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ABSTRACT

We report on the synthesis of new magneto-optical materials with excellent optical and magneto-optical (MO) properties for visible-range and near-infrared applications. Bi-substituted composite garnet films fabricated with excess bismuth oxide content using RF co-sputtering and conventional oven-annealing processes are found to possess simultaneously a record-high MO quality and strong uniaxial magnetic anisotropy. The films demonstrate nearly-square hysteresis loops with specific Faraday rotations of up to 10.1 deg/μm at 532 nm and up to 2.6 deg/μm at 635 nm, which are significantly larger than these measured in garnet films of the same composition prepared without extra bismuth oxide content. Record-high MO figures of merit are demonstrated in our composite garnet materials due to a significant reduction in the optical absorption coefficients achieved across the visible spectral range, thus making garnet-oxide composites highly attractive for use in a range of magneto-optical applications.

Keywords: Bi-substituted iron garnet, magneto-optical materials, MO figure of merit, optical absorption, Faraday rotation, uniaxial magnetic anisotropy.

1. INTRODUCTION

The unique magneto-optical (MO) properties of Bi-substituted iron garnet (Bi:IG) materials are very attractive for use in MO devices and can lead to functional improvements in next-generation photonic integrated circuits. Bismuth-substituted iron garnets are considered to be the most attractive class of MO materials for use in various multifunctional device applications including polarization control, latent marking, bank-note testing, light beam scanning, MO flaw detection, high-density MO data storage, high-speed spatial light modulators,[1-3] as well as magnetic photonic crystals (MPC) for the development of next-generation integrated devices. Recently, some new bismuth-substituted iron garnet-based structures have been suggested and investigated for various applications in nanophotonics.[4, 5, 11] Although Bi:IG films possess excellent optical transparency and MO figure of merit in the near-infrared region, the high optical absorption (especially in sputtered films) in the visible wavelength range and the typical absence of uniaxial magnetic anisotropy in high-bismuth-content films make their practical use very limited in visible-range magneto-optics applications. RF magnetron sputtered films are attractive because the sputtering procedure is very suitable for the integration of Bi:IG films into optical devices.

Bi:IG films with a high bismuth substitution (in excess of 1.5 Bi atoms per formula unit) produced by different techniques including RF magnetron sputtering, ion beam sputtering and pulsed laser deposition (PLD) typically show very high optical absorption coefficients ranging between $3\text{-}5\times10^{3}$ cm^{-1} at 633 nm.[3, 4] The maximum specific Faraday rotation reported so far in $Bi_3Fe_5O_{12}$ was Θ_F = -8.09°/μm at 633 nm.[6, 7] Y. Zhang et al[8] prepared Bi-substituted dysprosium iron garnet films by a sol-gel process, which possessed the perpendicular magnetic anisotropy and strong coercivity, but had a very low figure of merit. Bi-doped iron garnet films of the reported composition $Bi_{2.0}Dy_{1.0}Fe_{3.5}Ga_{1.0}O_{12}$ demonstrating perpendicular magnetic anisotropy have been deposited by laser ablation technique featured a square hysteresis loop and 0.78°/μm of Faraday rotation at 628 nm at the remanent state of magnetization.[9] Also, BIGG ($Bi_3Fe_4Ga_1O_{12}$) films have been prepared for ultrafast switching applications by the PLD technique and demonstrated a MO figure of merit of (16.5°±1°) at 532 nm.[10] Bi:IG films often deviate from their nominal stoichiometric compositions as a result of various factors affecting the deposition process. For example, $Bi_3Fe_5O_{12}$ films produced by RF sputtering will likely possess an excess of iron and iron oxide(s) content, and a loss of bismuth and bismuth oxide content can occur during both the deposition and annealing processes. The latter is due to a rather large saturated vapour pressure of these compounds in comparison with other oxides. Since the iron oxides demonstrate a rather high optical absorption in the visible range, the presence of excess Fe_2O_3 or Fe_3O_4 phases residing outside the garnet grains (nanocrystallites) can dramatically increase the absorption losses in RF-sputtered doped iron garnet films. Based on the hypothesis that it is the presence of excess iron oxide phases that is largely responsible for the high absorption of sputtered garnet films (when compared to epitaxially-grown monocrystalline garnet layers), we have fabricated and characterized multiple batches of co-sputtered garnet-oxide composites of type $Bi_{3-x}Dy_xFe_{5-y}Ga_yO_{12}$:$Bi_2O_3$ (where x = 1 and y = 0.7; 1) using the sputtering targets of base garnet compositions $Bi_2Dy_1Fe_4Ga_1O_{12}$ and $Bi_2Dy_1Fe_{4.3}Ga_{0.7}O_{12}$ as well as a target of Bi_2O_3. The dysprosium-doped garnet compositions have been used to achieve the necessary level of uniaxial magnetic anisotropy in RF sputtered films, simultaneously with the improved optical transparency as reported in Ref.[11] The gallium doping diminishes the saturation magnetization, and also reduces the Faraday rotation, but increases the optical transmission, while the dysprosium substitution increases the magnetostriction coefficient of films. The presence of excess bismuth oxide content was intended to provide the improved transparency of films in the visible range, by forming an amorphous bismuth oxide-dominated matrix into which the garnet grains would be embedded after the crystallization process. Another purpose of adding the excess Bi_2O_3 was to provide an additional source of Bi atoms and therefore compensate for the possible loss of Bi content in the film, or to even increase the Bi substitution beyond two atoms per formula unit. The results of specific Faraday rotation measurements made with our composite films suggest that the latter goal has indeed been achieved (two Bi atoms per formula unit would result in only 2 °/μm of Faraday rotation at 633 nm in this type of garnet composition) whilst still keeping the magnetic moment in the direction perpendicular to the film's plane. The MO quality factors (figures of merit $Q = 2\Theta_F / \alpha$, where Θ_F is specific Faraday rotation measured in films at remanent magnetization state and α is the optical absorption coefficient measured at the same wavelength) of the composite films were nearly-doubled at 635 nm and also at 670 nm, and nearly-tripled at 532 nm compared to these measured in "undiluted" (base-composition) garnet films, which makes our synthetic materials very attractive for use in nano-structured magneto-photonic components and devices.

We have investigated the optical, magnetic, and MO performances of RF sputtered Bi/Dy-substituted Ga-doped iron garnet composite films containing different volumetric fractions of excess Bi_2O_3 co-sputtered from a separate target. The microstructural properties and the stoichiometries of our composite materials are being investigated, and the updated results will soon be reported elsewhere. In this paper, we report on the achievement of a large degree of control over the properties of MO garnets by means of varying their elemental content, as well as show some optical, magnetic, and magneto-optic characterization results. The combination of optical and MO properties of our garnet materials is very promising for the use in microphotonic device development, especially for the manufacture of magnetic photonic crystal structures. We also report achieving record-high MO figures of merit measured in our garnet-oxide composite materials across the visible spectral range.

2. RESULTS AND DISCUSSION

2.1 Deposition and annealing process parameters

The amorphous-phase garnet and garnet-oxide composite films were prepared by RF magnetron sputtering on Corning 1737 and polished monocrystalline GGG (111) substrates using low-pressure argon plasma according to the process conditions described in Table 1. No extra oxygen input was used during the deposition processes, and the substrate temperature was fixed at 250 °C for all film batches. Post-deposition annealing processes were run in a conventional temperature/ramp-controlled air-atmosphere oven (Sentrotech Inc.) to induce the polycrystalline (micro- or nanocrystalline) garnet phase formation. The crystallization temperatures of our garnet materials ranged between 480-700°C and were optimized carefully for each particular stoichiometry type. We used the annealing process durations of 30-120 minutes and temperature-ramp process rates of 3-5 ºC/min to crystallize the amorphous (as-deposited) layers into a high-quality nanocrystalline garnet phase with a grain size of about 50 nm.[12] In our experiments, we were able to optimize the crystallization processes for several types of garnet-bismuth oxide composites, however, the annealing processes suitable for crystallizing the highly-diluted composite garnet materials have been found to be particularly difficult to optimize. The high-quality microstructure and surfaces in garnet layers and their optical and MO performance are critically dependent on the optimization of the annealing processes. Our composite garnet films annealed using the optimized thermal treatment regimes demonstrated very attractive optical and MO properties in the visible wavelength region. The detailed experimental results related to the optimization of the annealing processes as well as the dynamics of such processes for various compositions of garnet and composite-garnet films will be reported elsewhere.

Table 1. Typical sputtering conditions for magneto-optic garnet layers and garnet-oxide composites fabricated by co-sputtering extra bismuth oxide from a second target.

Garnet target composition	$Bi_{3-x}Dy_xFe_{5-y}Ga_yO_{12,}$ where x=1 and y= 0.7, 1 (Kurt J. Lesker Co.)
Bismuth Oxide target	Bi_2O_3 (AJA International Inc.)
Background Pressure	P(base) < 1-2E-06 Torr
Process gas and pressure	Argon, P(Ar)=1-2 mTorr
RF power densities for garnets	3.3-7 W/cm^2
RF power densities for Bi_2O_3	0.44-3.9 W/cm^2
Substrate-target distance	15-20cm
Substrate temperature during deposition	250^{0}C
Deposition rates	3.5-8.7 nm/min(garnets); 1.2-5.4 nm/min (Bi_2O_3)

The garnet targets used had stoichiometric compositions $Bi_2Dy_1Fe_4Ga_1O_{12}$ and $Bi_2Dy_1Fe_{4.3}Ga_{0.7}O_{12}$ manufactured through sintering the mixes of bismuth, dysprosium, iron and gallium oxides. The RF magnetron sputtering system used was KVS-T 4065 (Korea Vacuum Technology Ltd.) with three RF guns using 3'' targets.

2.2 Material characterization results

A Beckman Coulter DU 640B UV-visible spectrophotometer was used to measure the transmission spectra of the $Bi_2Dy_1Fe_4Ga_1O_{12}$, $Bi_2Dy_1Fe_{4.3}Ga_{0.7}O_{12}$ and also of all composite garnet films. The close matching of the measured and modelled transmission spectra (within the spectral window between 500-1100 nm) of our films before and after annealing confirmed that the garnet and garnet-oxide composites had the refractive index spectra being very close to the reliably-known index spectra of $Bi_2Dy_1Fe_4Ga_1O_{12}$ in its amorphous and crystallized phases, which were measured using spectroscopic ellipsometry previously. Using the iterative fitting of the spectral features observed in the measured and modelled transmission spectra of films, the absorption spectra of our garnets and also garnet-oxide composite films, as well as the physical layer thicknesses were derived to within an estimated of ± 5% accuracy using custom-developed software.[13] The derived absorption spectra of high-quality garnet and garnet-oxide composite films (in their amorphous and polycrystalline phases) shown in Fig.1 reveal that the excess of Bi_2O_3 content reduces the optical absorption across most of the visible and near-infrared spectral regions. The low-absorption performance achieved in some of our garnet films is very comparable with that of monocrystalline films deposited epitaxially. The lowest possible absorption coefficients achieved in our composite films were in the range between 1100- 1200 cm^{-1} at 635 nm. At the same time, some of our best-performing garnet composite films showed a significantly larger Faraday rotation than that measured in the typical garnet films of similar compositions. The highest values of the specific Faraday rotation in our garnet-oxide films that were obtained were about 10.1°/µm at 532 nm, 2.6°/µm at 635 nm and 1.9°/µm at 670 nm. Fig. 2 shows the spectra of specific Faraday rotation measured in the typical garnet and garnet-oxide composite films grown on GGG (111) substrates. The measurements of Faraday rotation angles were performed using an electromagnet (custom-made) and a polarimeter (Thorlabs Inc.).

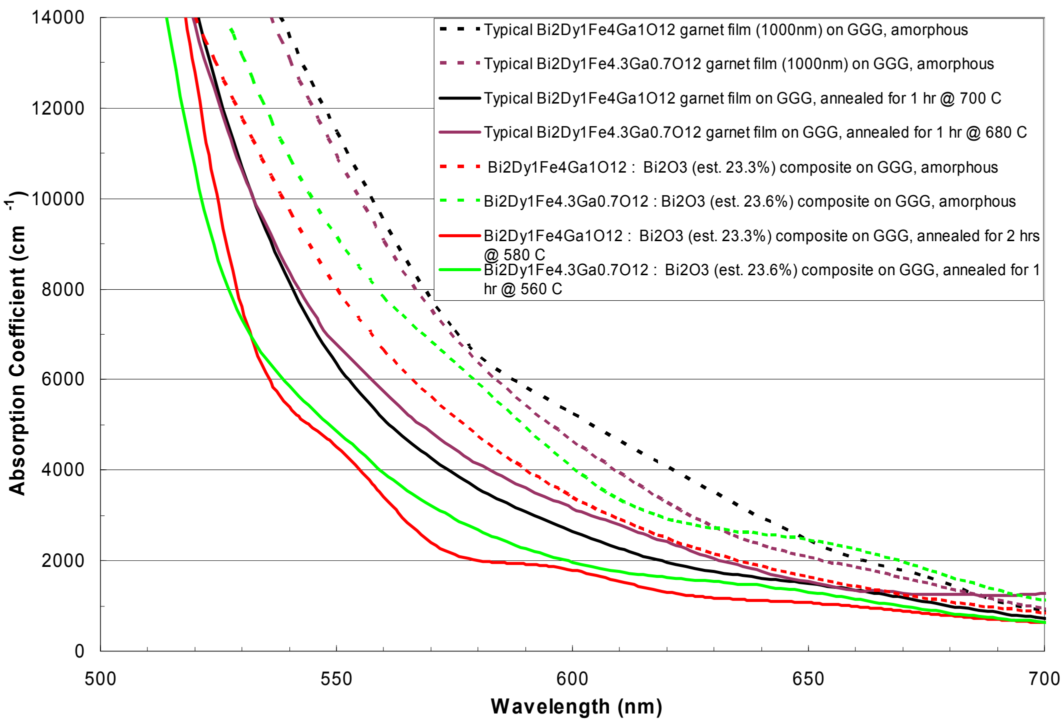

Figure 1. Derived absorption coefficients spectra of sputtered $Bi_2Dy_1Fe_4Ga_1O_{12}$ and $Bi_2Dy_1Fe_{4.3}Ga_{0.7}O_{12}$ garnet layers and these of the garnet-oxide composites (best-performing types) sputtered onto GGG (111) substrates (measured in amorphous-phase and optimally-annealed nanocrystalline films) prepared using RF co-sputtering followed by the conventional oven annealing in air atmosphere.

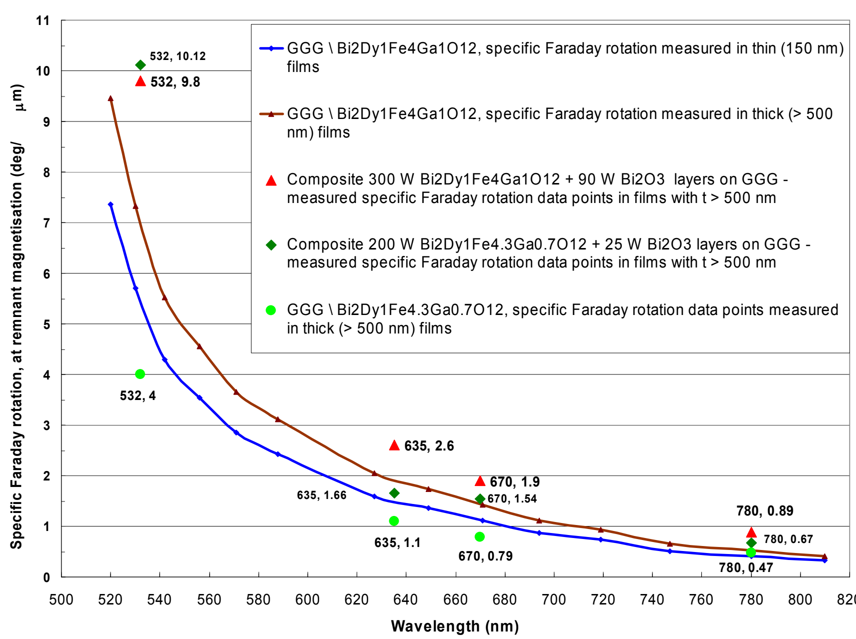

Figure 2. Spectra of specific Faraday rotation of the typical $Bi_2Dy_1Fe_4Ga_1O_{12}$ and $Bi_2Dy_1Fe_{4.3}Ga_{0.7}O_{12}$ garnet layers, and these of the best-performing garnet-oxide composite films prepared on GGG (111) substrates, measured at the remanent magnetization states.

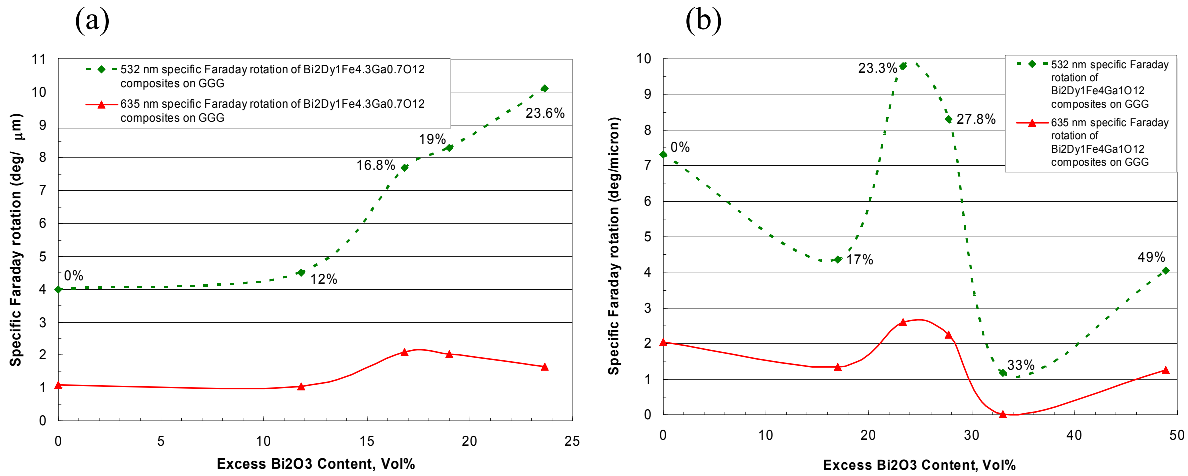

Figure 3. Specific Faraday rotation (measured at remanent magnetization states) of the co-sputtered annealed $Bi_2Dy_1Fe_{4.3}Ga_{0.7}O_{12}$: Bi_2O_3 (a) and $Bi_2Dy_1Fe_4Ga_1O_{12}$: Bi_2O_3 (b) composite garnet films deposited onto GGG (111) substrates at 532 nm (dotted lines) and 635 nm (solid lines) as a function of the estimated excess volumetric content of Bi_2O_3.

Fig. 3 shows the specific Faraday rotation for 532 nm (dotted line) and 635 nm (solid line) light, as a function of the estimated volumetric fraction (approximated quantification of the excess Bi_2O_3 fractions by volume, calculated using the partial and total deposition rates) of the excess bismuth oxide content within the deposited films. It can be noted that at 532 nm, the specific Faraday rotation increases with the increase of excess Bi_2O_3 content up to about 25 vol. %, while at 635 nm, the best specific Faraday rotation peaks at the range of excess oxide fractions of between 16-20 vol.%. At 635 nm, a drop in the specific Faraday rotation in observed after reaching about 25% excess Bi_2O_3 content in the film. This may be due to some impurity phases formation, but is mainly due to the increase in the volume of material in the amorphous matrix surrounding the garnet grains.

In films having the excess bismuth oxide content greater than about 25 vol. %, some surface degradation was often occurring after the annealing processes, which led to the significant scattering losses, and consequently, the reduction in the MO figures of merit. Nevertheless, films with up to 50 vol.% of excess bismuth oxide were synthesized and annealed rather successfully, and these showed about 55-60% of the specific Faraday rotation measured in the undiluted-garnet films. We believe that these highly-diluted composites have very small and isolated garnet grains embedded into the surrounding amorphous matrix filled predominantly with bismuth oxide, which would explain the remarkably-improved transparency of these films in the visible range. The study of these materials is still ongoing. The promising MO figures of merit achieved in our garnet films makes them very attractive for use in nano-structured magneto-photonic components as well as MPC-based devices, including magnetic field sensors and visualizers. The best MO figures of merit achieved in our garnet materials were as high as 29°(+/-1°) at 532 nm and 43°(+/-2°) at 635 nm. The measured data points for the MO figures of merit ($2\Theta_F/\alpha$) of several garnet-oxide composite films are shown in Fig. 4.

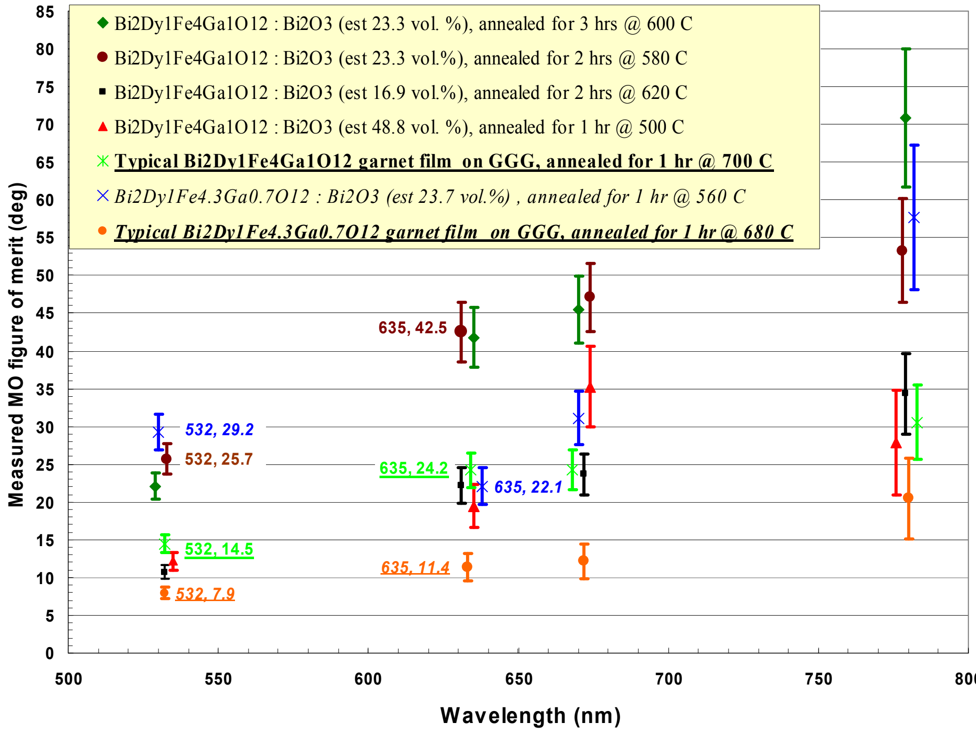

Figure 4. Measured MO figure of merit data points (taken at the wavelengths of 532, 635, 670 and 780 nm) of the typical $Bi_2Dy_1Fe_4Ga_1O_{12}$, $Bi_2Dy_1Fe_{4.3}Ga_{0.7}O_{12}$ layers, and of the various garnet-oxide composites of type $Bi_{3-x}Dy_xFe_{5-y}Ga_yO_{12}$: Bi_2O_3 deposited onto GGG (111) substrates having a record MO quality in the visible range.

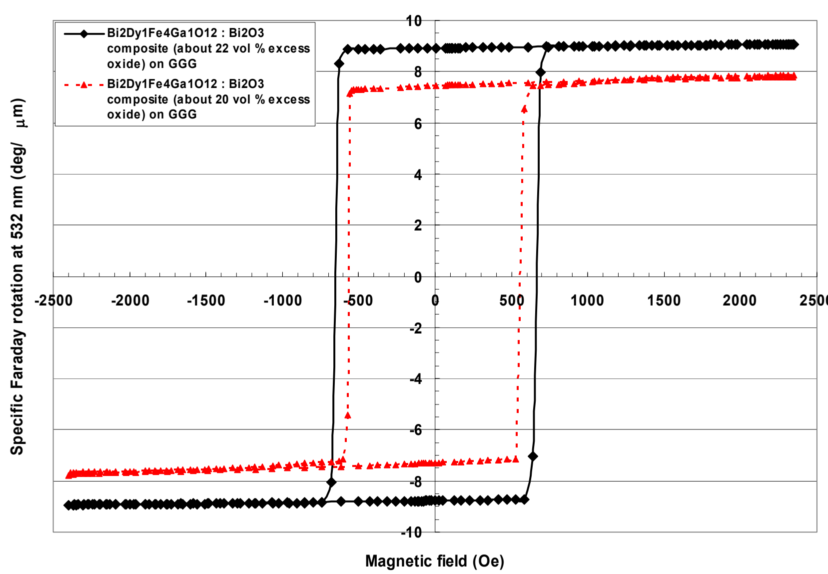

Figure 5. Hysteresis loops of Faraday rotation measured at 532 nm in two $Bi_2Dy_1Fe_4Ga_1O_{12}$: Bi_2O_3 composite films of slightly different excess Bi_2O_3 content having thicknesses of 1.1 µm (solid curve) and 0.74 µm (dashed curve) grown on GGG (111) substrates.

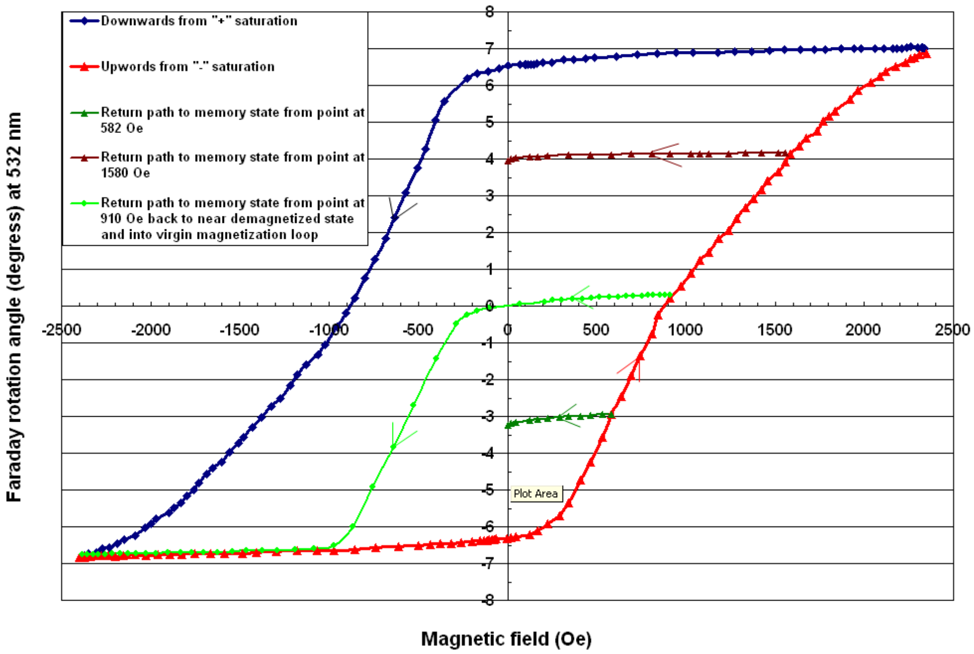

Figure 6. Hysteresis loop of Faraday rotation measured in $Bi_2Dy_1Fe_{4.3}Ga_{0.7}O_{12}$: Bi_2O_3 (est. 24 vol.% excess Bi_2O_3) composite film of 0.85 µm thickness grown on a Corning 1737 glass substrate measured using 532 nm light.

The nearly "square" hysteresis loops of Faraday rotation shown in Fig. 5 were measured at 532 nm in a 1.1 µm thick and 0.74 µm thick ($Bi_2Dy_1Fe_4Ga_1O_{12}$: Bi_2O_3) composite films having approximately 22 vol. % and 20 vol. % of added Bi_2O_3 content, grown on GGG (111) substrates. The specific Faraday rotation at 532 nm of more than 9 °/µm was measured at the remanent magnetization state in the film of thickness 1.1 µm. Fig. 6 shows the hysteresis loop of Faraday rotation measured at 532 nm in a 0.85 µm thick ($Bi_2Dy_1Fe_{4.3}Ga_{0.7}O_{12}$: Bi_2O_3) composite film having approximately 24 vol. % of added bismuth oxide, sputtered onto a Corning 1737 glass substrate. This film, like all films sputtered on glass substrates, exhibited a higher coercivity and a different dynamics of the magnetization switching process in comparison with other films from the same batch sputtered onto GGG (111) substrates. We found that the kinetics of the crystallization processes depends significantly on the substrate type, which is likely due to the difference in the grain nucleation and growth mechanisms. Also, the "return paths" towards the two different memory states from two different original magnetization states are shown in Fig. 6, illustrating the feasibility of ultra-fast magnetic field-driven polarization control devices that can be developed using our garnet films. The return path from the point at 910 Oe led to a nearly-demagnetized state, and from there, a magnetization path similar to the virgin magnetization loop was traced. All of our composite garnet films showed high-contrast magnetic domain patterns (observed in demagnetized films, immediately after the annealing processes, using a transmission-mode polarizing microscope). Near-100% remanence was observed in all garnet composite film batches (films with up to the estimated 40-50% of excess bismuth oxide content were tested), as a consequence of having a strong perpendicular magnetic anisotropy. In the remanently-magnetized states (at zero external field), all films were observed to be in the monodomain state.

3. CONCLUSION

We have demonstrated composite garnet-oxide films of record-high MO quality fabricated by adding the excess Bi_2O_3 content into the garnet structure of type $(BiDy)_3(FeGa)_5O_{12}$ and characterized the composite garnet materials optically, magnetically and magneto-optically. The new synthetic materials show great promise for the development of next-generation integrated-optics devices requiring the functionalities based on Faraday effect and magnetic memory.

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