

## MODIFIED REFRACTIVE INDEX OF ZINC SULFIDE NANOPARTICLES DOPED GLASSES

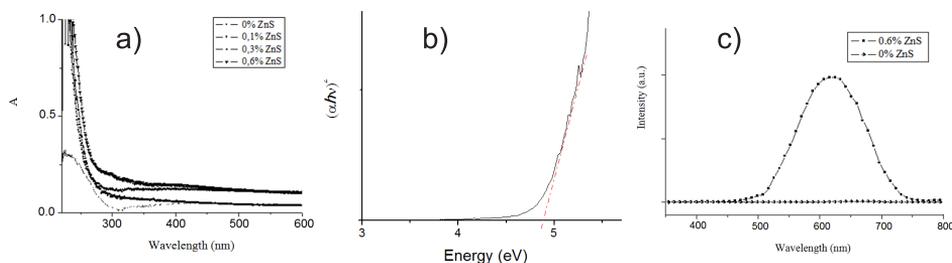
M. MOUSSAOUI,<sup>a</sup> R. SAOUDI,<sup>a\*</sup> S. TONCHEV,<sup>a,b</sup>  
S. PALLE,<sup>c</sup> AND A. V. TISHCHENKO<sup>a</sup>

**ABSTRACT.** ZnS nanoparticles (NPs) embedded in an oxide glass have been achieved in the present work by melting process. The UV-visible absorption and fluorescence properties of these doped and undoped glasses have been evaluated and compared. Studies on absorption spectra showed that the size of the ZnS NPs was near to 2 nm. Doped glass fluorescence characterized by laser confocale microscopy is centered at about 620 nm. We measured also the refractive index of ZnS doped glasses. The maximum refractive index difference between the undoped and ZnS doped glasses was found about 0.1 ( $\lambda = 632.8$  nm).

### 1. Introduction

Nanostructured materials represent a new class of materials. They exhibit novel optical properties which are potentially useful for technological applications and provide many opportunities for studying physics in low dimensions [1, 2]. Since the optoelectronic properties of semiconductor nanoparticles (NPs) differ from those of bulk material, nanostructured materials demonstrate a number of striking effects such as size quantification [3], unusual fluorescence [4], and non-linear optical behavior [5]. Previous studies have addressed the synthesis of semiconductor NPs embedded in a wide variety of matrices (glasses, polymers . . .) [6, 7]. Many research efforts concerned the use of supporting matrix like glasses to stabilize the NPs [8]. Glasses are expected to provide good mechanical and optical properties conferring high kinetic stability on semiconductor NPs. Therefore, the particles are embedded in the supporting media forming nanocomposite materials. Zinc sulfide (ZnS), which is a direct wide band gap ( $E_g = 3.6$  eV at 300 K) semiconductor, has attracted much attention owing to its wide applications including UV light emitting diodes, efficient phosphors in flat-panel displays, sensors and injection lasers, etc [9-10].

In the present paper we give experimental evidence of quantum confinement in ZnS doped oxide glasses. We controlled the NPs size with an adequate choice of ZnS initial concentration as glass dopant. This approach can be used to realize functionalized nanocomposite materials.



**Figure 1.** (a) UV-VIS absorption spectra of the ZnS NPs doped glasses. (b)  $(\alpha h\nu)^2$  vs.  $h\nu$  of the 0.6% ZnS sample. (c) Fluorescence spectra of the undoped and 0.6% ZnS NPs doped glasses.

## 2. Experiment

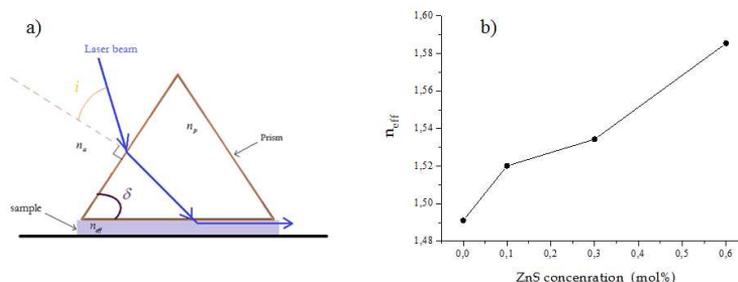
Experimental glasses were prepared by melting a glass host containing 75 SiO<sub>2</sub>, 5 CaCO<sub>3</sub>, 17Na<sub>2</sub>CO<sub>3</sub> mixed with 0 to 0.6 ZnS in mol%. We denote the samples as 0% ZnS, 0.1% ZnS, 0.3% ZnS and 0.6% ZnS. A mixture (10 g) of the raw materials was melted at 1350° for 2h. The resulting glass was cut and polished into a plate 0.5 mm thick.

The samples were characterised by UV-Vis absorption spectroscopy and Laser confocale microscopy. The absorption spectra in the UV and visible ranges were recorded with a lambda 900 Perkin-Elmer spectrophotometer in wavelength range 220–600 nm. Two-photon laser scanning microscopy was performed with a TCS-SP2 confocal microscope from Leica Microsystems attached to an upright microscope (Leica, Heidelberg, Germany). The system was equipped with a Ti:Sapphire MIRA 900 oscillator from coherent pumped with a 5W Verdi Nd:YAG laser at 532 nm. The laser system delivers typically 800 mW, 200 fs pulses with a 76 MHz repetition rate. The wavelength can be tuned in the range 710-890 nm with a maximum power around 800 nm. An electro-optical modulator (EOM) was used to adjust the laser power at the entrance of the confocal system. The microscope was controlled by the Leica Confocal Software. Series of spectra were collected in step of 10 nm from 350 to 800 nm.

Figure 1a shows the UV-Vis spectra of undoped, as well as 0.1% ZnS, 0.3% ZnS, and 0.6% ZnS doped samples. All glass samples present no absorption in the visible range. From the doped samples, we observe an increase in absorption with respect to the undoped glass and an absorption band edge peaking at about 300 nm. This blue shift from 345 nm ( $E_g=3.65$  eV) for bulk ZnS can be understood as a quantum size effect due to confinement of the electron and hole in ZnS nanoparticles volume [11]. With increasing ZnS initial concentration in samples, the absorption becomes more intense and present red shift. This is consistent with an interpretation of an increasing size and number of ZnS NPs with the ZnS initial concentration in doped glasses. This effect is particularly significant for 0.6% ZnS sample.

For direct interband transitions, Tauc's equation (1) is given by [11]:

$$(Ah\nu)^2 = C(h\nu - E_g) \quad (1)$$



**Figure 2.** Effective refractive index measurements of the ZnS NPs doped glasses at  $\lambda=632.8$  nm.

Where  $A$  is the molar absorption coefficient,  $h\nu$  is the photon energy,  $C$  is an arbitrary constant related effective masses of charge carriers associated with valence and conduction bands and  $E_g$  is the band gap of the nanoparticles. From the plot of  $(Ah\nu)^2$  versus  $h\nu$  as presented in fig. 1b, the value of  $E_g$  is obtained by extrapolating the linear fitted regions to  $(Ah\nu)^2$ . The band gap energy  $E_g$  of ZnS NPs was estimated using Tauc's plot which comes out to be 4.9 eV (253 nm) for 0.6% ZnS sample. This value of  $E_g$  is fairly large in comparison with the bulk ZnS (3.65 eV). It corresponds to the ZnS NPs diameters of 2.2 nm according to the tight-binding calculation [12]. Figure 1c presents the fluorescence of 0% ZnS and 0.6% ZnS samples under excitation at 800 nm. 0.6% ZnS NPs doped glass presents stable red emission at about 620 nm, whereas 0% ZnS shows none. This fluorescence is interpreted in literature as due to some surface states in ZnS NPs [13].

The effective refractive index  $n_{eff}$  of samples was determined by measurement of the critical angle using attenuated total reflection at the prism/sample interface as depicted in fig. 2a. All measurements were carried out at room temperature using He-Ne laser ( $\lambda = 632.8$  nm). This allows for refractive index measurements with precision of  $10^{-4}$ . Figure 2b shows the refractive index modification with ZnS initial concentration of samples. The refractive index of undoped sample was 1.4910. It increases with ZnS concentration in the glassy matrix. The maximum  $n_{eff}$  difference between the undoped and the 0.6% ZnS doped glass was found about 0.1. The refractive index of a sample is a function of NPs concentration, temperature, and the wavelength of the incident light. Since the temperature and the wavelength of the incident light do not change, the increase of refractive index samples is certainly due to the increase of the ZnS NPs concentration in glassy matrix as shown by UV-visible measurements. These results demonstrate that one can modify the  $n_{eff}$  in nanocomposite glasses by varying ZnS concentration in the host matrix.

### 3. Conclusions

We succeed in synthesis of ZnS NPs doped glasses with high refractive index difference by using melting process. The maximum refractive index change between the undoped and the 0.6% ZnS doped glass was found about 0.1. This makes such glasses prospective for fabrication of materials with optical adjustable properties.

## References

- [1] A. L. Rogach, *Semiconductor Nanocrystal Quantum Dots: Synthesis, Assembly, Spectroscopy and Applications* (Springer-Verlag/Wien, 2008).
- [2] V. Turco Liveri, *Controlled synthesis of nanoparticles in microheterogeneous systems* (Springer, 2006).
- [3] R. M. Richards, K. J. Klabunde, *Nanoscale materials in chemistry. 2nd ed.* (New York: John Wiley and Sons, 2009).
- [4] G. Schmid, *Nanoparticles from theory to application* (WILEY-VCH Verlag GmbH Co.KGAA, 2004).
- [5] C. Flytsanis, "Quantum electronics: A treatise", Vol. 1a, Academic Press, New York (1975).
- [6] H. Nalwa, *Handbook of nanostructured materials and nanotechnology*. Volume 3-Electrical Properties, (Academic Press 2000).
- [7] N. Taghavinia, H. Y. Lee, H. Makino, and T. Yao, "Evolution of roughness and photo-crystallization effect in ZnS-SiO<sub>2</sub> nanocomposite films", *Nanotechnology*, 16, 944-948 (2005).
- [8] A.A. Onushchenko and G.T. Petrovskii, "Size effects in phase transitions of semiconductor nanoparticles embedded in glass", *J. Non-Cryst. Solids*, 196, p. 73 (1996).
- [9] T. Yamamoto, S. kishimoto, and S. Lida, "Control of valence states for ZnS by triple-codoping method", *Physica B*, 308, 916 (2001).
- [10] G. Cao. *Nanostructures and nanomaterials*. (Imperial College Press, 2004).
- [11] C. Burda, X. Chen, R. Narayanan, M.A. El-Sayed, "Chemistry and Properties of Nanocrystals of Different Shapes", *Chem. Rev.* Vol. 105. p. 1025 (2005).
- [12] J.Tauc and A.Menth. "States in the gap". *Journal of Non-Crystalline Solids*. Vol. 569. p. 8 (1972).
- [13] H. Y. Lu, S. Y. Chu, S. S. Tan, "The characteristics of low-temperature-synthesized ZnS and ZnO nanoparticles", *J. Cryst. Growth*, 269, 385 (2004).

---

<sup>a</sup> Université de Lyon, Université Jean Monnet  
Laboratoire Hubert Curien CNRS UMR5516  
18 Rue du Professeur Benoit Laurus  
42000, Saint-Etienne, France

<sup>b</sup> The Institute of Solid State Physics  
Sofia, Bulgaria

<sup>c</sup> Centre de Microscopie Confocale Multiphotonique, Bt. F  
18 Rue du Professeur Benot Laurus  
42000 Saint-Etienne, France

\* To whom correspondence should be addressed | Email: saoudi@univ-st-etienne.fr

Paper presented at the ELS XIII Conference (Taormina, Italy, 2011), held under the APP patronage; published online 15 September 2011.

© 2011 by the Author(s); licensee *Accademia Peloritana dei Pericolanti*, Messina, Italy. This article is an open access article, licensed under a [Creative Commons Attribution 3.0 Unported License](https://creativecommons.org/licenses/by/3.0/).