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Optical limiting properties of composites of iron, nickel and cobalt phthalocyanine complexes with single-wall carbon nanotubes and assessment of their efficiency by latest correlation methods

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One of the strategic directions of scientific and technological development of the Russian Federation is the creation of highly effective protection against laser radiation attack. A small series of phthalocyanine complexes with 3*d*-row metals (iron (1a), cobalt (1b), and nickel (1c)) has been synthesized. It is shown that the enhancement of the nonlinear optical response (NOR) of these dyes is possible by simply adsorbing them on the surface of single-walled carbon nanotubes (SWCNTs). The efficiency of the nonlinear absorbers has been evaluated using open aperture *Z*-scan and fixed sample position methods. It is found that the nature of the metal complexing agent allows fine-tuning of NOR properties of the materials. Thus, the highest value of the nonlinear absorption coefficient ($\beta = 650$ cm/GW) was obtained for 1c (PcNi). The estimation of the optical confinement efficiency for the obtained complexes was performed using correlation relations derived in our previous works by the state-of-the-art high performance CORRELATO method. Special „efficiency"descriptors were used, which allowed us to classify our materials into three groups within the graphical analysis. As a result, composites SWCNTs/PcFe (2a) and SWCNTs/ PcCo (2b) are found to have the best combined limiting characteristics and can meet the design requirements.

Keywords: optical limiting, composites, phthalocyanines, single-walled carbon nanotubes, *Z*-scan, CORRELATO.

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Introduction

Development of a highly effective protection against laser radiation damage is a critical issue. In industry, military affairs and geodesy, there are cases of using lasers to deal with the everyday issues. First of all, this is due to the use of lidars to automate many processes [1–3]. Pulsed laser radiation is needed for their operation, and they shall detect weak feedback signals. Avalanche photodiodes, which can be used as receiving devices, fail relatively easily when exposed to intense light [4]. In cases where CMOS and CCD cameras are used, there is also a risk of damage by laser radiation at a slightly higher threshold of destruction [5,6] in the case of re-reflection from closely located objects, especially for the long-range lidars [7,8]. Such consequences can also occur when using ultrashort pulses [9]. Only passive laser protection devices can provide sufficient performance. However, widely used light filters usually attenuate both strong and weak radiation, which prevents their use in the case of lidars. Laser radiation limiters based on nonlinear absorbers have the required properties [10]. For their use the efficient nonlinear-optical materials are required that can be characterized minimum by six parameters [11]: linear transmission, optical layer thickness, nonlinear absorption coefficient, dynamic range, threshold exposure of laser radiation and attenuation coefficient.

Phthalocyanines have high thermal stability and acid resistance, which allows them to be used in solutions, while they have a significant nonlinear optical response [11–13]. Their key benefit is the possibility of pulses decay for a time period shorter than duration of the pulse itself, which makes it possible to limit the power of short pulses [14–16]. Phthalocyanines also have high values of the dynamic range of limitation [11,17,18]. However, to use materials that may be used as laser radiation limiters, the highest possible values of the attenuation coefficient are required; this may be achieved with composite structures, which, apart from forming the phthalocyanines complexes, combine various particles [10,19].

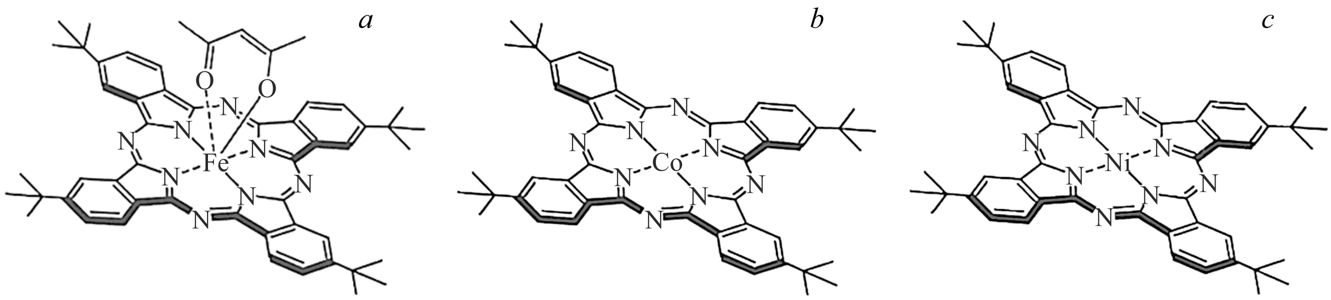

Figure 1. Structure formula of phthalocyanines with different central ions of metals: *a* — iron (1a); *b* — cobalt (1b); *c* — nickel (1c).

In this paper, single-walled carbon nanotubes (CNTs) were selected to prepare the composite structures. Phthalocyanines can be attached to them due to the formation of covalent [20] or ionic bonds [21,22], in particular, formation of dipole-ion bonds after functionalization of the nanotube surface with alkylammonium cations [23], as well as through Van der Waals forces [20], which are weaker and have an electrical nature. The dyes combine with SWCNT surface through Van der Waals forces, $\pi-\pi$ stacking, hydrophobic interactions, hydrogen bonds, and electrostatic interactions [24]. The optimal concentration of the dye for dispersion is achieved due to adsorption sites saturation on the nanotubes surface with dye molecules and formation of micelles in the solvent in case of surfactant application [25].

The created SWCNT composite structures and phthalocyanine complexes under the action of ultrasonic treatment with a submerged homogenizer have sustainable stability for a sufficient time. All prepared materials were examined by method of *Z* scanning with an open aperture, and the limiting curve was determined with a fixed position of the material.

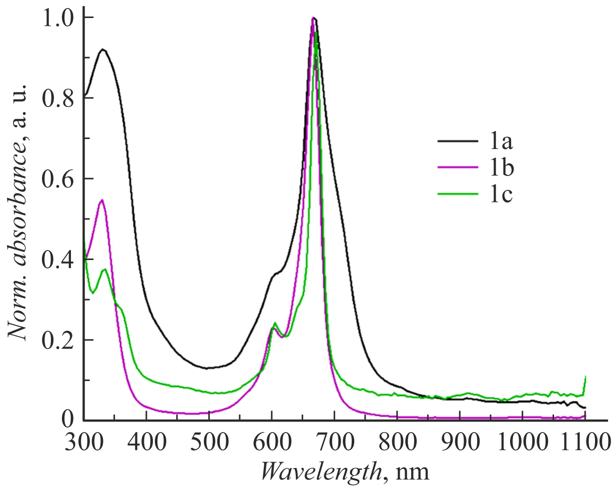

Figure 2. Electron spectra of absorption of phthalocyanine 1a–1c in DMFA (concentration $\sim 1.5 \cdot 10^{-4}$ M).

Next, the solutions of phthalocyanines 1a–c in DMFA were prepared. The dye concentration was selected based on the linear transmittance value of 75 % at a wavelength of 532 nm, at which laser measurements were carried out by recording the absorption spectra (Fig. 2).

The final stage was mixing the SWCNT dispersions in DMFA with each of the dye solutions 1a–c in the ratio of 10/3: SWCNT/iron phthalocyanine (2a), SWCNT/cobalt phthalocyanine (2b) and SWCNT/nickel phthalocyanine (2c). Mixing was carried out using an ultrasonic homogenizer at a volumetric energy density of 3230 J/ml for 10 min and a temperature of about 50 °C. One of the samples was made up of original SWCNT nanotubes and was further designated as 2d. Figure 3 shows the optical spectra of composite samples and original nanotubes.

1. Materials and research methods

1.1. Materials

Chemical structure of complexes of iron (1a), cobalt (1b) and nickel (1c) are shown in Fig. 1. The phthalocyanine ligand has a pseudo-symmetric structure, which is important for the isotropic properties of the final materials. The composite compounds of dyes 1a–c with SWCNT (TUBALL^{TM}, Russian Federation) were formed in three stages. First, the dispersions of SWCNT (0.01 mass%) in dimethylformamide (DMFA) were prepared using Soniqator Q700 ultrasonic homogenizer (Qsonica, USA) with a probe with a diameter of 13 mm operating at a frequency of 20 kHz. The processing time was 30 min at a volumetric energy density of 7560 J/ml, which was estimated using the method described in [26]. This value is determined by the rated power, the processing time and the amount of the processed sample. To avoid excessive heating during processing a cooling system was used.

1.2. *Z*-scanning with an open aperture

The studies were performed using *Z*-scanning with an open aperture [10] on the second harmonic (532 nm) of laser LS2147 (Lotis Tii Belarus) used as a radiation source. The exposure of initial (before focusing) incident pulse with a duration of 16 ns was 20 J/cm^2, which made it possible to

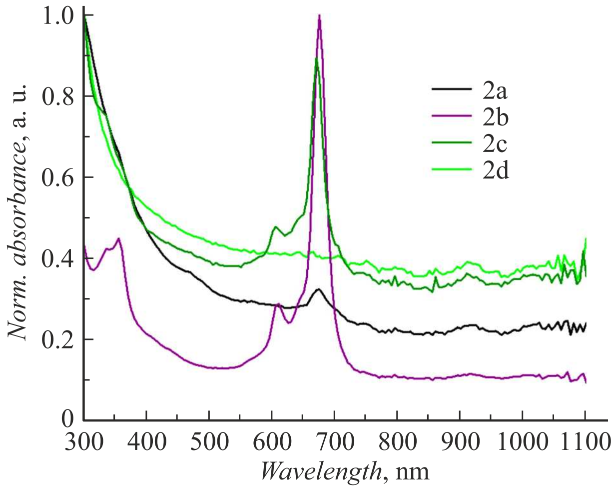

Figure 3. Electron spectra of absorption of composites dispersions 2a–2c and initial solutions of SWCNT (2d) in DMFA.

capture the area of linear interaction and the nonlinear area near the lens focus, where the greatest exposure of laser radiation was observed at constant energy of the initiating pulse.

To evaluate the material as a laser radiation limiter, it is necessary to quantify the shape of the optical limitation output signal. The measurements were performed when the sample was fixed in position of minimum normalized transmission according to the data from Zscanning with an open aperture. At this point, the value of the beam radius at the lens focus was 40 μm according to measurements by the charge-coupled device — camera SP620U (Ophir-Spiricon, Israel). The Glan-Taylor prism mounted in a rotating frame was used to smoothly change the incident energy of a single pulse.

2. Theory

The solution of the radiation transfer equation [21] for a square shape of the incident pulse with a threshold dependence of the absorption coefficient on the intensity is obtained analytically:

$$T_{\text{noom}} = \exp\left(\frac{\beta d}{\tau\sqrt{\pi}}\left(\frac{F_0}{w^2_{\text{noom}}} - F_x\right)\right). \tag{1}$$

where β — nonlinear absorption coefficient, [cm/W)]; F_0 — exposure of incident radiation; d — thickness of optical layer, [m]; τ — duration of pulse; F_x — threshold exposure of laser radiation [J/m2] defined by expression:

$$F_x = \frac{0,076}{\beta d}\frac{\tau\sqrt{\pi}}{2}, \tag{2}$$

exposure of incident laser radiation is designated F_0, [J/m^2]; τ — pulse duration, [s]; w_{norm} — normalized beam radius defined from the expression:

$$w_{\text{norm}} = \sqrt{1 + \frac{z^2\lambda^2}{\pi^2 w_0^4}}, \tag{3}$$

where z — shift of the sample relative to the lens focus, [m]; λ — wavelength, [m]; w_0 — beam radius in the lens focus, [m].

To assess the efficiency of laser radiation limiter it is required to take into account minimum five parameters: linear transmission T_0, thickness of optical layer d, nonlinear absorption coefficient β, dynamic range DR, threshold exposure of laser radiation F_x and attenuation coefficient k_A. Each value is of an individual interest. High linear transmission allows working with low-intensity radiation with the ability to measure it or monitor the site of exposure (at values above 60 %, there is no noticeable data distortion). The layer thickness should be as small as possible, but when working with liquid dispersed media, it is difficult to work with a thickness less than 0.2 cm because of viscosity, therefore, the thickness is selected less than Rayleigh length. The values of nonlinear absorption coefficient should be maximized to ensure the best attenuation. Because the dynamic range is determined by the exposure values of the incident laser radiation and the threshold exposures of the beam, it is required to provide its maximal value. With its help, the energy range of the device's operation is characterized. At the same time, small values of the exposure threshold indicate the possibility of decay of small energy values, which may also pose a threat to photosensitive devices. The attenuation coefficient, which should be maximum, is also highlighted as the main parameter. To evaluate them together, we used correlation relations derived in our previous papers using CORRELATO algorithm, which later proved their correctness [27]. The values of descriptors σ_1 and σ_2 are given in the table and their analytical expression is given below:

$$\sigma_1 = \lg\left(\frac{d^2}{\beta\cdot\ln^2(T_0)}\right). \tag{4}$$

Descriptor σ_1 is responsible for the negative effect of aggregation on the effectiveness of optical limitation. The more its value is shifted to the negative area, the more pronounced is the effect of aggregation [11,28]. In turn, the descriptor σ_2, associated with the quantum-chemical description of the nonlinearity of optical properties, should have the highest possible value:

$$\sigma_2 = \frac{k_A\beta}{DR\cdot F_{\text{thr}}}. \tag{5}$$

Calculating the values of σ_1 and σ_2 is a necessary, but not sufficient criterion for the effectiveness of limitation within the functional analysis. At the moment, the relationship of these descriptors in the bilogarithmic scale ($\theta_2\ vs\ \theta_1$) may serve as a confirmation, when the calculated values fit into

Data for assessing the efficiency of optical limitation

Sample	T_0	β, cm·GW^{-1}	F_{th}, J/cm^2	k_A	DR	σ_1	σ_2	θ_1	θ_2
1a	0.81	1	0.18	1.01	110	0.30	0.05	−1.29	−3.64
1b	0.76	97	0.13	1.05	155	−1.90	5.05	0.70	1.96
1c	0.85	650	0.08	1.41	260	−2.28	44.06	1.64	4.00
2a	0.77	2800	0.07	4.35	260	−3.31	669.23	2.83	6.69
2b	0.80	2700	0.07	3.90	260	−3.17	578.57	2.76	6.53
2c	0.85	450	0.07	1.26	260	−2.15	31.15	1.49	3.65
2d	0.80	3000	0.11	4.25	170	−3.22	681.82	2.83	6.68

a straight line:

$$\theta_1 = \lg(\sigma_2), \tag{6}$$

$$\theta_2 = \lg(\sigma_1^2 \sigma_2^2). \tag{7}$$

3. Experiment

The properties of the non-linear optical response (NOR) were studied by means of single nano-second pulses in a 0.3 cm thick cuvette which is selected taking into account the Rayleigh length of 0.9 cm. Meeting this condition makes it possible to neglect changes in the size of the laser beam inside the sample. The sample was shifted in the range from −4 to 4 cm with a spacing of 0.05 cm which is close to the lens focal distance of 6 cm.

3.1. Z-scanning with an open aperture

For all complexes of phthalocyanines 1a−c, the effect of nonlinear attenuation was obtained upon exposure to laser radiation exceeding the corresponding threshold value (Fig. 4). The nonlinear properties of free dyes were determined using the formula (1).

In Fig. 5 the data for dispersion media of composites 2a−c and free SWCNT are shown. In a similar way using the expression (1) the characteristics of these materials were obtained. The non-linear decay is clearly shown for composite 2a and in lower extent — for composites 2b and 2d.

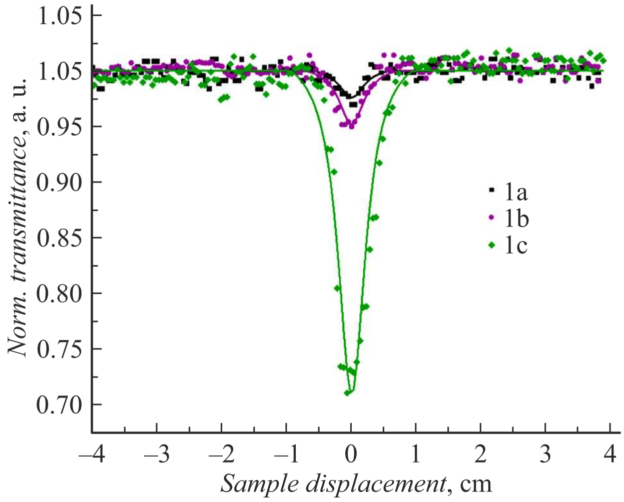

Figure 4. Change of transmission based on the data of Z-scanning with an open aperture for the phthalocyanine complexes 1a−1c. The samples were shifted relative to the lens focus in the range from −4 to +4 cm.

In contrast to the initial dyes 1a−c, in case of composites 2a−c, the optical limitation curves show a distinct deviation from the linear dependence. Nickel composite 2c exhibits the least attenuation which is evidenced by the presence of weak nonlinearity. Fig. 7 shows the results of the studies of dispersion media of composites 2a−c and free SWCNT (2d).

3.2. Effect of optical limitation

The properties of the laser radiation limiter make it possible to study the optical limitation curve, which in our study was obtained based on measurements of the nonlinear transmission at a fixed location of the material relative to the lens focus. The range from 0.04 to 15 J/cm^2 was selected for the measurements. For complexes of phthalocyanines 1a−c in DMFA, no noticeable deviation from the linear dependence was found, which is associated with a relatively small value of the nonlinear absorption coefficient β (Fig. 6).

3.3. Results

To perform correlation analysis, it is necessary to use expressions (4)−(7), substituting in them the values in dimensions from the table.

In Fig. 8, a we may see that the non-linear absorbers are grouped into individual zones. According to the boundary conditions for σ_1 and σ_2, the materials 2a,b,d, attributed to a „strong“, group may, in practice, demonstrate the best NOR properties acceptable for creation of the high-speed optical limiters. The materials 1a−c and 2c are,

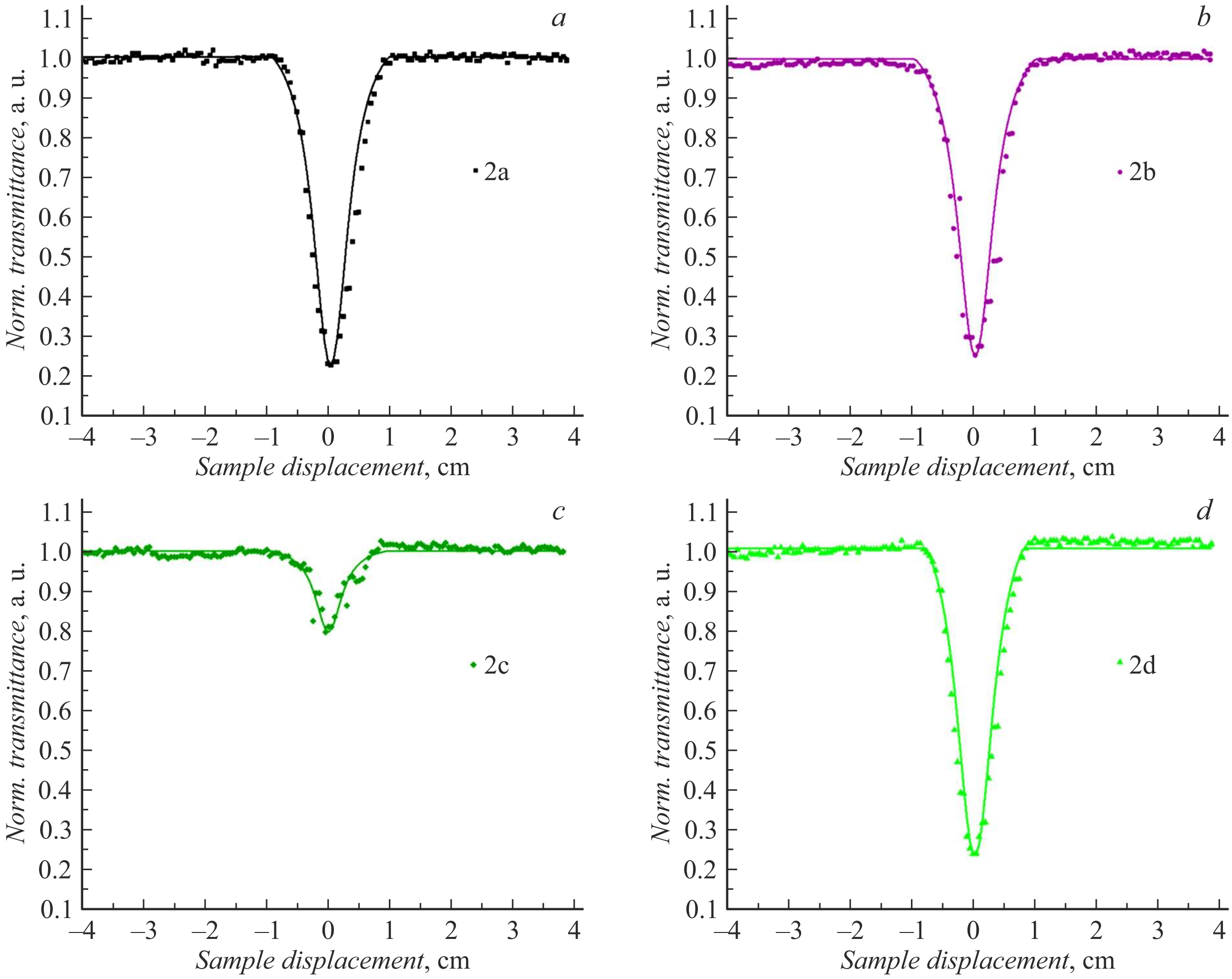

Figure 5. Change of transmission based on the data of *Z*-scanning with an open aperture for the composites and original nanotubes: *a* — 2a; *b* — 2b; *c* — 2c; *d* — 2d.

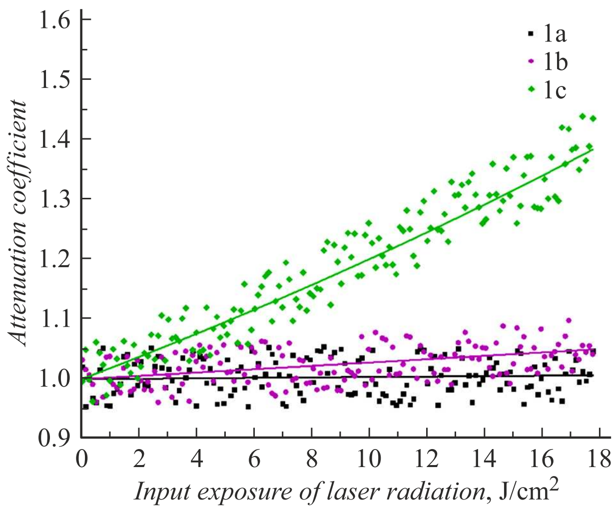

Figure 6. Attenuation coefficient versus laser radiation exposure for the complexes of phthalocyanines 1a–1c in DMFA.

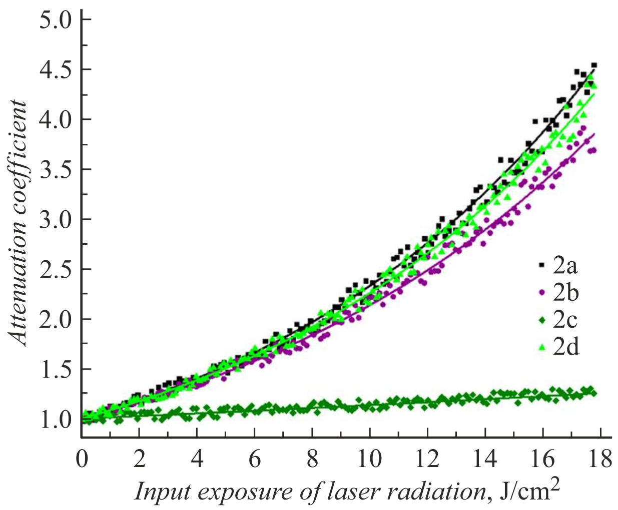

Figure 7. Attenuation coefficient versus laser radiation exposure for the composites and nanotubes 2a–2d.

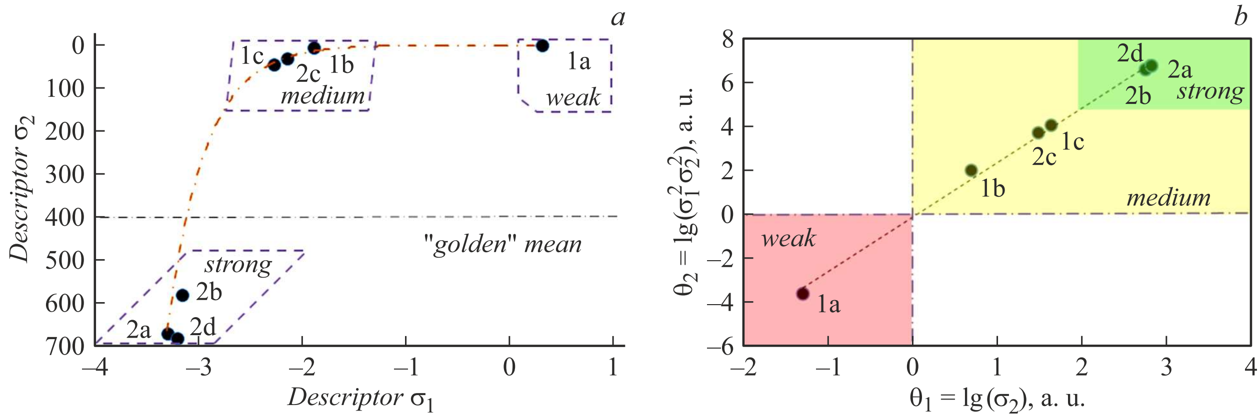

Figure 8. Zone parametric analysis of the laser radiation limiters efficiency based on the expressions (4)–(7): *a* — ratio of descriptors σ_2 *vs* σ_1; *b* — checking the validity of correlation on a bilogarithmic scale (θ_2 *vs* θ_1) to clarify the obtained result.

in their turn, located on one line. For this reason, it is needed to look at the bilogarithmic scale (Fig. 8, *b*), which allows straightening out the resulting indefinite nonlinearity. Finally, it turns out that materials 1b,c and 2c have an intermediate position in terms of efficiency and shall be attributed to group „medium", whereas nanomaterials 2a,b,d may be the most suitable ones in terms of design. It also follows from the bilogarithmic analysis that if a material falls into the range of negative values θ_1 and θ_2, then its properties in practice are likely to be unattractive and will belong to the „weak" series. Interesting is that while iron phthalocyanine 1a, by itself, has the least activity in optical limitation, after it is attached to SWCNT the final material becomes more active. The same relation is also true for the cobalt complex 1b, which after absorption on the surface of SWCNT leaves the yellow zone (Fig. 8, *b*). But for nickel phthalocyanine 1c, combining with nanotubes does not give any significant benefit. We conclude that although phthalocyanine composites with SWCNT in most cases give an increase in activity in optical limitation, such adduction itself does not guarantee the desired result.

Conclusion

In this work, three composites 2a, 2b, and 2c were created for which optical limitation properties were studied. By evaluating their efficiency with new correlation methods it was found that phthalocyanine complex of iron with SWCNT 2a manifests better combination of the non-linear optical parameters: linear transmission 0.77, non-linear absorption coefficient 2800 cm·GW^{-1}, dynamic range 260, threshold exposure of laser radiation 0.07 J/cm^2 and attenuation coefficient 4.35. This was found when comparing the prepared materials by descriptors σ_2 and σ_1 according to the results of the zone parametric analysis, which was supplemented by a bilogarithmic scale θ_2 and θ_1, which are inter-related with σ_2 and σ_1 by the relations described herein. The analysis with the use of only σ_2 and σ_1 is insufficient. It was also found that among phthalocyanines, sample 1c has the best optical limitation properties. The materials obtained by the advanced high-performance method CORRELATO are featuring the best combined optical limitation characteristics and are able to meet the design requirements for use as a working substance in laser radiation limiters.

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Conflict of interest

The authors declare that they have no conflict of interest.

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