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Writing of crystal line patterns in glass by laser irradiation

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Abstract

We examined the laser-induced crystallization to form the fresnoite type $Ba_2TiGe_2O_8$ crystal line patterns in transition metal ion doped BaO–TiO_2–GeO_2 glass. $Ba_2TiGe_2O_8$ crystal line was written in 0.6FeO–33.3BaO–16.7TiO_2–50GeO_2 glass by continuous wave yttrium–aluminum–garnet (YAG) laser irradiation. We obtained polarization dependence of Raman spectra in crystal line pattern. Second harmonic generation (SHG) indicated unique fringe patterns from $Ba_2TiGe_2O_8$ crystal lines.

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1. Introduction

Laser irradiation to glass has been regarded as a process for spatially selected structural modification and/or crystallization in glass [1,2]. The present authors' group [3–7] has proposed that the irradiation of a cw Nd:YAG laser with $\lambda = 1064$ nm induces the formation of dot/line shape crystallite in Sm^{3+} and Dy^{3+} containing oxide glasses. The laser-induced crystallization behavior in samarium ion heat processing with the use of fundamental wavelength of YAG laser ($\lambda = 1064$ nm) is examined by Sato et al. [3]. They confirmed the formation of $Sm_2Te_6O_{15}$ micro-crystalline dots on 10Sm_2O_3–10BaO–80TeO_2 glass and proposed the crystallization mechanism as follows: Since Sm^{3+} has an absorption band around 1064 nm, some energy of cw Nd:YAG laser is absorbed by Sm^{3+} in glass through f–f transitions ($^6F_{9/2} \rightarrow {}^6H_{5/2}$), consequently inducing thermal effects through continuous electron–phonon coupling. We found the same behavior in dysprosium (Dy^{3+}) ion containing glasses [4]. This technique for the writing of crystal dots and lines in glasses might be, therefore, called 'Rare-earth ion heat processing' (REIH). By using REIH technique, present authors have succeeded in patterning of single crystal lines consisting of β-BaB_2O_4 (designated as β-BBO) nonlinear optical crystals in some glasses [4]. Ihara et al. [5] have reported the writing of two-dimensional crystal curved or bending lines consisting of rare-earth ion doped $BiBO_3$ crystals showing a second harmonic generation (SHG). Recently, Gupta et al. [8] fabricated $Nd_{0.2}La_{0.8}BGeO_5$ crystallites by the irradiation of titanium-sapphire light source of wavelength $\lambda = 800$ nm to Nd_2O_3–La_2O_3–B_2O_3–GeO_2 glass. Nd^{3+} has the absorption band around 800 nm and shows the non-radiative relaxation inducing thermal effects.

Furthermore, the present authors' group proposed a transition metal ion (such as V^{3+}, V^{4+}, Fe^{2+}, Ni^{2+}, Cu^{2+}) heat processing technique (TMIH), instead of REIH processing [9]. The doping amount of transition metal ions for inducing crystallization in glass is small compared to rare-earth ions such as Sm^{3+} and Dy^{3+}.

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In this paper, we examined the writing of crystal line patterning consisting of $Ba_2TiGe_2O_8$ (BTG) optical nonlinear crystal in $BaO–TiO_2–GeO_2$ glass TMIH processing. Second ordered optical nonlinearity of BTG crystal is examined by Takahashi et al. [10] They fabricated transparent surface crystallized glasses consisting of BTG crystals and found that they show large second order optical nonlinearity ($d_{eff} \sim 22$ pm/V) comparable to that of $LiNbO_3$ single crystal. We discuss about the morphology and second harmonic generation of BTG crystal lines compared with β-BBO crystal line [4,6,7].

2. Experimental procedure

The composition of the glasses examined in this study is $0.6FeO–33.3BaO–16.7TiO_2–50GeO_2$ (0.6FeO–BTG50 glass) and prepared by a conventional melt quenching method. The glass transition, T_g, and crystallization onset, T_x, temperatures were determined using differential thermal analysis (DTA) at a heating rate of 10 K/min. The glasses were mechanically polished to a mirror finish with ceria powders. In TMIH technique a continuous wave Nd:YAG laser with $\lambda = 1064$ nm irradiated the surface of the glass using an objective lens (60×). The glasses were moved at the speeds of 7 μm/s. Micro-Raman scattering spectra of fresnoite crystal lines were measured with a three-dimensional spatially resolved laser microscope (Tokyo Instruments Co. Nanofinder) operated at Ar^+ ($\lambda = 488$ nm) laser. In detail of the measurement of Raman spectra is described elsewhere [6,7]. To investigate the polarization dependence of second harmonic intensity from crystal lines, we established the second harmonic microscope technique, and the configuration of sample and incident laser is illustrated in Fig. 1. The second harmonic intensity of crystal lines was measured by using a fundamental wave of Q-switched Nd:YAG laser with $\lambda = 1064$ nm as a laser source, in which linearly polarized fundamental laser beams were introduced into crystal lines perpendicularly and the azimuthal dependence of SHG signals was measured by rotating the sample with the analyzer parallel to the polarized direction of a normally incident fundamental beam.

3. Results

Fig. 2 shows the optical absorption spectra at room temperature for 0.6FeO–BTG50 glasses. The absorption coefficients, α, at 1064 nm has a value of 6.3 cm^{-1} for 0.6FeO–BTG50 glass. This value is much higher than a value of 4.5 cm^{-1} for $10Sm_2O_3–40BaO–50B_2O_3$ glass.

Fig. 3 shows the polarized optical micrographs of crystallized line fabricated by cw YAG laser irradiation (power: 1.0 W, scanning speed: 7 μm/s) in 0.6FeO–BTG50 glass. The structural modifications with a width of approximately 2 μm are observed. We carried out the polarized micro-Raman scattering measurements to obtain the information of orientation in the crystallized pattern, and the results are shown in Fig. 4. We also indicated the spectra for β-BBO crystal line in Fig. 4. The sharp peaks are obtained in both cases and all peaks correspond to the β-BBO and BTG crystalline phase. In measurements of polarized Raman scattering spectra, various configurations about the

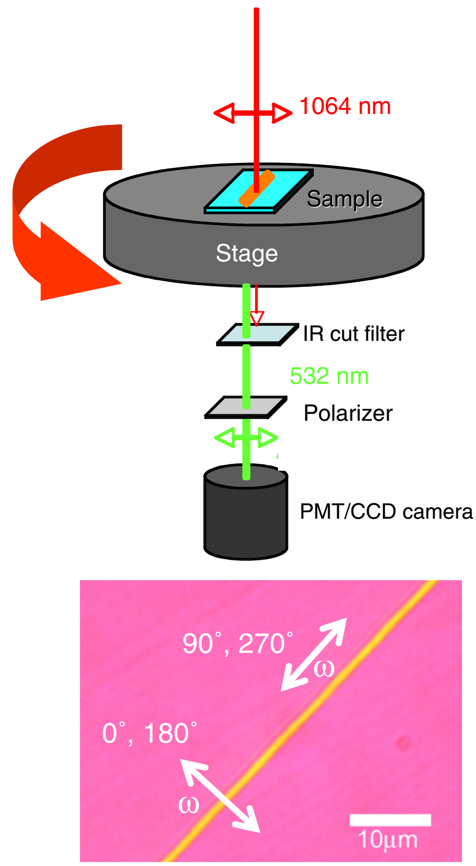

Fig. 1. Configurations of sample and incident laser for azimuthal dependences of SH intensity by second harmonic microscope. We decided the azimuth of 0° (180°) which polarization of fundamental wave (ω) is normal to the scanning direction.

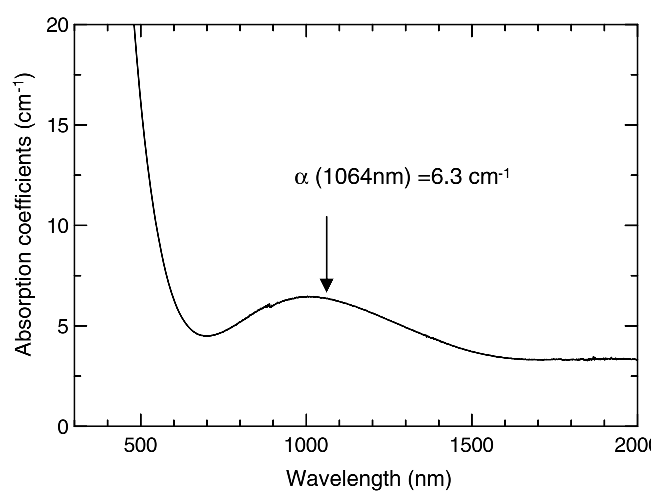

Fig. 2. Optical absorption spectra at room temperature for the 0.6FeO–BTG50 glass.