

New efficient laser dyes for the red region of the spectrum.

Part 1. Peri-indenones

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Abstract. We report the generation characteristics of ethanol solutions of twenty newly synthesised dyes belonging to peri-indenones, including benzantrones and phenalemines. The tuning curves of these dyes, generating light in the orange and red spectral regions, are measured, and the wavelength tuning ranges are determined. The dependence of the generation energy on the pump energy in a non-selective cavity is measured. It is shown that some of the synthesised dyes surpass the widely used laser dyes in the energy efficiency and the width of the wavelength tuning range.

Keywords: dye laser, generation characteristics, benzantrones, phenalemines, tuning range, energy efficiency

1. Introduction

Dye lasers have been extensively studied and improved for more than 40 years. Thanks to the possibility of the radiation wavelength tuning within a wide spectral range, such lasers became widely used as ultra-short pulse (USP) lasers, as well as in spectroscopy, medicine, etc. At present the field of dye laser applications became significantly narrower, since the USPs are now generated by titanium–sapphire, chromium forsterite, and chromium LiSAF and LiCAF lasers. For the photodynamic cancer therapy, it is more convenient to use cheaper, high-power semiconductor lasers. However, the application fields still exist where dye lasers cannot be replaced. This is, e.g., spectroscopy or laser-assisted isotope separation, where it is often necessary to generate radiation with any required wavelength and very narrow line. In particular, the production of the ^{168}Yb isotope requires the radiation with a

wavelength of 581.067 nm [1]. This wavelength is hard to obtain using a titanium–sapphire laser, chromium laser, or harmonics of their radiation. Parametric oscillators, present in the market, allow generating the radiation tunable within a very broad spectral band, but do not provide the line width smaller than a few inverse centimetres. The authors of book [2] considered the dye lasers as the main type of tunable lasers suitable for laser isotope separation.

New fields of application for dye lasers also continue to arise. For example, the dyes as active laser substances are used in plasmonic nanolasers and nanoscopic coherent optical sources [3–5]. Distributed-feedback dye lasers are used as sensors of small variations of the refractive index in biological solutions [6].

Dye lasers cover the spectral range 310–1800 nm, do not require pump powers close to the breakdown thresholds of optical materials, allow easy generation of radiation lines as narrow as a few picometres and smaller, and can be scaled for high powers and energies. However, the most efficient dyes are mainly concentrated in the yellow and orange spectral regions (rhodamines and pyrromethenes), their efficiency achieving the values above 80% [7, 8]. The efficiency of dyes generating in other regions of the spectrum is considerably lower, although this fact has no apparent physical reasons. Probably, good dyes for these spectral regions will be found in the future. Therefore, the search for new dyes with increased efficiency in the green and red regions of spectrum is still urgent.

The efficiency of laser dyes depends on many factors, the most essential ones being the triplet–triplet absorption and singlet–singlet absorption of excited molecules at the lasing wavelength at the expense of the $S_1 \rightarrow S_n$ transitions to higher excited states. At present, it is impossible to calculate the probabilities of these processes with acceptable accuracy. Their measurement is more difficult than that of the generation characteristics of new substances. Certain attempts were undertaken to establish the rules allowing the prediction of the generation efficiency in different compounds [9–12]. However these rules either possess too general character, as, e.g., the undoubtedly useful Drexhage’s “loop rule” [9], stating that the molecules with a closed chromophore system possess a higher probability of a transition to the triplet state, which hampers efficient generation, or are related to a narrow group of substances. For example, in Ref. [12] it is shown that among the four most widespread pyrromethene dyes and the three phenalimine ones the highest efficiency within one class is inherent in the molecules with the maximal relative (normalised to the absorption spectrum width) Stokes shift between the maxima of absorption and fluorescence spectra. However, among other classes of dyes one can find multiple examples of

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substances with a large Stokes shift that do not generate at all under any pump level. Therefore, it seems impossible to elaborate clear recommendations for targeted synthesis of new efficient dyes. Nevertheless, the practical experience allows reasonable choice when planning the synthesis of new dyes, but for the final evaluation of the synthesised dyes, the measurements of generation efficiency are necessary.

One of the major drawbacks of most widespread lasers on dye solutions is the necessity to provide the active medium circulation because of thermo-optical distortions and fast 'burning' of dye molecules, which stimulated the development of solid-state dye lasers based on polymers, sol-gel and porous glasses [13–16]. In the active elements of such lasers, the same active substances as in solutions were used. The solid-state compositions with the resource of more than a million pump pulses at one point were reported [17].

Another essential disadvantage of dye lasers is the complexity of pump systems. Due to the short lifetime of dye

molecules in the excited state, the excitation power density necessary to provide a considerable gain is on the order of 1 MW cm^{-2} (for longitudinal pumping). Due to this fact, they have to use for pumping either the well-focused laser radiation, or the pulsed lamps with complex high-voltage power supply systems. As a result, the entire system becomes complicated and expensive. This drawback will most probably vanish, when it will become possible to use semiconductor lasers for pumping, but for this aim the dyes with minimal pump thresholds are to be found.

In the present work the generation characteristics of several tens of newly synthesised dyes, belonging to the class of peri-indenones, were measured. The derivatives of peri-indenones, in particular, benzanthrone and phenalene, presently attract great interest. Among them not only the efficient lumino-phores of different purpose were found, but also the stable compounds with a high lasing efficiency [18–20]. Particular attention was attracted by the phosphorus-containing deriva-

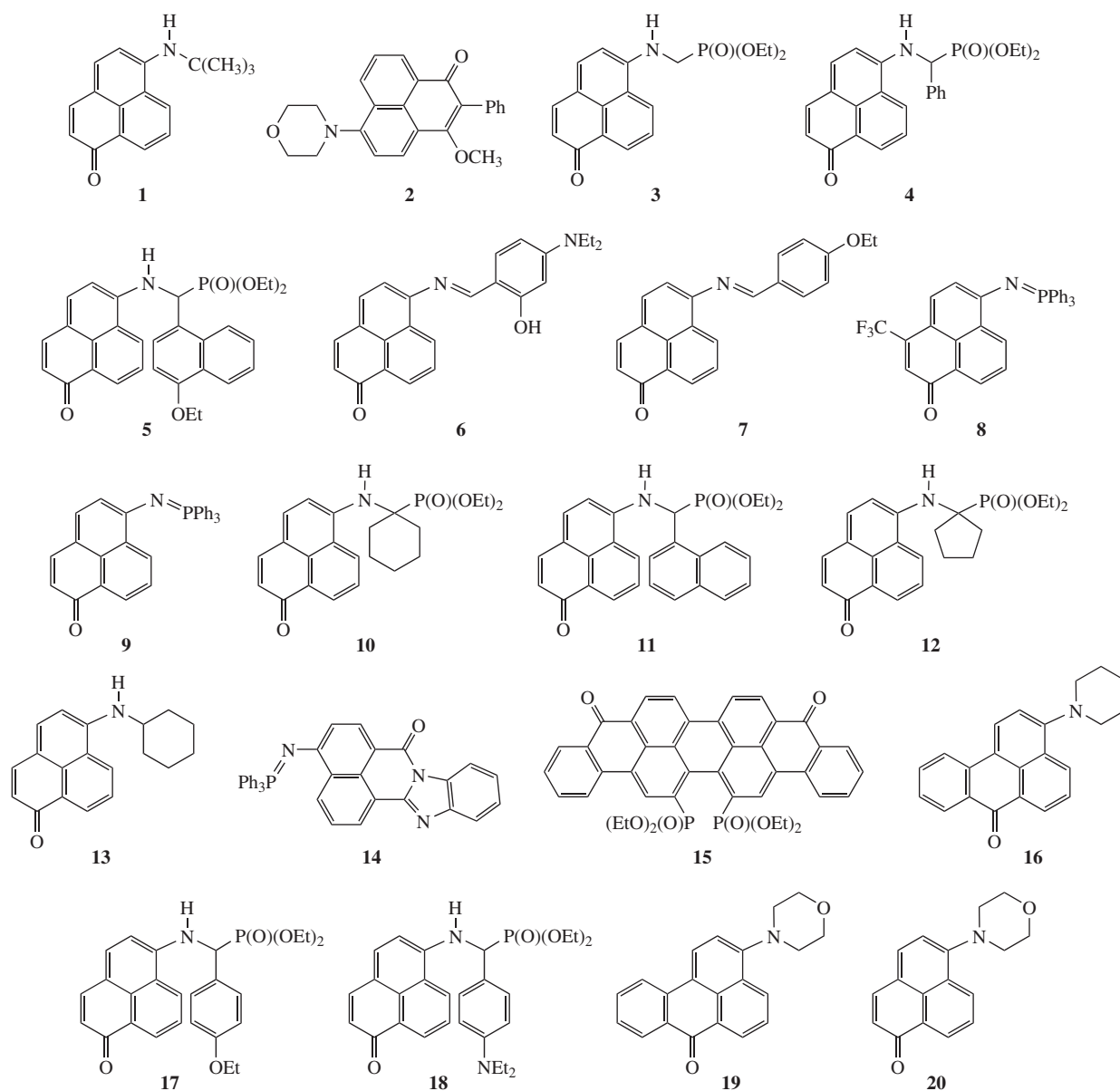


Figure 1. Structural formulae of the studied substances. The numbers of dyes correspond to those in Table 1.

tives of these dyes with iminophosphoryl and phosphonate groups, which possess a considerable Stokes shift (to 150 nm), a high quantum yield of the fluorescence, and high generation parameters [21–24].

2. Experiment

The synthesis of peri-indenones and model compounds was implemented following different, previously described schemes [23–25]. The structure formulas of the molecules of the studied substances are presented in Fig. 1.

We measured the tuning curves, i.e., the dependences of the output laser energy on the laser wavelength under longitudinal pumping having the fixed energy, similar for all substances. For the most efficient dyes, we also measured the dependences of the generation energy in a non-selective cavity on the pump energy with the aim to determine the pump thresholds and slope efficiencies of lasing. Ethanol was used as a solvent in all cases.

The solutions were pumped using the second harmonic of the radiation from an Nd:YAG laser having a pulse duration of 25 ns. The optical scheme of the setup for measuring the tuning curves is presented in Fig. 2. The studied solutions were poured into a rectangular glass cuvette with the thickness of the dye layer 5 mm. The concentration of the solution for each substance was chosen such that the dye layer absorbed practically all the pump radiation, and the transmission amounted to a few fractions of per cent. The cuvette was placed at the Brewster angle in the dispersion cavity formed by the Brewster roof prism and the stack of two glass plates, used as the exit mirror. The wavelength selection was implemented using two Brewster prisms made of TF-1 glass. This cavity provided practically the same Q -factor at the chosen wavelength for all substances, generating in different spectral regions. The pump radiation was focused into a spot with a diameter ~ 0.8 mm, the pump energy being equal to 7 mJ. At each wavelength, several measurements were carried out with subsequent averaging of the results. No circulation was provided, and to eliminate the influence of thermo-optical distortions a sufficiently long interval of nearly 1 min was set between the pump pulses. The generated wavelength was

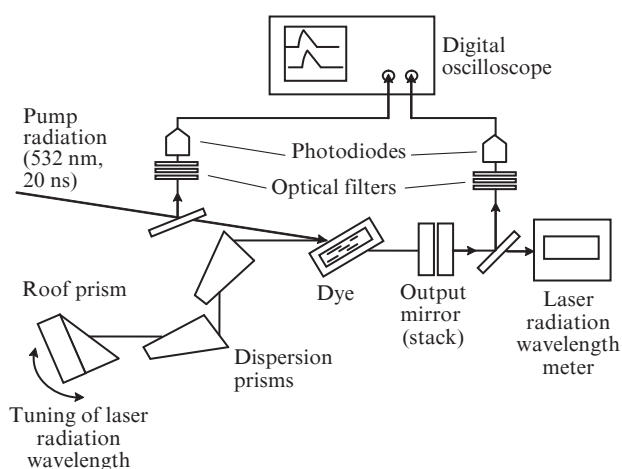


Figure 2. Schematic of the setup for measuring the tuning curves of laser dyes.

recorded using the laser radiation wavelength meter (Physics Instrumentation Center at GPI, Russia) with an accuracy of 0.01 nm. The pump and generation energy was measured in relative units by means of the FD-24 photodiodes with the correction for their spectral sensitivity. The signals from the photodiodes were recorded using a digital Goodwil Instek GDS-2104 oscilloscope. For comparing the studied dyes with the known substances under the same conditions, the generation characteristics of Rhodamine 6G, Rhodamine 101 and DCM were measured.

To measure the dependence of the generation energy on the pump energy, the solutions of the studied dyes were placed into a cylindrical cuvette, in which one of the windows was a plate of TF-1 glass. The outer surface of this plate played the role of an exit mirror with a reflection coefficient of 6%. At the outer surface of the second window that played the role of a highly reflecting mirror the reflecting coating with a reflection coefficient of $\sim 99\%$ was deposited. The thickness of the dye layer was 8 mm, and the total cavity length was 2.4 cm. The concentration of dyes was chosen similarly to the previous case to provide a virtually total absorption of the pump radiation.

The schematic of the measurement setup is shown in Fig. 3. The pumping was implemented through the exit mirror at a small angle to the cavity axis in the spot with the diameter 3 mm with sharp edges and the intensity distribution over the area close to uniform. This allows determination of the threshold pump energy density with a minimal error. The uniform intensity distribution was achieved at the expense of cutting the central part of the pump beam by means of a circular diaphragm, which was then imaged by the lens onto the cuvette with the dye. The pump and generation energy was measured with two calorimetric VChD-2 heads (Special Design Bureau at the Lebedev Physics Institute of the Russian Academy of Sciences, Troitsk, Russia). The heads were calibrated using an IMO-2N laser radiation energy meter. The signals from the calorimetric heads were digitized with a 14-bit USB-3000 ADC and stored in the memory of a personal computer. The processing of the measurement results has shown that the dependences of the generation energy on the pump, above-the-threshold energy are straight lines only in the first approximation: the tangent of the slope angle decreases with exceeding the threshold by several times. For definiteness, the slope efficiency was determined as the slope angle tangent at exceeding the threshold by two–three times. The threshold pump energies were determined by extrapolating the initial linear segment to the region of the zero generation energy.

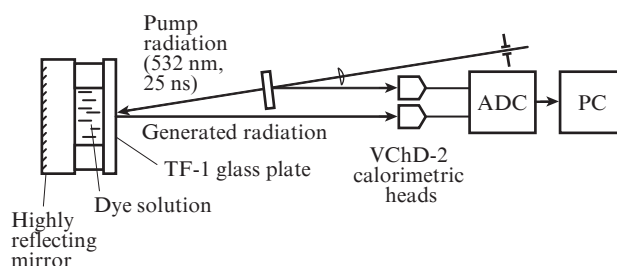


Figure 3. Schematic of the setup for measuring the dependence of generation energy on the pump energy.

3. Results and discussion

The tuning curves of the studied dyes are presented in Fig. 4. Figure 5 presents the dependences of the generation energy on

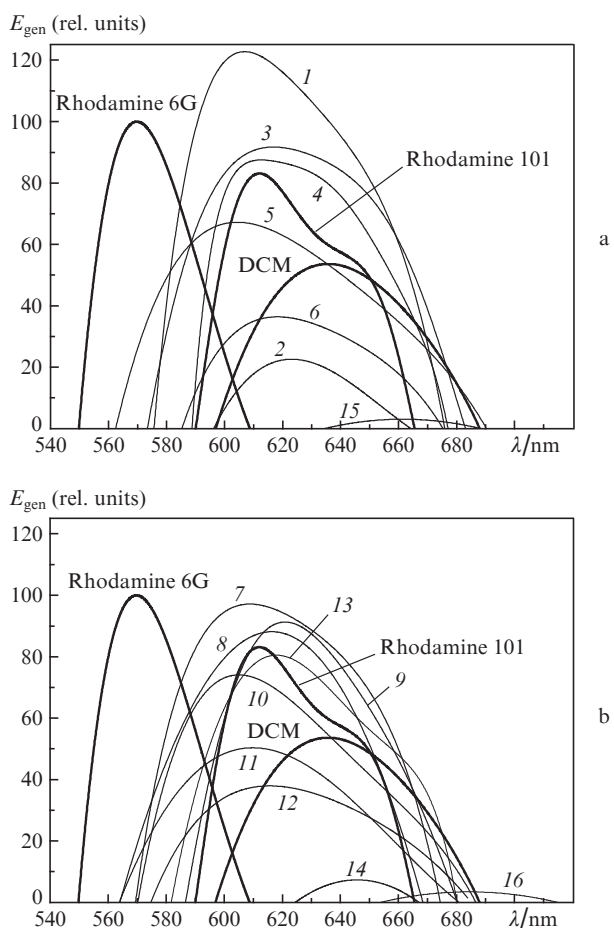


Figure 4. Dependences of the dye generation energy on the wavelength in a selective cavity. The numbers of the curves correspond to those in Table 1. The vertical scale is chosen such that the generation energy for Rhodamine 6G in the maximum equals 100.

Table 1. Peri-indenones and etalon substances.

Substance	$\lambda_{\text{abs}}^{\text{max}}/\text{nm}$	Selective cavity		Broadband cavity	
		$\lambda_{\text{gen}}^{\text{max}}/\text{nm}$	$\Delta\lambda/\text{nm}$	η (%)	$E_{\text{pump}}^{\text{th}}/\text{mJ}$
1	522	605	576–674	40.6	6.7
2	454	623	596–663	23.0	11.0
3	518	619	577–681	43.1	7.4
4	503	612	565–666	40.3	7.7
5	506	603	565–689	35.4	9.3
6	537	618	585–674	39.4	9.8
7	503	607	570–673	45.7	7.9
8	538	615	590–675	43.6	6.6
9	552	620	578–677	45.4	5.9
10	515	604	572–687	39.1	7.3
11	501	610	565–681	30.3	10.0
12	519	615	576–681	27.6	9.45
13	552	623	583–680	46.7	5.5
14	495	644	627–667		
15	610	670	636–687		
16	457	690	656–715		
17	519		Generation at the threshold	13.5	20.0
18	499		No generation		
19	444		No generation*		
20	462		No generation		
Rhodamine 6G	570		550–618	50.9	4.9
Rhodamine 101	612		593–665	42.3	4.6
DCM	635		595–691	28.9	7.4

* Weak absorption at the pump wavelength, insufficient solubility. Note: $\lambda_{\text{abs}}^{\text{max}}$ is the wavelength at the maximum of absorption; $\lambda_{\text{gen}}^{\text{max}}$ is the wavelength at the maximum of generation; $\Delta\lambda$ is the width of the tuning range; η is the slope efficiency; and $E_{\text{pump}}^{\text{th}}$ is the threshold pump energy.

the pump energy for the most efficient dyes in the broadband cavity. In this case, the pump energy is understood as the energy of radiation passed through the exit mirror and actually reaching the dye solution. The results of the measurements are summarised in Table 1.

From Fig. 4 one can see that some of the new dyes have a high efficiency, comparable with that of widely used dyes (Rhodamine 6G, Rhodamine 101, DCM) or even exceeding it. All studied substances absorb well the second harmonic of

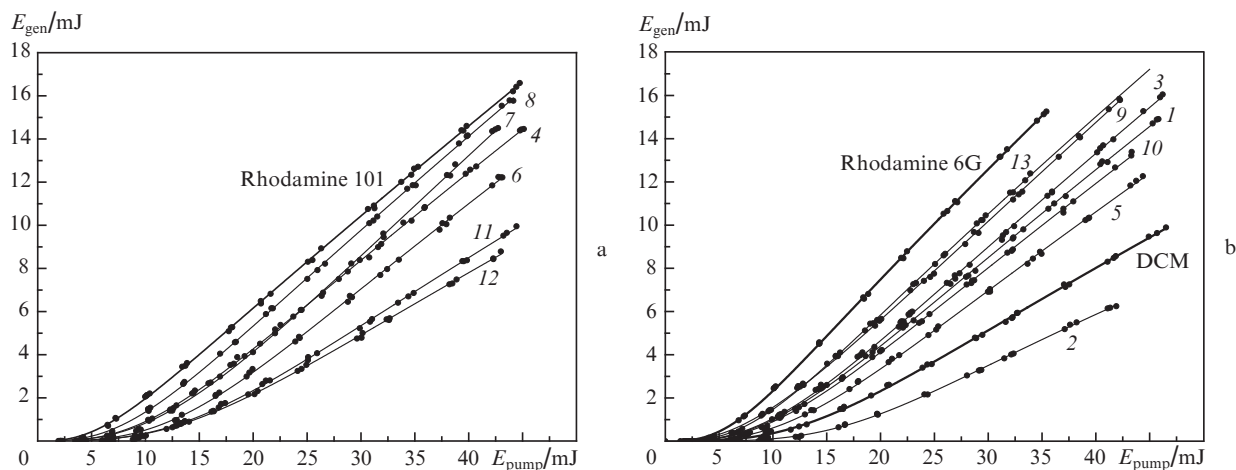


Figure 5. Dependences of the dye generation energy on the pump energy in the broadband cavity. The numbers of curves correspond to those in Table 1.

the neodymium laser radiation. At the same time, the new dyes provide a wide tuning range, essentially exceeding that of rhodamine dyes. This fact allows one to recommend them for application. Some dyes are promising for pumping semiconductor lasers. For example, the substances with numbers 9 and 13 are good absorbers of the radiation of green laser diodes (520 nm), insignificantly yield to Rhodamine 6G in the threshold pump energy and slope efficiency, but have the tuning range that is one and a half wider.

4. Conclusions

For the solutions of 20 dyes synthesised for the first time, we have measured the generation characteristics in a selective and broadband cavity. The studied dyes generate in the orange and red spectral regions. Some of the dyes possess the wavelength tuning range considerably exceeding 100 nm, which is larger than in the DCM dye and essentially larger than in rhodamine dyes. The dependences of the generation energy on the pump energy in a non-selective cavity were measured. The energy efficiency of the best of the studied dyes is inferior to the efficiency in widely used ones.

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References

1. Tkachev A.N., Yakovlenko S.I. *Kvantovaya Elektron.*, **33**, 581 (2003) [*Quantum Electron.*, **33**, 581 (2003)].
2. Bokhan P.A., Buchanov B.B., Zakrevskii D.E., Kazaryan M.A., Prokhorov A.M., Fateev N.V. *Opicheskoye i lazerno-khimi-cheskoye razdeleniye izotopov v atomarnykh parakh* (Optical and Laser-Chemical Separation of Isotopes in Atomic vapours) (Moscow: Fizmatlit, 2010).
3. Noginov M.A., Zhu G., Belgrave A.M., Bakker R., Shalaev V.M., Narimanov E.E., Stout S., Herz E., Suteewong T., Wiesner U. *Nature*, **460**, 08318 (2009).
4. Meng X., Liu J., Kildishev A.V., Shalaev V.M. *Laser Photonics Rev.*, **8**, 896 (2014).
5. Yang A., Hoang T.B., Dridi M., Deeb C., Mikkelsen M.H., Schatz G.C., Odom T.W. *Nat. Commun.*, **6**, 6939 (2015).
6. Vannahme C., Dufva M., Kristensen A. *Light: Science & Applications*, **4**, e269 (2015).
7. Hermes R.E., Allik T.H., Chandra S., Hutchinson A. *Appl. Phys. Lett.*, **63**, 877 (1993).
8. Allik T.H., Hermes R.E. *Proc. SPIE Int. Soc. Opt. Eng.*, **2115**, 240 (1994).
9. Drexhage K.H. *Proc. VII Int. Quantum Electronics Conf.* (Monreal, Canada, 1972).
10. Pavlopoulos T.G. *Opt. Commun.*, **38**, 397 (1981).
11. Bondar M.V., Przhonskaya O.V., Tikhonov E.A., Fedotkina N.M. *Zh. Prikl. Spektrosk.*, **52**, 554 (1990) [*J. Appl. Spectrosc.*, **52**, 352 (1990)].
12. Koldunov M.F., Kravchenko Ya.V., Manenkov A.A., Pokotilo I.L. *Kvantovaya Elektron.*, **34**, 115 (2004) [*Quantum Electron.*, **34**, 115 (2004)].
13. Rahn M.D., King T.A. *Appl. Opt.*, **34**, 8260 (1995).
14. Kopylova T.N., Maier G.V., Reznichenko A.V., et al. *Kvantovaya Elektron.*, **30**, 387 (2000) [*Quantum Electron.*, **30**, 387 (2000)].
15. Bezrodnyi V.I., Derevyanko N.A., Ishchenko A.A., Karabanova L.V. *Zh. Tekh. Fiz.*, **71**, 72 (2001) [*Tech. Phys.*, **46**, 858 (2001)].
16. Dolotov S.M., Koldunov M.F., Kravchenko Ya.V., Lugovoy V.B., Manenkov A.A., Petukhov V.A., Ponomarenko E.P., Roskova G.P., Tsekhomskaya T.S. *Kvantovaya Elektron.*, **32**, 669 (2002) [*Quantum Electron.*, **32**, 669 (2002)].
17. Yuji Oki, Shinichi Miyamoto, Mitsuo Maeda. *Opt. Lett.*, **14**, 1220 (2002).
18. Samsonova L.G., Kopylova T.N., Narozhnaya L.G., et al. *Opt. Atmos. Okeana*, **15**, 251 (2002) [*Atmos. Ocean. Opt.*, **15**, 189 (2002)].
19. Kopylova T.N., Samsonova L.G., Zemlyanov A.A., Ushakova V.G., Maier G.V., Donchenko V.A., Vasil'ev A.V. *Izv. Vyssh. Uchebn. Zaved., Ser. Fiz.*, **45**, 10 (2002) [*Russ. Phys. J.*, **45** (4), 336 (2002)].
20. Zhytniakivska O., Trusova V., Gorbenko G., Kirilova E., Kalnina I., Kirilov G., Kinnunen P. *J. Lumin.*, **146**, 307 (2014).
21. Khrolova O.R., Kunavin N.I., Komlev I.V., Tavrizova M.A., Trofimova S.I., Madiy V.A., Petukhov V.A. *Zh. Prikl. Spektrosk.*, **41**, 53 (1984) [*J. Appl. Spectrosc.*, **41**, 771 (1984)].
22. Krymova A.I., Petukhov V.A. *Kvantovaya Elektron.*, **13**, 657 (1986) [*Sov. J. Quantum Electron.*, **16** (3), 429 (1986)].
23. Komlev I.V., Mezentseva G.A., Reznichenko A.V., Tavrizova M.A., Khrolova O.R., Petukhov V.A., Semenov M.A. *Proc. SPIE Int. Soc. Opt. Eng.*, **4761**, 188 (2002).
24. Nifantsev E.E., Belov S.P., Komlev I.V., Petukhov V.A., Semenov M.A., Mezentseva G.A., Tavrizova M.F., Ponomareva O.V. *Zh. Obshch. Khim.*, **78**, 400 (2008) [*Russ. J. Gen. Chem.*, **78**, 383 (2008)].
25. Belov S.P., Komlev I.V., Kuznetsov S.V., Nifantsev E.E. *Zh. Obshch. Khim.*, **79**, 2061 (2009) [*Russ. J. Gen. Chem.*, **79**, 2698 (2009)].