

PACS numbers: 42.65.An; 42.65.Hw
DOI: 10.1070/QE2002v032n02ABEH002145

Anomalous large nonlinearity of thin $SnCl_2$ phthalocyanine films observed upon pulsed laser excitation

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Abstract. **The nonlinear susceptibility of thin stannum dichloride phthalocyanine ($SnCl_2Pc$) films was studied by the method of degenerate four-wave mixing (DFWM) using the second-harmonic 532-nm, 10-ns pulses from a single-mode, TEM_{00}, 1.5-mJ Nd^{3+}:YAG laser and by the method of nonlinear lens (the Z-scan method). The intensity of the first-order self-diffraction upon the DFWM on dynamic gratings induced in $SnCl_2Pc$ films has a cubic dependence on the recording-beam intensity, indicating to the third-order nonlinear response of the films. The value of the nonlinear susceptibility $\chi^{(3)}(\omega;\omega,-\omega,\omega,) = (4.4 \pm 0.5) \times 10^{-7}$ esu noticeably exceeds this value for phthalocyanines known in the literature. The mechanisms that can be responsible for the nonlinear response of the new synthesised material are discussed.**

Keywords: *phthalocyanines, nonlinear refraction, nonlinear optical susceptibility, nonlinear absorption.*

1. Introduction

The nonlinear properties of some metallophthalocyanine films were earlier studied in detail mainly upon pulsed laser excitation into a strong absorption Q band, where the contribution from localised Frenkel excitons dominates. The third-order nonlinear susceptibility $\chi^{(3)}$ of these films obtained in the experiments depends on the nature of the central atom (group) and is $10^{-11} - 10^{-10}$ esu [1, 2].

In this paper, we studied the nonlinear properties of phthalocyanine films observed upon pulsed laser excitation into a weak absorption band, where the contribution from direct transitions accompanied by the formation of charge-transfer states (CT states) is substantial for asymmetrical molecules [3]. As a model object, we studied stannum dichloride ($SnCl_2Pc$) films because the contribution of CT states near the 532-nm second-harmonic of a Nd^{3+} : YAG laser used in our experiments should be dominant.

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Received 15 August 2001; revision received 19 November 2001
Kvantovaya Elektronika **32** (2) 140 – 142 (2002)
Translated by M.N.Sapozhnikov

2. Experimental

The $SnCl_2Pc$ films were prepared by thermal deposition on a quartz substrate in high vacuum at room temperature. The film thickness was controlled during the deposition with a quartz thickness meter with an accuracy of 10 nm. To study the influence of polymorph modifications on the nonlinear susceptibility, 800-nm thick films obtained simultaneously during one deposition were annealed at different temperatures in the temperature range between 60 and 200 °C in air (in an oven) in dark for three hours.

Fig. 1 shows the absorption spectrum of the $SnCl_2Pc$ film recorded with a Specord M40 spectrophotometer (the arrow shows the wavelength of the Nd^{3+} : YAG laser). We measured the nonlinear susceptibility of samples by the method of degenerate four-wave mixing (the self-diffraction method) [5] and the method of nonlinear lens (the *Z*-scan method) [6, 7]. We determined by these methods the nonlinear susceptibility, the type of nonlinearity (by the self-diffraction method), as well as the sign of nonlinearity (by the method of nonlinear lens) and the character of nonlinear absorption. We used in our experiments a frequency-doubled 0.532-μm single-mode Nd^{3+} : YAG laser. The laser emitted 10-ns, 1-mJ Gaussian pulses.

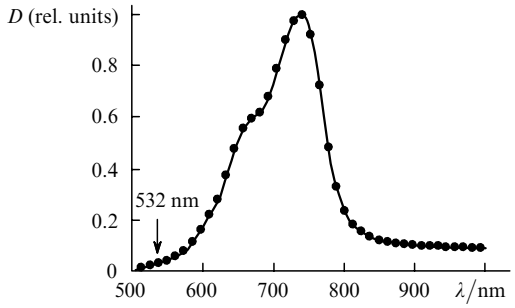

Figure 1. Absorption spectrum of the $SnCl_2Pc$ film.

3. Experimental results and discussion

Our experiments showed that the self-diffraction efficiency η (the ratio of the light intensity I_1 in the first diffraction order to the recording beam intensity I_0) first increased from 1.5×10^{-5} to 1.65×10^{-4} with increasing film thickness d and then gradually saturated at $d > 800$ nm. We measured the nonlinear characteristics of 800-nm thick films.

The measurements of the exposure characteristic of dynamic gratings, i.e., of the dependence of the intensity I_1 of the first-order diffraction beam on the recording beam intensity I_0 showed that the experimental data are well described by a cubic curve $y = a + bx^3$ (the solid curve in Fig. 2), where y is the intensity of the beam diffracted in the first order and x is the intensity of the recording beam. This shows that the material under study exhibits the third-order nonlinear response.

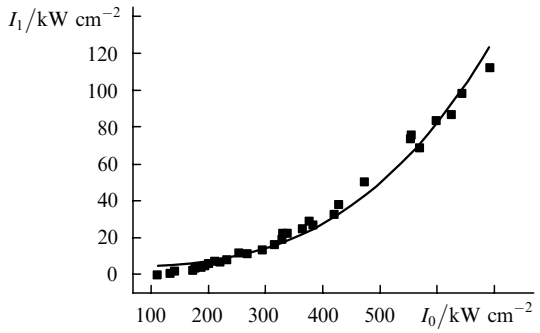

Figure 2. Exposure characteristic of the dynamic grating recorded in a thin $SnCl_2$2Pc film by laser pulses. Squares are measurements, the solid curve is a fitting cubic curve.

The cubic nonlinear susceptibility for unannealed films was determined from the obtained values of η using the relations [5]:

$$n_2 = \frac{\lambda\sqrt{\eta}}{\pi d I_0} = (8.8 \pm 0.9) \times 10^{-6} \text{ cm}^2 \text{ kW}^{-1}, \quad (1)$$

$$\chi^{(3)} = 3\left(\frac{n_0}{4\pi}\right)^2 n_2 = (4.4 \pm 0.5) \times 10^{-7} \text{ esu}, \quad (2)$$

where λ is the wavelength of incident radiation; n_0 is the linear refractive index; n_2 is the nonlinear refractive index.

The unannealed sample was also studied by the method of nonlinear lens (Fig. 3). One can see from Fig. 3 that the refractive index exhibits a positive change ($\Delta n > 0$) in the laser-wave field [measurements with a diaphragm, curve (*1*)], which is accompanied by bleaching of the medium [measurements without a diaphragm, curve (*2*)]. Having measured the difference ΔT_{pv} of transitions at the maximum and minimum, we determined the nonlinear refractive index n_2 [8]

$$n_2 = \frac{\Delta T_{pv}}{0.406(1-S)^{0.25} k_0 I_0 L_{eff}} = (4.8 \pm 2.4) \times 10^{-6} \text{ cm}^2 \text{ kW}^{-1}, \quad (3)$$

which gives the cubic nonlinear susceptibility

$$\chi^{(3)} = (2.3 \pm 1.2) \times 10^{-7} \text{ esu}, \quad (4)$$

where $k_0 = 2\pi/\lambda$; $L_{eff} = [1 - \exp(-\alpha d)]/\alpha$; and α is the absorption coefficient. The results of our measurements show that the values of $\chi^{(3)}$ obtained by the two methods coincide by an order of magnitude within the measurement error.

To determine the influence of polymorphous modifications of $SnCl_2$Pc, we measured the nonlinear optical susceptibility $\chi^{(3)}$ and optical density D for seven 800-nm thick films, which were preliminary annealed at different temperatures in the range from 60 to 200 °C. The results of the measurements are presented in Fig. 4. One can see that the values of $\chi^{(3)}$ and D decrease nonmonotonically with increasing the annealing temperature. Both dependences exhibit two maxima at temperatures ~ 80 and ~ 140 °C. Because the relative error of measurements of $\chi^{(3)}$ and D is lower than their changes observed in experiments, these changes can be explained by the formation of two stable polymorphous modifications at these annealing temperatures.

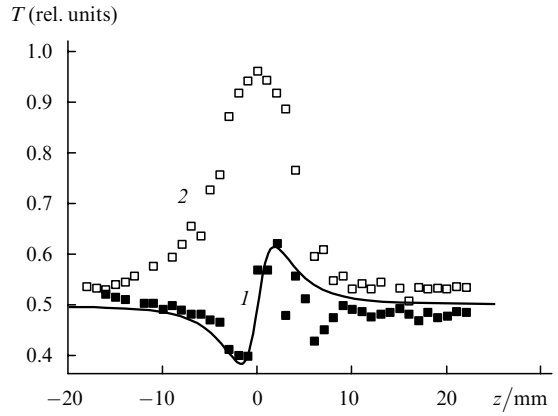

Figure 3. Nonlinear response measured by the method of nonlinear lens with a diaphragm (*1*) and without it (*2*); T is the transmission, z is the displacement of a sample from the laser beam waist.

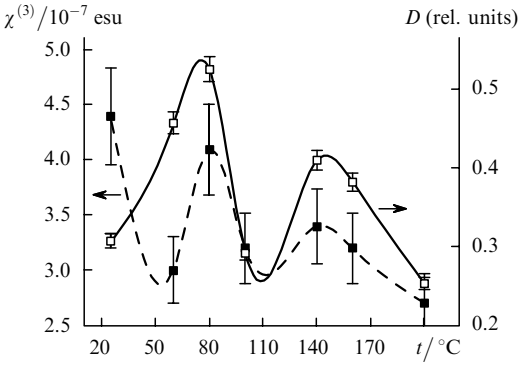

Figure 4. Dependences of the third-order nonlinear susceptibility $\chi^{(3)}$ and the optical density D of 800-nm thick films on the annealing temperature.

Note that such behaviour is observed for films of most metallophthalocyanines, in particular for Pb and VO phthalocyanine films [9, 10]. This is confirmed by our measurements of the optical density at 532 nm for thermally deposited PbPc and VOPc films annealed at different temperatures (Fig. 5). One can see from Fig. 5 that the temperature dependences of the optical density for these two phthalocyanines are similar to that for $SnCl_2$Pc (the temperature dependence for VOPc being slightly shifted to lower temperatures). Phase III that was found for other phthalocyanines is formed at a higher annealing temperature (above 200 °C) [3, 9].

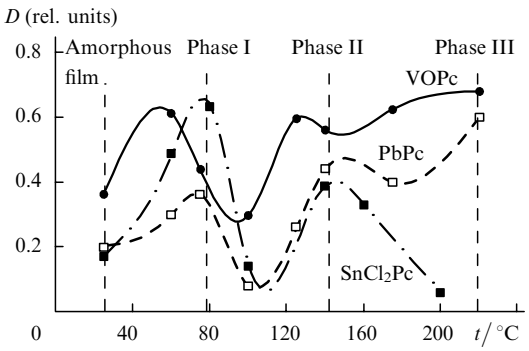

Figure 5. Optical density of thermally deposited $SnCl_2Pc$, PbPc, and VOPc films at 532 nm annealed at different temperatures.

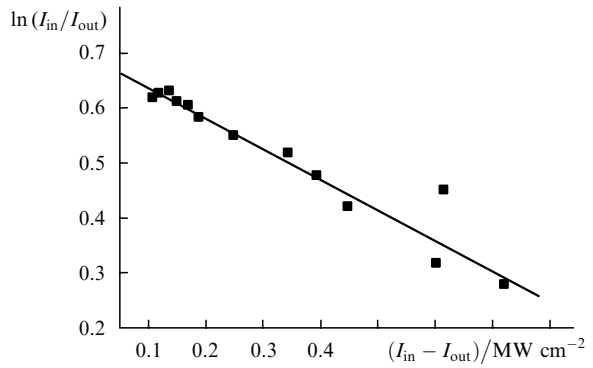

Figure 6. Dependence (*5*) and experimental data (squares) presented in Fig. 3 [(curve (*2*)].

Thus, the dependence of $\chi^{(3)}$ on the annealing temperature of the films can be explained by a change in the optical density of the films at the recording wavelength caused by a change in their crystalline structure.

Analysis of the possible mechanisms of nonlinear refraction in $SnCl_2Pc$ shows that the CT states can make a certain contribution to the nonlinear refraction of the $SnCl_2Pc$ films. This is confirmed by the correlation between the temperature dependences of the nonlinear susceptibility $\chi^{(3)}$ and the optical density D (Fig. 4) and by a noticeable role of CT states in different structural modifications of $SnCl_2Pc$ [4]. In addition, the absorption saturation (bleaching) of $SnCl_2Pc$ films at 532 nm can make a substantial contribution to their nonlinear refractive index. The bleaching of the film is clearly observed in measurements of the nonlinear susceptibility by the method of nonlinear lens [curve (*2*) in Fig. 3]. By using the data presented in Fig. 3, we can calculate the saturation intensity I_s from the expression [11]

$$\ln \frac{I_{in}}{I_{out}} + \frac{I_{in} - I_{out}}{I_s} = \alpha d, \tag{5}$$

where I_{in} and I_{out} are the radiation intensities at the input and output from a sample. Fig. 6 shows the dependence of $\ln (I_{in}/I_{out})$ on $I_{in} - I_{out}$. The slope of this dependence gives the saturation intensity $I_s \approx 1.7$ MW cm^{-2}. By expanding the expression [5]

$$\chi(I) = \frac{\chi_0}{1 + I/I_s} \tag{6}$$

for the optical susceptibility caused by the absorption saturation in a series in a small parameter $I/I_s \ll 1$ (where χ_0 is the linear optical susceptibility), we estimate the cubic nonlinear susceptibility $\chi^{(3)}$ caused by the absorption saturation. The estimate gives the value $\chi^{(3)} \approx 10^{-5}$ esu, which, however, exceeds the cubic nonlinear susceptibility obtained in the experiment. This discrepancy can be explained by the fact that the experimental cubic susceptibility $\chi^{(3)}$ is determined by different competing nonlinearity mechanisms. Thus, taking into account that the absorption of our samples at 532 nm is rather high ($\alpha \sim 3.7 \times 10^3$ cm^{-1}), we can assume that the thermal mechanism can also make contribution along with nonlinearity mechanism considered above. This contribution can be negative, resulting in a decrease in the total nonlinear susceptibility $\chi^{(3)}$ compared to its value estimated taking into account only the absorption saturation.

The mechanisms of nonlinearity of $SnCl_2Pc$ films call for further detailed investigation of the dynamics of their nonlinear response, as well as of the effect of polymorphism of the films on their nonlinear properties, which will be the subject of our further studies.

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