High Figure of Merit Magneto-Optical Ce- and Bi-Substituted Terbium Iron Garnet Films Integrated on Si

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Films of polycrystalline terbium iron garnet (TbIG), cerium-substituted TbIG (CeTbIG), and bismuth-substituted TbIG (BiTbIG) are grown on Si substrates by pulsed laser deposition. The films grow under tensile strain due to thermal mismatch with the Si substrate, resulting in a dominant magnetoelastic anisotropy which, combined with shape anisotropy, leads to in-plane magnetization. TbIG has a compensation temperature of 253 K which is reduced by substitution of Ce and Bi. The Faraday rotation at 1550 nm of the TbIG, Ce$_{0.36}$Tb$_{1}$IG, and Bi$_{0.03}$Tb$_{1}$IG films is $5400 \pm 600$° cm$^{-1}$, $4500 \pm 100$° cm$^{-1}$, and $6200 \pm 300$° cm$^{-1}$, respectively, while Ce$_{0.36}$Tb$_{1}$IG and Bi$_{0.03}$Tb$_{1}$IG exhibit lower optical absorption than TbIG, attributed to a reduction in Fe$^{2+}$ and Tb$^{4+}$ absorption pathways. The high Faraday rotation of the films, and in particular the high magneto-optical figure of merit of the Bi$_{0.03}$Tb$_{1}$IG of 720° dB$^{-1}$ at 1550 nm, make these polycrystalline films valuable for applications in integrated photonics.

1. Introduction

Magneto-optical (MO) materials provide nonreciprocal functionality in optical circuits and networks. In particular, optical isolators based on nonreciprocal mode conversion or phase shift are key components of optical networks, ensuring unidirectional propagation of light.[1–6] The nonreciprocity of a MO material is given by the off-diagonal terms of the permittivity tensor, and can be characterized by measuring the Faraday rotation. For the near-IR optical communications bands, materials based on ferrimagnetic yttrium iron garnet (YIG, Y$_3$Fe$_5$O$_{12}$) offer a desirable combination of a high Faraday rotation and low optical absorption. Cerium- and bismuth-substituted yttrium iron garnet (CeYIG, BiYIG) have an excellent MO figure of merit (FoM, the ratio of Faraday rotation to optical absorption).[3–18] and bismuth iron garnet and paramagnetic terbium gallium garnet are both used in bulk optical isolators.

In order to incorporate these complex oxides into photonic integrated circuits, films with high FoM must be grown onto photonic substrates and devices. Although YIG crystallizes readily on non-garnet substrates, it has a low Faraday rotation ($\approx +100^\circ$ cm$^{-1}$ at 1550 nm)[29] and FoM. Crystallization of CeYIG or BiYIG without secondary phases can be accomplished by deposition then annealing the film directly or by annealing a bilayer consisting of a YIG seedlayer placed either above or below the active MO layer.[12,13] When a seed layer is included, a top seed layer is preferable as it maximizes coupling of the MO garnet with an optical mode propagating through an underlying waveguide.

Like YIG, rare earth garnets such as terbium iron garnet (TbIG) or dysprosium iron garnet[19,20] can crystallize directly on non-garnet substrates to form polycrystalline films. TbIG is a thermodynamically stable phase like YIG[21,22] which promotes garnet-phase crystallization without a seed layer. TbIG has a Faraday rotation in 1100–1550 nm wavelength range of $\approx +270$ to $+1000^\circ$ cm$^{-1}$.[23–25] Bi-substituted TbIG has been grown by liquid-phase epitaxy and flux methods[23–27] or sol-gel methods[28] and more recently thin films of Ce- and Bi-substituted TbIG (CeTbIG, BiTbIG) were grown on Si by sputtering.[29–34] Sputtered BiTbIG with Bi substitution of 14% of the Tb sites has a Faraday rotation of $\approx -500^\circ$ cm$^{-1}$ at 1550 nm,[29] the same sign as that of CeYIG, which at 1550 nm wavelength had a Faraday rotation of at least $\approx -3700^\circ$ cm$^{-1}$.[29] CeTbIG films with Ce substituting up to 25% of the Tb sites showed a Faraday rotation above $\approx -3200 \pm 200^\circ$ cm$^{-1}$,[31,32] but a 44 nm thick magnetic dead layer formed between the waveguide and the CeTbIG, hindering the interaction of evanescent light with the MO garnet cladding.[12] However, the optical absorption and FoM of these Bi- and Ce-substituted TbIG materials have not yet been reported.

In this paper, we report the growth, magnetic, and optical characteristics of polycrystalline thin films of TbIG, CeTbIG, and BiTbIG synthesized using pulsed laser deposition (PLD) on
Si substrates. The effect of the growth conditions on the stoichiometry of TbIG, CeTbIG, and BiTbIG films is discussed. We show that by composition control of the Ce- and Bi-substituted TbIG, high Faraday rotation is achievable, up to 6200° cm⁻¹ at 1550 nm wavelength. The optical absorption of the TbIG garnet films can be reduced by addition of Bi³⁺ and Ce³⁺ and the possible mechanisms of optical absorption in these films are discussed. The FoM reached 720° dB⁻¹, the highest reported for polycrystalline garnet films with the added benefit of improved device performance due to the absence of a seed layer. The temperature dependence of the MO and magnetic properties of these thin films are also characterized.

2. Results

2.1. Structural, Compositional, and Surface Characterization of TbIG/Si, CeTbIG/Si, and BiTbIG/Si

TbIG, CeTbIG, and BiTbIG films were grown on Si substrates with native oxide by PLD as described in the Experimental Section by codeposition from Tb₂Fe₅O₁₂, Ce₂Tb₂Fe₅O₁₂, and Bi₁₀⁻₃Tb₂₇Fe₅O₁₂ targets. Iron garnets such as Tb₂Fe₅O₁₂ form cubic crystals with lattice parameter of ≈1.2 nm and 8 formula units per unit cell, illustrated in Figure 1a. Tb, Bi, and Ce are expected to occupy 3 dodecahedral sites per formula unit whereas the Fe occupies 2 octahedral and 3 tetrahedral sites. We define a composition parameter R as the ratio of \( \frac{Tb + Ce + Bi}{Fe} \) which characterizes how close the film is to the ideal cation stoichiometric ratio of \( R = 0.6 \). Table S1, Supporting Information, shows the cation ratios of films made in this study determined by wavelength dispersive X-ray spectroscopy (WDS).

Figure 1b–d shows the X-ray diffraction (XRD) patterns and R ratios for several samples of TbIG, CeTbIG, and BiTbIG after rapid thermal annealing (RTA) at 900 °C for 3 min. The nominally TbIG samples have an R ratio of 0.70, 0.57, and 0.54 (Figure 1b), yet they each crystallize well on Si, showing the characteristic garnet (400), (420), and (422) powder peaks near \( 2\theta = 30° \) with no detectable peaks from secondary phases. An iron deficiency similar to that of the TbIG with \( R = 0.70 \) has also been reported for single crystal TbIG films with the excess Tb incorporated into the octahedral sites usually occupied by

![Figure 1](https://example.com/figure1.png)

**Figure 1.** a) Cubic unit cell of TbIG showing octahedral (pink), tetrahedral (purple), and dodecahedral (yellow) sites. The cation sites are surrounded by \( O^− \) (indicated by black spheres) at the vertices of the polyhedrons. Magnetization directions of the Tb³⁺ and Fe³⁺ cations are shown using red arrows. b–d) XRD θ-2θ scans for polycrystalline b) TbIG, c) CeTbIG, and d) BiTbIG films on silicon after RTA at 900 °C for 3 min.
Fe. The iron deficiency of the films in this study was reduced by using a lower laser fluence which is believed to result in less scattering of Fe atoms in the PLD plume compared to the rare earth.

In the case of CeTbIG, while all the compositions shown in Figure 1c form garnet phases, only the Ce0.36TbIG film, which has an R ratio that is closest to 0.6, crystallizes with all three of the garnet peaks near 2θ = 30°. Increasing Ce content led to the formation of broad garnet peaks or secondary phase formation. For BiTbIG, most of the films have very low bismuth content compared to the target. This is due to the volatility of bismuth, which is commonly depleted during high-temperature deposition or annealing. By using a lower substrate temperature of 700 °C and a higher oxygen pressure of 100 mTorr, the Bi content was greatly enriched, forming Bi0.79TbIG with an R ratio of 0.66, but this composition did not crystallize as a single-phase garnet according to the XRD data (Figure 1d).

Based on the structural and compositional analysis we selected three exemplary films for further magnetic and MO characterization. The films, of composition TbIG (123 nm thick, measured composition Tb:Fe = 2.9:5.1, R = 0.57), Ce0.36TbIG (72 nm, Ce:Tb:Fe = 0.36:2.59:5.05, R = 0.58) and Bi0.03TbIG (79.8 nm, Bi:Tb:Fe = 0.03:3.06:4.9, R = 0.63), consist of polycrystalline single-phase garnet. Atomic force microscopy (AFM) images of these three films in Figure 2a–c and Figure S1a–c, Supporting Information, show that the TbIG has a grain size of the order of 100–150 nm, the CeTbIG exhibits a range of grain sizes from 20–100 nm, and the Bi0.03TbIG had a grain size of

![AFM images](image-url)

Figure 2. AFM height images post-RTA for a) TbIG/Si (R = 0.57), b) Ce0.36TbIG/Si, c) Bi0.03TbIG/Si. In-plane and out-of-plane VSM room temperature hysteresis loops of d) TbIG (R = 0.57), e) Ce0.36TbIG, and f) Bi0.03TbIG films on Si after RTA. Temperature dependent magnetization measured in a SQUID magnetometer for g) TbIG (R = 0.70, 0.57 and 0.54), h) Ce0.36TbIG, and i) Bi0.03TbIG.
10–30 nm with the grains forming larger clusters. Even though the final Bi content in the film is small, we expect that the film contained a much greater fraction of Bi prior to RTA which was lost on annealing, and this affected the microstructural development compared to that of TbIG.

### 2.2. Magnetic Characterization

Magnetic hysteresis of the films was measured with the magnetic field applied both in-plane and out-of-plane (perpendicular to the films) using a vibrating sample magnetometer (VSM), and temperature-dependent in-plane magnetic hysteresis measurements were carried out using a SQUID magnetometer. The VSM hysteresis loops at room temperature are given in Figure 2d–f. The TbIG ($R = 0.57$), Ce$_{0.36}$TbIG and Bi$_{0.03}$TbIG films have room temperature saturation magnetization ($M_s$) of 43, 26 and 38 kA m$^{-1}$ respectively. The total anisotropy of the films includes the sum of magnetoelastic, magnetoelastic and thermal properties of polycrystalline garnet are then given by

$$K_u = K_{me} + K_{an} = \frac{3}{2} \frac{\lambda}{1 - \nu} (\epsilon_z - \epsilon_x) - \frac{\mu_s}{2} M_s^2$$

where $\lambda$ is the magnetostriction coefficient for the polycrystal, $E$ is Young's modulus, $\nu$ is the Poisson's ratio and $\epsilon_x$ and $\epsilon_z$ are the in-plane and out-of-plane strain. Iron garnet is close to being elastically isotropic, with an elastic anisotropy factor $2c_{44} / (c_{11} + c_{12}) = 0.947$ calculated for YIG$^{[36]}$ where $c_{11}$, $c_{12}$, and $c_{44}$ are the three independent cubic elastic constants. The elastic properties of polycrystalline garnet are then given by $E = \left(\frac{c_{11} + 2c_{12}}{c_{11} + c_{12}}\right) c_{11} - c_{12}$ and $\nu = \frac{c_{44}}{c_{11} + c_{12}}$. The room temperature magnetostriction coefficients of single-crystal TbIG are $\lambda_{100} = -3.3 \times 10^{-6}$ and $\lambda_{111} = +12 \times 10^{-6}$. The approximation for the magnetostriction $\lambda$ of a polycrystal proposed by Akulov$^{[38]}$ is

$$\lambda = \frac{2}{3} \lambda_{100} + \frac{3}{5} \lambda_{111}$$

which yields $\lambda = +5.88 \times 10^{-6}$ for TbIG. An approximation of Callen and Goldberg$^{[39,40]}$ which assumes non-uniform mechanical stress within the polycrystalline aggregate gives a similar result of $\lambda = +5.73 \times 10^{-6}$ based on the elastic constants of TbIG$^{[38]}$.

The strain state in the garnet films on Si is dominated by thermal expansion mismatch. The in-plane strain is $\epsilon_x = \epsilon_y = -\epsilon_z = \alpha \Delta T$ where $\alpha = \alpha_{film} - \alpha_{substrate}$ is the mismatch between the thermal expansion coefficient ($\alpha$) of the film and substrate and $\Delta T$ is the temperature change. We assume for TbIG that $\alpha$ has little variation within the temperature range, which is a reasonable approximation for iron garnets.$^{[37]}$ The TbIG film on Si will experience an in-plane tensile strain after cooling down from 900 °C. For an isotropic film under biaxial stress, the out-of-plane strain is $\epsilon_z = \epsilon_y = - \frac{1}{1-\nu} \epsilon_x$.

Both magnetoelastic and shape anisotropy favor an in-plane easy axis, though the magnetoelastic contribution for TbIG $R = 0.57$ is more than 2 times greater than the shape anisotropy. The total anisotropy for the films, $K_u$, is calculated from the predicted thermal mismatch, magnetostriction, and magnetization and is shown in Table 1. The values of $K_u$ have the same sign and indicate an in-plane easy magnetization direction for all the films. The calculated anisotropy for TbIG $R = 0.57$ agrees well with the anisotropy determined experimentally from the difference in area between the in-plane and out-of-plane anhysteretic loops (i.e., the measured loops with hysteresis subtracted)$^{[40]}$ suggesting that thermal mismatch provides a reasonable estimation of the strain state and the bulk magnetostriction values are appropriate.

In contrast, the measured anisotropy of the Bi$_{0.03}$TbIG is 5 times higher than that of the TbIG, exceeding the value predicted from the magnetostriction and thermal mismatch strain. This suggests that the strain or the magnetostriction are higher than those of TbIG, or there may be another source of anisotropy. The magnetostriction is likely similar to that of TbIG due to the small Bi content, but Bi loss on annealing and the subsequent volume reduction could account for an increase in the in-plane tensile strain, and the Bi may also affect strain relaxation mechanisms$^{[42]}$ or produce a growth-induced anisotropy.

The magnetostriction of Ce-substituted garnets is not well characterized, but magnetostriction coefficients of $\lambda_{100} = +120 \times 10^{-6}$ and $\lambda_{111} = +50 \times 10^{-6}$. They have been extrapolated for the theoretical garnet Ce$_{2}$Fe$_{5}$O$_{12}$ based on data from YIG with small substitutions of Ce. Ce provides a positive contribution to the magnetostriction of YIG, and extrapolating from data

| Sample | Calculated $\lambda$ from Refs. $^{[38,43]}$ ($10^{-6}$) | Calculated $K_{me}$ [kJ m$^{-3}$] | Calculated $K_u = K_{me} + K_{an}$ [kJ m$^{-3}$] | Measured Anisotropy from anhysteretic loops [kJ m$^{-3}$] | Model $T_{comp}$ [kK] | Measured $T_{comp}$ [kK] | Faraday Rotation at 1550 nm $2\nu$ [° cm$^{-1}$] | Optical Loss at 1550 nm [dB cm$^{-1}$] | MO FoM $at$ 1550 nm [° dB$^{-1}$] |
|--------|-------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| TbIG (95 nm)/Si, R = 0.70 | 5.73 | −2.8 | −0.57 | −3.37 | −2.99 | 266 | 259.9 ± 2.5 | 3500 ± 300 | 19.9 | 175 |
| TbIG (123 nm)/Si, R = 0.70 | −1.16 | −3.96 | −3.42 | 243 | 252.6 ± 2.5 | 5400 ± 600 | 17.4 | 310 |
| TbIG (300 nm)/Si, R = 0.54 | −0.20 | −3.00 | −0.97 | 237 | 244.6 ± 2.4 | 1800 ± 240 | – | – |
| Bi$_{0.03}$TbIG (80 nm)/Si | 5.73 | −2.8 | −0.91 | −3.71 | −15.01 | 236 | 229.9 ± 2.2 | 6200 ± 300 | 8.6 | 720 |
| Ce$_{0.36}$TbIG (72 nm)/Si | 35.4 | −17.5 | −0.42 | −17.92 | −9.09 | 193 | 145.8 ± 1.4 | 4500 ± 100 | 8.3 | 540 |
reported by Wijn[43] we estimate $\lambda = +35 \times 10^{-6}$ for polycrystalline Ce$_{0.36}$TbIG. This is 6 times larger than the magnetostriction of polycrystalline TbIG, and could account for the larger anisotropy of Ce$_{0.36}$TbIG compared to TbIG even if the actual value of magnetostriction is not as large as the extrapolated value.[33,43]

We now describe the trends in magnetic compensation temperature with composition. In iron garnets, the strongest superexchange interactions occur between the octahedral Fe$^{3+}$ and tetrahedral Fe$^{3+}$ moments leading to ferrimagnetic ordering. The moment of the rare earth (here Tb$^{3+}$) in the dodecahedral site is coupled antiparallel to the tetrahedral Fe$^{3+}$ as shown in Figure 1a. The dodecahedral Tb moments are canted at low temperatures around the [111] directions.[46,47] The different temperature-dependences of the Tb$^{3+}$ and Fe$^{3+}$ moments and the canting lead to a compensation temperature $T_{\text{comp}}$ where the net Tb moment plus the octahedral Fe moment balances the tetrahedral Fe moment and the total moment is zero, that is, at $T_{\text{comp}}$ three dodecahedral Tb contribute the same net magnetic moment as one tetrahedral Fe$^{3+}$.

The polycrystalline TbIG ($R = 0.57$) has a $T_{\text{comp}}$ of 252.6 K [$\pm$2.5 K] which is near the bulk $T_{\text{comp}}$ of 248.6 K.[35] The iron deficient TbIG ($R = 0.70$) has a $T_{\text{comp}}$ of 260 K [$\pm$2.6 K], while the iron rich TbIG ($R = 0.54$) has $T_{\text{comp}}$ of 244.6 K [$\pm$2.4 K] as shown in Figure 2g, which also demonstrates that an increase in Tb:Fe ratio raises the magnetization below $T_{\text{comp}}$. The increase in compensation temperature with Tb enrichment is similar to observations of Rosenberg et al.[35] and can be attributed to excess Tb occupying octahedral sites. Tb can also be tetrahedral, and is present in the films (see below); in Tb-rich TbIG the Tb$^{4+}$ (4f$^0$) is more likely to occupy the smaller octahedral sites. When Tb is on the octahedral sites it is expected to exhibit stronger exchange coupling to the Fe$^{3+}$ and less canting than dodecahedral Tb. This raises the magnetic moment of the octahedral sublattice relative to that of the tetrahedral sublattice which increases $T_{\text{comp}}$ and the low-temperature net magnetization.

To compare with experimental data, a modified version of Dionne’s molecular field coefficient model for garnets was employed.[48,49] The model was modified to account for off-stoichiometry in the films by assuming that excess rare-earth occupies the octahedral sites, whereas excess iron occupies the dodecahedral sites. The molecular field coefficients are assumed to be independent of the site occupancy, and other defects such as cation vacancies, Tb$^{4+}$ and Fe$^{2+}$ are neglected. Comparison with experimentally measured compensation temperatures for the TbIG shows good agreement, with the trend of higher $R$ values leading to higher compensation temperatures as shown in Figure S2, Supporting Information.

Replacing Tb$^{3+}$ (4f$^0$) with Bi$^{3+}$ (5d$^{10}$6s$^2$) or Ce$^{3+}$ (4f$^1$) is expected to reduce the magnetization of the dodecahedral sublattice and lower $T_{\text{comp}}$, with Bi having a larger effect than Ce. To estimate $T_{\text{comp}}$ for Ce$_{0.36}$TbIG and Bi$_{0.03}$TbIG we assume that the contribution to the magnetic moment from the octahedral and tetrahedral Fe$^{3+}$ is the same as that of YIG.[46,50–52] The Tb$^{3+}$ sublattice magnetization can then be obtained by subtracting the magnetization of YIG[46] from that of TbIG,

$$[M_{\text{IG}}]_T = [M_{\text{IG}}]_T - [M_{\text{YIG}}]_T$$

The resulting temperature-dependent sublattice magnetization of Tb$^{3+}$, $[M_{\text{IG}}]_T$, is then scaled to account for Bi$^{3+}$ or Ce$^{3+}$ substitution and added back to the temperature-dependent magnetization of YIG, $[M_{\text{IG}}]_T$, to obtain the thermomagnetic curves for Bi$_{0.03}$TbIG and Ce$_{0.36}$TbIG. The predicted values of $T_{\text{comp}}$ are shown in Table 1. The measured $T_{\text{comp}}$ for Bi$_{0.03}$TbIG is lower than that of bulk TbIG by 19 K (Figure 2i), whereas the model predicted a decrease by 13 K. As a comparison, sol-gel Bi$_x$Tb$_{1-x}$IG showed a decrease in $T_{\text{comp}}$ by 80 K for $x = 0.5$.[28] In the case of Ce$_{0.36}$TbIG, the measured reduction in $T_{\text{comp}}$ by 103 K (Figure 2h) is much larger than predicted by the model (56 K). A significant Ce$^{4+}$ content appears unlikely since it would be associated with Fe$^{2+}$ and a higher optical absorption,[53] and there was no detectable CeO$_2$ found from XRD. The results show that both the Bi and Ce lower $T_{\text{comp}}$ further than would be expected from a model based on simple dilution of the rare earth moment, which may indicate that the Ce or Bi affects the cation site occupancy in the films or the canting which is present at and below $T_{\text{comp}}$.[47]

2.3. MO Characterization

The temperature and spectral dependences of MO effects were obtained using a high precision MO spectrometer with a rotating analyzer, which enabled Faraday effect measurements to an accuracy of $\pm$1 mdeg. Saturation Faraday rotation at 1550 nm at room temperature for the TbIG ($R = 0.57$), Ce$_{0.36}$TbIG and Bi$_{0.03}$TbIG films was $5400 \pm 600$ mdeg cm$^{-1}$, $4500 \pm 100$ mdeg cm$^{-1}$, and $6200 \pm 300$ mdeg cm$^{-1}$ respectively as shown in Figure 3a. The greater Faraday rotation of TbIG in comparison to YIG at energies around 1 eV is due to strong optical transitions at higher energies induced by Tb$^{3+}$.[54] Tb$^{3+}$ is reported to increase the splitting of oscillator strength for left and right circularly polarized light above 4 eV in iron garnets due to exchange interactions between Tb$^{3+}$ and tetrahedral Fe$^{3+}$.[54] The Faraday rotation of TbIG is thus proportional to the magnetic moment of the ions involved in this charge transfer process.[52,54] Bi$^{3+}$ and Ce$^{3+}$ both have a negative contribution to the Faraday rotation of YIG[55–57] and in Ce$_{0.36}$TbIG the positive Faraday rotation is lower in comparison to TbIG as expected. However, in Bi$_{0.03}$TbIG the Bi content is small and the Faraday rotation of TbIG and BiTbIG agree within the error range.

The polar Kerr rotation spectrum of the TbIG film shown in Figure 3b resembles prior results[54] for single crystal TbIG. In TbIG, optical transitions located between 3–4 eV originate from Fe$^{3+}$ crystal-field transitions.[54] The amplitude of the Kerr effect is lower than the results of single crystals in Ref.[54] Figure 3c shows longitudinal Kerr spectra of Ce$_{0.36}$TbIG at temperatures above and below $T_{\text{comp}}$. Below $T_{\text{comp}}$ the octahedral Fe$^{3+}$ and dodecahedral Tb$^{3+}$ plus Ce$^{3+}$ moments are oriented parallel to the field while the tetrahedral Fe$^{3+}$ moments are antiparallel.[58] The Kerr rotation of the two datasets at 120 and 320 K have opposite signs as the orientation of the sublattices reverses at $T_{\text{comp}}$. This change in sign is because the Kerr rotation like Faraday rotation is sensitive to the magnetic sublattices rather than the net magnetization.[58,59] Ce$_{0.36}$TbIG has a polar Kerr spectrum similar to that of single-crystal CeYIG.[17] Figure 3d displays the temperature-dependent polar Kerr
rotation of Bi0.03TbIG at 2.5 eV. The change in sign indicates $T_{\text{comp}}$ in the range of $\approx 220$ K, similar to the value of $\approx 230$ K found using SQUID magnetometry.

3. Optical Characterization

A spectroscopic ellipsometer (J.A. Woollam RC2) was employed to acquire the spectra of the ellipsometric parameters PSI and DELTA. A set of three measurements at different angles of incidence were performed to enlarge the experimental dataset for subsequent fitting. For the fitting, a model structure of a TbIG, Ce0.36TbIG, or Bi0.03TbIG layer on an oxidized Si substrate was considered. The spectral dependence of complex refractive index ($N=n+ik$) of each garnet layer was parametrized by the sum of 4 Cody-Lorentz oscillators and their parameters were fitted together with the layer thickness and surface roughness. The resulting spectra of refraction index and extinction coefficient, $n$ and $k$, for the three TbIG, CeTbIG, and BiTbIG samples are shown in Figure 4a,b and the spectrally dependent absorption coefficient is shown in Figure 4c. The spectral behavior of $n$ and $k$ in Figure 4a,b is typical for ferrimagnetic garnets,[12,56,57,60,61] with the absorption edge around 2 eV. We were unable to estimate the absorption of the 300 nm TbIG ($R = 0.54$ eV) film under 2 eV from ellipsometric measurements since this particular thickness leads to high interference in the low energy region and large depolarization. From Figure 4b, one can see a slight red shift of the onset of absorption for Bi and Ce samples. The shift towards lower energies induced by increasing the amount of Bi in YIG is well reported.[56,62]

The CeTbIG and BiTbIG had lower absorption than the TbIG at 1550 nm as shown in Table 1. The absorption of TbIG at 1550 nm can be attributed to the tail extending from a Faraday rotation and optical absorption line at $\lambda = 1850$ nm from inner 4f electronic transitions in the Tb$^{3+}$ ion.[23,27,63] While rare earths predominately occur in the trivalent state, Tb$^{3+}$ only has one electron above the half-filled 4f shell and therefore is known to readily oxidize to Tb$^{4+}$, especially in cubic materials.[35,64–66] Tb$^{4+}$ has been reported to be a quenching site of fluorescence for its strong and broad absorption in the visible region.[64]

High-resolution XPS data from the TbIG, CeTbIG, and BiTbIG films show the presence of Tb$^{4+}$ in all three films, Figure 4e which is in accordance with results from single crystal TbIG films.[35] The higher intensity of the Tb$^{4+}$ peak can be qualitatively interpreted as a larger proportion of Tb$^{4+}$ than Tb$^{3+}$ in these films.[15,30] Moreover, the intensity of Tb$^{4+}$ relative to Tb$^{3+}$ peaks was stronger in the TbIG film compared to Ce0.36TbIG and Bi0.03TbIG films pointing towards a higher fraction of Tb$^{4+}$ in TbIG compared to the other two films. The XPS spectra of Fe 2p in TbIG reveal a shift to lower binding energy compared
A shift to lower binding energy of the Fe 2p3/2 peak in Fe3O4 has been associated with a reduction of Fe3+ to Fe2+ due to the lower binding energies associated with Fe2+ compounds than Fe3+ compounds. This higher amount of Fe2+ in the TbIG films correlates with the higher amount of Tb4+, and has been reported in other rare earth iron garnets as a result of the presence of tetravalent ion impurities. This higher amount of Fe2+ in the TbIG films correlates with the higher amount of Tb4+, and has been reported in other rare earth iron garnets as a result of the presence of tetravalent ion impurities. The electron donor behavior of Tb3+ allows an electron promoted by a photon in Fe2+ to transfer to a nearby Fe3+ ion. This relaxation process is associated with a large change in dipole moment and strong absorption, and at high concentrations of tetravalent ions the absorption is reported to be proportional to the amount of tetravalent ions (here Tb4+) because they increase the number of Fe2+ ions.

In addition to Fe3+-Fe2+ relaxation, the simultaneous presence of Tb4+ and Tb3+ can also affect the optical properties of the garnet films. The electron donor behavior of Tb3+ allows

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Figure 4. Refractive index (n) and extinction coefficient (k) spectra of a) TbIG (R = 0.54, 0.57, 0.7), b) Ce0.36TbIG and Bi0.03TbIG films. c) Spectral dependence of absorption coefficient of TbIG, Ce0.36TbIG, and Bi0.03TbIG films. d) MO FoM versus energy for TbIG (R = 0.57, 0.7), Ce0.36TbIG and Bi0.03TbIG films. High resolution XPS spectra of e) Tb 4d and f) Fe 2p of the TbIG (R = 0.57), Ce0.36TbIG, and Bi0.03TbIG films.
electronic transitions from 4f → 4f and 4f → 5d between 1.2 and 6 eV while the electron acceptor behavior of Tb4+ allows charge transfer from ligand orbitals to rare earth or Fe3+ ions.\[64\] These additional absorption pathways result in TbIG having higher absorption than YIG or BiYIG.\[12\] However, we find moderate additions of Ce3+ and very small additions of Bi3+ are able to reduce this absorption to less than half as shown in Table 1 and also depicted in Figure 4c. The Bi3+ and Ce3+ ions are associated with lower amounts of Tb4+ and Fe2+ as indicated by XPS, lowering the absorption coefficient significantly. Nonetheless, the TbIG (R = 0.57) has a good MO FoM of 310° dB⁻¹ compared to the FoM of 38° dB⁻¹ for polycrystalline CeYIG.\[12\]

As a result of having both a lower absorption than TbIG albeit a slightly smaller Faraday rotation due to the negative contribution of Ce3+, the Ce0.36TbIG film has a FoM almost 2 times higher than that of TbIG. Bi0.03TbIG triumphs with an FoM of 720° dB⁻¹ as shown in Figure 4c. The small amount of Bi3+ does not negatively impact the Faraday rotation but it reduces the optical absorption significantly. So far, the highest FoM of 769° dB⁻¹ was reported\[12\] for polycrystalline BiYIG with a 40 nm bottom YIG seed layer, and the Bi0.1TbIG in this work has the advantage of having a similarly high FoM while allowing for simpler fabrication and better device performance by eliminating the seed layer.

4. Conclusion

TbIG, CeTbIG, and BiTbIG films were grown directly on Si via PLD without a seed layer. The films exhibit the highest reported Faraday rotation for polycrystalline films at 1550 nm wavelength, up to 6200° cm⁻¹ for Bi0.03TbIG films and a similar value for TbIG. Despite its high Faraday rotation, the TbIG films exhibited a higher optical absorption than that of CeTbIG and BiTbIG, attributed to both the greater concentration of Tb4+ and Fe3+ that can facilitate absorption through Fe3+-Fe2+ relaxation and charge transfer from ligand orbitals, and the 4f electronic transitions of Tb4+. Addition of Ce and Bi lowered the absorption significantly by reducing absorption pathways related to the presence of Tb4+, thus improving the overall FoM of these films. This work emphasizes the critical importance of controlling the Tb3+/Tb4+ ratio, analogous to the improvement in MO performance obtained by controlling Ce4+ in CeYIG via growth conditions.\[73\] The high FoM and the single-layer growth process make Ce and especially Bi-substituted TbIG attractive materials for integrated nonreciprocal photonic devices or for other applications requiring MO materials such as magnetophotonic crystals or other nonreciprocal MO metamaterials.\[74,75\]

5. Experimental Section

**Thin Film Growth**: TbIG, CeTbIG, and BiTbIG films were grown on Si substrates by PLD from targets of composition Tb2Fe2O12, CeTb2Fe2O12, and Bi3Tb2Fe2O12 using a 248 nm wavelength 45 KrF excimer laser (Coherent, COMPex Pro 205). The targets were prepared by mixed oxide sintering\[72\] of 99.999% pure Tb2O3, CeO2, Bi2O3, and Fe2O3 powders. The films were grown at a repetition rate of 10 Hz and laser fluence of 1.5 and 2.5 J cm⁻². The substrate heater setpoint temperature was 900 °C which correspond to a substrate temperature of approximately 750 °C, and an oxygen pressure of 10 mTorr. Afterward, the films were RTA at 900 °C for 3 min in oxygen. Different compositions for the CeTbIG and BiTbIG films were achieved by codeposition with the TbIG target, by alternately ablating the targets using 25 laser shots on TbIG target and between 4–15 laser shots on the CeTbIG and BiTbIG targets.

**Material Characterization**: θ–2θ x-ray diffraction data of the polycrystalline films were carried out using a PANalytical X'pert Pro MPD diffractometer. Compositional analysis was done by WDS using a JEOL-JXA-8200 Superprobe. The cation ratios in the thin films were calculated using the GMR electron probe thin-film microanalysis program\[76\] which takes into account the substrate contributions to the WDS spectrum and the effect of the substrate-film interface. AFM measurements were performed using a Cypher-S AFM, equipped with blueDrive (Asylum Research, an Oxford Instruments company). The bimodal technique, called DualAC, was employed for high-quality images of the lateral microstructure of the thin films. Also, the photothermal excitation technique, called blueDrive, was utilized to tune both the primary and second-order resonance peaks. In particular, the signal from the minute amplitude of oscillation of the second mode for an Olympus AC160TSA-R3 cantilever was used to present the AFM images in Figure S1, Supporting Information. The thickness was measured by surface profilometry on a KLA-Tencor P-1600 stylus profiler. Room temperature magnetic properties were characterized by VSM using an ADE Technologies VSM Model 1660. Temperature-dependent magnetic characterization was performed using Quantum Design’s Magnetic Properties Measurement System (MPMS 3) that allows measurements in the temperature range of 1.8 to 400 K with magnetic fields up to ~70 kOe and temperature accuracy specification of better than +/- 1% at low temperatures. Spectroscopic ellipsometry was performed on a J.A. Woollam RC2 ellipsometer for three light incident angles ranging from 55° to 65°. The experimental data were processed using proprietary software CompleteEase by J. A. Woollam.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.
Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
Faraday rotation, magneto-optical figure of merit, magneto-optical materials, optical absorption, rare-earth iron garnets

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