



# Influence of annealing on the scintillation properties of zinc oxide powders and ceramics



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## HIGHLIGHTS

- Different annealing atmospheres produce different luminescence centers in powders.
- Luminescence of each center is accompanied by specific decay curve.
- Intensity of emission of ceramics can be increased by hydrogenous annealing.
- Depth of hydrogenous annealing effect in ceramics is about 100  $\mu\text{m}$ .

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## ABSTRACT

It was shown that annealing ZnO and ZnO:Ga initial powders and ceramics in different atmospheres significantly changes the characteristics of the studied samples. Two main luminescence bands of different origins were observed in powders at 540 nm and 580 nm. Annealing either in vacuum or in Ar:H<sub>2</sub> atmosphere increased intensity of green luminescence with peak at 540 nm whereas annealing in air enhanced a luminescence band with peak at 580 nm in the powders. Corresponding changes in luminescence kinetic properties were observed. Annealing of the ceramics in vacuum and air did not affect the luminescence properties, while annealing them in Ar:H<sub>2</sub> atmosphere increased green luminescence intensity of undoped ceramics and excitonic luminescence intensity of doped ones. Comparison of the X-ray, gamma-ray and cathode-ray excited luminescence lead to conclusion that the enhancement of luminescence intensity took place in surface layer of about 100  $\mu\text{m}$  thickness.

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## 1. Introduction

Zinc oxide (ZnO) is known as an efficient phosphor, besides it finds application in scintillation techniques (Moses, 2002). Generally, various forms of ZnO exhibit two emission bands. One of them is a narrow band located near the absorption edge of the crystal; therefore it is called near-band-edge luminescence (NBEL). Another one is a broad band, its maximum usually lies in the green-yellow spectral range and it is called green luminescence (GL). The NBEL has exciton nature, and the GL is associated with native defects (Chen et al., 2011). The NBEL shows a decay time of subnanosecond

range, and therefore it is most important for high-speed photonic devices.

In order to use this material as fast scintillator one has to suppress the GL and enhance the NBEL intensity. This task was solved on powders and nanocrystals (Berseth et al., 2006; Ton-That et al., 2012; Bourret-Courchesne et al., 2009) with annealing in different atmospheres. For scintillator applications, bulk and transparent materials (such as optical ceramics) are required. Therefore, it is interesting to study the influence of annealing on optical ceramics.

In this paper, the influence of annealing in vacuum, air and Ar:H<sub>2</sub> atmospheres on luminescence characteristics of ZnO and ZnO:Ga ceramic samples and its initial powders was studied.

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## 2. Materials and methods

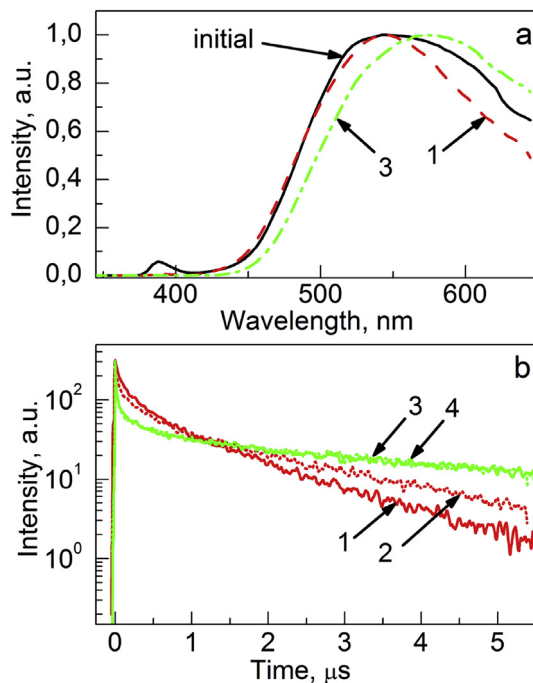
The chemical purity (99.9%, Russia) zinc oxide powders were used for manufacturing of ZnO by the method of uniaxial hot pressing in a high vacuum furnace (Demidenko et al., 2007). Hot pressing was produced at temperature 1000–1100 °C under pressure of 100–200 MPa for 60 min. The gallium doped ceramics (ZnO:Ga) contained 0.075% of Ga<sup>3+</sup> that was introduced in the initial powder in the form of gallium oxide. Samples had the form of discs with a diameter of 24 mm and after polishing they had thickness of 0.5 mm. Transmittance of undoped ceramics was more than 50% in range of 450–900 nm. Transmittance of ZnO:Ga ceramics was about 20% at 395 nm.

The X-ray excited luminescence (XRL) spectra were measured under steady state X-ray excitation (40 kV, 10 mA). The detection system consists of an MDR-2 grating monochromator with 1200 grooves/mm and a FEU-106 PMT. The spectra were corrected for the quantum efficiency of the PMT and for monochromator transmission. The decay time curves were recorded by the setup described in (Rodnyi et al., 2001). The XRL spectra and decay time curves were measured in the reflection mode. The cathodoluminescence (CL) spectra under 20 keV electron beam on 1 mm<sup>2</sup> spots were recorded with a scanning electron microscope (SEM) coupled with an optical fiber to the Ocean Optics QE65000 USB-spectrometer.

## 3. Results

### 3.1. Annealing of powders

Normalized XRL spectra of the powders are presented in Fig. 1a. Mainly the broad GL band with maximum at 550 nm was observed in the XRL spectrum of the initial powder. The NBEL with relatively small intensity was detected at 388 nm. Annealing of the initial powder was performed at 800 or 1050 °C for 120 min in vacuum



**Fig. 1.** X-ray excited luminescence spectra (a) and decay curves (b) of initial undoped powder and undoped powders after vacuum (1–1050 °C, 2–800 °C) and air (3–1050 °C, 4–800 °C) annealing. Intensities are normalized.

and air. After the vacuum annealing, intensities of the GL were about 10 (for 800 °C) and 20 (for 1050 °C) times higher than intensity of the initial powder while the GL intensities of both air annealed powders were 5 times greater than the initial ones. Shift of the GL peak position was observed for the vacuum (540 nm) and the air (580 nm) annealed powders.

A change in the decay kinetics corresponding to the shift of the GL peak position was detected (Fig. 1b). All the powders had a complicated decay law, which could be quantitatively described by 3-exponential decay. For the air annealed powders the estimated decay time constants were 5 ns, 100–200 ns, and 4000–5000 ns. Approximation of the decay curves of the vacuum annealed powders by three exponential decays gave time constants of: 10–50 ns, 100–200 ns, and a third slow decay time component. For the powder annealed at 800 °C the decay time of the slow component was about 1600 ns and for the powder annealed at 1050 °C the decay time of the slow component was about 1100 ns. After vacuum or air annealing, the powders were annealed in gas mixture of 85% Ar and 15% H<sub>2</sub> (Ar:H<sub>2</sub>) at 800 °C for 15–60 min. For the vacuum annealed powders, the Ar:H<sub>2</sub> annealing had no significant effect on peak position or intensity (Fig. 2). For the air annealed powder, subsequent Ar:H<sub>2</sub> annealing for 30 min significantly decreased the intensity of the red shifted GL. In the same time, an increase of the NBEL intensity was observed. Annealing in hydrogenous atmosphere for longer time leads to an intensity increase of the GL band peaking at 540 nm. The luminescence decay curves of the powders annealed for a long time in Ar:H<sub>2</sub> gas mixture were the same as the luminescence decay curves of the powders annealed in vacuum.

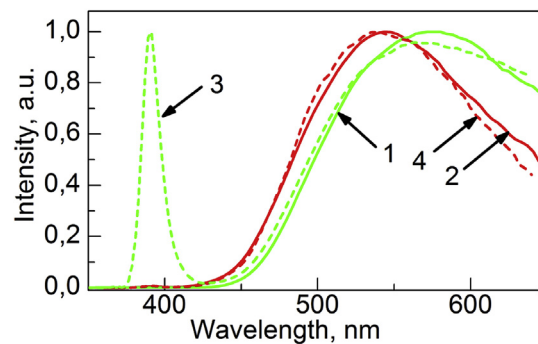
### 3.2. Annealing of ceramics

Vacuum and air annealing of the ceramics was performed at 1050 °C for 120 min. Unlike the powders, air and vacuum annealing do not affect the emission intensity, peak position or decay kinetics of the ceramic samples.

The optimization of the annealing conditions in hydrogenous atmosphere was made for the gallium doped ceramics. The ceramic samples were annealed in the gas mixture of 5% H<sub>2</sub> and 95% Ar at 600 or 700 °C for 30 or 120 min and characterized by CL (Fig. 3a). The highest increase of the NBEL intensity was detected when the annealing was performed at 600 °C for 120 min.

SEM photos of the samples (Fig. 3b) show that Ar:H<sub>2</sub> annealing leads to thermochemical etching of surface. No grain morphology changes are observed.

ZnO and ZnO:Ga ceramics were annealed at the best conditions (600 °C, 120 min) and characterized by XRL and CL. In the ZnO



**Fig. 2.** Comparison of X-ray excited luminescence spectra of powders that were annealed in air (1), annealed vacuum (2), subsequently annealed in air and then in Ar:H<sub>2</sub> gas mixture (3), subsequently annealed in vacuum and then in Ar:H<sub>2</sub> gas mixture (4). The Ar:H<sub>2</sub> annealing was performed at 800 °C for 30 min. Intensities are normalized.

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