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Synthesis and laser patterning of Bi-doped $Y_3Fe_5O_{12}$ crystals in germanosilicate glasses

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ABSTRACT

New germanosilicate glasses giving the crystallization of yttrium iron garnet $Y_3Fe_5O_{12}$ (YIG) and Bi-doped YIG, $23Na_2O$–xBi_2O_3–$(12-x)Y_2O_3$–$25Fe_2O_3$–$20SiO_2$–$20GeO_2$ (mol%), are developed, and the laser-induced crystallization technique is applied to the glasses to pattern YIG and Bi-doped YIG crystals on the glass surface. It is clarified from the Mössbauer effect measurements that iron ions in the glasses are present mainly as Fe^{3+}. It is suggested from the X-ray diffraction analyses and magnetization measurements that Si^{4+} ions are incorporated into YIG crystals formed in the crystallization of glasses. The irradiations (laser power: 32–60 mW and laser scanning speed: 7 μm/s) of continuous wave $Yb:YVO_4$ fiber laser (wavelength: 1080 nm) are found to induce YIG and Bi-doped YIG crystals, indicating that Fe^{3+} ions in the glasses act as suitable transition metal ions for the laser-induced crystallization. It is suggested that YIG and Bi-doped YIG crystals in the laser irradiated part might orient. The present study will be a first step for the patterning of magnetic crystals containing iron ions in glasses.

1. Introduction

Glasses having high transparency, high chemical durability, and excellent thermal properties are key materials in microelectronics, optics, and optical fiber technology. It is known that glasses containing a large amount of rare-earth (RE) ions such as Pr^{3+}, Tb^{3+}, and Eu^{2+} exhibit large Faraday effects in the visible to ultraviolet range [1–5]. Such glasses have high potentials for active devices such as magneto-optic switches, laser isolators, and sensors of magnetic field based on Faraday effects. On the other hand, it is also well known that yttrium iron garnet (YIG) with a chemical formula of $Y_3Fe_5O_{12}$, which was first developed by Bertaut and Forrat [6], is one of the most famous and important magneto-optic crystals and is transparent in the near-infrared region. Furthermore, it is noted that bismuth-substituted $Y_{3-x}Bi_xFe_5O_{12}$ (Bi–YIG) crystals exhibit stronger Faraday effects compared with bismuth non-doped YIG [7,8].

Crystallization of glass is a method for fabrication of transparent and dense condensed materials with desired shapes, and various transparent functional crystallized glasses have been synthesized so far [9–17]. It is of interest to fabricate glasses consisting of YIG and Bi-doped YIG crystals from a viewpoint of the design of light control devices. There have been several reports on the fabrication of crystallized glasses with YIG crystals [18–22]. For instance, Bahadur et al. [18–21] reported the crystallization of YIG in Na_2O–Y_2O_3–Fe_2O_3–SiO_2 glasses. At this moment, however, information on the crystallization behavior of YIG in glasses is limited [18–21], and there have been no reports on the crystallization of Bi-doped YIG crystals in glasses.

The purpose of this study is to find suitable glasses for the crystallization of YIG and Bi-doped YIG and to pattern those crystals on the glass surface by laser irradiations. Laser irradiation to glass has been regarded as a process for spatially selected structural modification and/or crystallization in glass, and laser-induced crystallization techniques have been applied to various glasses in order to pattern functional crystals in glasses [23–30]. It is of interest to apply the laser-induced crystallization technique for the patterning of YIG crystals. The patterning of YIG crystals in glasses would be a good step for the design of magneto-optic devices. In this study, glasses in the Na_2O–Bi_2O_3–Y_2O_3–Fe_2O_3–SiO_2–GeO_2 system were developed as precursors for the crystallization of YIG and Bi–YIG crystals.

2. Experimental

Glasses in the system of Na_2O–Bi_2O_3–Y_2O_3–Fe_2O_3–SiO_2–GeO_2 were prepared by using a conventional melt-quenching method, and the compositions of some glasses are shown in Table 1. Raw materials Na_2CO_3, Bi_2O_3, Y_2O_3, Fe_2O_3, SiO_2, and GeO_2 were mixed

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Table 1
Glass compositions, glass transition temperature (T_g), and crystallization peak (T_{p1}, T_{p2}, T_{p3},) temperatures in the glasses examined in this study. The errors in the values are ± 2 °C.

Sample	Glass composition (mol%)	T_g (°C)	T_{p1} (°C)	T_{p2} (°C)	T_{p3} (°C)
Sample A	$23Na_2O–12Y_2O_3–25Fe_2O_3–40SiO_2$	569	617	690	–
Sample B	$23Na_2O–12Y_2O_3–25Fe_2O_3–20SiO_2–20GeO_2$	541	589	682	762
Sample C	$23Na_2O–2Bi_2O_3–10Y_2O_3–25Fe_2O_3–20SiO_2–20GeO_2$	527	569	644	714
Sample D	$23Na_2O–4Bi_2O_3–8Y_2O_3–25Fe_2O_3–20SiO_2–20GeO_2$	475	571	609	689
Sample E	$23Na_2O–5Bi_2O_3–7Y_2O_3–25Fe_2O_3–20SiO_2–20GeO_2$	486	563	597	688
Sample F	$23Na_2O–6Bi_2O_3–6Y_2O_3–25Fe_2O_3–20SiO_2–20GeO_2$	485	552	595	697

and melted in a platinum crucible at 1400–1450 °C for 30 min in air in an electric furnace. The melts were poured onto an iron plate and pressed to a thickness about 1 mm with another iron plate. The glass transition, T_g, and crystallization peak, T_p, temperatures were determined using differential thermal analysis (DTA) at a heating rate of 10 K/min. To eliminate residual internal stresses, the as-quenched glasses were annealed (not crystallization) at T_g for 30 min in air. In order to clarify the valence of iron ions in the glasses, the Mössbauer effect measurements were conducted on powder samples ($\sim$120 mg) spread on an aluminum foil ($\sim$2 cm $\times$ 2 cm) at room temperature using an equipment of VT-6000 (Laboratory Equipment Co.). A radioactive ^{57}Co in Pd matrix was used as the γ-ray source, and the velocity calibration was obtained from the 6-line hyperfine spectra of iron foil [31].

The glasses were mechanically polished to a mirror finish with CeO_2 powders, and heat-treated at various temperatures. The crystalline phases present in heat-treated samples were examined from the X-ray diffraction (XRD) analyses at room temperature by using Cu $K\alpha$ radiation. Magnetization curves at room temperature for crystallized samples were measured by using a vibrating sample magnetometer (VSM). Yb:YVO_4 fiber lasers with λ=1080 nm were irradiated onto the surface of the polished glass samples using objective lens (magnification: 50, numerical aperture: NA=0.8). The glass samples were put on the stage and mechanically moved during laser irradiations to pattern crystals. Laser powers were 20–500 mW and scanning speeds were 5–20 μm/s.

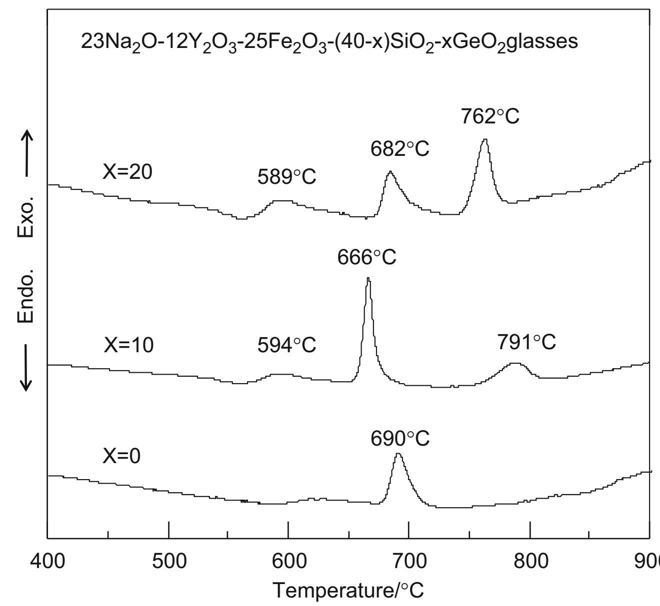

Fig. 1. DTA patterns for the bulk samples of $23Na_2O–12Y_2O_3–25Fe_2O_3–(40-x)SiO_2–xGeO_2$ with x=0, 10, and 20. The heating rate was 10 K/min.

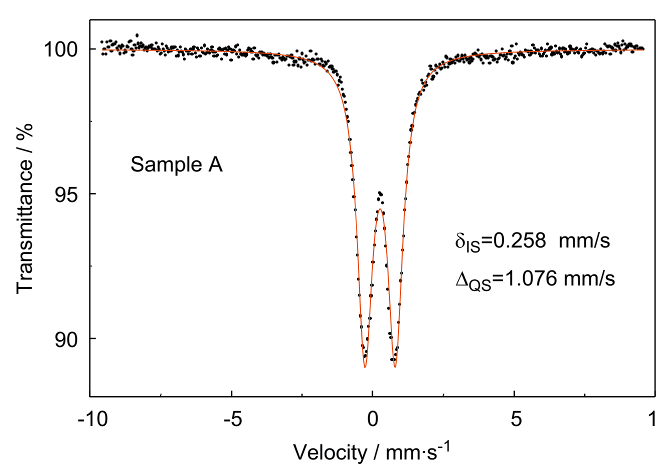

Fig. 2. The Mössbauer spectrum at room temperature for Sample A ($23Na_2O–12Y_2O_3–25Fe_2O_3–40SiO_2$ glass).

3. Results and discussion

3.1. Formation of YIG crystals

In order to fabricate crystallized glasses consisting of YIG and Bi–YIG crystals and to pattern those crystals by laser irradiations, search and development of suitable precursor glasses are one of the most important steps. So far, glasses with the compositions such as $34Na_2O–6Y_2O_3–10Fe_2O_3–50SiO_2$ and $26Na_2O–9Y_2O_3–15Fe_2O_3–50SiO_2$ have been developed for the crystallization of YIG [18–22]. We first examined the samples with the compositions of $23Na_2O–12Y_2O_3–25Fe_2O_3–(40-x)SiO_2–xGeO_2$, x=0, 5, 10, and 20, in which relatively large amounts of Y_2O_3 and Fe_2O_3 are included and GeO_2 is added to decrease glass preparation temperature.

All melt-quenched samples of $23Na_2O–12Y_2O_3–25Fe_2O_3–(40-x)SiO_2–xGeO_2$ showed only halo patterns in the XRD patterns. The DTA data for the melt-quenched samples with x=0, 10, and 20 are shown in Fig. 1. Endothermic peaks due to the glass transition and exothermic peaks due to the crystallization are observed. These results (XRD and DTA) indicate that the melt-quenched samples are glass. The DTA patterns shown in Fig. 1 suggest that the crystallization behavior of the glasses change depending on the SiO_2/GeO_2 ratio. In particular, three clear crystallization peaks are detected in the glass with x=20. The values of T_g and T_p for the glasses with x=0 (Glass A) and 20 (Glass B) are given in Table 1. It is seen that the glass transition and crystallization temperatures decrease with the substitution of GeO_2 for SiO_2. The glass with GeO_2/SiO_2=1 shows the values of T_g=541, T_{p1}=589, T_{p2}=682, and T_{p3}=762 °C.

The valence of iron ions in the glasses was examined from the Mössbauer effect measurements [31] and a cerium redox titration