

# Nonlinear optical and optical limiting properties of new structures of organic nonlinear optical materials for photonic applications

A. Jawad Almosawe and H. L. Saadon\*

Department of Physics, College of Science, University of Basrah, Iraq

\*Corresponding author: haithamsaadon@yahoo.com

Received October 26, 2012; accepted November 19, 2012; posted online March 20, 2013

The nonlinear optical (NLO) and optical limiting (OL) properties of three new structures of organic NLO guest–host Poly(N-vinylcarbazole)/disperse orange 3 (PVK/DO3), PVK/disperse orange 13 (PVK/DO13), and PVK/disperse orange 25 (PVK/DO25) as a solution at different concentrations and as a thin-film sample are studied using continuous wave  $z$ -scan system at 532 nm. The open-aperture  $z$ -scan data of the NLO materials in the solution and thin-film samples displayed two-photon and saturable absorptions, respectively. The PVK/DO13 exhibits the largest and best values of the nonlinearities, such as  $n_2$ ,  $\beta$ ,  $\chi^{(3)}$ , compared with those of PVK/DO3 and PVK/DO25. This nonlinearity increases as the concentration increases. The results indicate that these NLO materials are good candidates for optical switching and OL devices.

OCIS codes: 190.0190, 190.4710, 160.5470, 160.4890, 130.4815.

doi: 10.3788/COL201311.041902.

Organic nonlinear optical (NLO) materials have been exploited as bases for photonic devices. Recently, a growing interest has come up on the third-order nonlinearity of azo-dye-doped polymer materials because of their large optical nonlinearity, broadband spectral response, and fast response time, which are interesting features in the optical switching, optical limiting (OL), and photonic applications<sup>[1–3]</sup>.

Concentration dependence has been known to play a very important role in the NLO and OL investigations. Several groups have studied the effect of concentration on the NLO and OL behavior of organic dye polymer<sup>[4–9]</sup>. Thus, the pursuit for new materials or structures suitable for constructing high-performance all-optical switching and OL has opened up new avenues in material research.

In this letter, we report the experimental studies on the NLO and OL properties of new structures of disperse-dye polymer in a solution with different concentrations and in a thin-film sample using a modified  $z$ -scan system at 532 nm. Disperse orange 3 (DO3), disperse orange 13 (DO13), and disperse orange 25 (DO25) were chosen as NLO active chromophores (guests), whose broadband spectral response was doped with Poly(N-vinylcarbazole) (PVK). Finally, the results are discussed and compared with one another.

The nonlinear refractive index  $n_2$ , nonlinear absorption  $\beta$ , and OL of NLO polymers were investigated by a modified  $z$ -scan system. The system is shown in Fig. 1. A laser beam that propagated through the NLO polymer experienced both amplitude (intensity) and phase variations. The beam was focused by a small spot using a lens with a 5-cm focal length, and the sample was mounted on a translation stage and moved along the  $z$ -axis using a computer-controlled stepper motor. The laser beam waist  $\omega_0$  at the focus was measured as 16  $\mu\text{m}$ , and the Rayleigh length  $z_0$  was equal to 1.51 mm.

Figure 1 shows that, to measure the nonlinear refractive index, the transmission of the laser beam through

the aperture (or closed aperture) must be placed in the far field. In this case, the transmission of the beam is sensitive to both nonlinear absorption and nonlinear refraction. Meanwhile, the nonlinear absorption measurements are performed by removing the aperture (or opened aperture). Here, transmission of the beam is sensitive only to the nonlinear absorption. In both cases, the detected signal is received by a photodetection system (PDS). The PDS consists of a photodiode (PD) and its associated high-gain PD amplifier, followed by a low-noise amplifier. The output of the entire photodetection system is conveyed to a data acquisition (DAQ) controller and then processed by a computer.

In the case of the open-aperture system, the transmission of the laser beam measured by the PDS is sensitive only to the intensity variations. The absorption  $\alpha$  of the material is intensity-dependent and is given by<sup>[10]</sup>

$$\alpha = \alpha_0 + \beta I, \quad (1)$$

where  $\alpha_0$  is the linear absorption coefficient and  $\beta$  is the nonlinear absorption coefficient.

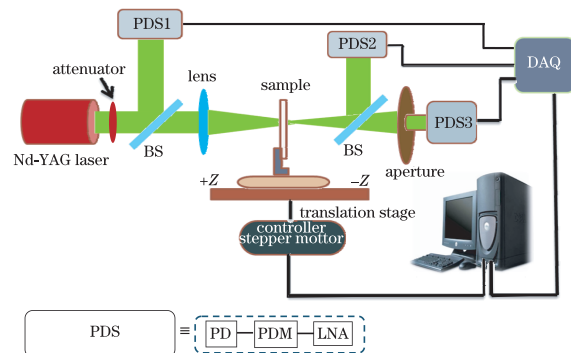


Fig. 1. Modified  $z$ -scan system for measuring the NLO and OL properties. BS: beam splitter.

The normalized transmittance of the sample under the open-aperture condition is written as<sup>[10]</sup>

$$T(z, s = 1) = 1 - \frac{q_0(z)}{2\sqrt{2}} \quad \text{for } |q_0(z)| < 1, \quad (2)$$

where  $q_0(z) = I_0\beta L_{\text{eff}}/(z^2/z_0)$ .  $z_0 = k\omega_0^2/2$  is the Rayleigh (diffraction) length of the beam,  $k = 2\pi/\lambda$  is the wave factor,  $\omega_0$  is the beam waist radius at the focal point,  $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0$  is the effective thickness of the sample,  $I_0 = 2P/\pi\omega_0^2$  is the peak intensity within the sample, and  $P$  is the peak power.

From the closed-aperture system, the index of refraction of the material is intensity-dependent and is given as<sup>[10]</sup>

$$n = n_0 + n_2 I, \quad (3)$$

where  $n_0$  is the linear refractive index and  $n_2$  is the nonlinear refractive index.

The normalized transmittance of the sample under the closed-aperture condition is given by<sup>[10]</sup>

$$T(z, \Delta\phi_0) = 1 - \frac{4(z/z_0)}{\left[\left(\frac{z^2}{z_0^2}\right) + 9\right] \left[\left(\frac{z^2}{z_0^2}\right) + 1\right]} \Delta\phi_0, \quad (4)$$

$$\Delta T_{P-V} = 0.406(1 - S)^{0.25} \Delta\phi_0 \quad \text{for } |\Delta\phi_0| \leq \pi, \quad (5)$$

where  $\Delta T_{P-V}$  is the difference between the normalized peak and valley transmittance and  $S = 1 - \exp(-2r_a^2/\omega_0^2)$  is the aperture linear transmittance with  $r_a$  denoting the aperture radius. The nonlinear phase shift  $\Delta\phi_0$  can be calculated from<sup>[10]</sup>

$$\Delta\phi_0 = n_2 I_0 L_{\text{eff}} k. \quad (6)$$

The nonlinear refractive index  $n_2$  and the nonlinear absorption coefficient  $\beta$  are related to the real and imaginary parts of third-order susceptibility  $\chi^{(3)}$ . The relations are defined as<sup>[10]</sup>

$$\text{Re}[\chi^{(3)}](\text{esu}) = 10^{-4} \frac{\varepsilon_0 c^2 n_0^2}{\pi} n_2 \quad (\text{cm}^2/\text{W}), \quad (7)$$

$$\text{Im}[\chi^{(3)}](\text{esu}) = 10^{-2} \frac{\varepsilon_0 c^2 n_0^2 \lambda}{4\pi^2} \beta \quad (\text{cm}^2/\text{W}), \quad (8)$$

where  $\varepsilon_0$  is the vacuum permittivity and  $c$  is the velocity of light.

From the real and imaginary parts of  $\chi^{(3)}$ , the absolute value of the third-order NLO susceptibility is given by

$$|\chi^{(3)}| = \sqrt{(\text{Re}\chi^{(3)} + \text{Im}\chi^{(3)})^2}. \quad (9)$$

The specific materials studied include a series of NLO guest-host systems formed by individually dissolving the dyes DO3, DO13, and DO25 in PVK. The molecular structures of the disperse dyes and the polymer are shown in Fig. 2. The dyes and the polymer were obtained from Sigma-Aldrich Company.

The samples were prepared as follows. The glass plates and quartz cuvette were washed in acetone, ethanol, and distilled water and then dried. Different ratios of DO3, DO13, and DO25 were used to prepare a NLO guest-host

polymer system with chromophore (dye) weight ratios of 10 wt.-% in the host polymer PVK; they were designated as NLO guest-host PVK/DO3, PVK/DO13, and PVK/DO25 polymer systems, respectively.

The azo-polymer powder was dissolved in chloroform. To increase the solubility, the solution was heated at 60 °C for 30 min and stirred at room temperature for 24 h. Then, four concentrations of 0.08, 0.2, 0.6, and 1 mmol/L were prepared as solution in a 1-mm quartz cuvette. For the thin-film sample, a thin azo-polymer layer with 1 mmol/L concentration was cast to commercially available microscope slides (glass plates). After the casting, the NLO samples were dried in an oven at 60 °C for 12 h to remove the residual solvent. The obtained polymer film thickness was from 9 to 10  $\mu\text{m}$ .

The ultraviolet (UV)-visible absorption spectra of the PVK/DO3, PVK/DO13, and PVK/DO25 solution samples at different concentrations of 0.08, 0.2, 0.6, and 1 mmol/L and the thin-film sample at a concentration of 1 mmol/L were recorded using the spectrophotometer. The absorption spectra are shown in Fig. 3. The solid line represents the absorption spectra of the solution, and the dotted line represents the absorption spectra of the thin film.

Figures 4(a) and (c) show the open- and closed-aperture  $z$ -scan curves, respectively, obtained from the PVK/DO3 (sample solution) at different concentrations of 0.08, 0.2, 0.6, and 1 mmol/L. Figures 4(b) and (d) show the open- and closed-aperture  $z$ -scan curves (thin-film sample), respectively, at a concentration of 1 mmol/L.

For the PVK/DO13 sample solution, the open- and closed-aperture  $z$ -scan results are shown in Figs. 5(a)

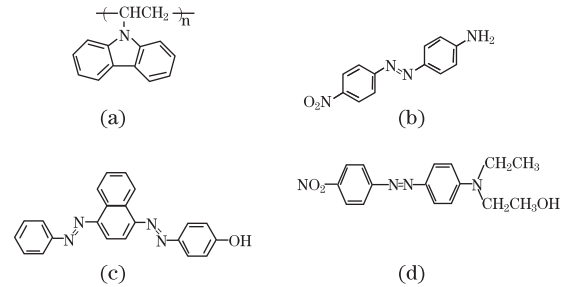


Fig. 2. Chemical structures for (a) PVK, (b) DO3, (c) DO13, and (d) DO25.

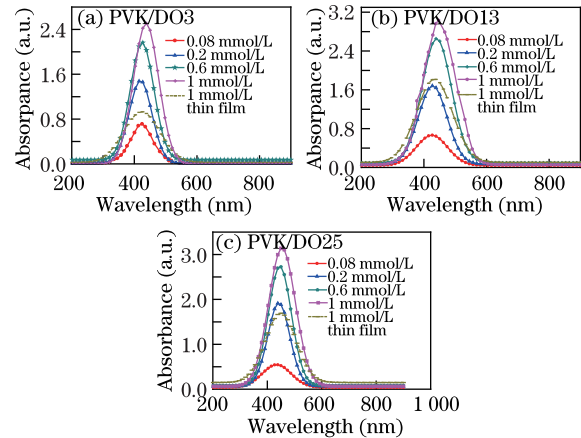


Fig. 3. Absorption spectra at different concentrations for (a) PVK/DO3, (b) PVK/DO13, and (c) PVK/DO25.

and (c), respectively, at different concentrations of 0.08, 0.2, 0.6, and 1 mmol/L. For the PVK/DO13 thin-film sample, the open- and closed-aperture  $z$ -scan results are shown in Figs. 5(b) and (d) at a concentration of 1 mmol/L.

Figures 6(a)–(d) show the open- and closed-aperture  $z$ -scan curves obtained from PVK/DO25 at different concentrations (sample solution) and at a concentration of 1 mmol/L (thin-film sample), respectively.

For the OL measurement, the sample solution in the 1-mm quartz cuvette was placed just under the focus of the lens (focal length of 5 cm) where the defocusing occurred. The OL experiment was investigated by the open-aperture  $z$ -scan system. Figure 7 shows the OL curves at different concentrations of 0.08, 0.2, 0.6, and 1 mmol/L from the PVK/DO3, PVK/DO13, and PVK/DO25.

First, we must note that the modified  $z$ -scan technique

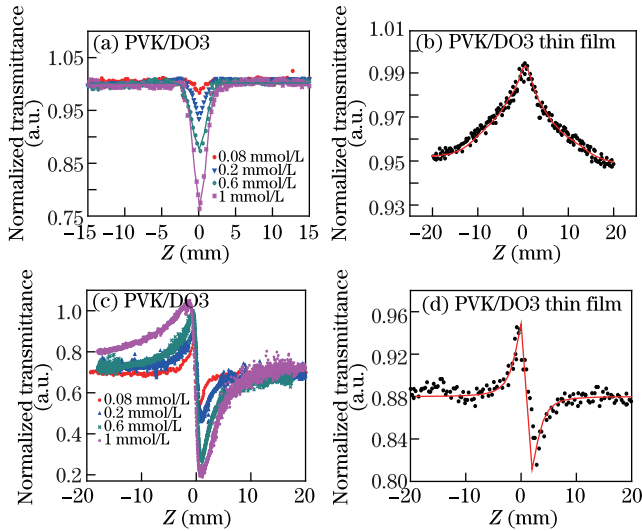


Fig. 4. Open-aperture  $z$ -scans of (a) the PVK/DO3 solution and (b) the thin film. Closed-aperture  $z$ -scans of (c) the PVK/DO3 solution and (d) the thin film.

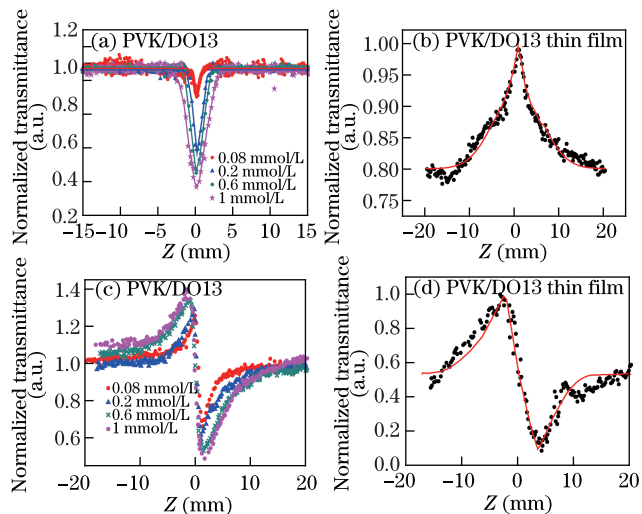


Fig. 5. Open-aperture  $z$ -scans of (a) the PVK/DO13 solution and (b) the thin film. Closed-aperture  $z$ -scans of (c) the PVK/DO13 solution and (d) the thin film.

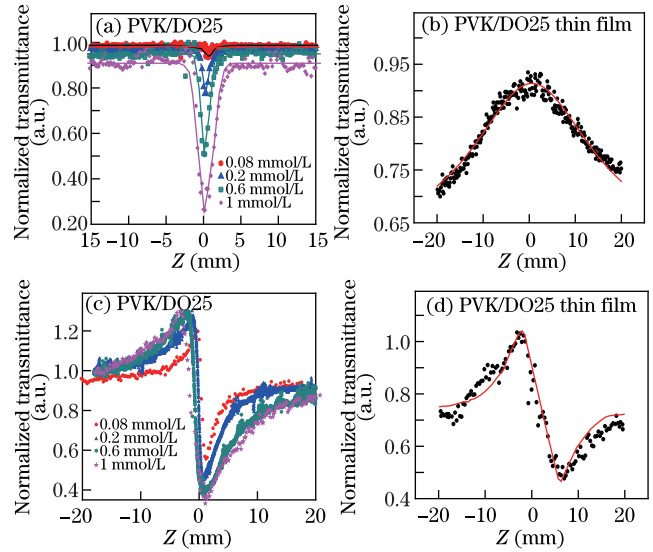


Fig. 6. Open-aperture  $z$ -scans of (a) the PVK/DO25 solution and (b) the thin film. Closed aperture  $z$ -scans of (c) the PVK/DO25 solution and (d) the thin film.

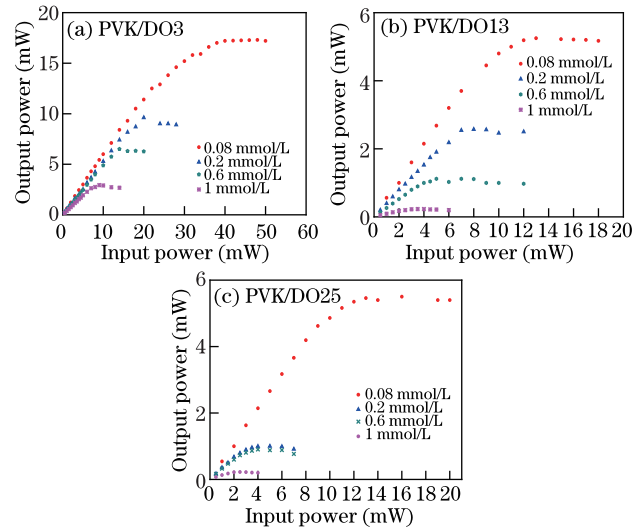


Fig. 7. Optical limiting effect for the (a) PVK/DO3, (b) PVK/DO13, and (c) PVK/DO25 solutions at different concentrations.

used in this work not only has the accuracy and versatility advantages of the method but also is satisfactorily reliable.

The nonlinear absorption coefficient  $\beta$  is an important parameter in photonic applications. From Figs. 4(a), 5(a), and 6(a), the samples exhibit a normalized transmittance valley, indicating an induced absorption (i.e., two-photon absorption). Meanwhile, from Figs. 4(b), 5(b), and 6(b), the open-aperture curves exhibit a transmittance peak, indicating a saturable absorption. This result shows an interesting effect, and the NLO samples can be used for another application such as in passive  $Q$ -switching laser. This difference in the behavior of the solutions and the thin film from the NLO polymer materials can be attributed to the thickness of the sample of  $\sim 10 \mu\text{m}$ , similar to the case in Refs. [6,11], and the increase in the laser beam intensity, which induces bleaching in the ground-state absorption, increases the

**Table 1. Summary of the Nonlinear Optical Properties of PVK/DO3, PVK/DO13, and PVK/DO25 Solution Samples at Different Concentrations and for the Thin-film Sample at a Concentration of 1 mmol/L**

Material	Form of Sample Solution at Concentration	$\Delta T_{P-V}$	$n_2$ ( $\times 10^{-7}$ cm <sup>2</sup> /W)	$\beta$ (cm/kW)	$ \chi^{(3)} $ ( $\times 10^{-6}$ esu)
PVK/DO3	0.08	0.3	-0.70	1.52	4.8
	0.2	0.433	-1.02	2.02	6.8
	0.6	0.711	-1.83	4.08	12.2
	1	0.85	-2.33	8.07	27.8
	Thin Film at 1 mmol/L	0.117	-32.1	28.33	300
PVK/DO13	0.08	0.599	-2.13	8.22	8.9
	0.2	0.7	-3.49	29.04	17.7
	0.6	0.82	-9.32	86.45	45.7
	1	0.92	-18.27	163.7	109.3
	Thin Film at 1 mmol/L	0.87	-32.8	384.7	5894
PVK/DO25	0.08	0.64	-1.66	1.75	6.8
	0.2	0.795	-2.29	12.12	10.2
	0.6	0.9	-3.21	26.752	16.5
	1	0.954	-5.08	58.66	35.19
	Thin Film at 1 mmol/L	0.5	-1.37	127.5	1614

transmittance. Using Eq. (2) with the obtained  $\Delta T$  from the curves, the nonlinear absorption coefficient  $\beta$  can be determined.

The nonlinear refractive index  $n_2$  is another important parameter used in optical switching or OL in photonic applications. From Figs. 4(c) and (d), 5(c) and (d), and 6(c) and (d), the closed-aperture curves exhibit a peak-valley shape, indicating a negative value for the nonlinear refractive index  $n_2$ . The negative sign confirms that the nonlinear phenomena are caused by the self-defocusing and can be attributed to the local variation in the refractive index with the temperature and to the thermal nonlinearity resulting from the absorption of an irradiation wavelength of 532 nm. Using Eqs. (5) and (6) with the obtained data of  $\Delta T_{P-V}$ , the nonlinear refractive index  $n_2$  can be determined. Table 1 summarizes the values of the nonlinear refractive indexes, nonlinear absorption coefficients, and the third-order susceptibilities of both NLO samples in the solution and the thin-film sample.

Table 1 shows that the values of  $\Delta T_{P-V}$  increase with the increase in the concentration. Further, when the concentration increases, the values of  $n_2$ ,  $\beta$ , and  $\chi^{(3)}$  increase. In the solution and the thin-film samples, PVK/DO13 exhibits the best and highest values for  $n_2$ ,  $\beta$ , and  $\chi^{(3)}$  compared with those of the PVK/DO3 and PVK/DO25 materials. Thus, the large values of  $n_2$ ,  $\beta$ , and  $\chi^{(3)}$  for the NLO PVK/DO13 polymer system make it a promising material for used in photonic applications, such as for an all-optical switching.

Figure 7 shows that the important parameter for the OL properties is the limiting threshold, and it is inversely proportional to the concentration. The OL responses of the low-concentration solution are generally much weaker than those of the more concentrated solutions. However, the highly concentrated solutions exhibit strong OL,

which indicates that a NLO sample with high concentration has more molecules per unit volume that participate in the interaction during the nonlinear absorption process. Hence, the concentration of the NLO sample must be considered carefully. In addition, at high concentration, the transmission is very poor. Meanwhile, at low concentration, the transmission is good, and beyond this concentration, the OL effect could disappear. The observed results confirm that the concentration threshold is very important in the OL measurements. Therefore, in these materials, the two-photon-assisted state absorptions, which lead to reverse saturable absorption, may be responsible for the OL action. In addition, our initial studies do not display appropriate OL behavior in the thin-film sample probably because of scattering or bleaching. The OL threshold values for all sample concentrations are shown in Table 2. The present results show that the NLO samples exhibit remarkable optical responses, which help in designing organic NLO materials suitable for optical limiters.

In conclusion, new structures of organic NLO guest-host PVK/DO3, PVK/DO13, and PVK/DO25 polymer systems are studied as NLO materials, and

**Table 2. Summary of the Optical Limiting Threshold of the New Structures of Organic NLO Guest-host Polymer Systems at Different Concentrations**

Material	Optical Limiting Threshold (mW)			
	Concentration (mmol/L)			
	0.08	0.2	0.6	1
PVK/DO3	29	15	13.3	6.3
PVK/DO13	9.5	6.4	3.8	1.1
PVK/DO25	10.4	2.9	2.8	1.3

their NLO and OL properties are investigated using the continuous wave (CW)  $z$ -scan system at 532 nm. The nonlinear refractive index  $n_2$ , nonlinear absorption coefficient  $\beta$ , and the third-order nonlinear susceptibility  $\chi^{(3)}$  are estimated and shown as linear functions of the concentration. They increase with the increase in the concentration of all NLO samples. Our studies show that the PVK/DO13 has the largest and best values of  $n_2$ ,  $\beta$ , and  $\chi^{(3)}$ . All films exhibited saturable absorption, which can be attributed to the film thickness. These results suggest that the NLO PVK/D03, PVK/D013, and PVK/D025 materials are good candidates for photonic applications such as optical limiter and optical switches. The large nonlinearity may be due to the strong donor/acceptor groups; thus, tailoring the NLO property is possible via structure modification in this class of materials.

## References

1. Y. Zhang, X. Hu, H. Yang, and Q. Gong, *Appl. Phys. Lett.* **99**, 141113 (2011).
2. G. Balaji, R. K. Rekha, and A. Ramalingam, *Acta Phys. Polon. A* **119**, 359 (2011).
3. T. Huang, Z. Hao, H. Gong, Z. Liu, S. Xiao, and S. Li, *Chem. Phys. Lett.* **451**, 213 (2007).
4. P. Poornesh, P. K. Hegde, G. Umesh, M. G. Manjunatha, K. M. Manjunatha, and A. V. Adhkari, *Opt. Laser Technol.* **42**, 230 (2010).
5. M. D. Zidan and Z. Ajji, *Opt. Laser Technol.* **43**, 934 (2011).
6. P. Poornesh, G. Umesh, and P. K. Hegde, *Appl. Phys. B* **97**, 117 (2009).
7. Y. Wang, Y. Jiang, J. Hua, H. Tian, and S. Qian, *J. Appl. Phys.* **110**, 033518 (2011).
8. M. D. Zidan, A. W. Allaf, Z. Ajji, and A. Allahham, *Opt. Laser Technol.* **42**, 531 (2010).
9. K. Naseema, K. B. Banjunatha, K. V. Sujith, G. Umesh, B. Kalluraya, and V. Rao, *Opt. Mater.* **34**, 1751 (2012).
10. M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Vanstrylound, *IEEE J. Quantum Electron.* **26**, 760 (1990).
11. S. J. Mathews, S. C. Kumar, L. Giribabu, and S. V. Rao, *Opt. Commun.* **280**, 206 (2007).