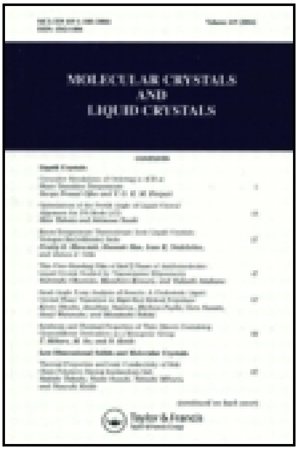
This article was downloaded by: [University of Haifa Library]
On: 09 August 2012, At: 14:09
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Chiral Azobenzene Nematics Phototunable with a Green Laser Beam

Svetlana V. Serak [a], Nelson V. Tabiryan [a], Guram Chilaya [b], Andro Chanishvili [b] & Gia Petriashvili [b]

[a] Beam Engineering for Advanced Measurements Co., Winter Park, Florida, USA
[b] Institute of Cybernetics, Tbilisi, Georgia

Version of record first published: 22 Sep 2010

To cite this article: Svetlana V. Serak, Nelson V. Tabiryan, Guram Chilaya, Andro Chanishvili & Gia Petriashvili (2008): Chiral Azobenzene Nematics Phototunable with a Green Laser Beam, Molecular Crystals and Liquid Crystals, 488:1, 42-55

To link to this article: http://dx.doi.org/10.1080/15421400802240144

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of Haifa Library] at 14:09 09 August 2012

Mol. Cryst. Liq. Cryst., Vol. 488, pp. 42–55, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802240144

Downloaded by [University of Haifa Library] at 14:09 09 August 2012

Chiral Azobenzene Nematics Phototunable with a Green Laser Beam

Svetlana V. Serak[1], Nelson V. Tabiryan[1], Guram Chilaya[2], Andro Chanishvili[2], and Gia Petriashvili[2]
[1]Beam Engineering for Advanced Measurements Co., Winter Park, Florida, USA
[2]Institute of Cybernetics, Tbilisi, Georgia

Phototuning of Bragg reflection bandgap from green to blue and from red to green wavelengths was induced with a green ($\lambda = 532\,nm$) laser beam in a cholesteric liquid crystal based on highly sensitive azobenzene nematic BEAM 1005 (BEAM Co.) and UV transparent non-photoisomerizable optically active dopant ZLI-6248 (R-2011) (Merck Ltd.). Optical switching between reflected and transmitted beams, as well as nonlinear transmission and reflection due to Bragg reflection band shift are studied in detail.

Keywords: azobenzene; Bragg reflection; chiral dopants; laser; liquid crystals

1. INTRODUCTION

Many interesting studies of liquid crystals (LCs) are related with controlling material parameters with light beams [1–3]. Optically induced processes are most efficient in LCs containing azobenzene in their molecular structure (azo LCs). Azobenzene molecules are distinguished with drastic change in their molecular structure as a result of photoisomerization [4]. The *trans*-isomer, 9 Å in length, is highly anisotropic and mesogenic, whereas the *cis*-isomer is 5 Å in size, rather symmetric and non-mesogenic. Azo LCs are in the mesophase when their molecules are in the state of *trans* isomers, and they can be transformed into isotropic phase when *cis* isomers are created by UV radiation. Generation of *cis* molecules destabilizes the LC ordering. The LC is transformed to the isotropic phase when the concentration of *cis* molecules reaches a certain value.

Address correspondence to Nelson V. Tabiryan, Beam Engineering for Advanced Measurements Co., 809 S. Orlando Ave., Suite 1,Winter Park, FL 32789, USA. E-mail: nelson@beamco.com

Downloaded by [University of Haifa Library] at 14:09 09 August 2012

Azo LCs are highly photosensitive materials for radiation of UV-green wavelengths. The constant of nonlinear refraction reaches values $\sim 0.4\,\mathrm{cm}^2/\mathrm{W}$ in the LC phase and it is only one order of magnitude smaller for photoinduced isotropic phase at $\lambda = 532\,\mathrm{nm}$ wavelength [5].

In cholesteric LCs (CLCs), the photoinduced isomerization of azobenzene molecules can cause a change of the pitch, and thus a shift of the wavelength of the selective reflection band (SRB). For a light propagating along the CLC axes, the peak of SRB occurs at the wavelength $\lambda_o = Pn$, where n is the average refractive index $n = (n_e + n_o)/2$ and n_e, n_o are the extraordinary and ordinary indices of refraction, respectively. The full width at half maximum of the SRB ($\delta\lambda$) is equal to $P\delta n$, where $\delta n = n_e - n_o$. The reflected light is circularly polarized with the sign of polarization related to the sign of the cholesterics helix.

A colour shift of the reflected light has been observed when a conformationally active dye has been added to a CLC [6,7], a photoisomerizable chiral compound has been used as a chiral dopant in a cholesteric mixture [8–13], as well as when photosensitive nematics were mixed with cholesteric LCs [14]. In all cases the shift can be attributed to a light induced change of the helical twisting power of the chiral photoisomerizable component. The majority of investigations were devoted to *trans-cis* transformations observed in different chiral or achiral azobenzene derivatives [15–27].

Azobenzene materials appear to be very attractive for applications, several papers were published on investigations of a large variety of novel mixtures including chiral and achiral azobenzene derivatives. Notably, a blue shift of more than 400 nm was achieved for the selective reflection band of CLCs containing azobenzene derivatives due to UV light emitting diode (LED) irradiation [14]. Later a reversible tuning in CLCs containing nematic azo- or azoxy- photo-sensitive components and photo- insensitive chiral dopants was observed with LEDs: by irradiating samples at 405 nm wavelength (blue shift) and at 466 nm wavelength (red shift) [28]. The maximum exposure times varied from 1.5 min for mixtures with azo-compounds to 10 minutes for mixtures with azoxy-compounds.

In this paper we report about phototuning of Bragg reflection bandgap with a green laser beam (532 nm) of low power density ($20\,\mathrm{mW/cm}^2$) in highly sensitive azobenzene nematic LC (BEAM Co.) doped with an optically active chiral dopant. The green laser beam changes the green reflective material into blue reflective, as well as red reflective into green. Nonlinear optical switching due to changes of transmission and reflection was studied. We observed formation

Downloaded by [University of Haifa Library] at 14:09 09 August 2012

of two-dimensional periodic structures preceding the color shift. Previously we described 2D gratings induced with violet light from low power LED ($\lambda_{\rm exp} = 395\,{\rm nm}$, $I = 3\,{\rm mW/cm^2}$) or diode laser ($\lambda_{\rm exp} = 409\,{\rm nm}$, $I = 10\,{\rm mW/cm^2}$) in cholesteric LCs doped with up to 25 wt.% azobenzene nematics [29]. In the new material compositions under study, 2D periodic structures were formed with a low power green laser beam.

2. EXPERIMENTAL RESULTS

The azo NLC 1005 was used as a photoizomerizable nematic. The material 1005 is a multi-component compound based on a series of 4-*n*-alkyl-4′-*n*-alkoxyazobenzenes [30]. It is photosensitive in a large temperature range including room temperature, 7°C–49°C. In Figure 1 the absorption spectra of *trans* and *cis* isomers of 1005 are shown. The absorption wavelength of azobenzenes depends on the particular molecular structure. Unsubstituted azobenzenes exhibit a low-intensity n-π^* absorption in the visible region ($\lambda_{\rm max} = 446\,{\rm nm}$), and a much higher intensity π-π^* absorption in the ultraviolet ($\lambda_{\rm max} = 345\,{\rm nm}$). The spectra measurements were made for thin cell with thickness of the LC layer 340 nm at room temperature using a fiber spectrophotometer. The spectrum of *cis*-isomers obtained after

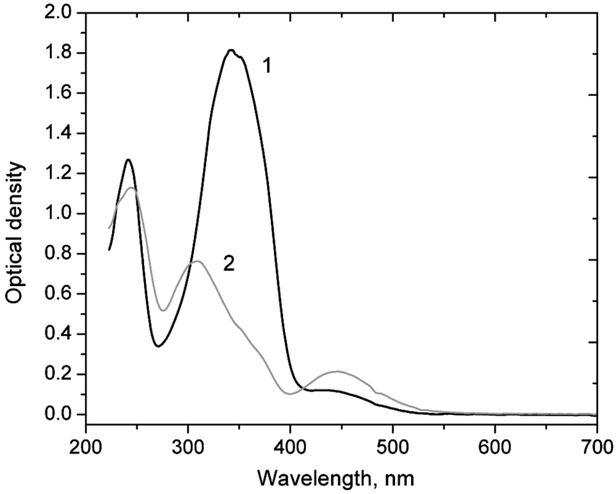


FIGURE 1 Absorbance spectrum of azo LC 1005 (BEAM Co.) in *trans* (1) and *cis* (2) forms. The thickness of the LC layer is $L = 340\,{\rm nm}$. The power density of the UV source is $8\,{\rm mW/cm^2}$.

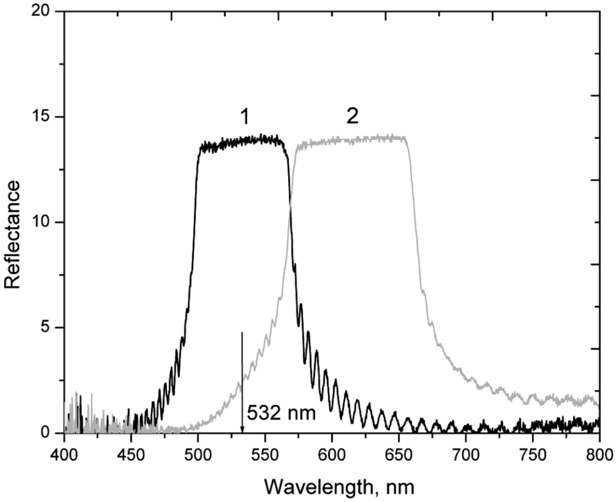


FIGURE 2 Reflectance spectra of CLC 1 (1) and CLC 2 (2) at 20°C.

30 s UV exposure ($\lambda_{\text{exp}} = 365\,\text{nm}$) did not change at longer UV exposure times.

We studied the mixtures of nematic azo LC 1005 with UV transparent non-photoisomerizable optically active dopant (OAD) ZLI-6248 (Merck). Two mixtures, 6248(30.6%)/1005(69.4%) (CLC 1) and 6248(26%)/1005(74%) (CLC 2), were fabricated and filled in planarly oriented cells. Two 2-mm thick plane-parallel glass substrates were coated with polyvinyl alcohol and then unidirectionally rubbed with cloth to promote planar alignment of the LC molecules. Thickness of the LC layer was 6 µm. Bragg reflection wavelength λ_B was 532 nm for the cell filled with the CLC 1 and 614 nm for the cell filled the CLC 2, Figure 2. Helical twisting power (HTP) β of chiral compounds was defined as $\beta = n/\lambda_B(0.01\,C)$, where λ_B was measured in microns (μm), C was the relative OAD concentration in weight percent. Its value is $\beta \cong 10\,\mu\text{m}^{-1}$ and sign of HTP is positive because material ZLI-6248 named as R-2011 has right-handed helix.

The CLC samples were exposed to an expanded and collimated green laser beam of 8 mm size and up to 14 mW/cm^2 power density. The CLC color was changed during irradiation from green to blue for the CLC 1 and from red to green for the CLC 2, Figure 3. The dependencies of Bragg reflection wavelength for both mixtures on exposure time to the green laser beam are shown in Figure 4. For comparison, phototuning upon illumination with a UV light at 365 nm was measured as well.

Downloaded by [University of Haifa Library] at 14:09 09 August 2012

Downloaded by [University of Haifa Library] at 14:09 09 August 2012

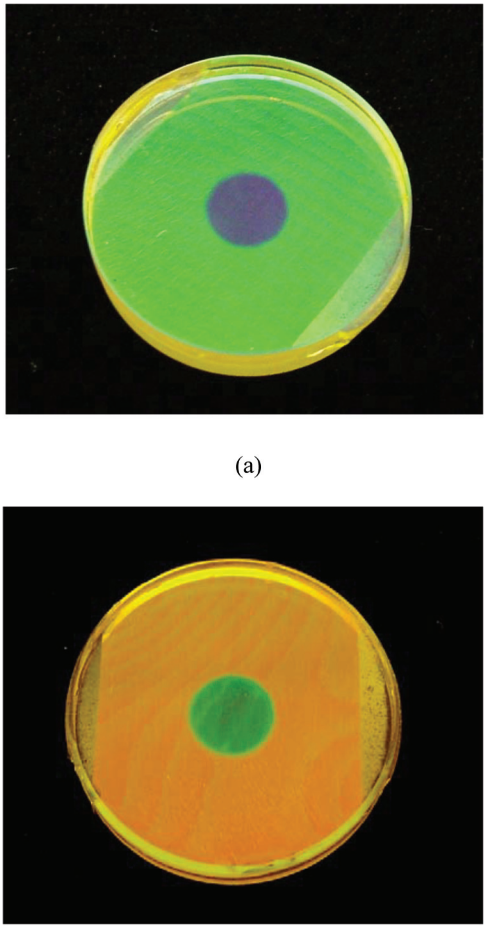
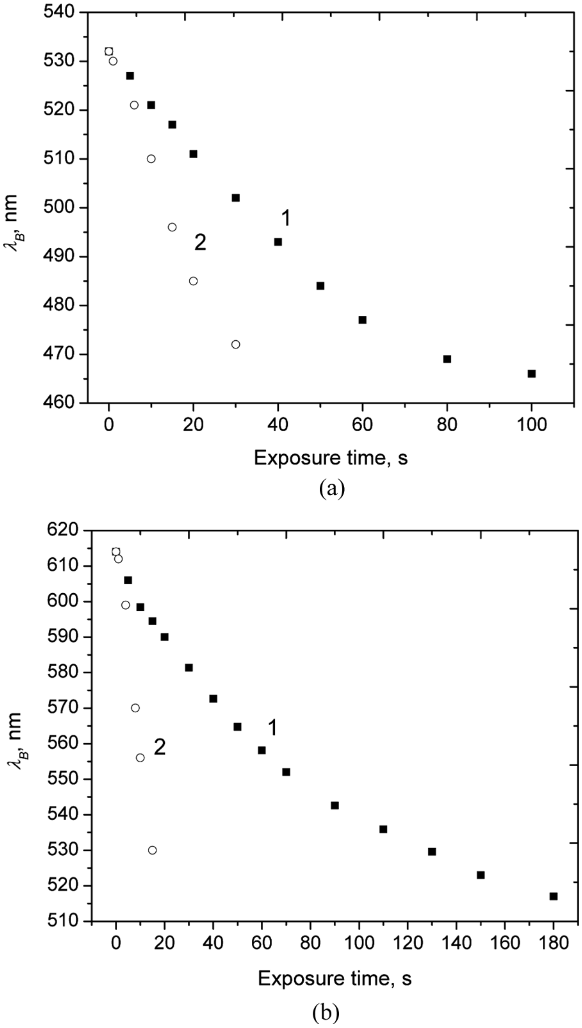


FIGURE 3 (a) Photo of the CLC 1 cell with initial green reflection bandgap shifting into blue reflection after 5 min exposure to a green laser beam (spot in the center of the cell). (b) Photo of the CLC 2 cell with initial red reflection transforming into green reflection after 10 min exposure to a green laser beam (spot in the center of the cell). The power density is 7.6 mW/cm^2.

The azo NLCs doped with OAD demonstrate "blue shift" of Bragg reflection band. Both materials are transformed into isotropic state at prolonged UV exposure: 30 s for the CLC 1 and 15 s for the CLC 2. Spontaneous relaxation of the materials back to the initial reflection state takes tens of hours for UV pre-exposed materials. No photo-induced phase transition is observed even at prolonged (20 min at

Downloaded by [University of Haifa Library] at 14:09 09 August 2012



(a)

(b)

FIGURE 4 Bragg reflection wavelength for CLCs 1 (a) and 2 (b) as a function of the exposure time to (1) a green laser beam ($I = 14\,\mathrm{mW/cm^2}$) and (2) to a UV radiation ($I = 10\,\mathrm{mW/cm^2}$).

$14\,\mathrm{mW/cm^2}$) exposure times to a green laser beam. The laser beam induces blue shift equal to $\Delta\lambda_B = 66\,\mathrm{nm}$ during 100 s for the material 1, and equal to 97 nm during 180 s for the material 2.

The decrease of Bragg wavelength is a result of decreasing order parameter. Indeed, blue shift of the Bragg wavelength is observed also when heating these materials, Figure 5. The shift is smaller in this

Downloaded by [University of Haifa Library] at 14:09 09 August 2012

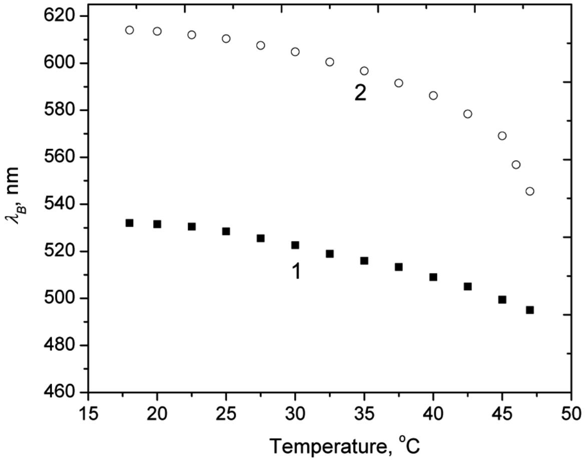


FIGURE 5 Bragg reflection wavelength vs temperature for the CLCs 6248(30.6%)/1005 (1) and 6248(26%)/1005 (2).

case compared to the effect of a light beam: $\delta\lambda_B = 37$ nm for the CLC 1 and 68 nm for the CLC 2. The clearing temperature of the materials ($T_{cl} = 47$°C) is close to the clearing temperature of the host nematic azo NLC, 49°C.

Transmission and reflection dynamics was measured using the optical set-up shown in Figure 6. A green laser beam linearly polarized with a polarizing cube was expanded, and its central part was selected with a diaphragm of 6 mm opening to get homogeneous distribution of the beam intensity. The beam after the diaphragm was slightly focused on the cell into a spot of 0.2 mm size with a lens of 200 mm focal length. A zeroth order quarter waveplate was adjusted for maximal reflection at the wavelength 532 nm. Transmitted and reflected

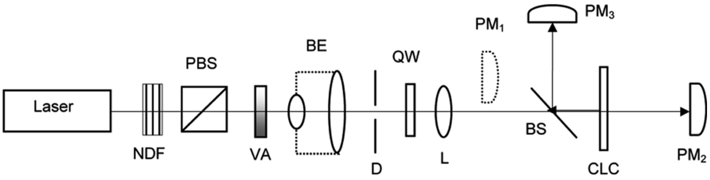
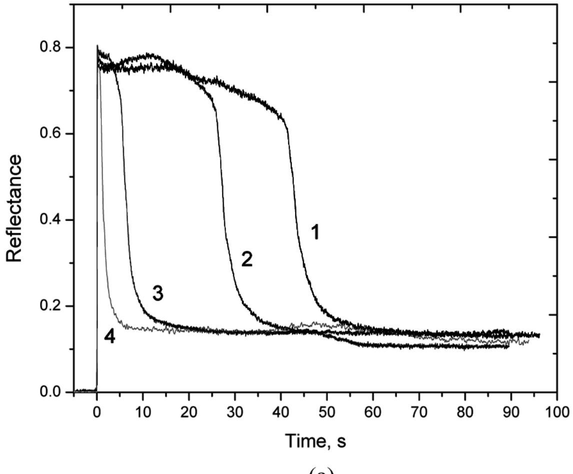
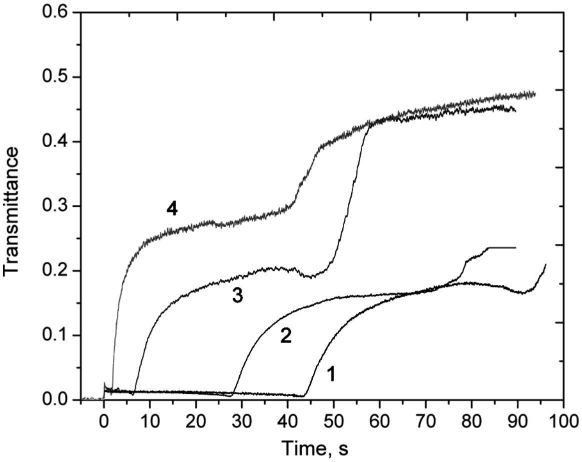


FIGURE 6 Experimental set-up for characterization of nonlinear reflection and transmission of CLCs: NDF – a set of neutral density filters; PBS – polarizing beam splitter; VA – variable attenuator; BE – beam expander; D – diaphragm; QW – zero order quarter waveplate; L – focusing lens; PM$_1$, PM$_2$ and PM$_3$ – power meters; BS – beam sampling plate.

Downloaded by [University of Haifa Library] at 14:09 09 August 2012



(a)



(b)

FIGURE 7 Reflection (a) and transmission (b) dynamics of the CLC 1 for several power values of a green laser beam: (1) 5.5 μW; (2) 7 μW; (3) 10 μW; (4) 20 μW.

powers of the beams were registered using power meters PM_2 and PM_3, correspondingly. The removable power meter PM_1 was used for measuring the input power of the laser beam. Neutral density filters NDF and a variable attenuator allowed controlling the beam power with a small graduation.

The blue shift of the Bragg reflection band for the green reflective sample results in decreasing reflection and increasing transmission.

By that, the transmission increases in two stages, Figure 7. During the time corresponding to the first stage, the transmitted beam diffracts on the 2D gratings which was observed on the screen behind the sample, Figure 8. The second stage of increasing transmission is related to erasure of these gratings.

Transmission and reflection dynamics for the material 2 are more complicated, Figure 9. Both the reflection and transmission decrease during illumination for a low beam power, Figure 9(a). This may be a result of scattering of the beam on the spontaneously formed 2D gratings. The 2D pattern appears at 2-μW ($I = 6.4\,\mathrm{mW/cm^2}$) power of a green laser beam. For comparison, periodical structures described previously [29] were generated by a violet laser beam with power density of $10\,\mathrm{mW/cm^2}$. CLCs described in this paper are considerably more sensitive even for longer wavelength that is due to high concentration of azobenzene molecules in CLC mixtures.

Depending on radiation power, the transmittance and reflectance dynamics in CLC 2 with higher concentration of azo NLC is, apparently, determined by three factors: spontaneous pattern formation; bandgap shift; and critical opalescence. The first process, spontaneous pattern formation, is substantial only at lower power levels,

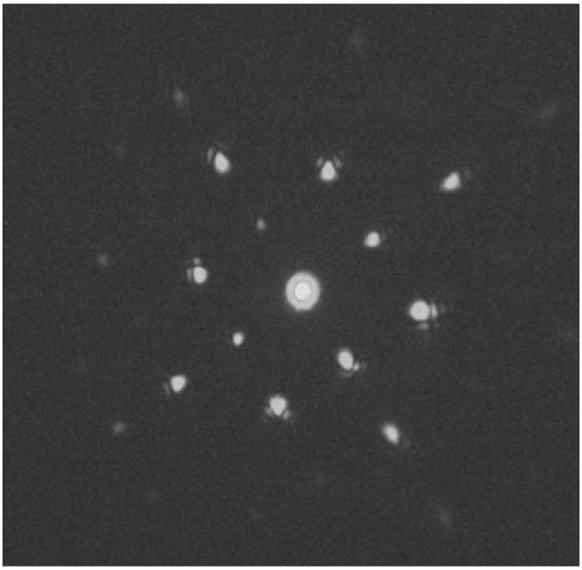
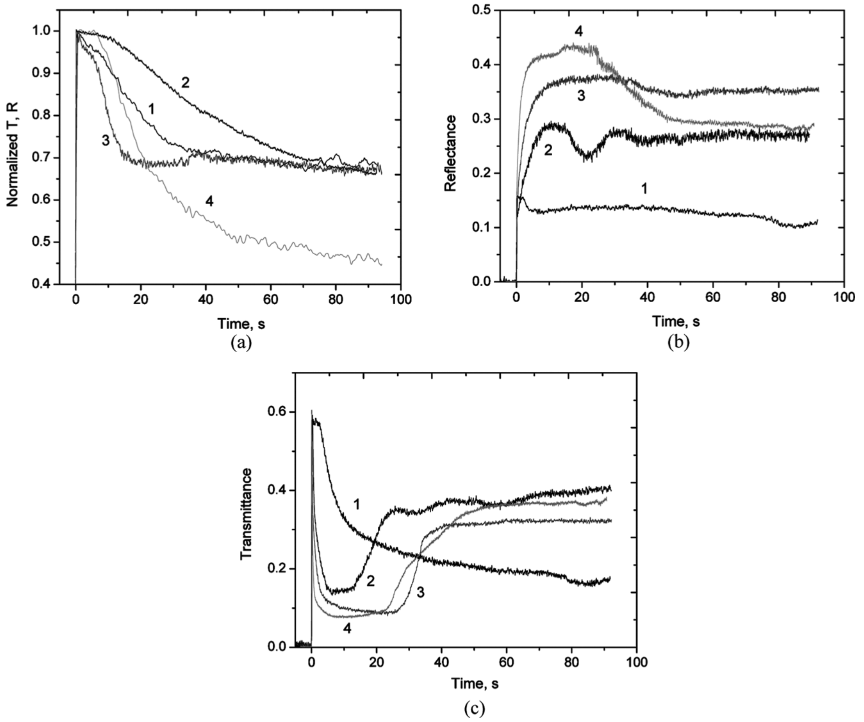


FIGURE 8 Diffraction pattern induced with a focused green laser beam of 20-μW power in the material CLC 1.

Downloaded by [University of Haifa Library] at 14:09 09 August 2012

Downloaded by [University of Haifa Library] at 14:09 09 August 2012



(a) (b) (c)

FIGURE 9 Reflection and transmission dynamics for CLC 2 at several beam power values of the laser beam. (a) Dynamics of normalized reflection (1, 3) and transmission (2, 4) at low power regime: (1, 2) 2 μW; (3, 4) 3 μW. (b) Reflectance dynamics for different power values: (1) 9 μW; (2) 75 μW; (3) 125 μW; (4) 400 μW. (c) Transmittance dynamics for different power values: (1) 9 μW; (2) 75 μW; (3) 125 μW; (4) 400 μW.

~1–4 μW, where the bandgap shift is practically absent. The role of critical opalescence becomes evident at high energy levels ~100 mJ/cm^2. The bandgap shift contributes into increasing of reflectance and decreasing transmittance starting form intermediate energy levels.

The time constants were calculated using exponential fit of the reflection decay curves for the CLC 1 and transmission decay curves for the CLC 2, Figure 10. The obtained characteristic time is hundreds of milliseconds at power density ~100 mW/cm^2. This time coincides with the formation time of 2D periodical structures. The time required for reaching the state of minimum transmission is inverse proportional to the radiation power as it is expected for

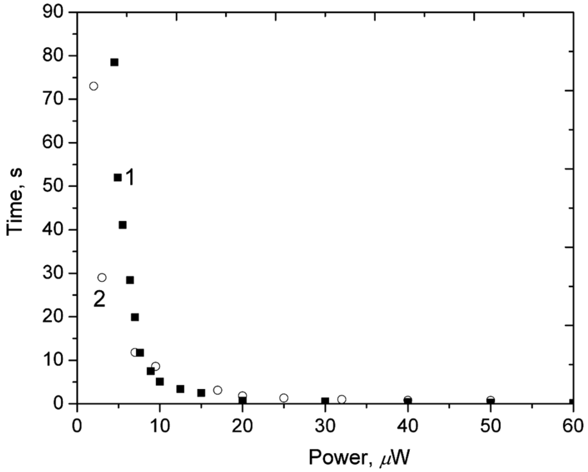


FIGURE 10 Time of appearance of scattering caused by formation of 2D gratings: (1) – CLC 1; (2) – CLC 2.

critical opalsecense requiring accumulation of a critical concentration of *cis*-isomers.

We measured transmission and reflection of the CLC 1 and CLC 2 cells changing power density of the laser beam, Figure 11. One can see that for CLC 1 the reflection is decreasing from 80% to 8% and the transmission increases from 5% to 65% when the power density is increased from 20 to 400 mW/cm^2. Photoinduced changes for CLC 2 are 40% in reflection and 48% in transmission. Note that the sum $(T + R)$ for both cells is smaller than the initial transmission of the cells. It can be caused by increasing absorption of azo LCs at accumulation of *cis*-isomers as well as by the enhanced scattering/diffraction due to formation of 2D spatial patterns.

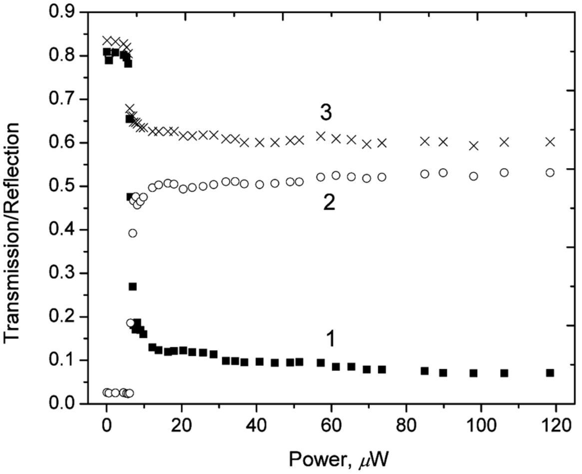
3. CONCLUSION

We have demonstrated laser-induced nonlinear optical switching of reflected and transmitted beams due to Bragg reflection shift between green and blue and between red and green wavelengths in CLCs based on azobenzene nematics and chiral dopants using low power radiation of 532 nm wavelength. The restoration of the initial reflection state takes over 60 hours after illuminating the CLC with a green laser beam and over 160 hours after UV exposure.

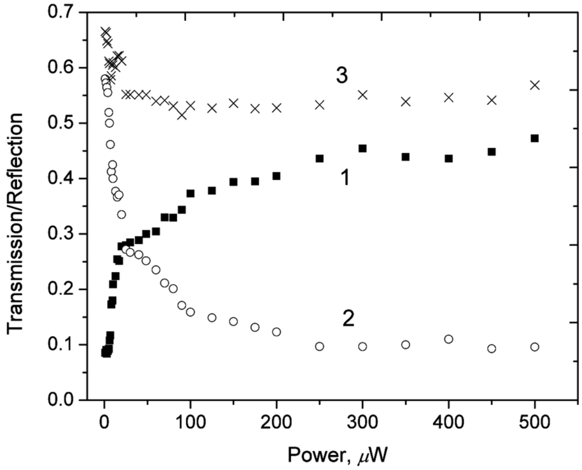
The shift of the photoinduced reflection band is accompanied with several phenomena such as formation of 2D periodic structures

Downloaded by [University of Haifa Library] at 14:09 09 August 2012

Downloaded by [University of Haifa Library] at 14:09 09 August 2012



(a)



(b)

FIGURE 11 Transmission (1), reflection (2) and the ratio $(T+R)/T_0$ (3) vs input power: (a) CLC 1; (b) CLC 2.

and critical opalescence near photoinduced isothermal phase transition. The 2D spatial structures are caused by undulation of CLC layers and are transient in nature taking place during adaptation of the helical structure to the new pitch value. These structures influence notably the transmitted beam only. At higher power levels, the transmission is influenced primarily by enhanced light scattering due to formation of isotropic microdroplets in the nematic phase at the vicinity of photoinduced phase transition (critical opalescence).

REFERENCES

[1] Tabirian, N. V., Sukhov, A. V., & Zel'dovich, B. Ya. (1986). *Mol. Cryst. Liq. Cryst.*, *136*, 1.

[2] Khoo, I. C. & Wu, S. T. (1993). *Optics and Nonlinear Optics in Liquid Crystals*, World Scientific: Singapore.

[3] Chilaya, G. (2000). Cholesteric liquid crystals: Optics, Electrooptics and Photooptics. In: *Chirality in Liquid Crystals*, Bahr, Ch. & Kitzerow, H. (Eds.), Springer Verlag: New York, Chapter 6, 159–185.

[4] Rau, H. (1990). Photochemistry of azobenzenes. In: *Photochemistry and Photophysics*, Rebek, J. (Ed.), CRC Press: Boca Raton, FL, Vol. 2, 119–141.

[5] Tabiryan, N., Hrozhyk, U., & Serak, S. (2004). *Phys. Rev. Lett.*, *93*, 113901.

[6] Sackmann, E. (1971). *J. Am. Chem. Soc.*, *93*, 7088.

[7] Schnuriger, B. & Bourdon, J. (1976). *J. Chim. Physique.*, *73*, 795.

[8] Vinogradov, V., Khizhniak, A., Kutulya, L., Reznikov, Yu., & Reshetnyak, V. (1990). *Mol. Cryst. Liq. Cryst.*, *192*, 273.

[9] Yarmolenko, S. N., Kutulya, L. A., Vaschenko, V. V., & Chepeleva, L. V. (1994). *Liq. Cryst.*, *16*, 877.

[10] Boiko, N. I., Kutulya, L. A., Reznikov, Yu. A., Sergan, T. A., & Shibaev, V. P. (1994). *Mol. Cryst. Liq. Cryst.*, *251*, 311.

[11] Bobrowski, A. Yu., Boiko, N. I., & Shibaev, V. P. (1999). *Liq. Cryst.*, *26*, 1749.

[12] Van de Witte, P., Brehmer, M., & Lub, J. (1999). *J. Mater. Chem.*, *9*, 2087.

[13] Vicentini, F., Cho, J., & Chien, L.-C. (1998). *Liq. Cryst.*, *24*, 483.

[14] Hrozhyk, U. A., Serak, S. V., Tabiryan, N. V., & Bunning, T. J. (2007). *Adv. Func. Mat.*, *17*, 1735.

[15] Kuruhara, K., Kanda, T., Nagase, T., & Nonaka, T. (1998). *Appl. Phys. Lett.*, *73*, 2081.

[16] Yamaguchi, T., Inagava, T., Nakazumi, H., & Irie, M. (2000). *Chem. Mater.*, *12*, 869.

[17] Ruslim, C. & Ichimura, K. (2000). *J. Phys. Chem.*, *B104*, 315.

[18] Lee, H., Doi, K., Harada, H., Tsustsumi, O., Kanazawa, A., Shiono, T., & Ikeda, T. (2000). *J. Phys. Chem.*, *B104*, 6529.

[19] Feringa, B. L., Van Delden, R. A., Koumura, N., & Geertsema, E. (2000). *Chem. Rev.*, *100*, 1789.

[20] Tamaoki, N. (2001). *Adv. Mat.*, *13*, 1135.

[21] Moriyama, M., Song, S., Matsuda, H., & Tamaoki, N. (2001). *J. Mater. Chem.*, *11*, 1003.

[22] Serak, S., Arikelian, E., Gleeson, H., Grozhik, V., Guillou, J., & Usova, N. (2002). *Liq. Cryst.*, *29*, 19.

[23] Tabiryan, N., Serak, S., & Grozhik, V. (2003). *J. Opt. Soc. Am.*, *B20*, 538.

[24] Ikeda, T. (2003). *J. Mater. Chem.*, *13*, 2037.

[25] Mallia, V. & Tamaoki, N. (2004). *Chem. Soc. Rev.*, *33*, 76.

[26] Chanishvili, A., Chilaya, G., Petriashvili, G., & Sikharulidze, D. (2004). *Mol. Cryst. Liq. Cryst.*, *409*, 209.

[27] Hrozhyk, U., Serak, S., Tabiryan, N., & Bunning, T. (2007). *J. Adv. Mat.*, *19*, 3244.

Downloaded by [University of Haifa Library] at 14:09 09 August 2012

[28] Chilaya, G., Chanishvili, A., Petriashvili, G., Barberi, R., Bartolino, R., Cipparrone, G., Mazzulla, A., & Shibaev, V. (2007). *Adv. Mat.*, *19*, 565.

[29] Hrozhyk, U. A., Serak, S. V., Tabiryan, N. V., & Bunning, T. J. (2007). *Optics Express*, *15*, 9273.

[30] Hrozhyk, U., Serak, S., Tabiryan, N., & Bunning, T. (2006). *Mol. Cryst. Liq. Cryst.*, *454*, 235.

Downloaded by [University of Haifa Library] at 14:09 09 August 2012