

Near-infrared sensitive photorefractive device using polymer dispersed liquid crystal and BSO:Ru hybrid structure

Ren Chung Liu,¹ Vera Marinova,^{1,2,*} Shiuan Huei Lin,³ Ming-Syuan Chen,¹ Yi-Hsin Lin,¹ and Ken Yuh Hsu¹

¹Department of Photonics, National Chiao Tung University, Hsinchu 30010, Taiwan

²Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

³Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan

*Corresponding author: veramarinova@nctu.edu.tw

Received March 11, 2014; revised April 24, 2014; accepted April 26, 2014;
posted April 28, 2014 (Doc. ID 207982); published May 30, 2014

A near-infrared sensitive hybrid device, based on a Ru-doped BSO photorefractive substrate and polymer dispersed liquid crystal (PDLC) layer, is reported. It is found that the photoexcited charge carriers generated in the BSO:Ru substrate create an optically induced space charge field, sufficient to penetrate into the PDLC layer and to re-orient the LC molecules inside the droplets. Beam-coupling measurements at the Bragg regime are performed showing prospective amplification values and high spatial resolution. The proposed structure does not require indium tin oxide (ITO) contacts and alignment layers. Such a device allows all the processes to be controlled by light, thus opening further potential for real-time image processing at the near-infrared range. © 2014 Optical Society of America

OCIS codes: (160.5320) Photorefractive materials; (230.3720) Liquid-crystal devices; (090.7330) Volume gratings.
<http://dx.doi.org/10.1364/OL.39.003320>

The development of hybrid structures based on a combination of organic and inorganic materials with nanoparticles or functional molecules has attracted essential scientific and technological interest due to outstanding properties such as the large anisotropy and strong birefringence typical of organics and high photosensitivity of inorganics [1,2]. Furthermore, the common feature between the above materials is the photorefractive effect, which refers to the spatial modulation of the refractive index in response to light. The photorefractive effect arises when the charge carriers, photogenerated by a spatially modulated light intensity, are trapped to produce a non-uniform space-charge distribution. The unique property of the photorefractive effect is the beam amplification, which allows a weak beam to grow exponentially with the distance, thus opening possibilities for practical applications of devices in nonlinear optics and photonics [3].

Significant beam amplification values have been achieved on several hybrid organic/inorganic structures [4,5]. However, the development of such structures is still challenging, especially at the near-infrared spectral range, because of the trade-off between the application of a high external voltage and enhancement of liquid crystals' (LCs) molecular reorientation. Tabiryan and Umeton [6] predicted theoretically that the space charge field (E_{sc}) created by the photogenerated charge carriers in inorganic substrates can penetrate into the LC layer, acting as a driving force to modulate the LC directors. This makes the hybrid structure simpler and avoids the external voltage application. Recently, a number of hybrid cells based on ferroelectrics such as KNbO_3 and SBN:Ce assembled with nematic LC layers have been successfully realized to support experimentally the above prediction at the visible spectral range [5,7]. Until now, only a limited number of near-infrared sensitive structures have been designed based on semiconductor substrates such as CdTe [8] or GaAs [9] and an LC layer, which also requires precise alignment processes.

Sillenite crystals are well known as excellent photoconductors, and due to their remarkable charge carrier mobility, these belong among the fastest materials for real-time image processing and related dynamic applications [10–12]. Furthermore, $\text{Bi}_{12}\text{SiO}_{20}$ (BSO) is an essential component for optically addressed spatial light modulators (SLM). Aubourg *et al.* [13] proposed monocrystalline BSO assembled with a LC layer into a coherent-to-incoherent image converter, or so-called liquid crystal light valve (LCLV). Later on, this idea was extended and several nonlinear applications of nondoped BSO/LCLV devices at the visible spectral range were demonstrated [14,15]. For the first time, Takizawa and co-workers [16,17] assembled BSO with polymer dispersed liquid crystal (PDLC) into a hybrid structure with high transmittance, high resolution, real-time operation, and no need of polarizers for projection displays applications. However, all the above proposed configurations using BSO substrates work under an external voltage and at the visible spectral range.

Recently [12], we found that Ru is very suitable as a dopant in BSO, which significantly improves the response time and the photosensitivity at 1064 nm. Moreover, the addition of Ru in the BSO structure shows promising features for beam transfer enhancement [18], which opens further opportunities for the development of near-infrared devices for bio-medical diagnostic and real-time image processing.

In this Letter, we present, for the first time to our knowledge, a Ru-doped BSO crystal combined with PDLC into a light valve hybrid structure, operating at near-infrared. In general, PDLC consists of micrometer-sized droplets of LC randomly dispersed in a transparent polymer matrix. Because of the randomness of LC droplets dispersed in a polymer matrix, PDLCs do not require use of polarizers in contrast to the conventional LCs [1]. Generally, PDLC can be switched between a light-scattering state and a transparent state by applying

an external electric field, which mainly results from mismatch or match of refractive indices between the LC and the polymer. Electrical driving of PDLC usually requires high electric voltage application (10–20 V/ μm). Alternatives have been proposed to re-orient the LC molecules either optically or by acoustic waves [19,20].

Here, we propose a hybrid structure combining the excellent photoconductivity of Ru-doped BSO crystal with the strong birefringence of PDLC. A near-infrared light is used to re-orient the LC molecules inside the LC droplets by the space charge field, created via a photogeneration of charge carriers in the BSO:Ru photoconductive layer. The near-infrared sensitivity and the charge carriers necessary to build up the space charge field come from the BSO:Ru plate, whereas the birefringent modulation is provided by PDLC. The proposed structure is very simple and easy to fabricate, without need of ITO layer deposition, alignment layers, polarizers, and an external voltage. All the processes are driven by the space charge field induced by infrared light.

The hybrid structure consists of a BSO:Ru substrate, PDLC film (10 μm thickness), and a glass substrate. The Ru-doped BSO plate was cut from the bulk crystal [21] and optically polished to 0.4 mm thickness. PDLC was fabricated by mixing UV-curable monomer NOA65 ($n_p = 1.515$ at 1064 nm, Norland) in a nematic LC host (E 48, $\Delta n = 0.16$ at $\lambda = 1064$ nm, Merck) at 30:70 wt% ratio. A LC/monomer mixture was injected into an empty cell composed of BSO:Ru and a glass substrate at the isotropic state at $T = 90^\circ\text{C}$. Then the sample was exposed with UV light ($\lambda = 365$ nm) with an intensity of 60 mW/cm^2 for 15 min at $T = 20^\circ\text{C}$. The PDLC phase separation morphology was observed by a polarizing optical microscopy, and the average diameter of the LC droplets was around $7.3 \mu\text{m}$.

To test the near-infrared properties, a diode-pumped solid state laser emitting at 1064 nm was used. First, a Gaussian laser beam (1 mm waist) was impinged on the BSO:Ru/PDLC structure, and the transmitted light intensity was detected. Figure 1(a) shows the time-dependent relative transmittance. The transmittance is small and does not change with time at low beam intensity, which indicates the structure scatters the incident

light because of the mismatch between the refractive indices of the LCs and the polymer binder. When the illuminated intensity is larger than 300 mW/cm^2 , the transmittance starts to increase with time, which means the BSO:Ru/PDLC starts to respond to light.

At some threshold value of 500 mW/cm^2 , the structure turns to a highly transparent state. The same test has been performed on a glass/PDLC/glass reference sample, made with the same thickness (as used for the hybrid structure) and layered between two glass substrates. No noticeable changes of the transmittance with the time have been detected on it, as is seen from Fig. 1(a).

Obviously, the light irradiation on BSO:Ru/PDLC leads to a reverse of its initial opaque state to the transparent state. We suppose the effect comes from BSO:Ru crystal. Because of its near-infrared absorption and high photoconductivity, the Gaussian beam illumination caused charge carriers' generation, which migrate by diffusion to form an inhomogeneous distribution. This photo-induced field, generated inside the BSO:Ru plate, can be strong enough (estimated later) to spread out into the PDLC surface layer, realigning the LC molecules' orientation inside the droplets and thus changing the LCs' director and, consequently, the refractive index and transparency of the structure. The effect of E_{sc} field is supported by monitoring the Gaussian beam on the structure, as shown in Fig. 1(b). The beam image when the infrared light is off/on is displayed at Fig. 1(c). Evidently, BSO:Ru/PDLC becomes more transparent in the area, where the space charge field is stronger. The presented results are in good agreement with the numerical calculation by Stevens *et al.* [22] about the Gaussian beam effect on electric field and charge density distribution in BSO crystal. In addition, we tested the thermal heating effect by adjusting the thermocouple very close to the laser spot. With increasing the light intensity, the temperature increased and saturated at $50 \pm 0.5^\circ\text{C}$; this occurs at 500 mW/cm^2 (when the structure becomes highly transparent). This value is still below the clearing point of the LCs; therefore, we suppose the E_{sc} field is the dominant factor contributing to the LCs' realignment and BSO:Ru/PDLC transparency.

Evidently, Ru-doped BSO possesses enough concentration of trap density necessary to support the charge carriers' generation and subsequent E_{sc} field distribution. Furthermore, the optical activity (typical for sillenites) becomes lower, when doped with Ru [11]. We measured a value of $1.6^\circ/\text{mm}$ at 1064 nm, which can be neglected.

Owing to the above demonstrated ability of the space-charge field to realign the LC molecules, two-beam coupling experiments have been performed. First, the input laser beam was split to two linearly polarized beams with 1:1 ratio [300 mW output power of each beam, Fig. 2(a)]. Figure 2(b) shows simultaneously detected behavior of both beams passing throughout the structure. As is seen, after the BSO:Ru/PDLC becomes transparent, a constructive and destructive depletion occurs, which is indication for a 90° phase shift between the light pattern and the index grating. No change between two beams has been detected on the glass/PDLC/glass reference sample. Next, the ratio between the pump and signal beam has been experimentally optimized to $I_s/I_p = 1/50$, where

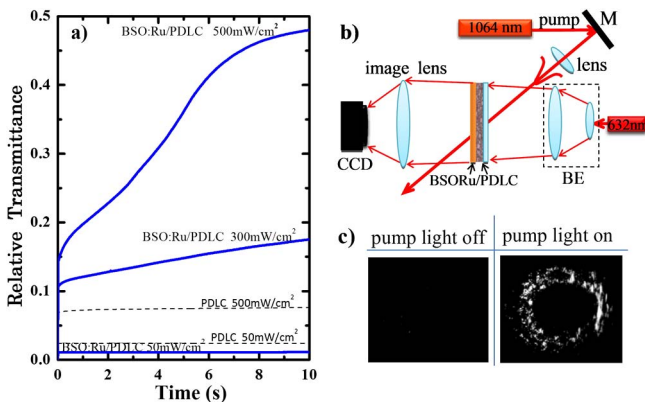


Fig. 1. (a) Relative transmittance under different 1064 nm intensities. Solid and dashed lines stand for BSO:Ru/PDLC and PDLC, respectively. (b) Experimental set-up for Gaussian beam illumination through BSO:Ru/PDLC. (c) Beam shape when infrared light is off and on.

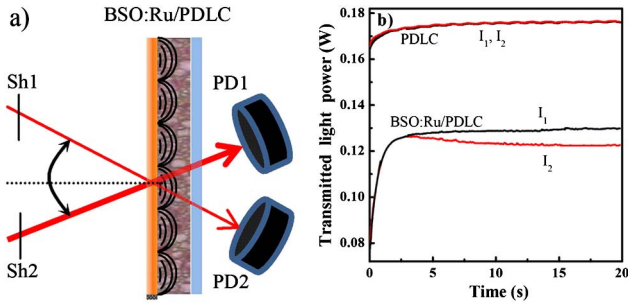


Fig. 2. (a) Two-beam coupling experiment. (b) Simultaneous behavior of both transmitted beams through hybrid structure and comparison with PDLC reference sample.

the full angle 2θ between the two interacting beams varies from 34° to 65° .

During the two-beam interference, the structure acts as a dynamic holographic grating at Bragg matched regime, where the grating period is much less than the PDLC layer thickness [5,6]. The gain ratio Γ , defined as the saturated value of the signal beam divided by the initial value of the signal beam after opening the shutter Sh2, gives the gain amplification by the following equation [3]:

$$\Gamma = 1/l \times \log_e(G), \quad (1)$$

where l is thickness of PDLC layer. The experimentally measured Γ (cm^{-1}) dependence on the grating spacing Λ (interacting angle) is presented in Fig. 3(a). As is seen, the gain coefficient can reach 45 cm^{-1} at $1 \mu\text{m}$ grating pitch. Obviously, the measured beam amplification exceeds several times the typical amplification values of bulk photorefractive crystals as nondoped BSO and Ru-doped BSO at 647 nm [3,18]. We also measured the gain of our BSO:Ru cubic crystal ($8 \text{ mm} \times 8 \text{ mm} \times 6 \text{ mm}$) using the same experimental conditions [shown at Fig. 2(a)] as a value of $\Gamma \sim 1 \text{ cm}^{-1}$. Furthermore, the experimentally measured gain ratio is almost three times higher than those reported for other near-infrared sensitive hybrid structures using two-side semiconductor substrates as CdTe (16 cm^{-1}) and GaAs (18 cm^{-1}) combined with LC layer [8,9]. We assume the effect is due to the higher concentration of Ru ions in the BSO crystal matrix, providing enough density of trap levels for space-charge generation. Much higher amplification values (over 450 cm^{-1}) have been reported for hybrid structures

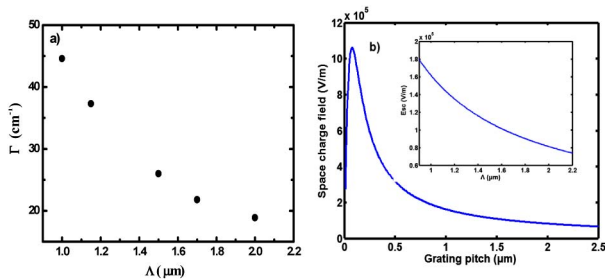


Fig. 3. (a) Γ (cm^{-1}) dependence on Λ (μm). (b) Theoretical simulation of E_{sc} dependence on Λ (μm). Inset graph: selected part interval as experimental one.

based on SBN:Ce crystal and LCs, which operate in the visible spectral range [5].

In addition, we estimated the gain coefficient of the PDLC layer assuming small index modulation (around 1%) by the following equation [3]:

$$\Gamma = \frac{2\pi \times \Delta n}{\lambda \times \cos \theta}, \quad (2)$$

where $\theta = 32.5^\circ$ and Δn can be estimated by the difference between the average refractive index (n_{av}) of randomly oriented LC molecules in droplets and the effective refractive index (n_o) of the incident (s -polarized) light, given by [23]

$$n_{av} = \frac{n_e + 2n_o}{3}, \quad (3)$$

Substituting $\Delta n = 1\% \times (n_{av} - n_o)$ into Eq. (2), the estimated gain coefficient of $\sim 37 \text{ cm}^{-1}$ is quite similar to the experimental result of 45 cm^{-1} .

Next, we estimated the space charge field E_{sc} induced in the BSO:Ru crystal plate, assuming sinusoidal charge density distribution [3]:

$$E_{sc} = \frac{iK \frac{k_B T}{q} I_1}{1 + \frac{K^2}{k_d^2} I_0}, \quad (4)$$

$$k_d^2 = \frac{q^2}{\epsilon \cdot k_B T} \frac{N_A}{N_D} (N_D - N_A), \quad (5)$$

where $K = 2\pi/\Lambda$ is the grating wave vector, k_d is the Debye wave number, $N_D = 6.1 \times 10^{23} \text{ (m}^{-3}\text{)}$ is the donor's density, $T = 300 \text{ K}$, $N_A = 0.9 \times N_D$ is the acceptor's density, k_B is the Boltzmann constant, and q -electron charge and $I_1/I_0 = 1$ (the intensity ratio required to achieve maximal E_{sc}). The experimentally measured threshold voltage of PDLC (assuming $7.3 \mu\text{m}$ droplet size) is 20 V , so the PDLC's threshold electric field is $E_{th(PDLC)} = 2 \times 10^6 \text{ (V/m)}$. Taking the dielectric constant of $\epsilon = 56$ for BSO:Ru and $\epsilon = 4$ for PDLC, the required space charge field in BSO:Ru crystal is $E_{sc} = 2 \times 10^6 \times (4/56) = 1.25 \times 10^5 \text{ V/m}$. The simulated E_{sc} field (according to the parameters of BSO:Ru crystal) in the range of grating period of 1 to $2.2 \mu\text{m}$ is compatible with the required E_{sc} field of $1.25 \times 10^5 \text{ V/m}$. Evidently, the E_{sc} field created in BSO:Ru is strong enough to penetrate into the PDLC layer and re-align the LCs molecules inside the droplets, consequently to modulate the LCs' director. This is a sign that Ru addition in the BSO crystal structure generates enough density of charge carriers' levels. Evidence of Ru-related high concentration of trap defects, acting as acceptor centers for photoexcited electrons, has been proved by [18,24].

Further, we theoretically simulated the strength of the E_{sc} versus the grating spacing Λ (μm) [presented in Fig. 3(b)], assuming the same charge carrier density parameters as discussed above. From the materials parameters, the calculated Debye screening length is $0.08 \mu\text{m}$. As is seen from Fig. 3(b), the diffusion field becomes dominant and the E_{sc} decreased with increas-

ing the grating spacing from 1 to 2 μm . Since the gain (related to the refractive index modulation, e.g., to the re-orientation of LCs molecules inside the droplets) is controlled by the E_{sc} , it follows the behavior of the space charge field on the way to decrease with increasing the grating spacing. In that aspect, a double side crystal structure can increase the effective interaction length and optimize the E_{sc} field penetration depth.

To the best of our knowledge, this is the first report on PDLC combined with inorganic substrate, where all the processes are controlled by near-infrared light. The proposed structure is very simple (without requirements of alignment layers), and due to the BSO:Ru high photoconductivity, the photogenerated space-charge field inside the crystal can spread out into the PDLC layer, reorienting the LC molecules inside the droplets. Furthermore, the proposed hybrid device allows one to realize the beam coupling at the Bragg matched regime, which is difficult to achieve in similar structures using an external electric field for LCs' realignment (the gratings there act as a thin hologram [15,16]).

In general, by controlling the droplet size and consequently the driving voltage of the LC molecules from one side and optimizing the Ru concentration in BSO matrix (providing high enough charge carriers density to turn out higher photocurrent) from another, the structure can be modified for further application as an optical switch at near-infrared. Therefore, the role of BSO:Ru substrate is twofold: to increase the light absorption at the near-infrared spectral range and to generate enough density of charge carriers for the space-charge field modulation.

In conclusion, we have demonstrated a simple near-infrared sensitive device assembled by PDLC layer on the BSO:Ru photoconductive substrate, where all the processes are controlled by light. The space-charge field, induced by photogenerated charge carriers inside the BSO:Ru substrate, acts as a driving force for the LC molecules' realignment inside the droplets. Holographic gratings have been recorded at a Bragg regime with promising beam amplification values for further near-infrared photonics applications. Furthermore, varying the transmitted light intensity through the device, it can operate as near-infrared optically addressed light valve.

Financial support by National Science Council, Taiwan under contracts NSC103-2911-I-009-516 and

NSC101-2221-E-009-111-MY3 and AUT Ministry of Education, Taiwan are gratefully acknowledged.

References

1. I. C. Khoo, *Liquid Crystals Physical Properties and Nonlinear Optical Phenomena* (Wiley, 1995).
2. D. R. Evans, G. Cook, and M. A. Saleh, *Opt. Mater.* **31**, 1059 (2009).
3. P. Yeh, *Introduction to Photorefractive Nonlinear Optics* (Wiley, 1993).
4. F. Kajzar, S. Bartkiewicz, and A. Miniewicz, *Appl. Phys. Lett.* **74**, 2924 (1999).
5. D. C. Jones and G. Cook, *Opt. Commun.* **232**, 399 (2004).
6. N. V. Tabiryan and C. Umeton, *J. Opt. Soc. Am. B* **15**, 1912 (1998).
7. M. J. Deer, *Appl. Phys. Lett.* **88**, 254107 (2006).
8. K. Gvozdosky, D. R. Shcherbin Evans, and G. Cook, *Appl. Phys. B* **104**, 883 (2011).
9. R. R. Garcia and C. B. Rodriguez, *Mol. Cryst. Liq. Cryst.* **561**, 68 (2012).
10. J. Frejlich, *Photorefractive Materials* (Wiley-Interscience, 2007).
11. V. Marinova, M. L. Hsieh, S. H. Lin, and K. Y. Hsu, *Opt. Commun.* **203**, 377 (2002).
12. V. Marinova, R. C. Liu, S. H. Lin, and K. Y. Hsu, *Opt. Lett.* **36**, 1981 (2011).
13. P. Aubourg, J. P. Huignard, M. Hareng, and R. A. Mullen, *Appl. Opt.* **21**, 3706 (1982).
14. U. Bortolozzo, S. Residori, and J. P. Huignard, *J. Nonlinear Opt. Phys. Mater.* **16**, 231 (2007).
15. U. Bortolozzo, S. Residori, and J. P. Huignard, *J. Phys. D* **41**, 224007 (2008).
16. K. Takizawa, H. Kikuchi, H. Fujikake, and M. Okada, *Appl. Phys. Lett.* **56**, 999 (1990).
17. K. Takizawa, H. Kikuchi, H. Fujikake, Y. Namikawa, and K. Tada, *Opt. Eng.* **32**, 1781 (1993).
18. F. Ramaz, L. Rakitina, M. Gospodinov, and B. Briat, *Opt. Mater.* **27**, 1547 (2005).
19. D. Coates, *J. Mater. Chem.* **5**, 2063 (1995).
20. Y. J. Liu, X. Ding, S. S. Lin, J. Shi, I. K. Chiang, and T. J. Huang, *Adv. Mater.* **23**, 1656 (2011).
21. P. Sveshtarov and M. Gospodinov, *J. Cryst. Growth* **113**, 186 (1991).
22. D. M. Stevens and P. P. Banerjee, *Opt. Lett.* **27**, 1333 (2002).
23. J. Li, G. Baird, Y.-H. Lin, H. Ren, and S.-T. Wu, *J. Soc. Inf. Disp.* **13/12**, 1017 (2005).
24. V. Marinova, I. Ahmad, and E. Goovaerts, *J. Appl. Phys.* **107**, 113106 (2010).