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Photoluminescence and Chromaticity Properties of ZnO Nanopowders Made by a Microwave Hydrothermal Method

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Four series of ZnO nanopowders obtained by a microwave hydrothermal method are examined. Two different solvents (ethanol and distilled water) and different values of pressure during heating in the reactor were used. The obtained nanopowders show a bright emission covering visible light spectral region, including the band edge emission. Results of scanning electron microscopy, X-ray diffraction, photo- and cathodoluminescence investigations and also CIE1961 chromaticity diagram are presented.

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1. Introduction

Despite the concentrated research of ZnO, this material still has several new opportunities for biological and medical applications as luminescence markers and drug delivery systems, and optoelectronic applications as a phosphor material. The first application requires nano ZnO with a relatively narrow particle size distribution [1]. The hydrothermal method (used in the present work) allows to obtain ZnO nanopowders with a narrow size distribution and good crystallographic quality. It was thus selected by us for preparation of several types of undoped and doped ZnO nanopowders. Here we examine properties of undoped ZnO particles and search for possibility of white color emission under blue/UV excitation.

2. Experimental procedure and the results

Two different solvents (ethanol and distilled water) were used for the preparation of ZnO nanopowders with the microwave hydrothermal method [2]. The MAGNUM II reactor from ERTEC Company was used.

A mixture of zinc hydroxides was obtained by addition of 2 M solution of NaOH to a 20% solution of $Zn(NO_3)_2{\cdot}6H_2O$ in water or ethanol. In the hydrothermal synthesis the obtained hydroxides were heated in the reactor by a microwave power. The microwave assisted synthesis was conducted under a pressure of 2–4 MPa (20–40 atm) during 15 min. The obtained product was filtered, dried and calcined at 750 °C for 1 h. After the reaction samples were dried and examined as-grown or after annealing at 750 °C for one hour.

Elemental composition and morphology of the samples were examined using scanning electron microscope (SEM) Hitachi SU-70. This system is combined with the energy dispersive spectroscopy (Thermo Scientific ultra dry silicon drift X-ray detector) allowing composition studies. Secondary electron signal was used in the SEM investigations. For cathodoluminescence (CL) investigations we used the GATAN Mono CL System. Optical investigations were performed within the spectral range of 200–850 nm.

Figure 1 presents the SEM results for the selected samples. We demonstrate that the annealing procedure has rather small (small increase of size) influence on the size and shape of nanopowders. SEM investigations indicate also that more regular nanopowders with spherical shape are produced in processes with ethanol as a solvent.

The crystallographic structure of the samples was determined using X-ray diffraction (XRD) (Cu K_α radiation, X'Pert Philips). Powder consists of ZnO crystallites of wurtzite structure. The mean crystallite size of the detected phases was determined using the Scherrer formula [3]. The deduced size of about 100 nm agrees well with the SEM investigations shown in Fig. 1.

XRD indicates that both solvents give similar results (Fig. 2). Moreover, we observe analogous XRD results for powders after annealing.

Figure 3 presents dependence of integrated intensity of visible CL on the pressure used during a heating in

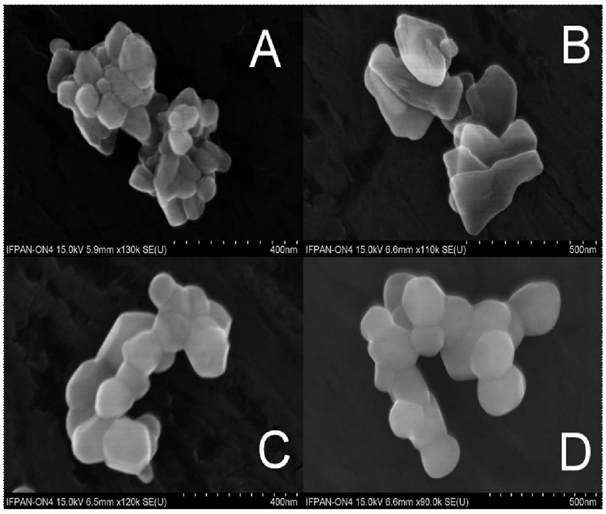

Fig. 1. SEM of ZnO nanopowders: (A) distilled water as solvent and as grown sample; (B) distilled water as solvent and after annealing at 750 °C; (C) ethanol as solvent and as grown sample; (D) ethanol as solvent after annealing at 750 °C.

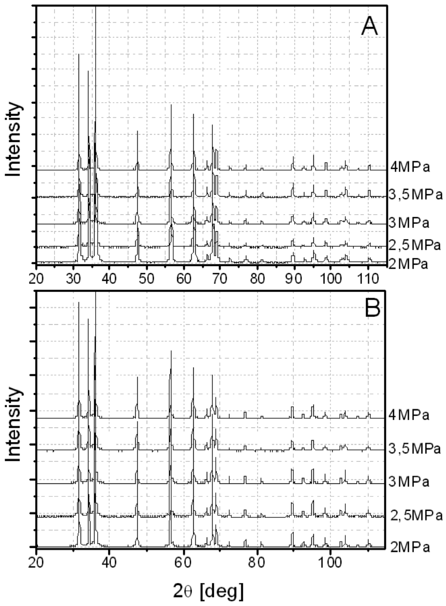

Fig. 2. XRD of ZnO nanopowders with two different solvents: (A) distilled water; (B) ethanol.

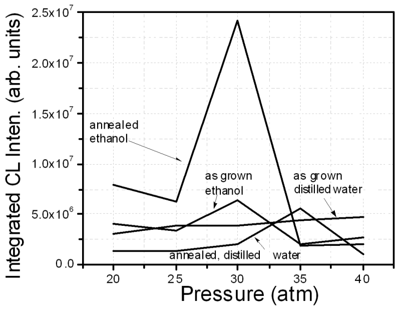

Fig. 3. Integrated CL intensity (visible light) of ZnO nanopowders as function of reaction pressure.

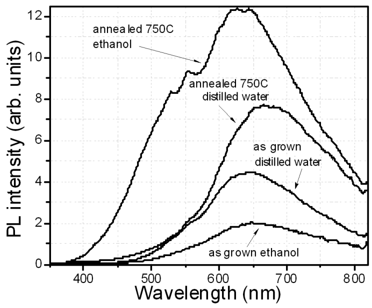

Fig. 4. Photoluminescence of ZnO nanopowders in the visible range.

the reactor. The 30 atm pressure and ethanol as solvent seem to be preferential to get a bright light emission.

The CM SOLAR 2203 spectrofluorometer was used for photoluminescence (PL) investigations. The spectral range was 340 nm to 820 nm and the optical resolution was 5 nm. In the PL spectra (see Fig. 4) we observed similar trend like in the CL spectra. The highest intensity of PL was obtained at reaction pressure of 30 atm.

Figure 4 presents PL spectra for samples obtained at the same condition (pressure in the reactor equal to 30 atm). PL was collected at low excitation density. At such conditions band edge PL is weak and a broad defect-related PL dominates the spectrum. PL intensity of our nanopowders significantly increases upon annealing.

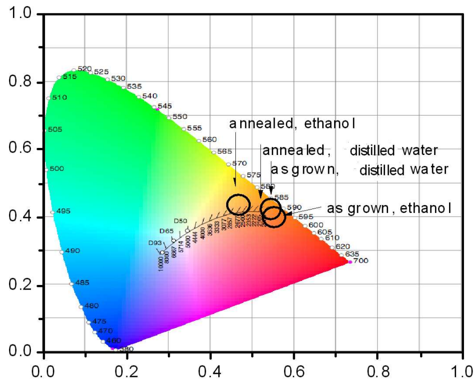

Fig. 5. Chromaticity diagram CIE1961 of ZnO nanopowders in the visible spectral range.

Samples showing a broad PL (covering nearly all visible light spectral region) were selected for chromaticity investigations using CIE1961 diagram (Fig. 5). Chromaticity calculation shows that the samples shine in a yellow-orange color.

This is an advantageous property of our nanopowders making them suitable for application in hybrid light emitting diodes (LEDs). Emission of GaN-based violet-blue LED excites powder emission and mixture of powder and LED emission gives the impression of a white color.

3. Summary

In this paper we analyze optical properties of ZnO nanopowders obtained by a hydrothermal method. After annealing nanopowders show intensive emission covering a wide spectral region of a visible light. Advantageous chromaticity parameters of nanopowders investigated make them suitable for phosphor applications.

Acknowledgments

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