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Writing of two-dimensional crystal curved lines at the surface of Sm_2O_3–Bi_2O_3–B_2O_3 glass by samarium atom heat processing

Rie Ihara[a], Tsuyoshi Honma[a,1], Yasuhiko Benino[a], Takumi Fujiwara[a], Ryuji Sato[b], Takayuki Komatsu[a,*]

[a] *Department of Chemistry, Nagaoka University of Technology, Nagaoka 940-2188, Japan*
[b] *Department of Materials Engineering, Tsuruoka National College of Technology, Tsuruoka 997-8511, Japan*

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Abstract

Two-dimensional crystal curved lines consisting of the nonlinear optical $Sm_xBi_{1-x}BO_3$ phase are fabricated at the surface of $8Sm_2O_3 \cdot 37Bi_2O_3 \cdot 55B_2O_3$ glass by continuous wave Nd:YAG laser (wavelength: 1064 nm) irradiation (samarium atom heat processing) with a power of ~0.9 W and a laser scanning speed of 5 μm/s. The curved lines with bending angles of 0–90° or with sine-shapes are written by just changing the laser scanning direction. The polarized micro-Raman scattering spectra for the line after bending are the same as those for the line before bending, indicating that the crystal plane of $Sm_xBi_{1-x}BO_3$ crystals to the crystal growth direction might be maintained even after the change in the laser scanning direction. It is found from laser scanning microscope observations that the crystal lines at the surface are swelled out smoothly, giving a height of about 10 μm.

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1. Introduction

Glass having high transparency, high chemical durability, excellent thermal and electrical properties is very important materials in microelectronics, optics and optical fiber technology. Micro-fabrication of glass, i.e. structural modifications, has found increasingly more applications in optoelectronics and telecommunication devices such as optical grating and waveguide. Recently, laser irradiation to glass has received much attention as a new tool of micro-fabrication, and many studies on laser-induced micro-fabrication in glass have been carried out so far, where the most of the target glasses are SiO_2-based glasses and source lasers are mainly short-wavelength excimer lasers or femtosecond pulsed lasers, and structural modifications are mainly refractive index changes (not crystallization) [1–7].

Recently, the present authors' group [8–14] proposed that the irradiation of a continuous wave (cw) Nd:YAG laser with a wavelength of $\lambda = 1064$ nm induces the formation of crystal dots and lines such as $Sm_xBi_{1-x}BO_3$, β-BaB_2O_4, and $KSm(PO_3)_4$ in glasses containing Sm_2O_3 or Dy_2O_3. In particular, it has been proposed that crystals of $Sm_xBi_{1-x}BO_3$ and β-BaB_2O_4 in the straight lines might be single crystals [11–13]. This technique is called 'samarium (rare-earth) atom heat processing' [11,12]. In the samarium atom

* Corresponding author. Tel.: +81 258 47 9313; fax: +81 258 47 9300.

E-mail address: komatsu@chem.nagaokaut.ac.jp (T. Komatsu).

[1] Present address: Advanced Technology R&D Center, Mitsubishi Electric Corporation, Sagamihara, Kanagawa 229-1195, Japan.

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heat processing, cw Nd:YAG laser with $\lambda = 1064$ nm is absorbed by Sm^{3+} in glass through f–f transitions ($^6F_{9/2} \leftarrow {}^6H_{5/2}$) and the surrounding of Sm^{3+} is heated through a nonradiative relaxation (electron–phonon coupling) [8–12]. Consequently, structural modification (refractive index change or crystallization) is induced.

Crystal lines written in glass have a potential use as optical waveguide with such active nonlinear functions as light-wave switching, modulation, and wavelength conversion. Usually, tunable optical waveguides have been fabricated by constructing curved lines with different refractive indices in substrates, e.g. Ti-doped ferroelectric $LiNbO_3$ single crystals. It is, therefore, of extremely importance to establish technique for the writing of crystal curved lines in glass. Although three-dimensional channels (structural damages with refractive index changes, not crystal lines) have been micro-machined in silica-based glasses by using femtosecond laser pulses [15–17], the micro-fabrication of crystal curved lines in glass by using laser is scarce [13]. Very recently, Honma et al. [13] tried to write curved lines of β-BaB_2O_4 crystals, but a discontinuous change has been observed at the bending point.

In this study, we tried to write crystal curved lines with various shapes in Sm_2O_3–Bi_2O_3–B_2O_3 glass by using the samarium atom heat processing and to clarify the quality of curved crystal lines from polarized micro-Raman scattering spectra and laser scanning microscope observations. In previous papers [10,11,13], it was demonstrated that straight lines consisting of $Sm_xBi_{1-x}BO_3$ crystals showing second harmonic generation (SHG) are written at the surface of Sm_2O_3–Bi_2O_3–B_2O_3 glasses by cw Nd:YAG laser irradiations.

2. Experimental

The glass composition examined in this study is $8Sm_2O_3 \cdot 37Bi_2O_3 \cdot 55B_2O_3$. The glass preparation method is described elsewhere [9–11]. The quenched glasses were annealed at around glass transition temperature to release internal stress and then mechanically polished to a mirror finish with CeO_2 powders. A cw Nd:YAG laser ($\lambda = 1064$ nm) with a power of ~ 0.9 W irradiated the surface of the glass using an objected lens (magnification 60), and the sample stage was automatically moved during laser irradiations to write curved lines. The moving speed of the sample stage, i.e. laser scanning speed, was 3 or 5 μm/s, and its speed was kept constant even at the bending point of curved lines. The crystal lines fabricated by YAG laser irradiations were observed with polarization optical and laser scanning (Keyence: VK-8550, $\lambda = 685$ nm) microscopes. Polarized micro-Raman scattering spectra were measured with a three-dimensional spatially resolved laser microscope (Tokyo Instruments Co. Nanofinder) operated at Ar^+ ($\lambda = 488$ nm) laser.

3. Results and discussion

The glass of $8Sm_2O_3 \cdot 37Bi_2O_3 \cdot 55B_2O_3$ has the glass transition temperature of $T_g = 454$ °C and crystallization onset temperature of $T_x = 571$ °C. The laser scanning microscope photograph for the curved line with a bending angle of 30° is shown in Fig. 1. The curved lines with a width of approximately 10 μm are clearly written by YAG laser irradiation. It is seen that the line at the surface is swelled out smoothly, giving a height of about 10 μm. Furthermore, it should be emphasized that any appreciable changes such as structural damages have not been observed even at the bending point. The curved lines with bending angles of 60 and 90° were also written, and it was confirmed from micro-Raman scattering spectra that these curved lines are crystals. The swelling at the surface shown in Fig. 1 suggests that melts are initially formed in YAG laser irradiated regions and then crystallization is induced.

It is of particular interest to examine the crystal growth direction of lines at just the bending points. Polarization optical micrograph observations were carried out for the line with a bending angle of 60°, where the line was rotated against the polarizer such as 45 and 90°. Since the angle between the polarizer and the line before bending differs from the angle between the polarizer and the line after bending, it is expected that the color of the polarization optical micrograph would change at the bending point. The obtained polarization optical micrographs, however, indicate that the color does not change suddenly at the bending point, but changes gradually extending over about 60 μm. The presence of such kinds of retardation in the polarized optical micrographs suggests that the plane of the crystal growth does not change suddenly just at the bending point, but changes gradually after bending.

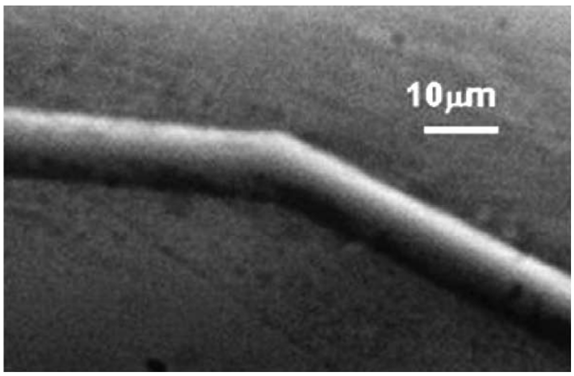

Fig. 1. Laser scanning microscope photograph for the curved line with a bending angle of 30° at the surface of glass written by YAG laser irradiation (power: ~ 0.9 W, scanning speed: 5 μm/s).

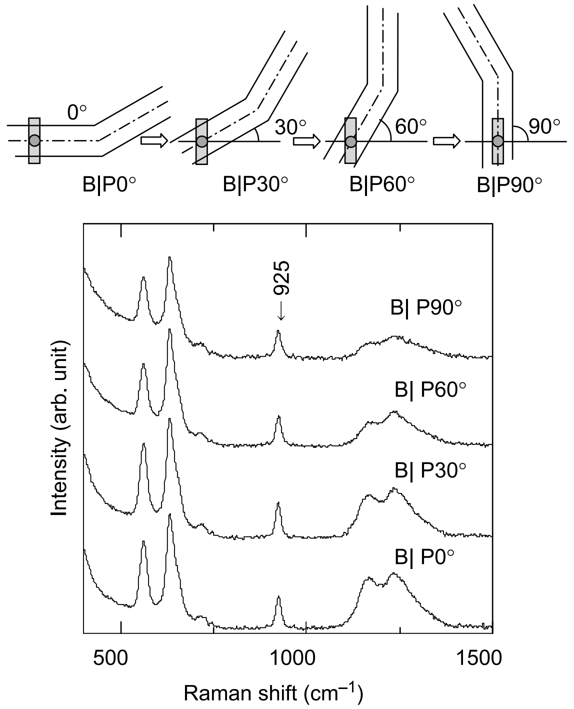

Fig. 2. Polarized micro-Raman scattering spectra for the line (at the position of ∼100 μm from the bending point) before bending with a bending angle of 30°. The angle between the polarized direction of incident laser and the line growth direction was changed from perpendicular (B|P0°) to parallel (B|P90°).

The polarized micro-Raman scattering spectra for the line (at the position of ∼100 μm from the bending point) before bending with a bending angle of 30° are shown in Fig. 2, where the angle between the polarized direction of incident laser and the line growth direction was changed from perpendicular to parallel. In these observations, for instance, the relation with the angle of 60° is designated here as B|P60°. In the Raman scattering spectra shown in Fig. 2, the sharp peaks are observed at 562, 633, and 925 cm^{-1}. These peaks are assigned to $Sm_xBi_{1-x}BO_3$ crystals showing SHGs [18,19]. Unfortunately, the crystal structure of the $Sm_xBi_{1-x}BO_3$ phase has not been clarified at this moment [18,19], but our preliminary experiments suggest that this crystalline phase might have an orthorhombic structure [20]. As seen in Fig. 2, the intensity of the peaks at around 1200 cm^{-1} changes largely by changing the angle between the polarized direction of incident laser and the line growth direction. We checked the relative (normalized) intensities of the peaks at around 1200 cm^{-1} against the peaks at 925 cm^{-1} for the relations of B|P0°, B|P30°, B|P60° and B|P90° and found that the relative intensity changes depending on the angle between the polarized direction of incident laser and the line growth direction. These results suggest that $Sm_xBi_{1-x}BO_3$ crystals in the line before bending are highly oriented, as already proposed in the previous paper [11]. If the crystal line consists of an assembly of $Sm_xBi_{1-x}BO_3$ crystals and thus is a polycrystalline line, the difference in the relative intensity would not be appeared.

Similar observations were carried out for the line (at the position of ∼100 μm from the bending point) after bending, where the notations such as A|P60° have been used. It was found that the polarized Raman spectra (not shown here: A|P0°, A|P30°, A|P60°, and A|P90°) for the line after bending are almost the same as those (Fig. 2) for the line before bending. That is, it is suggested that the line after bending also consists of $Sm_xBi_{1-x}BO_3$ crystals with a highly orientation. The relative (normalized) intensities of the peaks at around 1200 cm^{-1} against the peaks at 925 cm^{-1} for the relations of B|P0° and A|P0° are shown in Fig. 3. It is seen that both relations show the same data. Similar behaviors were observed for the relations of B|P0° and A|P0°, B|P30° and A|P30°, B|P60° and A|P60°, and B|P90° and A|P90°. The data shown in Fig. 3 strongly suggest that the crystal plane of $Sm_xBi_{1-x}BO_3$ crystals to the crystal growth direction might be maintained at the positions of over ∼100 μm from the bending point even after the change in the laser scanning direction.

The polarization optical micrographs for the sine-shape curved lines, which were written at a constant YAG laser

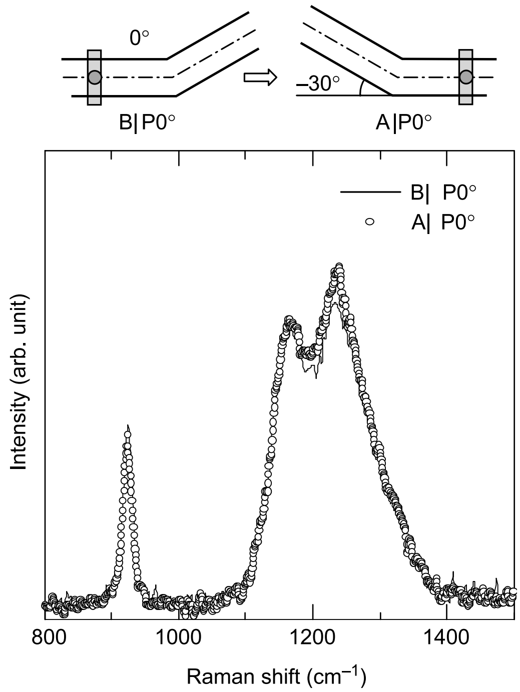

Fig. 3. Polarized micro-Raman scattering spectra for the line before and after bending with a bending angle of 30°. The relative (normalized) intensities of the peaks at around 1200 cm^{-1} against the peaks at 925 cm^{-1} for the relations of B|P0° and B|P0° are plotted.

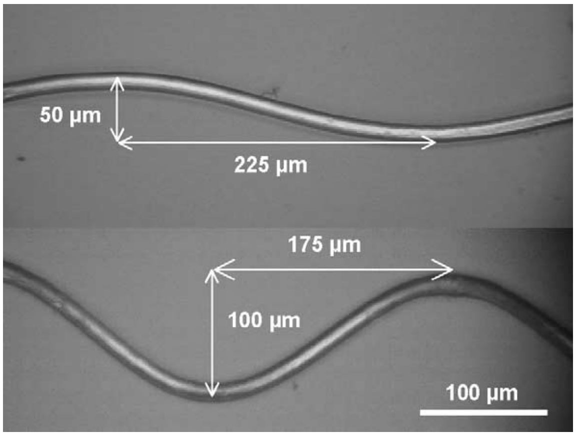

Fig. 4. Polarization optical micrographs for the sine-shape curved lines written at a constant YAG laser moving speed of 3 μm/s.

moving speed of 3 μm/s, are shown in Fig. 4. It was confirmed from micro-Raman scattering spectra that these sine-shape curved lines consist of $Sm_xBi_{1-x}BO_3$ crystals, demonstrating that two-dimensional crystal curved lines with desired bending angles can be designed at the surface of $8Sm_2O_3 \cdot 37Bi_2O_3 \cdot 55B_2O_3$ glass by using cw Nd:YAG laser irradiation (the samarium atom heat processing). As a preliminary experiments, the light ($\lambda = 632.8$ nm) transmission was examined for a crystal curved line (length: 4.5 mm) with a sine-shape (wavelength: 450 μm, amplitude: 50 μm), and, as a result, it was confirmed qualitatively that the crystal curved line acts as optical waveguide.

As one demonstration for the technique developed in this study, a famous ground picture (bird) in Nazca (Peru in South America) was designed on the surface of $8Sm_2O_3 \cdot 37Bi_2O_3 \cdot 55B_2O_3$ glass, where laser power was 0.8–0.9 W and laser scanning speed was 4 μm/s. The designed picture with various bending angles is shown in Fig. 5. Since the line consists of nonlinear optical $Sm_xBi_{1-x}BO_3$ crystals, the SHG (green light with $\lambda = 532$ nm for incident Nd:YAG laser with $\lambda = 1064$ nm) has been clearly observed from the designed lines, as seen in Fig. 5.

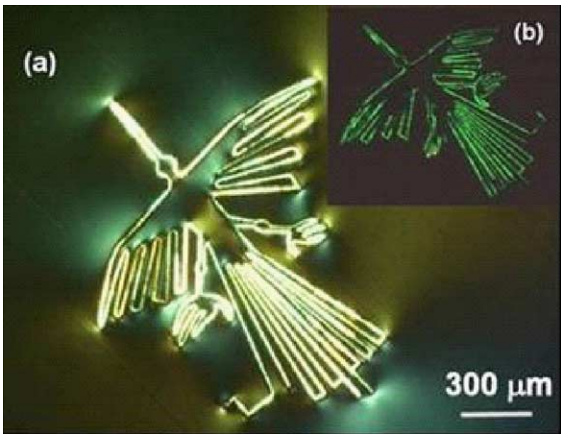

Fig. 5. Polarization optical micrograph (a) and SHG microscope observation (b) for the curved line (designed as a ground picture (bird) in Nazca) at the surface of glass written by YAG laser irradiation.

4. Conclusions

We succeeded in writing of two-dimensional crystal curved lines with bending angles of 0–90° and sine-shapes consisting of the nonlinear optical $Sm_xBi_{1-x}BO_3$ phase at the surface of $8Sm_2O_3 \cdot 37Bi_2O_3 \cdot 55B_2O_3$ glass by cw Nd:YAG laser ($\lambda = 1064$ nm) irradiations. It was suggested from the polarized micro-Raman scattering spectra that the crystal plane of $Sm_xBi_{1-x}BO_3$ crystals to the crystal growth direction might be maintained at the positions of over ~100 μm from the bending point even after the change in the laser scanning direction. In this study, the quality (e.g. quantitative light transfer loss) of crystal curved lines and the crystal growth direction have not been determined, but we can say that this success in the writing of nonlinear optical crystal curved lines in glass by laser irradiation opens a new door to a processing of active photonic devices in passive glass substrate. The study of the crystal growth mechanism in curved lines should be needed.

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