

Nonlinear absorption of laser radiation by zinc and lead phthalocyanines and zinc porphyrin in a nanoporous-glass/polymer composite

S.M. Dolotov, L.M. Koldunov, M.F. Koldunov, V.A. Petukhov, A.V. Sizyukhin

Abstract. We have studied the nonlinear absorption of nanosecond 532-nm laser pulses by zinc phthalocyanine (PcZn), lead phthalocyanine (PcPb) and zinc porphyrin (PrZn) incorporated into a nanoporous-glass/polymer composite and determined the basic nonlinear absorption characteristics of these compounds in the composite host. The composite is shown to be suitable for designing nonlinear optical elements activated with organic compounds. The correlation between the characteristics of the three compounds in the composite host and liquid solvents is analysed.

Keywords: nonlinear absorption, composite, solid host, nanoporous glass/polymer, lead phthalocyanine, zinc phthalocyanine, zinc porphyrin, functional organic compound.

1. Introduction

Nonlinear absorption in functional organic compounds (FOCs) has been the subject of intense research since the 1980s [1]. The interest in this phenomenon has been aroused by both the fundamental problem of identifying the mechanism of the nonlinear absorption in FOCs and the need for advanced nonlinear optical elements (power limiters, optical switches and others). From a practical point of view, solid optical elements are preferable, but most studies so far have been concerned with characteristics of nonlinear absorption by FOCs in a liquid solvent [2–4].

A solid host for FOCs must meet a number of requirements: it should be transparent in their working wavelength range, have a high laser damage threshold, be stable to temperature and humidity changes, etc. Moreover, the host material fabrication process should allow the addition of an FOC without breaking it down. Since the decomposition tempera-

ture of FOCs is typically below 200 °C, there is a limited range of suitable host materials. The possible types of hosts for FOCs include polymers [5–7], ormosils [8], sol–gel glasses [9] and nanoporous-glass/polymer (NPGP) composites [10].

The characteristics of FOC molecules (absorption cross section, internal and intercombination conversion rates and others) depend significantly on their environment [11, 12]. Distinctions between the characteristics of an FOC in a solid host and liquid solvent are likely to lead to changes in the characteristics and, possibly, mechanism of its nonlinear absorption. For this reason, the incorporation of an FOC (investigated previously in a liquid solvent) into a solid host requires additional studies of the characteristics and mechanism of its nonlinear absorption. Moreover, given the large amount of data on the nonlinear absorption by FOCs in liquid solutions, it is of great current interest to correlate the nonlinear absorption characteristics of FOCs in liquid solutions to those in solid hosts.

The objective of this work was to study nonlinear absorption by FOCs in an NPGP composite host and to correlate their nonlinear absorption characteristics in the NPGP composite to those in a liquid solvent. To this end, we measured the nonlinear absorption in zinc and lead phthalocyanines and zinc porphyrin incorporated into the NPGP composite and compared the results to relevant data in the literature.

2. Samples and their spectral characteristics

We studied NPGP composite optical elements activated with zinc porphyrin (PrZn) or modified zinc (PcZn) or lead phthalocyanine (PcPb). The samples were prepared as described elsewhere [10].

The NPGP composite [10] consisted of a nanoporous glass matrix and a polymer embedded in the pores of the glass. The composite was fabricated using glass of 40% porosity (pore volume to total volume ratio). The pore size distribution, determined using water porosimetry [13], was narrow and unimodal, with an average pore size of 5 nm and standard deviation of 2 nm. The polymer component of the composite was prepared from a monomer mixture that comprised methyl methacrylate purified by distillation, a low molecular weight additive and a reaction initiator. The FOCs were dissolved in the monomer mixture. The solubility limit of PcPb and PcZn was 10^{-3} M and that of PrZn was 5×10^{-3} M. In the fabrication of the composite, the highest FOC concentration in the monomer mixture was 30% below the solubility limit.

Next, the nanoporous glass was immersed in the monomer mixture. After the glass pores were filled with the mix-

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ture, free-radical polymerisation was carried out. The composite was then withdrawn from the polymer block and treated by a procedure common in the technology of optical glass.

The optical elements thus produced were $20 \times 14 \times 3$ mm in dimensions. Their surface was polished to the fourth finish class. All the elements had high optical quality and were uniformly infiltrated with one of the FOCs. Their absorbance at 532 nm was 0.38 (PcPb), 0.24 (PcZn) or 0.58 (PrZn).

In addition to the solid optical elements, we studied a PrZn solution in ethyl acetate as a control sample. Its absorbance at 532 nm was 0.47.

The absorption spectra of the FOCs, in both the monomer mixture and composite, were measured from 200 to 800 nm on a Solar SM 2203 spectrofluorometer. The FOC concentration in the monomer mixture was varied from 10^{-5} M to the solubility limit. To measure the spectra of concentrated FOC solutions, with a high absorbance, we used thin Schott glass cuvettes.

According to our results, the absorption spectra of the three FOCs in monomer solution were concentration-independent up to their solubility limit. Absorbance measurements at a number of wavelengths showed that, over the entire concentration range, Bouguer's law was obeyed: $A(\lambda) = \log(I_0/I) = \varepsilon(\lambda)cL$, where $A(\lambda)$ is optical absorbance; $\varepsilon(\lambda)$ is extinction; c is the dye concentration; L is the sample thickness; and I_0 and I are the incident and transmitted intensities. The absorption and extinction spectra of the FOCs in the composite coincided to within experimental uncertainty with those in the monomer mixture.

That the absorption spectra did not vary indicated that there were no associates at any FOC concentration in the solutions or composite, and the equal extinctions of the FOCs in solution and composite suggested that the transitions from the ground state to the first excited state had identical cross sections.

3. Measurements

We studied the transmittance of the samples at $\lambda = 532$ nm as a function of incident laser fluence, the photodegradation of the FOCs in the NPGP composite and the laser damage threshold of the composite at 532 nm.

Figure 1 shows a schematic of the experimental setup used to measure the transmittance of the FOCs as a function of incident laser fluence.

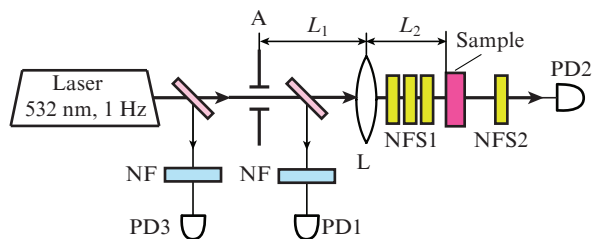


Figure 1. Schematic of the experimental setup used to measure the transmittance of optical elements: (A) 2-mm-diameter aperture, (NFS1, NFS2) neutral filter sets, (L) $f = 8$ cm lens, (PD1, PD2) photodetectors, (NF) neutral filter, (PD3) photodetector for pulse duration measurement.

As probe light, we used the second harmonic of a Nd:YAG laser pulsed at 1 Hz. The laser pulse duration (24 ± 1 ns full width at half maximum) was monitored with a LeCroy WaveRunner 6050A oscilloscope. The signal was fed to the oscilloscope from a Hamamatsu S7481 photodiode (PD3).

The transverse beam intensity profile was nearly Gaussian. The beam was passed through a 2-mm-diameter aperture (A) to give an almost top-hat profile, so in data processing the beam intensity was thought to be constant across the aperture. A lens (L) projected an image of the aperture onto the frontside of the sample. The aperture–lens distance, L_1 , was chosen so as to ensure a necessary range of laser fluences on the surface of the sample, which was placed between two neutral filter sets, NFS1 and NFS2. The laser intensity incident on the sample could be varied by putting a filter from NFS1 to NFS2. The laser pulse energy was measured in front and behind the sample by photodiodes PD1 and PD2, respectively, with a relative uncertainty of $\pm 1\%$.

In this experimental configuration, the transmittance of a sample, $T(W)$ (where W is the incident laser fluence), was proportional to the ratio of the signals from PD2 and PD1 normalised to the transmittance of the optical element in the linear regime: $T(0) = T_0$.

To identify the onset of FOC photodegradation in the NPGP composite, a particular region of the sample was exposed to 200 pulses with $W \leq 1$ J cm $^{-2}$, and the transmittance of the sample was measured. An increase in transmittance was interpreted as evidence for the onset of FOC photodegradation.

Laser damage to the FOC-activated NPGP composite was studied in the single shot regime: a region of an optical element was exposed to a single pulse. The incident laser intensity at which the damage probability was 0.5 was taken as the laser damage threshold of the NPGP composite.

4. Experimental results

Figure 2 shows transmittance T as a function of laser fluence W for the PcPb-activated sample. The $T(W)$ data for PcZn in the NPGP composite and for PrZn in the composite and ethyl acetate are presented in Fig. 3.

It is seen in Figs 2 and 3 that the $T(W)$ data are characterised by two transmittance values, at low and high laser fluences, $T(0)$ and $T(\infty)$, respectively, and by the corresponding laser fluences, W_{th} and W_{sat} (saturation fluence). There is no

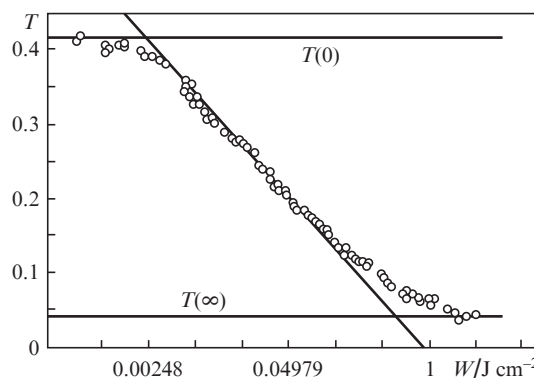


Figure 2. Transmittance T as a function of laser fluence W (J cm $^{-2}$) for PcPb.

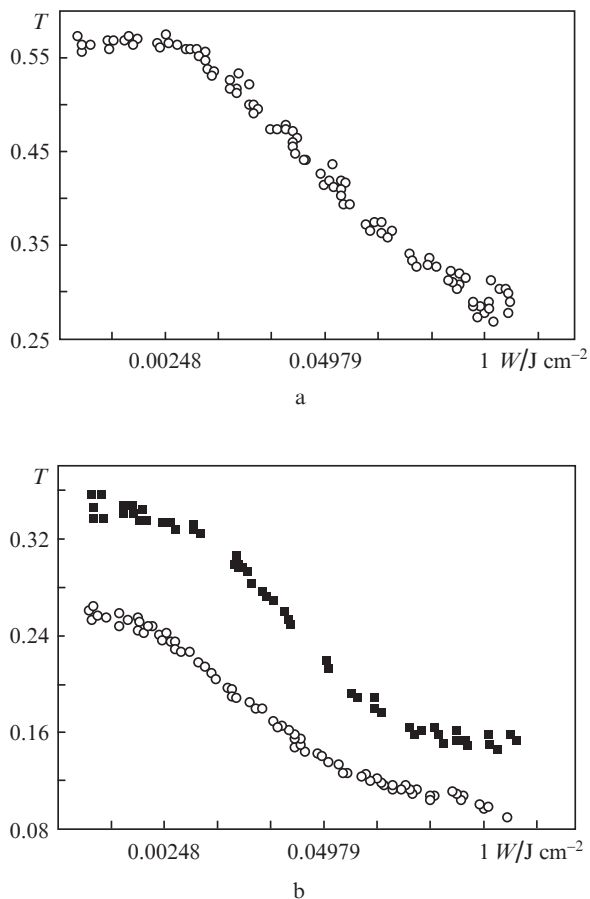


Figure 3. Transmittance T as a function of laser fluence W (J cm^{-2}) for (a) PcZn and (b) PrZn in ethyl acetate (■) and the composite (○).

commonly accepted technique for W_{th} and W_{sat} determination. In this study, these parameters are evaluated as illustrated in Fig. 2: W_{th} and W_{sat} are the fluences at which the tangent to the $T(W)$ curve at the inflection point intersects the straight lines $T(0)$ and $T(\infty)$, respectively.

There is also practical interest in other characteristics of nonlinear optical elements, derived from $T(0)$, $T(\infty)$, W_{th} , and W_{sat} , such as the transmittance ratio (contrast) $C = T(0)/T(\infty)$; nonlinear range $\Delta W = W_{\text{sat}} - W_{\text{th}}$ [fluence range where $T(W)$ varies]; and the slope of the transmittance as a function of fluence, $S = \Delta T/\Delta W$. These parameters of the compounds studied here are listed in Table 1.

A sufficient condition for stable operation of a nonlinear element is that the FOCs do not decompose in the working range of laser fluences, i.e. for $W < W_{\text{sat}}$. Studies of FOC photodegradation in the NPGP composite showed that, for $W \leq 1 \text{ J cm}^{-2}$ (which exceeds W_{sat} for the three compounds), there was no degradation.

Table 1.

FOC	A_0	C	R_A	$W_{\text{th}}/\text{J cm}^{-2}$	$W_{\text{sat}}/\text{J cm}^{-2}$	$S/\text{cm}^2 \text{J}^{-1}$
PcPb	0.38	10	3.7	0.002	0.51	0.7
PcZn	0.24	2.1	2.4	0.004	0.834	0.4
PrZn	0.58	2.5	1.7	0.001	0.121	1.3
PrZn (in ethyl acetate)	0.47	2.2	1.7	0.004	0.205	0.9

Note: A_0 is the absorbance of the samples at 532 nm and R_A is the ratio of the absorbances at high and low laser fluences.

In laser damage studies, we observed spatial fluctuations of the laser damage threshold. Such fluctuations are commonly interpreted in terms of the dominant role that absorbing inclusions play in the laser damage mechanism [14]. The damage threshold (50% probability of damage) was determined to be 35 J cm^{-2} , with a standard deviation of 7 J cm^{-2} . Thus, the damage threshold of the NPGP composite exceeds the threshold intensity for FOC photodegradation. Note [10] that the damage threshold of the composite at $\lambda = 1064 \text{ nm}$ is $\sim 70 \text{ J cm}^{-2}$, i.e. twice the threshold at 532 nm. This result is a natural consequence of the damage being due to absorbing inclusions. The absorption cross section of small inclusions is known to be inversely proportional to wavelength [15], whereas the damage threshold is proportional to the absorption cross section of the inclusions for laser radiation.

5. Discussion

Nonlinear absorption in FOCs is due to laser-induced changes in the population of energy levels of the FOC molecules (the energy level diagram of an FOC molecule is presented in Fig. 4). At intensities $I_0 \ll W_{\text{th}}/\tau_p$ (where τ_p is the laser pulse duration), the transmittance of the sample is $T(0) = \exp(-\sigma_{S_0}NL)$, where σ_{S_0} is the cross section of the $S_0 \rightarrow S_1$ transition and N is the FOC concentration. For $I_0 > W_{\text{sat}}/\tau_p$, the absorption on the $S_0 \rightarrow S_1$ transition is negligible because of the electron redistribution between the S_1 and T_1 levels, so that $T(\infty) = \exp(-\sigma_{\text{eff}}NL)$, where $\sigma_{\text{eff}} = \sigma_S h_{S_1} + \sigma_T h_{T_1}$ is the effective absorption cross section; $h_{S_1} = n_{S_1}/N$; $h_{T_1} = n_{T_1}/N$; n_{S_1} and n_{T_1} are the populations of the singlet and triplet levels. Therefore, the transmittance ratio is given by $C = \exp(\Delta\sigma NL)$ ($\Delta\sigma = \sigma_{\text{eff}} - \sigma_{S_0}$).

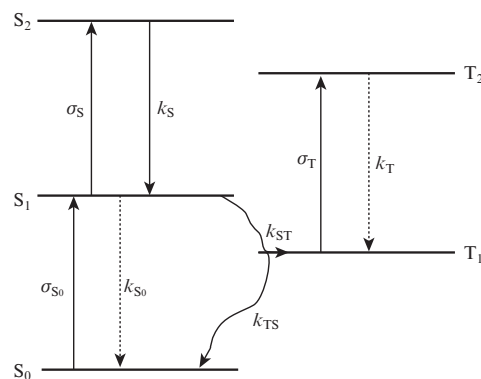


Figure 4. Energy level diagram of an FOC molecule: σ_{S_0} , σ_S and σ_T are the cross sections of the $S_0 \rightarrow S_1$, $S_1 \rightarrow S_2$ and $T_1 \rightarrow T_2$ transitions, respectively; k_{S_0} , k_S and k_T are the nonradiative transition rates; and k_{S_1} and k_{T_1} are the intercombination conversion rates.

Data in the literature are difficult to compare because the nonlinear absorption characteristics of optical elements depend on their geometric dimensions and FOC concentration. One example is the transmittance ratio, C , which explicitly depends on the concentration of FOC molecules, N , and sample thickness, L . Since the samples studied range widely in concentration and geometric dimensions, results reported by different groups are difficult or even impossible to compare.

Among the aforementioned nonlinear absorption characteristics, the following one is free of the above drawbacks:

$$R_A = \frac{\ln T(\infty)}{\ln T(0)} = \frac{\sigma_{\text{eff}}}{\sigma_{S_0}}$$

(the ratio of the absorbances at high and low laser fluences). It depends only on the properties of FOCs and can be evaluated from measured transmittance, T , as a function of laser fluence, W . Unfortunately, data presented in many reports (see e.g. Ref. [16]) are insufficient to evaluate R_A , which makes it impossible to adequately compare their results. The R_A values reported in Refs [4, 17–19] or evaluated from data therein differ drastically. For example, calculations give $R_A = 4.7$ for a PcPb solution in toluene [19] and $R_A = 9.6$ for a solution in CHCl_3 [4], whereas we obtained $R_A = 3.7$ for the PcPb in the composite. Similarly, Kuznetsova et al. [17] reported $R_A = 3.7$ – 4.7 for PrZn in ethyl acetate, whereas we obtained $R_A = 1.7$ in both ethyl acetate and the composite host.

The differences between the R_A values derived from earlier data are difficult to account for by the influence of the medium or substituents in the molecules. Spectroscopic data demonstrate that the absorption spectra of the three FOCs in different solvents (monomer mixture, ethyl acetate, and toluene) and the composite coincide to within experimental uncertainty. This suggests that solvation processes have no significant effect on the position of the energy levels of the molecules or the cross sections of the transitions between them. At the same time, the medium and substituents influence nonradiative conversion rates [12], which in turn changes W_{th} , W_{sat} , ΔW and S but is unlikely to influence C or R_A . Changes in conversion rates will of course lead to changes in level populations, i.e. in h_{S_1} and h_{T_1} , and hence in σ_{eff} . However, in the one-electron approximation, the configurations of the S_1 and T_1 states coincide, as do those of the S_2 and T_2 states. Therefore, $\sigma_S \sim \sigma_T$, and there are no grounds to expect drastic changes in σ_{eff} in response to changes in h_{S_1} and h_{T_1} .

Variations in the R_A of a particular FOC from report to report may be related either to the technique used to measure $T(W)$ or the data processing procedure. In Refs [4, 17–19], $T(W)$ was found by measuring the transmittance of a sample placed at the focus of a lens. This approach requires that the laser beam have a Gaussian transverse intensity profile, but this issue was not addressed in Refs [4, 17–19]. Moreover, the ‘tails’ of a Gaussian distribution impede accurate determination of the saturation fluence W_{sat} and, hence, $T(\infty)$, which is needed for FOC contrast calculation. The σ_{eff} values reported in Refs [18, 20] are also open to question because they were obtained by numerically calculating $T(W)$ using rate equations for molecular level populations. The cross sections σ_S and σ_T were adjusted so as to fit the calculated $T(W)$ to experimental data. In this way, Mansour et al. [18] obtained $R_A \approx 23$ for a PcPb solution in toluene and nanosecond pulses. At the same time, for the same compound, solvent and pulse duration Perry et al. [19] estimated R_A at 4.7, which is comparable to the 3.6 obtained in this study. Thus, the value $R_A = 23$ appears doubtful.

To find out the origin of the differences between the R_A 's of the FOCs in the composite and liquid solutions, we measured the nonlinear absorption by PrZn in the NPGP composite and ethyl acetate. The results are presented in Fig. 3. Under identical conditions, we obtained the same R_A value to within experimental uncertainty for the PrZn in the composite and ethyl acetate: $R_A = 1.7$.

6. Conclusions

The nonlinear absorption characteristics of FOCs incorporated into a composite host do not correlate with those reported for the same compounds in liquid solvents. Further work is needed to understand the origin of this distinction.

The NPGP composite studied here meets the requirements for nonlinear optical elements. The process used to fabricate the composite enables the addition of an FOC without destroying it. The laser damage threshold of the composite considerably exceeds its nonlinear absorption saturation fluence. The nonlinear absorption characteristics of the FOCs incorporated into the composite are identical to those of these compounds in liquid solutions.

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