Spectral and nonlinear optical characteristics of nanocomposites of ZnO–Ag

Litty Irimpan *, V.P.N. Nampoori, P. Radhakrishnan

International School of Photonics, Cochin University of Science and Technology, Cochin, Kerala, India

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ABSTRACT

In this Letter we present the spectral and nonlinear optical properties of ZnO–Ag nanocomposites prepared by colloidal chemical synthesis. Obvious enhancement of ultraviolet (UV) emission of the samples is observed and the strongest UV emission is over three times than that of pure ZnO. These nanocomposites show self-defocusing nonlinearity and good nonlinear absorption behaviour which increases with increasing Ag volume fraction. The observed nonlinear absorption is explained through two photon absorption followed by free carrier absorption. ZnO–Ag is a potential nanocomposite material for the UV light emission and for the development of nonlinear optical devices with a relatively small limiting threshold.

1. Introduction

The linear and nonlinear optical properties of semiconductors are the subject of much current theoretical and experimental interest [1]. Amongst the various nonlinear optical (NLO) materials investigated, wide bandgap semiconductors, especially zinc oxide (ZnO) have attractive nonlinear properties that make them ideal candidates for NLO based devices [2]. The field of nanocomposite materials has been widely recognized as one of the most promising and rapidly emerging research areas [3,4]. Recent investigations have shown that ceramic composites having nano-sized metal particulate dispersions show excellent optical, electrical and mechanical properties [5]. In this study, therefore, the nanocomposite techniques are applied to improve the spectral and optical properties of ZnO [6–9]. Optical nonlinearity of metal nanoparticles in a semiconductor has attracted much attention because of the high polarisability and fast nonlinear response that can be utilised in making them as potential optical devices [3,10]. It is well known that noble metal nanoparticles show an absorption due to surface plasmon resonance (SPR) in the visible region [3]. Out of various metal nanoparticles, silver, copper and gold are extensively studied in colloids, thin films and in different glass matrices for their nonlinear optical properties [11]. In this work Ag is selected to prepare metal-semiconductor nanocomposite with ZnO, because of their interesting optical properties in the visible range which gives rise to wide applications in optoelectronic devices.

2. Experiment

Colloids of ZnO are synthesized by a modified polyol precipitation method [12]. The stable ZnO colloidal spheres are produced by a two-stage reaction process. The method of preparation involves the hydrolysis of zinc acetate dihydrate (ZnAc) in diethylene glycol medium (DEG) and is explained in detail in the Ref. [12]. The silver nanocolloids are prepared by a conventional reduction method [13]. The method of preparation involves the reduction of a Silver nitrate in H_2O with 1% sodium citrate near boiling temperature. The molar concentration of precursor solution is 0.025 M. The concentration of sodium citrate employed for the reduction is kept low to avoid the presence of excess citric acid in the silver suspension. The solution is kept on boiling for one hour to get a monodisperse stable colloid.

The ZnO–Ag nanocomposites are prepared via colloidal chemical synthesis by mixing certain amounts of colloids of Ag to ZnO at 120 °C during its preparation stage and stirred for 1 h at that temperature. The volume fraction of Ag is changed keeping the volume of ZnO constant. The samples having the ZnO–xAg composition of (x=) 0.1%, 0.5%, 1%, 2% and 5% are named as ZnO–0.1Ag, ZnO–0.5Ag, ZnO–1Ag, ZnO–2Ag and ZnO–5Ag, respectively.

In the present investigation, we have employed the single beam z scan technique with nanosecond laser pulses to measure nonlinear optical absorptive and refractive properties of ZnO–Ag nanocomposites. Z scan technique developed by Sheik Bahae and his co-workers is a single beam method for measuring the sign and magnitude of nonlinear refractive index, n_2, and has a sensitivity comparable to interferometric methods [14,15]. A Q-switched Nd:YAG laser (Spectra Physics LAB-1760, 532 nm, 7 ns, 10 Hz) is used as the light source and the experimental set up is explained in detail in Ref. [15].

* Corresponding author. Fax: +91 484 2576714.
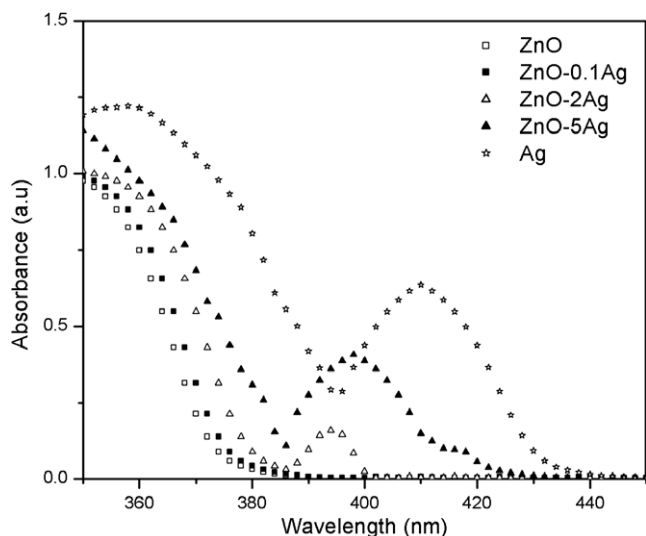 *E-mail address:* littyirimpan@yahoo.co.in (L. Irimpan).

Fig. 1. Absorption spectra of ZnO–Ag nanocomposites.

3. Results and discussion

Optical absorption measurement is an initial step to observe the single colloid and metal-semiconductor nanocomposite behaviour. Fig. 1 gives the room temperature absorption spectra of the ZnO–Ag nanocomposites. The excitonic peak of ZnO colloid is found to be blue shifted with respect to that of bulk ZnO which could be attributed to the confinement effects [16]. For silver nanocolloid, the surface plasmon absorption (SPA) band lies in the 410 nm region. Although the conduction and valence bands of semiconductors are separated by a well-defined band gap, metal nanoclusters have close-lying bands and electrons move quite freely. The free electrons give rise to a surface plasmon absorption band in metal clusters, which depends on both the cluster size and chemical surroundings [3]. The plasmon band of metal particles as explained on the basis of Mie theory involves dipolar oscillations of the free electrons in the conduction band that occupy energy states near the Fermi level [3]. The pronounced dependence of the absorption band gap on the size of semiconductor nano crystals and SPA band on the size of metal nano crystals is used to determine the particle size. An order of magnitude estimate of the particle size is possible from the absorption spectra. The size of ZnO and Ag nanocolloids are in the range of 10–20 nm. The presence of excitonic peak and SPA band itself indicates that the composites are of nanometer size. The size evolution of nanocomposites may also have some relation with optical characteristics in addition to the composition and the study is in progress.

For small volume fraction of Ag, the composite exhibits the characteristics of ZnO with a red shift in the excitonic peak. On the other hand, the ZnO–2Ag nanocomposite exhibits both the semiconductor and metallic behaviour with a blue shift in plasmon band. Optical absorption spectra indicate presence of well-defined ZnO excitonic feature along with the Ag surface plasmon absorption feature at 400 nm [17]. The optical absorption spectra of the clusters show a gradual shift in absorbance towards the visible region, over which an extremely weak surface plasmon resonance is superposed. The surface plasmon absorption band of metal nanoclusters is very sensitive to the surface-adsorbed species and dielectric of the medium. For example, I^- and $C_6H_5S^-$ ions result in damping of the surface plasmon band of colloidal silver particles [18]. Alternately, one can also observe bleaching of the surface plasmon band with electrons deposited from radiolytically produced radicals, which cause a blue shift and narrowing of the plasmon band. A more detailed discussion

on the damping effects caused by surrounding material can be found elsewhere [3]. When the volume fraction of Ag increases beyond 2%, the surface plasmon peak is shifted towards 410 nm. It has been established that the shift of the plasma band of silver observed is a result of accumulation of excess electrons on the ZnO/Ag particles which leads to equalization of the potentials of the conductions zones of the semiconductor and the metallic components of the nanocomposite [19].

Photoluminescence spectra of all samples measured at room temperature are shown in Fig. 2. The intensities of the emission peaks depend on the volume fraction of Ag of the samples. ZnO and ZnO–0.1Ag have only 385 nm emission, but the intensity of the peak of ZnO–0.1Ag is much stronger than that of ZnO. ZnO–1Ag has the strongest UV emission centered at 375 nm. ZnO–2Ag has UV emission centered at 365 nm, which can be fitted to two peaks centered at 348 and 382 nm. ZnO–5Ag and Ag have only a peak at 348 nm. It is obvious that the intensity of 348 nm peak agrees with the content of Ag nanocolloids. Fig. 3 shows the PL intensity as a function of the silver content. It is clear that the intensity of this peak increases with the increasing amount of the Ag and Zn acceptors. When the ZnO colloid is overdoped by
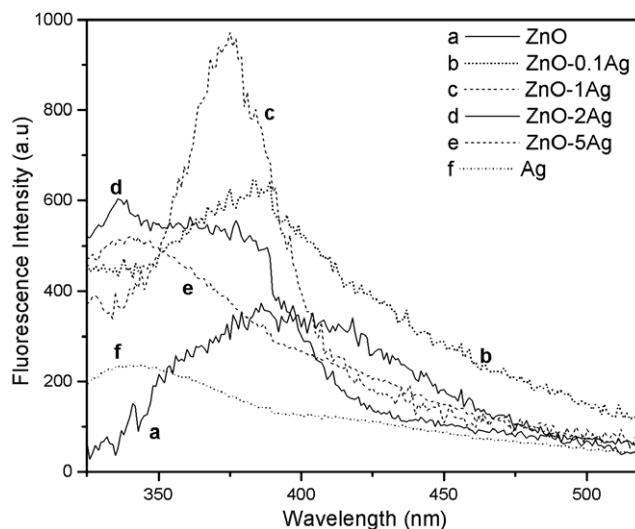

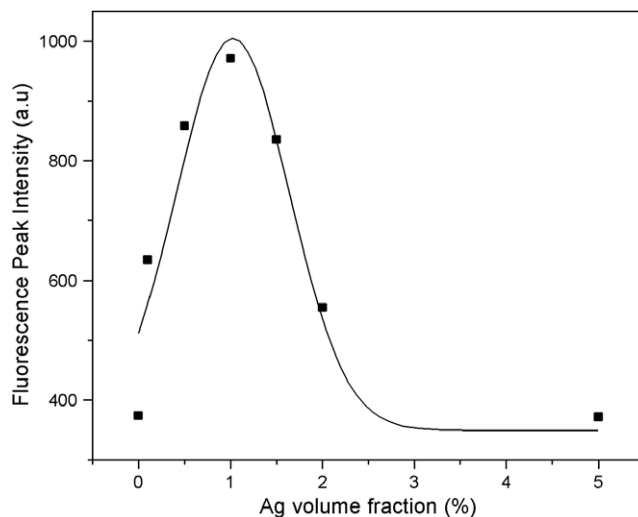**Fig. 2.** Fluorescence spectra of ZnO–Ag nanocomposites.

Fig. 3. The fluorescence intensity of UV peak as a function of the volume fraction of silver in ZnO–Ag nanocomposites.

Ag, the Ag_2O nanoclusters appears and hence there is reduction in PL intensity [20]. The emission of ZnO at 385 nm can be attributed to exciton transition. An undoped ZnO colloid has insufficient holes and so restricted exciton concentration. After Ag doping, Ag acceptors bring more holes to make the concentration of the excitons increase, so that the UV emission is enhanced accordingly as shown in Fig. 2. Nanostructural semiconductor materials generally have more holes accumulated on its surface or in the interface than common semiconductor material [21]. Therefore, there are many holes existing in the interface between Ag nanoclusters and ZnO grains. The electrons in ZnO arrive at the interface easily because of their short mean free paths and the Coulomb forces. Based on quantum confinement effects, plenty of excitons can be formed. Then the UV emission due to exciton transition is enhanced.

The optical absorption spectroscopy and photoluminescence studies reveal the reaction mechanism at the junction. A twofold enhancement of steady state luminescence of rhodamine 6 G has been observed when it is doped with silver [22]. The presence of silver aggregates causes substantial depolarization of the luminescence and the electromagnetic interaction between Ag surface plasmons and dye molecules can result, under certain conditions, in an enhanced fluorescence quantum efficiency and photostability of the dye. The strongest UV emission of a certain ZnO–Ag film is reported to be over ten times stronger than that of a pure ZnO film and the enhancement of UV emission is caused by excitons formed at the interface between Ag nanoclusters and ZnO grains [20].

Fig. 4 shows the nonlinear absorption of ZnO–Ag nanocomposites at a typical fluence of 300 MW/cm². The open aperture curve exhibits a normalized transmittance valley, indicating the presence of reverse saturable absorption in the colloids. The obtained nonlinearity is found to be of the third-order, as it fits to a two photon absorption process. The corresponding net transmission is given by [14]

$$T(z) = \frac{C}{q_0 \sqrt{\pi}} \int_{-\infty}^{\infty} \ln(1 + q_0 e^{-t^2}) \, dt \qquad \text{where } q_0(z, r, t) = \beta I_0(t) L_{\text{eff}}$$

(1)

Here, $L_{\text{eff}} = 1 - e^{-\alpha l}/\alpha$ is the effective thickness with linear absorption coefficient α, nonlinear absorption coefficient β and I_0 is the irradiance at focus. The solid curves in Fig. 4 are the theoretical fit to the experimental data. The obtained values of nonlinear absorption coefficient β at an intensity of 300 MW/cm² are shown in Table 1.

Interestingly, ZnO and Ag colloids show a minimum nonlinearity, while the ZnO–Ag nanocomposites clearly exhibit a larger in-
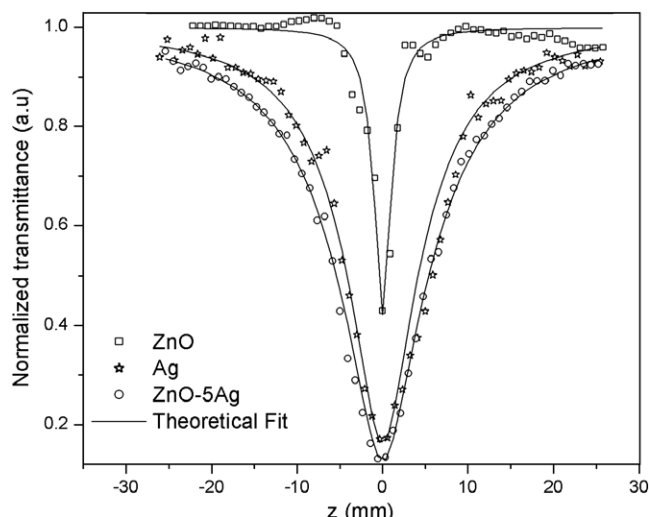

Fig. 4. Open aperture z scan traces of ZnO–Ag nanocomposites at an intensity of 300 MW/cm² for an irradiation wavelength of 532 nm.

Table 1
Measured values of nonlinear absorption coefficient and refractive index of ZnO–Ag nanocomposites at an intensity of 300 MW/cm² for an irradiation wavelength of 532 nm

ZnO–Ag nanocomposites	β (cm/GW)	n_2 (10^{-17} m²/W)
ZnO	20.7	1.5
Ag	121	2.9
ZnO–0.1Ag	138.2	4.4
ZnO–0.5Ag	155.5	5.9
ZnO–1Ag	172.8	7.3
ZnO–2Ag	190.1	11
ZnO–5Ag	207.4	12.3

duced absorption behavior. The calculated nonlinear coefficients given in Table 1 show fairly high values of nonlinearity. The nonlinear absorption coefficient increases substantially in the nanocomposites, as compared to pure ZnO and Ag colloids. It is reported that the nonlinear absorption coefficient increases in the bimetallic and core-shell nanocomposites, as compared to pure metals [23].

Different processes, like two photon absorption, free carrier absorption, transient absorption, interband absorption, photoejection of electrons and nonlinear scattering are reported to be operative in nanoclusters. In general, induced absorption can occur due to a variety of processes. The theory of two photon absorption process fitted well with the experimental curve infers that TPA is the basic mechanism. There is the possibility of higher order nonlinear processes such as free carrier absorption (FCA) contributing to induced absorption. The free carrier lifetime of ZnO is reported to be 2.8 ns [24]. Hence the 7 ns pulses used in the present study can excite the accumulated free carriers generated by TPA by the rising edge of the pulse. Silver nanoparticles are well known materials for nonlinear optical applications because of their subpicosecond time response of third-order optical nonlinearity. Transient absorption and nonlinear absorptive mechanisms are reported to lead to optical limiting in the case of Ag nanoparticles [25].

The surface plasmon band is sensitive to laser excitation. The plasmon band of metal particles as explained on the basis of Mie theory involves dipolar oscillations of the free electrons in the conduction band that occupy energy states near the Fermi level [3]. Once these electrons are excited by a laser pulse, they do not oscillate at the same frequency as that of the unexcited electrons, thus causing the plasmon absorption band to bleach [26]. In our case, the excitation energy (532 nm or 2.3 eV) is lower than the Ag SPR (410 nm or 3.02 eV) and as such the plasmon absorption is not possible. No plasmon bleach effects are seen when the samples are excited with nanosecond laser pulses at 532 nm. Instead, a reduced transmission behavior is observed, which fits to a two photon absorption mechanism. A laser pulse can cause an intraband or interband absorption in the metal nanoparticle system, depending on the excitation wavelength and incident intensity [27]. In our case, the excitation energy (532 nm or 2.3 eV) is lower than the interband threshold from d level to p levlel (E_{dp} = 2.5 eV), and hence interband absorption is not possible although strong optical limiting properties because of interband absorption accompanied by the absorption of free carriers generated in the conduction band are reported in different nanoparticle systems [28]. We propose that this nonlinearity is caused by two photon absorption followed by free carrier absorption occurring in the nanocomposites.

Fig. 5 gives the closed aperture z scan traces of ZnO–Ag nanocomposites at a fluence of 300 MW/cm². It is observed that the closed aperture z scan satisfies the condition $\Delta z \sim 1.7 z_0$, thus confirming the presence of pure electronic third-order nonlinearity [14]. The value of the difference between the normalised peak and valley transmittance, ΔT_{p-v} can be obtained by the best theoretical fit from the results of divided z scan curve. The nonlinear
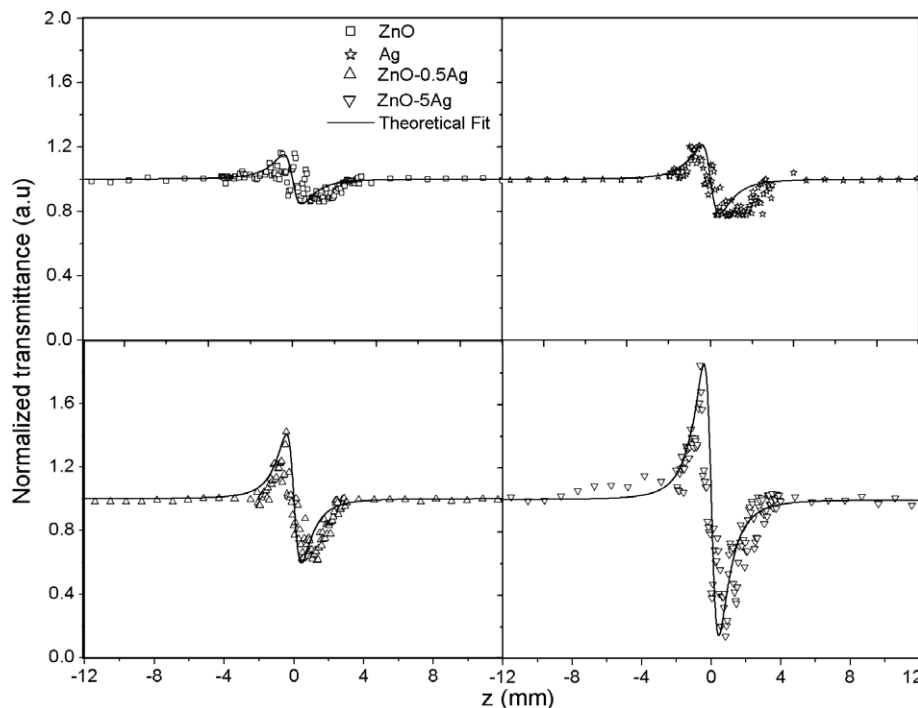
Fig. 5. Closed aperture z scan traces of ZnO–Ag nanocomposites at an intensity of 300 MW/cm^2 for an irradiation wavelength of 532 nm.

refractive index n$_2$ is calculated from ΔT_{p-v} in closed aperture z scan using Eq. (2) and is tabulated in Table 1

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\Phi_0| \qquad \text{where } |\Delta\Phi_0| = \frac{2\pi}{\lambda}n_2 I_0 L_{\text{eff}} \qquad (2)$$

The peak–valley trace in a closed aperture Z-scan shows that these samples have self-defocusing (negative, n$_2$ < 0) nonlinearity, though earlier reports with picosecond pulsed lasers have shown positive nonlinearity for individual Ag nanoclusters [29]. Though laser-induced permanent sign reversal of the nonlinear refractive index is reported in Ag nanoclusters in soda-lime glass, we have not observed any such permanent effect either in the intensity ranges (150–400 MW/cm^2) studied using the second harmonics of a Q-switched Nd:YAG laser or within the wavelength ranges 450–650 nm studied using a tunable laser (Quanta Ray MOPO, 5 ns, 10 Hz) [30]. The nanocomposites exhibit reverse saturable absorption at all wavelengths and good nonlinear absorption, which increases with increasing input intensity. The nonlinear refractive index increases substantially in the nanocomposites, as compared to pure ZnO and Ag colloids. The dramatically enhanced nonlinear refractive response is due to the enhanced electromagnetic field existing in the interface between Ag nanoclusters and ZnO grains [31]. Since n$_2$ increases with absorption, thermal nonlinearity is also taken into account. It is reported that if the thermal contributions are to dominate, then there will be increase in n$_2$ with increase of absorption [32]. The figure of merit for the third-order nonlinearity measured using a two-beam degenerate four-wave mixing configuration by Uchida et al. shows an increase with the particle size of Cu as well as Ag [11]. We therefore attribute the steady increase in the n$_2$ values to the increase of third-order susceptibility as a function of particle size from ZnO–0.1Ag to ZnO–5Ag.

The significant optical nonlinearities of the pure Ag colloid at 532 nm are reported to have the nonlinear refractive index of the order of 10^{-16}–10^{-17} m^2/W. The nonlinear coefficients of Ag films are about one order of magnitude larger than that of Ag colloids [33]. It is worth noting that certain representative third-order nonlinear optical materials, such as CuO chain compounds, Ag$_2$S/CdS

nanocomposites, organic coated quantum dots, metal clusters etc., yielded values of order of 10^{-9}–10^{-14} m/W for nonlinear absorption coefficient at a wavelength of 532 nm [34,35]. These values are comparable to the value of β obtained for nanocomposites in the present investigation. Thus, the nonlinear absorption coefficient and nonlinear refractive index measured by the z scan technique reveals that the ZnO–Ag nanocomposites investigated in the present study have good nonlinear optical response and could be chosen as ideal candidates with potential applications in nonlinear optics.

To examine the viability of ZnO–Ag nanocomposites as optical limiters, the nonlinear transmission of the colloid is studied as a function of input fluence. The optical limiting property occurs mostly due to absorptive nonlinearity which corresponds to the imaginary part of third-order susceptibility [36]. From the value
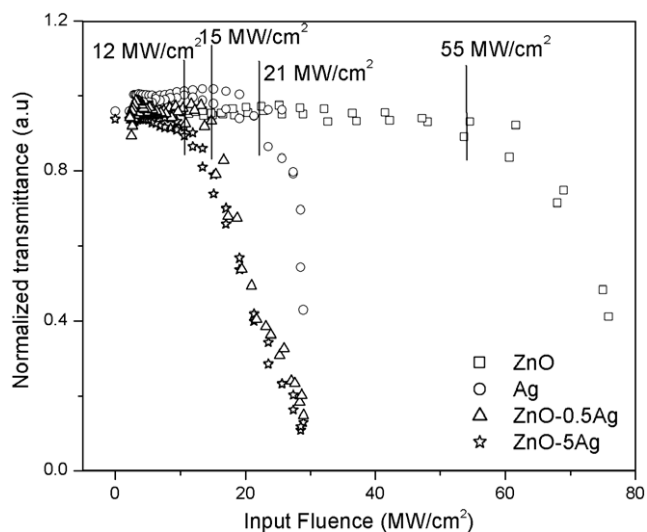

Fig. 6. Optical limiting response of ZnO-Ag nanocomposites generated from the open aperture z scan traces.

of fluence at focus, the fluence values at other positions could be calculated using the standard equations for Gaussian beam waist. Such plots represent a better comparison of the nonlinear absorption or transmission in these samples and are generated from z scan traces. Fig. 6 illustrates the influence of volume fraction of silver in ZnO–Ag nanocomposites on the optical limiting response.

The fluence value corresponding to the onset of optical limiting (optical limiting threshold) is found to be high in the case of ZnO colloids (55 MW/cm^2) in comparison to the Ag colloids (21 MW/cm^2). These values are comparable to the reported optical limiting threshold for CdS and ZnO nano colloids [37,15]. ZnO–Ag nanocomposites are found to be good optical limiters compared to ZnO and Ag and the optical limiting threshold of ZnO–5Ag nanocomposites is observed to be 12 MW/cm^2. The arrow in the figure indicates the approximate fluence at which the normalized transmission begins to deviate from linearity. Nanocomposites have a significant effect on the limiting performance and increasing the volume fraction of Ag reduces the limiting threshold and enhances the optical limiting performance.

4. Conclusion

The spectral and nonlinear optical properties of ZnO–Ag nanocomposites prepared through a colloidal chemical synthesis are investigated. Very strong UV emissions at room temperature are observed from ZnO–Ag nanocomposites. Compared with regular ZnO colloid, ZnO–Ag nanocomposite is advantageous due to its stronger UV emission. The strongest UV emission is observed to be over three times stronger than that of a pure ZnO. The enhancement of UV emission is caused by excitons formed at the interface between Ag and ZnO. These nanocomposites show self-defocusing nonlinearity and good nonlinear absorption behaviour. The nonlinear refractive index and the nonlinear absorption increases with increasing Ag volume fraction. The observed nonlinear absorption is explained through two photon absorption followed by free carrier absorption. These materials can be used as optical limiters and ZnO–Ag is a potential nanocomposite material for the UV light emission and for the development of nonlinear optical devices with a relatively small limiting threshold.

Acknowledgment

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