Fabrication and characterization of cerium-doped terbium gallium garnet with high magneto-optical properties

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High optical quality (Tb$_{1-x}$Ce$_x$)$_3$Ga$_2$O$_{12}$ (TCGG) single crystal has been grown by the Czochralski method. The optical and magneto-optical properties of the TCGG are analyzed in detail and the Verdet constant (V) of TCGG is compared with that of undoped terbium gallium garnet (TGG) crystal. TCGG presents a very high transmittance, particularly in the visible-near infrared (VIS-NIR) region, and its V is obviously larger than that of TGG in the VIS-NIR region. The figure of merit and optical features point out the superior characteristics of TCGG with respect to TGG. © 2015 Optical Society of America

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With the rapid advance in high-power solid-state lasers and the progress of different laser devices, the research and application of nonreciprocal magneto-optical devices become more and more important [1,2], especially the demand for Faraday isolators (FIs) at wavelengths of 400–1100 nm [3,4]. FIs are based on Faraday rotators (FRs) plus two polarizers and FRs-optical devices consist of a magneto-optical element (MOE) placed into the magnetic field. The MOE can be magneto-active materials made of single crystal, glass, or ceramic. For a given magnetic field and crystal length, it yields to a 45° rotation of the polarization plane to prevent optical feedback, which may cause instabilities in laser systems. However, yttrium iron garnet cannot be used at shorter wavelengths (<1100 nm) due to its poor transparency [5]. Terbium gallium garnet (TGG) and terbium aluminum garnet (TAG) crystals have excellent optical and magneto-optical properties, high damage threshold and low absorption coefficient, leading to the implementation of which in the FRs at shorter wavelengths. But TAG is extremely difficult to grow large size single crystal for its incongruent melting nature [6–8], hindering its practical use in the FRs.

The advantages of TGG crystal are high transparency in the visible-near infrared (VIS-NIR) region and a congruently melting-type material [9,10]. Thus, the TGG single crystal having a bulk size can be easily produced by the Czochralski (Cz) process. But the TGG has a comparatively low Verdet constant (V) (39.0 rad · m$^{-1}$ T$^{-1}$) at 1064 nm [11,12], so there is an urgent hope to find magneto-optical materials that have a larger V that can be effective in size-reduction of the crystals used in the magneto-optical devices. Larger V means that even a smaller size of crystal (length < 10 mm) can obtain a sufficient 45° rotation to avoid laser-induced damage under high-energy pulse operation and the thermal birefringence effect [13], improving the stability of the high-power laser systems [14].

Recently, researchers have found that fluoride single crystals with efficient paramagnetic RE ions in the ultraviolet-visible region had comparatively large V at room temperature [15,16]. Some magneto-optical glass doping more than one paramagnetic RE ion (Ce, Pr, Tb, Dy, Ho, Er) showed excellent Faraday effect [17,18]. Tb$_3$[$\text{Sc}_{1.95}$Lu$_{0.05}$]$\text{Al}_3$O$_{12}$ garnet single crystal presented superior magneto-optical properties to TGG crystal by doping the Lu$^{3+}$, Sc$^{3+}$, Al$^{3+}$ ions [19]. So we believed that the quantum-based superexchange interaction between Tb$^{3+}$ and other paramagnetic RE ions or two paramagnetic RE ions might occur, which can enhance the Faraday effect of the materials.

In the present work, we focus on the study of terbium-type paramagnetic garnet single crystal and we believe that it may have a larger V compared to TGG and we hope to provide a magneto-optical device using the terbium-type paramagnetic single crystal. Ce$^{3+}$ ion shows excellent Faraday effect in many materials and its ion radius is similar to that of Tb$^{3+}$, so a Ce$^{3+}$-doped terbium-type garnet crystal with larger V is possibly achievable.

High purity of Tb$_4$O$_7$, CeO$_2$, and Ga$_2$O$_3$ (5N) were weighted in the corresponding nominal cationic ratios. Mixtures were pressed to sheet and sintered at 1400°C for 20 h in air. The pulling and rotation rates were fixed to 3 mm/h and 12 rpm, respectively. (Tb$_{1-x}$Ce$_x$)$_3$Ga$_2$O$_{12}$ (TCGG) crystal was obtained by the Cz method, as shown in Fig. 1. TCGG and TGG samples were cut from the crystals shown in Fig. 2. Then the grounds were polished carefully for further measurements.

Figure 3 shows the x-ray diffraction patterns of TCGG. The result showed that TCGG had the pure phase which was almost identical to that of the standard cubic TGG. The unit-cell parameters are $a = b = c = 1.2396$ nm, slightly larger than that of pure TGG ($a = b = c = 1.2355$ nm). It can be explained by the reason that the radius of Ce$^{3+}$ is larger than Tb$^{3+}$. The full width at
The half-maximum of the rocking curve for the crystal is about 18.2 arcsec, which showed the high crystallinity of the crystal.

The element analysis of the crystal is measured by the inductively coupled plasma-atomic emission spectroscopy method [20]. The crystal grown from the melt can be expressed as \( \text{Tb}_{2.98}\text{Ce}_{0.02}\text{Ga}_5\text{O}_{12} \) according to the measured molar ratio of Tb:Ce:Ga.

The Faraday rotation of [111] oriented single crystal was measured at room temperature by the extinction method [21], using a homemade instrument consisting of light sources (Xe-lamp and monochromator), two polarizers, and an electromagnet. The accuracy of \( V \) measurement can reach to the 0.1 rad · m\(^{-1}\) T\(^{-1}\).

The results of the \( V \) measurements are displayed in Fig. 4, where the \( V \) dispersion of TCGG is shown in comparison with that of TGG. It can be seen that TCGG possesses a higher \( V \) value, with an obvious increment in wavelength of 400–1100 nm. For instance, the TCGG has a \( V \) of 53.2 rad · m\(^{-1}\) T\(^{-1}\) at 1064 nm, 36.4% larger than that of TGG (39.0 rad · m\(^{-1}\) T\(^{-1}\)).

According to the standard theory of Faraday rotation, the \( V \) is a dependence of the factor \( E \) (the transition probability) and the inverse of the wavelength square \( \lambda_0 \) as follows [22]:

\[
V = \frac{E}{\lambda^2 - \lambda_0^2}.
\]  

The optical transmittance spectra of TCGG is shown in Fig. 5. The absorption peak of S1 located at about 484 nm is due to the \( \text{Tb}^{3+}:7\text{F}^6 \rightarrow 5\text{D}^4 \). TCGG shows high degree of transmittance observed in the whole visible region. Therefore, it indicates that the as-grown single crystal in our work is suitable for application of apparatus used in the VIS–NIR Faraday rotator.

Absorption coefficient \( a_0 \) is an important parameter of magneto-optical properties. TCGG has a weak absorption loss in the working wavelength 550–1500 nm. The \( a_0 \) for TCGG crystal was measured by the photothermal common-path interferometer technique [23]. The peak is around 1800 ppm/cm at 1064 nm, as shown in Fig. 6. The magneto-optical figure of merit (MO) can generally represent the magneto-optical properties of the materials, which were shown in Table 1. The MO of TCGG at 1064 nm is 821.

![Fig. 1. Picture of as-grown bulk crystal by the Cz method.](image1)

![Fig. 2. TCGG and TGG samples with dimension Φ8 mm × 5 mm was polished for the measurements.](image2)

![Fig. 3. X-ray powder diffraction patterns of the powder specimen. The green peaks refer to the pure TGG while the red peaks refer to the TCGG.](image3)

![Fig. 4. Verdet constant dispersion of TCGG in comparison with that of TGG.](image4)

![Fig. 5. Transmission spectra of TCGG crystals.](image5)

![Fig. 6. Curve of the weak absorption of TCGG crystal at 1064 nm.](image6)
1064 nm was calculated according to $V/a_0$, that is $2.96 \times 10^2$ rad/T, 21.3% larger than that of TGG ($2.44 \times 10^2$ rad/T). Therefore, TCGG is an attractive candidate to substitute TGG crystal used in FIs for optical communication systems in wavelengths of 550–1500 nm.

TCGG single crystal was first grown by the Cz method. In conclusion, the presented results showed the superior properties of TCGG in comparison with the TGG. As we know, the magnetic properties of the garnets illustrate the theory of paramagnetism where the three sublattice magnetizations ($M_d, M_a, M_c$) correspond to the three magnetic ion crystallographic sites (tetrahedral, octahedral, and dodecahedral), respectively. In first approximations, the Faraday rotation is the sum of the three paramagnetic sublattices terms. Therefore, the probable reason for the increasing of the $V$ and specific Faraday rotation is that Ce$^{3+}$ changed the three sublattice magnetization contributing to the total magnetization. The doping of Ce$^{3+}$ may cause superexchange interaction, which produces a further splitting of the crystal field. The transition probability from the base 4f to 5d energy level contributing differently to the polarization light leads to the huge Faraday effect. A more theoretical interpretation of the increase in Faraday rotation will require further experiments concerning detailed crystal field analysis and quantum-based superexchange interaction.

Although the concentration of Ce$^{3+}$ is still small, the increase of $V$ is very significant, giving a huge expectation of getting a more excellent magneto-optical material from $(\text{Th}_{1-x}\text{Ce}_x)_3\text{Ga}_5\text{O}_{12}$ by adjusting the $X$ value. TCGG single crystal has great potential to substitute the commercial TGG crystals for magneto-optical devices in the VIS–NIR region.

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Table 1. Comparison of Main Magneto-Optical Properties between TGG and TCGG at 1064 nm

<table>
<thead>
<tr>
<th></th>
<th>TGG</th>
<th>$(\text{Th}_{1-x}\text{Ce}_x)_3\text{Ga}<em>5\text{O}</em>{12}$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>(Tb$^{3+}$)</td>
<td></td>
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<tr>
<td></td>
<td>$x=0.0133$</td>
<td></td>
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<tr>
<td></td>
<td>$x=0.0134$</td>
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<tr>
<td></td>
<td>$x=0.0135$</td>
<td></td>
</tr>
<tr>
<td>Absorption coefficient (cm$^{-1}$)</td>
<td>0.0016</td>
<td>0.0018</td>
</tr>
<tr>
<td>Verdet constant (rad$\cdot$m$^{-1}$T$^{-1}$)</td>
<td>−39.0</td>
<td>−53.2</td>
</tr>
<tr>
<td>Magneto-optical figure of merit (10$^2$ rad/T)</td>
<td>2.44</td>
<td>2.96</td>
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References