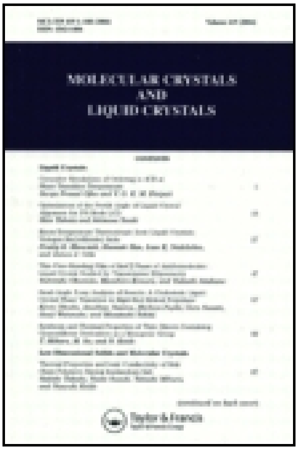

Molecular Crystals and Liquid Crystals

Photoinduced Phenomena in Conjugated Organic Systems Doped with Fullerenes

N. V. Kamanina [a], I. Yu. Denisyuk [a], A. V. Varnaev [a], A. P. Zhevlakov [b] & A. A. Nikitichev [b]

[a] Vavilov State Optical Institute, St. Petersburg, Russia

[b] Institute for Laser Physics, St. Petersburg, Russia

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Photoinduced Phenomena in Conjugated Organic Systems Doped with Fullerenes

N. V. Kamanina
I. Yu. Denisyuk
A. V. Varnaev
Vavilov State Optical Institute, St. Petersburg, Russia

A. P. Zhevlakov
A. A. Nikitichev
Institute for Laser Physics, St. Petersburg, Russia

Optical limiting properties of C_{60} and C_{70}-doped organic thin films (polyimide, 2-cyclooctylamino-5-nitropyridine) under a laser irradiation at wavelengths of 532, 1047, and 1315 nm have been studied. The films can be applied as laser power attenuators at a laser energy density of more than 2 $J \cdot cm^{-2}$ and at a laser energy density up to 0.8–1 $J \cdot cm^{-2}$ in the visible and near infrared spectral ranges, respectively. Reverse saturable absorption and the complex formation have been discussed to explain optical limiting results. The place of the materials studied can be predicted among other nonlinear optical systems attenuating high energy density in the near infrared.

Keywords: fullerene; laser-matter interaction; near infrared spectral range; optical limiting; organic structures

1. INTRODUCTION

Development of new fullerene-doped materials as effective optical limiting (OL) systems provokes the great interest in their optical properties [1–5]. These properties conditioned by the excitation of π-electrons

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Address correspondence to N. V. Kamanina, Vavilov State Optical Institute, 12 Birzhevaya Line, St. Petersburg, 199034 Russia. Tel.: 7-812-377-3422, Fax: 7-812-1017, E-mail: kamanin@ffm.ioffe.ru

demonstrate that a new charge transfer complex is formed between fullerene and a donor fragment of an organic molecule [6–9]. This complex is of a higher excited state absorption cross section than the ground state one. That is why fullerene-doped systems are reverse saturable absorption (RSA) materials and may be used for a sensor and eye protection as nonlinear optical absorbers.

In the present paper, the OL properties have been studied in the C_{60} and C_{70}-doped organic thin films, namely, polyimide and 2-cyclooctylamino-5-nitropyridine (COANP) structures under a laser irradiation at wavelengths of 532, 1047, and 1315 nm. It has been shown that the systems studied can be applied as laser power attenuators in the visible and near infrared spectral ranges.

2. EXPERIMENTAL CONDITIONS

3% solutions of conjugated materials in 1,1,2,2-tetrachloroethane (TClE) were used. The solutions were doped with fullerenes C_{60} or/and C_{70}. The fullerene concentration was varied from 0.2 wt.% to 5 wt.%. It should be noticed that fullerenes are of relatively high solubility (about 5.3 mg mL^{-1}) [10] in TClE. The 2.5–5 μm-thick films were spun on the glass or quartz substrates. A general view of the films obtained based on the materials treated is presented in Figure 1. The film structures after drying are shown in Figure 2. The homogeneity of the films was investigated with a scanning electron microscope (SEM) HU-11B at an accelerating voltage of 75 kV. The multiplication was 12500×. Spectroscopic measurements were carried out using a Perkin–Elmer Lambda 9 instrument in the wavelength range 200–3000 nm.

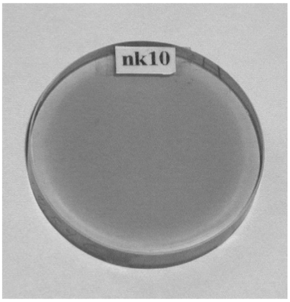

FIGURE 1 View of a fullerene-doped polyimide thin film on the glass (or quartz) substrate.

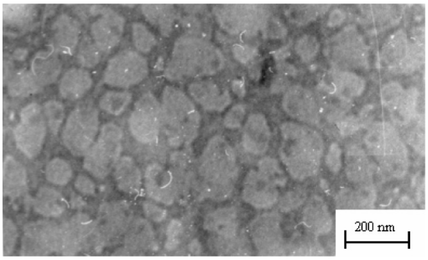

FIGURE 2 SEM image of a 6B polyimide film.

A pulsed Nd-YAG laser at a wavelength of 532 nm was applied as a radiation source to study OL in the structures. A pulse width was 20 ns and a laser spot on the sample surface was 3–3.5 mm in diameter. Beam energies incident on and transmitted through the sample were measured. The OL scheme was analogous to that presented in [11].

A pulsed Nd:YLiF$_4$-laser with a pulse width of 8 ns was applied as an irradiation source to investigate OL at a wavelength of 1047 nm. The spot diameter was about 2 mm.

To estimate the nonlinear transmission at 1315 nm, the dependence of the output energy on the input one was measured with a use of a photodissociative iodine laser. The first near-infrared OL results were published in [12]. The laser pulse width was 50 ns. A spot on the sample surface was 2 mm. It should be mentioned that, to control the OL level in the near infrared, an additional scheme solution was proposed [13].

3. RESULTS AND DISCUSSION

One of the most important processes observed in fullerene-doped media is OL. The study of this effect allows the laser-matter interaction to be investigated and the search for the new materials to protect the human eyes and technical devices against laser radiation to be solved.

The dependence of the output energy density W_{out} on the input one W_{in} for the polyimide and COANP thin films with different fullerene concentrations followed by different numbers of excited molecules is shown in Figure 3. The same dependence for a 1 μm-thick pure fullerene film is shown in the inset. On synthesis of thin films, the preference has been given to C_{70} because the molecule is anisotropic. As a result, the compound with C_{70} has 3–10 times more absorption than

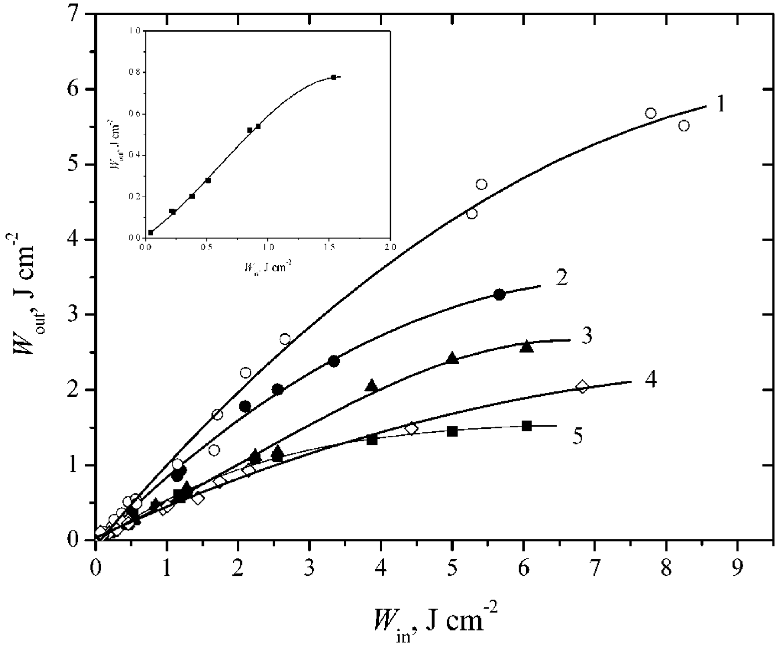

FIGURE 3 Dependence of the output energy density (W_{out}) on the input one (W_{in}) for films: 1 – COANP with 0.5 wt.% C_{70}; 2 – polyimide with 0.2 wt.% C_{70}; 3 – polyimide with 0.5 wt.% C_{70}; 4 – COANP with 5 wt.% C_{70}; 5 – polyimide with 0.7 wt.% C_{70}. In the inset: Dependence of the output energy density (W_{out}) on the input one (W_{in}) for 1 μm pure fullerene thin film. ($\lambda = 532$ nm).

the one with C_{60} in the range 400–700 nm [14]. The absorption spectra of the films with C_{70} are red-shifted 20–30 nm and 50–70 nm for PI [15] and COANP [16], respectively. Because the lifetime of C_{70} in triplet T_1 state is one order of magnitude longer than that of C_{60} [17], more pronounced responses and their clear detection have been obtained over the visible spectral range.

From the intersection of linear and nonlinear parts of the dependence $W_{out} = f(W_{in})$ (Fig. 3), the OL level can be estimated. It corresponds to the input energy density of 1.1–1.3 J · cm^{-2} and 2.2–2.5 J · cm^{-2} for polyimide with 0.7 wt.% C_{70} and COANP with 5 wt.% C_{70}, respectively. The 3-fold attenuation of the laser beam has been established for these structures that is close to that for 1 μm pure fullerene thin film (see the inset in Fig. 3). It should be mentioned that the level of input energy density, at which the saturation of the transmission takes place, decreases as the fullerene concentration increases.

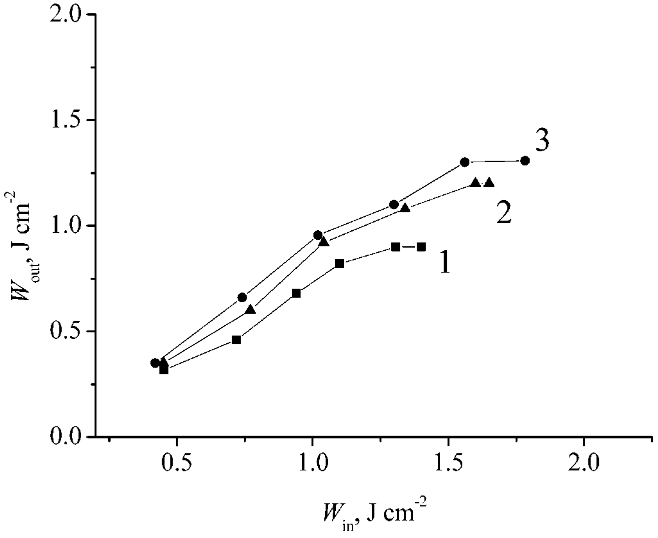

FIGURE 4 Dependence of the output energy density (W_{out}) on the input one (W_{in}) for polyimide films: 1 – 0.5 wt % C_{70}; 2 – 0.2 wt % C_{70}; 3 – 0.1 wt % C_{70} at 1047 nm.

The dependence of the output energy density (W_{out}) on the input one (W_{in}) for 2.5–5 μm-thick polyimide films studied at 1047 nm is shown in Figure 4. One can see from Figure 4 that the more than 2-fold attenuation has been observed.

It should be noticed that the drastic spectral dependence of photoconductivity has been revealed for the fullerene-doped polyimide system. It should be noticed that the photoconductivity of pure fullerenes (C_{60} and C_{70}) decreases drastically [18] in the near-infrared range ($\lambda > 700$ nm), while the one of fullerene-doped polyimide continues to rise. Using this peculiarity the OL effect has been studied for the structure of C_{70}-doped polyimide with 0.5 wt.% of fullerenes with a pulsed iodine laser ($\lambda = 1315$ nm) with a pulse width of 50 ns. The results for the near-infrared range are presented in Figure 5.

The effect began at the input energy density of 0.25–0.3 J $\cdot$ cm^{-2}, while the 16-fold attenuation was observed when the incident energy density reached 0.8 J $\cdot$ cm^{-2}. Furthermore, the initial input energy density of 0.25–0.3 J $\cdot$ cm^{-2} can be reduced down to 0.1 J $\cdot$ cm^{-2} by using a Xe flash-lamp with a broad spectral band (see the inset in Fig. 5). The filter with the transmission peak at 470 nm that corresponded to the resonant line of C_{70}, was applied. The flash-lamp irradiation was incident on the back surface of the film. The flash preceded the

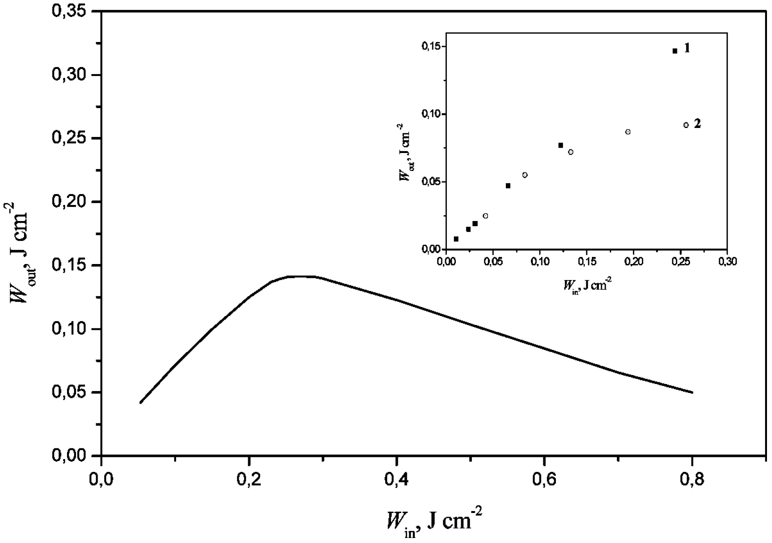

FIGURE 5 Dependence of W_{out} on W_{in} in polyimide 6B film with 0.57 wt.% of fullerene C_{70} ($\lambda = 1315$ nm). In the inset: Dependence of W_{out} on W_{in} in C_{70}-polyimide 6B films using an additional scheme solution [13].

laser pulse with the time interval of 5 μs. Thus, the fullerene-doped polyimide film may be applied as an optical limiter operating in the infrared spectral range. The OL effect level can be controlled by the low-power irradiation of a flash-lamp.

To discuss the OL mechanisms which are responsible for the OL effect in fullerene-doped polyimide and COANP structures, the reverse saturable absorption (RSA) and complex formation have been considered. Moreover, the additional Förster energy transfer process and the dipole-dipole interaction have been taken into account. Really, from data of the Z-scan and electrophotographic methods, the absorption cross-section for the ground and excited states has been estimated. It has been shown that the excited state absorption cross-section is larger than that for the ground state [5,19]. Thus, fullerene-doped polyimide and COANP can be testified as RSA structures. Therefore, the difference between the transmission of samples with various fullerene concentrations (see Fig. 3, curves 1, 4 and 2, 3, 5) and, hence, the OL effect can be explained in the framework of the RSA mechanism.

Furthermore, an additional absorption at 532 nm due to the Förster mechanism should be take into account for the fullerene-doped polyimide system. T. Förster considered possibilities for the energy transfer via a resonant mechanism if the fluorescence spectrum overlapped with the absorption one [20]. From the comparison of the absorption spectra of C_{60} and C_{70} solutions in different solvents (hexane, toluene, benzene, tetrachloroethane) and the fluorescence spectrum of the polyimide matrix, it follows that there is the essential overlapping band which extends from 500 nm to 700 nm [11]. In our case, the overlapping of the fluorescence spectrum of the polyimide matrix and the absorption one of C_{70}-doped polyimide is observed at an excitation wavelength of 532 nm. As a result, polyimide doped with fullerenes C_{70} should attenuate the laser beam stronger due to the resonance absorption at 532 nm via the Förster mechanism.

As for C_{70}-doped COANP compounds, one can note that the electronic states of COANP corresponding to the red edge absorption near 430 nm, are in the same spectral region as the C_{70} electronic states. As a result, the theoretical model for the absorption spectra under consideration based on the electric dipole-dipole interaction between the electronic degrees of freedom of C_{70} and COANP molecules has been proposed [16]. Due to this rather close energy splitting one deal here with a possibility of the quasi-resonant dipole-dipole interaction between COANP and C_{70} states. This model explains the absorption enhancement at 532 nm and does not contradict the complex formation in the COANP-C_{70} system.

It should be mentioned that the fullerene sensitization provokes the creation of a charge transfer complex between the donor fragment of photosensitive conjugated molecules and fullerene ones. The charge-transfer complex formation should influence OL due to an additional absorption by the complex. The structural peculiarities of polyimide are favorable for the complex formation between the polyimide donor fragment (triphenylamine) and fullerene. The excitation causes a conformational transformation of the triphenylamine fragment from the neutral tetrahedral form to the ionized planar one. The parallel arrangement of these planes creates a necessary condition for the charge transfer. Fullerenes have electron affinity of 2.65–2.7 eV. They are stronger sensitizers than the intramolecular acceptor fragment (diimide) and hence, they increase the charge phototransfer in that system. Really, the fullerene doping of polyimide results in a significant increase in photocurrent. The increase is at least one order of magnitude at a potential of 70 V [12]. The acceptor fragment of a COANP molecule is an NO_2 group, which is bound with the donor fragment by a benzene ring. The electron affinity of an individual molecule or radical NO_2 is 2.3 eV, but the electron affinity of the NO_2 group bounded with a benzene ring is only 0.54 eV [21] that is four times less than that of fullerene. Thus, the fullerene molecule

TABLE 1 Comparative Data on Optical Limiting Over the IR Range

System	Initial transmission, %	Wavelength, nm	Pulse width, ns	Limiting threshold, $J \cdot cm^{-2}$	Destruction threshold, $J \cdot cm^{-2}$	Possible optical limiting mechanisms	Ref.
Composite based on silver halide with nanoparticles of metallic silver		3800–4200	250	0.005–0.025		Shift of the absorption band related to plasmon resonance with simultaneous increase in absorption coefficient; thermal change in permittivity of the components	[22]
2-(n-prolinol)-5-nitropyridine-C_{60}	65–70	2940	500 μs	0.9–1	≥ 1.5	Light-induced complex formation	[23]
Polyimide-C_{70}	~ 80	1315	50	0.08–0.1	~ 2	Light-induced complex formation; effect of two-spectral control	[12,13]
Zn-Pc-C_{60}	75–80	1064	nanoseconds			Light-induced complex formation	[24]
Carbon-black suspensions (SBS) both in water and in CS_2	~ 80	1064	10	0.12–0.7		Thermodynamic processes in suspensions caused by laser pulse heating with input energy density of more than 10 $J \cdot cm^{-2}$	[25]

Carbon nanotube suspensions both in water and in chloroform	≥ 90	1064	6	0.15–0.35		Nonlinear scattering; sublimation of carbon nanoparticles	[26]
C_{60} (solution)	~ 85	1064	35 ps	~ 3		Two-photon absorption	[27]
Polyimide-C_{70}	~ 79–85	1047	8	0.6–0.7	~ 2.5–3	Two-photon absorption of fullerene C_{70}; multi-photon absorption of polyimide matrix; possible change of refractive index related to RF Kerr effect	[28]
Mg-Pc-C_{60}	70	1047	8	1.5	> 3	Multiphoton processes, complex formation	[29]
C_{60} (solution)	84	710–740	10	2		Reverse saturable absorption	[30]

dominates the acceptor NO_2 group in COANP and changes the intramolecular donor-acceptor interaction. The mass spectroscopy data pointed to the charge transfer complex formation between fullerene and triphenylamine and between fullerene and the HN group in the C_{70}-polyimide and C_{70}-COANP systems. The photoconductivity measurements [12] and the mass spectroscopy investigations [19] of the fullerene-polyimide and fullerene-COANP systems give additional arguments in favor of the charge transfer complex formation and can explain OL results in the near infrared.

The basic OL results of the present study and those shown in the other papers for the near infrared are placed in Table 1.

4. CONCLUSION

Optical limiting properties of the fullerene-doped conjugated structures based on polyimide and 2-cyclooctylamino-5-nitropyridine have been studied to apply these materials as an effective nonlinear absorber in the visible and in the near-infrared spectral ranges. For the thin C_{70}-polyimide and C_{70}-COANP films, the more than 3-fold attenuation was observed in the visible spectral range. The 16-fold attenuation of a laser beam was found for the thin C_{70}-polyimide film with a fullerene concentration of 0.5 wt.% in the near infrared. It has been shown that the OL level can be controlled by the low-power irradiation of a flashlamp. The RSA mechanism and the complex formation between the organic molecules and fullerenes, as well as the Förster energy transfer and the dipole-dipole interaction, have been discussed.

The place of the materials studied can be predicted among other nonlinear optical systems attenuating high energy density. It should be noticed that we consider thin films, neither solutions nor solid bulk materials. This is a specific feature of our study. It is important to apply these structures in different areas, where the dimensions of systems play a key role.

REFERENCES

[1] Tutt, L. W. & Boggess, T. F. (1993). *Prog. Quant. Electron.*, *17*, 299.
[2] Kost, A., Tutt, L., Klein, M. B., Dougherty, T. K., & Elias, W. E. (1993). *Opt. Lett.*, *18*, 334.
[3] Kajzar, F., Taliani, C., Zamboni, R., Rossini, S., & Danieli, R. (1996). *Synth. Met.*, *77*, 257.
[4] Kamanina, N. V., Kaporskii, L. N., & Kotov, B. V. (1998). *Opt. Commun.*, *152*, 280.
[5] Kamanina, N. V. (2002). *Synth. Met.*, *127*, 121.
[6] Itaya, A., Sizzuki, I., Tsuboi, Y., & Miyasaaka, H. (1997). *J. Phys. Chem.*, *B101*, 5118.

[7] Konarev, D. V., Zubavichus, Y. V., Slovokhotov, Yu. L., Shul'ga, V. N., Drichko, N. V., & Lyubovskaya, R. N. (1998). *Synth. Met.*, *92*, 1.

[8] Du, Ch., Li, Yu., Wang, Sh., Shi, Zh., Xiao, Sh., & Zhu, D. (2001). *Synth. Met.*, *124*, 287.

[9] Kamanina, N. V. (2001). *J. Opt. A: Pure Appl. Opt.*, *3*, 321.

[10] Ruoff, R. S., Tse, D. S., Malhotra, R., & Lorets, D. S. (1993). *J. Phys. Chem.*, *97*, 3379.

[11] Kamanina, N. V. (1999). *Opt. Commun.*, *162*, 228.

[12] Kamanina, N. V., Bagrov, I. V., Belousova, I. M., Kognovitskii, S. O., & Zhevlakov, A. P. (2001). *Opt. Commun.*, *194*, 367.

[13] Kamanina, N. V., Bagrov, I. V., Belousova, I. M., & Zhevlakov, A. P. (2001). *Opt. Spectrosc.*, *91*, 1.

[14] Bensasson, R. V., Hill, T., Lambert, C., Land, E. J., Leach, S., & Truscott, T. G. (1993). *Chem. Phys. Lett.*, *206*, 197.

[15] Kamanina, N. V., Kaporskii, L. N., Pozdnyakov, A., & Kotov, B. V. (2000). *Proceed. SPIE*, *3939*, 228.

[16] Kamanina, N., Barrientos, A., Leyderman, A., Cui, Y., Vikhnin, V., & Vlasse, M. (2000). *Mol. Mater.*, *13*, 275.

[17] Razbirin, B. S. (2002). *Private communication*.

[18] Hosoya, M., Ichimura, K., Wang, Z. H., Dresselhaus, G., Dresselhaus, M. S., & Eklund, P. C. (1994). *Phys. Rev.*, *B49*, 4981.

[19] Kamanina, N. V. & Plekhanov, A. I. (2002). *Opt. Spectrosc.*, *93*, 408.

[20] Förster, T. (1959). *Disc. Farad. Soc.*, *27*, 7.

[21] Gurvich, L. V., *et al.* (1974). Energies of chemical bond breaking, ionization potentials and electron affinity, Nauka, Moscow: USSR [in Russian].

[22] Bagrov, I. V., Zhevlakov, A. P., Mikheeva, O. P., Sidorov, A. I., & Sudarikov, V. V. (2002). *Techn. Phys. Lett.*, *28*, 552.

[23] Kamanina, N. V., Iskandarov, M. O., & Nikitichev, A. A. (2003). *Techn. Phys. Lett.*, *29*, 337.

[24] Ruani, G., Biscarini, M., Cavallini, M., Fontnini, C., Murgia, M., & Taliani, C. (2000). *Abstract 2nd Intern. Symp. Optical Power Limiting*, Venice (Italy), *69*.

[25] Riehl, D. & Fougeanet, F. (1999). *Nonlin. Opt.*, *21*, 391.

[26] Vivien, L., Riehl, D., Lancon, P., Hache, F., & Anglaret, E. (2001). *Nonlin. Opt.*, *27*, 395.

[27] Ganeev, R. A., Kamanina, N. V., Kulagin, I. A., Ryasnyansky, A. I., Tugushev, R. I., & Usmanov, T. (2002). *Quantum Electron.*, *32*, 781.

[28] Kamanina, N. V., Iskandarov, M. O., & Nikitichev, A. A. (2003). *Techn. Phys. Lett.*, *29*, 672.

[29] Kamanina, N. V. & Denisyuk, I. Yu. (2004). *Optics and Spectroscopy*, *96*, 77.

[30] Mishra, S. R., Rawat, H. S., & Mehendale, S. C. (1997). *J. Appl. Phys. Lett.*, *71*, 46.