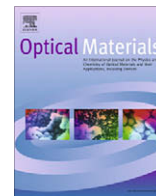




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## Excitonic luminescence in ZnO nanopowders and ceramics

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## ABSTRACT

Fast photoluminescence spectra in the spectral region of 3.1–3.45 eV in ZnO and ZnO:Al ceramics were studied at 14 and 300 K. Ceramics with grains smaller than 100 nm were sintered from nanopowders by high pressure (8 GPa) and low temperature (350 °C). Ceramics with grain sizes 1–5 μm were sintered at 1400 °C. It is shown that excitonic luminescence spectra depend on the ceramics grain size, post preparing annealing and doping. The excitonic luminescence decay time was faster than 2 ns and the afterglow at 30 ns was ~0.05%.

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## 1. Introduction

The research of scintillator materials and scintillation properties has been active during last years [1,2]. The free exciton (Ex) luminescence on a ZnO single crystal is faster than the core-valence luminescence on BaF<sub>2</sub>: 0.44 ns on ZnO [3] and 0.6 ns on BaF<sub>2</sub> [1]. ZnO crystals could have a potential scintillator application, but due to the complicate single crystal growth process the crystal cost is high. Ceramics have a lower cost, but it is difficult to get transparent ceramics from ZnO having a hexagonal symmetry. Recently, it has been reported [4] that partly transparent ZnO:Zn ceramics were prepared at the temperature ~1300 °C and the pressure of ≤300 MPa.

The excitonic luminescence on a ZnO single crystal has been studied in detail [5]. At low temperature, the main band is at 3.359 eV and it is due to an exciton bound at a neutral donor (Ex<sub>D</sub><sup>0</sup>). At 300 K in an undoped ZnO single crystal the main band is due to a phonon associated free exciton state (1LO<sub>Ex</sub>) and is peaking at ≈3.26 eV.

In this paper, the sintering of ZnO ceramics with grains ~100 nm and 1–5 μm in size is reported. The luminescence spectra in a spectral region of 3.10–3.45 eV were studied on different ZnO

ceramics and compared with the known exciton luminescence in a ZnO single crystal.

## 2. Experimental

ZnO ceramic samples were sintered from nanopowders. Undoped and Al doped nanopowders were obtained by different methods: hydrothermal synthesis (HY) [6], plasma (PI) [7] and a vapor condensation (VC) process in a solar reactor [7–9]. All VC powders were prepared in the same conditions: the power density of 950 W/m<sup>2</sup>; the air pressure of 80 Torr in the reactor. The high temperature (HT) sintering and high pressure (HP) at low temperature methods were used to prepare the ceramics. A toroidal press, a calcite matrix and a graphite heater were used for the high pressure technique. The ceramic pellets were 7 mm in diameter; the pressure of sintering was 8 GPa; the time of sintering was 5 min; the temperature of sintering was 350 °C. The ceramics were prepared in the Institute of High Pressure Physics, Polish Academy of Science.

Another method for ceramic sintering was HT sintering, using slightly pressed ZnO pellets. The sintering temperature was 1400 °C and the sintering time was 1–3 min.

The morphology of the obtained powders and ceramics was controlled by the SEM method. SEM images of powders and ceramics

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were obtained using a LEO1530 field emission scanning electron microscope.

The luminescence spectra and luminescence decay kinetics were measured at 14 and 300 K. A YAG:Nd laser (266 nm, 2 ns pulse duration) was used for the photoluminescence excitation. The luminescence measurements were carried out with a photon counting head (HAMAMATSU H8259-2) and a photon counting card (FastComTec Communication Technology module P 7888-1E) with time bins of 2 ns. The spectra were measured in a time gate of 250 ns. The equipment time resolution was 2 ns.

### 3. Results and discussion

Fig. 1 shows SEM images of the powders used for ceramic sintering and the ceramics obtained by the HP method from this powder.

The powders prepared by the HY method have spherical grains, but the powders obtained by VC have whiskers and a tetrapod structure.

The grains of the ceramics were  $\sim 100$ – $200$  nm in size. The morphology of the ceramics prepared from the HY powder (Fig. 1b) and the VC powder (Fig. 1d) differs markedly.

Fig. 2 shows SEM images of the initial powder and the ceramic sintered from this powder using the HT method. During the HT sintering the grain growth was very rapid and ceramics with grains  $1$ – $3$   $\mu\text{m}$  in size were obtained within  $1$ – $3$  min. In Fig. 2b, a whisker can be seen on the surface of the grains. Therefore, simple HT sintering is not a good tool for preparation of nanostructured ceramics, even if the nanopowder was used as an initial material.

The results of the excitonic luminescence studies in ZnO ceramics are shown in Fig. 3. All the luminescence spectra were mea-

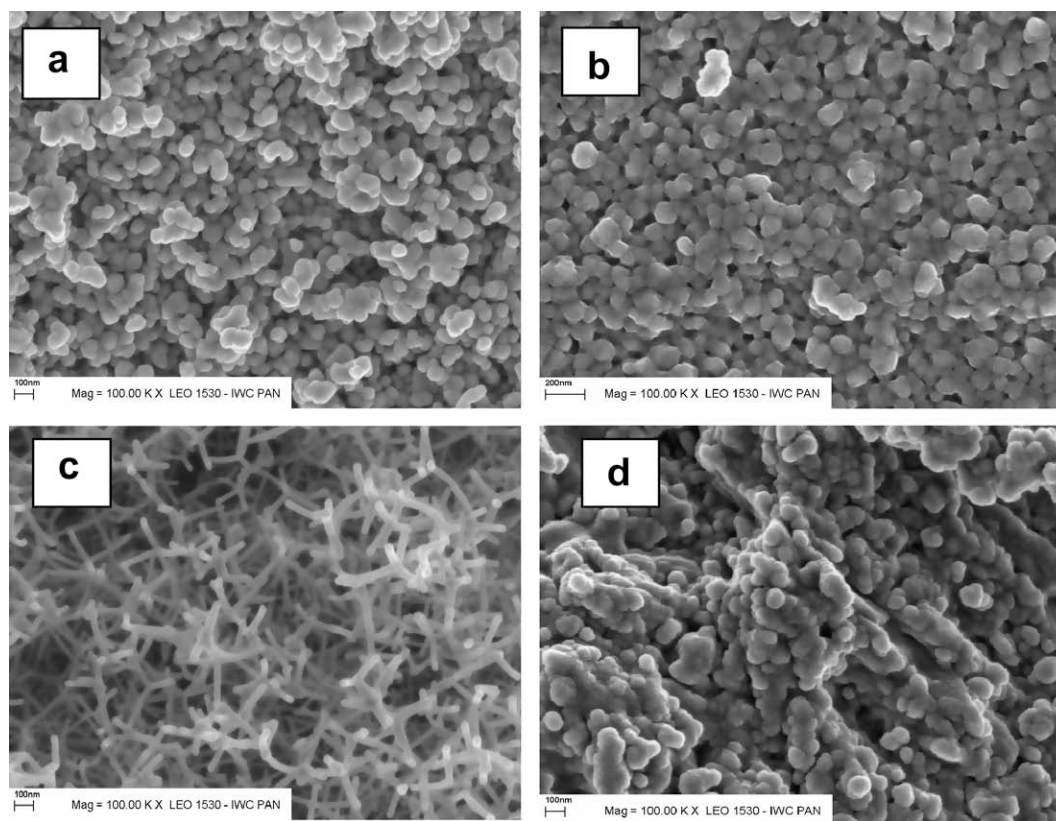


Fig. 1. SEM images: (a) ZnO undoped HY powder; (b) ZnO ceramic prepared from HY powder; (c) ZnO:Al powder obtained by the VC process from PI powder; (d) ZnO:Al ceramic prepared from the powder shown at (c).

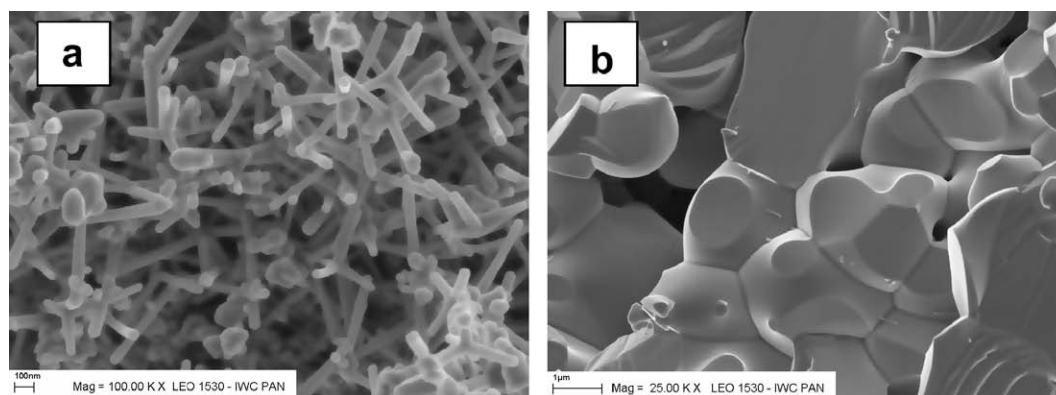
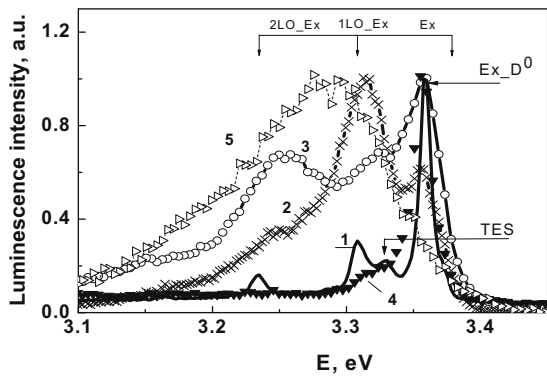
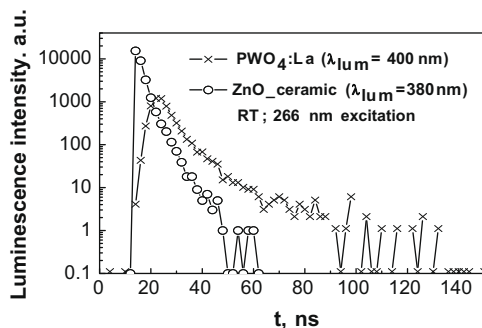


Fig. 2. SEM images: (a) undoped ZnO nanopowder prepared by the PI method and (b) ZnO ceramic prepared by the HT method from this powder; sintering temperature  $1400$   $^{\circ}\text{C}$ , sintering time  $3$  min.



**Fig. 3.** Normalized luminescence spectra of ZnO single crystal 1 and ceramics: 2 and 5 – HP obtained from HY undoped ZnO nanopowder; 3 – HP obtained from VC PI ZnO:Al powder; 4 – HT obtained from undoped VC PI powder. Spectra 1–4 were measured at 14 K; spectrum 5 was measured at 300 K.



**Fig. 4.** Luminescence decay kinetics: comparison of PbWO<sub>4</sub>:La and ZnO ceramics sintered at 1400 °C.

sured in the same experimental conditions. The spectra of a ZnO single crystal are shown for a comparison and interpretation of the excitonic band according to the review [5] for a single crystal. The luminescence intensity of ceramic samples was considerably lower than that for a single crystal. Broadening and overlapping lines of two electron satellites (TES), 1LO\_Ex and 1LO\_ExD<sup>0</sup> were detected in the HP ceramics. The HP ceramics are brown in colour and the fundamental absorption edge is shifted to the low energy side. We suggest that the ExD<sup>0</sup> band could be distorted

due to the near band absorption. An additional luminescence band at 3.25 eV appeared on the ZnO:Al ceramic; similar luminescence was observed in the Al doped powders [7].

The luminescence decay kinetics obtained under the same experimental conditions for the well known fast scintillator PbWO<sub>4</sub>:La and the ZnO ceramic sintered at 1400 °C are compared (Fig. 4). The luminescence decay is considerably faster for the ZnO ceramic. The light yield (the area under the decay curve) at first 50 ns exceeds that for PbWO<sub>4</sub>:La and the afterglow level at 40 ns is less than 0.02%. Therefore, the ZnO ceramic could be used as a fast scintillator.

#### 4. Conclusions

Ceramics with grains smaller than 100 nm can be obtained from ZnO nanopowders by *High Pressure Low Temperature Sintering*. The grains have a micrometer size in simple high temperature sintering. The excitonic luminescence characteristics depend on the grain size, the method of preparing and the doping. The light yield in the fast component for a ZnO ceramic is considerably higher than that for PbWO<sub>4</sub>:La and has a low afterglow level. Therefore, ZnO ceramics are prospective materials for fast scintillators. The ZnO ceramic sintering process will be developed with the main goal to obtain a transparent or partly transparent ZnO ceramic.

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