Nonlinear optical crystal-line writing in glass by yttrium aluminum garnet laser irradiation

Tsuyoshi Honma, Yasuhiko Benino, Takumi Fujiwara, Takayuki Komatsu, and Ryuji Sato

Citation: Applied Physics Letters **82**, 892 (2003); doi: 10.1063/1.1544059
View online: http://dx.doi.org/10.1063/1.1544059
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/82/6?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS VOLUME 82, NUMBER 6 10 FEBRUARY 2003

Nonlinear optical crystal-line writing in glass by yttrium aluminum garnet laser irradiation

Tsuyoshi Honma, Yasuhiko Benino, Takumi Fujiwara, and Takayuki Komatsu[a)]
Department of Chemistry, Nagaoka University of Technology, Nagaoka 940-2188, Japan

Ryuji Sato
Department of Materials Engineering, Tsuruoka National College of Technology, Tsuruoka 997-8511, Japan

(Received 5 November 2002; accepted 16 December 2002)

Crystal lines with second-order optical nonlinearity have been successfully fabricated at the surface of $10Sm_2O_3.35Bi_2O_3.55B_2O_3$ glass by continuous irradiation of Nd:YAG laser. The laser-induced crystalline phase was confirmed to be $Bi_{0.7}Sm_{0.3}BO_3$ by x-ray diffraction measurements, and second-harmonic generation (SHG) from the phase was clearly observed. An array structure of crystal lines was fabricated by laser writing under automatic computer control, and Maker fringe patterns of SHG were observed, indicating that the direction of polarization in the structure with a crystal line array was parallel to the sample surface. In addition, we measured polarization optical microphotographs, and found uniform phase retardation for a whole length of crystal lines. It is strongly suggested from these results that crystal lines by laser irradiation are formed in single-domain crystalline phase (single crystal) with second-order nonlinearity. [DOI: 10.1063/1.1544059]

Laser irradiation of glass materials has received much attention, because this technique is regarded as a new processing method for spatially selected structural modification and/or crystallization in glass.[1–4] For instance, a permanent change of refractive index can be induced in Ge-doped SiO_2 optical fibers by ultraviolet laser irradiation to produce Bragg gratings under suitable exposure conditions.[1] Sato *et al.*[3] found that crystalline dots consisting of the $Sm_2Te_6O_{15}$ phase are induced by irradiation of a cw Nd^{3+}:yttrium–aluminum–garnet (YAG) laser operating at $\lambda = 1064$ nm in $BaO-Sm_2O_3-TeO_2$ glasses. Fujiwara *et al.*[4] succeeded in fabrication of a periodic structure consisting of ordered nanocrystal arrangements using photoinduced crystallization in $K_2O-Nb_2O_5-TeO_2$ glasses through a XeCl excimer laser ($\lambda = 308$ nm).

Very recently, Honma *et al.*[5,6] discovered the formation of new nonlinear optical crystalline phases, $Bi_{0.7}Ln_{0.3}BO_3$, in the crystallized glasses of $Ln_2O_3-Bi_2O_3-B_2O_3$ (Ln: La, Gd, Sm) and found, furthermore, that some glasses, such as $12.5Sm_2O_3.30Bi_2O_3.57.5B_2O_3$, are crystallized by irradiation of cw Nd:YAG laser at $\lambda = 1064$ nm, resulting in the formation of nonlinear optical crystalline dots consisting of the $Bi_{0.7}Sm_{0.3}BO_3$ phase. It has been proposed that cw YAG laser irradiations to glass containing Sm^{3+} ions cause continuous $f-f$ transitions ($^6F_{9/2} \leftarrow {}^6H_{5/2}$) in Sm^{3+} and continuous electron–phonon coupling, consequently inducing thermal effects.[3,5,6] That is, in the YAG laser irradiation processing, local regions centered round Sm^{3+} ions are selectively heated. This technique might be called, therefore, "selective atom heat processing." The purpose of this study is to fabricate a structure of nonlinear optical crystal lines by cw Nd:YAG laser irradiation in $Sm_2O_3-Bi_2O_3-B_2O_3$ glasses, and to clarify the direction of polarization in the lines by means of a Maker fringe technique in second-harmonic intensity measurements.

The glass composition examined in this study is $10Sm_2O_3.35Bi_2O_3.55B_2O_3$. The glass preparation method is described elsewhere.[5,6] A cw YAG laser with $\lambda = 1064$ nm was used to irradiate the surface of the glass using an objective lens ($60\times$), and the sample stage was mechanically moved during laser irradiations to construct the line patterns. For an example of optimum conditions to induce the crystal-line phase, we obtained 0.66 W for laser power, and 10 $\mu m\, s^{-1}$ for scanning speed of sample stage.

The crystal lines fabricated by YAG laser irradiation were observed with a polarization optical microscope. The second-harmonic (SH) intensity of crystal lines was measured by using a fundamental wave of Q-switched Nd:YAG laser with $\lambda = 1064$ nm as a function of the angle of incident light, that is, the Maker fringe method. The coefficient d_{11} of second-order nonlinearity in α-quartz (z-cut α-quartz with a thickness of 0.6 mm) was used as a reference of SH intensity.

The glass of $10Sm_2O_3.35Bi_2O_3.55B_2O_3$ has a glass transition temperature of $T_g = 474\,°C$ and crystallization onset temperature of $T_x = 574\,°C$. The polarization optical microphotographs for the sample obtained by YAG laser irradiation (power: 0.66 W, scanning speed: 10 $\mu m\, s^{-1}$) are shown in Fig. 1. The lines with a width of approximately 5 μm, separated by 20-μm pitch from each other, are clearly written by laser irradiations. As discussed subsequently, it was confirmed from x-ray diffraction (XRD) analysis that the lines prepared in this study are crystalline. In Fig. 1, it is found in a cross-sectional view that a crystal grows toward interior, to a depth of about 15 μm. It is also seen that a structural change (not crystallization), which gives a refractive index change, is induced around crystals. In a side view, a homogeneous color/tone is observed for an area of crystal line, suggesting that there is no grain boundary in the crystal-

[a)]Author to whom correspondence should be addressed; electronic mail: komatsu@chem.nagaokaut.ac.jp

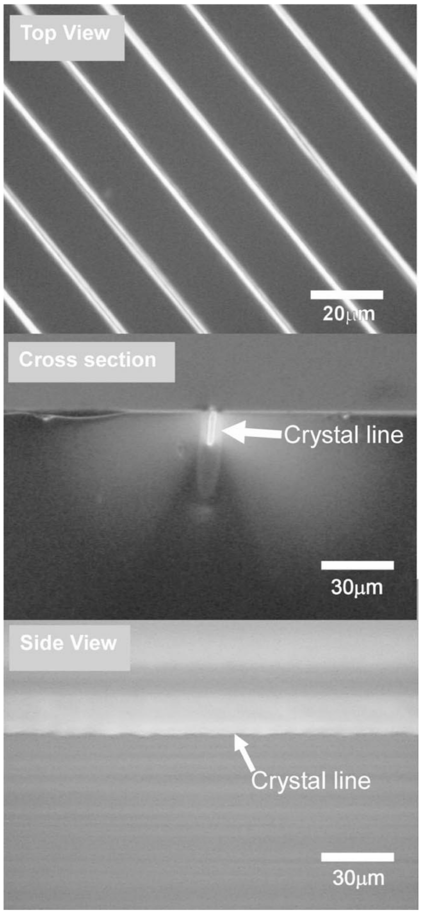

FIG. 1. Polarization optical microphotographs [top (surface), cross-section, side views] for the sample obtained by YAG laser irradiation (power: 0.66 W, scanning speed: 10 μm s^{-1}).

line region. The dependence of the retardation in the crystallized line on rotation angles of polarizer in the microscope is shown in Fig. 2. It is found that the same color/tone is observed at any angles except of 0° and 90°, strongly suggesting again the presence of no grains, and in addition, formation of single-domain crystalline phase. For comparison, the polarization optical microphotograph of the surface crystallized glass obtained by uniform heat-treatment in an electric furnace is also shown in Fig. 2. In this case, in contrast with that in laser writing, many different color/tone caused by multidomains are observed, because crystals grow randomly at the surface and various crystal planes are exhibited.

A crystal-line array of 100 lines was prepared by scanning YAG laser irradiation, where the length of each crystal line is 8 mm and a distance between lines (pitch) is 20 μm, as shown in Fig. 1 (top view). The XRD pattern for such a crystal-line array with 100 components is shown in Fig. 3, together with those for a surface crystallized glass and a crystalline dot array. The presence of a few peaks is confirmed, indicating that the lines are crystals (that is, $Bi_{0.7}Sm_{0.3}BO_3$).[5,6] It should be pointed out that the number of peaks for a crystal-line array is small compared with those for the surface crystallized glass and a crystalline dot array, suggesting that the crystals in the lines may be highly oriented. The crystal structure of the $Bi_{0.7}Sm_{0.3}BO_3$ phase has not been clarified as yet, and thus the crystal planes shown in Fig. 3, that is, the prior direction of crystal growth by YAG laser irradiation, are unclear at this moment.

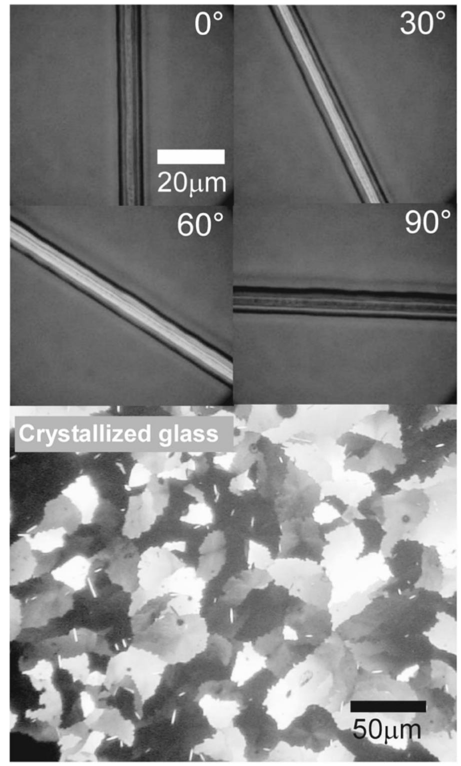

FIG. 2. Polarization optical microphotographs for the sample obtained by YAG laser irradiation. The angle of the polarizer with respect to the sample was changed. The data for the surface crystallized glass obtained by heat treatment in an electric furnace is also shown.

The SH intensity of this crystal-line array was measured using a Maker fringe method. Two different sample locations against the direction of incident laser polarization, as shown in Fig. 4, were taken. That is, the direction of crystal-line array is parallel or perpendicular to the rotational axis of the sample. In both cases, the front plane of crystal-line pattern was irradiated by a fundamental YAG laser with $\lambda = 1064$ nm, and generated SH waves with $\lambda = 532$ nm coming out from the back side of the sample were measured. The Maker fringe patterns obtained for such arrangements are shown in Fig. 4. In both cases, the second-harmonic generation (SHG) is clearly observed and the maximum SH intensity is positioned at $\theta = 0°$, the laser incident angle. These results indicate that the direction of polarization in crystal-

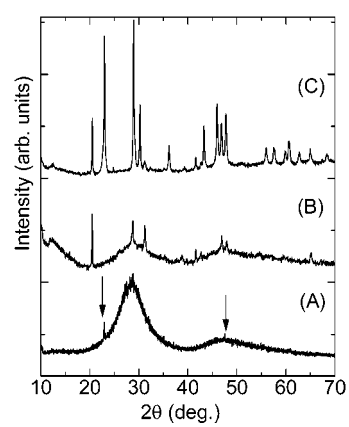

FIG. 3. XRD patterns for a crystal-line array (a) obtained by YAG laser irradiation in $10Sm_2O_3 \cdot 35Bi_2O_3 \cdot 55B_2O_3$ glass. The data for a crystalline dot array (b) and surface crystallized glass (c) are also shown.

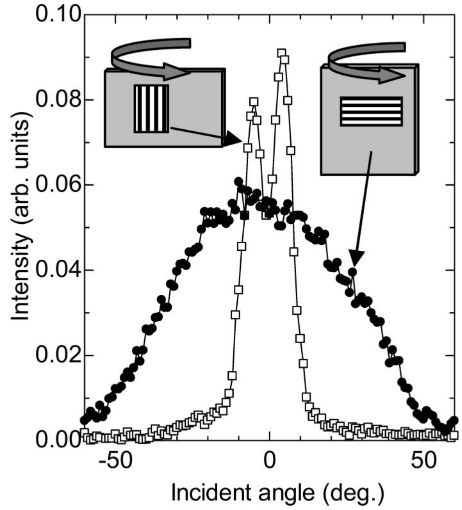

FIG. 4. Maker fringe patterns for the crystal-line array (100 lines) prepared by cw Nd:YAG laser irradiation.

lines is parallel to the sample surface; that is, parallel to the direction of crystal-line growth, because a p-excitation laser is used as an incident light source. Two possible directions of polarization, both parallel to the surface, are still remaining for a principal polarization; however, this is of particular interest, because in typical surface crystallized glasses showing SHG, the direction of polarization is perpendicular to the surface.[7–10] As shown in Fig. 4, in the case of the parallel relation to rotational axis, the Maker fringe pattern is sharp, giving steep drops at around $\theta = 10°$ in the SH intensity. This behavior suggests that generated SH waves from crystal lines are diffracted by crystal-line array, just like the behavior of Bragg gratings. Combined with the data shown in Figs. 2, 3, and 4, it is proposed that the line prepared by YAG laser irradiation in $10Sm_2O_3.35Bi_2O_3.55B_2O_3$ glass is a nonlinear optical single crystal. As a preliminary study of propagating light waves in the lines, it was confirmed that a nonlinear optical crystal line works as an optical waveguide.

In crystal-line writing experiments, we used the following technique. A crystalline dot was first formed at a given spot before laser scanning, and a YAG laser was then scanned at a constant speed. The formation of a crystalline dot at the starting point in a line is very important for the fabrication of smooth crystal lines, seeming to be required for seeding. This technique of crystal-line writing using YAG laser irradiation is just like the so-called zone melting method for single-crystal growth. Since crystal lines are clearly written by YAG laser irradiations at the scanning speed of $10\ \mu m\, s^{-1}$, the crystal growth rate of the $Bi_{0.7}Sm_{0.3}BO_3$ phase in $10Sm_2O_3.35Bi_2O_3.55B_2O_3$ glass would be at least higher than $10\ \mu m\, s^{-1}$. Very recently, Maciente *et al.*[11] succeeded in forming highly oriented β-BaB_2O_4 crystals at the surface of $BaO-B_2O_3-TiO_2$ glass using CO_2 laser ($\lambda = 10.6\ \mu m$) irradiations and reported that the crystal growth rate seems to be higher than that obtained by heating in an electric furnace. It is desirable to estimate temperatures in YAG laser irradiated regions, because the rate of crystal growth in glass is a function of temperature.

In summary, nonlinear optical crystal lines with a thickness of $\sim 5\ \mu m$ and a depth of $\sim 15\ \mu m$ were fabricated at the surface of $10Sm_2O_3.35Bi_2O_3.55B_2O_3$ glass by irradiation of continuous Nd^{3+}:YAG laser (power: 0.66 W, scanning speed: $10\ \mu m\, s^{-1}$). The crystalline phase in lines was $Bi_{0.7}Sm_{0.3}BO_3$, and SHG was observed from crystal lines. It is proposed, from obtained results of polarized optical microphotographs and Maker fringe patterns, that the lines are in the phase of single crystals and that the direction of polarization in crystal lines is parallel to the surface of lines. The crystal lines have a potential use as optical waveguides with such active nonlinear functions as light-wave switching, modulation, and wavelength conversion.

This work was supported from Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan. One of the authors (T.H.) would like to thank the Sasakawa Scientific Research Grant from The Japan Science Society for the partial financial support to this work.

[1] K. O. Hill, B. Malo, F. Bilodeau, D. C. Johnson, and J. Albert, Appl. Phys. Lett. **62**, 1035 (1993).
[2] J. Qiu, K. Miura, and K. Hirao, Jpn. J. Appl. Phys. **37**, 2263 (1998).
[3] R. Sato, Y. Benino, T. Fujiwara, and T. Komatsu, J. Non-Cryst. Solids **289**, 228 (2001).
[4] T. Fujiwara, R. Ogawa, Y. Takahashi, Y. Benino, T. Komatsu, and J. Nishii, Phys. Chem. Glasses (in press).
[5] T. Honma, Y. Benino, T. Fujiwara, R. Sato, and T. Komatsu, Opt. Mater. **20**, 27 (2002).
[6] T. Honma, Y. Benino, T. Fujiwara, R. Sato, and T. Komatsu, J. Ceram. Soc. Jpn. **20**, 27 (2002).
[7] R. Sakai, Y. Benino, and T. Komatsu, Appl. Phys. Lett. **77**, 2118 (2000).
[8] Y. Takahashi, Y. Benino, T. Fujiwara, and T. Komatsu, J. Appl. Phys. **89**, 5282 (2001).
[9] Y. Takahashi, Y. Benino, T. Fujiwara, K. B. R. Varma, and T. Komatsu, J. Ceram. Soc. Jpn. **110**, 22 (2002).
[10] Y. Takahashi, Y. Benino, T. Fujiwara, and T. Komatsu, Appl. Phys. Lett. **81**, 223 (2002).
[11] A. F. Maciente, V. R. Mastelaro, A. L. Martinez, A. C. Hernandes, and C. A. Carneiro, J. Non-Cryst. Solids **306**, 309 (2002).