



## The luminescence of ZnO ceramics

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### ARTICLE INFO

#### Article history:

Received 17 August 2009

Received in revised form

15 February 2010

Accepted 30 March 2010

#### Keywords:

ZnO

Time-resolved luminescence

Nanostructured ceramic

### ABSTRACT

The luminescence properties of ZnO ceramics with grains 100–5000 nm sintered by different techniques from nanopowders were studied. The luminescence decay times were compared with that obtained for ZnO single crystal. The temperature dependence of non-exponential decay of defect luminescence (2.0–2.6 eV) was measured in wide time, intensity and temperature range. The luminescence decay kinetic at  $T \leq 20$  K shows the decay close to  $I(t) \sim t^{-1}$  dependence. At temperature region 50–250 K the decay kinetics is more complicate since the TSL was observed in this temperature region. It is shown that the luminescence properties of NP and ceramics strongly depend on defect distribution on grains surface and the volume/surface ratio determine the luminescence decay in ZnO nanostructures and ceramics.

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### 1. Introduction/scope

The lately extensive research of ZnO has been carried out due to wide applications including luminescent devices, transparent conductive coatings and others. One of the important applications is a fast scintillators since the ZnO excitonic luminescence has known faster decay time and low level of afterglow (Wilkinson et al., 2004, 2005; Grigorjeva et al., 2008). However there are some open questions in the field of ZnO luminescence (e.g., the mechanisms of fast excitonic luminescence and the origin of green–yellow luminescence).

The luminescence properties of ZnO powders (with nano- and microsize grains easy obtained by different synthesis methods) as well as ZnO coatings were widely studied. However, for luminescence detector practical application preferably are a single crystal or ceramic. It is known the attempt to obtain partly transparent ZnO ceramic (Demidenko et al., 2007).

In present work the luminescence properties of ZnO ceramics sintered by different techniques we studied by using time-resolved luminescence method.

### 2. Sample preparation

The undoped and Al doped nanopowders (NP) prepared by plasma (PL) method (Grabis, 2007) were used for ceramic sintering. Two different methods for ZnO ceramic sintering were used: *high*

*temperature sintering* (HT) and *high pressure low temperature sintering* (HPLT). For the HT sintering method the pellets have been pressed under 290 MPa and then annealed in air at 1200 °C for 10 min. For the HPLT sintering the toroidal press, calcite matrix and graphite heater were used. Diameter of the pellet was 5 mm, pressure of sintering 8 GPa, time of sintering 1 min, sintering temperature 150 °C.

### 3. Experimental

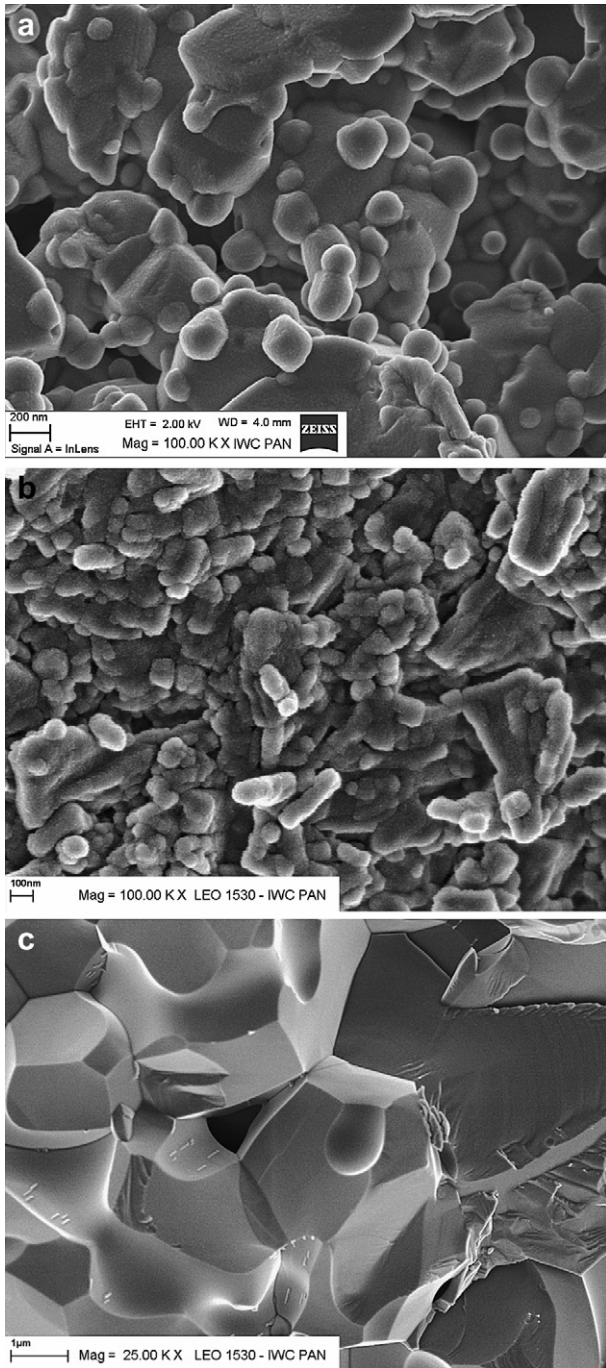
YAG:Nd laser (CryLas FQSS266-Q, 266 nm, 1 ns pulse width FWHM, pulse energy 0.42 μJ, laser beam was focused into 2 mm spot, 2.5 kHz) was used for photoluminescence excitation. Luminescence measurements were carried out with a photon counting head (HAMAMATSU H8259-2) and photon counting board (module P 7887) with minimal time bins 250 ps. Thermally stimulated luminescence (TSL) was measured after 10 min X-ray excitation at 4.5 K with heating rate 5 K/min. SEM images were measured by scanning electron microscope ZEISS LEO1530.

### 4. Results and discussion

The morphology and grain size of ceramics were estimated from SEM images (Fig. 1). The ceramics obtained by HT sintering has wide grain size distribution 100 nm–5 μm (Fig. 1a,c). The nanostructured ceramics with grains 100–500 nm have been prepared by HPLT method (Fig. 1b). It is significant to note that the morphology of ceramics is depending not only on sintering condition, but also from the morphology and doping of used raw NP (Grigorjeva et al., 2009).

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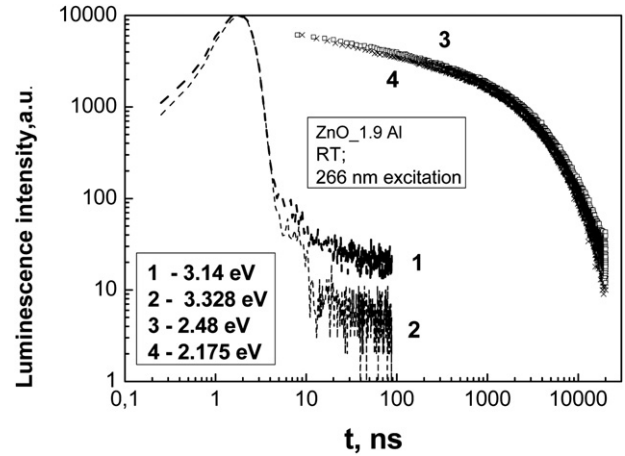
E-mail address: [lgrig@latnet.lv](mailto:lgrig@latnet.lv) (L. Grigorjeva).



**Fig. 1.** SEM images of ceramics prepared from PL NP: ZnO:Al (1.9 wt.%) by HT sintering (a), undoped ZnO by HPLT sintering (b) and undoped ZnO by HT (6 min 1200 °C) sintering (c).

The ZnO native luminescence is due to exciton annihilation (blue spectral range) and to defect states (yellow and/or green luminescence). It is known that the photoluminescence is one of the popular tools for ZnO testing. The luminescence decay kinetics of ZnO:Al ceramic detected at RT at different spectral points are shown in Fig. 2. The decay time of excitonic bands is very fast (<1 ns) and luminescence pulse follows the excitation pulse (Fig. 2).

The green–yellow defect luminescence of ZnO has been studied for a long time, but the common point of view for the origin of this luminescence not exists. The prevailing view is that the green luminescence was from the photogenerated hole recombination



**Fig. 2.** Luminescence decay kinetics of HT ZnO:Al ceramic.

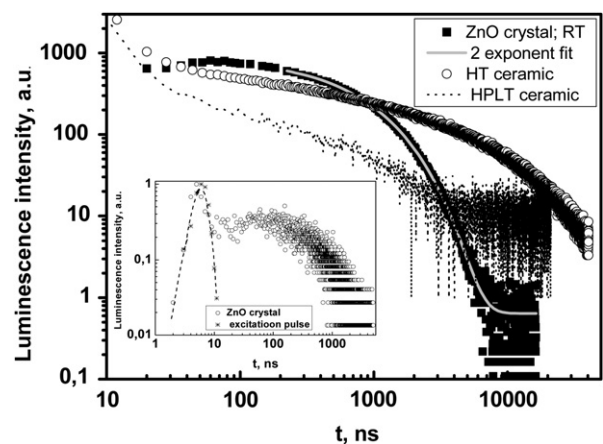
with electron at the singly ionized oxygen vacancy (Vanheusden et al., 1996; Ozgur et al., 2005). In that case the defect luminescence properties (intensity, spectrum, decay kinetics) evidently depend strongly on oxygen vacancy concentration, nanostructure morphology and grain size, dopant concentration. The decay process in green and yellow luminescence bands is the same in wide intensity range.

The coincidence of luminescence decay at 2.17 eV and 2.48 eV (Fig. 2) are due to the same recombination process until excited state formation of different luminescence centers in assumption that life-time of excited state is short.

Fig. 3 shows the luminescence decay kinetics measured at 2.48 eV at RT of ZnO crystal and ceramics prepared by HPLT and HT methods.

The HPLT ceramics has high ratio of grain surface area to volume and color of prepared ceramics is brown. The color is due to unknown defects mainly on grains boundaries. The ceramics prepared by HPLT shows low light yield due to additional defects created under high pressure sintering.

The studies of ZnO crystal luminescence show that the initial part of luminescence kinetics has a raising stage due to luminescence center creation. This stage is not observed in ceramic samples. The analysis of decay process is possible to start with ~200 ns. For a single crystal the luminescence decay is described with sum of two exponents with 375 ns and 900 ns decay times (see Fig. 3). The decay process in ceramics is more complicated.



**Fig. 3.** The luminescence decay kinetics of ZnO ceramics and ZnO crystal measured at 2.48 eV. In inset the initial part of decay process in ZnO single crystal are shown.

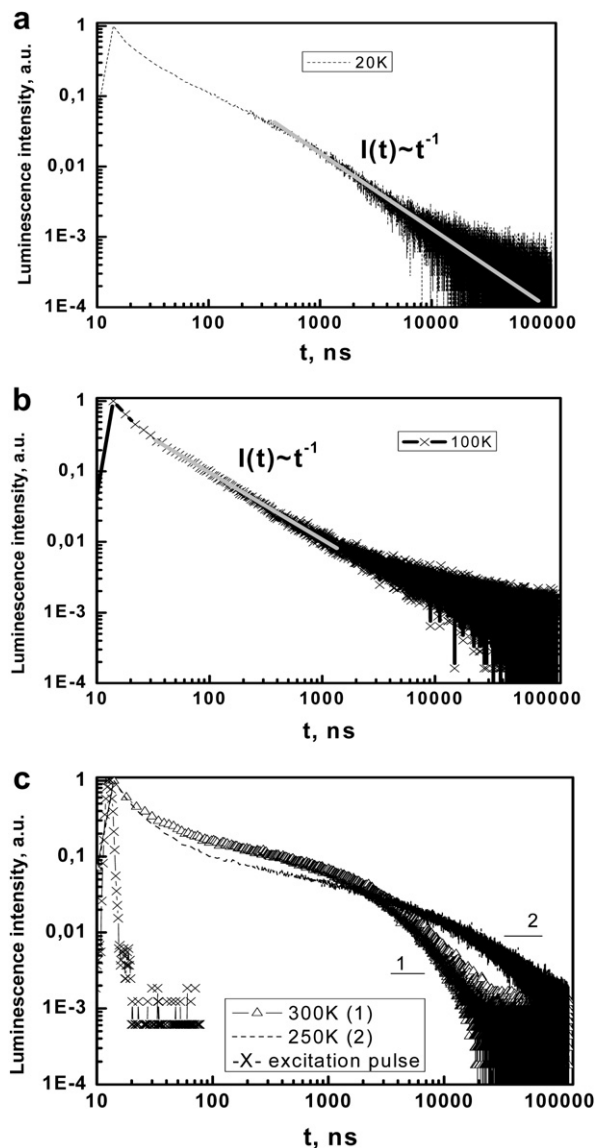


Fig. 4. Temperature dependence of luminescence decay kinetics of HT ZnO:3Al ceramic.

The luminescence decay did not obey the simple exponential decay law; surely, the recombination mechanism is evident, however the origin of recombination process and electron/hole nature is not clear. The donor–acceptor pair recombination was suggested in ZnO films (Nikl et al., 2009). It is well known that the tunnel recombination did not depend on temperature within some temperature range. Thus we recorded the luminescence decay kinetics at 2.48 eV within 20–300 K (Fig. 4). It is detected that at 20 K the stage close to  $I(t) \sim t^{-1}$  gives the contribution at the kinetic tail (gray line in Fig. 4a). Such behavior is known for tunneling recombination of separate pairs. Our TSL measurements shows

wide TSL peak in 40–250 K. It means that in this temperature region the part of shallow traps will be released and take a part in recombination process. The decay kinetic at 100 K shows the additional recombination channel in the tail of decay kinetics (Fig. 4 b). At higher temperature the decay kinetic became faster, but the probability of charge re-trapping is very high and this is the reason why the decay kinetic at 300 K is complicate. For example, the model with sum of four exponents gives a satisfactory result.

Therefore the luminescence properties of NP and ceramics strongly depend on defect distribution on grains surface and the volume/surface ratio determine the luminescence decay in ZnO nanostructures and ceramics.

## 5. Conclusions

The ceramics with grains less than 100 nm were prepared from ZnO NP by HPLT. During HT sintering the grains grown up to a micrometer size. The luminescence properties of ZnO ceramics depend on grain size, sintering conditions, doping and post preparing annealing. The luminescence decay at spectral region 2.0–2.6 eV defect band is complicate, does not possess simple donor–acceptor pair recombination and at 300 K will be described in model of 3–4 exponents. The decay process is the same within the broad band from 2.2 to 2.6 eV. At low temperature the tunneling recombination process was suggested, whereas at 300 K the complicate process due to high probability of re-tapping takes place.

## Acknowledgments

Supported by Latvian Material Science Program and LZP grant 09.1126. Authors thanks A. Presz for SEM images measurements and Tiit Kerner for the assistant the TSL measurements.

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