

Intense photoluminescence of slightly doped ZnO–SiO₂ matrix

M. Bouguerra^{a,*}, M. Samah^a, M.A. Belkhir^a, A. Chergui^e, L. Gerbous^b, G. Nouet^c,
D. Chateigner^d, R. Madelon^c

^a *Département de physique, Laboratoire de physique théorique (LPT), Université de Bejaia 06000, Algeria*

^b *Centre de recherche nucléaire, d'Alger (CRNA), 02 Bd de Frantz, Fanon BP 399, Alger, Algeria*

^c *SIFCOM-ENSICAEN 6, Bld Maréchal Juin, 14050 Caen cedex, France*

^d *CRIS-MAT. ENSICAEN 6 Bld Maréchal Juin, Université de, Caen-Basse Normandie, 14050 Caen cedex, France*

^e *Département de Physique, Université F. Abbas de Sétif, 19000, Algeria*

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Abstract

ZnO nanocrystals are embedded in an amorphous matrix of SiO₂ using the sol-gel method and their optical properties were studied. A strong Blue-violet luminescence was observed. The photoluminescence's maximum, located at 400 nm approximately, depends on the rate of the gelation process and also shows a slight dependence with the wavelength of excitation. The mean size of ZnO particles is about 27 nm leading with a weak quantum confinement. XRD patterns did not reveal the presence of ZnO particles but TEM investigation demonstrates agglomeration of ZnO crystallites in the composite with different sizes and shapes.

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1. Introduction

Optical devices, such as diodes and lasers, stimulated great interest particularly due to their several potential applications in communication's instruments as well in medicine. Multiple technological and fundamental imperatives such as doping processes and wavelength emission constrain the manufacture of these instruments.

At present, it seems that wide gap semiconductor nanocrystals, namely ZnSe, GaN and ZnO, were strongly favourable for visible and ultraviolet emission of spectral range [1–4].

Optical properties of nanocrystals depend strongly on the nature of the host's media [11]. The luminescence of ZnO particles, embedded in different matrices is dominated by the well known green band luminescence [5–10].

A number of articles relate the use of sol-gel method for including nanoparticles and report different optical properties of ZnO particles in amorphous and semi-crystalline SiO₂ matrix [13–16].

In this Letter, monolithic SiO₂ matrix was doped with ZnO particles using the sol-gel method. Optical properties, photoluminescence (PL) and photoluminescence-excitation (PLE) measurements at room temperature (RT), have been studied. The gelation rate process, X-rays diffraction (XRD) patterns and transmission electron microscopy (TEM) analysis were also investigated.

2. Experiment

The method adopted for sample elaboration is the same as that cited in Ref. [12] with some modifications.

Tetraethoxysilane (TEOS), water and ethanol were mixed with the following quantities; 21.4, 2.25 and 13.6 ml, respectively. Then, the solution was catalysed by traces of HCl acid ($\approx 5 \mu\text{l}$). The mixture was stirred for 24 h at ambient temperature (32 °C) to obtain a complete hydrolyse process. Another solution was obtained by mixing 70 ml of acetone, 4.5 ml of deionized water and 0.2 ml of hydroxide ammonium and stirred for several minutes.

The two solutions are shaken and jiggled. Before the end of gelification process, 2 mg of ZnO fine powder (99.95 Prolabo) is added to this final solution and also shaken

* Corresponding author.

E-mail address: bouguerradjitou@yahoo.fr (M. Bouguerra).

for homogenization. This mixture was divided into two solutions. The first one is continuously stirred until the gelification is accomplished. Thus, it forms the sample named S_1 . The second one is left some hours to let the biggest ZnO particles be precipitated. Then, the colourless solution above was used to obtain the second sample S_2 .

The obtained xerogels were stored at 30 °C during eight weeks. The very slow storage is important to avoid the formation of Zn_2SiO_4 and related compounds [16] and, on the other hand, to eliminate the residues of sols in samples.

XRD patterns, PL and PLE spectra were measured to characterize these samples. PL and PLE measurements were performed on a Hitachi 850 Fluorescence spectrometer at room temperature. The excitation wavelength was produced by a xenon lamp equipped with a grating monochromator. The Microscope type is Jeol 2011 'Field emission gun'. Since the samples are flimsy and easily damaged, we have milled them to obtain a powder deposited on a copper grille and covered up by a carbon membrane (Lacey carbon film, 300 mesh).

3. Results and discussion

Fig. 1 presents typical curves of both PL and PLE spectra of ZnO nanoparticles prepared in SiO_2 matrix for both samples, S_1 and S_2 . On PLE spectra, monitored at wavelength of 410 and 400 nm, absorption edges are located at 3.24 and 3.34 eV for S_1 and S_2 , respectively. The first value is slightly below the band gap of ZnO. This red-shift is estimated about 180 meV with good agreement with the value found by Chang et al. [13]. The average particle sizes, using the effective mass approximation, are estimated around 27 and 21 nm for S_1 and S_2 , respectively.

This difference in peak position for these samples is explained by different mean sizes of ZnO nanoparticles

within the samples. It seems that S_1 sample contains the biggest ZnO particles because the elaboration is made by a continuous stirring until end of gelation process. PLE spectra exhibit also four peaks. No significant differences between S_1 and S_2 samples are seen except that S_1 PLE is more intense than S_2 one. Radiative transitions via matrix, impurities and defects levels seem to be the plausible explanation. The two like-bands located in the interval of 300–340 nm are attributed to transition between different ZnO particle sizes [13,17] and references therein.

Room temperature PL spectra monitored at 325 nm, for both samples exhibit an identical shape. A strong band appears at 409 and 392 nm for S_1 and S_2 , respectively. Weak and broadened shoulders belonging approximately at 475 and 525 nm for both samples appear also. The well known green-band [5–9] dominating the luminescence spectrum of ZnO is not visible. It is interpreted by surface passivation of ZnO particles by the surrounding media. The responsible oxygen vacancies (V_O) are filled by the so rich oxygen SiO_2 media. Mahmuni et al. have reported the same spectra on passivated ZnO nanoparticles with tetraoctylammoniumbromide (TOAB) fabricated by electrochemical way. They also reported two other peaks at 420 and 485 nm [19].

Elsewhere, Gil and Kavokin [18] theoretically predicted that coupling between electromagnetic field of the light and exciton in ZnO nanoparticles arises its maximum value for mean size about 30 nm. It is exactly the situation of our samples.

A deep investigation of PL spectra was done by fitting the curves by four Gaussian functions based on Mahmuni et al. [19] works. Table 1 summarizes these results (see Fig. 2).

The first peak, noted 1, is due to phonon replica emissions and/or bound exciton recombinations [20]. The second one, located at 401 and 399 nm for S_1 and S_2 , respectively, is rarely reported in the literature. Wei et al.

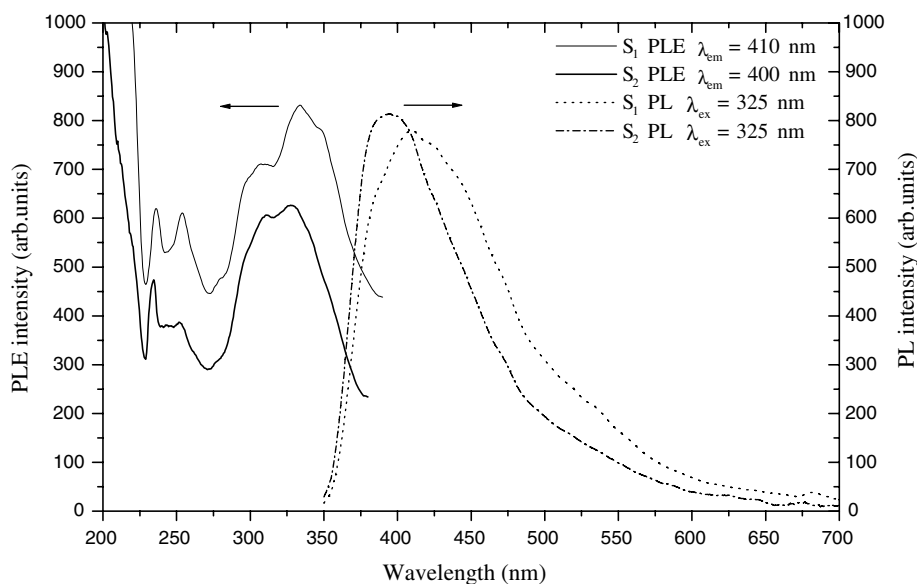


Fig. 1. Photoluminescence (PL) and photoluminescence-excitation (PLE) spectra of ZnO nanoparticles embedded in SiO_2 matrix. Photoluminescence spectra were recorded with excitation at 325 nm and PLE with emission at 410 and 400 nm for S_1 and S_2 , respectively.

Table 1
Fit results by four Gaussians for both samples PL spectra

Sample	Peak 1 (nm)	Peak 2 (nm)	Peak 3 (nm)	Peak 4 (nm)
S ₁	379	401	435	491
S ₂	377	399	434	486

[21] explain this band by radiative transition of electron from shallow donor levels, created by oxygen vacancy, to valence band. We note that this peak was most intense in S₂ sample containing the smallest ZnO particles. Consequently, defect density, proportional to surface-volume ratio, becomes important.

Peak 3 is attributed to emission from trap levels and/or acceptor–donor recombinations. The nature of these trap levels stays controversial. However, most authors agree

to consider oxygen vacancy as responsible [13,22]. The mechanism of this emission is as follows: firstly, a hole is photogenerated and immediately trapped on an oxygen vacancy (V_{O}^{**}). Consequently, a (V_{O}^*) is created above 1 eV of valence band and an electron recombines radiatively with this site. The broadening of this band is due to several factors: size distribution, surrounding environment and participation of trapped electron within and on surface of ZnO crystallites.

Hreniak et al. [23] attributed the fourth peak (4), located at 491 and 486 nm for S₁ and S₂, respectively, to Si–OH radicals.

Opposing to ZnO–SiO₂, the luminescence of free ZnO powder was dominated by a broad green-yellow luminescence (GYL) with maximum located at 560 nm. The

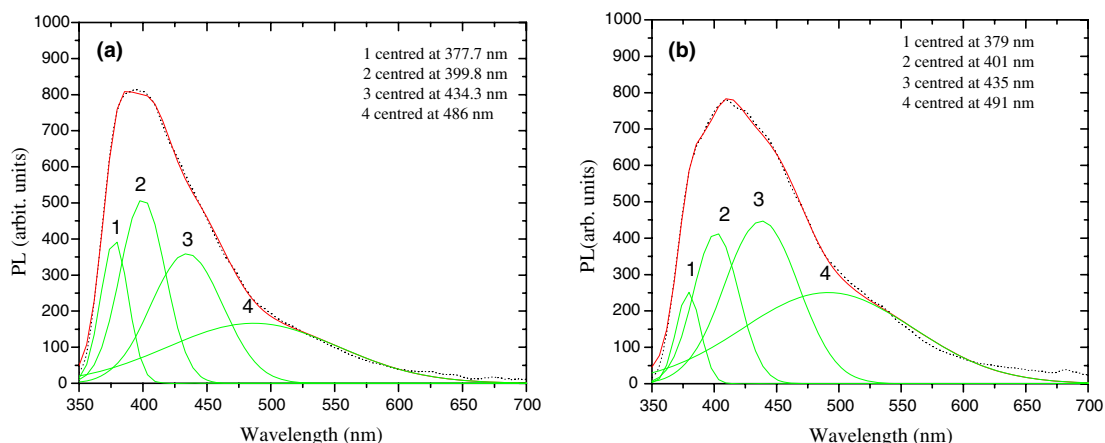


Fig. 2. PL spectra at ambient temperature of S₁ (a) and S₂ (b) samples. The red line is the sum of the fitting by four Gaussian functions (green lines). Black dotted lines are the experimental results. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

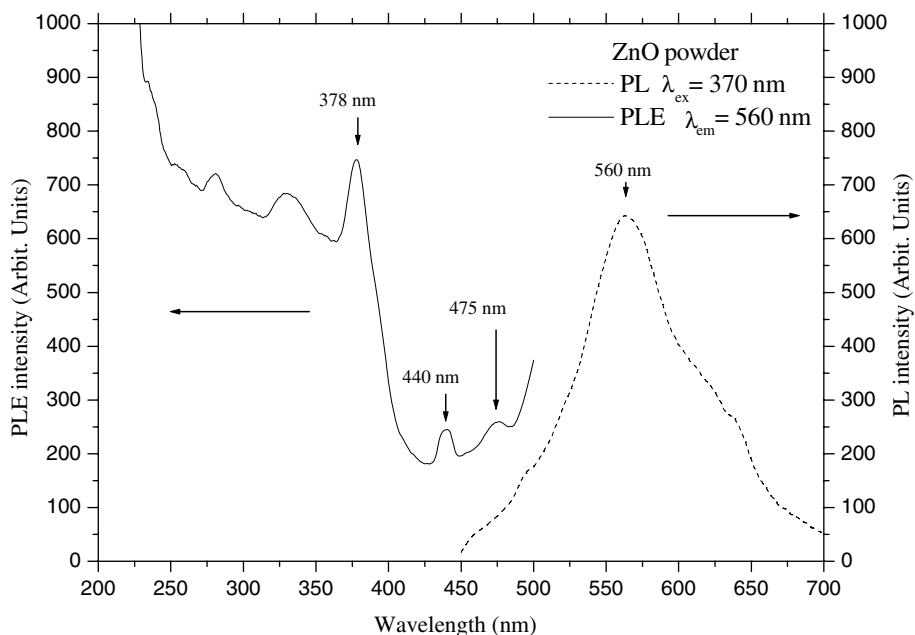


Fig. 3. PL and PLE spectra of ZnO powder at room temperature. The PL spectrum is monitored with excitation at 370 nm.

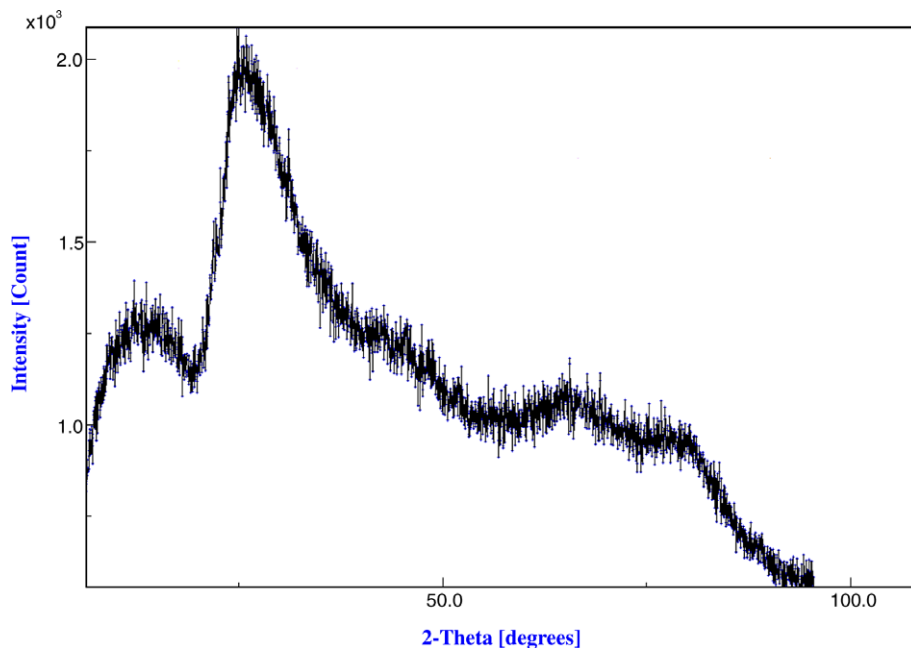


Fig. 4. X-ray diffraction patterns of S_1 (same as S_2). No evident peaks corresponding to ZnO wurtzite phase due to the little amount of ZnO in the sample.

superposition of several GYL-related defects and strong electron–phonon coupling accounted for the GYL broadening. The same luminescence contrast behaviour between ZnO powder and ZnO embedded into synthetic opal was recently reported [25]. The GYL quenching in the case of ZnO crystallites embedded in SiO_2 matrix provides evidence that the GYL-related defects were located in the surface of the crystallites.

The luminescence intensities comparison between the powder and ZnO– SiO_2 composite (sample 1) in which the ZnO amount is several orders of magnitude little than the powder revealed that the powder PL intensity do not reach the PL intensity value of ZnO– SiO_2 composite. This strong luminescence is visible to the naked-eye. Yang et al. [17] observe the same behaviour of ZnO nanocrystals embedded in SiO_2 opal.

The high peak at 378 nm depicted in PLE of the powder corresponds to band gap of ZnO crystallites. This peak is observed as well since near-band-gap absorption coefficient increases considerably; thus high density pair electron–hole was generated near the crystallites surface where they recombined giving rise to GYL. The two weak peaks located at 475 nm (~ 2.61 eV) and 440 nm (2.82 eV) observed on PLE correspond to the ionization of GYL-related defects, presumably the V_{O} . Other defects may be envisaged such as Cu^+ or $V_{\text{Zn}}\text{-Cl}_{\text{O}}$ acceptors giving rise to broad luminescence centred at 500 nm [26,27] (see Fig. 3).

The XRD pattern is represented in Fig. 4. Both samples are represented with the same spectrum and no difference exists between the two samples. Even though the samples exhibit a strong luminescence, the XRD study do not reveal significant intense diffraction lines because of the little amount of ZnO powder used for doping SiO_2 matrix.

Similar results were reported by Lidia et al. [24]. Unclear with XRD, they observed the ZnO particles under TEM investigation.

TEM characterization reveals an agglomeration of ZnO crystallites in the composite (see Fig. 5). This latter fact increases drastically the complexity of crystallites size estimation. The evident statement is that the major crystallites are rod-like with very different diameters and lengths. A small number of crystallites dot-like having small size was also observed. The tripod morphology is so infrequent, but not extraordinary since tetrapod-like and T-like structure have been reported recently [28–30]. A typical high-resolution TEM image of the arm (shown in Fig. 5c) indicates that the arms are single-crystal ZnO structures. The interplanar spacing of around 0.52 nm corresponds to the distance between two (001) planes, revealing (001) as growth direction for the arms. A bad crystallized crystallite-matrix space is noted and consequently the most defects are located near the surface.

4. Conclusion

In summary, ZnO particles with mean size of 27 and 21 nm are embedded in SiO_2 matrix elaborated by sol-gel method. Despite the little amount of ZnO particle within SiO_2 matrix, optical measurements showed a very strong luminescence. This luminescence is interpreted by a strong coupling of electromagnetic field and exciton in ZnO particles. This coupling claims to its maximum for ZnO particles of mean size about 30 nm. PL spectra showed a slight shift towards high energy with increasing excitation energy. The green band does not appear because of the passivation phenomenon by the surrounding medium. XRD patterns did

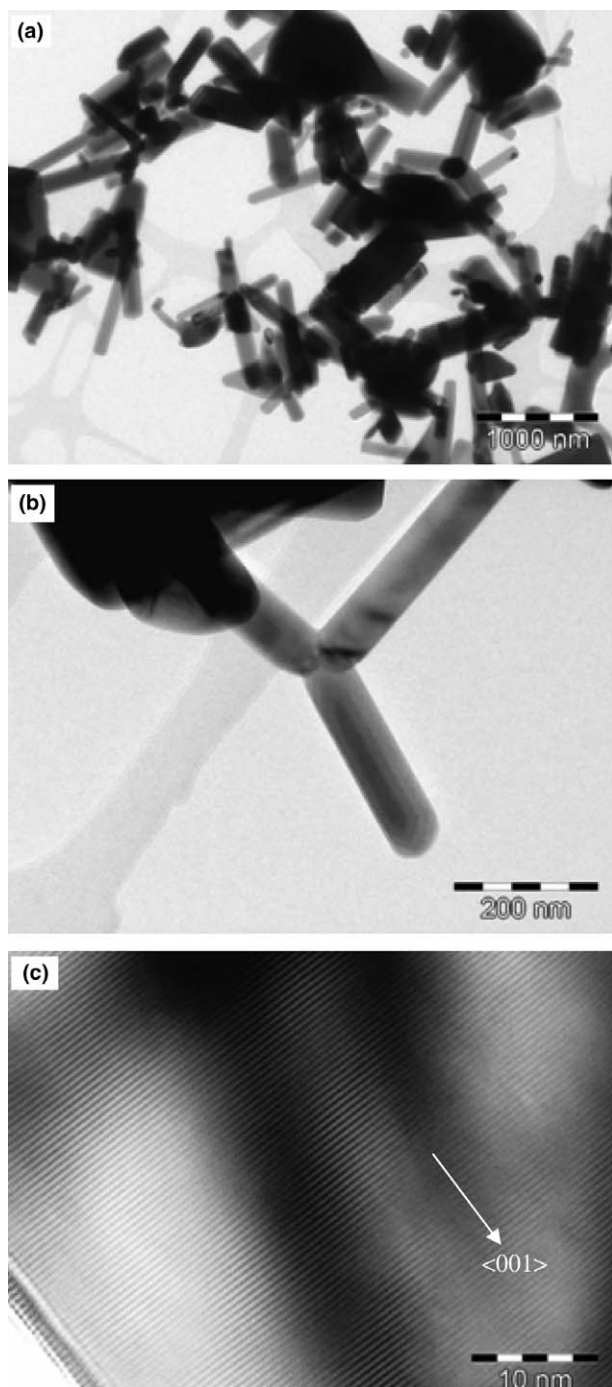


Fig. 5. TEM images with different magnifications scales of S_1 sample. ZnO microparticles with a variety of well defined morphologies, including rod-like, dot-like, further, tripod-like morphologies, have been observed.

not reveal any diffraction lines due to the presence of ZnO particles but TEM investigation demonstrates agglomeration of ZnO crystallites in the composite with different

forms like nano-rods, tri-pods and small dots crystallized in wurtzite structure.

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