SOME ASPECTS OF THE MATERIALS' OPTICAL LIMITING FEATURES

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Abstract: Due to the effective use of the fullerenes and other nanoparticles in the materials for the general optoelectronic, laser and display technique, as well as for biomedicine, the different mechanisms to attenuate the light intensity are considered with good advantage in order to protect the human eyes and technical devices from high laser irradiation. Reverse saturation absorption, complex formation, scattering, etc. are taken into account. In the current paper the influence of the content of the nanoobjects on the interface relief is shown and considered as an additional possible optical limiting mechanism. Moreover, the diffraction from the nanostructured materials via high frequency Kerr effect is added to extend the numbers of the optical limiting mechanisms. Different experimental instruments and supporting models are presented. VIS lasers, AFM, OCA devices are applied to test and visualize the results. Theoretical and experimental data are in good coincidence.

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Introduction

The problem of limiting of the laser radiation of high intensity (or energy density in the pulsed mode) is one of the first places in the design of the complex optoelectronic circuits and the technical devices used in eye microsurgery and other biomedical applications. This is due to the necessary protection of the service personnel and sensitive photo electronic converters from laser breakdown. Thus, it becomes necessary to solve the problem of searching and modifying the properties of new sensitized materials, as well as to study the mechanisms responsible for limiting the radiation passing through such types of the materials.

Due to unique properties of the fullerenes (Krätschmer, 1990; Krätschmer, 1990; Liu, 1994) and carbon nanotubes (Robertson, 2004; Namila, 2004; Ould-Moussa, 2013), these sensitizers are occupying the special place in the area of the materials parameters optimization, including the features to attenuate the laser beam. Moreover, the π -conjugated organic materials (such as pyridines, polyvinyl carbazole, polysilanes, poly(3-hexylthiophene), polyimide, liquid crystal matrixes, etc.) sensitized with the mentioned above nanoobjects are the promising compounds for these purposes (Brabec, 1999; Sapurina, 2000; Kamanina, 2001; Kamanina, 2002) because they allow their physical-chemical characteristics to be modified by doping with a varied amount of these impurities.

Among different mechanisms, the optical limiting (OL) effect, a reverse saturable absorption (Couris, 1995; Belousov, 1997), intermolecular charge transfer complex formation (Hosoda, 1997; Kamanina, 2005), light-induced change of the refractive index (Kamanina, 2008; Kamanina, 2012), scattering (Belousov, 1999; Belousova, 2001), etc. can be considered.

In the current paper the novel approach to explain the OL mechanism is proposed. It is based on the nanoobjects varied content influence on the surface relief, thus, on the additional reflection from the surface. Moreover, the novel results are shown to support the OL mechanism via high-frequency Kerr effects for the sensitized liquid crystal matrix with the fullerene-containing polyaniline via energy losses due to diffraction.

Experimental conditions, materials and results

The possible model on how the content of the nanoobjects influences the interface relief is shown in Fig.1 via checking the wetting angle at the material surface. The organics matrix can be presented as the polyimides, polyvinyl alcohol (PVA), etc. compounds. It has been shown before that the change of the nanoobjects (fullerene) content in the polyimide matrix from 0.5 to 1.0 wt.% permitted to increase of the wetting angle up to 72 and 103 degrees respectively; when the content of the carbon nanotubes (CNTs) in the PVA matrix is 1.0 wt.%, the change of the wetting angle can be changed from 40 to 82 degrees (Kamanina, 2019). This content of the CNTs in the PVA can be increase up to 5.0 wt. before the saturation, that provokes the change of the wetting angle at the PVA surface up to 28-130 degrees. As a result, the scattering from these modified surfaces should be taken into account under the condition of the OL effect explanation.

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It should be remarked that the fullerenes powder with a purity of 97% and single wall carbon nanotubes (SWCNTs), type #704121, with the diameter placed in the range of 0.7-1.1 nm, have been purchased from Alfa Aesar and Aldrich Co., respectively, and used in the current experiment. Moreover, the pure PVA water solution was made with the content of the dry PVA in water being 8.0 wt.%. Furthermore, the OCA 15EC instrument, which has been purchased from LabTech Co. (Saint-Petersburg-Moscow, Russia), has been applied in order to reveal the change of the wetting angle at the modified surfaces. The measured increased wetting angle directly showed the surface relief modification via the influence of the nanoobjects hexagonal and pentagonal core structures.

Figure 1: Change of the wetting angle from the organics after the body sensitization (a) and model presentation of the light beams reflection (see the multidirectional arrows marked with a yellow marker) from the sensitized organics, when the core of the nanoobjects modifies the surface relief of the organic matrix (b).

Source: Author

Figure 2: Analog scheme of the four-wave mixing technique, which permit to register the efficiency in the first order diffraction when the light beam diffracted at the nanostructured materials. 1- nanosecond pulsed Nd-YAG-laser with the converter at 532 nm, 2- filters, 3 – 49.9% mirror, 4 – 99.8% mirror, 5 – He-Ne-laser to visualize the diffraction effect in the non-reversible mode, 6 - Nd-laser to check the diffraction in the reversible mode, 7 – filters, 8 – 99.9% mirror, 9 – sample (sensitized organics), 10 – photodetector, 11 – the picture of the registered diffraction order under the Raman-Nath diffraction conditions (colored and grey ones).

Source: Author

Moreover, other OL mechanism responsible for the dramatic attenuation of the laser beam can be taken into account using the energy losses via diffraction through the sensitized organics. In this case the polyimide and polyaniline matrixes can be considered effectively.

The following results obtained via the checking the diffraction efficiency in the scheme that is analogous shown before for the four-wave mixing technique (Kamanina, 1995; Kamanina, 1997) is

presented in Fig.2. The pulsed nanosecond Nd-laser with the second harmonic generation was used as the main irradiation source. One can testify that the light beams create the interference pictures at the organic thin films structured with nanoobjects, but this interference pattern diffracts at the nanostructured materials body. As the results, the energy can be distributed at 10 or more diffracted orders, if the Λ^{-1} is more than the thickness of the thin films. Here Λ is the spatial frequency and Λ^{-1} is the period of the recorded grating. Thus, the energy losses via diffraction can be taken account to explain the attenuation of the laser beam via the OL effect.

Some results of the laser induced refractive index that change in the sensitized organic media are shown in Table 1. The data is comparatively presented for the pure LC, LC doped with the complex of polyimide+C₇₀ and the LC doped with the complex PANI-C₆₀.

Table 1: Comparative laser-induced change of the refractive index Δn_i in the liquid crystal thin films doped with the complex: PANI-C ₆₀ .						
	Materials	Content of the sensitizer wt. %	W, J×cm ⁻²	τ, ns	Δn_i	Ref.
	LC	0.0	0.2		0.16×10 ⁻³	Khoo, 1994
	LC doped with polyimide+C ₇₀	0.2	0.1-0.3	20	1.2×10 ⁻³	Kamanina, 2013
	LC doped with PANI+C ₆₀	1	0.3	20	1.1×10 ⁻³	current
	LC doped with PANI+C ₆₀	6	0.3	20	1.3×10 ⁻³	current
Source: Author						

It should be remarked once again, that the change of the refractive index has been estimated under the Raman-Nath diffraction conditions. The following equation has been made (Akhmanov, 1997), which firstly has been applied for the calculations for the structured organic media in paper (Kamanina, 2005):

$$\eta = \frac{I_1}{I_0} = \left(\frac{\pi \Delta n_i d}{2\lambda} \right)^2,$$

where Δn_i – induced change of the refractive index, I_1 is the intensity in the first diffraction order, I_0 is the input laser intensity, d is the thickness of the medium, λ is the wavelength of the light incident on the medium. In the current experiment the wavelength of the laser beam was 532 nm, as the second harmonic of the pulsed Nd-laser, and the pulse width τ was close to 20 ns.

Conclusion

To summarize the obtained results and proposed consideration, one can testify towards the following aspects. Different physical mechanisms can be considered in order to explain the OL effect. Among them, indeed, the reverse saturable absorption is the main mechanism, which is responsible for the OL process in the visible spectral range. Under the sensibilization model matrix conditions the bathochromic shift can be found, thus, the intermolecular complex formation can be used too as the OL mechanism, which permits to extend the spectral range up to IR one. Moreover, the energy losses via diffraction from the nanostructured organics can extend the number of the OL mechanism efficiently. As the novel additional mechanism, shown in the current paper, the energy losses via reflection from the surfaces can be considered under the condition when the material body has been sensitized with the varied content of the nanoobjects. The core of the nanoobjects influences on the surface relief of the materials dramatically, which takes part in the attenuation of the laser beam. As the more perspective nanoobjects, which provoke the surface relief change, namely the CNTs can be used. Based on the data presented one can conclude that the area of the OL process application can be extended and supported by a different model of the OL mechanism.

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