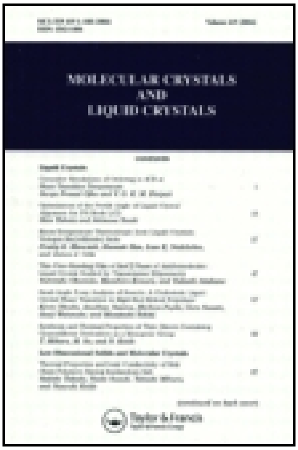

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Laser-Induced Change in the Refractive Index in the Systems Based on Nanostructured Polyimide: Comparative Study with Other Photosensitive Structures

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Laser-Induced Change in the Refractive Index in the Systems Based on Nanostructured Polyimide: Comparative Study with Other Photosensitive Structures

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The fullerene- and nanotubes-doping effect on spectral and photorefractive properties of conjugated organic systems based on polyimide have been studied. A fullerene introduction in these materials has been used due to high electron affinity of fullerenes that allows the intermolecular donor-acceptor interaction to be reinforced. The nanotubes doping has been made due to a large increase in photoconductivity of the new composites. Drastic increase in delta n has been observed under condition of nanoobjects introduction. The data presented in the current study testified that these materials could be used as new reversible holographic recording elements, new optical limiting systems, as well as new high-speed switchers.

Keywords: fullerenes; laser-induced change in the refractive index; nanotubes; organic electrooptical nanostructures; polyimide

1. INTRODUCTION

Last decade the organic electrooptical systems doped with fullerenes and carbon nanotubes (CNTs) were used in a hologram recording [1–8] and a laser frequency multiplication [9,10] with good advantage.

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A fullerenes concentration effect and an influence of the laser recording beam intensity on the diffraction efficiency of photorefractive polymers were studied [1]. In the pico- and femtosecond ranges of the recording pulses, the response was found to be increased significantly because of the charge transfer at a complex formation in the fullerene-containing compounds [3]. The holographic gratings were recorded in polyvinyl carbazole and in polymethyl metacrylate [2,4]. In the polymethyl metacrylate thin films the first diffraction order was exhibited at the recording energy density of 25–30 $\mathrm{mJ \cdot cm^{-2}}$ [4]. The second and third diffraction orders were revealed at a higher recording energy density. Erasure of the holographic grating in the fullerene-containing organic compounds was investigated in paper [6]. Dynamic holographic recording was first studied in fullerene-containing polyimides and 2-cyclooctylamino-5-nitropyridine (COANP), as well as in the dispersed liquid crystal structures based on them [7,8]. It should be mentioned that the investigations of the optical properties in the fullerene- or nanotubes-containing systems determined by the excitation of π electrons show the evidence of the effective light absorption by charge-transfer complexes formed both between the donor part of an organic matrix molecule and fullerene (electron acceptor), as well as between the CNT odd electrons and organic media [11–17]. The affinity of fullerene in this complex exceeds the one of the intramolecular organic acceptor. In the systems with CNTs, it is necessary to take into account the absorption of light by odd electrons as free charge carriers and light-induced scattering.

In the present paper the fullerene- and nanotubes-doping effect on the photorefractive properties of conjugated organic systems based on polyimide have been studied. Dramatic increase in the laser-induced change of the refractive index has been observed under condition of nanoobjects introduction. The data presented in the current study allow these materials to be applying as effective reversible holographic elements, and promising optical limiting systems, as well as high-speed light switchers of new generation.

2. THEORETICAL AND EXPERIMENTAL CONDITIONS

2.1. Theoretical Background

It is well known that at high laser intensity the refractive index of the media became dependent on the laser intensity. As the results, the high frequency Kerr effect was achieved in these structures [18]. The basic equation of this process to reveal the change in the nonlinear refraction n_2 and third order susceptibility $\chi^{(3)}$ (the last parameter is the lowest nontrivial nonlinearity, coincides with the dipole polarizability of the local volume of the system, and can be observed for both the centresymmetric and noncentresymmetric structures) can be written as follow:

$$P = \chi^{(1)}E + \chi^{(3)}E^3, \tag{1}$$

where P is nonlinear polarization of the systems, E is field intensity of the light beam, $\chi^{(1)}$ and $\chi^{(3)}$ are linear and nonlinear optical susceptibilities, respectively. In that approximation, the refractive index n is defined by the following equations:

$$D = E + 4\pi P = \varepsilon E = n^2 E, \tag{2}$$

that yields

$$n = \sqrt{1 + 4\pi P/E} \tag{3}$$

with Eq. (1) and neglecting an infinitesimal term, we get:

$$n = n_0 + \frac{2\pi}{n_0}\chi^{(3)}E^2 \tag{4}$$

where

$$n_0 = \sqrt{1 + 4\pi\chi^{(1)}} \tag{5}$$

The light intensity is $I = cE^2/8\pi$. Therefore,

$$n = n_0 + n_2 I, \tag{6}$$

where

$$n_2 = \frac{16\pi^2}{n_0 c}\chi^{(3)}. \tag{7}$$

n_0 is the linear refractive index and c is the light velocity.

It follows from Eq. (6) that the refractive index depends on the light intensity in the media with the cubic nonlinearity. This effect causes self-interaction of the light waves; resulting in self-focusing of a light beam, phase self-modulation of pulses, bistability of a resonator filed with the nonlinear medium, etc. n_2 is adequate characteristic of the cubic nonlinearity and local system polarizability. The mechanisms of an anisotropic electrooptical molecule turn can result in the Eq. (6)

nonlinearity under the effect of the intense polarized light wave. The process is quite slow in comparison to the electron polarizability of the medium. Because this mechanism provides the birefringence induced by the dc field (direct Kerr effect), the dependence of the refractive index on the light intensity is named as the high frequency Kerr effect, and the Eq. (6) nonlinearity is the Kerr nonlinearity.

One can found from the Eq. (6) that n_2 can be written:

$$n_2 = \frac{\Delta n_i}{I}, \tag{8}$$

where Δn_i – induced change in the refractive index.

It should be noticed that using condition of the Raman-Nath diffraction [19], the value of the laser-induced change in the refractive index could be estimated from the diffraction efficiency in the first order diffraction:

$$\eta = I_1/I_0 = (\pi \Delta n_i d/2\lambda)^2, \tag{9}$$

where η is the diffraction efficiency; I_0 and I_1 are the beam intensities (energy densities in the pulsed laser regime) incident on and transmitted through the sample in the first order diffraction; d is the thickness of the medium, λ is the wavelength of the light incident on the medium.

It should be mentioned that actual values of n_2 and $\chi^{(3)}$, for example, for the quartz, as the classical materials traditionally used for nonlinear optics, are $(2.5\text{–}3) \times 10^{-16}\,\text{cm}^{-2} \cdot \text{W}^{-1}$ and $10^{-14}\,\text{cm}^3\,\text{erg}^{-1}$ (esu), respectively. However, there are materials with higher optical nonlinear refraction and susceptibility. Ones of those materials are fullerenes, nanotubes and π-conjugated structures doped with them, for example, electrooptical polyimide as the system of the current study. These data will be given below, in the paragraph Results and Discussion.

2.2. Experiments

The experiments were performed with 3%–6.5 solutions of photosensitive polyimide in tetrachloroethane or chloroform, which were sensitized by fullerenes (C_{60} and/or C_{70}) or CNTs with content from 0.1 to 1 wt%. Thin films were deposited at the glass or quartz substrates, the thickness of the films after drying were placed in the range of 1–5 micrometers.

The second harmonic of the pulsed neodymium laser at wavelength of 532 nm with a pulse width of 20 ns was applied as an irradiation source to investigate the diffractive efficiency under Raman-Nath diffraction conditions. The sport of the beam was 3–5 mm. The write energy density was 0.01–2 $\mathrm{J \cdot cm^{-2}}$. The spatial frequency was ranged at 50–100 $\mathrm{mm^{-1}}$. The AFM-image of the grating obtained at spatial frequency of 50 $\mathrm{mm^{-1}}$ is shown in Figure 1. In this case the polyimide film doped with 0.2 wt.% of fullerene C_{70} has been treated. One can see the relief with dimension of 20 micrometers that is more than the thickness of the polyimide structures studied in the current paper. Thus, the Raman-Nath diffraction condition is realized in this case. It can be supported by the fact that $\Lambda^{-1} \geq d$, where Λ is the spatial frequency, d is the thickness of the film. Beam energies incident on and transmitted through the sample in the first order diffraction were measured. The holographic recording scheme was analogous to that presented in paper [20], it presents in Figure 2. It should be noticed that the data of delta n for polyimide treated at wavelength of 1315 nm was obtained using pulsed iodine laser with pulsewidth of 50 ns.

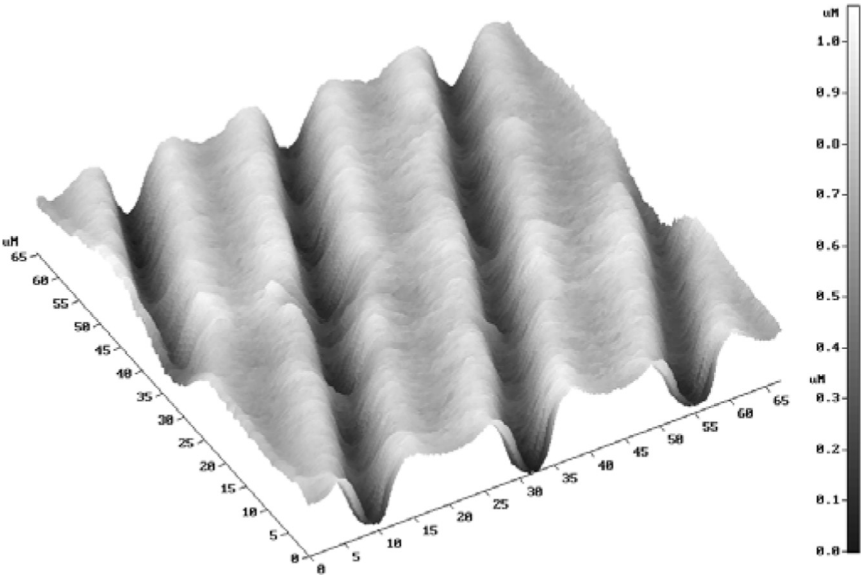

FIGURE 1 The AFM-image of the thin grating formation on the polyimide structure after laser irradiation, when reversible process has been transferred to unreversible one.

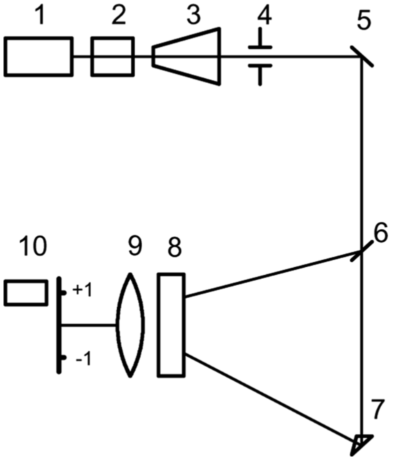

FIGURE 2 The experimental scheme: 1 – Nd: YAG laser; 2 – the crystal for 2nd harmonic conversion, 3 – telescope; 4 – diafragm; 5 – rotation mirrow (R ~ 99.9% at $\lambda = 532\,\text{nm}$); 6 – splitting mirrow (R ~ 49.9% at $\lambda = 532\,\text{nm}$); 7 – prism; 8 – the sample; 9 – lens; 10 – photoresponse detector.

3. RESULTS AND DISCUSSION

The results of the investigations are presented in the Table 1.

The increase in the diffraction efficiency and hence in the light-induced refractive index change could be explained from spectral peculiarities and thermal behavior of the nanoobjects-doped polyimide structure as well as by the photorefractive effect.

Really, the electron affinity of fullerenes is ~2.65 eV, it is twice as large as that of an intramolecular acceptor fragment of polyimide.

TABLE 1 Laser Induced Change in the Refractive Index (Δn_i) in the Organic Matrixes Based on Polyimide

Structures	Nanoobjects contents, wt.%	Wavelength, nm	Energy density, $J \cdot cm^{-2}$	Laser pulse width, ns	Change in the refractive index, Δn
Pure polyimide	0	532	0.6	20	10^{-4}–10^{-5}
Polyimide + malachite green dye	0.2	532	0.6	20	2.87×10^{-4}
Polyimide + C_{70}	0.2	532	0.6	20	4.68×10^{-3}
Polyimide + C_{70}	0.5	532	0.6	20	4.87×10^{-3}
Polyimide + nanotubes	0.1	532	0.5–0.8	10–20	5.7×10^{-3}
Polyimide + C_{70}	0.1–0.5	1315	0.2–0.8	50	$\cong 10^{-3}$

Therefore, fullerenes are stronger sensitizers and they dominate the acceptor fragments of intramolecular complexes. As results, complex between fullerenes and polyimide donor fragment (triphenylamine) are formed enhancing phototransfer of charge in these systems. The path of the charge transfer changes from the intramolecular donor fragment of polyimide not to its acceptor fragment but to fullerene. In this case the field gradient is formed, that causes the photorefractive effect in these structures under laser irradiation of the visible spectral range. It should be noticed that the changes of the photorefractive properties correlated with a long-wave shift of the absorption spectrum and with the occurrence of an additional absorption band in the near IR range. Moreover, structural changes of the systems were observed. They were associated with a transition of the polyimide donor fragment from its tetragonal form to the ionized planar one under the laser irradiation. As results, electron shells of polyimide and fullerene overlapped, this effect was conducive to the complex formation between donor fragment and fullerene.

To support the charge transfer complex formation, for example, in the systems based on fullerene-doped polyimide, the following evidences could be done. The mass-spectrometry data, the dipole moment and mobility increase via fullerene introduction, the spectral shift, the absorption cross section increase due to charge transfer complex formation, etc. have been presented in the papers [21–25]. The data regarding the dependence of the dark and photocurrent on bias voltage of polyimide with 0.2 wt.% of fullerene C_{70} is shown in Figure 3. The behavior of the curves testifies that the charge transfer process significantly influences the photorefractivity of the systems studied. Moreover, the dependence of the photoconductivity on wave length can be presented to support this idea (see Fig. 4). It should be noticed that for pure fullerene molecules the conductivity is drastically decreased after 700 nm.

From the data obtained by us for C_{70}-doped polyimide, Δn_i changes from 2.15×10^{-4} to 4.68×10^{-3} for the nanosecond pulsed laser irradiation as the incident energy density increases from 0.03 to $0.6\,\mathrm{J \cdot cm^{-2}}$. At the same time, minor changes in Δn_i have been obtained for pure polyimide. It has been compared with thermal nonlinearity of 10^{-4}–10^{-5} for nanosecond pulse regime. Moreover, the same evidence can be found when these structures would be treated at wavelength of 1315 nm. It should be remembered that the compounds investigated are the systems with intramolecular charge transfer complex. Let us remain that mass-spectrometry data, photoconductive experiments, quantum-chemical simulations, etc. have supported the evidences of the charge transfer process in the fullerene-doped

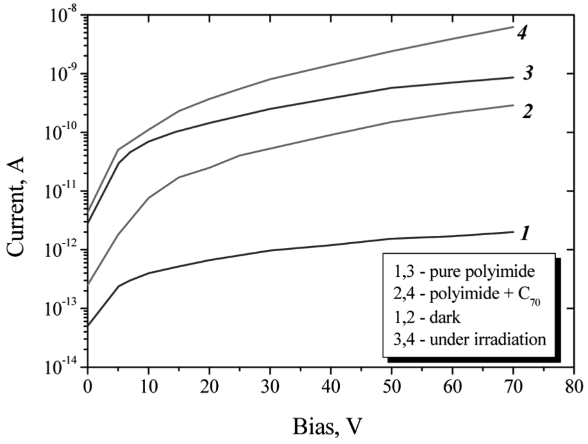

FIGURE 3 The dependence of the current on bias voltage of polyimide with 0.2 wt.% of fullerene C_{70}.

polyimide materials. It should be noticed when organic polyimide matrix had been doped with carbon CNTs the change in Δn_i can be obtained up to 5.7×10^{-3} due to larger increase in the photoconductivity. It is not contradicted with the data obtained by authors of paper [26], where it has been shown that the electrical conductivity of

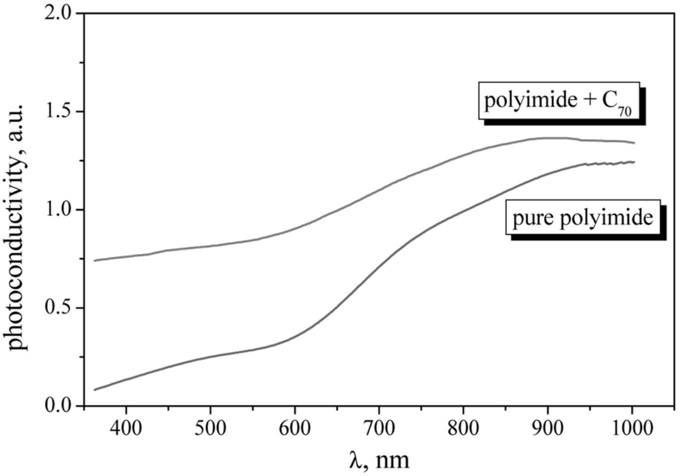

FIGURE 4 The dependence of the photoconductivity on wavelength of polyimide doped with 0.2 wt.% fullerene C_{70}.

TABLE 2 Nonlinear Optical Parameters of the Materials

Structure	n_2, $cm^2 W^{-1}$	$\chi^{(3)}$, $cm^3 erg^{-1}$ (esu)	Ref.
CS_2	3×10^{-14}	10^{-12}	[18]
SiO_2	3×10^{-16}	10^{-14}	[18]
C_{60} film		0.7×10^{-11}	[27]
C_{60} film		8.7×10^{-11}	[28]
C_{60} film		2×10^{-10}	[29]
C_{70} film		1.2×10^{-11}	[30]
C_{70} film		2.6×10^{-11}	[28]
Cu – phthalocyanine		$2.1 \pm 0.2 \times 10^{-12}$	[31]
Pb – phthalocyanine		2×10^{-11}	[32]
α-TiO-phthalocyanine		1.59×10^{-10}	[33]
bis-phthalocyanine	-2.87×10^{-9}	$2–5 \times 10^{-9}$	[34]
Polyimide – C_{70}	0.78×10^{-10}	2.64×10^{-9}	[35,36]
Polyimide – C_{70}	-1.2×10^{-9}	1.9×10^{-10}	[37]
2-cyclooctylamine-5-nitropyridine (COANP) – C_{60}	$0{,}69 \times 10^{-10}$	$2{,}14 \times 10^{-9}$	[17]
COANP – C_{70}	$0{,}77 \times 10^{-10}$	$2{,}4 \times 10^{-9}$	[17,38]
PDLC based on COANP – C_{70}	1.6×10^{-9}	4.86×10^{-8}	[39]
Si	10^{-10}	10^{-8}	[18]
Liquid crystal	10^{-4}	10^{-3}	[18]

nanotube-doped materials from polyimide group has been increased by more than 11 orders of magnitude. Thus, after nanoobjects doping the refractive parameters of the organic materials such as polyimide can be improved drastically.

The place of the structure investigated among other nonlinear optical systems has been indicated. The data are shown in the Table 2.

One can see from the data of Table 2 that nonlinear optical parameters of the nanoobjects-doped conjugated structures are larger than those obtained for traditional nonlinear systems that permit to apply these materials as effective holographic recording element, spatial light modulator, switchers, nonlinear absorber in the visible and in the near-infrared spectral ranges. Moreover, the data testify that nonlinear characteristics of the materials studied are close to the Si-based structures that provoke the polyimide with nanoobjects to be used in organic solar energy technique.

4. CONCLUSION

The results of the study can permit to postulate that: the main basic first improvement of the optical properties of nanoobjects-doped polyimide is connected with dramatic change in the refractive index.

It permits the area of nonlinear optical application to be extended drastically. The second improvement is coincided with the dramatic shift in the IR range when π-conjugated polyimide can be doped with nanoobjects. It provokes the operation in the near IR range, for example, at the wavelength of 1315 nm. The third problem is connected with good light stability of polyimide doped with nanoobjects that is more than the one regarded to polyimide doped with dyes. The fourth improvement is connected with the good laser strange of the polyimide layer due to large number of C–C bond in the nanoobjects, which are hard to brake and can be compared with diamond.

The basic mechanisms responsible for the laser-induced change in the refractive index have been discussed. The place of the materials studied has been shown among other nonlinear optical systems applied for nonlinear optics.

REFERENCES

[1] Silence, S. M., Walsh, C. A., Scott, J. C., & Moerner, W. E. (1992). *Appl. Phys. Lett.*, *61*, 2967.

[2] Orczyk, M. E., Zieba, J., & Prasad, P. N. (1993). *Proceed. SPIE*, *2025*, 298.

[3] McBranch, D. W., Maniloff, E. S., Vacar, D., & Heeger, A. J. (1997). *Proceed. SPIE*, *3142*, 161.

[4] Belousov, V. P., Belousova, I. M., Bespalov, V. G., Budtov, V. P., Volynkin, V. M., Grigor'ev, V. A., Danilov, O. B., Zhevlakov, A. P., Kalintsev, A. G., Ponomarev A. N., Tul'skii, S. A., & Yutanova, E. Yu. (1997). *J. Opt. Technol.*, *64*, 870.

[5] Ono, H., Saito, I., & Kawatsuki, N. (1998). *Applied Physics B*, *B66*, 527.

[6] Cui, Y., Swedek, B., Cheng, N., Zieba, J., & Prasad, P. N. (1999). *Journal of Applied Physics*, *85*, 38.

[7] Kamanina, N. V., Kaporskii, L. N., Sizov, V. N., & Stasel'ko, D. I. (2000). *Opt. Commun.*, *185*, 363.

[8] Kamanina, N. V., Sizov, V. N., & Stasel'ko, D. I. (2001). *Optics and Spectroscopy*, *90*, 1.

[9] Hoshi, H., Nakamura, N., Maruyama, Y., Nakagawa, T., Suzuki, S., Shiromaru, H., & Achiba, Y. (1991). *Jap. J. Appl. Phys., Part 2*, *30*, L1397.

[10] Ganeev, R. A., Ryasnuansky, A. I., Kamanina, N. V., Kulagin, I. A., Kodirov, M. K., & Usmanov, T. J. (2001). *Optics B: Quantum and Semiclassical Optics*, *3*, 88.

[11] Guldi, D. M., Rahman, G. M. A., Zebretto, F., & Prato, M. (2005). *Acc. Chem. Res.*, *38*, 871.

[12] Kajzar, F., Taliani, C., Zamboni, R., Rossini, S., & Danieli, R. (1996). *Synth. Met.*, *77*, 257.

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

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

[15] Vivien, L., Riehl, D., Hache, F., & Anglaret, E. J. (2000). *Nonlinear Opt. Phys. Mater.*, *9*, 297.

[16] Zhang, T., Xi, K., Yu, X., Gu, M., Guo, Sh., Gu, B., & Wang, H. (2003). *Polymer*, *44*, 2647.

[17] Kamanina, N. V. & Sheka, E. F. (2004). *Opt. Spectrosc.*, *96*, 599.

[18] Akhmanov, S. A. & Nikitin, S. Yu. (1998). *Physical Optics*, Moscow University Press: Moscow, [in Russia]; Akhmanov, S. A. & Nikitin, S. Yu. (1997). *Physical Optics*, Oxford University Press: USA, 270.

[19] Collier, R. J., Burckhardt, C. B., & Lin, L. H. (1971). *Optical Holography*, Academic Press: New York and London.

[20] Kamanina, N. V. & Vasilenko, N. A. (1997). *Opt. Quantum Electron.*, *29*, 1.

[21] Kamanina, N. V. (2002). *Synthetic Metals*, *127*, 121.

[22] Kamanina, N. V. & Plekhanov, A. I. (2002). *Optics and Spectroscopy*, *93*, 408.

[23] Mikhailova, M. M., Kosyreva, M. M., & Kamanina, N. V. (2002). *Tech. Phys. Lett.*, *28*, 450.

[24] Varnaev, A. V., Zhevlakov, A. P., & Kamanina, N. V. (2002). *Optics and Spectroscopy*, *93*, 327.

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

[26] Xiaowen Jiang, Yuezhen Bin, & Masaru Matsuo. (2005). *J. Polymer*, *46*, 7418.

[27] Liu Huimin, Taheri B., & Weiyi Jia. (1994). *Phys. Rev.*, *B49*, 10166.

[28] Kajzar, F., Taliani, C., Muccini, M., Zamboni, R., Rossini, S., & Danieli, R. (1994). *Proceed. SPIE*, *2284*, 58.

[29] Li, J., Feng, J., & Sun, J. (1993). *J. Chem. Phys.*, *203*, 560.

[30] Krätschmer, W., Lamb, L. D., Fostiropoulos, K., & Huffman, D. R. (1990). *Nature*, *347*, 354.

[31] Chollet, P. A., Kajzar, F., & Le Moigne. (1990). *J. Proceed. SPIE*, *1273*, 87.

[32] Shirk, J. S., Lindle, J. R., Bartoli, F. J., Hoffman, C. A., Kafafi, Z. H., & Snow, A. W. (1989). *Applied Physics Letters*, *55*, 1287.

[33] Singh Nalwa, H., Saito, T., Kakuta, A., & Iwayanagi, T. (1993). *Journal of Physical Chemistry*, *97*, 10515.

[34] Wen, T. C. & Lian, I. D. (1996). *Synth. Metal.*, *83*, 111.

[35] Kamanina, N. V. (2001). *Optics and Spectroscopy*, *90*, 867.

[36] Kamanina, N. V. (2003). *Synthetic Metals*, *139*, 547.

[37] Ganeev, R. A., Ryasnyansky, A. I., Kodirov, M. K., & Usmanov, T. (2000). *Opt. Commun.*, *185*, 473.

[38] Kamanina, N. V. (2001). *Journal of Optics A: Pure and Applied Optics*, *3*, 321.

[39] Kamanina, N. V. (2002). *Journal of Optics A: Pure and Applied Optics*, *4*, 571.