# TIME-RESOLVED LUMINESCENCE IN MICRO AND NANOSTRUCTURED ZnO POWDERS

*Kalinko A.*[1], *Grigorjeva L.*[1], *Millers D.*[2], *Grabis J.*[3], *Lojkowski W.*[4], *Monty C.J.*
[1] *Institute of Solid State Physics, University of Latvia, Riga, Latvia, E-mail: akalin@latnet.lv*
[2] *Institute of Inorganic Chemistry, Riga Technical University, Salaspils, Riga, Latvia*
[3] *Procèdès Matèriauux et Energie Solaire (PROMES), Font-Romeu, France*
[4] *Institute of High Pressure Physics, Polish Academy of Sciences, Warsaw, Poland*

# S ČASOM MIZNÚCA LUMINISCENCIA V MIKRO- A NANOŠTRUKTÚRNYCH ZnO PRÁŠKOCH

*Kalinko A.*[1], *Grigorjeva L.*[1], *Millers D.*[2], *Grabis J.*[3], *Lojkowski W.*[4], *Monty C.J.*
[1] *Ústav fyziky tuhých látok, Univerzita v Litve, Riga,*
[2] *Ústav anorganickej chémie, Technická Univerzita v Rige, Salaspils, Riga, Livtva*
[3] *Pracovné postupy v oblasti materiálov a solárnej energie (PROMES), Font-Romeu, France*
[4] *Ústav fyziky vysokých tlakov, Poľská Akadémia vied, Varšava, Poľsko*

**Abstrakt**

S použitím metód mikrovlnením poháňaného hydrotermálneho procesu, plazmovej syntézy a odparovania-kondenzácie boli v solárnej peci syntetizované 3 druhy ZnO prášku. Veľkosť zrna pripravených práškov bola určená zo snímkov REM a táto sa pohybovala od niekoľkých málo mikrometrov až po 30 nm.

Ďalej boli študované časovo- rozložené luminiscenčné spektrá a kinetika rozpadu luminiscencie pôsobením nanosekundových laserových pulzov (YAG:Nd laser, 266nm, 10ns). S použitím fotónového čítacieho systému bola v širokom intervale časov a rozsahu intenzít meraná kinetika rozpadu luminiscencie. Bolo zistené, že intenzita luminiscencie v oblasti žlto-zeleného spektra aj excitačný pás veľmi silne závisia od techniky syntézy. Proces luminiscenčného rozkladu je v širokom spektrálnom pásme (2.0 – 2.6 eV) rovnaký, je však závislý od technológie prípravy práškov. Kinetika rozkladu bola analyzovaná v log-log súradniciach (log $I$ – log $t$), pričom pre charakterizáciu procesu bol použitý sklon kinetiky rozkladu. Zistilo sa, že kinetika luminiscenčného rozkladu je v log $I$-log $t$ súradniciach pre $t >> \Delta t$ priamka, pričom $\Delta t$ je trvanie excitačného pásu. Sklon čiary závisí od hodnoty špecifického povrchu ($S_{BET}$).

**Abstract**

ZnO powders were synthesized using microwave driven hydrothermal process, plasma synthesis and evaporation-condensation in solar furnace. The grain size of prepared powders was estimated using SEM images and was from few micrometers down to 30 nm.

Time-resolved luminescence spectra and luminescence decay kinetics under nanosecond laser pulses (YAG:Nd laser, 266nm, 10ns) were studied. The decay kinetics was measured in wide time and intensity range using photon counting system. It was shown that the luminescence intensity in yellow-green spectral region as well as the excitation band strongly depends on synthesis technique. Luminescence decay process is the same within wide spectral region (2.0 – 2.6 eV), but it depends on powder preparation technology. Decay kinetics were analyzed in double logarithmic coordinates (log $I$ – log $t$) and decay kinetic slope was used for

process characterization. It was determined that the luminescence decay kinetic in log $I$-log $t$ coordinates is a straight line at $t >> \Delta t$, where $\Delta t$ is the excitation pulse duration. The line slope depends on specific surface area ($S_{BET}$).

**Key words**: ZnO, luminescence spectra, luminescence decay kinetic, nanopowders.

## 1. Introduction

Zinc oxide (ZnO) is a semiconductor with wurtzite structure and has a direct band $E_g$= 3.37 eV. Though the ZnO:Zn is well known luminescent material for displays, the luminescence mechanism and defects in ZnO are not clear up to now. The interest to nanostructured ZnO is stimulated by the potential application of this material to blue-light emission devices. The luminescence of ZnO crystal, thin films and nanopowders has been widely studied [1-4]. Two groups of luminescence bands were known: (i) in the region 1.8 eV – 2.4 eV due to defects; and (ii) in the region 3.1-3.3 eV due to excitons [5]. The exciton luminescence lifetime is below 1 ns in ZnO [6]. The mechanisms of the defect luminescence are under discussion up to now. Only a few papers are devoted to luminescence decay process study [3,6,7] and different decay times (from ns up to ms) for defect bands are reported. Millers *et al.* showed that the luminescence decay is not exponential and suggested a diffusion controlled recombination mechanism [3]. The reason for different results might be the different experiment details (e.g. excitation pulse duration) and/or in different types of nanostructures used for experiments. Therefore, in this work the luminescence spectra and decay of ZnO nanocrystals produced by different methods has been studied.

## 2. Experimental

The ZnO powders were prepared by different methods: hydrothermal synthesis (HY), plazma synthesis (PL) and vaporization-condensation in solar reactor from HY synthesized powder (HY-VC). Time-resolved luminescence characteristics of the ZnO single crystal have been measured for comparison in some cases. Scanning electron microscope (SEM) images were studied for sample microstructure analysis. Sample A090 consists of hexagonal microcrystals, while samples A055 and J003 contain spherical nanograins. Samples G2 and R6019 looks like very thin (10-50 nm) and some micrometers long whiskers. The specific surface area $S_{BET}$ was determined by nitrogen absorption and the average grain size $d$ have been calculated.

Table 1 ZnO sample characteristics

| Sample | Synthesis method | $S_{BET}$ ($m^2/g$) | Density ρ ($g/cm^3$) | Grain size $d$ (nm) |
|---|---|---|---|---|
| A090 | HY(Zn acetate) | 0.66 | 5.1519 | 2000-5000 |
| A055 | HY (Zn oxalate) | 40.86 | 5.489 | ~50 |
| J003 | HY ($ZnCl_2$) | 4.929 | 5.5302 | ~80 |
| G2 | PL | 25 | - | ~50 |
| R6019 | HY-VC | 37.62 | 4.777 | 33 |

The pulsed YAG:Nd laser operating at 266 nm with pulse duration 10 ns ($\Delta t$) was used for luminescence excitation. The luminescence decay was measured by photon counting system, time resolution of this system was from 2 ns up to 160 ns. All experiments have been performed at room temperature.

## 3. Results and discussion

The luminescence spectra in defect band spectral region depend on the sample preparation method and change from yellow (HY in Fig.1a) to yellow-green (PL) and green (HY-VC in Fig.2a). By the comparison of luminescence decay kinetics at different points of spectra it was shown that the decay process is the same within wide spectral region (see e.g. Fig. 2.b). However, the luminescence decay kinetic depends on powder preparation technology. The decay kinetics was measured in wide time and intensity range. The decay process is non-exponential and more then three exponents will be used for decay process analysis. It is suggested that the process obey to Becquerel law: recombination luminescence involving different defect states take place ($\log I \sim -p \log t$, were $p$ is constant). Hence in the present investigation all decay kinetics were analyzed in double logarithmic coordinates ($\log I$ - $\log t$). In Figs.1b. and 2b the decay kinetics for two samples are shown. The slope of luminescence decay kinetic ($\log I$ / $\log t$) was used for decay process rate characterization.

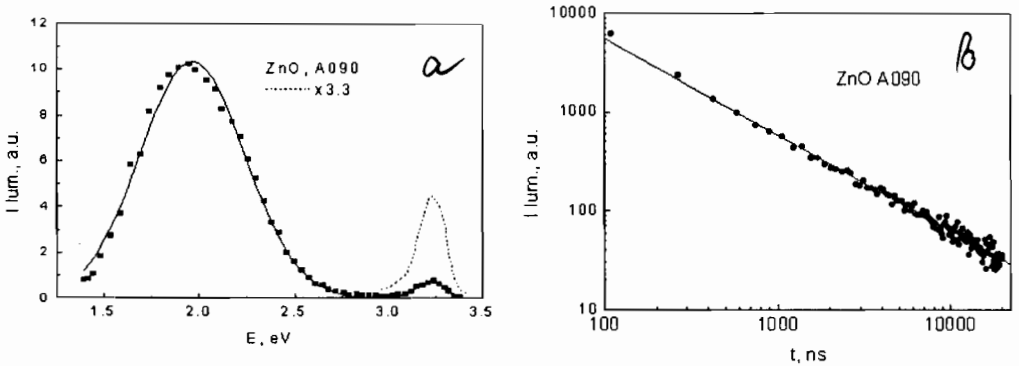


Fig.1 Luminescence spectra (a) and luminescence decay kinetic (b) of HY synthesis ZnO nanopowder

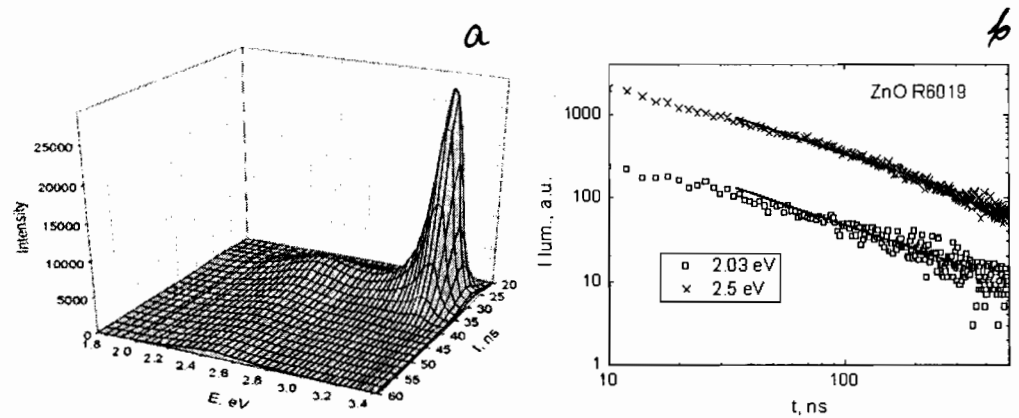


Fig.2 Luminescence spectra (a) and luminescence decay kinetic (b) of HY-VC ZnO nanopowder

The dependence of the luminescence kinetic slope on $S_{BET}$ is shown in Fig.3. The luminescence kinetic in double logarithmic coordinates at $t>>\Delta t$ for HY synthesized ZnO is a strain line and the slope of this line depends on specific BET surface area (Fig.3).

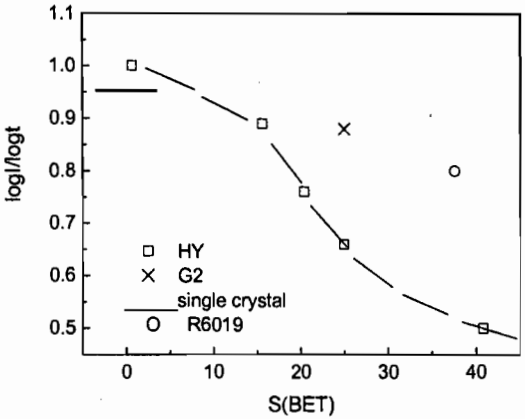


Fig.3 The luminescence decay process dependence of HY ZnO micro and nanopowders on the specific surface area $S_{BET}$. The result obtained for whiskers and single crystals are shown by symbols

## 4. Conclusions

The photoluminescence spectra and luminescence decay kinetics of hydrothermally synthesized (HY), plazma synthesized (PL) and vaporization-condensation synthesized (HY-VC) ZnO powders has been studied. Broad luminescence band peaking at ~2.0 eV was detected in HY synthesized powders, whereas after vaporization-condensation the peak position was at 2.4 eV. In PL synthesized ZnO powders the both type of luminescence was observed. The luminescence decay kinetic for 2.0 eV and 2.4 eV coincides for each sample, but are different for samples obtained by different techniques. It was found that the luminescence decay kinetic in log*I*-log*t* coordinates is a straight line and the line slope depends on $S_{BET}$ for HY synthesized ZnO powders. It means that by changing the synthesis condition the rate of luminescence decay will be changed. The HY-VC samples show low defect luminescence intensity level and intensive exciton luminescence.

## Acknowledgments

*The authors are gratefully acknowledged for financial support of this work by SOLFACE European project of the PROMES laboratory, France, Latvian National Program Material Science Nr.1-23/37 and SPUB COST. NETWORK NAMIC.*

## Literature

[1] Vanheusden K, Warren W.L., Seager C.H., Tallant D.R., Voigt J.A.: J. Appl. Phys., vol.36, 1996, pp.7983-7987.
[2] Lim J., Shin K., Kim H.W., Lee Ch.: J. Lumin., vol.109, 2004, pp.181-185.
[3] Millers D., Grigorjeva L., Lojkowski W., Strachowski T.: Radiation Meas., vol.38, 2004, pp. 589-591.
[4] Ozaki K., Gomi M.: Jpn. J. Appl. Phys., vol.41, 2002, pp.5614-5617.
[5] Look D.c., Reynolds D.C., Litton C.W., Jones R.L., Eason D.B., Cantwell G.: Appl. Phys. Lett., vol.81, 1996, pp.1830-1834.
[6] Xiong G., Ucer K.B., Williams R.T.: J. Appl. Physics, vol.97, 2006, pp. 043528-1-4.
[7] Gaspar C., Costa F., Monteiro T.: J. Mater. Sci.: Materials in electronics, vol.12, 2001, pp.269-271.