Optical, magneto-optical and holographic study of $Bi_4Ge_3O_{12}$ crystals doped with transition elements

Petya Petkova [a], Vera Marinova [b*], Ilia Iliev [a], Todor Dimov [a], Shiuan H. Lin [c], Ken. Y. Hsu [d]
[a] Shoumen University "K. Preslavski", Shoumen, Bulgaria
[b] Central Laboratory of Optical Storage and Processing of Information, Bulgarian Academy of Science, P.O. Box 95, Sofia 1113, Bulgaria
[c] Department of Electrophysics National Chiao Tung University, HsinChu 30050, Taiwan
[d] Institute of Electro-Optical Engineering, National Chiao Tung University, HsinChu 30050, Taiwan

ABSTRACT

Bismuth germanate $Bi_3Ge_4O_{12}$ (BGO) single crystals doped with ruthenium, manganese and ruthenium plus manganese are grown by Czohralski technique with automatically diameter-weight control method. The effect of doping on the light-induced, magneto-optical and holographic properties of BGO single crystals is studied. It was found that the optical transmission spectrum of doped samples is modified strongly under thermal annealing and homogeneous illumination with UV light as well as the photochromic effect is fully reversible. The magneto-optical rotation was measured and Verdet constant was calculated at visible spectral range. Holographic grating are successfully recorded at 633 nm.

Keywords: doped crystals, optical properties, magneto-optical rotation, photochromic effect, photorefractive effect

1. INTRODUCTION

In spite of the many advantages of BGO crystals as scintillator materials[1], voltage and electric field sensors in opto-electronic devices[2] or laser host materials[3] they has not been widely studied for photorefractive applications because of the limited dynamic range. Similar to $LiNbO_3$, non-doped BGO is one of the few crystals in which it is possible to record holographic gratings at shorter UV wavelengths at room temperature[4]. However there is not enough density of traps in the energy gap in order a refractive index modulation at visible spectral range to be induced.

One of the easiest ways to optimize physical properties and to improve response time and photosensitivity at visible wavelengths is by doping of BGO crystals with appropriate elements.

Fortunately, BGO has a large energy gap and can accept a wide variety of extrinsic impurities, such as transition metals or rare-earth elements. Using the doping effect, holographic gratings were successfully recorded in Cr-doped BGO crystals[5], in Fe-doped and Mn-doped BGO in a blue-green[6] and in a red spectral range[7], as well as in Co- and V-doped crystals[8,9]. Recently, we found that Ru and Mn addition in BGO crystal structure generates enough density of suitable traps for photo-induced charge carriers and photorefractive behavior has been detected [7,10,11], however the effect of co-doping combination is still missing.

In this paper, we have preliminary characterized the influence of Ru and Mn co-doping on photochromic and holographic properties of BGO crystals. For the first time results of magneto-optical rotation measurements are reported.

2. EXPERIMENT

2.1. Crystal growth and sample preparation.

* e-mail: vera_marinova@yahoo.com

Holography 2005: Intl. Conf. on Holography, Optical Recording, and Processing of Information, Yury Denisyuk, Ventseslav Sainov, Elena Stoykova, Eds., Proceedings of SPIE Vol. 6252, 62520O, (2006) · 0277-786X/06/$15 · doi: 10.1117/12.676940

BGO single crystals doped with Ru, Mn and Ru+Mn were obtained by Czochralski technique. A stoihiometric Bi_2O_3:GeO_2 powders were mixed in molar proportion 2:3. Crystals growing was performed from melts in pure platinum crucibles of diameter100 mm and 120 mm high. The growth conditions for BGO crystals have been established by adjusting the temperature gradient above the melt. Dopants were introduced into the melt in form of oxides. The doping element content was determined by the atomic absorption spectrometry analysis. The concentrations of Ru, Mn and Ru+Mn doped BGO crystals are summarized in Table 1.

Table 1. Summary of doping concentration

doping element	Ru	Mn	Ru+Mn
concentration $x10^{18}$ cm^{-3}	6.1	5	Ru - 3 Mn - 1

After the growth process the crystals were oriented and cut into pieces: double polished plates with thickness less than 1 mm for optical measurements and parallelepipeds with edges, oriented with respect to the crystallographic [110], [$\bar{1}$10] and [001] directions were prepared for holographic experiments.

2.2. Optical measurements

Optical transmission spectra were measured in the wavelength range 250-800 nm using the Cary 5E model spectrophotometer with accuracy 0.5% [12]. The transmission spectra were measured on two different initial states of the crystals: (1) after thermal annealing at 450°C in oxygen atmosphere for 3 hours (so called annealed state) and (2) after preliminary illumination with ultraviolet light coming from mercury lamp (colored state). UV illumination durations were between 80 and 100 min in order to obtain the saturation state (maximum value of the transmission coefficient change).

2.3. Magneto-optical effect

Magneto-optical rotation was measured by the modulation method (φ-modulation) using a vibrating polarizer in the system Polarizer-Crystal-Analyzer (P-C-A). The beam transmitted through P-C-A system depends linearly on the angle between P and A, and the signal can be measured using photomultiplier and band-pass amplifier.

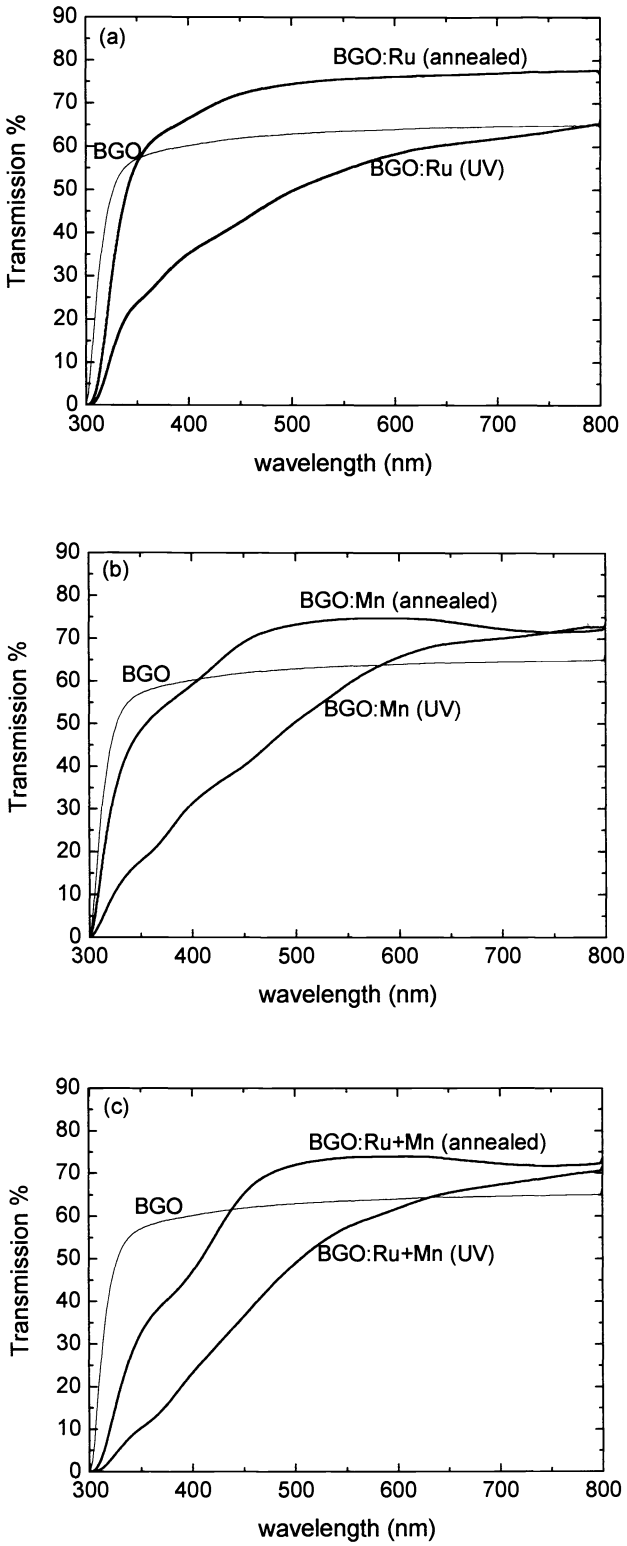

Fig.1. Transmission spectra of Ru (a), Mn (b) and Ru+Mn (c) doped BGO crystals after thermal annealing and after UV exposure.

The magneto-optical rotation was investigated in absorption edge vicinity and in the transmission region, where the ratio $\hbar\omega/E_0 \approx 0{,}1-1$ (E_0 is the edge energy) is fulfilled. Therefore, the observed magneto-optical effect in doped BGO crystals was determined principally from the inter-band rotation.

2.4. Holographic recording

Holographic gratings were recorded by two-wave mixing set-up using He-Ne laser source. The angle θ between two writing beams was 15° and the

grating vector was perpendicular to the [001] direction. During the writing, one of the recording beams (signal beam) was blocked for about 0.1s and the other beam (reference beam) was used to monitor the grating build-up.

During the erasure, only the reference beam was incident on the crystal by completely blocking the signal beam with a shutter.

Diffraction efficiency η was defined as the ratio between the diffracted intensity and the input beam intensity. No external electric field was applied.

Before each holographic experiment the samples were thermally annealed and after that illuminated with UV light for 1 hour.

3. RESULTS AND DISCUSSIONS

3.1. Transmission spectra

Figure 1 (a,b,c) show the Ru, Mn and Ru+Mn doping effect on optical transmission spectra of BGO crystals. As it seen, all doped samples shift the transmission shoulder to the visible spectral range in comparison with non-doped BGO (BGO transmission spectra is presented for reference) as well as the shifting is stronger in case of Ru+Mn co-doping effect .

Furthermore, the investigated samples show a significant change of optical transmission after thermal annealing and homogeneous illumination with UV light. Ru, Mn and Ru+Mn doped crystals exhibited photochromic effect at room temperature, which is fully reversible, i.e., the light -induced absorption is possible to be reduced by subsequent thermal annealing. In doped BGO crystals the photochromic phenomenon is associated mainly with the presence of dopants since the non-doped BGO does not exhibit any appreciable photochromic effect[13]. The magnitude of photochromism is stronger in case of Ru-doped

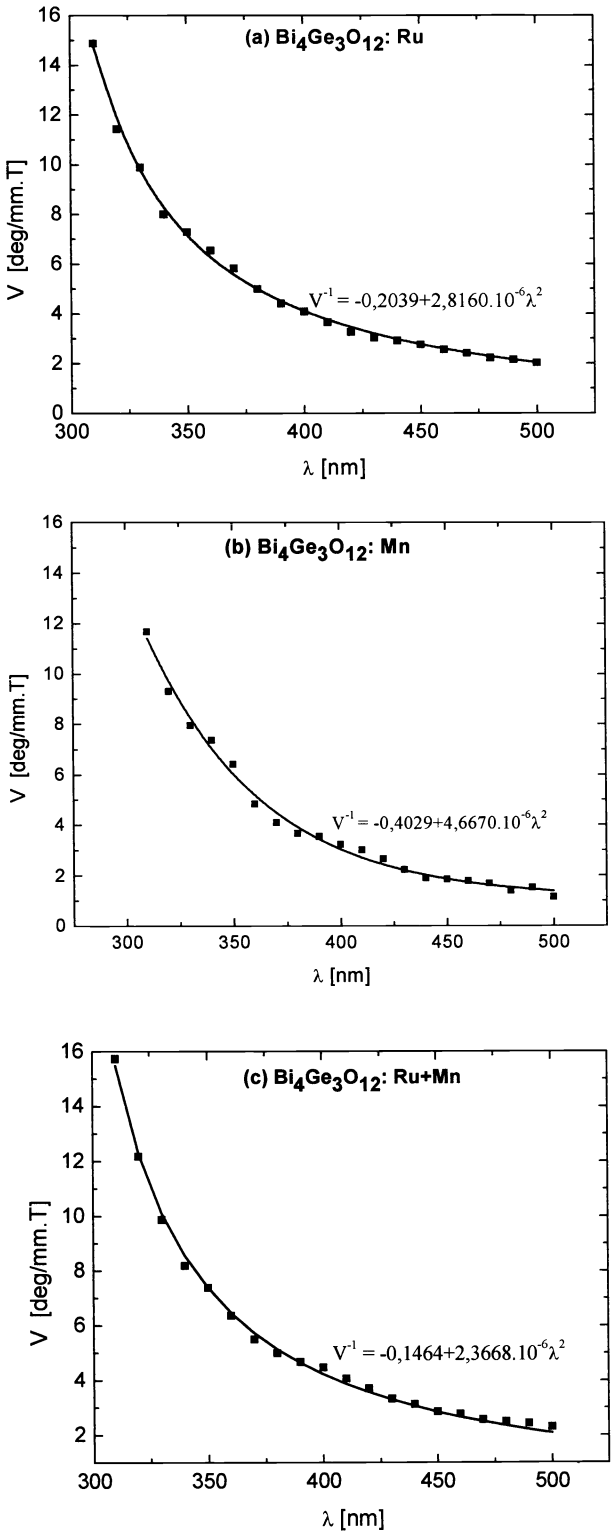

Fig.2 (a,b,c). Verdet constant versus wavelengths. The symbols represent experimental data, the solid lines are theoretical fitting.

BGO. Such preliminary treatments have been used to modify the defect structure in a crystal lattice and the corresponding absorption bands during further holographic testing.

We suppose that the observed photochromic effect is due to the valence change of doping elements caused by the photoinduced charge transfer from the UV sensitive absorption centers via the conduction (valence) band. The impurities charge transfer transition probably is due to the charge carrier redistribution between different traps, which exist simultaneously in samples at different oxidation states.

3.2. Magneto-optical properties

The results from Faraday's effect are analyzed using Bequerel formula:

$$\varphi(\lambda) = \frac{A}{\lambda^2 - \lambda_0^2} \qquad (1)$$

where: A is a constant, determined from the matrix elements of the corresponding inter-band transitions; λ_0 is the wavelength related to the inter-band transitions and corresponding to the natural frequency ω_0 of a harmonic effective oscillator. In addition, the Verdet constant as a function of the wavelength is calculated by:

$$V = \varphi / B.d \qquad (2)$$

where: φ is magneto-optical rotation, V is the Verdet constant, d is the sample thickness and B is magnetic induction. Figure 2 (a,b,c) show the Verdet constant dependence on the wavelength where the symbols present the experimental data and the solid lines are theoretical fitting. As can be seen the dependence is quadratic for all investigated samples. Deviation from the quadratic dependence (the step structure in the interval between 350 nm to 450 nm) appeared in the regions where the Urbach rule is fulfilled. We suppose that this step structure probably is due to the bound excitons just before the absorption edge.

Holographic properties.

Ru, Mn and Ru+Mn co-doped BGO crystals have been tested for holographic recording at 633 nm wavelength. Figure 3 compare the recording and erasure characteristics measured at the same writing geometry and beam intensities. The observed temporal behavior of writing dynamics for Ru- and Mn-doped BGO follows single exponential law. However for Ru+Mn co-doped BGO the behavior is more complex, starting with fast growth, decreasing and approaching to the steady-state value after long recording. The last behavior is similar to those reported for Co-doped BGO crystal[8] and recently observed in case of Fe+Mn doubly doped BGO[7]. Furthermore, the erasure time constant is slower in case of co-doping effect. Probably, such transient dynamic is due to the competitive redistribution of electrons and holes, which reduces the space charge electric field. The evolution of build-up and dark decay of light-induced absorption measurements are under investigations in order to estimate the contribution of photochromic effect during holographic recording.

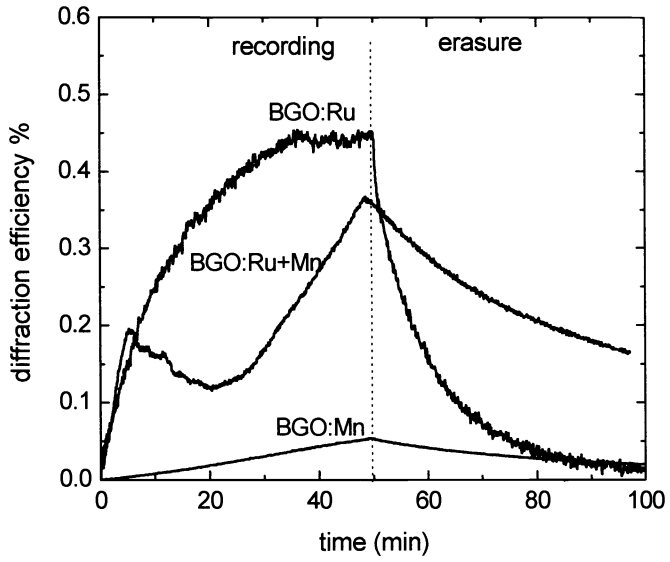

Fig.3. Holographic recording-erasure cycle at λ = 633 nm for Ru, Mn and Ru+Mn doped BGO crystals. Experimental conditions: grating spacing Λ = 0.61 μm, recording intensity 38 mW/cm^2, no external electric field.

CONCLUSIONS

Ru, Mn and Ru+Mn-doubly doped BGO crystals exhibited a reversible photochromic effect at room temperature. The magnitude of photochromism is larger in case of Ru-doped BGO. Irradiation with UV light induced a new absorption band, which could be bleached by thermal annealing. It was concluded that UV illumination creates new defect centers in the BGO host as well as the states of the trap centers can be manipulated by UV or visible light illuminations.
Photorefractive behavior has been observed in all doped BGO crystals at 633 nm and the diffraction efficiency and writing kinetics of the recorded holograms depend on the concrete dopants and previous illumination with UV light.
We suppose with suitable doping concentration as well as the wavelength and beam intensity selection doped with transition elements BGO crystals to have promising potential for non-volatile holographic storage using a two-step sensitization method.

ACKNOWLEDGEMENTS

This work was supported by the National Science Found, Bulgaria, contract # F-1405.

REFERENCES

1. B. C. Grabmaier, "Crystal scintillators," IEEE Trans. Nucl. Sci. **NS-31** 372-376 (1984).
2. O. Kamada and K. Kakishita, "Electro-optical effect of $Bi_4Ge_3O_{12}$ crystals for optical voltage sensors," Jap. J. Appl. Phys. **32** 4288-4291, 1993.
3. A. A. Kaminskii, S. E. Sarkisov, G. A. Denisenko, V. V. Ryabchenkov, V. A. Lomonov, Yu E. Perlin, M. G. Blaza, D. Shultze, B. Hermoneit and P. Reiche, "Growth, spectral and luminescence study of cubic $Bi_4Ge_3O_{12}:Pr^{3+}$ crystals," Phys. Status Solidi A **85** 553-567, 1984.
4. G. Montemezzani, St. Pfandler and P. Gunter, "Electro-optic and photorefractive properties of $Bi_4Ge_3O_{12}$ crystals in the ultraviolet spectral range", *JOSA* B, **9** 1110-1117, 1992.
5. E. Moya, L. Contreras and C. Zaldo, " $Bi_4Ge_3O_{12}$:Cr: a new photorefractive materials," *JOSA B* **5** 1737-1742, 1988.
6. C. Zaldo, E. Moya, F. Magana, L. Kovacs and K. Polgar, "Optically induced gratings in Fe- and Mn-doped $Bi_4Ge_3O_{12}$ single crystals," *J. Appl. Phys.* **73** 2114-2121, 1993.
7. V. Marinova, S. H. Lin, Ken Y. *Hsu* "Light-induced and holographic properties of Fe, Mn and Fe+Mn doubly doped $Bi_4Ge_3O_{12}$ crystals" *OSA Tops* 2005 in press.
8. C. Zaldo and E. Dieguez, "On the microscopic origin of the photochromic and photorefractive behaviour of doped $Bi_4Ge_3O_{12}$ single crystals," *Opt. Mat.* **1** 171-176, 1992.
9. V. Marinova, Shiuan Huei Lin, Mei-Li Hsieh, M. M. Gospodinov and Ken Yuh Hsu, "Photochromic effect and holographic recording in V, Co and Co+V doped $Bi_4Ge_3O_{12}$ single crystals," *Optical Memory & Neural Network* **11** 211-218, 2002.
10. V. Marinova, S. H. Lin, Mei-Li Hsieh, Ken Y. Hsu, M. M. Gospodinov and V. Sainov, "Optical properties of $Bi_4Ge_3O_{12}$ crystals doped with ruthenium," *J. Mat. Sci. & Mat. Elect.* **14** 857-858, 2003.
11. Marinova, Ken Y. Hsu and S. H. Lin,"Light-induced properties of ruthenium-doped $Bi_4Ge_3O_{12}$ crystals," *J. Appl. Phys.* in press 2005.
12. I. Konstantinov, Tz. Babeva and S. Kitova "Analysis of the errors in thin film optical parameter derived from spectrophotometric measurements at normal light incidence," *Appl. Opt.* **37** (19) 4260-4267, 1996.
13. L. Kovacs, E. Moya, K. Polgar, F. J. Lopez and C. Zaldo, "Photochromic behavior of doped $Bi_4Ge_3O_{12}$ single crystals," *Appl. Phys.* A **52** 307-312, 1991.