Analysis of the Features of Two-Photon-Excited Luminescence in Micropowders of Zinc Oxide and Zinc Selenide at High Optical Excitation Lewels

Ilyos Rakhmatullaev[1*], Quvonchbek Hoshimov[2], Bobur Abdusattarov[3]

[1] Department of Mathematics and Physics, Alfraganus University, Tashkent, Uzbekistan, https://orcid.org/0000-0002-2348-7099
[2] Department of Theoretical Physics and Quantum Electronics, Samarkand State University, Samarkand, Uzbekistan, https://orcid.org/0009-0009-8304-2209
[3] Department of Exact and Natural Sciences, Kattakurgan Branch of Samarkand State University, Kattakurgan, Uzbekistan, https://orcid.org/0009-0003-5262-4544

**Corresponding author: Ilyos Rakhmatullaev (Email: i.rakhmatullaev@afu.uz)*

Abstract

The spectra of two-photon-excited luminescence (TPEL) of zinc oxide and zinc selenide micropowders under pulsed-periodic emission of a copper vapour laser have been investigated. The mechanisms of formation of TPEL spectra of the studied materials have been revealed. It was found that at laser irradiation intensities of 10^7 W/cm^2 the superluminescence effect is observed in zinc oxide and zinc selenide micropowders. This is confirmed by the increase of TPEL intensity with increasing intensity of excitation radiation. It was found that with increasing the intensity of excitation radiation in the studied samples a shift of the maximum of the TPEL spectrum band to 4-5 nm is observed.

Keywords: two-photon-excited luminescence, zinc oxide, zinc selenide, micropowder, spectrum.

INTRODUCTION

Zinc oxide (ZnO) is a versatile material that has attracted interest due to its excellent electrical, optical, piezoelectric and pyroelectric properties. ZnO semiconductors are used widely in ultraviolet detectors, emission devices, thin film transistors and surface acoustic wave systems. The large exciton binding energy (60 meV) allows to obtain intense ultraviolet luminescence in ZnO due to radiative recombination of excitons at room temperature and above (up to 550 K) [1].

Zinc selenide (ZnSe) crystals are wide-gap semiconductors with $A^{II}B^{VI}$-type structure. These crystals are characterised by relatively high mobility reaching 700 cm^2/(V·s) at room temperature [2]. Intense edge luminescence in the short-wave part of the visible spectrum makes ZnSe a promising material for the fabrication of blue light guides [3,4].

To date, very diverse methods have been developed for the preparation of micro- and, especially, nanomaterials (including nanopowders) and the properties of these structures strongly depend on the methods of their synthesis [3-9]. The choice of synthesis method is determined by the following relationship: 'Synthesis method - Morphology - Functional properties' [10-12].

At present, one of the most effective methods for analysing electronic and vibrational spectra of condensed media is laser spectroscopy of secondary radiation [13,14]. When pulsed laser radiation is applied to condensed media, both linear and nonlinear optical processes can be observed in them. In contrast to linear optical processes, two or more photons are involved in the processes of nonlinear interaction of radiation with the medium. As a result, the probabilities of

 https://doi.org/10.5281/zenodo.15811842

multiphoton processes of light scattering in the medium depend nonlinearly on the intensity of the excitation radiation [15-17].

The phenomenon of two-photon excitation was theoretically developed long ago in quantum optics. It was first discussed in Maria Geppert-Mayer's doctoral thesis and experimentally confirmed thirty years later, shortly after the invention of the laser. Since two-photon excitation depends on simultaneous absorption, the induced fluorescence emission varies in proportion to the square of the excitation light intensity. This quadratic relationship between excitation and emission is the reason for many important advantages with two-photon excitation. Consequently, to generate sufficient two-photon-excited luminescence (TPEL), extremely high power lasers are required.

Previously, pulsed solid-state lasers with modulated goodness-of-field, passive or active mode synchronisation, providing high pulse power, were used to excite TPEL. Examples of such lasers are ruby laser (λ=694.3 nm) and neodymium laser (λ=1064 nm), generating pulses of short duration (~10^{-8} s) with small pulse repetition rate (1-50 Hz). The single-pulse mode significantly complicates the registration of TPEL spectra and makes inefficient spectrometric methods based on continuous spectrum scanning with diffraction monochromators. In addition, the generation lines of the above lasers fall into narrow ranges of the visible and near-infrared (IR) spectral region, which limits the range of objects under study.

For TPEL observation in wide-gap semiconductors and in most dielectric materials it is necessary to use laser sources generating simultaneously in the green or yellow regions of the spectrum. Recently, due to the further development of laser technology, high-power pulse-periodic lasers on copper vapour and gold with high pulse repetition rate (up to ~20 kHz) have been used for TPEL observation in such media [18]. The copper vapour laser (CVL), which operated in the pulse-periodic mode, turned out to be the most promising for these purposes. CVL is the most powerful and efficient laser in the visible region of the spectrum (λ=510.6 and λ=578.2 nm) [19]. The conversion coefficient of electric energy into light energy for these lasers is ten times higher than for such well-known lasers as ‘argon’ and ‘helium-neon’ lasers.

The basic properties of TPEL in condensed media have been studied in numerous works. However, the excitation and basic characteristics of TPELs in fine and ultradisperse media have remained poorly studied until recently. In addition, under sufficiently intense irradiations of pulsed lasers, the initial characteristics of powdery substances are strongly changed: the medium is strongly heated and even photodestruction of the substance can occur [20-22].

In this regard, the aim of the present study is to investigate the mechanisms of TPEL spectra formation of ZnO and ZnSe micropowders under pulsed-periodic laser excitation.

MATERIALS AND METHODS

Ready-made white coloured ZnO and ZnSe micropowders from Sigma-Aldrich of 99% purity were used for the study. For excitation and registration of TPEL spectra, we used optic technique described in detail in [9,20-23]. The green generation line of the copper vapour laser (λ=510.6 nm) was used as the excitation source, while the yellow line (λ=578.2 nm) of the laser was suppressed by a filter. The average emission power of the laser is 10 W. The radiation is generated in pulse-periodic mode with a high repetition rate (10^4 Hz) of short (20 ns) generation pulses with a peak power of 10^5 W. Calibrated neutral light filters of type (ND) were used to analyse the TPEL intensity. Samples of micropowders were tightly clamped between plane-parallel quartz windows of the cuvette. Quartz cuvettes for spectrophotometry are made of ‘KU’ (‘Quartz UV’) brand quartz glass. The thickness of the layer was about 1 mm. The resolution at registration of spectra in the measured wavelength range was 0.1 nm. Measurements were made at room temperature.

 https://doi.org/10.5281/zenodo.15811842

ISSN: 0369-8963

RESULTS AND DISCUSSION

TPEL spectra of ZnSe micropowders (d_{mean}=5 μm) at different excitation intensities of the excitation radiation by the green line of the copper vapour laser (λ_{exc}=51056 nm) are shown in Fig. 1. The data obtained in [24]: photoluminescence spectrum of ZnSe micropowders obtained by the third optical harmonic of the YAG:Nd^{3+} laser (λ_{exc}=355 nm) are also presented in the inset for comparison. As follows from this figure, the TPEL spectrum observed by us has a peak in the 440-460 nm region. First of all, we note that the emission maximum at 470-480 nm is closer to the width of the forbidden zone E_g, and secondly, the position of the maximum depends on the excitation level, shifting towards lower energies with increasing I_{exc}. All of the above features in the 460-480 nm region are typical for the annihilation of excitons during their inelastic scattering on free charge carriers [2,16]. At 77 K ZnSe, the spectrum of the main band (2.789 eV) has a simple character: the band splits into tri-basic components with maxima at 2.793 (E_x), 2.775 (I_1) and 2.745 eV (I^{LO}), respectively. A series of peaks at 2.705 (A), 2.676 (A^{LO}), 2.645 (A^{2LO}) and 2.611 eV (A^{3LO}) are observed in the additional low-energy region of the spectrum. The intensity maximum in the TPEL spectrum (λ_{max}=475 nm) obtained in our work corresponds to the three-phonon repeat (A^{3LO}). The origin of this emission band is attributed to the decay of free excitons interacting with free carriers and with trapped carriers. The behaviour of bound exciton lines and 'edge emission' bands under the same excitation is briefly described [25]. As is known [2,16,25], the spectra of single- and two-photon-excited luminescence differ from each other: in the dipole approximation, two-photon transitions are resolved between states of equal parity, in contrast to single-photon transitions. Note that luminescence in the case of TPEL is observed in the anti-Stokes region of the spectrum, which is convenient for experimental detuning of the useful signal from the excitation radiation and the continuous background of secondary radiation.

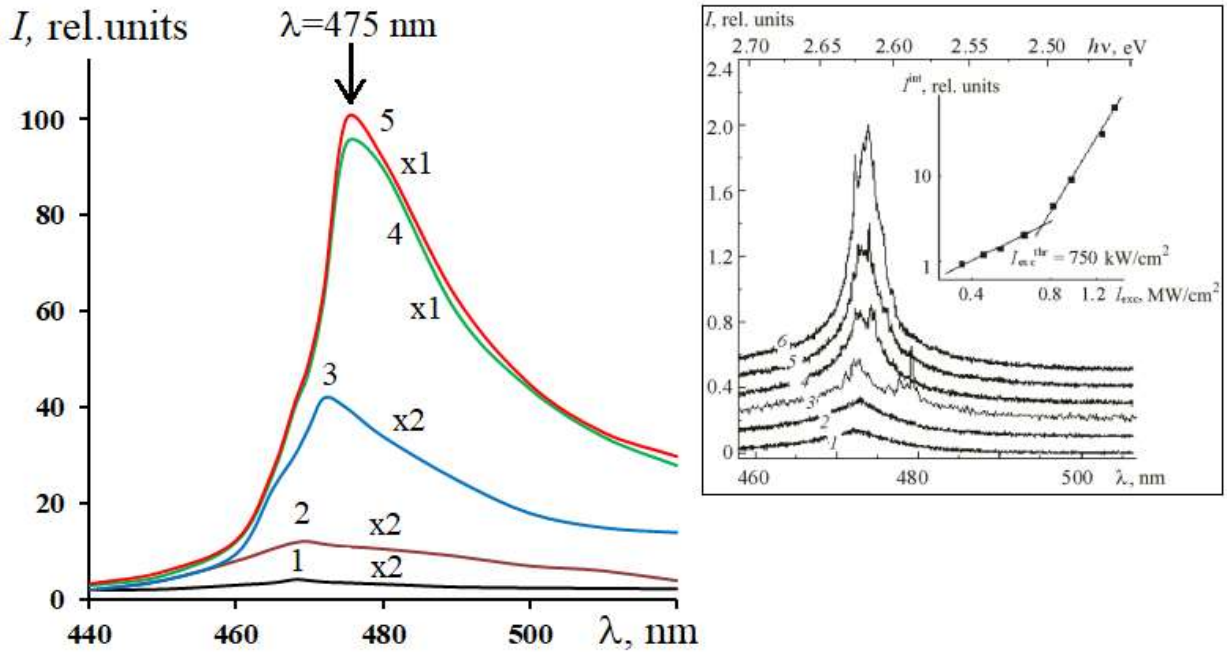

Fig. 1. TPEL spectra in ZnSe micropowders (d_{mean}=5 μm) obtained at different pumping intensities: curve (1) corresponds to pumping intensity I_{exc}=0.8; (2) - I_{exc}=1.4; (3) - I_{exc}=2.0; (4) - I_{exc}=2.6; (5) - I_{exc}=3.2 (where I_{exc} values are given in units of 10^7 W/cm^2). The data obtained in [24] are shown in the inset.

https://doi.org/10.5281/zenodo.15811842

At low pump intensities (Figure 1, curves 1-2), the observed maximum of the TPEL spectrum corresponds to ~470 nm. When the laser intensity is increased (curves 3-5), the TPEL intensity increases; in addition, the contour is 'deformed' with an increase in the relative intensity of the long-wavelength wing; the position of the maximum starts to shift to 5 nm and becomes equal to 475 nm (Figure 1, curves 4-5). The observed spectrum is similar to the TPEL spectrum obtained in ZnSe single crystal in [16] and in ZnSe micropowders in [24] at high pumping intensity.
Figure 2 shows the relationship between the TPEL intensity and the intensity of the excitation radiation. The dependence corresponds to the wavelength λ=475 nm. As can be seen from this figure, at rather low intensities of excitation radiation, the dependence of $I(I_{exc})$ is quadratic. When I_{exc} increases, this relationship is characterised by a clear deviation from the quadratic one. This effect can be explained by the transition at high pumping intensities from spontaneous luminescence to stimulated luminescence, i.e., superluminescence.

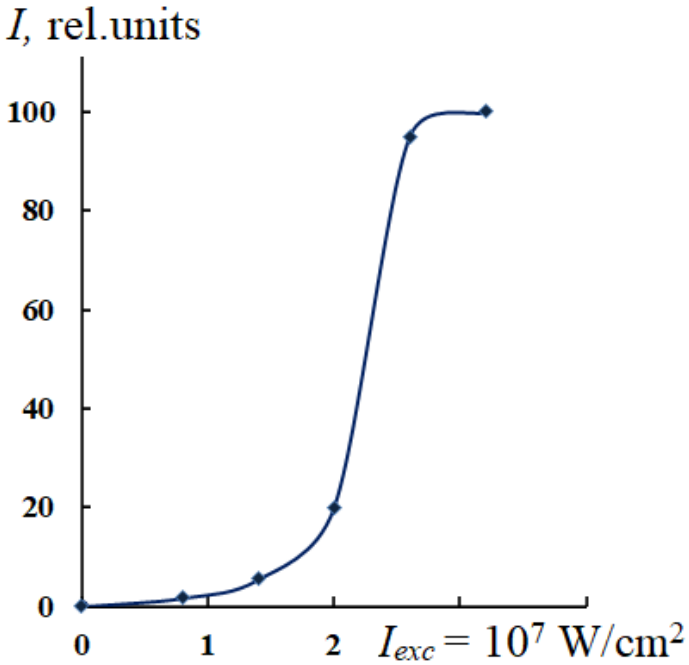

Fig. 2. Dependence of the TPEL intensity *I* on the pump intensity I_{exc}. The curve corresponds to the wavelength λ=475 nm.

Figure 3 shows the TPEL spectra of ZnO micropowders obtained at different pump intensities. Earlier in our study [23] it was shown that at room temperature the TPEL spectrum of ZnO polycrystals possesses a broad structureless band with a maximum at 390 nm. In [26], the room temperature photoluminescence spectra under one-photon excitation (with a wavelength of 313 nm of a mercury lamp) and under two-photon excitation with a ruby laser were investigated. In this work, it was found that these spectra differ in shape. In addition, it was found that at room temperature the TPEL spectrum of epitaxial ZnO layers has a broad structureless band with a maximum at 390 nm, which decays into a series of narrow equidistant bands when the sample is cooled to 80 K. As can be seen from Figure 3, the TPEL spectrum observed by us at low intensity of excitation radiation has a maximum at 390 nm. This peak corresponds to the position of the 3L0 band from the multiphonon annihilation series of A-exitons [14,23,26]. When the intensity of the excitation radiation increases, the intensity of the TPEL spectrum, rapidly increases (Figure 4). At the same time, the maximum intensity of the TPEL spectrum shifts to the short-wavelength region up to 4 nm. At high powers of excitation radiation (Figure 4), the TPEL intensity grows more steeply than according to the quadratic law. The reason for this may be the process of transition from spontaneous luminescence to forced luminescence. However,

 https://doi.org/10.5281/zenodo.15811842

ISSN: 0369-8963

the absence of a significant narrowing of the spectrum indicates that in our experiments only threshold effects for forced TPEL are realised.

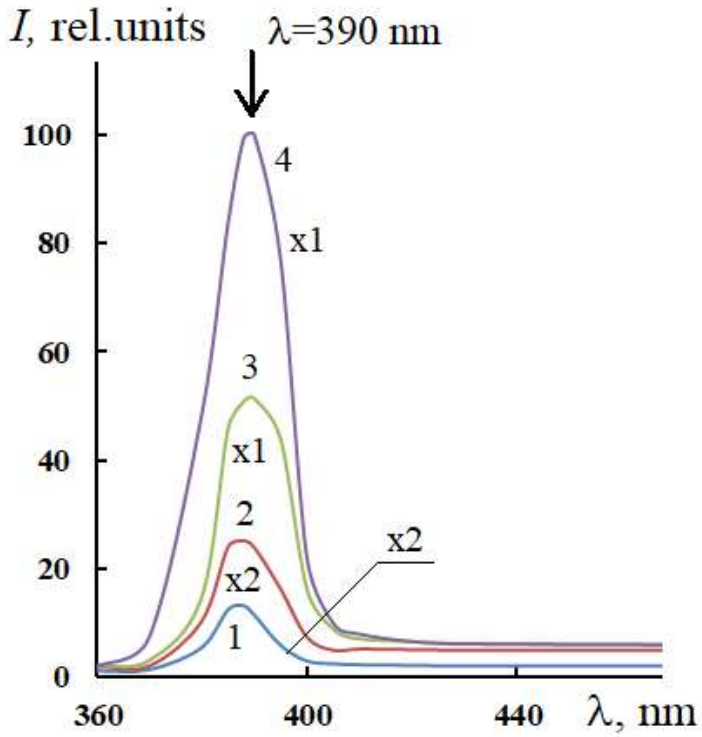

Fig. 3. TPEL spectra in ZnO micropowder (d_{mean}=5 μm) obtained at different pumping intensities: curve (1) corresponds to pumping intensity I_{exc}=0.8; (2) - I_{exc}=1.4; (3) - I_{exc}=2.0; (4) - I_{exc}=2.6 (where I_{exc} values are given in units of 10^7 W/cm^2).

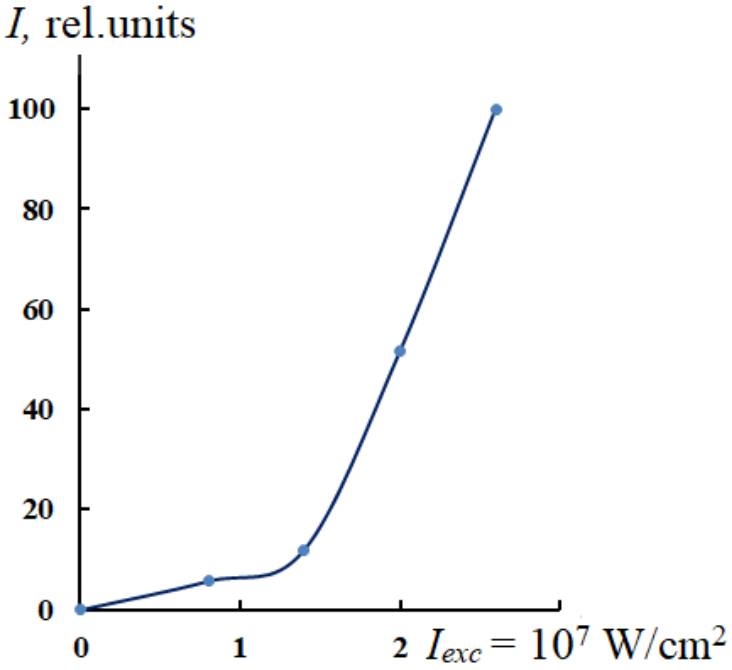

Fig. 4. Dependence of the TPEL intensity *I* on the pump intensity I_{exc}. The curve corresponds to the wavelength λ = 390 nm.

CONCLUSION

https://doi.org/10.5281/zenodo.15811842

Thus, in our experiments at intensities of 10^7 W/cm^2 of laser radiation, superluminescence effects are observed in zinc oxide and selenide micropowders. It was found that a shift of the band maximum to 4-5 nm is observed when the excitation radiation intensities of both samples are increased. It is experimentally found that at room temperature laser effects are clearly observed in ZnO and ZnSe micropowders. The high radial strength of the studied objects opens wide possibilities for realisation of effective transducers of radiation frequency in the visible and near-UV regions based on the stimulated TPEL effect.

Author contribution: All authors have accepted responsibility for the entire content of this manuscript and consented to its submission to the journal, reviewed all the results, and approved the final version of the manuscript.

Conflict of interest: The Authors state no conflict of interest.

Financing: The study was performed without financial support.

Data availability: Manuscript has no associated data.

Use of artificial intelligence: The authors confirm that they did not use artificial intelligence technologies when creating the current work

REFERENCES

1. Burakov, V.S., Tarasenko, N.V., Nevar, E.A. et al. (2011). Morphology and Optical Properties of Zinc Oxide Nanostructures Synthesized By the Methods of Thermal and Discharge Sputtering. Technical Physics. **56** (2): 245-253. https://doi.org/10.1134/s1063784211020071
2. Nedeoglo, D.D., Simashkevich, A.V. (1984). Electrical and Luminescent Properties of Zinc Selenide. Chișinău: Shtiyintsa. 165 p.
3. Dmitruk I., Berezovska, N., Degoda, V. et al. (2021). Luminescence of Femtosecond Laser-Processed ZnSe Crystal. Journal of Nanomaterials. **21(**1): 206–208. https://doi.org/10.1155/2021/6683040
4. Li, H.Y., Jie, W.Q., Zhang, S.A. et al. (2006). The Photoluminescence of ZnSe Bulk Single Crystals Excited by Femtosecond Pulse. Chinese Physics. **15**: 2407. https://doi.org/10.1088/1009-1963/15/10/037
5. Averin, I.A., Pronin, I.A., Yakushova, N.D. et al. (2019). Analysis of the Structural Evolution of Zinc Oxide Powders Obtained by Mechanical High-Energy Grinding. Technical Physics. **64**(9): 1330–1335. https://doi.org/10.1134/S1063784219090020
6. Ong, C.B., Ng, L.Y., Mohammad, A.W. (2018). A Review of ZnO Nanoparticles as Solar Photocatalysts: Synthesis, Mechanisms and Applications. Renewable and Sustainable Energy Review. **81**: 536–551. https://doi.org/10.1016/j.rser.2017.08.020
7. Hamid, H.A., Miswan, N., Kunakornwattana, P. et al. (2024). ZnO Nanorods Prepared By Hydrothermal Method as a Sensitive Nanosensor for Methanol Detection in Aqueous Solution. Journal of Physical Science. **35**(1):67–78. https://doi.org/10.21315/jps2024.35.1.6
8. Gorokhova, E.I., Anan'eva, G.V., Demidenko, V.A. et al. (2008). Optical, Luminescence and Scintillation Properties of ZnO and ZnO:Ga Ceramics. Journal of Optical Technology. **75**(11): 741-746. https://doi.org/10.1364/JOT.75.000741
9. Rakhmatullaev, I.A., Bunkin, N.F., Davronov, M.K. (2025). Effect of Raman Opalescence on Titanium Dioxide Micropowders Under Pulse-Periodic Laser Excitation.Journal of Applied Spectroscopy. **91**(6):1256–1260. https://doi.org/10.1007/s10812-025-01846-9
10. Tarasov, A.P. (2019). Luminescence of Zinc Oxide Microstructures and Influence of Surface Plasma Resonance and Magnetic Field on it. [in Russian]. Physics-Mathematics Candidate's Dissertation, Moscow Institute of Physics and Technology, Moscow, Russia. 125 p.

11. Neshchimenko, V. V. (2016). Structure, Properties and Resistance to Radiation of Oxide Micro and Nanopowders and Derived Reflecting Surfaces [in Russian]. Physics-Mathematics Doctoral Dissertation, Tomsk State University of Control Systems and Radioelectronics, Tomsk, Russia. 273 p.
12. Chernenko, K.A. (2016). Luminescence and Scintillation Processes in Oxide Matrices. [in Russian]. Physics-Mathematics Candidate's Dissertation, Peter the Great St. Petersburg Polytechnic University, Saint-Petersburg, Russia. 150 p.
13. Gorelik, V.S. (2002). Visible and Near- Visible Light Scattering. Raman Scattering. in "Scattering. Scattering and Inverse Scattering in Pure and Applied Science". Edited by Pike and Pierre Sabatier. Academic Press. San Diego, San Francisco, New York, Boston, Sydney, Tokyo. Topic 2.3: 828-848.
14. Rakhmatullaev, I.A. (2008). Secondary Radiation in Condensed Media Upon PulsePeriodic Laser Excitation. Physics-Mathematics Doctoral Dissertation, Department of Thermal Physics of the Academy of Sciences of the Republic of Uzbekistan. 260 p.
15. Terhune, R.W., Maker, P.D., Savage, C.M. (1965). Measurements of Nonlinear Light Scattering. Physical Review Letters. **14**: 681-684. https://doi.org/10.1103/PhysRevLett.14.681
16. Agal'tsov, A.M., Gorelik, V.S., Rakhmatullaev, I.A. (1997). Spectral, Energy, and Temporal Characteristics of Two-Photon-Excited Fluorescence of ZnSe Single Crystal in the Blue Region of the Spectrum. Semiconductors. **31**(12): 1228–1230. https://doi.org/10.1134/1.1187299
17. Dong, H., Zhou, B., Li, J. et al. (2017). Ultraviolet Lasing Behavior in ZnO Optical Microcavities. Journal of Materiomics. **3**: 255-266. https://doi.org/10.1016/j.jmat.2017.06.001
18. Lyubin, N.A., Chursin, A.D., Ugolnikov, S.A. et al. (2001). Development, Production and Application of Desoldered Copper Vapour Lasers (in Russian). Quantum Electronics. **31(**3): 191-202.
19. Isaev, A.A., Kazaryan, M.A., Petrash, G.G. (1972). Effective Pulsed Laser on Copper Vapour with High Average Power (in Russian). Letters in ZhETF. **16**: 40-42.
20. Gorelik, V.S., Rakhmatullaev, I.A. (2005). Excitation of Raman Optical Processes in an Ultradispersed Medium by Radiation from a Pulsed-Periodic Laser. Technical Physics. **50**(1): 61-64. https://doi.org/10.1134/1.1854824
21. Gorelik, V.S., Rakhmatullaev, I.A. (2005). Combination Optical Processes in Superdispersed Media under Pulse-Periodic Laser Excitation. Journal of Russian Laser Research. **26**(1): 66-82. https://doi.org/10.1007/s10946-005-0007-3
22. Gorelik, V.S., Rakhmatullaev, I.A. (2004). Photoluminescence of Diamond Films and Ultrafine Diamond under UV Laser Excitation. Inorganic Materials. **40**(7): 686–689. https://doi.org/10.1023/B:INMA.0000034766.98987.de
23. Agal'tsov, A.M., Gorelik, V.S., Rakhmatullaev, I.A. (1996). Two-Photon Excitation of Fluorescence in Polycrystalline ZnO. Physics of the Solid State. **38**(11): 1812-1814.
24. Leanenya, M.S., Lutsenko, E.V., Pavlovskii, V.N. et al. (2015). Luminescence and Lasing in ZnSe Micropowders at High Optical Excitation Levels. Journal of Applied Spectroscopy. **82**(1): 53-57. https://doi.org/10.1007/s10812-015-0063-6
25. Era K., Langer D.W. (1970). Luminescence of ZnSe Near the Band Edge under Strong Laser Light Excitation. Journal of Luminescence. **1–2**: 514-527. https://doi.org/10.1016/0022-2313(70)90064-5
26. Abduev, A.Kh., Adukov A.D., Ataev B.M. et al. (1978). Ultraviolet Luminescence of Zinc Oxide Epitaxial Layers under One- and Two-Photon Excitations. (in Russian). Quantum Electronics. **5**(1): 206–208.