Fabrication and Magneto-Optical Property of (Dy₀.7Y₀.25La₀.05)₂O₃ Transparent Ceramics by PLSH Technology

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Abstract: (Dy₀.7Y₀.25La₀.05)₂O₃ magneto-optical transparent ceramics were successfully fabricated by pressureless sintering in reductive H₂ atmosphere (PLSH). The raw powder of (Dy₀.7Y₀.25La₀.05)₂O₃ was synthesized by a modified self-propagating high-temperature synthesis (SHS) and sintered to transparent ceramics at 1400–1600 °C in a flowing H₂ atmosphere, showing good sinterability of the as-synthesized raw powder. The magneto-optical Verdet constant of (Dy₀.7Y₀.25La₀.05)₂O₃ transparent ceramics was measured to be −191.57 rad/(T·m) at a wavelength of 632.8 nm. In this magneto-optical material of (Dy₀.7Y₀.25La₀.05)₂O₃, relative cheaper Dy and Y were used to replace Tb, and the low cost and good magneto-optical property showed the advantage of application on Faraday isolators (FIs) and Faraday rotators (FRs).

Keywords: (Dy₀.7Y₀.25La₀.05)₂O₃; transparent ceramics; magneto-optical property; rare earth sesquioxide

1. Introduction

Magneto-optical (M-O) material is an essential component of Faraday isolators (FIs) and Faraday rotators (FRs), which can be used in fiber-optic communication to effectively isolate external light from the light sources [1–3]. With the development of science and technology, FI and FR devices are also developing towards miniaturization, which puts forward higher requirement on the performance of M-O materials. Tb₃Ga₅O₁₂(TGG) with garnet structure is widely used as a magneto-optical material, and its Verdet constant is −134 rad/(T·m) [4] at 632.8 nm. However, the garnet structure limits the terbium concentration of Tb³⁺ and therefore limits the Verdet constant [5]. In recent years, it has been found that rare-earth sesquioxide RE₂O₃ (RE = Tb, Dy) of paramagnetic RE³⁺ ions has a higher Verdet constant than TGG crystal [6–8]. In 2015, Veber et al. [6] grew the firstly Tb₂O₃ single crystal with a size of about 5 × 5 × 2 mm³ by flux method. The Verdet constant of single crystal Tb₂O₃ is at least three times larger than that of a commercial TGG crystal. In 2018, Snetkov and Balabalnov et al. [9] prepared Y, La-doped (DyₓYₓ₋₀.₉₅₋₁₋₀.₀₂₅₋₀.₀₅ₓLa₀.₀₅ₓ)₂O₃ transparent ceramics using a vacuum sintering method at an extremely high temperature of 1780 °C. Recently, Aung et al. [10] showed the possibility of obtaining ceramics (Dy₀.₇Y₀.₂₅La₀.₀₅)₂O₃ with ZrO₂ sintering aid. Despite the high achieved quality of ceramics, the use of such a sintering additive can limit the service life of magneto-optical elements due to a change in the oxidation state of zirconium ions under the laser radiation, the appearance of free charge carriers and, accordingly, a sharp increase in absorption.
In this paper, 5 at. % lanthanum oxide was used as sintering aid. (Dy\textsubscript{0.7}Y\textsubscript{0.25}La\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} powders were synthesized by self-propagating high-temperature synthesis (SHS) method. The transparent ceramics of (Dy\textsubscript{0.7}Y\textsubscript{0.25}La\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} was obtained by pressureless sintering in reductive H\textsubscript{2} atmosphere (PLSH) technology at relatively low temperature. The microstructure, optical quality and magneto-optical Verdet constant of the ceramics were characterized as well.

2. Results and Discussion

Figure 1 shows the X-ray diffraction pattern of (Dy\textsubscript{0.7}Y\textsubscript{0.25}La\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} powder synthesized by SHS method. It can be seen from the figure that the diffraction peaks of the (Dy\textsubscript{0.7}Y\textsubscript{0.25}La\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} powder corresponds to the Dy\textsubscript{2}O\textsubscript{3} and Y\textsubscript{2}O\textsubscript{3} standard cards (PDF#22-0612, PDF#43-1036). The main diffraction peaks of the powder are located between the peaks of two standard cards, indicating that Y\textsubscript{2}O\textsubscript{3} have entered the crystal lattice of Dy\textsubscript{2}O\textsubscript{3} and they formed a substitutional solid solution. The crystal grain size of (Dy\textsubscript{0.7}Y\textsubscript{0.25}La\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} powder is 15.5 nm, calculated by the Sherer formula.

![X-ray diffraction pattern of (Dy\textsubscript{0.7}Y\textsubscript{0.25}La\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} powder.](image)

Figure 1. X-ray diffraction pattern of (Dy\textsubscript{0.7}Y\textsubscript{0.25}La\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} powder.

Figure 2 is a scanning electron microscope image of (Dy\textsubscript{0.7}Y\textsubscript{0.25}La\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} powder synthesized by SHS. The powders consist of irregular primary particles, which are combined to form loose agglomerates with a porous structure [11]. The formation of this structure is determined by the mechanism of the SHS, where the propagation of the reaction front causes the precursor to foam, followed by the start of the combustion reaction and the discharge of a large amount of gaseous product [12–14].

To characterize the microstructure of as-sintered transparent ceramics, the fracture of (Dy\textsubscript{0.7}Y\textsubscript{0.25}La\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} ceramic is observed by SEM. As shown in the Figure 3a, there are many micro-pores in the ceramics sintered at 1400 °C by PLSH technology. When the temperature increased to 1450 °C, a small amount of pores can still be found in the ceramic matrix, marked with white circles, as shown in Figure 3b. It is demonstrated in Figure 3c,e that the ceramics have homogeneous microstructures without abnormal grain growth and the fracture mode of (Dy\textsubscript{0.7}Y\textsubscript{0.25}La\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} transparent ceramics is mainly trans-granular. However, in Figure 3d, abnormal grain growth can be observed in 1600 °C PLSH sintered ceramic, which leads to the degradation of optical transmittance in the visible wavelength to a certain extent. The appearance of the (Dy\textsubscript{0.7}Y\textsubscript{0.25}La\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} transparent ceramics, before and after annealing at 900 °C for 5 h in air are shown in the Figure 3f. The transmittance curves of (Dy\textsubscript{0.7}Y\textsubscript{0.25}La\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} transparent ceramics before and after annealing at 900 °C in a muffle furnace are given in Figure 4. Annealing in air did not affect the transmittance in the infrared range of the spectrum, but reduced the transmission in the visible range.
The Verdet constant of (Dy0.7Y0.25La0.05)2O3 transparent ceramics was characterized as well. The transmittance in the IR range (1895 nm to 2000 nm) is significantly higher than that previously published on ceramics of the same composition [9] and in Dy2O3 transparent ceramics with ZrO2 sintering aid by vacuum sintering [10]. Therefore, PLSH sintering should be recognized as an effective method for producing transparent ceramics. However, the existing scattering in the visible range in such ceramics indicates the presence of defects on the nanoscale-submicron scale. There is a possibility that with a large element length required for an FI (about 25 mm at a magnetic field of 2.5 T), scattering by these defects can become noticeable at a wavelength of 2000 nm. The Verdet constant of (Dy0.7Y0.25La0.05)2O3 transparent ceramics is −191.57 rad/(T·m) (λ = 632.8 nm), which is 1.43 times that of a commercial TGG crystal.

Figure 2. Scanning electron microscope micrograph of (Dy0.7Y0.25La0.05)2O3 powder prepared by self-propagating high-temperature synthesis (SHS).

Figure 3. SEM micrographs of the fracture surface of (Dy0.7Y0.25La0.05)2O3 ceramics: (a) 1400 °C/6 h; (b) 1450 °C/6 h; (c) 1500 °C/6 h; (d) 1600 °C/6 h; (e) 1550 °C/6 h; (f) the appearance of the (Dy0.7Y0.25La0.05)2O3 transparent ceramics sintered at 1550 °C: as-sintered and annealed at 900 °C for 5 h in air.

The transmittance in the IR range (1895 nm to 2000 nm) is significantly higher than that previously published on ceramics of the same composition [9] and in Dy2O3 transparent ceramics with ZrO2 sintering aid by vacuum sintering [10]. Therefore, PLSH sintering should be recognized as an effective method for producing transparent ceramics. However, the existing scattering in the visible range in such ceramics indicates the presence of defects on the nanoscale-submicron scale. There is a possibility that with a large element length required for an FI (about 25 mm at a magnetic field of 2.5 T), scattering by these defects can become noticeable at a wavelength of 2000 nm. The Verdet constant of
(Dy$_{0.7}$Y$_{0.25}$La$_{0.05}$)$_2$O$_3$ transparent ceramics is $-191.57$ rad/(T·m) ($\lambda = 632.8$ nm), which is 1.43 times that of a commercial TGG crystal.

Figure 4. Transmittance curves of the (Dy$_{0.7}$Y$_{0.25}$La$_{0.05}$)$_2$O$_3$ ceramics: as-sintered and additionally annealed at 900 °C for 5 h in air.

Figure 5 shows X-ray diffraction patterns of (Dy$_{0.7}$Y$_{0.25}$La$_{0.05}$)$_2$O$_3$ ceramics before and after annealing at 900 °C for 5 h in air. After annealing in air, the XRD data completely coincide with the card (PDF#22-0612) for cubic Dy$_2$O$_3$; the relative intensities of the peaks also correspond to these data, and no impurities or secondary phases are detected. In the as-sintered (Dy$_{0.7}$Y$_{0.25}$La$_{0.05}$)$_2$O$_3$ ceramic, the relative intensities of the peaks significantly deviate from the card (PDF#22-0612) for cubic Dy$_2$O$_3$. However, the peak at 2θ = 26° is not related to Dy$_2$O$_3$ but coincides with the La$_2$O$_3$ (PDF#05-0602). It can be associated with a significant effect of oxygen vacancies and, probably, Dy$^{2+}$ ions on the phase formation in the Dy$_2$O$_3$-Y$_2$O$_3$-La$_2$O$_3$ system. When the ceramic sample is annealed in the muffle furnace at 900 °C for 5 h, the La$_2$O$_3$ phase disappeared, characterized by XRD, as shown in Figure 5. After annealing, the Dy$^{2+}$ ions are oxidized, oxygen vacancies decrease, and the solubility of La$_2$O$_3$ in the solid solution increases. We attribute the decrease in the transmission of ceramics in the visible range after annealing in air to the presence of hydrogen in residual pores and interstices.

Further progress in improving the quality of ceramics (Dy$_{0.7}$Y$_{0.25}$La$_{0.05}$)$_2$O$_3$ can be associated with a thorough study of the phase diagrams in this system, taking into account the calcination atmosphere and finding the exact technological path to prevent the formation of secondary phases. Another or parallel possibility is to change the sintering technological route. Moreover, the combination of PLSH sintering at a low temperature (about 1400 °C) with subsequent hot isostatic pressing (HIP) and annealing in air seems to be promising.

The magneto-optical Verdet constant, which was recorded by the magneto-optical measurement system with a He-Ne laser, two polarizers and an electromagnet coil, was measured to be $-191.57$ rad/(T·m) at a wavelength of 632.8 nm, which is 1.43 times larger than that of commercial terbium gallium garnet (Tb$_3$Ga$_5$O$_{12}$, TGG) crystal. Andrzej Kruk et al. [15] proposed using MO-FOM (magneto-optical figure of merit) factor to describe the comprehensive magneto-optical property of Faraday materials. In this paper, the FOM of the (Dy$_{0.7}$Y$_{0.25}$La$_{0.05}$)$_2$O$_3$ transparent ceramic is calculation to be 0.66584 rad/T (38.15deg/T), which shows good prospects for magneto-optical applications.
1.1% was determined by the scanning electron microscope (COXEM, Daejeon, Korea). The UV-vis-NIR absorption spectrum of the aqueous solution was recorded to determine the concentration of the solution was determined by the gravimetric method at 500 °C. The stoichiometric amount of metal cations dysprosium, yttrium, and lanthanum are prepared by dissolving the respective metal oxides in nitric acid mixed with water under heating. The concentration of the solution was determined by the gravimetric method at 500 °C. Then, the nitrate solution is diluted to the desired concentration. Moreover, the solution of glycine and metal nitrates was prepared with the ratio of 1:1. The SHS redox reactions of precursor in a quartz flask were initiated in the furnace preheated at 500 °C. Then, the highly dispersed powders were formed. The (Dy0.7Y0.25La0.05)2O3 powder was pressed and sintered in a flowing hydrogen atmosphere at 1400–1600 °C for 6 h to obtain (Dy0.7Y0.25La0.05)2O3 ceramics.

The X-ray diffractometer (Rigaku, Tokyo, Japan) as the detective method equipped with graphite monochromatized Cu Ka radiation (λ = 1.5406 Å, 40 kV/200 mA) was used to investigate the crystal structure of ceramic powders in the range of 2θ = 10–80°. The microscopic morphology of the samples was determined by the scanning electron microscope (COXEM, Daejeon, Korea). The UV-vis-NIR spectrophotometer (Agilent, Palo Alto, CA, USA) was used to record the linear transmittance of transparent ceramics. The device of the magneto-optical measurement system (Fudan Tianxin, Shanghai, China) was used to measure the Verdet constant at 632.8 nm. The crystal grain size of (Dy0.7Y0.25La0.05)2O3 powder calculated by Sherer formula [20]:

$$D = \frac{K\lambda}{B\cos\theta}$$  \hspace{1cm} (1)

4. Conclusions

(Dy0.7Y0.25La0.05)2O3 powder was synthesized by the self-propagating high-temperature synthesis method. The compact green bodies of (Dy0.7Y0.25La0.05)2O3 can be sintered to be transparent ceramics by pressureless sintering in a reducing H2 atmosphere method at 1400–1600 °C. The inline transmittance of 1550 °C sintered ceramic at 2000 nm was measured to be 78%, which is the highest published
inline transmittance till now. Further improvement of the optical quality in the visible range of \((\text{Dy}_{0.7}\text{Y}_{0.25}\text{La}_{0.05})_2\text{O}_3\) ceramics shed light on the application of magneto-optical isolators.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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