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Bicolor laser stimulated elastooptical effect in the 2-cyclooctylamino-5-nitropyridine-C_{70} system

Abstract

For the first time the piezooptical effect has been observed in the 2-cyclooctylamino-5-nitropyridine doped with intermolecular strong acceptor—fullerene C_{70}. The observed effect may be used for optically operated acoustootpical modulators. Both contribution of electronic as well as phonon subsystem is crucial here. The laser induced changes were performed by 1,064 and 532 nm nanosecond laser pulses. The possible mechanisms of the observed phenomena are discussed within a framework of photoinduced electron-phonon anharmonicities.

Introduction

Modern innovation problems and development of high-power laser and acoustic sources has stimulated an interest and extensive research in designing new nonlinear optical, piezooptical and mechanooptical systems doped with effective nanoparticles for information processing, holographic recording, optical limiting, etc. [*1*–*7*]. These problems have stirred a search, namely for optical materials, the characteristics of which can be simply changed via intermolecular charge transfer complex formation. Among these materials the systems based on 2-cyclooctylamino-5-nitropyridine (COANP) occupy an exceptional place due to their highly delocalized π-conjugated electron states. It should be stressed that this system has been carefully studied so that it could be shown in the papers [*8*–*13*].

2-cyclooctylamino-5-nitropyridine system is a good model material with effective intra-molecular charge transfer process between NH-donor group and NO_2-accceptor. This intra-molecular interaction can be easily modified via nanoobjects sensitization. Indeed, electron affinity energies of intra-molecular acceptor fragments of COANP are close to 0.4–0.54 eV. The electron affinity energy of, for example, fullerenes C_{60} and C_{70} is ~2.65 eV. Thus, the inter-molecular acceptor fragment electron affinity energy is at least five times larger. Therefore, incorporated nano objects are stronger sensitizers and they dominate the acceptor fragments of intra-molecular complexes. In this case the field gradient favours an enhanced ground state dipole moment. So the increase of local volume polarizability favours an increase of dipole polarizability as well as the increase of charge carrier mobility.

In the current paper the new feature of optically induced COANP system doped with fullerene C_{70} is presented. It may be recommended for use as promising material for photoinduced acoustooptical modulators operated by external light.

Experiment

In our experiments, the fullerene-doped COANP films of about 3–4 μm thick were prepared by spin-coating of the solution in 1,1,2,2-tetrachloroetane on a glass substrate. A small amount of non-photosensitive polyimide structure has been used as plasticizer in order to form the homogenous solid film. The fullerene concentration was varied within 0.5 … 5 wt%. Absorption spectra of the investigated systems were measured by a Perkin Elmer Lambda 9 spectrometer in the 200–3,000 nm region with spectral resolution about 0.5 nm.

The photoinduced changes were stimulated by Nd:YAG laser operating at 1,064 nm in 15 ns regime with frequency repetition up to 1 kHz which has been used in order to form the induced piezooptical effect in the COANP materials. The pulse energy of the 1,064 nm photoinducing laser was varied within the 40–70 mJ and of the doubled frequency using BiB_3O_6 single crystal was equal to 20–30 mJ. Its diameter was fixed at 3…4 mm and the Gaussian-like contour was used. The incident angle of the photoinducing laser beam was equal to about the 24°. The probing of the piezooptical effect was performed by cw He–Ne laser with powered density 3 mW, which avoid any overheating. The traditional Senarmont method used for analogous studies of other polymer composites was applied. Usually the mechanical field was applied by external piezoelectric transducer which have formed the mechanical field at frequency of about 1 MHz. The set-up allows for registration of the changes of the birefringence with a precision up to 10^{-6}. The photoinducing process was performed simultaneously with the microsecond CO2 laser treatment. The observed effect achieved its maximum after 4–6 min. Of the photoinduced treatment and was controlled by the saturation of a CO_2 laser beam.

Results and discussion

Absorption spectra of the system studied are shown in Fig. 1. Absorption spectrum of COANP-polyimide-fullerene composite shows substantially different spectral features than spectra of COANP-polyimide or polyimide-C_{70} systems. There are two additional absorption peaks-at 490 nm and 810–820 nm. In the present paper we explain these peculiarities with inter-molecular charge transfer features and support them via analytic calculations, mass-spectrometry and nonlinear optical experiments [*11–13*]. It should be emphasized, that for all investigated COANP systems the nonlinear characteristics lie within the range: $n_2 = 10^{-10}–10^{-9}$ cm$^2 \times W^{-1}$ and $\chi^{(3)} = 10^{-10}–10^{-9}$ cm$^3 \times$ erg^{-1}. In comparison, for quartz, which is a classical material traditionally used for nonlinear optics, the values of n_2 and $\chi^{(3)}$ are $(2.5–3) \times 10^{-16}$ cm$^{-2}\cdot W^{-1}$ and 10^{-14} cm^3 erg^{-1} (esu), respectively. Thus, the systems studied reveal increased nonlinear optical parameters via photorefractive estimation.

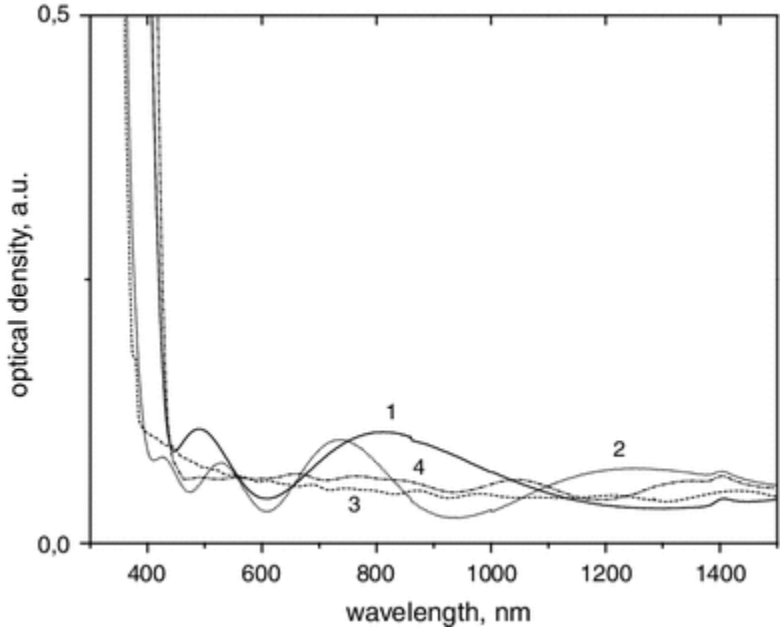

Fig. 1

Absorption spectra: 1 – fullerene-doped COANP-polyimide structure; 2 – pure polyimide; 3 – C_{70}-doped polyimide; and 4 – fullerene-free COANP-polyimide

The performed experiments have shown that the maximal photoinduced piezooptical effect was achieved for fullerene-doped COANP structure. For the remaining three structures this effect was at least one order less. Moreover, the illumination by 532 nm gives the photoinduced changes at least three times higher (see Fig. 2). It is interesting that the maximal effect was observed at power density equal to about 260 mW/cm^2. At higher intensities there occurs some material's photodestruction.

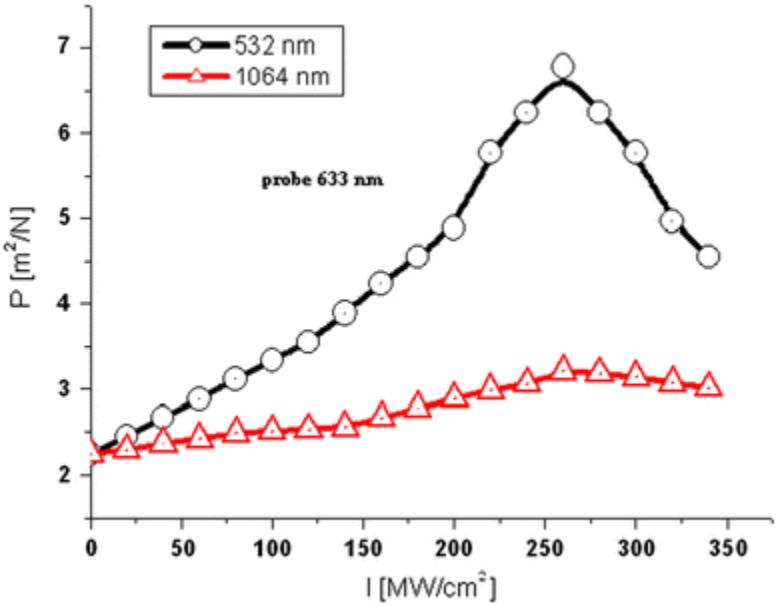

Fig. 2

Photoinduced piezooptical effect for diagonal tensor coefficient at different photoinducing wavelengths for fullerene-doped COANP-polyimide structure

After switching off of the photoinducing laser beam the sample returns to its initial state within the 6 min. The existence of the effect for fullerene-doped COANP-polyimide structure may be caused by existence of effective charge transfer which is demonstrated by the absorption spectra presented in the Fig. 1 together with the specific contribution of the electron-phonon interaction. It is well known that the third-order nonlinear piezooptical effects as well as other third order nonlinear optical susceptibilities are very sensitive to the contribution of the electron-phonon interactions [*14*, *15*]. Additionally very crucial are interfaces separating the polymers and the embedded chromophores [*16*, *17*]. It is caused by some flattering of the delocalized states due to the low-dimensional periodicity [*18*] and electron-phonon anharmonicities [*19*].

Conclusion

The photoinduced piezooptical effect was discovered under influence of the optical treatment by the 1,064 nm nanosecond and its second harmonic generation. Moreover the illumination by 532 nm shows the photoinduced changes are at least three times higher. It is interesting that the maximal effect was observed at power density equal to about 260 mW/cm^2. The observed effect is a consequence of

substantial contribution of the photoexcited phonon subsystem and photoexcited electron-phonon anharmonicity. The comparison with the similar chormophore confirms a principal role of the π-conjugated charge transfer due to interaction with electron-phonon subsystem.

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