Improvement of the scintillating properties of ZnO ceramics by the precipitation of initial powder

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Abstract. One of the applications of zinc oxide is a scintillator or phosphor. Both of its emission bands, fast near-band-edge or slow green luminescence, can be used, depending on the application. In any case it is essential to obtain the sample of high transparency in the range of a certain luminescence band. In this work ceramic samples made of undoped ZnO micro- and nanocrystalline powders, where the latter was made by precipitation of initial microcrystalline powder, were studied. Ceramics showed significant differences in their optical and luminescent properties. The reasons for observed changes are discussed.

1. Introduction
Zinc oxide (ZnO), as a wide-band-gap (Eg = 3.37 eV) semiconductor, possesses excellent optical and luminescent properties. It finds application as a material of phosphors, scintillators, transparent contacts, varistors, etc. The structural, optical, and luminescent characteristics of ZnO have been described in a series of reviews [1–3]. Various ZnO forms (single crystals, thin films and filaments, nanocrystals, needles, etc.) exhibit, as a rule, two luminescence bands, namely, a short-wavelength band near the absorption edge of the crystal, which is usually called near-band-edge (NBE) luminescence and a broad long-wavelength band peaking in the green spectral region, so-called green luminescence (GL). Under particular conditions, yellow (YL) and red (RL) luminescence of zinc oxide were also recorded [1, 3]. The edge luminescence with a maximum at 3.35 eV and a decay time of ~ 0.7 ns has an excitonic nature. The luminescence characteristics of excitons of different types in ZnO have been studied in detail in [4, 5].

To use zinc oxide in fast scintillation detectors, it is necessary to increase the intensity of NBE luminescence and suppress the GL. One of the ways to suppress GL and to increase the intensity of NBE luminescence is to introduce trivalent gallium and/or indium ions into ZnO [6]. Recently, researchers have used new approaches to solve this problem, in particular, the introduction of La3+ [7], Mg2+, Cd2+ [8], Al3+ [9] ions into ZnO:Ga. Various types of annealing [10] and cooling [11] are also used.

Another challenge is to increase transparency of the sample in the range of NBE luminescence, thus increasing the amount of light escaping the bulk that can reach the detector. In the present work,
an attempt was made to obtain transparent scintillation ceramics from ZnO micro- and nanopowders of various origins.

2. Experimental
As an initial material, we used 99% pure ZnO microcrystalline powder (Sigma-Aldrich). Part of the powder was processed by abundance of NH$_4$HCO$_3$ water solution at 25°C under vigorous stirring within 1 h to form the Zn$_x$(OH)$_y$(CO$_3$)$_z$ precipitate of mixed zinc hydroxide carbonates. Then the Zn$_x$(OH)$_y$(CO$_3$)$_z$ precipitate was filtered, dried and annealed on air at 600°C for 24 h to obtain a nanocrystalline ZnO powder. Average particle size varied from 100 to 500 nm and from 20 to 40 nm for microcrystalline and nanocrystalline powder, respectively.

The ceramic samples were prepared by uniaxial hot pressing of initial powders in a high-temperature vacuum furnace. After mechanical treatment they had a diameter of 24 mm and a thickness of 0.5 mm. Small pieces were cut from initial samples to perform independent measurements. Thus, we studied two ceramics samples, which were synthesized from initial microcrystalline powder (ZnO-1) and from the nanocrystalline powder obtained by precipitation method (ZnO-2).

The luminescence spectra were measured in the range from 350 to 650 nm under continuous X-ray excitation (40 kV, 10 mA) in “reflection” geometry. The luminescence was detected with the use of diffraction grating monochromator MDR-2 and Hamamatsu H8259-01 photon counting head. The spectra recorded were corrected taking into account the photodetector sensitivity and the monochromator transmittance.

The transmittance spectra were measured in the range from 350 to 1100 nm by the UV/Vis double-beam spectrophotometer SPECORD 200 PLUS with an integrating sphere attachment.

3. Results and discussion
Figure 1 shows the photo of the obtained samples. There are significant differences between their optical properties. The ZnO-1 sample, made directly from Sigma-Aldrich powder, has an intense red color which is uncommon for pure zinc oxide and sample ZnO-2 is painted in a light greenish color. The text is clearly visible through the ZnO-1 sample.

![Figure 1. Photos of ZnO-1 (left) and ZnO-2 (right) ceramic samples.](image)

Basic explanation of the observed sample coloration is the difference in impurity content. Initial Sigma-Aldrich powder is 99% pure meaning that it can contain a lot of elements which can have absorption bands in blue and green spectral regions. The precipitation involved in the powder preparation for the second sample assures smaller concentration of impurities in the ceramic. On the other hand, this method produces powders of a much smaller grain size which could have lead to higher level of refraction in the sample making it more opaque.

To prove this point the microphotographs of the ceramic surfaces were made and shown at figure 2. The intense progress of recrystallization processes during the formation of the ZnO ceramic resulted in 1.5-2 orders of magnitude increase of the grain size in comparison with the size of the original particles [12, 13]. The microstructure of ZnO-1 ceramic made of microcrystalline powder is
represented by grains with clearly defined boundaries, the size of which is on average 25–40 µm, and the shape approaches isometric. The microstructure of ZnO-2 ceramic made of nanocrystalline powder is composed of various grains from isometric, rounded to indefinite grains. The grain size of the ZnO-2 ceramics is significantly smaller than that of the ZnO-1 ceramics, and ranges from 3 to 25 µm.

Figure 2. Microstructure of ZnO-1 (left) and ZnO-2 (right) samples. The dash in the bottom right angle equals to 10 micrometers.

Figure 3 shows the X-ray luminescence spectra of the obtained ceramics, corrected for the sensitivity of the setup. Both samples show two luminescence bands: NBE luminescence with the maximum at 390 nm and GL with the maximum around 525 nm which corresponds to the emission of oxygen vacancies [14]. All curves have a similar shape. Ceramic pressed from a nanoscale powder has slightly higher (~ 20 %) intensity of defect-related luminescence. The intensity of the excitonic luminescence in ZnO-2 is lower than in the sample made of the original powder.

Figure 3. X-ray luminescence spectra of ZnO ceramics. Figure 4. Full transmittance spectra of ZnO ceramics.

Figure 4 shows the full transmittance spectra of ceramics. The transmission of the ZnO-1 sample is shifted to the long-wavelength region, with which the reddish tint of ceramics is associated. The transmission of the ZnO-2 sample obtained from nanocrystalline powders is 1.5–2 times lower in absolute value than that of the ZnO-1 sample, while the transmission spectrum is not shifted. The similarity of the shape of the spectra and the higher intensity of the excitonic emission band in ZnO-1 ceramic despite the lower transmittance is due to the fact that the X-ray spectra were taken in reflection-like geometry.
4. Conclusions

Two ZnO ceramic samples have been studied. It was observed that the luminescent properties of the samples do not undergo significant changes. ZnO-2 sample prepared from nanocrystalline powder showed 20% higher intensity of the green luminescence band and lower intensity of the NBE luminescence. The shape of the bands remained unchanged.

Optical properties on the other hand are quite different. The precipitation process used to obtain nanocrystalline powder resulted in a much smaller grain size of the ceramic sample. This may have caused overall decrease of the sample transparency due to much higher internal refraction on multiple interfaces or due to higher concentration of surface defects. At the same time the transmittance significantly improved in the range from 400 to 500 nm where NBE luminescence is usually present. The reason is most probably the purification effect of the precipitation process.

To obtain fast ZnO based scintillator it is necessary to increase transparency in the NBE luminescence region, particularly 380-420 nm. The results of this study indicate that precipitation method may be useful for increasing the transmittance in that spectral range. To improve the transmittance even more it is necessary to either increase the ceramic grain size or decrease the amount of defects. Both can be done by additional treatment of initial powder or by tweaking the pressing conditions. Further improvement of the method and estimation of its effect on the ZnO:Ga ceramics will be the topic of the future work.

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References

[1] Meyer B K et al 2004 Phys. Stat. Sol. B 241 231-60
[2] Ozgur U, Alivov Ya I, Liu C, Teke A, Reshchikov M A, Dogan S, Avrutin V, Cho S -J and Morkoc H 2005 J. Appl. Phys. 98 041301
[3] Rodnyi P A and Khoduk I V 2011 Opt. Spectrosc. 111 814-24
[4] Wagner M R et al 2011 Phys. Rev. B 84 035313
[5] Heinhold R, Neiman A, Kennedy J V, Markwitz A, Reeves R J and Allen M W 2017 Phys. Rev. B 95 054120
[6] Chernenko K A, Gorokhova E I, Eron’ko S B, Sandulenko A V, Venetsev I D, Wieczorek H and Rodnyi P A 2018 IEEE Trans. Nucl. Sci. 65 2196-202
[7] Prochazkova L, Gbur T, Cuba V, Jary V and Nikl M 2015 Opt. Mat. 47 67-71
[8] Prochazkova L, Cuba V, Beiliterova A, Jary V, Omelkov S and Nikl M 2018 Opt. Express 26 29482-94
[9] Ungula J, Dejene B F and Swart H C 2017 J. Lumin. 195 54-60
[10] Hur T B, Yoo D H, Jeen G S, Hwang Y H and Kim H K 2003 J. Korean Phys. Soc. 42 S1283
[11] Ghosh S and Basak D 2017 Royal Soc Chem. 7 694-703
[12] Gorokhova E I, Anan’eva G V, Demidenko V A, Rodnyi P A, Khodyuk I V and Bourret-Coucharnes E D 2008 J. Opt. Technol. 75 741-46
[13] Gorokhova E I, Eron’ko S B, Oreshchenko E A, Sandulenko A V, Rodnyi P A, Chernenko K A, Venetsev I D, Kul’kov A M, Muktepavela F and Boutachkov P 2018 J. Opt. Technol. 85 729-39
[14] Rodnyi P A, Chernenko K A and Venetsev I D 2018 Opt. Spectrosc. 125 357-63