Semiconductor Physics, Quantum Electronics & Optoelectronics, 2025. V. 28, No 1. P. 083-092.

Optoelectronics and optoelectronic devices

Efficient passive laser Q-switches based on dye-doped polyurethane for high-energy neodymium lasers

T.V. Bezrodna[1], A.M. Negriyko[1], V.I. Bezrodnyi[1], I.V. Matsnev[1], L.F. Kosyanchuk[2], O.I. Antonenko[2]

[1]*Institute of Physics, NAS of Ukraine, 46 Nauky Avenue, 03028 Kyiv, Ukraine*
[2]*Institute of Macromolecular Chemistry, NAS of Ukraine, 48 Kharkivske Avenue, 02160 Kyiv, Ukraine*
[*]*Corresponding author e-mail: tomaalone@yahoo.com*

Abstract. This paper studies energy and time operation characteristics of a laser on a Nd^{3+}:YAG crystal with passive Q-switches based on a dye-activated aliphatic polyurethane matrix with high radiation strength. A high efficiency of laser generation both in a free mode and at single pulse generation in the Q-switched regime is obtained using a samarium diffuse reflector with a $BaSO_4$ filler. A single pulse energy and duration for the lasers with passive Q-switches based on organo-nickel complex BDN and polymethine dye IR-1061 in an aliphatic polyurethane matrix polymerized by the polycondensation method from 1.6-diisocyanatohexane, poly[di(ethylene glycol) adipate] and trimethylolpropane as starting components were compared. A powerful single pulse with an energy of ~1 J was obtained in the Q-switching mode using polymethine thiopyrylo-4-tricarbocyanine dye (IR-1061). The highly efficient Q-switching caused by the use of passive laser Q-switch based on the IR-1061 dye is shown to be due to its specific linear and nonlinear spectral properties.

Keywords: solid-state laser, nonlinear absorption, saturable absorber, passive Q-switching, polyurethane matrix, dyes.

https://doi.org/10.15407/spqeo28.01.083
PACS 42.55.-f, 42.70.Hj

Manuscript received 24.07.24; revised version received 12.01.25; accepted for publication 12.03.25;

1. Introduction

Industrial need for lasers emitting light with high energy and power is constantly growing. Powerful pulsed lasers of infrared (IR) spectral region are used in a variety of applications such as ranging, marking, cutting, welding and time-resolved spectroscopy. Solid-state lasers with high output radiation energies can be implemented with lamp pumping. Such a system, unlike diode-pumped lasers, will be weakly sensitive to changes in ambient temperature. Under free-running conditions, a laser emits an irregular sequence of low-power light pulses, the total duration of which is hundreds of microseconds depending on the parameters of the pump lamp. To obtain high-power single pulses, a change (increase) in the optical cavity quality factor, the so-called Q-switching, is used. There are four types of methods that provide Q-switching: mechanical, electro-optical, acousto-optical methods and application of saturable absorption filters. Passively Q-switched lasers are the most reliable because passive Q-switches are based on a mechanism that changes the laser cavity losses in response to the changes in the laser internal photon density. Passive Q-switching elements do not require high voltage, high voltage switching electronics, acoustic transducers, and other complex devices to control Q-switching processes.

Solid-state laser passive Q-switches fully meet the modern operational requirements for the elements of laser technology. For neodymium lasers with a lasing wavelength of ~1 µm, the solid-state Q-switches are LiF:F_2^- crystals with color centers [1–3] and garnets with tetrahedrally coordinated tetravalent chromium ions, Cr^{4+}:YAG [4–6].

With a relatively high value of the absorption cross-section, $\sigma_{gs} = 1.5\cdot10^{-17}$ cm^2, LiF:F_2^- crystal-based Q-switches are applied in low- and medium-power lasers due to their good thermophysical properties and weak thermal dependence of the refractive index. However, use of LiF:F_2^- crystals is associated with a number of problems. These crystals are sensitive to temperature changes, have long relaxation times of the bleached state (~100 ns) [3], are destroyed under the influence of powerful laser radiation [7], and the color centers in them are subject to degradation over time. Due to the presence of birefringence, such Q-switches have an anisotropy that is inhomogeneous over a cross-section. This anisotropy causes abrupt changes in the direction of polarization by ±90° from pulse to pulse. Moreover, production of Q-switches encounters some technological challenges in creating active color centers in the LiF crystals. To obtain high initial absorption by the color centers at a wavelength $\lambda = 1.064\ \mu m$, which is on the long-wave edge of their absorption band, very large concentrations of the centers are required. The latter is achieved by γ-irradiation of crystals with doses of 10^6 to 10^8 R. Such irradiation conditions induce appearance of colloidal particles of alkali metal and inactive centers with parasitic absorption at $\lambda = 1.064\ \mu m$, which deteriorate the parameters of the LiF:F_2^--based Q-switches.

Cr^{4+}:YAG-based Q-switches are characterized by the nonlinear absorption anisotropy, which leads to self-induced rotation of the radiation polarization plane [4, 5], as well as by a relatively low beam strength of $E_d \sim 5\ J/cm^2$ and a small absorption cross-section at a wavelength of $1.064\ \mu m$ ($\sigma_{gs} \approx 5.7 \cdot 10^{-18}\ cm^2$). The relaxation time of the Cr^{4+}:YAG first excited state is ~3.4 µs, which significantly deteriorates the multispike mode parameters [8]. Cr^{4+}:YAG crystals make it possible to develop compact, medium-power lasers that generate nanosecond pulses with an energy of several tens mJ.

Solid-state Q-switches with organic dyes incorporated in polymer matrices do not have these disadvantages [8–11]. They are not sensitive to the polarization quality of radiation, are isotropic in both the initial and bleached states, and do not require polarizers or other anisotropic cavity elements for their operation (active Q-switching). Long duration of a linear part during formation of a single pulse in dye lasers with Q-switches results in mode discrimination on losses, which narrows the spectrum of the generated radiation. The absorption cross-section for most dyes in the ground state σ_{gs} is quite large ($\sim 10^{16}\ cm^2$). This parameter is important for implementation of Q-switching as the inequality $\sigma_{gs} >> \sigma_a$, where σ_a is the absorption cross-section of neodymium ions in the active laser element, must be fulfilled. This is necessary for the absorption saturation of the passive Q-switch to occur at a much lower intensity than the gain saturation of the active medium. For example, the σ_a value for a Nd^{3+}:YAG crystal is $8.8 \cdot 10^{-19}\ cm^2$.

In this work, optical and nonlinear optical properties of Q-switches based on organic dyes incorporated in a polyurethane matrix are investigated. A possibility of generating nanosecond powerful single pulses in a neodymium laser is tested. The pulse energy and time characteristics are studied.

2. Experimental

2.1. Polymer matrix and its properties

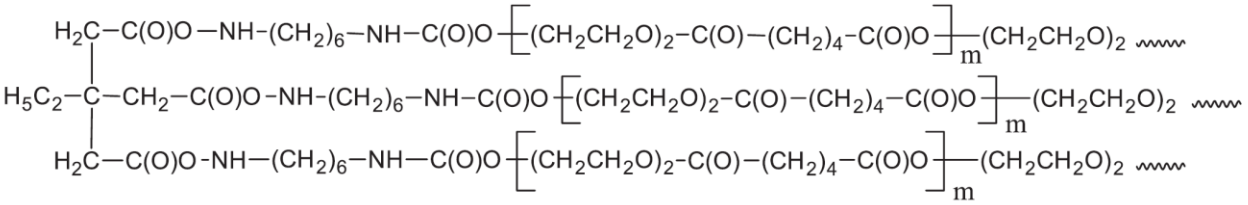
Development of high-power pulsed lasers with a single-pulse energy of ~1 J requires a set of optical components with high beam resistance. The studies [12–14] have been directed to elucidation of laser beam-induced destruction mechanisms of polymer matrices. It has been concluded that use of elastic materials exhibiting significant elastic deformations in a wide range of operating temperatures is needed to avoid such destruction. This is because a powerful radiation effect on Q-switches is associated with a pulsed thermomechanical shock that occurs during dissipation of the absorbed energy. Dealing with such conditions caused by a laser pulse, viscoelastic properties of a polymethyl methacrylate polymer matrix were improved by introducing a plasticizer (for example, ethanol), as was shown in [12, 14]. Another approach to solving the beam strength problem of polymer laser elements was to use elastomers based on polyurethane acrylate as a matrix [13, 15]. These polyurethane acrylate matrices [13, 15], whose elastic properties were preserved even in the absence of plasticizing additives, made it possible to significantly improve the radiation resistance of the laser elements at the energy densities $\geq 10\ J/cm^2$.

However, organic dyes in the polymer matrices, being obtained by the method of radical hardening (polymerization) and including, in particular, polyurethane acrylate [13, 15] and polymethyl methacrylate [12, 14], are subject to photodestruction as a result of interactions with chemically active free radicals at the stages of production and operation of such composites.

The Q-switches studied in this work are based on a colored polyurethane matrix obtained from the following components:

1.6-diisocyanatohexane $C_8H_{12}N_2O_2$,
poly[di(ethylene glycol) adipate] $HO(\text{-}CH_2CH_2O)_2\text{-}[C(O)\text{-}(CH_2)_4\text{-}C(O)O\text{-}(CH_2CH_2O)_2]_m\text{-}H$,
trimethylolpropane $C_6H_{14}O_3$.

The polymer synthesis method is based on the polycondensation reaction of an aliphatic diisocyanate with a hydroxyl-containing polyester and a low-molecular-weight diol. Scheme 1 presents a chemical structure of the produced polyurethane matrix:



Scheme 1.

The obtained multicomponent urethane polymer composition (PU) is a network elastomer, *i.e.* a continuous three-dimensional formation, in which all the constituent molecules are connected by chemical bonds of various types. An important property of this polymer is that it allows dissolving the main classes of organic dyes used in laser technology, with little formation of dimers or other more complex compounds [16]. Dealing with the polyurethanes, the probability of the appearance of dye associates in these polymers can be significantly reduced by increasing the number of functional groups in the matrix that can strongly solvate dye molecules. By varying the ratio of the components, such chemical groups can be created in the polyurethanes, which makes the latter promising for developing efficient dye laser elements [17, 18].

In this work, hardening of the polymer composition is carried out by the polycondensation method without any polymerization initiators at $t = 60$ °C. Spectral measurements have shown that the transparency window of an uncolored polymer matrix is in the region of 0.24 to 2.20 µm. Fig. 1 presents the short-wavelength transmission edge and the integral light transmission in the visible and near-IR regions that reaches $T \sim 100\%$. By varying the ratio of the components in the polymer, it is possible to change the polymer refractive index from 1.48 to 1.52, which allows obtaining almost complete immersion at the polymer-optical substrate interface when the Q-switch is fabricated in the form of triplexes. In addition to the requirements of high optical transparency in a wide spectral range, high solubility of dyes, stability of the latter during storage and operation, the polymer matrices for the dye laser elements should provide sufficient beam strength, *i.e.* resistance to powerful light radiation. This parameter of the PU exceeds 18 J/cm^2 [19].

High radiation resistance of the PU is associated with the high flexibility of its macromolecules caused by the presence of isocyanate and oligoester methylene chains. The chain fragments of the latter include oxygen atoms, which reduce the potential barrier to rotation around the –C–O– bond and, consequently, increase the macromolecule flexibility (Scheme 1). The highly elastic state of the PU matrix dissipates elastic stresses that arise due to both local thermal effects and mechanical stresses caused by electrostriction under exposure to a powerful laser pulse.

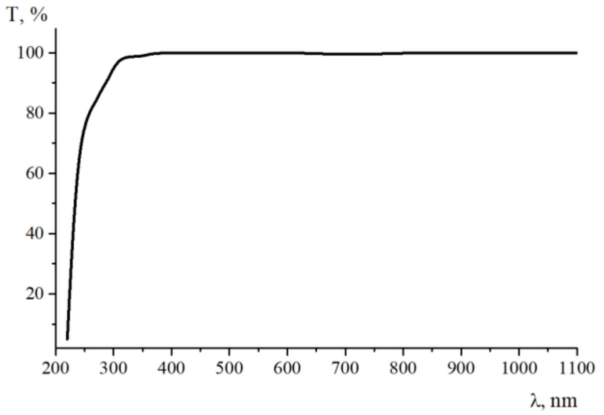
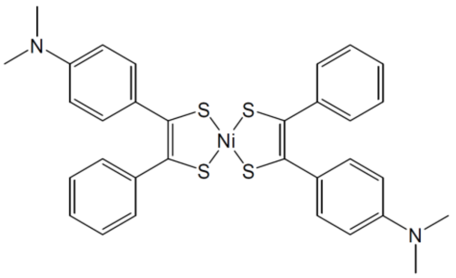


Fig. 1. Transmission spectrum of a 1 mm thick polyurethane matrix.

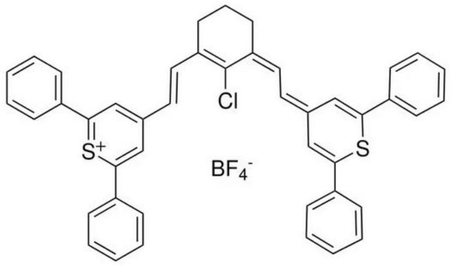
2.2. Dyes

Organic dyes operating as passive Q-switches should meet certain requirements. These compounds should have strong absorption band that coincides with the laser spectral line. The dye absorption cross-section at the band maximum should be large enough for absorption saturation of the passive Q-switch to occur at a much lower intensity than the gain saturation of the active medium.

In this work, two organic dyes were used as phototropic centers in the polymer matrix for producing Q-switches. The structures of these dye molecules are shown in Schemes 2 and 3. The absorption maximum of the main electronic transition for both dyes is located around 1.06 µm. These dyes are an organo-nickel complex BDN (bis-(4-dimethylaminodithiobenzil)-nickel) (Scheme 2), well-known for its use for creating passive Q-switches [8, 20, 21], and a poor-studied dye IR-1061 (4-[2-[2-chloro-3-[(2,6-diphenyl-4H-thiopyran-4-ylidene) ethylydene]-1-cyclohexen-1-yl]ethenyl]-2,6-diphenylthio pyriliumtetrafluoroborate) (Scheme 3) [22–24]. The mentioned compounds were purchased from Sigma-Aldrich and used without further purification.



Scheme 2.



Scheme 3.

The best operation results on the passive Q-switching of neodymium lasers in the nanosecond pulse regime have been obtained with a use of the BDN dye, compared to the other known dyes [8, 20, 21]. This dye has an absorption peak at 1.06 µm. The absorption cross-section at this wavelength is $\sigma_{gs} \approx 5.6 \cdot 10^{-17}$ cm^2. The fluorescence lifetime of the excited state is 1.5 ns. The disadvantages of this substance include the fact that it decomposes into vinyl and polymethyl methacrylate polymers even at the production stage of the composite materials [25].

The cationic dye IR-1061 is a meso-chloro-substituted thiopyrilo-4-tricarbocyanine with a trimethylene bridge group in the polymethine chain. It combines modulation and generation properties [11, 26]. The absorption

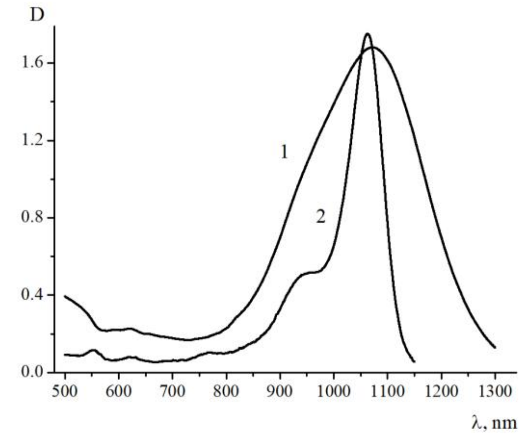


Fig. 2. Absorption spectra of the BDN (*1*) and IR-1061 (*2*) dyes in the polyurethane matrix.

at around 1.06 µm is primarily achieved by elongation of the polymethine chain. Its molecule contains 7 methine groups, which result in a high value of the absorption cross-section equal to $12.4 \cdot 10^{-16}\,\text{cm}^2$ at the generation wavelength of a neodymium laser of 1.06 µm [27]. Inclusion of a trimethylene bridging group and a chlorine atom into the polymethine chain significantly increases the IR-1061 photostability in polymer matrices [11, 16, 22]. Its fluorescence lifetime of the excited state becomes 50 ps.

The polymer Q-switches with BDN and IR-1061 dyes produced according to [8, 9, 15] were triplexes. Their optical substrates were made of K8 glass. A colored PU composition was used as a polymer layer between the glass surfaces. The production method of these Q-switches is acceptable for laboratory conditions. The electronic absorption spectra of the Q-switches measured on a Shimadzu UV-3100 spectrophotometer are presented in Fig. 2. The curves have a shape of a long-wave absorption band [16, 22] with the maxima around 1.06 µm, characteristic of typical organic dyes.

3. Theoretical

To study the possibility of obtaining high-power single-pulse laser generation, it is necessary to optimize the cavity elements, including the Q-switch. To estimate the parameters of the laser elements and Q-switched generation, we use a system of rate equations [28], which describe the rate of the photon density change inside the cavity, the numerical value of population inversion in the active medium, and the population density at the lower molecular level of the passive Q-switch:

$$\frac{d\Phi}{dt} = \frac{\Phi}{t_c}\left(2\sigma_a n_a l_a - 2\sigma_{gs} n_{gs} l_s - 2\sigma_{es} n_{es} l_s - \ln\frac{1}{R} - L\right) \quad (1)$$

$$\frac{dn_a}{dt} = R_p - c\sigma_a n_a \Phi\,, \quad (2)$$

$$\frac{dn_{gs}}{dt} - c\sigma_{gs} n_{gs}\Phi + \frac{n_{es}}{\tau_s}\,, \quad (3)$$

$$n_{gs} + n_{es} = n_0\,, \quad (4)$$

Here, Φ is the photon density inside the cavity, n_a is the inverse population in the active medium, σ_a is the effective cross-section of stimulated emission in the active element, l_a is the active medium length, n_{gs} and n_{es} are the populations of the Q-switch centers in the ground and excited states, n_0 is the initial density of the absorption centers, σ_{gs} and σ_{es} are the absorption cross-sections from the ground and excited states of the Q-switch centers, l_s is the Q-switch length, τ_s is the relaxation time of the dye excited state, R is the reflection coefficient of the output mirror, L is the passive losses of the cavity, R_p is the pump speed, c is the speed of light in vacuum, and $t_c = 2L_c/c$ is the complete round trip time of the cavity optical length L_c, respectively.

Eqs. (1) to (3) are the coupled rate equations that describe evolution of a single passively Q-switched laser pulse, the Q-switch initial state before bleaching starts and its excited state, using a four-level energy model of phototropic centers.

The presented system of the rate equations assumes presence of a plane wave and a uniform population inversion in the gain medium. This approach neglects the duration of a lamp pump pulse and spontaneous emission in the active element because of to the rapid switching of the quality factor of the cavity. Therefore, the change in inversion due to lamp pumping and spontaneous emission is quite small during Q-switching and pulse generation.

The necessary condition for effective Q-switching is $\sigma_{gs} >> \sigma_a$ for our choice of dyes. This condition is met by an active laser medium (Nd^{3+}:YAG). The values of the cross-sections of the Q-switch absorbing centers and the laser element are mentioned above. The energy and duration of laser pulses with passive Q-switching depend on the Q-switch initial transmission coefficient T_0. Lowering the T_0 value broadens the range of the changes in losses and inverse population. As a result, the pulse duration decreases and the pulse amplitude increases. The system of equations (1)–(4) allows a qualitative estimation of the dependence of laser output generation on the pump pulse energy and the Q-switch parameters.

From Eqs. (1)–(4), we can obtain the intensity-dependent absorption coefficient [28]:

$$\alpha_0(I) = \frac{\alpha_0}{1 + I_i/I_s}\,, \quad (5)$$

where α_0 is the weak signal absorption coefficient, I_i is the current intensity value, and I_s is the saturation intensity determined from

$$I_s = \frac{h\nu}{\sigma_{gs}}\,, \quad (6)$$

Here, h is the Planck's constant and ν is the transition frequency, respectively. Important characteristics of Q-switches are T_0, the saturation intensity I_s and the maximum transmission coefficient in the cleared state $T_{\max}$. The initial transmittance T_0 can be determined from

$$T_0 = \exp\left(-\alpha_0 l_s\right) = \exp\left(-n_0 \sigma_{gs} l_s\right). \tag{7}$$

Moreover, the value of T_0 can be directly measured by spectral instruments such as spectrophotometers. The current value of the Q-switch transmittance with an ideal nonlinear absorber T_i as a function of the radiation intensity I_i is expressed by the following equation:

$$T_i = \frac{I_s}{I_i}\ln\left[1+\left(e^{I_i/I_s}-1\right)T_0\right]. \tag{8}$$

This expression reduces to $T_i = T_0$ at $I_i < I_s$ and $T_i = 1$ at $I_i > I_s$. For a non-ideal absorber in the Q-switch (presence of absorption from the S_1 level, uncontrolled scattering, *etc.*), the transmission coefficient T_n can be approximated by the following expression:

$$T_n = T_0 + \frac{T_i - T_0}{1 - T_0}\left(T_{\max} - T_0\right) \tag{9}$$

and the maximum transmittance $T_{\max}$ is given by

$$T_{\max} = \exp\left(-n_0 \sigma_{es} l_s\right). \tag{10}$$

The cross-sections σ_{gs} and σ_{es} are needed to set the optimal absorption value of a real saturable element. The first parameter is found from the absorption spectra using the Bouguer–Lambert law. The value of the second parameter is determined using a complex flash photolysis technique. However, in the absence of additional absorption, except from the S_0 and S_1 levels, the following equations may be used [28]:

$$2\sigma_{gs} n_0 l_a = \ln\left(1/T_0^2\right), \tag{11}$$

$$2\sigma_{es} n_0 l_a = \ln\left(1/T_{\max}^2\right). \tag{12}$$

The value of σ_{es} for a given T_0 can be obtained from these equations by experimentally determining $T_{\max}$. Knowing the values of T_0 and $T_{\max}$, the parameter δ, being a contrast (the ratio of the optical densities D of the absorber in the initial D_0 and bleached D_s state), can be introduced. The value of δ is defined by the residual losses in the cleared state and depends on the energy structure of the saturated dye. Alternatively, a difference between the transmittance value in the cleared state and T_0, ΔT, can be introduced. Comparison of the values of ΔT for the two Q-switches is applicable if the T_0 values for both switches are the same or close.

4. Results and discussion

Neodymium-doped yttrium aluminum garnet (Nd^{3+}:YAG) crystals are the most commonly used active media for high- and medium-power solid-state lasers. In our work, we used Nd^{3+}:YAG with the dimensions of Ø6×110 mm (Altechna, Lithuania), placed in a single-lamp monoblock illuminator (Kigre, Inc, USA). A distinctive feature of this illuminator is that it uses a samarium diffuse reflector with a highly reflective $BaSO_4$ filler, which ensures a high degree of gain uniformity over a cross-section of the active element. In high-gain active laser environments, parasitic oscillations, especially when using specular reflectors, can limit the maximum stored energy and, therefore, the maximum gain. This is particularly true for Nd^{3+}:YAG active elements used as high-power Q-switched oscillators. A diffuse reflector provides a nearly homogeneous distribution of the excited Nd^{3+} ions in the active medium, reducing the possibility of parasitic oscillations. Optical pumping was carried out with a QXF-series pulsed lamp (Perkin-Elmer Optoelectronics) with xenon filling. A flat cavity with a length $L_c = 24$ cm was formed by two mirrors with the reflection coefficient $R_1 = 100\%$ and output $R_2 = 27\%$. The energy efficiency of the laser was tested in the free lasing mode. The pulse lamp was pumped using power supplies LTI-5 (pump range from 4.5 to 37.5 J) and BPL 66/33 (pump range from 43 to 65 J).

Fig. 3 shows the output/pump energy dependence when Q-switching elements were not used. At the electrical pumping energy of 65 J, the laser output energy in the free-running mode is 2.87 J, which corresponds to an efficiency of 4.4%. The laser generates radiation with a wavelength $\lambda = 1.064$ µm at the $^4F_{3/2}$–$^4F_{11/2}$ transitions of neodymium atoms. The pumping efficiency from the BPL 66/33 unit is somewhat lower, since its storage capacitor discharge time is 100 µs. In its turn, the discharge time of LTI-5 is 180 µs, which is close to the upper level lifetime of laser transitions, *i.e.* the fluorescence lifetime, of Nd^{3+}:YAG equal to 230 µs. The laser efficiency in the free-running mode with a LTI-5 power supply is 5.1%, which is reflected in Fig. 3. Namely, the left part of the curve has a larger slope as compared to its right side (obtained with a BPL 66/33 power supply) corresponding to the efficiency of 4.4%. Therefore, the lighting duration of the pump lamp in the pulsed laser generation mode should be close to the upper level lifetime of laser transitions in neodymium ions.

Along with the high beam resistance, Q-switches should have the highest possible efficiency when generating a single pulse. Efficiency of passive Q-switching η,

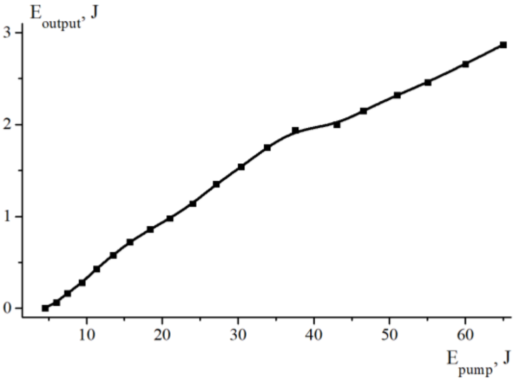


Fig. 3. Laser output energy *versus* pumping input energy in a free-running mode.

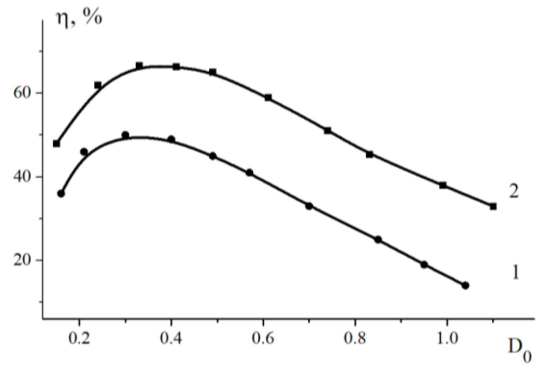
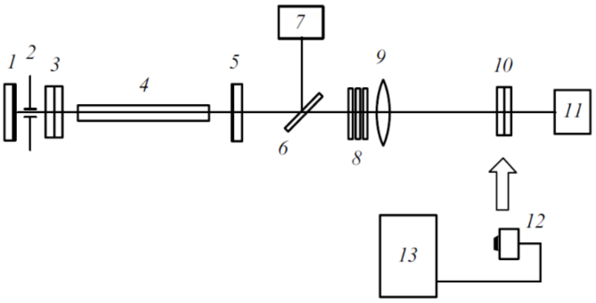


Fig. 4. Free generation conversion efficiency into a single pulse *versus* initial optical density of a polymer Q-switch on BDN (*1*) and IR-1061 (*2*) dyes.

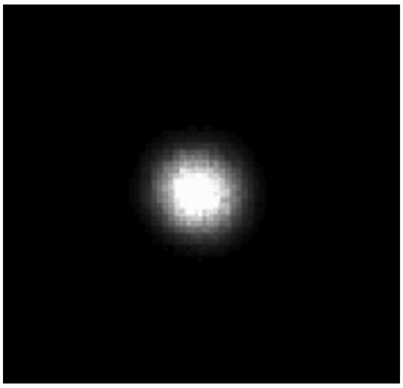
defined as the ratio of the energy of a single pulse at the lasing threshold and free lasing at equal pumping, was studied on a Q-switch for the cases of BDN and IR-1061 dyes in a PU matrix. Fig. 4 presents characteristic curves of the efficiency η *versus* initial density D_0, obtained using a Nd^{3+}:YAG laser in a multimode operation. The free generation and single pulse energies were measured with an IMO-2N calorimeter by a standard method. The obtained data indicate more effective clearing of the Q-switch on the IR-1061 dye as compared to the BDN based one.

To reveal the reasons for different values of η of the studied Q-switches, their nonlinear transmission (the output/input energy ratio) was measured. For this purpose, a laser operating in a single-mode (transverse index) regime was assembled. Optical scheme of the Nd:YAG laser cavity and nonlinear transmission detection is shown in Fig. 5a. The test laser operating in a Q-switching mode provided the following single pulse parameters: duration τ_p = 18 ns and energy W_p = 20 mJ. The samples under study were placed in a focus of the lens. The cross-section area of the beam in the lens focal point was measured with a laser radiation analyzer from SPIRICON (LBA-300PC with a FTS170 camera). Fig. 5b presents a cross-section of a radiation beam incident on the studied Q-switch samples. The nonlinear transmission was defined as the ratio of the light energy transmitted through the sample to the incident one. The energy of the incident beam was varied by neutral light filters (*8*, Fig. 5a). The signals from photodiodes (*7, 11*, Fig. 5a) were fed to a S1-104 oscillograph.

The transmission curves in Fig. 6 indicate a nonlinear dependence of the absorption coefficient on the energy density of the incident radiation. Practically, saturable absorbers never reach the transmission $T = 100\%$. The modulation depth defined as $\Delta T = T_{\max} - T_0$ is determined by the spectroscopic characteristics of the dye molecules, which mainly define the loss of the radiation energy to maintaining the clearing state. The residual losses and, hence, the efficiency of Q-switching η are largely dependent on the interaction of the high-power laser radiation not only with the Q-switch molecules in the ground electronic state S_0, but also with the electronically excited molecules on the levels S_1, S_2. To study absorption spectra at these levels, special techniques (such as laser flash photolysis) are required, the use of which is not the scope of the present research. Qualitative information about the absorption cross-section ratio for the $S_0 \rightarrow S_1, S_2$ transitions around $\lambda = 0.532$ µm (at which two-photon absorption of laser radiation occurs) can be retrieved from the absorption spectra of the BDN and IR-1061 dyes (Fig. 2). This ratio for the IR-1061 dye is smaller than for BDN, which has a positive effect on the increase in the modulation depth ΔT of the polymethine dye in comparison with that of a Ni complex (Fig. 6).



(a)



(b)

Fig. 5. Experimental scheme for studying nonlinear transmission (a) and a laser beam cross-section at the sample location (b): *1* – “deaf” mirror, *2* – diaphragm, *3* – Q-switch, *4* – Nd^{3+}:YAG rod, *5* – output mirror, *6* – beam splitter, *7, 11* – photodiodes, *8* – neutral density filters, *9* – lens, *10* – sample under study, *12* – CCD camera, *13* – oscilloscope.

Moreover, and this is most likely the main positive factor, the ground state absorption cross-section of the IR-1061 dye at $\lambda = 0.1064$ µm is significantly higher (22 times) than that of BDN. The consequence of the mentioned difference is a greater value of the modulation depth for the IR-1061 dye ($\Delta T = 51.3\%$) as compared to the BDN ($\Delta T = 37.6\%$) at equal T_0 values. The efficiency of Q-switching η tested in a laser is higher when the IR-1061 dye is used than that for the BDN dye (Fig. 4). Moreover, when the absorption cross-sections of the IR-1061 dye with the widely used Cr^{4+}:YAG Q-switch

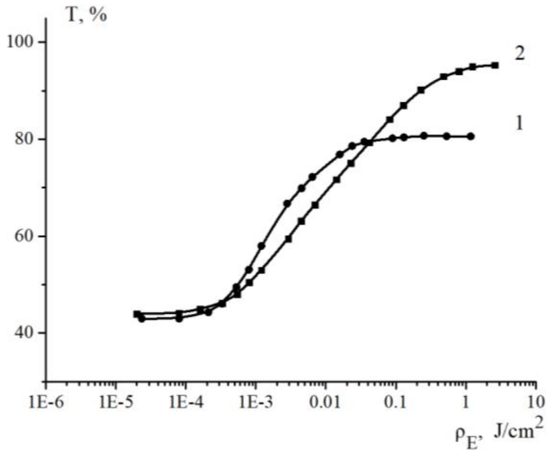


Fig. 6. Nonlinear transmission *versus* energy density of radiation incident on the Q-switch: for the BDN (*1*) and IR-1061 (*2*) dyes.

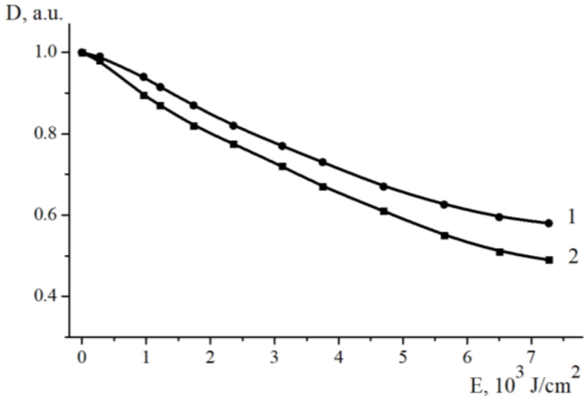


Fig. 7. Optical density of the dyes at the absorption maximum of the polymer matrix *versus* energy dose of irradiation with a mercury lamp: for the BDN (1) and IR-1061 (2) dyes.

are compared, this difference is even greater (more than 200 times), which results in $\Delta T = 30\%$ for a Cr^{4+}:YAG [4]. According to Fig. 6, the saturation intensity I_s for BDN is significantly smaller than that for the IR-1061 dye due to the large difference in the excited state relaxation times τ_s, 1.5 ns and 50 ps, respectively. For this reason, to obtain the same single-pulse energy, one needs to use a Q-switch on the IR-1061 dye with a larger T_0 value. Therefore, there is a qualitative correlation with Eqs. (7)–(10).

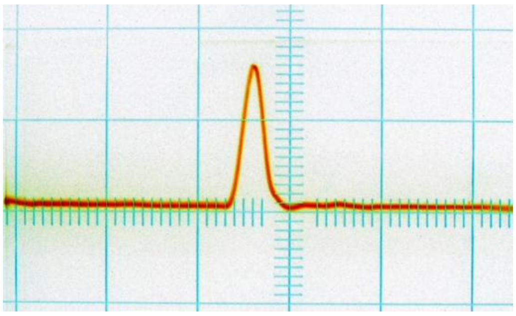


Fig. 8. Oscillogram of a laser single pulse with the Q-switch on the IR-1061 dye (T0 = 10%). The time scale is 50 ns/div.

For practical use, colored polymer elements should have maximum dark and photochemical stability. There is a correlation between these characteristics. For a quick experiment, we used irradiation with an ultra-high pressure mercury lamp DRK-120. To study photostability, polymer samples in the form of triplexes based on quartz glass as the substrates were prepared. The optical density D at the main electronic transition maximum of the BDN and IR-1061 dyes was equal to unity. The thickness of the dye-doped PU was ~400 µm. The light intensity in the irradiation zone of the samples was ~45 mW/cm^2. The change in the optical density D with the dose E of the incident light was monitored at the maximum of the dye main absorption band using a Shimadzu UV-1800 spectrophotometer. The kinetics of sample bleaching is shown in Fig. 7. The photostability of the IR-1061 based sample was somewhat lower than that of the BDN one. Oxygen, in particular high-reactivity singlet oxygen, is known for its ability to oxidize polymethine dyes more efficiently than organometallic complexes [16, 22, 27]. The subject of our further research is to search the ways to increase the stability of polymethine dyes in polymer matrices by removing oxygen or neutralizing it with various impurities.

Analysis of Eqs. (7)–(12) derived from Eqs. (1)–(3) shows that an output mirror of a cavity with a reflection coefficient ~ 20–35% and initial transmission of the dye-based Q-switch T_0 = 5–20% should be used to obtain a single pulse of high energy and power. The pumping threshold should be determined experimentally, since the value of the ratio of the gain and dissipative losses is unknown. These hard-to-quantify losses include non-saturable ones within the saturable absorber as well as all the useless losses such as those due to non-ideality of the transmitting and reflecting surfaces in the cavity, scattering or absorption in the laser crystal or other intracavity optics, and diffraction losses.

Using the above-described emitter and the BPL 66/33 power supply with an electric pump energy of 65 J, a single pulse of 0.96 J was obtained on the IR-1061 dye Q-switch at T_0 = 10%. The duration of a single pulse at half maximum was 11 ns (Fig. 8). The oscillogram was taken from the oscilloscope screen. The generated pulse had a symmetrical shape, high amplitude and temporal stability. The energy of the laser generation pulse was measured using a standard method with an IMO-2N device. The temporal characteristics of generation (duration and profile of a single pulse) were recorded by a FK-19 photodetector and a S7-19 oscilloscope. In a case of T_0 = 8%, a single pulse with a duration of 16 ns and an energy of 0.78 J was obtained. The pulse shape was also symmetrical, similar to that shown in Fig. 8.

5. Conclusions

This work showed that passive Q-switches based on highly resistant aliphatic polyurethane matrix activated with a thiopyrylo-4-tricarbocyanine dye provided powerful single pulses of an energy ~1 J. Efficient Q-switching with a polymethine dye is a result of more optimal linear and nonlinear spectral properties as compared to those of a widely used organo-nickel complex. Laser performance of a neodymium laser with a Nd^{3+}:YAG active element placed in a highly reflective samarium diffuse reflector was tested. The pumping efficiency as a function of the capacitor discharge time was investigated. It was shown that to obtain the maximum generation energy, the pumping duration by a flash lamp should be close to the upper level lifetime of the laser transition in the active element. The efficiency in the free mode of 5.1% was obtained, which was close to that of $Nd^{3+}:KGd(WO_4)_2$ lasers. However, the latter have significantly worse thermo-mechanical properties as compared to Nd^{3+}:YAG [29].

Highly efficient generation of powerful single pulses obtained in this work exceeds the best analogues of Q-switched lasers due to use of a highly beam resistant original polymer matrix in aliphatic polyurethane based Q-switches. Use of polymethine dye in the Q-switches provided significantly higher efficiency of a pulsed neodymium laser with passive Q-switching.

Acknowledgements

The work was partially supported by the Project B/210 “Generation of highly coherent laser fields, development of methods and means of controlling their characteristics, and research of quantum effects in the interaction of atoms, molecules, nano- and microparticles with laser fields with controlled parameters” of the National Academy of Sciences of Ukraine.

References

1. Chen J., Fu I.K., Lee S.P. LiF:F_2^- as a high repetition rate Nd:YAG laser passive modulator. *Appl. Opt.* 1990. **29**, No 18. P. 2669–2674. https://doi.org/10.1364/AO.29.002669.
2. Chen Y.F., Tsai S.W., Wang S.C., Chen J. A diode-pumped high power Q-switched and self-mode-locked Nd:YVO_4 laser with a LiF:F_2^- saturable absorber. *Appl. Phys. B.* 2001. **73**. P. 115–118. https://doi.org/10.1007/s003400100615.
3. Carson C.G., Goueguel C.L., Sanghapi H. *et al.* Evaluation of a commercially available passively Q-switched Nd:YAG laser with LiF:F_2^- saturable absorber for laser-induced breakdown spectroscopy. *Opt. Laser Technol.* 2016. **79**. P. 146–152. http://doi.org/10.1016/j.optlastec.2015.12.004.
4. Shimony Y., Burshtein Z., Kalisky Y. Cr^{4+}:YAG as passive Q-switch and Brewster plate in a pulsed Nd:YAG laser. *IEEE J. Quantum Electron*. 1995. **QE-31**, No 10. P. 1738–1741. https://doi.org/10.1109/3.466043.
5. Jazi M.E., Baghi M.D., Hajimahmodzadeh, Soltanolkotabi M. Pulsed Nd:YAG passive Q-switched laser using Cr^{4+}:YAG crystal. *Opt. M. Laser Technol.* 2012. **44**. P. 522–527. https://doi.org/10.1016/j.optlastec.2011.08.013.
6. Maleki A., Dindarlu M.H.M., Saghafifar H. *et al.* 57 mJ with 10 ns passively Q-switched diode pumped Nd:YAG laser using Cr^{4+}:YAG crystal. *Opt. Quant. Electron*. 2016. **48**. P. 1–12. https://doi.org/10.1007/s11082-015-0332-x.
7. Efimov O.M., Mekryukov A.M., Reiterov V.M. Optical breakdown of crystals containing radiation-generated color centers. *Sov. J. Quantum Electron.* 1989. **19**, No 12. P. 1620–1623. https://doi.org/10.1070/QE1989v019n12ABEH009838.
8. Bezrodnyi V.I., Ishchenko A.A. High-energy single pulse and multi-spike operation with a passive polymer Q-switch. *Opt. Laser Technol.* 2002. **34**. P. 7–13. https://doi.org/10.1016/S0030-3992(01)00080-9.
9. Bezrodnyi V.I., Vovk L.V., Derevyanko N.A. *et al.* nanosecond polymer passive switch for neodymium lasers. *Quantum Electron.* 1995. **25**. P. 229–231. https://doi.org/10.1070/QE1995v025n03ABEH000332.
10. Chen J., Kung H.-Ch., Yau H.-F. *et al.* Passive Q-switches for Nd:hosted solid state lasers. *Opt. Rev*. 2000. **7**, No 6. P. 511–519. https://doi.org/10.1007/s10043-000-0511-1.
11. Bezrodnyi V.I., Derevyanko N.A., Ishchenko A.A., Kropachev A.V. Highly efficient passive Q-switches for a neodymium laser based on thiopyrylotricarbocyanine dyes. *Quantum Electron*. 2009. **39**, No 1. P. 79–83. https://doi.org/10.1070/QE2009V039N01ABEH013832.
12. Gromov D.A., Dyumaev K.M., Manenkov A.A. *et al.* Efficient plastic-host dye lasers. *J. Opt. Soc. Am. B.* 1985. **2**. P. 1028–1031. https://doi.org/10.1364/JOSAB.2.001028.
13. Bezrodnyi V.I., Tikhonov E.A. Polymer passive Q-switch. *Quantum Electron*. 1986. **13**, No 12. P. 2486–2490. https://doi.org/10.1070/QE1986v016n12ABEH008515.
14. Dyumaev K.M., Manenkov A.A., Maslyukov A.P. *et al.* Dyes in modified polymers: problems of photostability and conversion efficiency at high intensities. *J. Opt. Soc. Am. B*. 1992. **9**. P. 143–151. https://doi.org/10.1364/JOSAB.2.001028.
15. Bezrodna T.V., Bezrodnyi V.I., Negriyko A.M., Kosyanchuk L.F. Spectral, photophysical and lasing properties of Rhodamine dyes in the polyurethane acrylate matrix. *Opt. Laser Technol.* 2021. **138**. P. 106868. https://doi.org/10.1016/j.optlastec.2020.106868.
16. Ishchenko A.A. Molecular engineering of dye-doped polymers for optoelectronics. *Polym. Adv. Technol.* 2002. **13**, No 10–12. P. 744–752. https://doi.org/10.1002/pat.269.

17. Kosyanchuk L.F., Kozak N.V., Babkina N.V. *et al.* Irradiation effects and beam strength in polyurethane materials for laser elements. *Opt. Mater*. 2018. **85**. P. 408–413. https://doi.org/10.1016/j.optmat.2018.09.010.
18. Bezrodna T., Negryiko A., Bezrodnyi V., Kosyanchuk L. Dipole moments of phenalenone dyes determined in liquid and polymer polar media. *J. Mol. Liq*. 2018. **267**. P. 89–95. https://doi.org/10.1016/j.molliq.2018.02.071.
19. Kosyanchuk L.F., Kozak N.V., Babkina N.V. *et al*. The dynamic characteristics of polyurethane matrix of dye laser solid-state active elements. *Fr.-Ukr. J. Chem*. 2016. **4**, No 2. P. 40–46. https://doi.org/10.17721/fujcV4I2P40-46.
20. Purnima, Mohan D., Gupta U., Jyoti D. Laser induced optical bistability in nickel-complex dye. *J. Opt*. 2012. **41**, No 3. P. 173–177. https://doi.org/10.1007/s12596-012-0081-1.
21. Purnima, Mohan D., Rani S. Optical nonlinear refractive and limiting behavior of nickel complex dye doped solid-state matrix for both visible and near infra-red nanosecond excitations. *Optik*. 2013. **124**. P. 1741–1745. http://doi.org/10.1016/j.ijleo.2012.05.011.
22. Ishchenko A.A. *Structure and Spectral-Luminescent Properties of Polymethine Dyes*. Naukova Dumka, Kiev, 1994.
23. Prosposito P., Casalboni M., De Matteis F. *et al.* IR-luminescent molecules in hybrid materials. *J. Sol-Gel Sci. Technol.* 2003. **26**. P. 909–913. https://doi.org/10.1023/A:1020732623656.
24. Bogdanovich M.V., Bondarev S.L., Dudikov V.N. et al. Polymethine dye-based optical compounds for diode pumped Nd:YAG laser systems. *Optik*. 2021. **245**. P. 167634. https://doi.org/10.1016/j.ijleo.2021.167634.
25. Enmanji K. Bleaching of bis[l-(4-dimethylamino phenyl)-2-phenylethanedithione]-nickel(0) in polymer solution and polymer matrix. *Bull. Chem. Soc. Jpn.* 1987. **60**, No 9. P. 3087–3092. https://doi.org/10.1246/bcsj.60.3087.
26. Bezrodnyi V.I., Ishchenko A.A. High efficiency lasing of a dye-doped polymer laser with 1.06 μm pumping. *Appl. Phys. B*. 2001. **73**, No 3. P. 283–285. https://doi.org/10.1007/s003400100646.
27. Ishchenko A.A., Kurdyukova I.V., Bogdanovich M.V. *et al.* Electronic structure and spectral-fluorescent properties of thiopyrylo-4-tricarbocyanine laser dyes. *Opt. Spectrosc*. 2021. **129**. P. 926–934. https://doi.org/10.1134/S0030400X21070080.
28. Degnan J.J. Optimization of passively Q-switched lasers. *IEEE J. Quantum Electron*. 1995. **31**, No 11. P. 1890–1901. https://doi.org/10.1109/3.469267.
29. Musset O., Boquillon J.P. Flashlamp-pumped Nd:KGW laser at repetition rates up to 50 Hz. *Appl. Phys. B*. 1997. **65**. P. 13–18. https://doi.org/10.1007/s003400050242.

Authors and CV

Tamara V. Bezrodna, PhD, Senior Researcher at the Photoactivity Department of the Institute of Physics, NAS of Ukraine. Author of more than 150 scientific publications. Her research field is development of new nanocomposite functional materials based on organic matrices of various types (liquid crystals, polymers), doped with inorganic nanoparticles (aerosil, clay minerals, carbon nanotubes), as well as polymer materials based on aliphatic and aromatic polyurethanes doped with organic laser dyes; the structure, phase transitions and spectral properties of such nanocomposite systems.
https://orcid.org/0000-0003-1935-7475

Anatoliy M. Negriyko, DrSci, Corresponding Member of the NAS of Ukraine, Head of the Laser Spectroscopy Department at the Institute of Physics, NAS of Ukraine. His current research activities are laser physics, high resolution laser spectroscopy, interaction of laser radiation with matter, laser applications. He is the author of more than 140 scientific papers and 2 books.
E-mail: negriyko@iop.kiev.ua,
https://orcid.org/0000-0002-2954-5157

Volodymyr I. Bezrodnyi, PhD, Leading Researcher at the Laser Spectroscopy Department of the Institute of Physics, NAS of Ukraine. Author of more than 130 scientific publications. His scientific interests include complex research and development of new functional materials based on polyurethane polymers and laser dyes of various classes; structure, spectral and photophysical properties, aggregation and intermolecular interactions of dye molecules in the polymers, factors that affect dye photostability in such materials during their synthesis and applications.
E-mail: bezrod@iop.kiev.ua,
https://orcid.org/0000-0001-9965-8707

Igor V. Matsnev, Junior Researcher at the Institute of Physics, NAS of Ukraine. Authored 16 scientific publications. The area of his scientific interests is nonlinear laser spectroscopy of atoms and molecules, laser physics.
E-mail: matsnev.igor@gmail.com,
https://orcid.org/0000-0002-5716-2081

Lyudmila F. Kosyanchuk, PhD, Senior Researcher at the Department of Physical-Chemical Polymers, Institute of Macromolecular Chemistry, NAS of Ukraine. Author of more 140 publications. Her scientific interests are polyurethanes doped with dyes of various classes (phenalenone, xanthene, polymethine, oxazine) as appropriate polymer matrices in active elements of solid-state lasers based on organic dyes. E-mail: lkosyanchuk@ukr.net, https://orcid.org/0000-0002-3617-9538

Oksana I. Antonenko, PhD, Senior Researcher at the Department of Physical-Chemical Polymers, Institute of Macromolecular Chemistry, NAS of Ukraine. Author of more 60 publications. Her scientific interests are dye-PU covalent bonding and inorganic nanofiller doping and their effects on spectral-luminescence characteristics of dyes.
E-mail: ant111@i.ua,
https://orsid.org/0000-0002-6451-7944

Authors' contributions

Bezrodna T.V.: validation, formal analysis, writing – review & editing.
Negriyko A.M.: conceptualization, project administration.
Bezrodnyi V.I.: investigation, formal analysis, writing – original draft.
Matsnev I.V.: methodology, software, investigation.
Kosyanchuk L.F.: validation, writing – review & editing.
Antonenko O.I.: resources, visualization.

Ефективні пасивні лазерні затвори на основі забарвленого поліуретану для високоенергетичних неодимових лазерів

Т.В. Безродна, А.М. Негрійко, В.І. Безродний, І.В. Мацнєв, Л.Ф. Косянчук, О.І. Антоненко

Анотація. Досліджено енергетичні та часові характеристики роботи лазера на кристалі Nd^{3+}:YAG з пасивними модуляторами добротності на основі активованої барвником аліфатичної поліуретанової матриці високої радіаційної стійкості. При використанні самарієвого дифузного відбивача з наповнювачем $BaSO_4$ отримано високу ефективність генерації лазера як у вільному режимі, так і під час генерації одиночного імпульсу в режимі модуляції добротності. Проведено порівняння енергії та тривалості одиночного імпульсу для лазерів з пасивними модуляторами добротності на основі нікельорганічного комплексу BDN та поліметинового барвника IR-1061 в аліфатичній поліуретановій матриці, полімеризованій методом поліконденсації з таких вихідних сполук: 1,6-дизоціанатогексан, полі[ді(етиленгліколь)адипат] і триметилолпропан. При використанні поліметинового тіопірило-4-трикарбоціанінового барвника (IR-1061) в режимі модуляції добротності отримано одиночний потужний імпульс з енергією ~1 Дж. Показано, що високоефективна модуляція добротності за допомогою пасивного лазерного затвора на барвнику IR-1061 спричинена його специфічними лінійними та нелінійними спектральними властивостями.

Ключові слова: твердотільний лазер, нелінійне поглинання, насичуваний поглинач, пасивна модуляція добротності, поліуретанова матриця, барвники.