Faraday rotation and photoluminescence in heavily Tb$^{3+}$-doped GeO$_2$-B$_2$O$_3$-Al$_2$O$_3$-Ga$_2$O$_3$ glasses for fiber-integrated magneto-optics

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We report on the magneto-optical (MO) properties of heavily Tb$^{3+}$-doped GeO$_2$-B$_2$O$_3$-Al$_2$O$_3$-Ga$_2$O$_3$ glasses towards fiber-integrated paramagnetic MO devices. For a Tb$^{3+}$ ion concentration of up to $9.7 \times 10^{21}$ cm$^{-3}$, the reported glass exhibits an absolute negative Faraday rotation of $\sim 120$ rad/T/m at 632.8 nm. The optimum spectral ratio between Verdet constant and light transmittance over the spectral window of 400–1500 nm is found for a Tb$^{3+}$ concentration of $\sim 6.5 \times 10^{21}$ cm$^{-3}$. For this glass, the crystallization stability, expressed as the difference between glass transition temperature and onset temperature of melt crystallization exceeds 100 K, which is a prerequisite for fiber drawing. In addition, a high activation energy of crystallization is achieved at this composition. Optical absorption occurs in the NUV and blue spectral region, accompanied by Tb$^{3+}$ photoluminescence. In the heavily doped materials, a UV/blue-to-green photo-conversion gain of $\sim 43\%$ is achieved. The lifetime of photoluminescence is $\sim 2.2$ ms at a stimulated emission cross-section $\sigma_{em}$ of $\sim 1.1 \times 10^{-21}$ cm$^2$ for $\sim 5.0 \times 10^{21}$ cm$^{-3}$ Tb$^{3+}$. This results in an optical gain parameter $\sigma_{em} \tau$ of $\sim 2.5 \times 10^{-24}$ cm$^2$s, what could be of interest for implementation of a Tb$^{3+}$ fiber laser.

The Faraday effect reflects the ability of a material to - in the presence of a magnetic field being parallel to the incident light beam - rotate the polarization plane of linear polarized light by a certain angle$^{1-3}$. The material’s magneto-optical (MO) performance is typically described by the Verdet constant $V_B$, which represents the degree of rotation as a function of the acting magnetic field strength and the geometrical path length within the material. High performance can hence be achieved via large rotation efficiency or a long path length. Applications of MO materials range from magnetic field sensing and security encoding to optical modulators, diodes, isolators and switches$^{1-6}$. Key for the design of an efficient, optically transparent (bulk) MO material is the incorporation of a high atom concentration of paramagnetic species while, at the same time, avoiding optical absorption to the highest possible degree. While some transition metals have also been considered for this purpose, at present, this calls for the use of rare earth species$^2$. Here, due to the electronic transition of 4f$^7$-4f$^5$5d$^1$, the Tb$^{3+}$ ion offers one of the highest paramagnetic susceptibilities ($J = 6, g = 1.46$) and magnetic moments (9.5–9.72 $\mu_B$) of all rare earth ions. Consequently, the most promising bulk MO material is terbium aluminum garnet (Tb$_3$Al$_5$O$_{12}$, TAG, $V_B \sim 180$ rad/T/m)$^{10,11}$, which is not yet available commercially, though. Instead, terbium gallium garnet single crystals (Tb$_3$Ga$_5$O$_{13}$, TGG, $V_B \sim 134$ rad/T/m)$^{12}$ are presently the most widely used commercial MO materials. But also all commercially available MO glasses rely on massive Tb$^{3+}$-doping$^{13-16}$. As an alternative to the MO crystals, glassy materials offer a much improved flexibility of forming and processing. Especially glass compositions which are suitable for fiber fabrication could enable fiber-integrated devices. In addition, the higher interaction length which can be achieved in fiber devices could further compensate eventual losses in Faraday rotation efficiency. In this regard, besides the primary optical properties, the thermo-physical stability and the rheological properties of the considered glass and its corresponding (supercooled) melt are key parameters: in order to avoid crystallization of the melt during fiber drawing, a certain crystallization stability is required. This is often expressed as the difference, $\Delta T$, between the glass transition temperature $T_g$ and the onset temperature of crystallization $T_c$ or through various other empirical stability indicators such as the Hrubý parameter which is derived from this difference, sometimes further relating...
it to the liquidus temperature of the melt or other properties\textsuperscript{17,18}. Typically, a large value of $\Delta T$ is sought for two reasons: fiber drawing must be performed at a temperature sufficiently above $T_g$ so that a sufficiently low viscosity is reached and the interval of processing temperature must be sufficiently wide to tolerate a certain degree of processing-induced temperature variability. On the other hand, for many of the specialty (non-silica) compositions with often high liquid fragility, fiber drawing cannot be performed above the liquidus temperature (where there would not be any risk of crystallization) because then, the viscosity would be too low.

Here, we consider glass forming liquids of the type GeO$_2$-B$_2$O$_3$-Al$_2$O$_3$-Ga$_2$O$_3$ enabling high rare earth solubility. In this system, we achieve a Tb$_2$O$_3$ doping concentration of up to 25 mol\%. The glass stability parameters are controlled through tailoring the matrix composition in order to provide the possibility of fiber drawing. We then report on the MO and photoluminescence properties of this material.

**Results**

**Magneto-optical properties.** The chemical composition and physical properties of all samples are summarized in Tables 1–2. Figure 1a shows the room-temperature wavelength dependence of $V_R$ for the full series of GBAG-xTb ($x = 14, 18, 22$ and 25). As expected, all samples exhibit paramagnetic behaviour over the full range of studied wavelengths, with a strong absolute increase towards the blue. Secondly, there is a notable increase with range of studied wavelengths, with a strong absolute increase expected, all samples exhibit paramagnetic behaviour over the full range of studied wavelengths, with a strong absolute increase expected.

In the framework of the Van Vleck-Hebb model of single-oscillator paramagnetic rare earth ions, the relationship between $V$ and $\lambda^2$ can be written as\textsuperscript{24,25}

\[
V_B^{-1} = \frac{g_B \mu_B \lambda^2}{4\pi^2 \gamma_{CI}} (1 - \frac{\lambda^2}{\lambda_1^2})
\]

In Eq. (1), $g$ is the Landé factor, $c$ the velocity of light, $h$ is the Planck constant, $\gamma_{CI}$ is the effective transition probability, and $\lambda_1$ is the effective transition wavelength. $\lambda$ is a weighted average value which is taken as the origin of the paramagnetic Faraday rotation. In rare earth ions, it is close to the position of the electric transition of $4f^8 \leftrightarrow 4f^75d^{\alpha}$\textsuperscript{26}. Plotting $V^{-1}$ over $\lambda^2$ therefore yields a linear relationship (Fig. 1c). Here, $\lambda_1$ is the intersection with the $\lambda^2$ axis which results from extrapolation of the data. The value of $\lambda_1$ is dependent on Tb$_2$O$_3$ concentration (inset of Fig. 1c). It increases with Tb$_2$O$_3$ concentration, i.e., from $\sim$225 to 300 nm when $x \leq 22$. A decrease back to $\sim$280 nm is observed for the highest Tb$_2$O$_3$ concentration.

As expected, these values are close to the $4f^8 \leftrightarrow 4f^55d$ transition of the Tb$^{3+}$ ion ($\sim$250 nm)$\textsuperscript{3}$, and are also similar to other reported values, e.g., Tb$^{3+}$-doped phosphate ($\sim$250 nm)$\textsuperscript{27}$, borosilicate ($\sim$259–280 nm)$\textsuperscript{28}$, aluminoborate ($\sim$250 nm)$\textsuperscript{29}$, sodium borate ($\sim$220 nm)$\textsuperscript{a}$ and fluorophosphate glasses ($\sim$217 nm)$\textsuperscript{26}$.

Fig. 1d shows the UV-NIR optical absorption spectra of GBAG-xTb ($x = 14, 18, 22$ and 25). The absorption spectra consist of several strongly overlapping but sharp absorption bands in the 300 to 390 nm range, and another sharp band at $\sim$484 nm. These bands can readily be assigned to the $4f^8 \leftrightarrow 4f^6$ electronic transitions of Tb$^{3+}$ from the ground state of $^7F_6$ to the labeled excited states (inset of Fig. 1d and Fig. 2e)$\textsuperscript{29,30}$. The intensity of all bands follows well Lambert-Beer’s power law. All glasses exhibit high transparency in the 400 to 1500 nm range with a transmittance of $\sim$58% ($\sim$95%) with a thickness of 1 cm (mm). The increasing absorption intensity with increasing Tb$^{3+}$ content in the near-UV region results in a shift of the absorption edge and an apparent coloration under sunlight, gradually varying from colorless to brown (inset of Fig. 1e).

The MO figure of merit (FoM) which is an important parameter for practical applications results from the ratio of $V_B/a$, where $a$ is absorption coefficient\textsuperscript{c}. As displayed in Fig. 1e, the spectral FoM exhibits a sharp dip at 484 nm, resulting from the $^7F_6 \leftrightarrow ^3D_4$ absorption band of Tb$^{3+}$. In the present case, the glass of GBAG-18Tb exhibits the best trade-off between $V_B$ and $a$ over the whole spectrum. The highest FoM performance of $\sim$0.049/\text{dB} is found at

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|c|}
\hline
Glass sample & GBAG-14Tb & GBAG-18Tb & GBAG-22Tb & GBAG-25Tb \\
\hline
GeO$_2$ & 16.5/17.3 & 16.5/18.0 & 16.5/16.4 & 16.5/17.0 \\
B$_2$O$_3$ & 21.5/25.3 & 21.5/25.0 & 21.5/21.4 & 21.5/23.0 \\
Al$_2$O$_3$ & 37.0/27.2 & 37.0/28.0 & 37.0/37.0 & 37.0/32.0 \\
Ga$_2$O$_3$ & 11.0/15.1 & 7.0/11.0 & 3.0/3.2 & 0.0/0.0 \\
Tb$_2$O$_3$ & 14.0/15.1 & 18.0/18.0 & 22/22.0 & 25.0/28.0 \\
\hline
\end{tabular}
\caption{Nominal and analyzed compositions of the studied glasses (data given in the form ‘nominal/as-analyzed’, mol\%)}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|c|}
\hline
Glass sample & GBAG-14Tb & GBAG-18Tb & GBAG-22Tb & GBAG-25Tb \\
\hline
$\rho$ (g/cm$^3$) & 4.08 & 4.53 & 4.79 & 4.85 \\
Tb$^{3+}$ ion concentration (10$^{21}$ cm$^{-3}$) & 5.0 & 6.5 & 8.1 & 9.7 \\
$n_d$ at 632.8 nm & 1.69 & 1.73 & 1.74 & 1.75 \\
$V_B$ (rad/T/m) & $-48$ & $-71$ & $-91$ & $-119$ \\
FoM (1/\text{dB}) & $-0.029$ & $-0.049$ & $-0.023$ & $-0.008$ \\
$t$ (ms) & 2.23 & 1.23 & 0.26 & 0.10 \\
$T_g \pm 1 \, [\text{C}]$ & 740 & 767 & 772 & 777 \\
$T_e \pm 1 \, [\text{C}]$ & 848 & 880 & 905 & 928 \\
$\Delta T \pm 1 \, [\text{K}]$ & 108 & 113 & 133 & 151 \\
$E_a$ (kJ/mol/K) & 520 & 593 & 533 & 482 \\
\hline
\end{tabular}
\caption{Experimental data of density $\rho$, Tb$^{3+}$ ion concentration, refractive index $n_d$, Verdet constant $V_B$ (at 632.8 nm), FoM (at 435 nm), $t$, $T_g$, $T_e$, $\Delta T$ and $E_a$ for the studied glasses}
\end{table}
~435 nm, which matches the emission characteristics of various blue laser diodes.

**Photoluminescence properties.** Fig. 2a and 2b present static photoexcitation (PLE) and luminescence (PL) spectra of Tb\(^{3+}\) in GBAG-xTb (x = 14, 18, 22 and 25) at room temperature. Fully consistent with the optical absorption data (Fig. 1d), the PLE spectra of Tb\(^{3+}\) consist of a series of sharp overlapping PLE bands in the NUV region with maxima at 378, 368, 358, 350, 340, 325, 317 and 303 nm, and another sharp PLE line in the blue with a maximum at 484 nm. These bands are attributed to the intra-configurational parity-forbidden 4f\(^8\)R\(^{4f8}\) electronic transitions from the ground state 7F\(_6\) to the labeled excited states, also indicated in energy level diagram of Tb\(^{3+}\) (Fig. 2a and 2e). The strongest PLE band is the 7F\(_6\)R\(^{5L9}\) at 350 nm, used in the following as excitation wavelength to record the PL spectra. Here, the five typical PL bands of Tb\(^{3+}\) are observed, i.e., at 488, 542, 585, 622 and 655 nm, deriving again from the intra-configurational parity-forbidden 4f\(^8\)R\(^{4f8}\) transitions from 5D\(_4\) to the 7F\(_J\) (J = 6, 5, 4, 3 and 2) multiplet, Fig. 2b and 2e. The green PL line of the magnetic dipole allowed transition (D = 1) Tb\(^{3+}\): 5D\(_4\)R\(^{7F5}\) at 542 nm with a full width at half maximum (FWHM) of ~10 nm (~337 cm\(^{-1}\)) dominates the PL spectra for all samples. As a result, the corresponding International Commission on Illumination (CIE) 1931 PL chromaticity coordinates of all samples are (~0.342 ± 0.002, ~0.667 ± 0.003), which are located in the green region. The aforementioned green PL band is Stark-split into two peaks due to the distorting effect of the disordered glass network on the Tb\(^{3+}\) ions (Fig. 2b). For lower amounts of Tb\(_2\)O\(_3\) loading (x ≤ 18), the intensity of all PL lines of Tb\(^{3+}\) decreases only slightly with Tb\(_2\)O\(_3\) concentration while for x ≥ 18, we observe strong concentration quenching. This is related to an increasing probability for the formation of Tb-O-Tb entities in the first coordination shell of Tb\(^{3+}\). The concentration quenching effect is further confirmed by the decay data of the Tb\(^{3+}\): 5D\(_4\)R\(^{7F5}\) emission (Fig. 2c). All decay curves follow a single exponential function of the form \(I = I_0 \exp(-t/\tau)\) (with time t and intensity I). The effective lifetime \(\tau\) decreases with increasing Tb\(^{3+}\) concentration,
i.e., from ~2.2 to ~1.2 ms when \( x \leq 18 \), and further to ~0.1 ms for \( x > 18 \) (Fig. 2b and 2c). The lifetime of \( \text{Tb}^{3+} \); \( \text{D}_4 \rightarrow \text{F}_2 \) PL for GBAG-14Tb glass (~2.23 ms) is larger than what is found in similar \( \text{B}_2\text{O}_3-\text{Ge}_2\text{O}_2-\text{Gd}_2\text{O}_3 \) glasses before concentration quenching, ~1.80 ms\(^{-}\). This further indicates that particularly weak concentration quenching occurs in the present case. The internal quantum efficiency \( \eta_{\text{QE}} \) for GBAG-14Tb is ~63\%. This value is close to the highest reported \( \eta_{\text{QE}} \) of \( \text{Tb}^{3+} \)-doped phosphor glass (~78\%)\(^{-}\) and silicone hybrid materials (~68\%)\(^{-}\). For higher doping concentration, it decreases to only 0.3\% at \( x = 25 \). The high \( \text{Tb}^{3+} \) loading results in a large absorption cross-section of incoming light and, hence, high photoluminescence. That is, the absorbance of GBAG-14Tb at 350 nm is ~69\%. Thus, the external quantum efficiency \( \eta_{\text{OE}} \) is ~43\%, meaning that at the considered excitation wavelength, ~43\% of the incoming photons are converted through photoluminescence.

PL of \( \text{Tb}^{3+} \) from the higher excited states, i.e., \( \text{D}_3 \rightarrow \text{F}_1 \) \( (\lambda = 6, 5, 4, 3, \) and 1) is almost fully quenched even in GBAG-14Tb glass (Fig. 2d). This is a result of the strong cross-relaxation processes which occur at the high doping levels used in this study. The cross-relaxation process is caused by the closeness of the \( \text{D}_3 \) and \( \text{D}_4 \) (~5629 cm\(^{-}\)) and the \( \text{F}_6 \) and \( \text{F}_5 \) energy levels (~5791 cm\(^{-}\)), Fig. 2e\(^{-}\).

\[ \text{Tb}^{3+}(\text{D}_3) + \text{Tb}^{3+}(\text{F}_6) \rightarrow \text{Tb}^{3+}(\text{D}_4) + \text{Tb}^{3+}(\text{F}_5) \] \tag{2}

The absorption cross-section \( \sigma_{\text{abs}} \) of \( \text{Tb}^{3+} \) at 350 (\( \text{Tb}^{3+} \); \( \text{F}_6 \rightarrow \text{L}_9 \)) and 484 nm (\( \text{Tb}^{3+} \); \( \text{F}_6 \rightarrow \text{D}_4 \)), and stimulated emission cross-section \( \sigma_{\text{em}} \) of \( \text{Tb}^{3+} \) PL at 542 nm (\( \text{Tb}^{3+} \); \( \text{D}_4 \rightarrow \text{F}_5 \)) can be estimated through McCumber’s and Fuchtbauer-Ladenburg’s equation\(^{43-45}\),

\[ \sigma_{\text{abs}} = \frac{2.303OD(\lambda)}{N_0d} \] \tag{3}

\[ \sigma_{\text{em}} = \frac{\lambda^2\eta}{4\pi cn^2\tau \Delta

In Eqs. (3)–(4), \( N_0 \) is the ion concentration of \( \text{Tb}^{3+} \), \( d \) is the sample thickness, \( \lambda_0 \) is the emission wavelength, \( OD(\lambda) \) is the optical density, \( \eta \) is the internal quantum efficiency, \( n \) is the refractive index of the host material, \( \tau \) is the emission lifetime and \( \Delta

The values of \( \rho \), \( n_0 \), \( T_g \), \( T_c \), and \( \Delta \) of GBAG-xTb are summarized in Tab. 1. Density and refractive index increase from ~4.08 to 4.85 g/cm\(^{3}\) and from 1.69 to 1.75 respectively with increasing \( \text{Tb}_2\text{O}_3 \) concentration due to the much higher molar mass of \( \text{Tb}_2\text{O}_3 \) (365.85 g/mol) as compared to \( \text{Ga}_2\text{O}_3 \) (187.44 g/mol) (Fig. 3a).

Figure 3b shows DSC curves of GBAG-xTb. Here, \( T_g \) and \( T_c \) gradually increase from 740 to 777°C and from 848 to 928°C, respectively, with increasing \( \text{Tb}_2\text{O}_3 \) concentration (Fig. 3c). In order to empirically judge glass stability, \( \Delta \) = \( T_c - T_g \) is calculated from these data.

Generally speaking, larger values of \( \Delta \) reflect an improved stability against crystallization. Here, \( \Delta \) increases from 108 to 151 K with increasing of \( \text{Tb}_2\text{O}_3 \) concentration (Fig. 3c). Overall, this suggests a comparably high crystallization stability of the glasses of this study.

The apparent activation energy \( E_a \) of crystallization is calculated from the DSC data for varying heating rates by a Kissinger equation\(^{46}\),

\[ \ln \left( \frac{\phi}{T_s^{\alpha}} \right) = \frac{-E_a}{RT_s} + \text{constant} \] \tag{5}

In Eq. (5), \( R \) is the ideal gas constant, \( T_s \) is the temperature of crystallization, and \( \phi \) is the heating rate of the DSC experiment. \( E_a \) can
therefore be estimated from the slope of a linear fit of ln(β/βx) versus 1/Tx plot. The obtained value depends on Tb3O5 concentration. It reaches a maximum of −593 kJ/(mol × K) at GBAG-18Tb and decreases to 482 kJ/(mol × K) for x = 25 (Fig. 3e). Hence, while, GBAG-18Tb and GBAG-14Tb exhibit the highest MO FoM and the highest PL performance, they also exhibit large ΔT and comparatively high E.

Conclusions

In summary, we reported on the magneto-optical (MO) properties of Tb3+-doped GeO2-B2O3-Al2O3-Ga2O3 glasses toward fiber-integrated magnetic MO devices. For Tb3+ ion concentrations of up to 9.7 mol% the reported glass exhibits an absolute negative Faraday rotation of ~120 rad/Tm at 632.8 nm. The underlying effective transition wavelength λ0 is close to the 4e ↔ 4f5d transition of the Tb3+ ion, ~250 nm. The optimum FoM is found for a Tb3+ concentration of ~6.5 × 1022 cm−3 (GBAG-18Tb), ~0.05°/dB at ~435 nm, matching the emission characteristics of blue light-emitting diodes. For this glass, the crystallization stability, expressed as the difference between glass transition temperature and onset temperature of melt crystallization exceeds 100 K, which is a prerequisite for fiber drawing. In addition, a high activation energy of crystallization is achieved using this composition. Optical absorption occurs in the NUV and blue spectral region, accompanied by Tb3+ photoluminescence. In the heavily doped materials, a UV/blue-to-green photoconversion gain of ~43% is achieved. The Tb3+ ions are well dispersed in GBAG-xTb glasses without notable concentration quenching of photoluminescence up to a dopant concentration of ~14 mol% of Tb2O3 (GBAG-14Tb). The lifetime of photoluminescence is ~2.2 ms with a stimulated emission cross-section σem of ~1.1 × 10−21 cm2 for ~5.0 × 1022 cm−3 Tb3+. This results in an optical gain parameter σem*τ of ~2.5 × 10−24 cm²/s, what could be of interest for implementation of a Tb3+ fiber laser.

Methods

Synthesis of Glasses. Precursor glasses with nominal compositions of 16.5GeO2-21.5B2O3-37Al2O3-(25-x)Ga2O3-xTb2O3 (GBAG-xTb with x = 14, 18, 22 and 25 mol%) were prepared by conventional melting and quenching. Batches of ~50 g of GeO2 (99.99%), H3BO3 (99.99%), Ga2O3 (99.99%) and Tb2O3 (99.99%) were thoroughly mixed and melted in a resistive heating furnace at 1500°C for 3 h in Al2O3 crucibles, heating to 700°C at 5 K/min and to 1500°C at 10 K/min. Melting conditions were kept identical for all batches to ensure a homogenous dilution of Al2O3 in the melt. Subsequently, melts were poured onto preheated brass plates, annealed for 1 h and finally cooled down to room temperature at the intrinsic furnace rate (~1 K/min). The obtained glass slabs were cut and polished on both sides for optical characterization.

Magneto-optical properties. Frequency-dependent MO analyses were done by using a series of laser diodes as light sources (405, 488, 635, 705 and 830 nm) and fitting the obtained data of Faraday rotation to a power function of the form Vp = a(1-B) for wavelength λ. Vp is calculated from the Faraday rotation angle θ (°) as Vp = (θ × L) / (2π × n) 1. The strength of the MO effect is characterized by the Faraday rotation angle θ (°) at a given wavelength λ. The obtained data of Faraday rotation to a power function of the form Vp = a(1-B) for wavelength λ. Vp is calculated from the Faraday rotation angle θ (°) as Vp = (θ × L) / (2π × n) 1. The strength of the MO effect is characterized by the Faraday rotation angle θ (°) at a given wavelength λ. 5. Hayakawa, T., Nogami, M., Nishi, N. & Sawanobori, N. Faraday Rotation Effect of Highly Tb2O3-Doped Glasses: Characterization and Synthesis. J. Non-Cryst. Solids 10, 3232–3235 (2002).

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Author contributions
L.W. and M.S. conceived of the experiment. A.W. prepared all glass samples. G.G., A.W., O.S., J.D. and C.D. performed the experiments. G.G., A.W. and L.W. analyzed the data. G.G. and L.W. wrote the manuscript. All authors contributed to the scientific discussions and manuscript review.

Additional information
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