Writing of Nonlinear Optical Single Crystal-Lines in Glass by YAG Laser Scanning

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A continuous-wave (CW) Nd:YAG laser operating at a wavelength of 1064 nm is irradiated to Sm2O3 and Dy2O3 doped glasses under various conditions in the systems of La2O3–Bi2O3–B2O3 and La2O3–BaO–B2O3 (L: Sm and Dy), and nonlinear optical Bi3+-Sm3+BO3 and β-BaB2O4 (β-BBO) crystals with the shape of dot or line are formed on the surface of glass substrates. It is demonstrated from the azimuthal dependence of second harmonic intensity that β-BBO crystal-lines are single crystals with the c-axis orientation along the laser scanning direction. The photoluminescence spectra indicate that Sm3+ and Dy3+ are incorporated into β-BBO single crystal-lines. The present study proposes that CW Nd:YAG laser irradiation to glass with Sm3+ and Dy3+ is a novel technique for a spatially selected crystallization in glass. [Received July 30, 2003; Accepted December 11, 2003]

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1. Introduction

Laser irradiation to glass has received much attention, because this technique is regarded as a new processing for spatially selected structural modification and/or crystallization (crystal growth) in glass.1–4 A permanent refractive index change can be induced in Ge-doped SiO2 fibers by ultraviolet laser irradiation,5 producing Bragg gratings under suitable exposure conditions.

On the other hand, optically transparent crystallized glasses containing rare-earth ions or nonlinear optical crystals have also received much interest, because such materials have a high potential for laser materials, tunable waveguide, tunable fiber grating and so on.5–7 It is, therefore, of particular interest to form optical functional crystalline phases in glass through laser irradiation. Recently Fujiwara et al.8 succeeded in fabricating a periodic structure consisting of nanocrystal’s arrangements with a second ordered optical nonlinearity through XeCl eximer laser (λ = 308 nm) induced crystallization in K2O–Al2O3–TeO2 glasses. Sato et al.9 found that crystalline dots consisting of the Sm3+TeO2O2 phase are induced by irradiation of a continuous-wave (CW) Nd3+ : yttrium-aluminum-garnet (YAG) laser operating at λ = 1064 nm in BaO(MgO)–Sm2O3–TeO2 glasses. Recently, the present authors’ group10–12 proposed a new idea for the writing of crystalline dots and lines in glass, in which a CW Nd:YAG laser with a λ = 1064 nm is irradiated to the glasses containing Sm2O3. It has been proposed that CW YAG laser irradiations to glass containing Sm3+ cause continuous f–f transitions (6F7/2→5H9/2) in Sm3+ and continuous electron-phonon couplings (nonirradiated relaxation), consequently inducing thermal effect, i.e., laser-induced heating. This new technique for the writing of crystalline dots and lines in glasses might be, therefore, called “selective (samarium) atom heat processing”.

In a previous study13 it was unclear whether samarium ions are incorporated into the Bi3+-Sm3+BO3 crystal phase formed by YAG laser irradiation and also was unclear whether the formed crystalline phase is single crystal or polycrystal. If crystal-lines written by YAG laser irradiation in glass are single crystals with nonlinear optical performances, this technique will give a great impact not only in materials science and technology but also in device processing. In this study, we approach this problem using β-BaB2O4 crystals-written by CW Nd:YAG laser irradiation in Sm2O3–BaO–B2O3 glasses. β-BBO is developed by Chen et al.14 and crystal structures are well known.14–16

2. Experimental

The glass compositions examined in this study are 10Sm2O3, 40BaO.50B2O3 (designated as 10SmBBO), 10Dy2O3.45BaO.45B2O3 (designated as 10DyBBO) and 10Sm2O3.35Bi2O3.55B2O3. Commercial powders of reagent grade (99.9% purity) Sm2O3, Dy2O3, BaCO3, Bi2O3 and B2O3 were melted in a platinum crucible at 1200°C for 40 min in an electric furnace. The melts were poured on to an iron plate and pressed to a thickness of about 1.5 mm by another iron plate. The glass transition, Tg, and crystallization onset, Tc, temperatures were determined using differential thermal analysis (DTA) at a heating rate of 10 K/min. Optical absorption spectra were taken in the wavelength range of 190–3200 nm on Shimadzu UV–3150 spectrometer. The glasses were mechanically polished to obtain a mirror surface with CeO2 powder.

CW Nd:YAG laser with λ = 1064 nm was irradiated to the surface of the glasses using an objective lens (20 and 60x), and the sample stage was automatically moved during laser irradiations to write crystal-lines. The crystal-lines written by YAG laser irradiations were observed with a polarized optical microscope. The formation of the β-BBO crystalline phase was confirmed using X-ray diffraction (XRD) analysis (Cu-Kα radiation) at room temperature. The second harmonic (SH) intensity of crystal-lines was measured by using a fundamental wave of Q-switched Nd:YAG laser with λ = 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. A Y-cut quartz plate (0.6 mm thickness) was used as a reference of SH intensity. Micro-Raman and photoluminescence spectra of β-BBO and Bi3+-Sm3+BO3 crystal-lines were measured with a three-dimensional spatially resolved laser microscope (Tokyo Instruments. Co. Nanofinder®) operated at Ar+ (488 nm) laser.

3. Results and discussion

3.1 Formation of β-BBO crystal-lines

In 10SmBBO and 10DyBBO glasses, we confirmed that the crystalline phase obtained by a conventional heat treatment in an electric furnace is assigned to only the β-BaB2O4 (ICDD # 85–0914) phase. The absorption coefficients at 1064 nm were 7.9 cm−1 (F9/2 z→F3/2 H15/2) for 10SmBBO glass and of 4.5 cm−1 (F9/2 z→F3/2 H15/2) for 10DyBBO glass.
In order to write crystal-lines easily and stably in the glasses, the following techniques were used. At first, to avoid the fracture of glasses due to the thermal shock during laser irradiations, the glasses were heated at about 150°C using a hotplate. Secondly, to form easily crystal nuclei of β-BBO, β-BBO crystal grains with a diameter of 5–30 µm, which were prepared by a conventional powder sintering method, were put onto the surface of the glasses, and then, YAG laser was irradiated to the crystal grains on the surface. Through continuous YAG laser irradiations, β-BBO grains were firstly incorporated into the glass melts, and crystalline dots were formed. Finally, the glasses were moved automatically at the speeds of ~8 µm/s. The suitable YAG laser powers were 0.6 W for 10SmBBO glass and 0.9 W for 10DyBBO glass. By applying the above techniques and procedures, crystal-lines with a width of approximately 5 µm were stably written in the glasses. As an example, polarized optical microphotographs for the lines written by YAG laser irradiations in 10SmBBO glass are shown in Fig. 1. The rotation angle dependence of homogeneous retardations can be seen in the case of Bi15...Sm2O3 crystal-line in Sm2O3–Bi2O3–B2O3 glasses.11

3.2 Morphologies of β-BBO crystal-lines written by YAG laser irradiation

Figures 2 shows the micro-Raman spectrum for a crystal-line obtained by YAG laser irradiation. The peaks are attributed to the stretching mode of [B2O5]1− meta-borate ring. The spectrum shown in Fig. 2 is the same as that for a bulk single crystal β–BaB2O4.16,17 A crystal-line array of 15 lines was prepared by YAG laser scanning, where the length of each crystal-line is 10 mm and a distance between lines (pitch) is 50 µm. The XRD pattern for the crystal-line array is shown in Fig. 3, in which only the (110) plane is observed. These results demonstrate that β-BBO crystals are certainly formed by YAG laser irradiation in 10SmBBO glass. Furthermore, the results suggest that β-BBO crystals are highly oriented in the lines.

Figure 4 shows the second harmonic (SH) intensities observed from a crystal-line written in 10SmBBO and 10DyBBO glass with a second harmonic microscope pumped with Q-switched YAG laser operating at λ = 1064 nm. The SH intensity was measured by changing the angle between linearly
polarized incident laser and $\beta$-BBO crystal-line. The maximum SH intensities are observed at the rotation angles of $\sim 0^\circ$ and $\sim 180^\circ$, and the zero intensities are located at $\sim 90^\circ$ and $\sim 270^\circ$, i.e., two-fold angular dependence as the crystal-line was rotated. The same experiment was carried out for the $y$-cut $\beta$-BBO single crystal (0.5 mm thickness) obtained commercially. It is clear that the azimuthal dependence of second harmonic generation signals for $\beta$-BBO crystal-lines written by YAG laser irradiations in 10SmBBO and 10DyBBO glasses is almost the same as that for commercially available $y$-cut $\beta$-BBO single crystal. From these SHG results, therefore, it is concluded that the crystal-lines are $\beta$-BBO single crystals with the $c$-axis orientation along the laser scanning direction.

### 3.3 Photoluminescence spectra for $\text{Bi}_1-\text{Sm}_3\text{BO}_3$ and $\beta$-$\text{BaB}_2\text{O}_4$ crystal-lines

Figure 5 shows the micro-Raman spectrum for a crystal-line written by YAG laser irradiation (power 0.65 W, scanning speed 8 $\mu$m/s) in 10Sm$_3$O$_7$-35Bi$_2$O$_3$-55B$_2$O$_3$ glass. Some sharp peaks are observed from the crystal-line. This spectrum is almost the same as that of BIBO3 phase (type-2) proposed by Potter. The photoluminescence for the glassy part and the crystal-line part in 10Sm$_3$O$_7$-35Bi$_2$O$_3$-55B$_2$O$_3$ sample are shown in Fig. 6 (A). The peaks correspond to $f-f$ transitions of Sm$^{3+}$ ions. The intensities of the peaks in the crystal-line are larger than those in the glassy part. In the previous studies, we proposed that the crystal lines correspond to the BIBO$_3$ metastable crystalline phase and samarium ions are incorporated into the BIBO$_3$ phase. The results shown in Fig. 6 (A) demonstrate the formation of the $\text{Bi}_1-\text{Sm}_3\text{BO}_3$ crystalline phase.

Figure 6 (B) shows the photoluminescence spectrum of the $\beta$-BBO crystal-line written by YAG laser irradiation. The photoluminescence peaks correspond to the $f-f$ transition of Sm$^{3+}$. There is no peaks attributing to Sm$^{2+}$ in Fig. 6 (B). The peak intensities for the crystal-line are much larger than those for the glass, and the peak splittings, so-called Stark splitting, are observed in the crystal-line. The two-dimensional luminescence intensity map at $^2G_{5/2} \leftrightarrow ^4H_{15/2}$ ($\sim 600$ nm) peak is shown in Fig. 7. The data demonstrate that Sm$^{3+}$ ions are incorporated into the $\beta$-BBO crystal-line homogeneously. Considering the coordination number (eight-fold BaO$_6$) and ionic radius of Ba$^{2+}$ ions in $\beta$-BBO, Sm$^{3+}$ ions might substitute Ba$^{2+}$ sites in the structure of $\beta$-BBO single crystals written by YAG laser irradiations. If Sm$^{3+}$ ions are substituted for Ba$^{2+}$ ions, a charge compensation must be fulfilled by the generation of defects such as Ba$^{2+}$ site vacancies. The discussion on the charge compensations in Sm$^{3+}$ doped $\beta$-BBO will be the next stage in this study.

### Summary

CW Nd:YAG laser with $\lambda = 1064$ nm was irradiated to Sm$_2$O$_3$ and Dy$_2$O$_3$ doped glasses under various conditions in the systems of Ln$_2$O$_3$-Bi$_2$O$_3$-$\text{B}_2\text{O}_3$ and Ln$_2$O$_3$-BaO-$\text{B}_2\text{O}_3$ (Ln: Sm and Dy), and nonlinear optical $\text{Bi}_1-\text{Sm}_3\text{BO}_3$ and $\beta$-BBO crystals with the shape of line were formed on the surface of glass substrates. It was demonstrated from the azimuthal dependence of SH intensity that $\beta$-BBO crystal-lines are single crystals with the $c$-axis orientation along the laser scanning direction. The photoluminescence spectra indicated that Sm$^{3+}$...
ions are incorporated into Bi$_2$–Sm$_3$BO$_3$ and β-BBO single crystal-lines. We propose that CW Nd:YAG laser irradiation to glass with Sm$^{3+}$ and Dy$^{3+}$ is a nice technique for a spatially selected crystallization in glass and this technique has a high potential for preparation of tunable optical waveguides.

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