

Short Communication

## Mechanisms of optical limiting in a COANP solution contaning fullerenes C<sub>70</sub>: Applicability for the optoelectronics devices <sup>#</sup>

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## Abstract

The mechanisms describing the nonlinear-optical properties of COANP solution sensitized with fullerenes  $C_{70}$  have been described in this work. The data of a DSC technique for pure COANP and system COANP- $C_{70}$  have been presented. The experimental data regarding the transmission have been shown for the materials treated by laser irradiation.

Keywords: laser-matter interaction, fullerenes, polymer, charge transfer complexes

Fullerenes and carbon nanotubes are widely studied due to their unique properties [1–3]. Composite materials with fullerene and nanotubes can be used to limit a powerful laser radiation in the visible and near-infrared spectral ranges and to protect human eyes and photosensitive equipment including ceramics. Also fullerenes and nanotubes can be applied in a solar energy device as a new type of solar battery materials and in medicine to deliver medications.

In this paper we are discussing optical limiting properties of 2-cyclooctylamino-5-nitropyridine (COANP) solution containing fullerenes  $C_{70}$ . Currently the greatest interest is an investigation of mechanisms leading to the observed nonlinear-optical properties. There are several mechanisms explaining nonlinear-optical properties: reverse saturable absorption (RSA), photoinduced change in the refractive index, Förster mechanism, complex formation, etc.

The 10 mm thick of 1% COANP solution in tetrachlorethane sensitized with fullerenes  $C_{70}$  of 0.5, 1.0, 10 and 20 wt.% were investigated. A second harmonic of a pulsed a Nd:YAG-laser radiation ( $\lambda = 532$  nm) with a pulsewidht of 10 ns was used as a laser source. A diameter of input laser beam was 5 mm. The several neutral filters were used to vary the incident energy density. The scheme to treat the samples in order to activate the optical limiting features was analogous to that presented in the paper [4].

Experiments have demonstrated the limiting of the laser irradiation with energy density from 0.1 J/cm<sup>2</sup> to 0.6 J/cm<sup>2</sup> (see Fig. 1). We have obtained the maximum attenuation of the radiation with density energy of 0.35 J/cm<sup>2</sup> for the solution COANP-C<sub>70</sub> with fullerene content of 20 wt.%. The energy value passed through solution has been decreased up to 18 times.

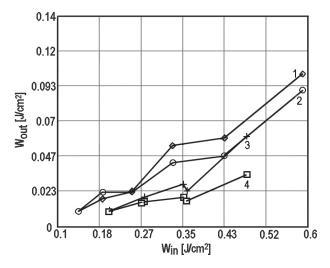


Figure 1. Dependence of the output energy density  $(W_{out})$  on the input energy density  $(W_{in})$  for COANP with fullerene  $C_{70}$ : 1) 0.5, 2) 1.0, 3) 10.0 and 4) 20.0 wt.%

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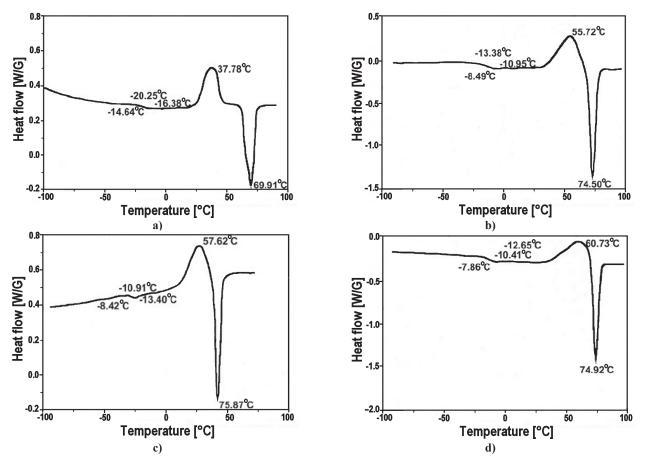


Figure 2. DSC analysis of: a) pure COANP (4.00 mg), and COANP with fullerene C<sub>70</sub>: b) 1.0 wt.% (5.00 mg), c) 2.0 wt.% (5.00 mg) and d) 5.0 wt.% (5.00 mg)

We are considering RSA and the complex formation as the mechanisms responsible for the optical limiting of COANP-C<sub>70</sub> system. The RSA mechanism is based on a difference in cross section for excited and unexcited fullerene molecule. The cross section of singlet-triplet excited state in the fullerene is larger than the one of the unexcited molecule. The population of excitation levels increases with laser energy increase, so absorption increases.

The intermolecular charge transfer complex with large cross section absorption can be formed in  $\pi$ -conjugated organic system containing C<sub>70</sub> due to the large electron affinity energy of fullerene [5,6]. The electron affinity of acceptor fragment in COANP is close to 0.45 eV. This parameter for fullerene is 2.65 eV. To support an evidence of the intermolecular charge transfer complex formation, we present results of DSC analysis (see Fig. 2). One can see that all transition temperature values shifting (such as a melting point, a point of crystallization and a glass transition temperature) in the case of adding some amount of fullerene C<sub>70</sub> in COANP.

It should be mentioned that the DSC results are correlated with mass spectrometry data shown previously in the paper [7]. As it has been revealed that mass spectrometry data point out to the formation of the fullerene–HN-group charge transfer complexes (CTCs) for the COANP– $C_{70}$ system. It has been shown the rate of release of  $C_{70}$  from the sensitized COANP on heating. Two mass spectrometry peaks have been observed. The first one, at a temperature of about 400°C, relates to the release of fragments with the mass of a fullerene molecule. The second peak is shifted to the temperature range from 400°C up to around 520°C and corresponds to the decomposition of HN-group–fullerene complexes. Based on the DSC experiment the shift of the characteristic temperatures to larger temperature region also has been obtained. Thus, CTCs have been supported by DSC method as an additional one.

## Conclusions

According to the experimental results the  $\pi$ -conjugated organic system COANP with C<sub>70</sub> could be used in techniques and equipments including ceramics as a medium for an effective absorption of a laser radiation. The mechanism related to the formation of the intermolecular charge transfer complex has been supported by the results of DSC analysis.

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## References

 J. Wang, W.J. Blau, "Inorganic and hybrid nanostructures for optical limiting", *J. Opt. A: Pure Appl. Opt.*, 11 [2] (2009) 1–16.

- N.V. Kamanina, V.N. Sizov, D.I. Stasel'ko, "Recording of thin phase holograms in polymer-dispersed liquid-crystal composites based on fullerene-containing π-conjugated organic systems", *Opt. Spectrosc.*, **90** [1] (2001) 1–3.
- 3. T. Hsinhan, X. Zhihua, K. Ranjith, W. Leeyith, A.M. Dattelbaum, A.P. Shreve, H. Wang, M. Cotlet, "Structural dynamics and charge transfer via complexation with fullerene in large area conjugated polymer honeycomb thin films", *Chem. Mater.*, **23** [3] (2011) 759–761.
- 4. N.V. Kamanina, "Reverse saturable absorption in fullerene-containing polyimides. Applicability of the Förster model", *Opt. Commun.*, **162** [4-6] (1999) 228–232.
- N.V. Kamanina, "Fullerene-dispersed nematic liquid crystal structures: dynamic characteristics and self-organization processes", *Physics-Uspekhi*, 48 [4] (2005) 419–427.
- N.V. Kamanina, N.A. Shurpo, S.V. Likhomanova, S.V. Serov, P.Ya. Vasilyev, V.G. Pogareva, V.I. Studenov, D.P. Uskokovic, "Influence of the Nanostructures on the Surface and Bulk Physical Properties of Materials", *Acta Physica Polonica A*, **119** [2] (2011) 256– 259.
- N.V. Kamanina, A.I. Plekhanov, "Mechanisms of optical limiting in fullerene-doped π-conjugated organic structures demonstrated with polyimide and COANP molecules", *Opt. Spectrosc.*, **93** [3] (2002) 408–415.