bonds breaking cause the opposite charge on the sides of the cracks. In [11] formation of different possible radicals is considered. Simultaneously with radicals appearance and defect formation high-speed electrons are formed. It was shown yet in 1955 in [14]. The authors registered such electrons in the process of tearing off high polymer film from the glass in a vacuum. Obreimov was the first who observed X-ray emission in the process of triboluminescence [15]. In 1930 he registered X-ray during mica splitting. In [16] triboluminescence and X-ray emission were registered in the process of peeling pressure-sensitive adhesive tape.

In nanomaterials, the strong impact of laser pulses leads to efficient vibrations of nanoparticles [5]. In theopal matrix, these vibrations lead to the siloxane bonds breaking and high-speed particles appearing, which can lead through the bremsstrahlung to the X-ray arising. Physically, this process is similar to the processes considered in [16]. The main difference is that the mechanical impact on the system under consideration in our case is realized by pulsed laser radiation through ponderomotive interaction. This enables the most effective acoustic excitation of the medium compared to a purely mechanical effect.

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