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About self-activated orange emission in ZnO

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Abstract. Nominally undoped ZnO ceramics were sintered in air and N₂ flow at 1000 °C. Room temperature photoluminescence (PL) spectra of the samples were measured and analyzed using Gaussian fitting. The self-activated orange PL band peaking at 610 nm was separated by Gaussian deconvolution. Based on the obtained results compared with some literature data, it has been concluded that the defects responsible for self-activated orange emission in ZnO are zinc vacancies.

Keywords: ZnO ceramics, photoluminescence.

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1. Introduction

Among numerous applications of zinc oxide in optoelectronics, development of light emitters is one of the most important. In fact, it was shown that ZnO single crystals, ceramics, films and nanostructures with both intense excitonic UV and bright defect-related visible emissions could be prepared [1, 2]. Based on careful study for several decades, origin of the most of UV bands in ZnO has been established quite unambiguously. At the same time, the electron-hole transitions responsible for defect-related emission and the origin of emitting centers are thus far the matter of discussion.

In undoped ZnO, defect-related emission is known to exhibit itself as a broad structureless green-orange band which is stated to consist of several overlapping ones [1, 2]. However, the number of the components and their peak positions are still debated through the literature. The majority of investigators believe that, in undoped ZnO, two bands are observed in green spectral range, one of which is related to native defects, while the other is caused by residual copper impurity [1, 2]. Emission in the red spectral range which exhibited itself as a shoulder at the longwave side of orange emission [3, 4] or as a

separate band peaked at about 700 nm [4-6] was also reported. In yellow-orange spectral region, intense impurity-related PL bands peaked at 600 and 570 nm were found to appear due to doping with Li and Na accordingly [1, 2, 7]. As for self-activated orange emission, various bands peaked at 570...590 nm [9-12], 610 nm [8, 9, 12], 614 nm [3], 620...630 nm [14, 15] and 640 nm [9, 13, 15] have been reported. This variety is usually related to the creation of different defects depending on the preparation method and ambient gas used. However, one of the reasons of such a discrepancy can be the fact that peak positions of emission bands are often determined using Gaussian fitting procedure. At the same time, Gaussian deconvolution of a broad structureless band will be rather ambiguous, if the number and peak positions of components are completely indeterminate. More reliable results can be obtained when the positions of some of components are established. In the present work, photoluminescence (PL) spectra of undoped ZnO ceramics were analyzed by Gaussian fitting. Deconvolution was made taking into account the positions of self-activated and Cu-related green bands determined experimentally, as well as the position of self-activated red band taken from the literature.

2. Experimental procedure

The samples were formed of the mixture of ZnO (99.99% purity) powder with distilled water, dried at room temperature, sintered for 3 hours at 1000 °C in air, N₂ flow or Zn vapor and cooled with the furnace. In the latter case, the samples were located in a closed crucible with metallic zinc scraps and annealed in N₂ flow. Several samples sintered in air were doped with Cu by adding CuCl₂ aqueous solution to the initial mixture. Obtained ceramics were cut transversally and defect-related PL spectra in 400...800 nm spectral range were measured at room temperature from both the surface and bulk of the samples. Xe-lamp light passing through grating monochromator was used as the exciting source, the wavelength 360 nm being chosen for PL excitation.

3. Results and discussion

In undoped samples sintered in air or N₂ flow, a broad green-orange PL band with a noticeable “tail” in the red spectral region was observed. This emission was well seen by naked eye, but its intensity was not too high (Fig. 1, curve 1). The samples sintered in Zn vapor exhibited very intense and comparatively narrow green PL band peaked at 515 nm (Fig. 1, curve 3). The green band with almost the same width, weaker intensity and peak position at 540 nm was demonstrated by the samples doped with Cu (Fig. 1, curve 2).

Surface and bulk PL spectra of ceramics sintered in air and N₂ flow are plotted in Figs 2 and 3. One can see that the curves have different shape and peak positions. Deconvolution of these curves by Gaussian fitting testifies, however, that, after separation of two green bands peaked at 515 and 540 nm as well as the red band peaked at 700 nm, the residual orange band with peak position 610 nm manifests itself in all cases. The contribution of this band to PL spectrum is more considerable in the samples sintered in N₂ flow with respect to that sintered in air and its intensity is higher at the surface of the samples with respect to that in the bulk.

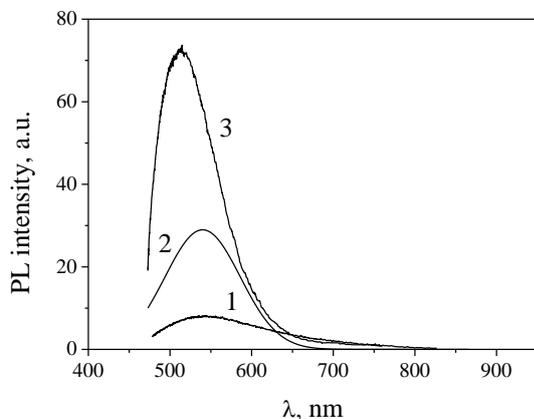


Fig. 1. PL spectra of ZnO ceramics sintered in air (1) undoped, (2) doped with Cu and (3) sintered in Zn vapor.

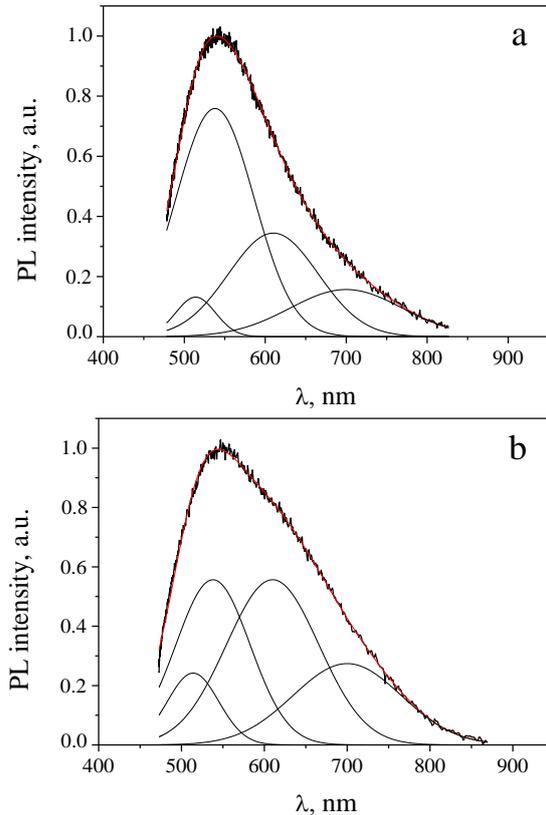


Fig. 2. PL spectra of undoped ZnO ceramics sintered in air: bulk (a) and surface (b) of the sample.

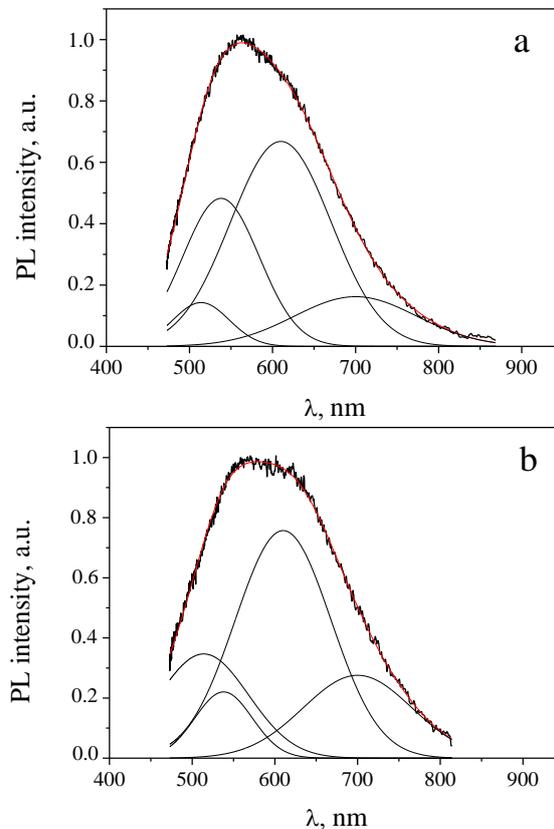


Fig. 3. PL spectra of undoped ZnO ceramics sintered in N₂ flow: bulk (a) and surface (b) of the sample.

The results of Gaussian deconvolution also show that self-activated green emission is the brightest one only in the samples sintered in Zn vapor, whereas in the samples sintered in air or N₂ flow its intensity is rather low and Cu-related band dominates in the green spectral region.

As literature survey has shown, orange emission in ZnO crystals, films, powders and nanostructures can be obtained by the annealing in air or oxygen ambient, and it is associated with stoichiometric oxygen excess in the form of oxygen interstitials [1-3, 9, 11-14, 16]. In [8], however, bright orange PL was obtained by annealing in vacuum of high-purity ZnO powder that demonstrated initially intense green PL band. With increasing the annealing temperature T_{ann} from 500 up to 800 °C, gradual conversion of green band peaked at 515 nm into the orange one peaked at 610 nm was observed, a layer of metallic Zn being formed on the cold end of the silica tube in which the annealing was performed [8]. Based on these facts, it was stated that emitting centers responsible for orange PL were related to zinc vacancies V_{Zn} created due to zinc evaporation [8]. The annealing of the same powder in air resulted in the appearance of both orange and red PL bands, which relative intensities were dependent on T_{ann} [4]. The red band arose at $T_{ann} = 450$ °C and enhanced up to $T_{ann} = 600$ °C as a separate band, then exhibited itself as a shoulder of growing orange band and at last hid in the tail of the latter at $T_{ann} \geq 800$ °C [4]. When the initial powder was annealed with Cu or Fe oxide, orange emission disappeared, and only the intense red PL band was observed [4]. This effect can be accounted for by the incorporation of impurity atoms into zinc vacancies, which is consistent with made in [8] conclusion about the origin of emitting centers responsible for self-activated orange PL band in ZnO.

Results obtained in the present work confirmed the role of zinc vacancies in formation of orange emission in intentionally undoped zinc oxide. In fact, one can expect that more intense Zn evaporation will occur, and the higher density of zinc vacancies will be created: i) on the surface of the sample than that in its bulk; ii) under annealing in N₂ flow with respect to that in immobile air due to removal of evaporated Zn from annealing zone by gas stream. As Figs 2 and 3 show, contribution of the orange band to PL spectrum is greater on the surface of the samples than in their bulk and after annealing in N₂ flow than in air, indeed. The other evidence of Zn removal from undoped ceramics under annealing is a low intensity of self-activated green emission that is associated with stoichiometric excess of zinc [1, 2, 17].

4. Conclusion

In order to ascertain the position of self-activated orange emission in zinc oxide, surface and bulk PL spectra of nominally undoped ZnO ceramics sintered in air or N₂ flow were measured and analyzed using

Gaussian fitting. Gaussian deconvolution was made using experimentally obtained positions of the self-activated and Cu-related green PL bands as well as the self-activated red PL band position taken from the literature. After such a procedure, the same orange PL band peaked at 610 nm was separated in all the PL spectra. The contribution of this band to PL spectra was found to be greater in the samples sintered in N₂ flow than that in those sintered in air and for the surface of the samples with respect to their bulk. This effect was accounted for as caused by evaporation of zinc from the samples under annealing, which is confirmed by the weak self-activated green PL band related to stoichiometric Zn excess. The obtained results compared with some literature data led to the conclusion that native defects responsible for the self-activated orange band were zinc vacancies.

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