AIP | Applied Physics Letters

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Citation: Applied Physics Letters **93**, 183304 (2008); doi: 10.1063/1.3021364
View online: http://dx.doi.org/10.1063/1.3021364
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/93/18?ver=pdfcov
Published by the AIP Publishing

Influence of doping on the photorefractive properties of a polymer-dispersed liquid crystal

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(Received 20 June 2008; accepted 18 October 2008; published online 7 November 2008)

The photorefractive effect is studied in a photoconducting polysiloxane containing small droplets of a low molar mass liquid crystal. In order to vary the trap density for charge carriers, the system is doped with tetramethyl-phenylendiamine. The measured energy transfer from one beam to the other (two-beam coupling) indicates a high gain coefficient, which is enhanced by adding small concentrations of the dopant. Measurements of the phase and the amplitude of the refractive index modulation confirm that this behavior can be attributed to an increase in the trap density. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3021364]

Despite extensive research on photorefractivity in inorganic crystals[1] in the past, they are still an important subject for investigation. Photoconducting polymers and other organic glasses have been extensively studied for the past decade.[2–10] Photorefractive behavior was also observed in polymer-dispersed liquid crystals (PDLCs),[11–13] which are phase-separated liquid crystal/polymer composites, where the liquid crystal is used as the electro-optical component. The photorefractive effect is based on spatial modulation of the refractive index due to charge redistribution in optically nonlinear and electro-optic materials. The spatially modulated light intensity generates charge carriers, which move by diffusion or drift and finally become trapped thereby producing a nonuniform space-charge distribution. The internal space-charge field modulates the refractive index and creates a phase grating. Therefore, the incident light beams are diffracted. If the mirror symmetry of the setup with respect to the bisector of the interfering beams is broken, a phase shift φ_n occurs between the inducing intensity pattern and the induced phase grating.

While the appearance of the photorefractive effect in organic materials is in principle well known, improving the performance of particular systems by doping is a subject of topical research. Various kinds of additives may be used for this purpose. Meerholz *et al.*[4] succeeded in achieving orientational enhancement[5] by adding plasticizers that lower the glass transition temperature. In previously investigated PDLC systems[12,13] based on poly(methylmethacrylate), the photoconductivity was improved by adding a photosensitizer. Also Cipparrone *et al.*[14,15] used dye as a dopant in order to increase light absorption. Apart from the light-induced charge carrier generation, the photorefractive performance depends also on the charge trap density within the material. Improvements due to the latter aspect were achieved by Bolink *et al.*[16] in a homogeneous photorefractive organic glass by adding organic semiconductor molecules that act as traps for the charge carriers.

Here, the effect of a semiconducting dopant (as used by Bolink *et al.*)[16] in a PDLC system is reported. The investigated PDLC samples (prepared as described previously[17,18]) consist of the photoconductive matrix poly[methyl-3-(9-carbazolyl)-propyl)siloxan] (PSX3), fullerene C_{60} (Fluka) as the photosensitizer, and the nematic liquid crystal mixture TL202 (Merck, Darmstadt). These PDLCs were doped with tetramethyl-phenylendiamine (TMPD). For this purpose, (61.1-x)% PSX3, 38.3% TL202, 0.6% C_{60}, and x% TMPD were dissolved in toluene and mixed thoroughly. The solvent was completely evaporated at 100 °C. Test cells (E.H.C. Co., Japan) with indium tin oxide electrodes and a 50 μm cell gap were used in applying an external electric field. Capillary forces helped fill the cells at 80 °C with the mixture. The test cells were rapidly cooled to 0 °C in order to get sufficiently small liquid crystal droplets. The measurements were taken at room temperature.

The samples were investigated by two-beam coupling experiments. A tilted geometry (Fig. 1, inset) is used in measuring the gain coefficient Γ,[17]

$$\Gamma = \frac{1}{d}\left(\cos\,\theta_1 \ln\frac{I_1}{I_{10}} - \cos\,\theta_2 \ln\frac{I_2}{I_{20}}\right), \tag{1}$$

$$\Gamma = \frac{4\pi\Delta n\,\sin(\varphi_n)}{\lambda\,\cos[(\theta_1+\theta_2)/2]}.$$

In addition, a moving grating experiment[18,19] was used to determine the phase φ_n and the amplitude Δn of the induced refractive index modulation.

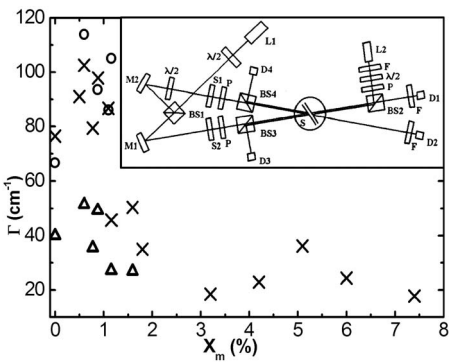

FIG. 1. Optical gain coefficient measured by two-beam coupling vs TMPD mass fraction (x_m) at different applied fields (△: 0.5 kV, ×: 1 kV, ○: 2 kV). Inset: experimental setup for two-beam coupling experiments. P: polarizers, S1, S2: shutters, BS: beam splitters, D: detectors, L1, L2: laser diodes, and $\lambda/2$: optical retarders.

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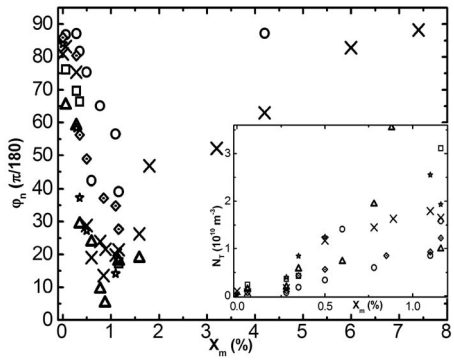

FIG. 2. Phase shift of the induced refractive index modulation as a function of TMPD mass fraction (x_m) at different applied fields (△: 0.5 kV, *: 0.75 kV, ×: 1 kV, ◇: 1.25 kV, □: 1.5 kV, ○: 2 kV). Inset: apparent trap density [calculated from φ_n using Eq. (3)] as a function of x_m.

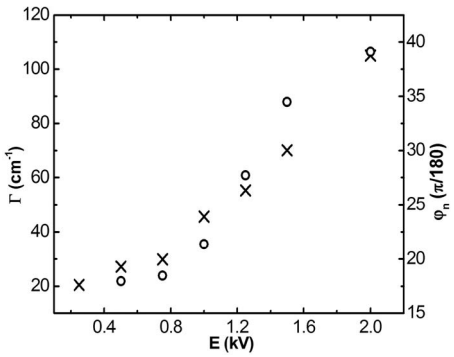

FIG. 3. Optical gain coefficient (×) and phase shift (○) in the sample with 1.16% TMPD vs applied field strength.

Samples with different mass fractions x_m of the dopant TMPD were investigated. The gain coefficient Γ increases with increasing amount of TMPD for small concentrations, $x_m < 1.1\%$ (Fig. 1). However, the gain decreases again for high dopant concentrations ($x_m > 1.1\%$). Samples with $x_m > 10\%$ show no photorefractive effect. This result shows that doping can indeed enhance the gain coefficient of the investigated PDLC, provided that the concentration of the dopant is not too high ($<1\%$) and the applied external field is sufficiently large (≥ 1 kV). In order to understand this behavior, the dependences of the gain on the external voltage and the TMPD mass fraction are studied in more detail and the results are discussed based on the standard model of photorefractivity.[20] The gain coefficient Γ depends on both the amplitude Δn and the phase φ_n of the induced phase grating. High Γ values are obtained for large Δn and large φ_n [$\approx \pi/2$, Eq. (1)]. The refractive index change Δn is proportional to the space charge field E_{SC}. According to the standard model of photorefractivity,[20] the applied field causes a migration of the charge carriers until they are captured in the traps. For moderate external voltages, the space charge field E_{SC} increases linearly with the component of the applied field strength E_K along the grating vector. For large voltages, the space charge field approaches a saturation field strength E_S,

$$|E_{SC}| \propto \frac{E_S E_K}{\sqrt{E_S^2 + E_K^2}}. \tag{2}$$

For high performance of the photorefractive effect, the saturation field E_S should be large, thereby enabling high values of E_{SC}, and thus high amplitudes Δn. However, for a large saturation field E_S, the external field E_K must also be large in order to achieve a large value of φ_n. The effective trap density N_T limits the maximum saturation field. If the diffusion field is neglected, the phase shift φ_n is given[3] by

$$\varphi_n \approx \arctan\frac{E_K}{E_S}, \quad \text{with} \quad E_S = \frac{e_0 N_T}{K\varepsilon\varepsilon_0}, \tag{3}$$

where K is the absolute value of the grating vector, e_0 is the elementary charge, ε_0 is the permittivity in vacuum, and ε is the relative permittivity. The results of the moving grating experiment indicate that the phase shift φ_n decreases with increasing dopant concentration for $x_m < 1.1\%$ (Fig. 2). This can be attributed to an increasing value of the saturation field E_S, which in turn corresponds to an increasing trap density N_T [Eq. (3) and Fig. 2]. In order to take advantage of the increase in E_S, the external field E_K has to be increased. If so, the gain coefficient is enhanced (Fig. 3), as expected. Surprisingly, the phase shift φ_n increases again with increasing TMPD concentration for $x_m > 1.1\%$, which seems to indicate a decrease in the apparent trap density. However, we suppose that the latter effect is due to changes in the sample morphology and that Eq. (3) is not valid for $x_m > 1.1\%$. The assumption of changing sample morphology is confirmed by the observations that the transmission changes considerably for concentrations $x_m > 2\%$ and that domains larger than the grating period are seen at higher x_m in the microscope.

In conclusion, TMPD proved to be suitable in order to increase the trap density and thus the gain coefficient. However, in the PDLC system described here, only small concentrations ($x_m < 1.1\%$) of the dopant are useful. In the best case, an increase in the gain coefficient Γ from 66.7 to 113.87 cm^{-1} could be achieved.

Financial support of this work by the European Science Foundation (EUROCORES, Grant No. 05-SONS-FP-014) and the German Research Foundation (DFG Grant No. KI 411/14-1) is gratefully acknowledged.

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