Improvement of magneto-optical quality of high purity $Bi_{12}GeO_{20}$ single crystal induced by femtosecond pulsed laser irradiation

G. S. I. ABUDAGEL[a], S. PETRIČEVIĆ[a], P. MIHAILOVIĆ[a], A. KOVAČEVIĆ[b], J. L. RISTIĆ-DJUROVIĆ[b], M. LEKIĆ[b], M. ROMČEVIĆ[b], S. ĆIRKOVIĆ[b], J. TRAJIĆ[b,*], N. ROMČEVIĆ[b]
[a]*School of Electrical Engineering, University of Belgrade, Bulevar kralja Aleksandra 73, 11000 Belgrade, Serbia*
[b]*Institute of Physics, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia*

Femtosecond pulsed laser irradiation can improve optical properties of $Bi_{12}GeO_{20}$ single crystals. We investigate if the effect occurs if the crystals are grown from high purity components. The samples are irradiated by a femtosecond pulsed laser beam of increasing power. The maximal transmittance of 44% occurs at the irradiating laser power of 451 mW. After irradiation, intensity of Raman spectra peaks increase, except for the peak at 203 cm^{-1}, whose intensity decreases. The irradiation also changes the sample colour. Although the Verdet constant does not change, the absorption coefficient decreases significantly, which leads to magneto-optical quality improvement of approximately 70%.

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1. Introduction

Bismuth germanium oxide ($Bi_{12}GeO_{20}$) from the sillenite group of cubic crystals is commonly abbreviated as BGO or s-BGO. Due to its fitting optical characteristics, such as photoconductivity, photochromism, photorefractivity, piezoelectricity, as well as to electro-optic and magneto-optic effects it supports [1, 2], it has been used in a wide range of optical applications and devices [2–6]. Its cubic cell unit is composed of two formula units, namely of 24 Bi, 40 O and 2 Ge. The Ge atoms positioned in the centre and the vertices of a cube are tetrahedrally coordinated by the oxygen atoms, whereas the Bi atoms are heptacoordinated [7–9]. There are numerous studies that considered properties of doped and un-doped BGO, see for example [10–18], as well as those investigating property changes induced by a wide variety of exposure types such as thermal treatments, particle beams or light treatments [3, 12–16, 19–25].

BGO is a good example of a Faraday rotator crystal possibly applicable in sensor systems. In order to evaluate usability of a crystal for sensing purposes not only its Faraday rotation capability, but its ability to be integrated into a sensing optical system must be considered. In general, in fiber-optic sensing systems optical beams used to sense the measured quantity are guided through the fibers, giving rise to the absorption coefficient as the most important optical property. Crystals with high absorption coefficient are in general less useful for sensor systems because they absorb much of the light and cause low signal-to-noise ratio at the receiving photo diode. If the magnetic field is to be detected, the intensity of light caused by magnetic field modulation is proportional to the Verdet constant, whereas the intensity of light reaching the photodiode as well as the photocurrent is inversely proportional to the crystal absorption. The noise in a fiber optic sensing system is predominantly determined by the noise in the processing electronics and can be expressed as the noise present in the photocurrent. Therefore, the signal-to-noise ratio of the magnetic field sensor is proportional to the Verdet constant and inversely proportional to the absorption coefficient of a crystal. Consequently, due to its proportionality to the signal-to-noise ratio, the magneto-optical quality of a crystal defined as a ratio of the Faraday rotation, which is proportional to the Verdet constant, and the absorption coefficient can be used as a measure of a crystal's applicability in a magnetic field sensing system.

When $Bi_{12}GeO_{20}$ crystals were exposed to pulsed laser beam irradiation, there are examples of laser beam operating in the nanosecond [3], picosecond [23–25], or femtosecond range [26]. In [26] it was determined that femtosecond pulsed laser irradiation of increasing power causes significant changes in the transmittance, transmission spectra, sample colour, Raman spectra, X-ray diffraction pattern, Verdet constant, magneto-optical property, and absorption coefficient of lower quality black $Bi_{12}GeO_{20}$ single crystals. Here we analyze if the same increasing power pattern of femtosecond pulsed laser irradiation has similar effect on the high quality yellow $Bi_{12}GeO_{20}$ single crystals, i.e., on the crystals that were grown from the components whose purity is higher than that of the black crystals, and whose magneto-optical quality is the maximal obtainable by the applied crystal growth technique.

2. Experimental procedure

2.1. Preparation of crystal samples

Single crystals of $Bi_{12}GeO_{20}$ were grown in the air by the Czochralski technique using the MSR 2 crystal puller, Eurotherm temperature controller and the calculated critical crystal diameter, critical rotation rate and pulling rate, as explained in detail in [17, 26]. The system provided small fluctuations in crystal diameter size as well as in melting temperature. The $Bi_{12}GeO_{20}$ seed was oriented in the ⟨111⟩ direction and the charge was a mixture of Bi_2O_3 and GeO_2 in the stoichiometric ratio 6:1. The light yellow crystal samples were obtained using the Bi_2O_3 and GeO_2 purity of 99.999 wt.% and 99.9999 wt.%, respectively. Crystal samples of size 4 mm × 4 mm × 10 mm were cut from the boule and mechanically as well as chemically polished. The technique used to prepare the samples insured maximal sample quality within the limits corresponding to their purity [17].

2.2. Crystal irradiation and characterization

The equipment used to produce the femtosecond pulsed laser beam and establish its wavelength was the Coherent Mira 900F femtosecond laser, Coherent Verdi V-10 pump laser that provided a 532 nm continuous wave pump beam, and Ocean Optics HR2000CG UV-NIR spectrometer. Crystal samples were irradiated along the crystal growth direction (*z*), i.e. along the samples' longest axis. The irradiating laser beam radius provided partial irradiation of the exposed crystal facet. The beam wavelength was 800 nm, whereas its power was increased from 50 mW to 950 mW and was adjusted by a graded filter. The pulses were 90 fs long and had repetition rate of 76 MHz. The samples were irradiated by each beam power for 3 s. The beam power was measured with the Ophir power meter with the thermal and photometric heads. In order to enable comparison of the irradiation effects on the single crystal samples of different purity, i.e., on yellow and black $Bi_{12}GeO_{20}$ samples, the irradiation conditions were intentionally chosen to be identical to those applied to the lower purity black crystals in [26].

The sample colour was calculated from the transmission spectra measured by the Beckman Coulter DU 720 General Purpose UV/VIS spectrometer.

The micro-Raman spectra were recorded at room temperature in the spectral range between 100 and 1100 cm^{-1} with 1 cm^{-1} resolution using the backscattering configuration and the 532 nm line of Verdi G optically pumped semiconductor laser as an excitation source, and the Jobin Yvon T64000 spectrometer, which has nitrogen cooled charge-coupled-device detector.

The Faraday rotation and optical activity were measured by Δ/Σ method at the wavelength of $\lambda = 632.8$ nm. After the BGO crystal the orthogonal polarizations of the light beam were separated by the $CaCO_3$ crystal into two parallel beams 3 mm apart. The quadrant photodiode connected into transimpedance stages was used for optoelectronic conversion. This method is described in more details in [26].

3. Results and discussion

The irradiation pattern applied here to the higher purity yellow crystals is identical to the one utilized in [26] to irradiate black crystals grown from the components of lesser purity. Consequently, the obtained results can be compared and the differences can be attributed solely to different sample purity. With the increase of irradiating laser power, the transmittance of irradiated sample undergoes initial growth followed by a decrease, as can be seen in Fig. 1. Comparison with the dependence corresponding to the black crystal given in [26] reveals that the transmittance curves for the black as well as for the yellow crystal has the same shape and that the slopes of the two curves appear to be approximately equal. The curve corresponding to the yellow crystal is shifted to the larger values by approximately 18.8% compared to the curve corresponding to the black crystal. For the yellow crystal, the maximal transmittance of 44.0% occurs at the irradiating laser power of 451 mW, whereas the lower purity black crystal was reported in [26] to have the smaller maximal transmittance value of 25.1% corresponding to 455 mW. It seems that both curves exhibit local irregularities which occur at 197.4–249.7 mW, 552–605 mW and 800–857 mW for the black crystal and at 593–641 mW for the yellow crystal. It is possible that the irregularity in the yellow sample curve for large values of incident power P_0 is not visible because it is outside the considered range of irradiating laser power, or due to insufficient measurement accuracy achieved for yellow crystal data points above 700 mW.

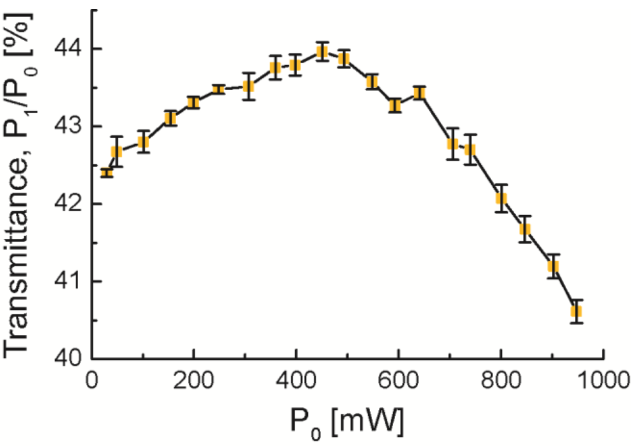

Fig. 1. Change of crystal transmittance with increase of irradiating laser power. For each value of the incident power P_0, a sample is irradiated by the femtosecond laser beam for 3 s. The transmittance is given as P_1/P_0, where P_1 is the transmitted power. The error bars were calculated from the uncertainties of measured values of the incident and transmitted power, ΔP_0 and ΔP_1.

The sample colours before and after irradiation were calculated using the CIE chromaticity coordinates and are given in Fig. 2. Comparison with the results corresponding to the black crystal given in [26] revealed that the change of black crystal colour was more pronounced than that of the yellow crystal presented here.

The Raman spectra of unirradiated and irradiated samples are recorded at room temperature in the spectral range from 150 to 800 cm^{-1} and are shown in Fig. 3. The results obtained for unirradiated crystals are in agreement with those given in [8, 17]. After irradiation the intensity of the $F(TO)$ peak at 203 cm^{-1} decreased, whereas all other peaks became more pronounced. Despite the difference in purity between the yellow samples studied here and the black crystals considered in [26] the Raman spectra of unirradiated crystals do not differ significantly. As reported in [26], irradiation of the black crystal caused all the peaks of symmetry type E, i.e., the peaks at 234, 454, and 619.6 cm^{-1}, to disappear and intensity increase of all other peaks. The change in the same Raman spectrum peaks of $Bi_{12}GeO_{20}$ was reported in [16]; however, the most, medium, and least intense peaks correspond to the annealed, doped, and untreated samples, respectively.

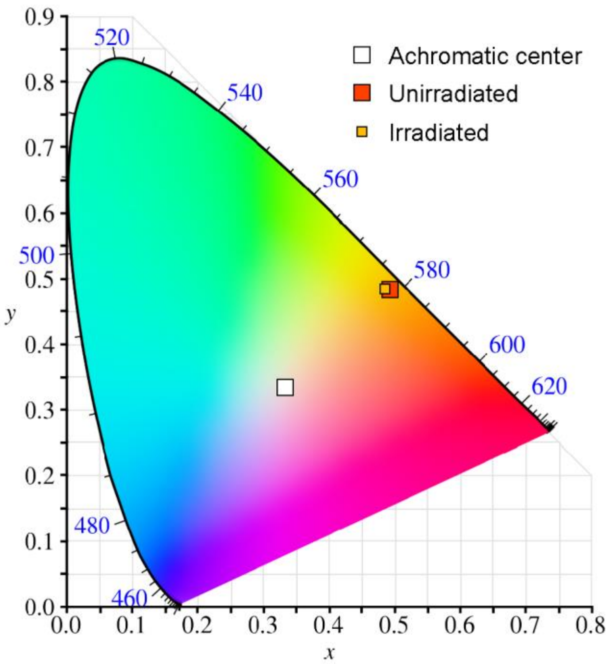

Fig. 2. Colours of irradiated and unirradiated samples in CIE chromaticity diagram.

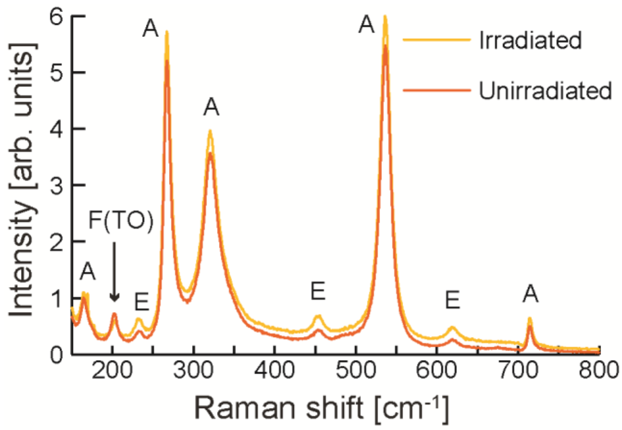

Fig. 3. Raman spectra. Irradiation caused a small upward shift of the crystal spectrum except for the F(TO) type peak at 203 cm^{-1}.

The Verdet constant is calculated from

$$V = \frac{\theta_{0AC}}{B_0 l} = \frac{1}{2B_0 l}\sin^{-1}\left(\frac{U_1 - U_2}{U_1 + U_2}\right)_{0AC} \quad (1)$$

where θ_{0AC} is the amplitude of the AC signal, B_0 is the amplitude of the magnetic induction, whereas U_1 and U_2, are the output signal voltages obtained after transimpedance stages from the vertically and horizontally polarized components, respectively. The FFT was used to separate spectral components of U_1 and U_2. The Faraday rotation was determined from the magnitude of the 50 Hz component.

The absorption coefficients were obtained by measuring the difference in beam intensities at the quadrant photodiode [26] with and without BGO crystal in the beam path. The reflection on the BGO crystal was calculated using the normal incidence and BGO refraction index of $n_{BGO} = 2.55$.

The absorption coefficient, α, was calculated from the beam intensities with and without the crystal present in the beam path, $I(x)$ and $I(0)$, and the known crystal length l = 9.8 mm as

$$I(l) = I_0 e^{-\alpha l} \Rightarrow \alpha = -\frac{1}{l}\ln\frac{I(l)}{I_0} \quad (2)$$

The magneto-optical quality is calculated by dividing the Verdet constant by the absorption coefficient. The obtained results are given in Table 1.

Table 1. Magneto-optical properties of irradiated and unirradiated high purity crystal samples.

Property	Unirradiated sample	Irradiated sample
Verdet constant (rad $T^{-1}m^{-1}$)	72	72
Absorption coefficient (cm^{-1})	0.58	0.34
Magneto-optical quality (rad T^{-1})	1.24	2.1

The data given in Table 1 show the effects of femtosecond laser irradiation on the magneto-optical properties of the high purity BGO crystal. The irradiation caused 41.4% decrease in the absorption coefficient and did not influence the Faraday constant. Consequently, the increase in crystal transparency resulted in a significant 70% increase in the magneto-optical quality. As explained earlier, increase in crystal transparency is an important gain from the point of view of a sensor system since the system-level signal-to-noise ratio is directly proportional to the magneto-optical quality of a crystal. Therefore, it is expected that the signal-to-noise ratio of a sensor system would be improved by the same amount as the improvement in the magneto-optical quality induced by the irradiation. Consequently, it can be concluded that the femtosecond pulsed laser irradiation affects the crystal in a positive manner.

4. Conclusions

Femtosecond pulsed laser irradiation of increasing power caused significant changes in optical properties of $Bi_{12}GeO_{20}$ single crystals grown from the components of high purity, as was the case in [26] when the component purity was not so high. The transmittance dependence on the applied irradiation power had the same shape regardless of the purity of the components the crystals were grown from. The curve corresponding to the higher purity crystal, i.e., the yellow crystal, is shifted to the larger values by approximately 18.8%. For the black and yellow crystal, the maximal transmittance of 25.1% and 44.0% occurred at 455 mW and 451 mW, respectively. The Raman spectra peaks became somewhat stronger, except for the *E* type peaks at 234, 454, and 619.6 cm^{-1} in the lower purity black crystal, which disappeared and the yellow crystal peak at 203 cm^{-1} whose intensity decreased. Irradiation also caused slight colour change of the yellow crystal and significant change of the black crystal colour. The Verdet constant did not change; however, the absorption coefficient significantly decreased leading to equally significant increase of the magneto-optical quality of the sample. Consequently, it can be concluded that optical properties of high quality $Bi_{12}GeO_{20}$ single crystals can be improved by irradiation with the femtosecond pulsed laser beam.

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*Corresponding author: jelena@ipb.ac.rs