Line narrowing effects and enhanced back scattering from ZnO colloids

B. KRISHNAN*
International School of Photonics, Cochin University of Science and Technology, Cochin, Kerala, India; Centre for Materials for Electronics Technology, Athani P. O. Thrissur, Kerala, India
E-mail: bindukrish23@yahoo.co.in

V P N NAMPOORI
International School of Photonics, Cochin University of Science and Technology, Cochin, Kerala, India

Published online: 3 March 2006

The dependence of the fluorescence emission intensity from nano ZnO colloid as a function of incident laser power is investigated. Emission in the near UV region from ZnO particles in diethylene glycol medium is studied using frequency tripled radiations at 355 nm from Nd-YAG laser. The spectrum, which was broad at lower pump intensities, exhibits an increase in the intensity as well as line narrowing above a threshold. The emission occurs in all directions and varies with pumping area. Results indicate the phenomenon of random lasing action due to multiple scattering inside the highly disordered medium. Coherent back scattering experiments confirm multiple scattering and weak localization effects in these samples. These preliminary studies show that colloidal nano ZnO medium is a promising candidate for random lasers.

1. Introduction

Semiconductor nano particles have received much attention from both scientific and technological circles because of their unique quantum nature. There are many ways of looking at a system of semiconductor nano particles. One possibility is viewing the system of nanosized particles as a highly disordered random medium. Many intriguing phenomenon occurs when we study the light propagation through such a random medium. Most popular candidates among them are disordered materials that are optically active which both strongly scatter light as well as amplify it. When the size of the particles is of the order of the optical wavelength and when such a random medium is optically excited, the emission originating from a spontaneous process gets amplified as it undergoes multiple scattering which also provides feed back if they form closed loops. When we probe such a random medium with a wavelength far away from the absorption wavelength, on the other hand, constructive interference of waves scattered along the same path in opposite directions can take place. In lower orders of multiple scattering, this effects results in a phenomenon of enhanced back scattering- also known as weak localization.

There are many candidates for random lasers like submicron powders of semiconductors like GaN and ZnO powders, TiO_2 suspended in dye solutions etc [1–4]. Interest in ZnO has intensified as a result of the discovery of mirrorless lasing action shown by nanosized ZnO powder by Cao *et al*. in 2000 [5], there by getting the status of the first powder laser. Polycrystalline ZnO thin films and ZnO powders suspended in dye solutions are also reported to show lasing action [6, 7].But here we have studied dilute colloids of ZnO to check if the multiple scattering is strong enough to show line narrowing effects. Colloidal ZnO exhibits efficient blue-green emission and is a promising candidate for Field emission displays [8]. We attempted pumping different nano ZnO colloidal samples with different preparation history, at different laser intensities and the emission is studied. A threshold behaviour and line narrowing is observed. Back scattering experiments using a green laser beam confirms multiple scattering and weak localization.

*Author to whom all correspondence should be addressed.

0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-006-7076-8

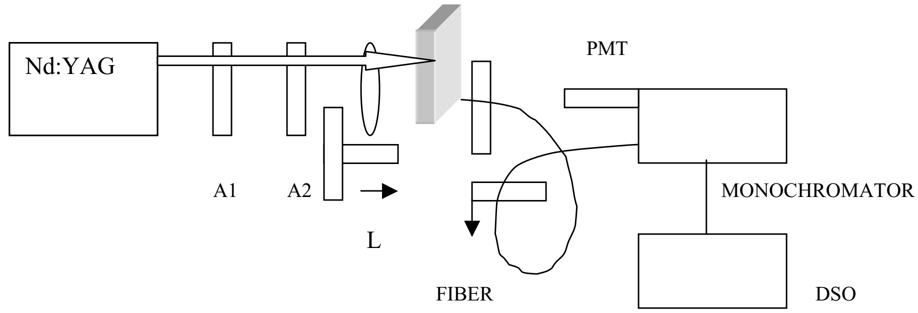

Figure 1 Experimental set up.

2. Experimental

2.1. Sample preparation

The ZnO colloids are synthesized by a polyol precipitation method. Synthesis in the polyol medium has the advantage that the high MP of the polyols offers a wider range of operating temperatures, which permit the precipitation to be conducted at atmospheric pressure. Among the different polyols, diethylene glycol (DEG) is chosen because it is reported to give powders with uniform shape and size distribution [9]. It involves the hydrolysis on Zinc acetate dihydrate in diethylene glycol medium. Different molar concentrations of salt is added to DEG and heated slowly to 160°C. The size of the particles and hence stability of the colloidal suspension depended both on ZnAc concentration and rate of heating. Upto molar conc. of 0.05 M colloids were highly stable for a heating rate of 4°C /minute. Above this concentration, colloids were stable only for 1-2 hours. After that, the particles aggregated and settled, but by ultrasonification, they could be dispersed again for further measurements. Even at lower concentrations, precipitation occurred if the heating rate was increased. A milky white precipitate is formed in a few minutes when the temp is reached 160°C. A short aging time is given to obtain high yield. Clusters composed of small crystallies of ZnO are formed.

2.2. Optical studies

The experimental set up as shown in Fig. 1.The samples taken in glass cuvette are optically pumped by the third harmonics ($\lambda = 355$ nm) of Nd-YAG laser (DCR-11Spectra Physics 10 Hz repetition rate, 15nm pulse width). The pump beam was passed through 2 attenuators A1 and A2 to limit the intensity. It was then focused as a circular spot onto the cuvette by means of a lens L, mounted on a translator stage. The pumping beam diameter was varied either by an aperture or by moving the lens. The beam is incident and collected at an angle of 30° to the cuvette surface. The pump beam intensity was measured by a power meter (Coherent Lab master). The spectrum of emission is collected by a microscope objective onto a UV sensitive fiber fixed on an XYZ precision translation stage, which is then coupled to a PMT (McPherson 0.2 m, Model no.275).the output of the PMT was given to a digital storage oscilloscope DSO. Absorption spectra are measured using the spectrophotometer JascoV-570(UV/Vis/IR).

Coherent back scattering experiments were done in the samples using 545 nm light from a DPSS. Polarization-preserving set up was used to eliminate stray effects [10] and the FWHM of the back scattering cone was measured.

3. Results and discussions

3.1. Powder characterization

Fig. 2 shows the XRD pattern of powder extracted from colloidal ZnO. The size of the clusters depend on the

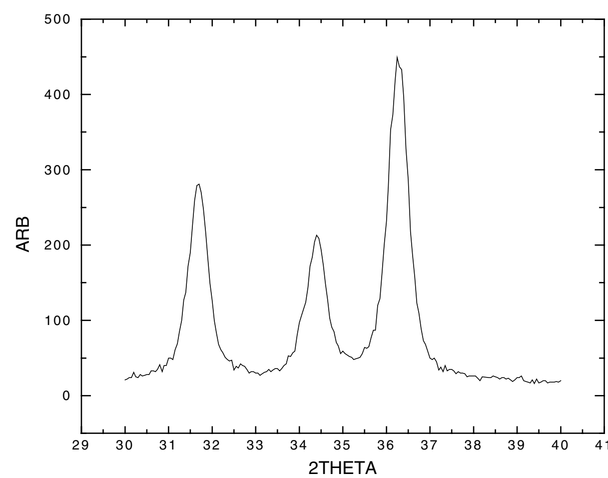

Figure 2 XRD pattern of ZnO powder extracted from 0.09 M sample.

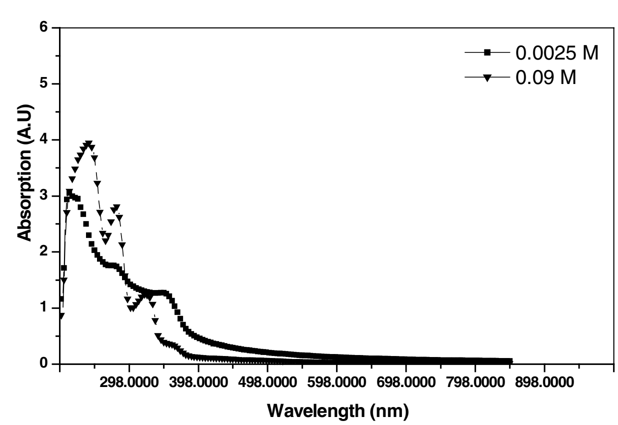

Figure 3 Absorption spectra of ZnO colloid samples.

heating rate as well as the initial concentration. The average crystallite size calculated by Scherrer's equation using the XRD line broadening method varied from 5nm to 10 nm. High surface area from BET measurements (37.79 m^2/g) shows the microporous nature of the clusters.

The absorption spectra of samples 1 and 2 (0.0025 M and 0.09 M precursor concentrations)are as shown in Fig. 3. The pronounced dependence of the absorption band gap on the size can be used to determine the particle size. To get a precise measure of the shift, the first derivative curve of the absorption spectrum is taken and the point of inflection is taken as the absorption edge. Usually size is calculated from the shift of the band edge by theories based on effective mass approximation (EMA) [11] which has the problem of overestimating the size in the small size region. Hence we have used the new empirical formula suggested by Ranjani Viswanatha *et al.* [12]. The cluster sizes are 8 nm and 12 nm for sample 1 and 2 respectively.

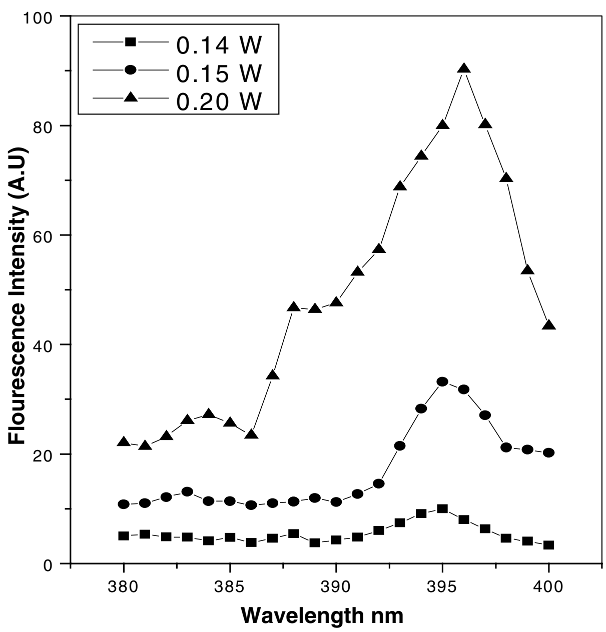

Figure 4 Fluorescence spectra of ZnO colloid sample (0.0025 M) at varying pump intensities.

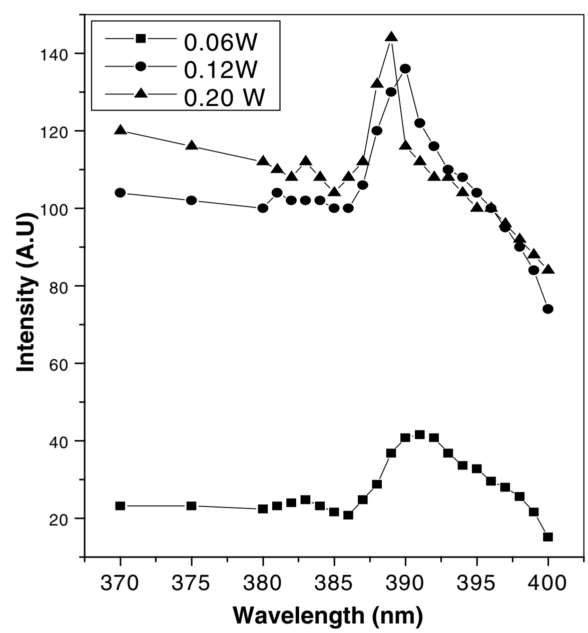

Figure 6 Fluorescence spectra of ZnO colloid (sample2 –0.09 M) at varying pump intensities.

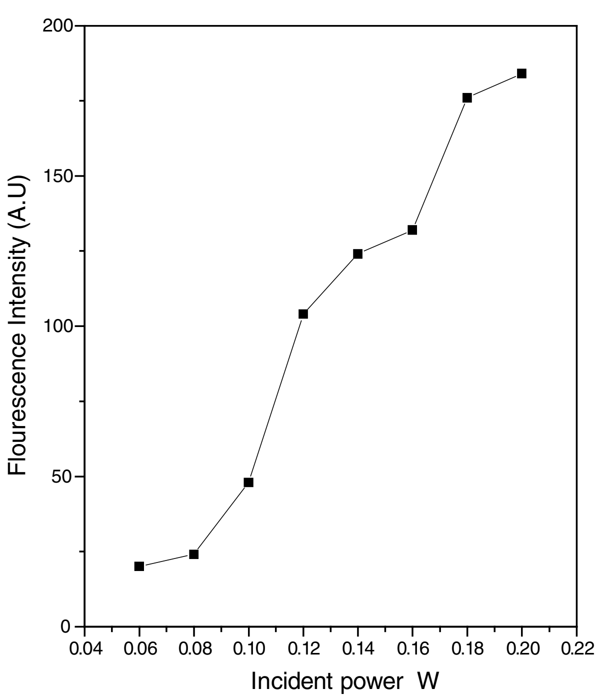

Figure 5 Threshold behaviour shown by the fluorescence spectrum on varying the pump laser power.

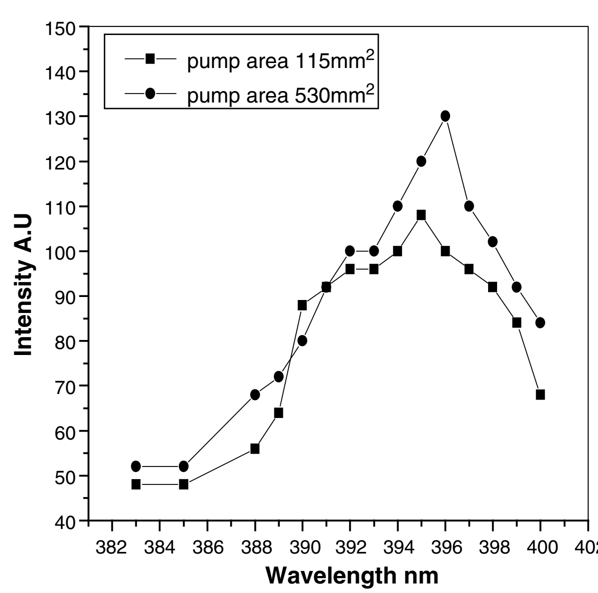

Figure 7 Effect of excitaion area on fluorescence—spectra from sample 2 when pumping area is limited using an aperture.

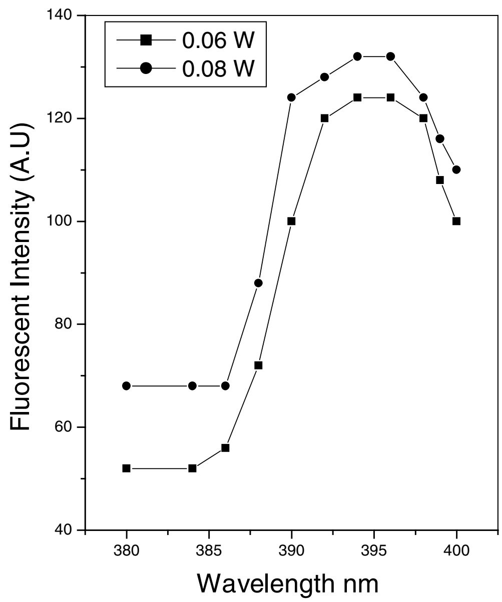

Figure 8 Fluorescence spectra of nano ZnO powder redispersed in methanol.

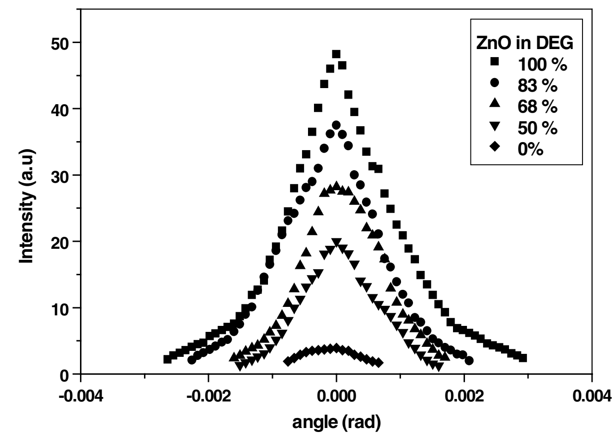

Figure 9 Measured back scattering cone from ZnO colloid.

We can see that the output intensity was enhanced as the refractive index contrast is more (refractive index of ZnO = 2.285 , DEG = 1.42, Methanol = 1.329). But the line narrowing or drastic increase in the output intensity above a threshold are not well pronounced.

3.2. Emission studies

Fig. 4 shows the emission spectrum from sample 1 at different pump energy levels. The laser beam was focused on to an area of 530 mm^2. The emission occurs at all angles. We collected and focused the emitted radiation using a large area lens onto the tip of the UV fiber. The peak is at around 395 nm. We can see that the spectrum is broad for lower pumping levels but above a threshold pump level, there is considerable line narrowing. Fig. 5 shows the plot of emitted intensity Vs excited intensity. Here also the emitted intensity increases drastically above a certain threshold value. Absence of very sharp peaks could be attributed to the limitations in increasing the pump level above a certain level and the limitations in the resolution and detection efficiency in the present experimental set up. However, a clear threshold behavior is exhibited which confirms that the medium is acting like a random lasing medium.

Fig. 6. Shows the emission from the sample 2 which is more concentrated .In this case, the intensity increase and line narrowing above a certain level of pumping intensity is much more evident. We also studied the effect of pumping area on the observed spectrum. The spot size was reduced from 530 to 115 mm^2 using an aperture and the spectrum was taken for sample 2. Fig. 7 shows the comparison of the spectrum at the same pumping intensity with and without aperture. We can see that line narrowing and intensity enhancement depends on area.

We have also observed that the line narrowing depends on the refractive index contrast between the scattering particles and the suspension medium. The ZnO powder extracted from sample 2 was redispersed in methanol and Fig. 8 shows the spectrum at different pumping intensities.

3.3. Back scattering studies

Back Scattering experiments were carried by an experimental set up similar to that ref.10. It gave a Lorentzian profile as expected (Fig. 9), confirming multiple scattering and weak localisation. The FWHM of the profile varied with the concentration of the colloid as expected.

4. Conclusions

Signature of gain is observed in ZnO nano particles in liquid medium. Existence of pronounced threshold in excitation is also exhibited. The observed enhanced back scattering indicated weak localization. All these indicate colloidal ZnO in ditheylene glycol is a promising random lasing medium.

Acknowledgments

One of the authors (B K) acknowledges C-MET for the support and permission to pursue this work.

References

1. N. M. LAWANDY, R. M. BALACHANDRAN, A. S. L. GOMES and E. SAUVAIN, *Nature* **368** (1994) 436.
2. D. S. WIERSMA, P. BARTOLINI, A. LAGENDIJJ and R. RIGHINI,*Nature* **390** (1997) 671.
3. R. M. BALACHANDRAN and N. M. LAWANDY, *Optics Letters*, **20**(1995) 1271.
4. A. MITRA and R. K. THERAJA, *J. Appl. Phy.*, **89** (4) (2001) 2025.
5. H. CAO, J. Y. XU, E. W. SEELIIG and R. P. H. CHANG, *Appl. Phys. Lett.* **76** (21) (2000) 2997.
6. H. CAO, Y. G. ZHAO, H. C. ONG, S. T. HO, J. Y. DAI, J. Y. WU and R. P. H.CHANG, *Appl. Phys. Lett.* **73** (1998) 3656.

7. H. CAO, J. Y. XU, S. H. CHANG and S. T. HO, *Phys. Rev. B*., **61** (2000) 1985.
8. A. VAN DIJKEN, E. A. MEULENKAMP, D. VANMAEKELBERGH and A. MEIJERINK, *Journal of Luminiscence*, **87**(2000) 454.
9. D. JEZEQUEL, J. GUENOT, N. JOUINI and F. FIEVET, *J. Mater. Res*. **10** (1) (1995) 77.
10. R. COREY, M. KISSNER and P. SAULNIER, *J. Am. Phys*. **63** (1995) 561.
11. L. BRUS, *J. Phys. Chem.* **90** (1986) 2555.
12. R. VISWANATHA, S. SAPRA, B. SATPATI, P. V. SATYAM, B. N. DEV and D. D. SHARMA, *J. Mater. Chem.* **14** (2004) 661.

Received 15 November 2004
and accepted 29 June 2005