Optical Materials 76 (2018) 174–177

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Large Faraday effect of borate glasses with high Tb^{3+} content prepared by containerless processing

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ARTICLE INFO

Article history:
Received 2 November 2017
Received in revised form
15 December 2017
Accepted 16 December 2017

Keywords:
Faraday rotation
Oxide glass
Containerless processing

ABSTRACT

Borate glasses containing a large amount of Tb^{3+} ions have been prepared by containerless processing. The content of Tb_2O_3 reached 60 mol%. The glass bearing the highest content of Tb^{3+} ions showed a large Faraday effect; the Verdet constant was 234 rad/T m. Annealing of the glasses in H_2/N_2 atmosphere resulted in a low optical absorption coefficient, leading to an extremely large magneto-optical figure of merit that was ~1.7 times higher than that of $Tb_3Ga_5O_{12}$ single crystal.

1. Introduction

The Faraday effect is one of the magneto-optical phenomena, that is, a rotation of the polarization plane of linearly polarized light that takes place when the light passes through a material in a magnetic field or ferro- and ferrimagnets. Materials with a large Faraday effect have been used as optical isolators, optical circulators, and sensors of electrical current or magnetic fields.

It is well known that garnet-type rare-earth ferrite crystals such as $Y_3Fe_5O_{12}$ (YIG), $Gd_3Fe_5O_{12}$, and $Bi_3Fe_5O_{12}$ exhibit an extremely large Faraday effect and are highly transparent to infrared light [1–6]. Therefore, the garnet-type ferrites have been practically utilized in the infrared range, for example, around a wavelength of 1550 nm, which is suitable for optical telecommunications. However, these ferrite crystals have rather intense optical absorption in the wavelength range below 1100 nm.

Recently, short-wavelength lasers typified by He-Ne lasers, laser diodes, and fiber lasers have been widely utilized for sensing, medical applications, and laser processing, for example. Optical isolators are an important element for laser systems. Thus, the demand for magneto-optical materials with both a large Faraday effect and high transparency in the visible to near-infrared (vis-NIR) region is steadily increasing.

The Faraday effect of paramagnetic materials is generally evaluated by the relation, $\theta_F = VHL$, where θ_F is the Faraday rotation angle, H is the external magnetic field, L is the length of the light pass in the material, and V is the Verdet constant for the material. Currently, terbium gallium garnet ($Tb_3Ga_5O_{12}$, TGG) is the most widely used as a magneto-optical material in the visible range. TGG is highly transparent in the visible range and its Verdet constant is ~134 rad/T m at 633 nm [7].

On the other hand, many studies have been carried out on the Faraday effect of rare-earth-containing glasses, because in general, glasses provide the advantages of tunable optical and mechanical properties by adjusting the chemical composition and controlling the shape of the product such as a plate, rod, or fiber [8–17]. Among the rare-earth ions, Tb^{3+} shows few optical absorption lines in a wide wavelength range from 400 to 1500 nm. Moreover, the large magnetic moment of the Tb^{3+} ion is fairly effective in generating a large Faraday effect. To achieve a large magneto-optical figure of merit as well as a large Faraday effect, it is important to incorporate a large amount of Tb^{3+} ions in glasses. However, it is not easy to avoid crystallization in the preparation of the glasses containing a high content of Tb^{3+} ions when the conventional melt-quenching method is employed with a crucible as a container for the melt. One way of circumventing the crystallization issue is to perform containerless processing, which has recently attracted attention as

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https://doi.org/10.1016/j.optmat.2017.12.031

an emerging glass-preparing method. This method enables the vitrification of materials in bulk form even if they have low glass-forming ability, because there is no contact with the container wall where heterogeneous nucleation occurs. Recently, glass formation through containerless processing has been performed for glass systems such as BaO-TiO_2, La_2O_3-TiO_2, La_2O_3-Nb_2O_5, and La_2O_3-WO_3 [18–21]. It is expected that glasses containing a high content of Tb_2O_3 can also be prepared by containerless processing.

In this research, we aim at the preparation of oxide glasses containing a large amount of Tb^{3+} to realize a magneto-optical material with a Verdet constant larger than that of a TGG single crystal and high transparency in the vis-NIR region.

2. Experimental procedure

Borate glasses containing a large amount of Tb_2O_3 (Tb_2O_3 concentrations of 45, 55, and 60 mol%) were prepared by containerless processing. Hereafter, these glasses are simply referred to as 45T, 55T, and 60T. Powders of reagent-grade Tb_4O_7, B_2O_3, SiO_2, and Al_2O_3 were weighed and mixed to obtain the designed proportions. The mixture of powders was placed on the nozzle of an aerodynamic levitation (ADL) furnace and levitated by nitrogen gas flow. The flow rate was monitored and controlled by a mass-flow meter. A high-resolution charge-coupled device (CCD) video camera equipped with telephoto objective lens was used to observe a magnified view of the samples. A CO_2 laser was used to melt the levitated sample and its temperature was measured by a pyrometer. The levitated melt was rapidly cooled to room temperature and solidified by turning off the laser.

The glass transition temperature (T_g) and crystallization temperature (T_c) were determined by differential thermal analysis (DTA) at a heating rate of 10 °C/min. Vitrified samples were annealed at their glass transition temperatures in 4%-H_2/96%-N_2 atmosphere for 10 h to reduce Tb^{4+} to Tb^{3+} then cooled slowly to release the thermal stress. The density of the glasses was measured by the Archimedes method. The transmittance spectra of glass plates 1 mm thick were obtained in the wavelength range of 300–1200 nm using a UV–vis spectrometer. The wavelength variation of the Faraday rotation angle was measured at room temperature by using a commercial measurement system for the Faraday and Kerr effects (Model K-250, JASCO). The light source was Xe lamp and the external magnetic field was 1.5 T.

3. Results and discussion

3.1. Transmittance

Glass spheres with a diameter of approximately 5 mm were prepared using an aerodynamic levitation furnace. Before annealing, the glass samples had brown color. After annealing at T_g in 4%-H_2/96%-N_2 atmosphere, they became colorless. Fig. 1 depicts the transmittance spectra of 60T before and after annealing. For comparison, the spectrum of a TGG single crystal (made by the Czochralski method, CASTECH Inc.) is also shown. In the spectrum of 60T before annealing, a broad optical absorption band can be seen at wavelengths shorter than 900 nm. The absorption is ascribable to the Tb^{4+} ion [22].

The spectra of 60T after annealing and TGG have similar absorption peaks at around 300–400 nm and ~480 nm. The absorption peaks corresponds to $^7F_6 \rightarrow {}^5H_7$, $^5L_9$, $^5D_3$, and $^5D_4$ transitions of the Tb^{3+} ion. It is considered that almost all the terbium ions in 60T are present as Tb^{3+} after the annealing, as suggested by the high similarity between the profiles of the spectra of the 60T glass after annealing and the TGG single crystal.

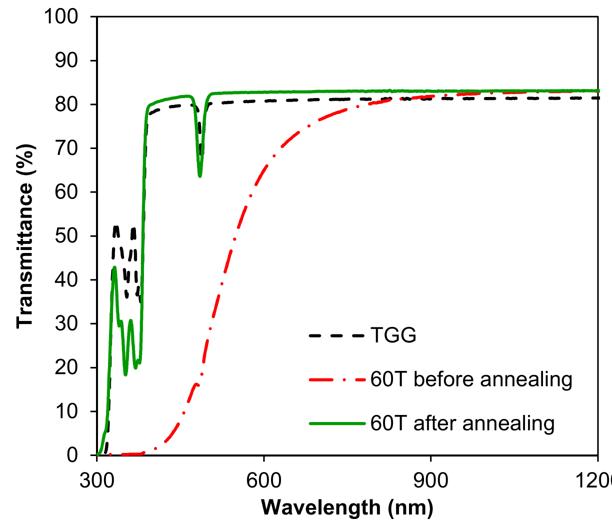

Fig. 1. Transmittance spectra of 60T before annealing, 60T after annealing, and $Tb_3Ga_5O_{12}$ (TGG).

3.2. Faraday effect

Fig. 2 illustrates the wavelength dependence of the Verdet constant at room temperature for 45T, 55T, 60T, and the TGG crystal. The Verdet constant is negative in the wavelength range studied, indicating that the Faraday rotation is caused by paramagnetic Tb^{3+} ions. The Verdet constant tends to increase with decreasing wavelength. Furthermore, all the glass samples have a larger Verdet constant than TGG in the entire wavelength range.

The density, Tb^{3+} ion concentration, and Verdet constant at 633 nm for each sample are summarized in Table 1, and the dependence of the Verdet constant at 633 nm on the Tb^{3+} ion concentration is shown in Fig. 3. It can be seen that the Verdet constant increases almost linearly with increasing Tb^{3+} ion concentration. A similar tendency was also found for other Tb^{3+}-containing glasses, such as silicate, phosphate, borate, and borogermanate glasses [15]. The largest Verdet constant reported thus far for Tb^{3+}-containing glasses is 185 rad/T m for $40Tb_2O_3$-$10Dy_2O_3$-$16.67B_2O_3$-$10Ga_2O_3$-$10SiO_2$-$3.33P_2O_5$ glass [14], but the present glasses exhibit larger Verdet constants; the largest value,

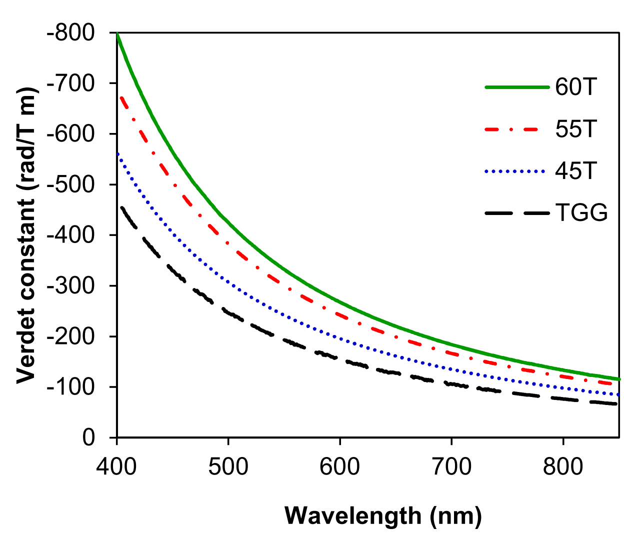

Fig. 2. Variation of Verdet constant with wavelength for 45T, 55T, 60T, and TGG at room temperature.