Fabrication and properties of non-stoichiometric Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ magneto-optical ceramics

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Abstract: Non-stoichiometric Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ ($x = -0.07$–0.45) magneto-optical ceramics were fabricated by solid-state reactive sintering in vacuum combined with hot isostatic pressing (HIP) post-treatment without any sintering aids. The phase composition, densification process, microstructure, optical transmittance, and Verdet constant of Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ ceramics were investigated. The in-line transmittance of (Tb$_{0.93}$Hf$_{0.07}$)$_2$Hf$_2$O$_{7.07}$ ceramics with a thickness of 2.0 mm reaches 74.6% at 1064 nm. The Verdet constant of Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ ceramics is $-153.4$, $-155.8$, and $-181.2$ rad/(T·m) at the wavelength of 633 nm when $x = -0.07$, 0, and 0.1, respectively. The Verdet constant increases with the increase of Tb content, and these values are higher than that of the commercial Tb$_3$Ga$_5$O$_{12}$ crystal, indicating that non-stoichiometric Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ ceramics have a great potential for the application in Faraday isolators.

Keywords: magneto-optical ceramics; Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ ceramics; reactive sintering; Verdet constant

1 Introduction

With the rapid development of laser technology, Faraday isolators have appealed much attention in these years [1–7]. The isolators can rotate the polarization plane of the light beam under an external magnetic field, making the Faraday isolators essential optical devices for optical isolation, polarization control, and birefringent compensation [8–14]. Magneto-optical materials play a vital role in Faraday isolators. Ideal magneto-optical materials should possess some important parameters including high Verdet constant, low absorption coefficient, low nonlinear refractive index, size scalability, high thermal strength, high laser-induced-damage threshold, and so on [8,10,14–20]. Terbium gallium garnet (TGG) crystal is one of the most widely applied magneto-optical materials because of the good comprehensive properties [14,15,21–27]. For high-power laser applications, however, TGG crystal is limited intrinsically by its absorption loss and thermo-optical coefficient, and thus serious thermal lensing and depolarization effects are nearly inevitable [14,15,28–34]. In general, efforts can be taken in two aspects: improving the performance of TGG crystal for high-
power laser uses or developing other suitable magneto-optical materials [35–40].

Transparent Tb$_2$Hf$_2$O$_7$ ceramics show high Verdet constant and high optical quality [41–43]. The Verdet constant of Tb$_3$Hf$_2$O$_7$ ceramics reaches about −159 rad/(T·m) at 633 nm and −50 rad/(T·m) at 1064 nm, which is 18.7% and 38.9% higher than that of commercial TGG crystal, respectively. The required length of Tb$_2$Hf$_2$O$_7$ ceramics is 28% shorter than that of TGG crystal when they are applied at 1064 nm under the same magnetic field intensity. Short magneto-optical elements have big advantages because they contribute to limiting the light absorption, minimizing the effects of self-focusing and other thermal-related effects [15].

Generally, the Verdet constant of the material increases with the increasing volume concentration of the paramagnetic metal ions according to Van Vleck et al.’s theory [44,45]:

\[
V = \frac{K}{T} (N n_{\text{eff}}^2 (g) \sum \frac{C_n}{(v^2 - v_n^2)^2})
\]  

(1)

where \( V \) is the Verdet constant, \( K = 4\pi^2\mu_b v^2/(3ckh) \), \( n_{\text{eff}} = g[J(J+1)]^{1/2}, N \) is the volume concentration of the paramagnetic ions, \( g \) is the Landé splitting coefficient, \( C_n \) denotes the transition moments, \( v \) is the frequency, \( v_n \) is the frequency corresponding to the splitting of excited states, \( J \) is the total angular momentum quantum number, \( k \) is the Boltzmann constant, and \( \mu_b \) is the Bohr magneton number, \( c \) is the speed of light in vacuum, \( h \) is the Plank constant, \( T \) is the absolute temperature. Considering the large solid solution range of the cubic phase shown in the phase diagram of HfO$_2$–Tb$_2$O$_3$ systems [46], transparent non-stoichiometric Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_7$ ceramics can be fabricated in theory. The non-stoichiometric Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_7$ ceramics with excess Tb will possess higher Verdet constants than the stoichiometric Tb$_3$Hf$_2$O$_7$ ceramics because of the higher volume concentration of the paramagnetic ions, \( N \) value in Eq. (1). In our previous work [43], high-optical-quality Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_7$ ceramics with \( x = 0.1 \) were fabricated successfully, while the properties of Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_7$ ceramics across a wider stoichiometric range are under expectation.

In this work, non-stoichiometric Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_7$ ceramics (\( x = -0.07–0.45 \)) were fabricated by solid-state reactive sintering in vacuum combined with hot isostatic pressing (HIP) post-treatment without any sintering aids. The phase composition, densification process, microstructure, optical transmittance, and Verdet constant of Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_7$ ceramics were discussed for the first time.

2 Experimental

Detailed information of the raw powders and experimental procedures were presented in our previous work [43]. Briefly, high-purity Tb$_2$O$_7$ powders and HfO$_2$ powders were mixed and ball-milled without any sintering aids. The milled slurry was dried and sieved through a screen. The mixed powders were calcined in a muffle furnace at 800 °C for 4 h and then uniaxially pressed into pellets. These pellets were treated at 800 °C for 10 h in NH$_3$ atmosphere to remove Tb$^{4+}$, preventing the ceramics from cracking during sintering. The pellets were cold isostatically pressed at 250 MPa for 5 min. These green bodies were pre-sintered at 1450–1750 °C for 3 h in vacuum and HIP post-treated at 1750 °C for 3 h under 176 MPa argon atmosphere. At last, the Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_7$ ceramics were mirror-polished on both surfaces to 2.0 mm.

Microstructure of the fracture and thermally etched surfaces, and energy-dispersive X-ray spectrometry (EDS) mapping were analyzed by field emission scanning electron microscopy (FESEM, SU-8220, Hitachi, Japan). Ceramic samples were thermally etched at 1300 °C for 10 h in high-purity argon atmosphere in a tube furnace. Linear intercept method was used to measure the grain sizes of the ceramics. Phase identification was performed by X-ray diffraction (XRD, D8 Advance, Bruker, Germany) equipped with a copper target X-ray tube in the 2θ range of 10°–80°. Bulk densities of the ceramic samples were measured using the Archimedes method. In-line transmittance of the ceramics with the wavelength range from 200 to 1800 nm was measured with ultraviolet–visible–near infrared (UV–vis–NIR) spectrophotometry (Cary-5000, Varian, USA). The Verdet constant at 633 nm of ceramics was determined at room temperature by an instrument consisting of a He–Ne laser, two polarizers, and an electromagnet.

3 Results and discussion

Figure 1(a) shows the XRD patterns of Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_7$ ceramics (\( x = -0.07–0.45 \)) ceramics pre-sintered at 1650 °C for 3 h and then HIP post-treated at 1750 °C for 3 h. A weak (311) characteristic peak of pyrochlore phase
(space group \(Fd\bar{3}m\), No. 227) can be seen at about 28.4° when \(x = 0\) shown in Fig. 1(a), confirming the pyrochlore phase of \(\text{Tb}_2\text{Hf}_2\text{O}_7\). No pyrochlore characteristic peaks can be detected when \(x \neq 0\) in this work. Thus, the main crystal phase of the non-stoichiometric ceramics can be regarded as a defect fluorite phase (space group \(Fm\bar{3}m\), No. 225) \([47–49]\), and this result is consistent with the phase diagram of \(\text{HfO}_2\)-\(\text{Tb}_2\text{O}_3\) binary systems \([46]\). An obvious peak shifting can be seen in the partial enlarged XRD patterns in Fig. 1(a) (the peak splitting in high angle is caused by Cu K\(\alpha_2\)). As the radius of Hf\(^{4+}\) is smaller than that of Tb\(^{3+}\) when six-coordinated, the lattice spacing increases with the increase of the \(x\) value, and the peak will shift to the low angle from the Bragg equation. No obvious peaks of the secondary phase can be found when \(x \leq 0.4\). However, when \(x = 0.45\), the full width at half-maximum (FWHM) of diffraction peaks increases evidently, and some diffraction peaks of a secondary phase can be detected, which is a solid solution of bixbyite \(\text{Tb}_2\text{O}_3\) phase with diffused \(\text{HfO}_2\). Based on the XRD data, the lattice parameters (or 1/2 of lattice parameter in pyrochlore crystal) and theoretical densities of \(\text{Tb}_2(\text{Hf}_{1-x}\text{Tb}_x)_2\text{O}_{7-x}\) (\(x = −0.07–0.45\)) are calculated and shown in Fig. 1(b). The calculated lattice parameters increase, and the theoretical densities decrease with the increase of Tb content. When \(-0.07 \leq x \leq 0.45\), the lattice parameters and theoretical densities change almost linearly.

Figure 2 shows the relative densities of \(\text{Tb}_2(\text{Hf}_{1-x}\text{Tb}_x)_2\text{O}_{7-x}\) (\(x = −0.07–0.45\)) ceramics pre-sintered at different temperatures for 3 h in vacuum. With the elevating pre-sintering temperature, the relative densities of \(\text{Tb}_2(\text{Hf}_{1-x}\text{Tb}_x)_2\text{O}_{7-x}\) (\(-0.07 \leq x \leq 0.3\)) ceramics increase basically, indicating the densification process. When \(-0.07 \leq x \leq 0.3\), with the increasing \(x\) value except \(x = 0\), the required pre-sintering temperature for achieving 95% relative density decreases. This suggests that excess Tb is favorable for the densification of \(\text{Tb}_2(\text{Hf}_{1-x}\text{Tb}_x)_2\text{O}_{7-x}\) ceramics because the oxygen vacancy (for charge compensation of \(\text{Tb}^{3+}\) replacing \(\text{Hf}^{4+}\)) can promote the lattice diffusion \([50]\). The densification process of \(\text{Tb}_2\text{Hf}_2\text{O}_7\) (\(x = 0\)) ceramics is singular in this work, which may be attributed to the different diffusion mobility in different phases as the \(\text{Tb}_2\text{Hf}_2\text{O}_7\) ceramics are the only specimens with pyrochlore phase shown in Fig. 1. After pre-sintered at 1650 °C for 3 h, the relative densities of \(\text{Tb}_2(\text{Hf}_{1-x}\text{Tb}_x)_2\text{O}_{7-x}\) (\(-0.07 \leq x \leq 0.3\)) ceramics are higher than 92%, and hence these pre-sintered specimens can be further densified during HIP post-treatment. The relative densities of \(\text{Tb}_2(\text{Hf}_{0.7}\text{Tb}_{0.3})_2\text{O}_{6.7}\) ceramics decrease slightly with the increase of pre-sintering temperature after 1650 °C. Furthermore, when \(x = 0.4\) and 0.45, the relative densities decrease abnormally with the increase of pre-sintering temperature. This converse densification phenomenon may associate with the complex behavior of the secondary phase during sintering.
In order to find out the cause of the converse densification when $x = 0.4$ and 0.45, XRD and FESEM were used to characterize the $\text{Tb}_2(\text{Hf}_{0.55}\text{Tb}_{0.45})_2\text{O}_{6.55}$ ceramics pre-sintered at different temperatures for 3 h, as shown in Figs. 3 and 4. It is clear that defect fluorite is the major crystal phase, and the secondary phase is observed shown in Fig. 3. It should be noted that the secondary phase is a Tb-rich solid solution with cubic bixbyite structure (space group $Ia\overline{3}$, No. 206) [46]. The bixbyite secondary phase cannot be eliminated even after sintered at 1750 °C for 3 h. The diffraction peak of bixbyite phase shifts to a higher angle with the increase of pre-sintering temperature, and the peak of defect fluorite phase shifts slightly to the lower angle, as shown in the partial enlarged patterns in Fig. 3. This phenomenon demonstrates the interdiffusion between defect fluorite phase and bixbyite phase. However, peak intensity of the secondary phase shows no sign of decrease, as shown in Fig. 3(a), implying that the bixbyite phase may be thermodynamically stable in $\text{Tb}_2(\text{Hf}_{0.55}\text{Tb}_{0.45})_2\text{O}_{6.55}$ ceramics during 1450 and 1750 °C. This result is inconsistent with the phase diagram in which $\text{Tb}_2(\text{Hf}_{0.55}\text{Tb}_{0.45})_2\text{O}_{6.55}$ compound is a single cubic phase with $x = 0.14$–0.47 over 1700 °C, and little phase diagram data below 1700 °C is available till now. Low diffusion rate between $\text{Tb}_3\text{O}_5$ and $\text{HfO}_2$ may be one of the causes for this inconsistence [46].

Figure 4 shows the FESEM images of the thermally etched surfaces of $\text{Tb}_2(\text{Hf}_{0.55}\text{Tb}_{0.45})_2\text{O}_{6.55}$ ceramics pre-sintered at different temperatures for 3 h. The grain size of the ceramics pre-sintered at a certain temperature is not uniform. Fine grains and larger grains are present in the ceramics. With the increase of pre-sintering temperature, all the grains grow up evidently but still nonuniformly. Meanwhile, the sizes of pores increase evidently. In general, grains grow up, and pores are gradually removed during the sintering process. The evolution of the pores shown in Fig. 4 is not the same with the usual sintering phenomenon. Figure 5 shows the EDS patterns of the $\text{Tb}_2(\text{Hf}_{0.55}\text{Tb}_{0.45})_2\text{O}_{6.55}$ ceramics pre-sintered at 1450 °C (unindexed peaks belong to Tb, Hf, and O). EDS patterns confirm that the fine grains are Tb-rich secondary phase, and the composition of larger grains is near the designed composition. Here we provide a hypothesis about the converse densification and microstructure evolution process. During the sintering process, the secondary phase particles with small grain size have high sintering activity, and they cause rapid grain boundary migration. The grain boundary migration is more sensitive to the temperature than the elimination rate of pores [51]. As a result, the grain boundary migration accelerates when the sintering temperature raises and the grain boundary closes, leading to the difficulty for pores to remove continually. The hindered pore removal process causes the abnormal densification shown in Fig. 2, and the porous ceramics with both intergranular and intragranular pores are formed as shown in Fig. 4. Further studies are eagerly needed to understand the causes of abnormal densification as well as the exact phase composition in $\text{Tb}_2\text{O}_3$–$\text{HfO}_2$ binary system under 1700 °C.

FESEM images of the thermally etched surfaces of $\text{Tb}_2(\text{Hf}_{1-x}\text{Tb}_x)\text{O}_7$ ($x = -0.07$–0.45) ceramics pre-sintered at 1650 °C for 3 h in vacuum are shown in Fig. 6. There are many pores in the pre-sintered specimens. The pores in the ceramics with $x = -0.07$, 0, and 0.1 are mainly intergranular pores and can be eliminated in the following HIP post-treatment, shown in Figs. 6(a)–6(c). The numbers of pores shown in FESEM images are in good agreement with the relative densities shown in Fig. 2. $\text{Tb}_3\text{Hf}_2\text{O}_9$ ($x = 0$) ceramics have the highest relative density and the fewest pores shown in Fig. 6(b) because of the distinct phase composition and diffusion mobility. A remarkable phenomenon shown in Figs. 6(c)–6(g) is that the excessive $\text{Tb}_2\text{O}_3$ can significantly promote the grain boundary migration and grain growth in $\text{Tb}_2(\text{Hf}_{1-x}\text{Tb}_x)\text{O}_7$ ceramics. The fast migration of grain boundaries results in larger grains and intragranular pores shown in Figs. 6(d)–6(g). Generally, intragranular pores are hard to be eliminated during HIP post-treatment, and those pores will remain in the ceramics becoming the optical scattering center [52], which brings a serious adverse effect on the optical quality of ceramics. In addition, some dark, small scattered
Fig. 4 FESEM images of the thermally etched surfaces of the 
Tb$_2$(Hf$_{0.55}$Tb$_{0.45}$)$_2$O$_{6.55}$ ceramics pre-sintered at different 
temperatures for 3 h: (a) 1450 °C, (b) 1500 °C, (c) 1550 °C, (d) 1600 °C, (e) 1650 °C, (f) 1700 °C, and (g) 1750 °C.

Fig. 5 EDS patterns of the Tb$_2$(Hf$_{0.55}$Tb$_{0.45}$)$_2$O$_{6.55}$ ceramics pre-sintered at 1450 °C for 3 h.

Points can be seen in the pre-sintered ceramics when $x \geq 0.1$, which are Tb-rich secondary phases. Some particles can be seen in Figs. 6(f) and 6(g), and they are impurities caused during the polishing process.

Figure 7 is the FESEM images of the thermally etched surfaces of 
Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ ($x = -0.07$–0.45) ceramics 
pre-sintered at 1650 °C for 3 h and HIPed at 1750 °C for 3 h. The relative densities and microstructures of pre-sintered ceramics have a distinct effect on the removal of pores during HIP post-treatment. Low-density pre-sintered ceramics with open and connected pores are hard to achieve full density after HIP post-treatment. Intragranular pores can hardly be removed either. Ideal pre-sintered ceramics for obtaining full density ceramics should possess small grain size and have no open or intragranular pores [52]. In general, pre-sintered ceramics with the relative densities of 92%–95% are suitable for the following HIP post-treatment to obtain pore-free ceramics [53,54]. Most of the intergranular pores in the specimens shown in Fig. 6(a) are eliminated after HIP
post-treatment. There are no obvious pores or secondary phase found in Fig. 7(a), implying the relatively high optical quality of the ceramics with $x = -0.07$. However, when $x = 0$, some small intergranular pores still exist because the sinterability of the pre-sintered Tb$_2$Hf$_2$O$_7$ ceramics is too low, resulting from the inappropriate pre-sintering temperature. When $x = 0.1$, shown in Fig. 7(c), no secondary phase can be found, which means that Tb-rich secondary phase diffuses and is mostly eliminated during HIP post-treatment. As the pre-sintering temperature is lower than that of the HIP post-treatment, this phenomenon indicates that enough sintering temperature and holding time may be needed for the diffusion between Tb$_2$O$_3$ and HfO$_2$ to obtain Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ with composition homogeneity. Some residual pores can be seen in grains when $x \geq 0.1$, proving that intragranular pores are hard to be eliminated during HIP post-treatment. Pre-sintering and HIP post-treatment temperatures can be further optimized to obtain fully dense Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ ($x = -0.07$–0.45). Figure 8 shows the EDS patterns of the Tb$_2$(Hf$_{0.8}$Tb$_{0.2}$)$_2$O$_{6.8}$ ceramics pre-sintered at 1650 °C with HIP post-treatment. The EDS patterns show that Tb-rich secondary phase remains in the ceramics when $x = 0.2$ even after HIP post-treatment, so the existence of secondary phase in Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ ceramics when $x > 0.2$ is predictable. Both pores and secondary phases scatter the incident light, so it is foreseeable that the Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ ceramics with $x \geq 0.2$ have relatively low optical quality.

Figure 9(a) shows the photograph of Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ ($x = -0.07$–0.45) ceramics after HIP post-treatment and mirror polishing. The Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ ceramics with $x = -0.07$, 0, and 0.1 are transparent, while the ceramics with $x \geq 0.2$ are opaque. The color of ceramics becomes deeper with increasing $x$ value from $-0.07$ to 0.3, which mainly corresponds to the increase of Tb$^{4+}$. The excess Tb in Tb$_2$(Hf$_{1-x}$Tb$_x$)$_2$O$_{7-x}$ ceramics are mostly in Hf$^{4+}$ site (Tb$^3Hf^+$) [55], so Tb$^{4+}$ can exist (Tb$^3Hf^+$) considering the charge balance. With increasing
Fig. 7 FESEM images of the thermally etched surfaces of Tb$_x$(Hf$_{1-x}$Tb)$_2$O$_{7-x}$ ceramics pre-sintered at 1650 °C for 3 h and HIPed at 1750 °C for 3 h: (a) $x = -0.07$, (b) $x = 0$, (c) $x = 0.1$, (d) $x = 0.2$, (e) $x = 0.3$, (f) $x = 0.4$, and (g) $x = 0.45$.

Fig. 8 EDS patterns of the Tb$_x$(Hf$_{0.8}$Tb$_{0.2}$)$_2$O$_{6.8}$ ceramics pre-sintered at 1650 °C for 3 h and HIPed at 1750 °C for 3 h (fracture surface).

$x$ value, the anti-site Tb increases, the concentration of Tb$^{3+}$ can be higher, and the brown color becomes deeper. The color of the Tb$_x$(Hf$_{1-x}$Tb)$_2$O$_{7-x}$ ceramics with $x = 0.4$ and 0.45 is lighter than that of the ceramics with $x = 0.3$, which may be attributed to the low relative density and high porosity because the light will be scattered and reflected more easily rather than absorbed in the ceramics. Figure 9(b) shows the in-line transmittance of the specimens. The transmittance of the ceramics is in good accordance with the microstructures shown in Fig. 7. When $x = -0.07$, the (Tb$_{0.93}$Hf$_{0.07}$)$_2$Hf$_2$O$_{7.07}$ ceramics show a relatively high optical quality. The in-line transmittance of (Tb$_{0.93}$Hf$_{0.07}$)$_2$Hf$_2$O$_{7.07}$ ceramics (2.0 mm thick) is higher than 70% at 600–1500 nm, and reaches 74.6% at 1064 nm. As a reference, the theoretical in-line transmittance of stoichiometric Tb$_2$Hf$_2$O$_7$ is 77.8% [41]. When $x = 0$ and 0.1, the in-line transmittance of the ceramics is 40.1% and
In addition, supplements are needed in the phase uniform, so the diffusion distance can be reduced greatly. Using the co-precipitation or combustion method to prepare non-reactive sintering may be an optional way, e.g., improvements on the optical quality of non-stoichiometric Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ ceramics are promising magneto-optical materials for Faraday rotators. Unfortunately, the Verdet constants of Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ ceramics with x ≥ 0.2 are difficult to measure because of the low optical transmittance. Further improvements on the optical quality of non-stoichiometric Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ ceramics with high Tb content are required at present for the application in Faraday isolators, and after that the service performance is expected to be evaluated as a new magneto-optical material.

The Verdet constant can be calculated by Eq. (2):
\[
V = \frac{\theta}{(Bd)}
\]
where V is the Verdet constant, \(\theta\) is the Faraday rotation angle, B is the magnetic field intensity, and d is the thickness of the sample. We measured the Faraday rotation angle under certain magnetic field intensity and sample thickness. The Verdet constants of Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ ceramics with x = −0.07, 0, and 0.1 are −153.4±1.8, −155.8±1.7, and −181.2±1.5 rad/(T·m) at the wavelength of 633 nm, respectively. Clearly, the Verdet constant of Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ ceramics increases with the increase of Tb content, which agrees with the Van Vleck et al.’s theory [45]. Increasing the Tb content in Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ ceramics is a practicable way to increase the Verdet constant and shorten the required length of magneto-optical materials when applied in Faraday isolators. The required lengths of Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ ceramics with x = −0.07, 0, and 0.1 are reduced to 87.4%, 86.0%, and 74.0% of TGG single crystal, respectively. Therefore, Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ ceramics are promising magneto-optical materials for Faraday rotators.

In summary, non-stoichiometric Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ (x = −0.07–0.45) magneto-optical ceramics were fabricated by solid-state reactive sintering in vacuum combined with HIP post-treatment without any sintering aids. The phase composition and lattice parameters change with the change of Tb content. The densification process of Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ ceramics was discussed, and the existence of Tb-rich bixbyite secondary phase was confirmed. The microstructures of Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ ceramics after HIP post-treatment show that when x = −0.07, the ceramics are nearly full dense without obvious pores or secondary phase, while there are numerous pores and Tb-rich secondary phase when x ≥ 0.2. The (Tb₀.⁶₉Hf₀.₀₇)₂Hf₂O₇.₇陶瓷s possess the highest optical quality in this work. The in-line transmittance of (Tb₀.⁶₉Hf₀.₀₇)₂Hf₂O₇.₇陶瓷s (2.0 mm thick) is 65.0% at 1064 nm, respectively. The main cause of the relatively low transmittance when x = 0 and 0.1 is the optical scattering from pores remained in ceramics, which can be improved promisingly by adjusting the pre-sintering and HIP schedule in the future [43]. However, when x ≥ 0.1, the in-line transmittance of Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ ceramics decreases with the increase of Tb content, which can be interpreted to the increase of secondary phase and pores as they both scatter the light severely. From the phase diagram of the binary system with hafnia and terbia [46], Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ can maintain single cubic phase (pyrochlore or defect fluorite phase) when −0.74 ≤ x ≤ 0.47 from 1700 to 2300 °C. However, the extremely low diffusion mobility in Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ ceramics limits the fabrication of single-phase ceramics by reactive sintering method. Hence, it is challenging to fabricate Tb₂(Hf₁−ₓTbₓ)₂O₇−ₓ ceramics with both high Tb content (x > 0.1) and high optical quality by this method. Improving the powder homogeneity and using non-reactive sintering may be an optional way, e.g., using the co-precipitation or combustion method to prepare the raw powder as the element distribution can be more uniform, so the diffusion distance can be reduced greatly. In addition, supplements are needed in the phase diagram of HfO₂–Tb₂O₃, especially the phase composition under 1700 °C.

The Verdet constant is one of the most important magneto-optical parameters. For paramagnetic materials, the Verdet constant can be calculated by Eq. (2):
\[
V = \frac{\theta}{(Bd)}
\]
thick) reaches 74.6% at 1064 nm. The Verdet constants of Tb₂(Hfₓ−ₓ,Tbₓ)₂O₇−ₓ ceramics reach −153.4±1.8, −155.8±1.7, and −181.2±1.5 rad/(T·m) when x = −0.07, 0, and 0.1 at the wavelength of 633 nm, respectively. The increasing Verdet constant with the increase of Tb content is confirmed, and these three values are higher than that of TGG crystal. Tb₂(Hf₁−ₓ,Tbₓ)₂O₇−ₓ ceramics show a good downsizing advantage and are promising magneto-optical materials for Faraday isolators.

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