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Microwave Synthesis and Study of Morphology, Structure and Luminescent Properties of Zinc Oxide Microstructures

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ABSTRACT: *The morphology of zinc oxide microstructures obtained by microwave synthesis has been studied and the features of its photoluminescence spectra have been revealed. X-ray diffraction analysis revealed that the synthesised zinc oxide samples have hexagonal crystalline structure. It was found that with increasing power density of excitation radiation in zinc oxide microstructures, band narrowing is observed and the maximum intensity of the photoluminescence spectrum shifts to the long-wave region. It is shown that zinc oxide microcrystalline structures obtained by microwave synthesis have a significant intensity of ultraviolet luminescence bands of free excitons at room temperature and are promising for the creation of short-wave light sources.*

Keywords: microwave synthesis, zinc oxide, microstructure, photon trap, photoluminescence

1. INTRODUCTION

In recent years, interest in zinc oxide (ZnO) has increased due to the high demand for this material.[1–3] This is primarily due to the huge potential of their practical use, as well as the unique combination of optical, chemical and electrophysical properties of ZnO.[4–10] To date, low-cost technologies for synthesising powders of inorganic compounds with controlled microstructure have attracted considerable attention of researchers. In particular, microwave synthesis is a relatively new area of inorganic chemistry, since the peculiarities of the interaction of microwave radiation with matter allows to obtain ordered structures of ZnO with controlled microstructure.[11–13] The growing conditions of ZnO structures significantly affect their luminescent properties, including due to the formation of intrinsic and impurity lattice defects. Producing bulk monocrystalline ZnO is a difficult, time-consuming and expensive technological process. At present, there are only isolated reports on the growth of single-crystal ZnO-based scintillators, in particular inidium-doped (ZnO:In) with millimeter dimensions.[14] In addition, fundamental knowledge of the spectral components of the emission of various ZnO structures is necessary for practical applications of such structures, including optoelectronics.[15–16] On the example of ZnO, a multiple enhancement of luminescence was obtained in some works.[17] However, such an effect is not always observed and obviously depends on many factors, the role of which should be studied. In this connection, the study of luminescent and laser properties of ZnO-based structures and the influence of various factors (growth conditions, doping, etc.) on them is of great interest. Despite the huge number of published works on synthesis and study of physical properties, many properties of ZnO still remain unexplained.

The aim of the present study is a comprehensive investigation of surface morphology, structure and luminescent properties of ZnO microstructures synthesised by the microwave decomposition method.

2. MATERIALS AND METHODS

In this work, synthesis of ZnO microstructures was carried out using Sigma-Aldrich reagents of 99% purity by microwave decomposition method; 2 g of ZnO powder and 1 mL of ethylene glycol solution were mixed and rubbed in an agate mortar for 20 min. Then, the mixed powder in an amount of 2 g was loaded into an aluminum oxide crucible and placed in the center of a microwave oven at room temperature under normal atmosphere. The microwave was processed for 15 min at 180°C and resulted in samples in the form of extended rods.[12] The surface morphology of ZnO microstructures were investigated by scanning

electron microscopy (SEM) on a SEM - EVO MA 10 electron microscope (Carl Zeiss, Germany). The elemental composition was determined using an AZtec energy dispersive elemental analyser (Oxford Instruments, UK). The structure and phase composition were studied on X-ray diffractometer, PANalytical Empyrean (Netherlands).

To measure photoluminescence (PL) spectra, we used a fibre-optic technique described in detail in a previous study; to amplify the PL signal in ultradisperse materials, we fabricated special constructions of miniresonator cuvettes of various designs - photon traps, i.e., cuvettes inside which radiation undergoes multiple reflection and scattering.[12,18] The idea of using photon traps is that a significant part of the primary (laser) radiation fraction entering the trap is converted into secondary radiation. A cavity was cut out in the trap body, which is the working volume and filled with the sample under study. It was found that the cone-shaped cavity proved to be the best option for amplifying the secondary radiation signals. The green line of the copper vapour laser generation (λ_{ex} = 510.6 nm) was used to excite the PL signals, while the yellow line (λ = 578.2 nm) of the laser was suppressed by the filter.

The average power of the laser radiation is 10 W. The radiation is generated in the 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.[18,19] The second optical harmonic (SOH) of the green line (510.6 nm) of laser generation, corresponding to the emission wavelength λ = 255.3 nm, turned out to be very effective for studying the PL spectra. The conversion efficiency of visible to ultraviolet (UV) radiation was about 1%. An effective doubling and addition of the frequencies of the laser generation lines was realised by using a nonlinear optical crystal BaB_2O_4.

3. RESULTS AND DISCUSSION

According to SEM data (see Figure 1), it can be seen that the investigated material consists mainly of particles in the form of micron-sized hexagonal rods (sticks). According to our estimates, the length of individual particles reaches 15 μm–18 μm with a thickness of 1 μm–8 μm. Similar results were obtained in.[11]

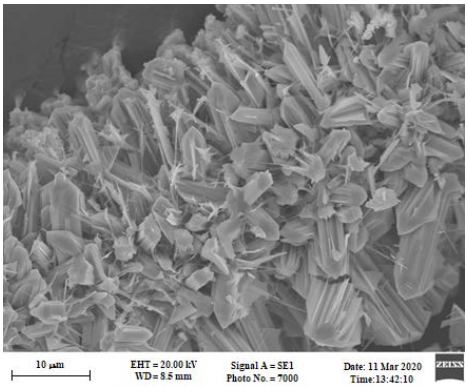

Figure 1: SEM image of ZnO microstructures.

It was found that the obtained samples possess significant photocatalytic activity despite the relatively low value of specific surface area. This fact may be explained by the extremely crystalline (see Figure 2) and low defectivity purity of ZnO samples (see Figure 3).[11] Figure 3 shows that the composition of the synthesised sample followed the stoichiometric formula of ZnO, indicating the presence of a well-balanced combination of O and Zn atoms in the material. No extraneous impurities were detected as energy dispersive X-ray (EDX) is sensitive to elements present on or near the surface of the sample.

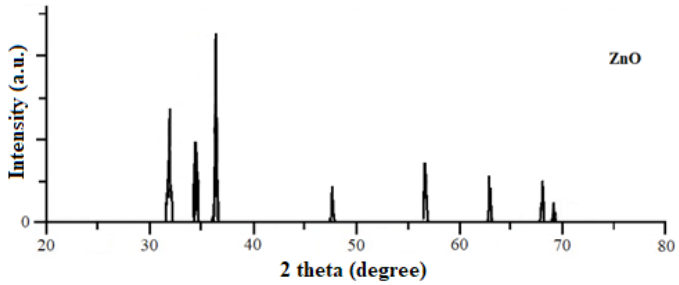

Figure 2: X-ray diffraction pattern of ZnO microstructures.

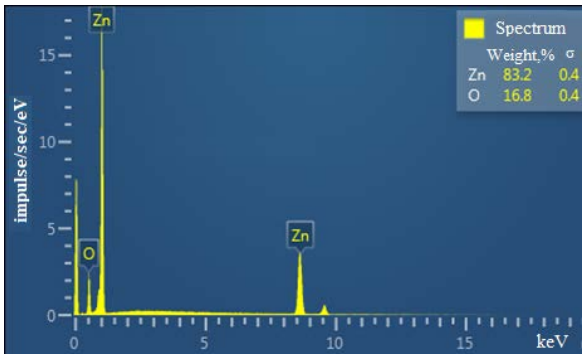

Figure 3: Elemental composition of ZnO microstructures.

X-ray diffraction analysis (see Figure 2) has established that the structure of synthesised ZnO samples contains one phase - ZnO of wurtzite $P6_3mc$ structural type.[1,4,20] The analysis of X-ray diffraction patterns showed that no additional peaks are observed in the investigated material. ZnO microstructure particles with average sizes of 1 μm, 2 μm and 8 μm were selected to investigate the PL spectra.

Figure 4 shows the PL spectra of ZnO microstructures obtained at different pump power densities (λ_{ex} = 255.3 nm). At low intensity of excitation radiation, the PL spectrum has a maximum in the region of 386 nm (curves 1 and 2). This peak corresponds to the position of the 3L0 band from the multiphonon annihilation series of A-exitons.[21]

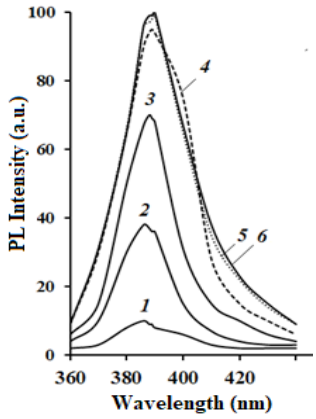

Figure 4: PL spectra of ZnO microstructures (d_{mean} = 2 μm), obtained at different intensities exciting radiation.

Note: Curve (1) corresponds power density (I_{ex}) = 5; curve (2) I_{ex}= 11; curve (3) I_{ex} = 15; curve (4) I_{ex} = 18; curve (5) I_{ex} = 21; curve (6) I_{ex} = 24 (where the values of I_{ex} are given in units of 10^3 W/cm^2).

At high intensity of excitating radiation in semiconductor materials with small concentrations of impurities and defects, saturation of the intensity of radiative transitions to impurity levels occurs and in this case the following aspect of multiphonon annihilation of free excitons is of special interest: the possibility of obtaining stimulated emission.[21] It is known that the inverse distribution on a free exciton is not feasible, while at the decay of an exciton with emission of a photon and a phonon the inversion occurs automatically.

At excitation intensities greater than $15 \cdot 10^3$ W/cm^2 (curve 3–curve 5), a narrowing of the exciton luminescence line is observed, the intensity of which grows nonlinearly with further increase in pumping intensity (see Figure 5). In addition, a narrowing of the PL band is observed and the maximum intensity of the PL spectrum shifts to the long-wavelength region up to 4 nm. At an excitation intensity of $24 \cdot 10^3$ W/cm^2 (curve 6), the dependence goes to saturation.

In order to observe the stimulated emission in ZnO microstructures, we have carried out the emission of UV luminescence from the intensity of two-photon excitation. The obtained results are presented in Figure 5. It can be seen that the indicated dependence is nonlinear and has a threshold character, and this is one of the signs of stimulated emission. However, the absence of a significant narrowing of the spectrum indicates that in our experiments only threshold effects for stimulated PL are realised.

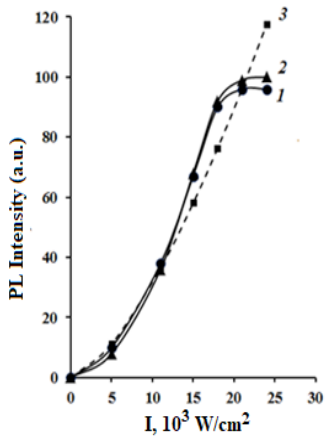

Figure 5: PL intensity dependences of ZnO microstructures (d_{mean} = 2 μm) (I) on the power density of the exciting radiation (I_{ex}).

Note: Curve (1) corresponds to the wavelength (l) = 386 nm; curve (2) l = 390 nm; curve (3) theoretical dependence, in accordance with the law $I = I_{ex}^{1.5}$.

In Sokolovsky's work, studies were carried out on the dynamics of exciton PL for ZnO depending on the structure of the sample and the power of exciting radiation in the range of 80 kW/cm^2–1000 kW/cm^2.[22] To analyse the PL intensity (I) we used the expression;

$$I = \eta . I_{ex}^{\alpha}$$

Where I_{ex} is the power density of the exciting radiation, η is the quantum yield, α characterises the mechanism of radiative recombination. For excitonic recombination $1 < \alpha < 2$, for fundamental radiation $\alpha \approx 2$ and for transitions from impurity levels $\alpha < 1$.

Indeed, under our experimental conditions ($I_{ex} \sim 10^3$ W/cm^2) for ZnO microstructures (see Figure 4) a power-law dependence with $\alpha \approx 1.5$ is observed (see Figure 5, curve 3), which corresponds to the value $\alpha = 1.5 \pm 0.2$ in the case of bulk ZnO, found in Sokolovsky's work.[22] At high power densities, a slowdown in the growth of PL intensity occurs, which can be caused either by thermal effects or by the generation of defects through photolysis and thermal destruction.

A similar pattern was observed in the work of Fonoberov et al. for single crystals and quantum dots (QDs) of ZnO.[23] The absence of visible PL in our samples indicates low concentration or absence of oxygen defects and high purity of the studied ZnO powders according to elemental analysis (see Figure 3).[24]

Figure 6 shows the PL spectra of ZnO microstructures of various sizes obtained under the same excitation conditions (λ_{ex} = 255.3 nm). As can be seen from the figure, as the size of the samples decreases, the maximum of the UV band moves slightly to the short wavelength region. The spectral intensity of the PL spectrum d_{mean} = 8 μm (λ_{max} = 390 nm) and d_{mean} = 2 μm (λ_{max} = 387 nm) is approximately 22 and 2 times less than the corresponding intensity of ZnO microparticles with d_{mean} = 1 μm (λ_{max} = 385 nm), respectively. The difference in intensity and position of the PL of these spectra is due to the fact that pores are formed between the particle faces, which contribute more to scattered light than to the effective absorption of exciting radiation quanta. In addition, if microparticles and nanoparticles (powders) are placed in an optical resonator (photon trap), then the intensity of PL signals can be increased many times.[5,18] In this regard, in recent years, a wide range of researchers have been attracted to UV lasers with an optical microcavity based on ZnO.[5] The quality factor of such resonators can be very high.[5] In an optical microcavity, the nano/microstructure itself and the material of the device

(cell) can serve as a gain medium. As a result, it is possible to obtain fairly intense signals in the UV region at the output and create mini-lasers operating at room temperature.[25,26]

4. CONCLUSIONS

Thus, the research results showed that the microwave decomposition method makes it possible to form crystallised microstructures of ZnO in the form of extended rods. Using the pulse-periodic laser excitation technique, UV luminescence spectra of free excitons at room temperature were obtained and studied depending on the pump power density and various sizes of ZnO microstructures. The observed changes in the PL spectra at high pump powers are explained by the manifestation of threshold effects of stimulated luminescence. The obtained data on the spectra of ZnO microstructures can be used to develop methods for analysing the characteristics of phosphors containing ZnO.

The high radiation resistance of ZnO opens up wide opportunities for the creation of new laser emitters with tunable wavelengths in the region (λ_{max} = 385 nm–390 nm).

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6. REFERENCES

1. Neschimenko, V. V. (2016). *Structure, properties and radiation resistance of oxide micro- and nanopowders and reflective coatings made on their basis.* DSc diss. Tomsk: Tomsk State University of Control Systems and Radioelectronics (in Russian).

2. Ong, C. B., Ng, L. Y. & Mohammad, A. W. (2018). A review of ZnO nanoparticles as solar photocatalysts: Synthesis, mechanisms and applications. *Renew. Sust. Ener. Rev*., 81(1), 536–551. https://doi.org/10.1016/j.rser.2017.08.020
3. Tarasov, A. P. (2019). *Luminescence of zinc oxide microstructures and the influence of surface plasma resonance and magnetic field on it*. PhD diss. Moscow: Moscow Institute of Physics and Technology (in Russian).
4. Mikhailov, M. M., Yuryev, S. A. & Lapin, A. N. (2022). The stability of optical properties under irradiation for ZnO micropowder modified with TiO_2 nanoparticles. *Mater. Chem. Phys*., 291, 126730. https://doi.org/10.1016/j.matchemphys.2022.126730
5. Dong, H. et al. (2017). Ultraviolet lasing behavior in ZnO optical microcavities. *J. Materiomics*., 3(4), 255–266. https://doi.org/10.1016/j.jmat.2017.06.001
6. Averin, I. A. et al. (2019). Analysis of structural evolution of zinc oxide powders obtained by mechanical high-energy milling method. *Tech. Phys.*, 89(9), 1406–1411. https://doi.org/10.21883/JTF.2019.09.48067.437-18
7. Mikhailov, M., Neschimenko, V. & Sokolovskiy, A. (2018). Features of degradation and recovery of the optical properties of coatings based on ZnO powder modified with nanoparticles after irradiation. *Rad. Eff. Def. in Sol*., 173(3–4), 198–209. https://doi.org/10.1080/10420150.2018.1424847
8. Sridev, D. & Rajendran, K. V. (2009). Synthesis and optical characteristics of ZnO nanocrystals. *Bull. Mater. Sci.*, 32(2), 165–168. https://doi.org/10.1007/s12034-009-0025-9
9. Kasim, A. W. (2024). Investigate the electrical and structural characteristics of the Si-ZnO diode. *J. Phys. Sci.*, 35(1), 13–20. https://doi.org/10.21315/jps2024.35.1.2
10. Hamid, H. A. et al. (2024). ZnO nanorods prepared by hydrothermal method as a nanosensor for methanol detection. *J. Phys. Sci.*, 35(1), 67–78. https://doi.org/10.21315/jps2024.35.1.6
11. Shaporev, A. S. et al. (2007). Rapid microwave synthesis of zinc oxide in salt matrices. *Inter. Sci. J. Alt. Ener. Ecol.*, 1(45), 44–47 (in Russian).
12. Vanetsev, A. S. & Tretyakov, Yu. D. (2007). Microwave-assisted synthesis of individual and multicomponent oxides. *Russ. Chem. Rev.*, 76(5), 435–453. https://doi.org/10.1070/rc2007v076n05abeh003650
13. Clark, D. E. et al. (1995). Microwaves: Theory and application in material processing. *Ceramic Transc*., 59, 24–28.
14. Gorokhova, E. I. et al. (2008). Optical, luminescence, and scintillation properties of ZnO and ZnO:Ga ceramics. *J. Opt. Technol.*, 75(11), 741–746. https://doi.org/10.1364/JOT.75.000741
15. Siregar, N. et al. (2023). Electroplated ZnO thin film: Influence of deposition time on optical and structural properties. *J. Phys. Sci.*, 34(1), 43–55. https://doi.org/10.21315/jps2023.34.1.4
16. Garcia-Gutierres, R. et al. (2016). Luminescent properties of ZnO microstructures grown on Au/Si substrate. *J. Ovon. Res.*, 12(5), 239–244.
17. Ali, A. T. et al. (2023). Random laser emission from fiber coated ZnO. *J. Phys. Sci.*, 34(2), 29–40. https://doi.org/10.21315/jps2023.34.2.3

18. Davronov, M. Kh., Makarov, N. V. & Rakhmatullaev, I. A. (2022). Study of the morphological, structural and optical properties of zinc oxide microstructures, produced by microwave deception. *Usp. xim.i xim. texn.* 36(10), 60–63 (in Russian).
19. Gorelik, V. S. & Rakhmatullaev, I. A. (2005). Excitation of Raman optical processes in an ultradispersed medium by radiation from a pulsed-periodic laser. *Tech. Phys.*, 50(1), 61–64. https://doi.org/10.1134/1.1854824
20. Burakov, V. S. et al. (2011). Morphology and optical properties of zinc oxide nanostructures synthesized by the methods of thermal and discharge sputtering. *Tech. Phys.*, 56(2), 245–253. https://doi.org/10.1134/S1063784211020071
21. Abduev, A. Kh. et al. (1978). Ultraviolet luminescence of zinc oxide epitaxial layers under one- and two-photon excitations. *Kvant .elek.*, 5(1), 206–208 (in Russian).
22. Sokolovskiy, M. I. (2006). *Secondary emission of nanocrystalline zinc oxide under laser excitation*. PhD diss. Ulyanovsk: Ulyanovsk State University (in Russian).
23. Fonoberov, V. A. et al. (2006). Photoluminescence investigation of the carrier recombination processes in ZnO quantum dots and nanocrystals. *Phys. Rev. B.*, 73, 165317. https://doi.org/10.1103/PhysRevB.73.165317
24. Emelchenko, G. A. et al. (2007). Luminescence of zinc oxide nanorods. *Fiz. i Tex. Polupr.*, 41(2), 182–185 (in Russian).
25. Johnson, J. C. et al. (2003). Optical cavity effects in ZnO nanowire lasers and waveguides. *J. Phys. Chem. B.*, 107(34), 8816–8828. https://doi.org/10.1021/jp034482n
26. Sun, X. W. et al. (2003). Room-temperature ultraviolet lasing from zinc oxide microtubes. *Jpn. J. Appl. Phys.*, 42(10), 1229–1231. https://doi.org/10.1143/JJAP.42.L1229