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UV Radiation of Powdered ZnO Pumped by Nanosecond Pulses

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Abstract—Since the intrinsic lifetime of spontaneous recombination UV radiation in zinc oxide amounts less than ~200 ps it is of interest to obtain stimulated UV radiation of powdered ZnO with pumping pulses of nanosecond duration. This will clarify the possibility of quasi-continuous laser radiation in disordered media. At the same time this effect can open the way for working out a cathodoluminescent screen with narrow spectrum and short persistence time. Investigations of UV radiation spectra of powdered zinc oxide were conducted. The samples were pumped by the 3rd harmonics of a two-stage Nd : YAG laser ($\lambda = 355$ nm) with pulse duration ~10 ns. The maximum energy density of pumping pulses was about 160 mJ/cm^2. Spectra of spontaneous emission were registered at 300 and 77 K. With some of our powdered samples we achieved lasing at 300 K. The threshold values of pumping energy density were higher than under picosecond pumping by approximately two orders of magnitude. Peculiarities of lasing of different samples are demonstrated and discussed.

1. INTRODUCTION

Stimulated radiation in randomly inhomogeneous media was predicted by Letokhov [1] and was first experimentally demonstrated on dielectric powders doped with neodymium [2]. The laser effect was then obtained and investigated in powdered zinc oxide excited by picosecond pumping [3]. ZnO is a wide-band-gap semiconductor where the binding energy of the exciton amounts to approximately 60 meV. The recombination of excitons in zinc oxide produces UV radiation in the region 380–390 nm with a lifetime of spontaneous emission of less than 200 ps. In such a situation it is relatively easy to excite zinc oxide by picosecond pumping, because during the pump pulse spontaneous decay is practically absent.

Quite another situation is seen in the case of nanosecond excitation, which we use in our research. Here the pumping must "surpass" spontaneous decay. In other words, the initial part of pumping pulse, which is considerably shorter than the spontaneous lifetime, must provide an excitation energy that is enough for lasing. Below we shall give a simplified estimation of the rise in the threshold at the transition from picosecond to nanosecond pumping. Under nanosecond pumping, we may expect quasicontinuous lasing, an effect that has not been previously investigated in these powders up to now. At the same time, this effect may open the way for working out cathodoluminescent screens with narrow spectrum and short persistence time. There is a paper [4] where pressed powder of ZnO was pumped by 5-ns pulses. The effect obtained in this research, however, could hardly be called lasing; in fact it closely resembles a fringe pattern.

Here we conducted investigations of UV radiation spectra of powders of zinc oxide. In some of the powdered samples under investigation, a narrowing of the UV band was observed with a rise in the pumping energy density. At the same time, a number of irregular narrow spikes appear in this band. We consider both of these facts as a manifestation of lasing in powdered ZnO excited by nanosecond pumping.

2. EXPERIMENT

In our experiments, the samples were pumped by 3rd harmonics ($\lambda = 355$ nm) of a two-stage Q-switched Nd : YAG laser with a pulse duration of approximately 10 ns and repetition rate 20 Hz. To vary the pumping power with the second stage (amplifier) or without it, we used a set of filters with different transmission at 355 nm. The average pumping power was ~0.5 mW without the amplifier and ~2.9 mW with it. The area of the pumping spot was approximately 9×10^{-4} cm^2. Thus, energy densities of up to 160 mJ/cm^2 were available.

The sample emission was directed to the monochromator MDR-23, which was in series with photo multiplier (PET-79) connected to boxcar integrator BCI-280. The resulting signal was registered by PC. The stepper motor was operated by the same PC and rotated the diffraction grating. The system could accumulate a given number of signals at every fixed wavelength.

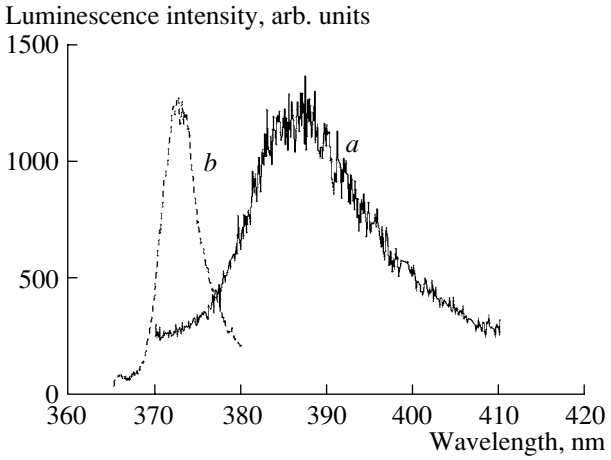

Fig. 1. Typical UV-emission spectra of ZnO powders at different temperatures: (*a*) 300 K; (*b*) 77 K.

In the experiment, powdered samples were placed in thin quartz test tubes. The main part of measurements was conducted at room temperature (300 K), and a few measurements were made at liquid-nitrogen temperature (77 K).

3. SIMPLIFIED ESTIMATION OF THE THRESHOLD RISE

It was interesting to estimate by how many times the thresholds of lasing under nanosecond pumping would exceed those under picosecond pumping. The simplest way is to take the pumping pulses as rectangular. Then the energy of pumping that falls on the sample during the lifetime of spontaneous emission (τ) under a long pump must be equal to the whole energy of a short pump E_{ps}. Since τ is less than 200 ps and the duration of nanosecond pulses is ~10 ns, the whole energy of a long pump E_{ns} must be more than 50 times greater than E_{ps}.

For a somewhat more accurate, but also simplified, estimation, we can proceed from the requirement of the equality of the carrier concentration maximum under both types of pumping. Using such an approach, we can take for a short pump $N_{max} = \frac{E_{ps}}{h\nu}$, since the pulse duration is much less than τ. In order to estimate N_{max} for a long pump, we will describe the time dependence of the pump by the expression $At\exp\left(-\frac{t}{t_m}\right)$, where t_m is the position of the pumping maximum, $A = \frac{E_{ns}}{(t_m)^2 h\nu}$. This expression is in good agreement for the pulses from our Q-switched Nd : YAG laser. The time dependence of the carrier concentration (N) is described by the balance equation $\frac{dN}{dt} = -\frac{N}{\tau} + At\exp\left(-\frac{t}{t_m}\right)$. The solution of this equation can be written as $N = AT^2\exp\left(-\frac{t}{\tau}\right)\left[1 + \exp\left(\frac{t}{T}\right)\left(\frac{t}{T} - 1\right)\right]$, where $\frac{1}{T} = \frac{1}{\tau} - \frac{1}{t_m}$. To determine N_{max} we must first find the time (T_0) when it will be reached and then put T_0 into the expression for N. From the condition $\frac{dN}{dt} = 0$, it follows that $\exp\left(\frac{T_0}{T}\right) = \frac{\frac{t_m}{\tau}}{\frac{t_m}{\tau} - \frac{T_0}{T}}$.

For the numerical computations we took $\tau = 0.2$ nc and $t_m = 4$ nc, which provides the pulse width ~10 nc. These values give $W = E_{ns}/E_{ps} \approx 54$. Thus, both our simplified estimations show that the threshold density of nanosecond pumping must be more than 50 times larger than that of picosecond pumping. Indeed, it turned out that W is several times larger.

4. RESULTS

4.1. Spontaneous Emission

At room temperature, the spectra of spontaneous UV emission of powdered zinc oxide have a maximum at 388–390 nm, and the bandwidth lies in the range 12–16 nm. An example of such a spectrum is depicted in Fig. 1, curve *a*. When the pumping energy increases, the bandwidth decreases. (This will be considered in detail in the next subsection). At liquid-nitrogen temperature, the maximum of UV spectrum is located at 372 nm and the bandwidth is approximately 5 times narrower than at room temperature, as demonstrated in Fig. 1, *b*.

It was observed that the intensity of the maximum of the UV spontaneous emission band of different samples has a tendency to increase with a an increase in the size of powder particles (in the range from ~150 nm to ~2–3 μm).

4.2. Lasing

When the energy density of pumping increases, stimulated emission arises. It manifests itself first in the band narrowing, and then lasing takes place. Different samples switch from spontaneous emission to lasing in different intervals of pumping values. The samples under investigation differ significantly one from another in the threshold, this interval, and the character of the lasing spectra. It is also necessary to point out that it is impossible to compare intensities corresponding to different curves in our figures, since each curve has its own scale. Micrographs of our samples made by scanning electron microscope (SEM) are shown below in the figures where the approximate grain sizes of these powders are indicated.

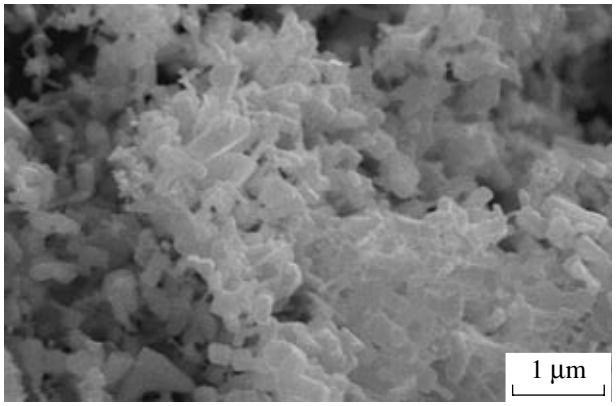

Fig. 2. Sample no. 1 (0.2–0.5 μm).

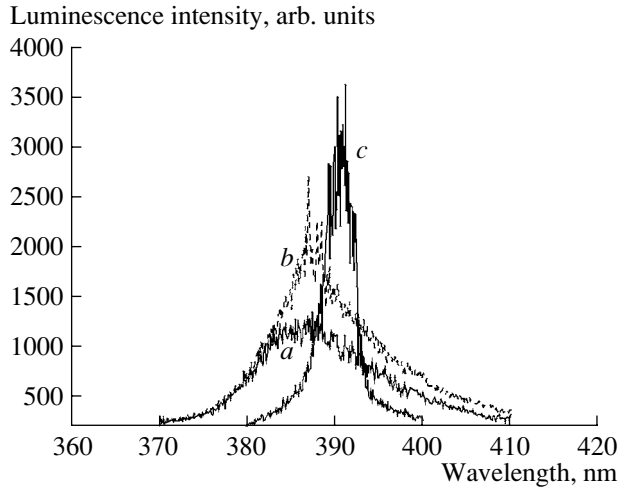

Fig. 3. UV-emission spectra of sample no. 1 at different levels of excitation: (*a*) 1.7 mJ/cm^2, (*b*) 2.7 mJ/cm^2, (*c*) 26.7 mJ/cm^2, T = 300 K.

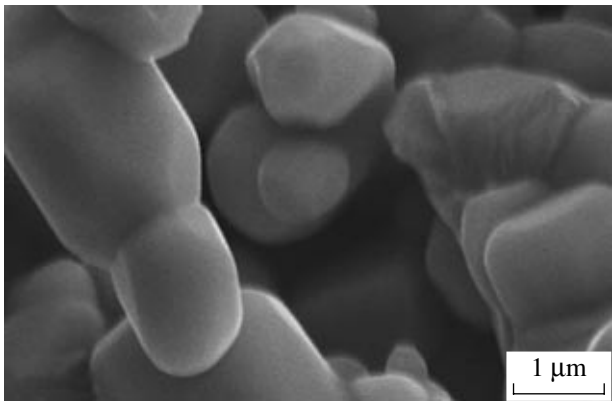

Fig. 4. Sample no. 5 (1–3 μm).

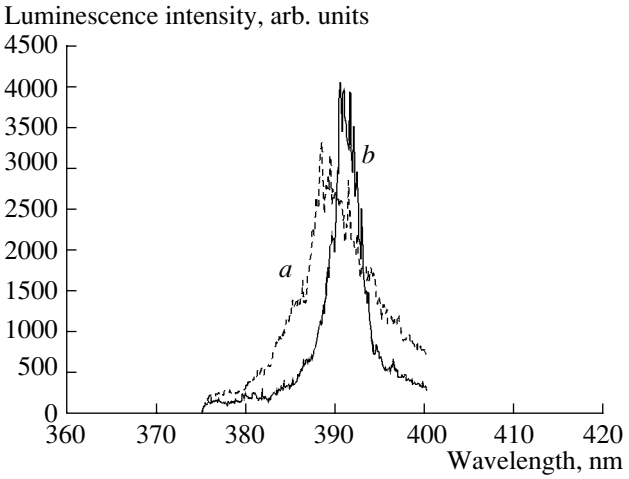

Fig. 5. UV-emission spectra of the sample no. 5 at different levels of excitation: (*a*) 2.7 mJ/cm^2, (*b*) 8 mJ/cm^2, T = 300 K.

The lowest threshold (~2.7 mJ/cm^2) was obtained for samples no. 1 (Fig. 2) and no. 5 (Fig. 4). As is demonstrated in Figs. 3 and 5, the spectra of these samples are rather narrow at 2.7 mJ/cm^2, and when the pumping increases further they become still narrower and spikes appear. At the same time, the maximum of the spectra shifts to the long-wavelength side. As can be seen in the figures for other samples, this shift takes place in all of our samples; the value of the shift amounts to ~3 nm.

The highest threshold (~27 mJ/cm^2) was found for sample no. 3 (Figs. 6 and 7). For this sample, it is characteristic that the switching from spontaneous emission to lasing occurs in a wide interval of pumping energy. The other peculiarity of this sample is the almost total lack of spikes even at a high level of pumping. It seems that here only amplified spontaneous emission takes place.

Samples no. 4 (Fig. 8) and no. 6 (Fig. 9) did not lase at all up to the maximum available energy density ~160 ml/cm^2.

The most interesting results were obtained with sample no. 2 (Fig. 11). It is practically monodisperse and its particles are spheres with diameter ~0.15 nm (Fig. 10). This sample demonstrates very weak spontaneous emission, but when pumping energy increases, the emission intensity increases sharply and the width of the band diminishes. As a result, in the spectra only a few narrow lines with width 0.5–1 nm exist. These lines differ from the spikes in Figs. 3 and 5 significantly. They have almost no pedestal, which is rather large in the case of samples no. 1 and no. 5, and it is

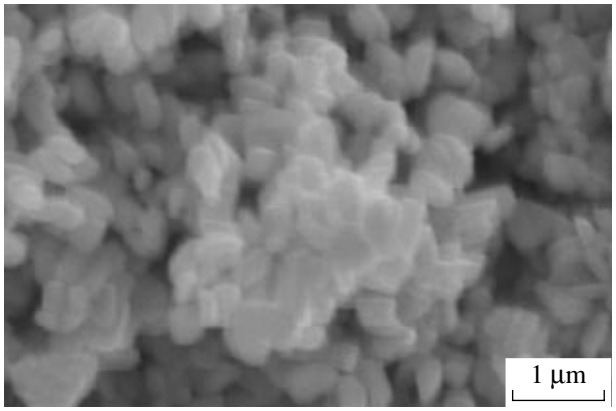

Fig. 6. Sample no. 3 (0.3–0.6 μm).

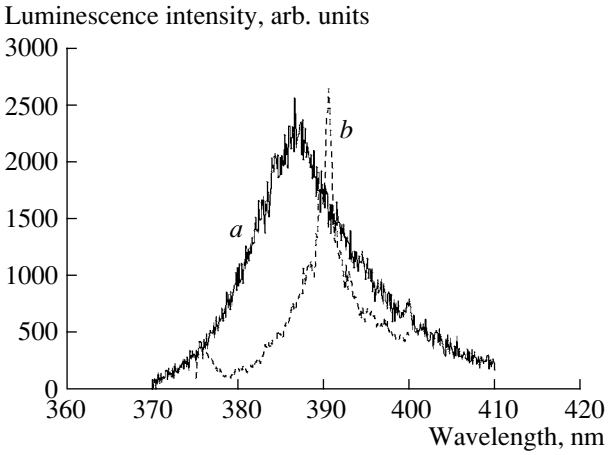

Fig. 7. UV-emission spectra of the sample no. 3 at different levels of excitation: (*a*) 27.7 mJ/cm^2, (*b*) 160 mJ/cm^2, $T = 300$ K.

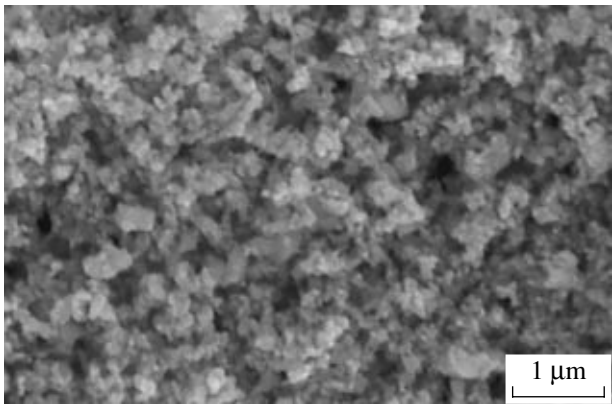

Fig. 8. Sample no. 4 (0.2–0.4 μm).

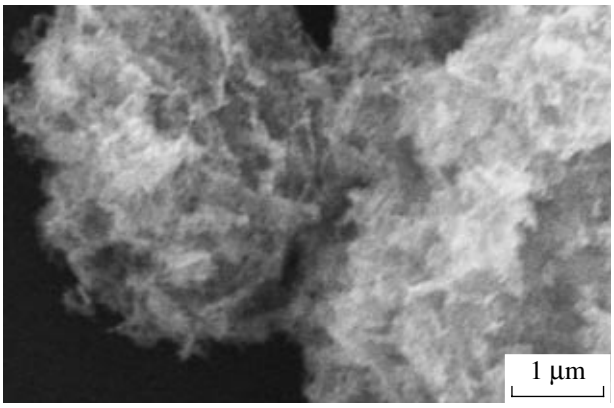

Fig. 9. Sample no. 6 (<0.2 μm).

very likely that this is the result of amplified spontaneous emission. It seems that, in sample no. 2, resonant feedback is considerably more effective than in others due to its monodispersivity.

It is necessary to emphasize that, in our method of registration, the sample emission due to different pumping pulses is registered at different wavelengths. We made all efforts to stabilize the pumping power; however, great variations of the signal from shot to shot were observed at fixed wavelength. These variations were significantly higher than the pumping instability could give. We consider these variations as manifestations of the chaotic character of lasing, similar to the effect observed in [5]. Thus, we can say that the fine structure of the spikes in our spectra sometimes do not exactly reflect their real shape. But some lines recur many times, for example in the spectra of sample no. 2, as is demonstrated in Fig. 12. This can be considered as evidence of the existence of such narrow lines, and they may be related to the resonant modes.

5. DISCUSSION

Let us briefly discuss the origin of UV radiation in our experiments. There are at least two possibilities: exciton recombination and recombination of electron–hole plasma (EHP). The characteristic peculiarity of the spectra obtained by us is the shift of the band maximum to the long-wavelength side when the pumping energy increases. It is known that the wavelength of exciton recombination radiation is shifted to the long-wavelength side when the recombination happens in the process of exciton–exciton scattering. (One of the two excitons recombines and the other goes over to the excited state.) The band corresponding to such recombination (the so-called P-line) appears when the pumping level is high enough and does not shift with further rise in pumping. But in our experiments, a continuous shift of the band maximum with the rise in pumping was observed. This is similar to the results obtained for ZnO epitaxial thin films in [6].

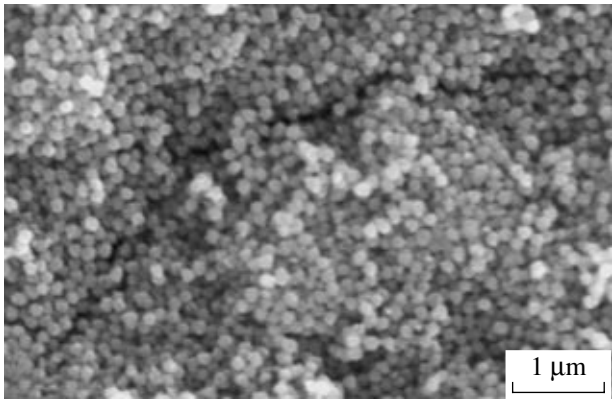

Fig. 10. Sample no. 2 (~0.15 μm).

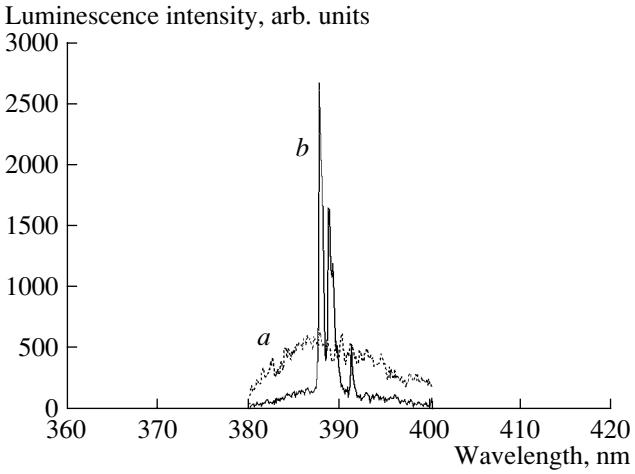

Fig. 11. UV-emission spectra of the sample no. 2 at different levels of excitation: (*a*) 2.7 mJ/cm^2, (*b*) 16 mJ/cm^2, $T = 300$ K.

The authors of [6] interpret their UV spectra as a result of EHP recombination and confirm this interpretation by comparison with calculations of the band-gap energy shift as a function of carrier density. It is most probable that, in our case also, EHP recombination takes place, since the pumping density is high enough for EHP formation. Indeed, the energy density 20 mJ/cm^2 corresponds to ~35×10^{15} photons/cm^2 for a pumping wavelength of 355 nm. Taking a penetration depth of ~0.1 μ, we get ~35×10^{20} photons/cm^3. But it is necessary to take into account that pumping pulse duration is much longer than the lifetime of carriers. This means that the maximum carrier concentration (N_{max}) will actually be noticeable smaller. To estimate this decrease, we can use the result of Section 3, where we found that when the lifetime of carriers is 0.2 ns

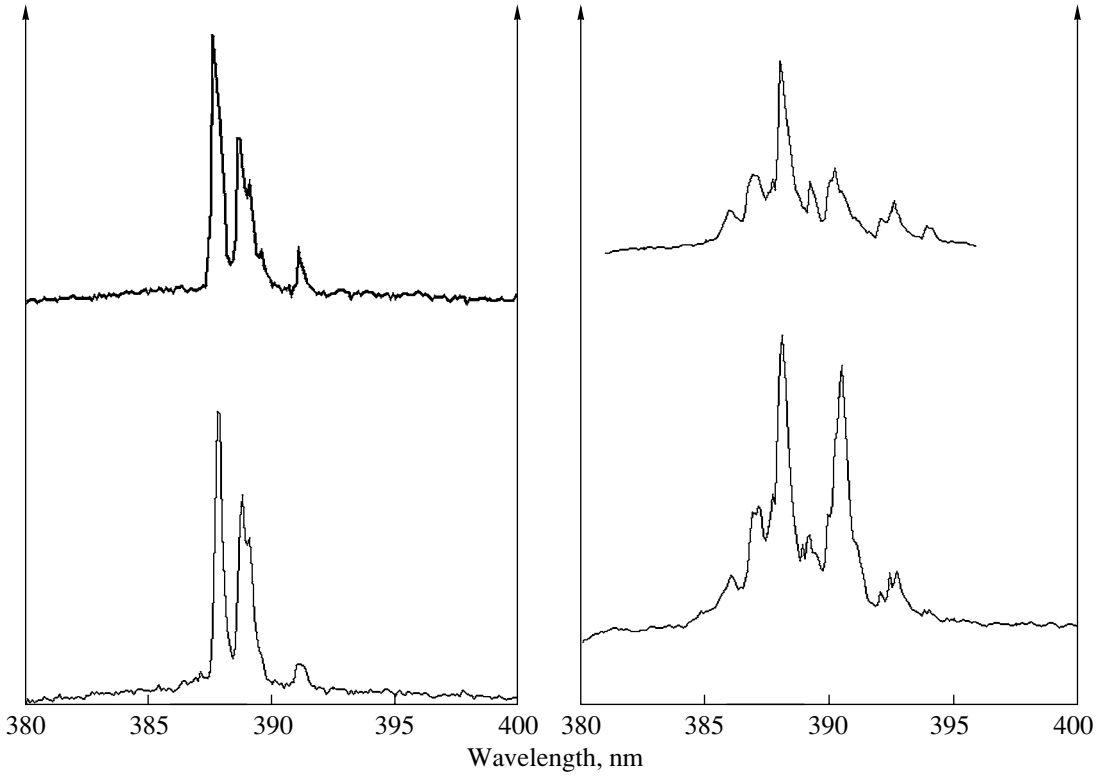

Fig. 12. Sample no. 2. Comparison of lasing spectra obtained with different pumping pulses. Pumping level 27.7 mJ/cm^2, $T = 300$ K.

N_{max} is approximately 50 times smaller than in the case when pulse duration is much shorter than lifetime. In other words, it is as if we have ~0.7×10^{20} photons/cm^3. So, if even only a small fraction of these photons is absorbed with free carrier generation, the concentration of the carriers can be higher than 10^{19} cm^{-3}.

6. CONCLUSIONS

Spectra of UV spontaneous emission and lasing for ZnO powders were investigated under nanosecond pumping. As expected, the threshold energy density of nanosecond pumping turned out to be considerably higher than that of picosecond pumping. Thus, under picosecond pumping, the threshold is usually not larger than 100 μJ/cm^2, while we obtained 2.7–26.7 mJ/cm^2, which is several hundred times higher. It seems that the short intrinsic lifetime of exciton recombination is not the only factor to play a role here; there are also some other factors of a still unknown nature. One such factor may be the role of EHP, whose lifetime must be shorter than the lifetime of excitons.

The samples investigated differ from one another significantly in the threshold and in the character of the lasing spectra. This seems to be the result of the different morphology of the particles forming different powders.

The chaotic character of lasing demonstrates itself by the irregular appearance and disappearance of radiation from shot to shot and was recorded for all samples investigated. The same effect was described in [5]. Its origin is still unknown and requires more detailed study.

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