

Transition metal atom heat processing for writing of crystal lines in glass

Tsuyoshi Honma, Yasuhiko Benino, Takumi Fujiwara, and Takayuki Komatsu^{a)}

Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka 940-2188, Japan

(Received 15 February 2006; accepted 28 April 2006; published online 7 June 2006)

A technique for the writing of crystal line in glass has been developed, in which a continuous-wave Nd:YAG laser (wavelength: $\lambda=1064$ nm) is irradiated to the glasses containing transition metal (TM) ions such as Fe^{2+} , Ni^{2+} , and V^{4+} . Laser energies are absorbed through $d-d$ transitions of TM ions and dissipated to the lattice surrounding TM ions by nonradiative relaxation process, giving the increase in temperature in the laser irradiated region and inducing crystallization. This technique has been demonstrated for the writing of crystal lines consisting of nonlinear optical fresnoite-type $\text{Ba}_2\text{TiGe}_2\text{O}_8$ and $\text{Ba}_2\text{TiSi}_2\text{O}_8$ crystals in NiO-, Fe_2O_3 -, and V_2O_5 -doped (0.3–1 mol %) BaO–TiO₂–GeO₂ and BaO–TiO₂–SiO₂ glasses. It is confirmed that crystals in the crystal lines are highly oriented along the laser scanning direction. The technique developed in this study is proposed to be called “transition metal atom heat processing.” © 2006 American Institute of Physics. [DOI: 10.1063/1.2212272]

Laser irradiation of glass has been regarded as a process for spatially selected structural modification and crystallization in glass. For instance, a permanent change of refractive index can be induced in Ge-doped SiO₂ optical fibers by ultraviolet laser irradiation to produce Bragg gratings under suitable exposure conditions.¹ A periodic structure consisting of the arrangement of ordered nanocrystals has been fabricated in TeO₂-based glasses through a photoinduced crystallization using XeCl excimer laser (wavelength: $\lambda=308$ nm) irradiation.²

Recently, the present authors' group^{3–7} developed a technique for laser-induced crystallization in glass, which is called rare-earth (samarium) atom heat processing [designated here as REAH (SAAH) processing]. In REAH processing, a continuous-wave (cw) Nd:yttrium aluminum garnet (YAG) laser with $\lambda=1064$ nm was irradiated to glasses containing Sm₂O₃ (or Dy₂O₃) and structural modification (refractive index change) or crystallization is induced through an absorption of an YAG laser by Sm³⁺ and a nonradiative relaxation in the $f-f$ transitions of Sm³⁺. Using this technique, Honma *et al.*^{4,5} have reported the patterning of single-like crystal lines consisting of nonlinear optical Sm_xBi_{1-x}BO₃ and β -BaB₂O₄ crystals in some glasses, and very recently, Ihara *et al.*⁸ have reported the writing of two-dimensional crystal curved or bending lines consisting of Sm_xBi_{1-x}BO₃ crystals showing a second harmonic generation (SHG) in Sm₂O₃–Bi₂O₃–B₂O₃ glasses.

A key point in REAH processing is a combination of rare-earth ions and cw Nd:YAG laser with $\lambda=1064$ nm, and it is, of course, prerequisite to prepare glasses with some amounts (approximately more than 8 mol %) of Sm₂O₃ (or Dy₂O₃), meaning some limitations of the application of REAH processing for the writing of crystal lines in glass. Considering the concept of REAH processing, other combinations would be possible for laser-induced crystallization in glass. In this study, we examined a combination of transition metal (TM) ions and cw Nd:YAG laser for the writing of crystal lines consisting of nonlinear optical fresnoite-type $\text{Ba}_2\text{TiGe}_2\text{O}_8$ and $\text{Ba}_2\text{TiSi}_2\text{O}_8$ crystals in TM ion-doped

BaO–TiO₂–GeO₂ and BaO–TiO₂–SiO₂ glasses, and consequently demonstrated that this combination works effectively. It should be pointed out that the doping amount of TM ions in the present technique is small, i.e., 0.3–1 mol % NiO, Fe₂O₃, or V₂O₅. It is known that the fresnoite-type $\text{Ba}_2\text{TiGe}_2\text{O}_8$ and $\text{Ba}_2\text{TiSi}_2\text{O}_8$ crystals reveal interesting dielectric and optical features such as piezoelectricity and ferroelectricity, and in addition, Takahashi *et al.*^{9,10} reported that surface crystallized glasses consisting of $\text{Ba}_2\text{TiGe}_2\text{O}_8$ crystals show the large second order optical nonlinearity comparable to that of LiNbO₃ single crystal. It is, therefore, of interest to write crystal lines consisting of $\text{Ba}_2\text{TiGe}_2\text{O}_8$ and $\text{Ba}_2\text{TiSi}_2\text{O}_8$ nonlinear optical crystal lines in glass.

The compositions of the base glasses examined in this study are 33.3BaO.16.7TiO₂.50GeO₂ (designated here as BTG50 glass) and 33.3BaO.16.7TiO₂.50SiO₂ (mol %) (BTS50 glass), and the base glasses were prepared by a conventional melt quenching method. Details of the base glass preparation have been described elsewhere.^{9,10} The plate shaped BTG50 and BTS50 glasses were pulverized, and glass powders were well mixed with Fe₂O₃, NiO, and V₂O₅ powders. The amounts of Fe₂O₃, NiO, and V₂O₅ powders were 0.3–1 mol %. The mixed powders were again melted at 1350 or 1500 °C for 10 min in a platinum crucible with a lid. By pouring and quenching the melts, the plate shaped BTG50 and BTS50 glasses containing transition metal ions with a thickness of ~1 mm were prepared.

The glass transition, T_g , and crystallization onset, T_x , temperatures were determined using differential thermal analyses (DTAs) at a heating rate of 10 K min⁻¹. The quenched glasses were annealed at around T_g to release internal stress and then polished mechanically to get a mirror finish with CeO₂ powders. Since iron and vanadium ions have polyvalent states such as Fe²⁺/Fe³⁺ and V⁴⁺/V⁵⁺, the valence states were changed by heat treatment at 670 °C for 1 h in 7% H₂–93% Ar mixed gas atmosphere. Optical absorption spectra at room temperature were taken in the wavelength range of 190–3200 nm on a Shimadzu UV-3150 spectrometer.

A cw Nd:YAG laser with $\lambda=1064$ nm was irradiated to the polished surface of the glasses. The laser beam was focused on the surface of the glasses using an objective lens

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

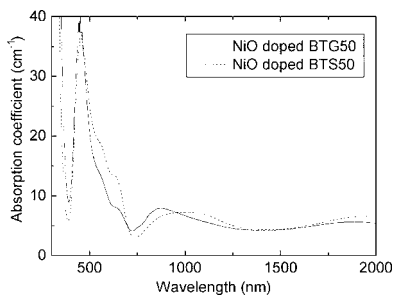


FIG. 1. Optical absorption spectra for the NiO (1 mol %)-doped BTG50 (solid line) and BTS50 (dashed line) glasses.

(magnifications 20 and 60) and the sample stage was automatically moved during laser irradiations to construct line patterns. Details of the laser irradiations were described elsewhere.^{4,5} Crystal lines written 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 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 against incident lasers. A *Y*-cut quartz crystal plate (0.6 mm thickness) was used as a reference of SH intensity.⁵ Micro-Raman-scattering spectra at room temperature for the precursor glasses and crystal lines written by YAG laser irradiation were measured with a laser microscope (Tokyo Instruments Co., Nanofinder) operated at an Ar⁺ (488 nm) laser.

Figure 1 shows the optical absorption spectra at room temperature for NiO (1 mol %)-doped BTG and BTS glasses. The absorption bands around 300–600 and 750–1400 nm are attributed to ${}^3A_2 \rightarrow {}^3T_1$ and ${}^3A_2 \rightarrow {}^3T_2$ transition in sixfold Ni²⁺ ions.¹¹ The absorption coefficients, α , at 1064 nm are $\alpha=6.01$ cm⁻¹ for NiO-doped BTG50 glass and $\alpha=7.18$ cm⁻¹ for NiO-doped BTS50 glass. These absorption coefficients are comparable to those for Sm₂O₃ (10 mol %)-doped glasses, e.g., $\alpha=4.5$ cm⁻¹ for 10Sm₂O₃.40BaO.50B₂O₃ glass,⁵ and it is expected that YAG laser irradiated spots in NiO-doped glasses would be heated.

The polarization optical micrographs for the samples obtained by YAG laser irradiation (power: $P=0.85$ W; scanning speed: $S=5$ μ m/s) in NiO-doped BTG50 and BTS50 glasses are shown in Fig. 2. The structural modifications with a width of approximately 5 μ m giving the refractive index changes are clearly observed in both samples. The micro-Raman-scattering spectra for the laser irradiated regions are also shown in Fig. 2, giving some sharp peaks and thus suggesting the formation of crystals. The positions of the peaks shown in Fig. 2 are well consistent with those for Ba₂TiGe₂O₈ and Ba₂TiSi₂O₈ single crystals.¹² It is, therefore, concluded that the lines written by YAG laser irradiation in NiO-doped BTG50 and BTS50 glasses consist of Ba₂TiGe₂O₈ and Ba₂TiSi₂O₈ crystals, respectively.

Considering the mechanism of YAG laser-induced crystallization in Sm₂O₃- or Dy₂O₃-doped glasses,^{3–8} YAG laser-induced crystallization in NiO-doped BTG50 and BTS50 glasses demonstrated in this study would be considered as follows. Some lasers irradiated to NiO-doped glasses are first absorbed through the *d-d* transitions (${}^3A_2 \rightarrow {}^3T_2$ transition) of Ni²⁺ ions, and then absorbed laser energies are dissipated to

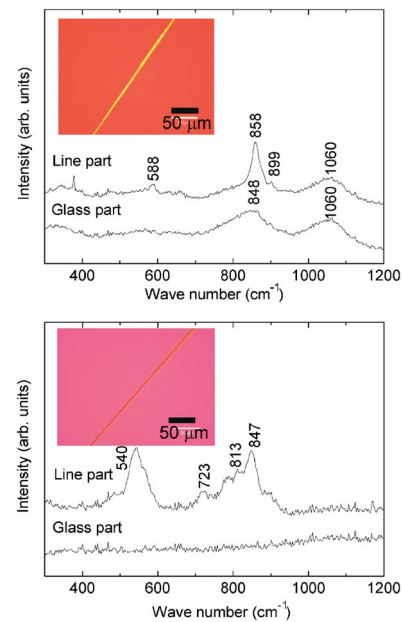


FIG. 2. (Color online) Polarization optical micrographs and micro-Raman-scattering spectra for the lines written by YAG laser irradiation. (a) NiO (1 mol %)-doped BTG50 glass and (b) NiO (1 mol %)-doped BTS50 glass.

the lattice surrounding TM ions by nonradiative relaxation process, consequently giving the increase in temperature in the laser irradiated region and inducing crystallization. The BTG50 glass has the values of $T_g=670$ and $T_x=780$ °C, and the BTS50 glass indicates $T_g=743$ and $T_x=846$ °C. It is, therefore, considered that the temperature of the YAG laser irradiated region in NiO-doped BTG50 and BTS50 glasses would rise at least up to around 850 °C. In other words, a small addition of 1 mol % NiO is effective in the heating of glasses by cw Nd:YAG laser irradiation.

Figure 3 shows the optical absorption spectra for V₂O₅ (0.7 mol %)- and Fe₂O₃ (0.3 mol %)-doped BTG50 glasses obtained by heat treatment at around T_g in 7% H₂–93% Ar mixed gas atmosphere. In both samples, the optical absorption coefficient at around $\lambda=1000$ nm increases due to the heat treatment in 7% H₂–93% Ar mixed gas atmosphere, i.e., in the reducing atmosphere. In the glass science field, it is well known that V³⁺, V⁴⁺, and Fe²⁺ ions in glass^{13,14} give optical absorptions at around $\lambda=1000$ nm. On the contrary, V⁵⁺ and Fe³⁺ ions do not show any strong absorption at around $\lambda=1000$ nm. The data shown in Fig. 3, therefore, indicate that some amounts of V⁵⁺ and Fe³⁺ ions present in the quenched glasses are reduced to V³⁺, V⁴⁺, and Fe²⁺ ions during the heat treatment at 670 °C for 1 h in 7% H₂–93% Ar mixed gas atmosphere. The absorption coefficients at 1064 nm were increased from 0.92 to 1.04 in V₂O₅-doped and 1.75 to 2.22 cm⁻¹ in Fe₂O₃-doped glasses due to the reducing treatment. Furthermore, from optical microscope observations for the cross section of the glass surface, it was confirmed that the thickness (depth) of the reducing layer at the surface is ~ 150 μ m. It is considered that the difference of the absorption coefficients between the quenched and reduced samples corresponds to the absorption coefficients of TM ions at the surface.

A cw Nd:YAG laser (power: ≤ 1.0 W) was irradiated to the quenched and reduced samples of V₂O₅- and Fe₂O₃-doped BTG50 glasses. In the case of the quenched samples without doing any reducing treatments, no crystallization was induced in both V₂O₅- and Fe₂O₃-doped BTG50

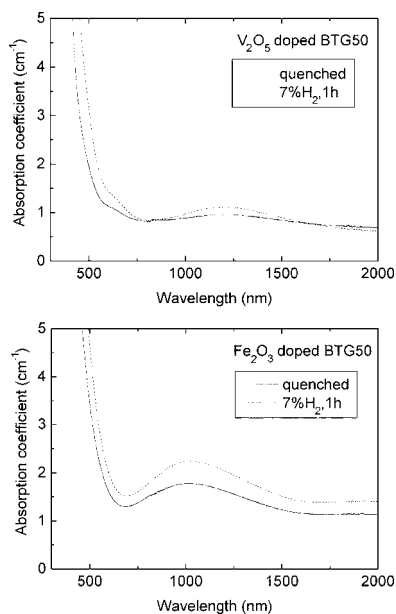


FIG. 3. Optical absorption spectra for V_2O_5 (0.7 mol %)- and Fe_2O_3 (0.3 mol %)-doped BTG50 glasses obtained by heat treatment ($670^\circ C$, 1 h) in 7% H_2 -93% Ar mixed gas atmosphere. The data on the quenched samples are also shown.

glasses. On the other hand, in the case of the samples reduced in 7% H_2 -93% Ar mixed gas atmosphere, it was confirmed from micro-Raman-scattering spectra that the crystallization is induced by Nd:YAG laser irradiation ($P=1.0$ W, $S=7\ \mu m\ s^{-1}$) and the lines consist of $Ba_2TiGe_2O_8$ crystals, similar to the case of NiO-doped BTG50 glass. It is considered that the temperature of the YAG laser irradiated region is very sensitive to the amount of V^{3+} , V^{4+} , and Fe^{2+} ions.

The SH wave images (the intensities of green light with $\lambda=532$ nm) observed from a crystal line written by YAG laser irradiation in Fe_2O_3 -doped BTG50 glass, i.e., the azimuthal dependence, are shown in Fig. 4. It is seen that the SH intensity is almost uniform over a whole line at each polarization angle (angle between the crystal line and linearly polarized incident laser). The maximum SH intensity is observed at the angle of 90° . This angle means that an electric field of incident light is perpendicular to the writing direction of crystal line, and it is considered that the polarization direction of $Ba_2TiGe_2O_8$ crystals in the crystal line is perpendicular to the writing direction. The same results have been observed in the case of β - BaB_2O_4 crystal lines written by YAG laser irradiation.⁵ It is necessary to study more for the determination of the growth direction of $Ba_2TiGe_2O_8$ crystals in the lines.

In the REAH processing, it is a key point to find glasses containing large amounts (8–15 mol %) of Sm_2O_3 or Dy_2O_3 . On the contrary, in the case of TM ions, the doping amount of NiO, Fe_2O_3 , or V_2O_5 is small, i.e., 0.3–1 mol %. Generally, transition metal ions such as nickel, iron, and vanadium in oxide glasses have broad $d-d$ band transitions compared to rare-earth ions ($f-f$ transitions). The absorption and nonradiative relaxation (electron-phonon coupling) in the outermost d electrons of TM ions might induce efficient YAG laser-induced heating. In the present study, crystal lines have been written on the surface of glasses, but controlling reducing positions of TM ions, it might be possible to write crystal lines in the interior of glasses. Finally, we propose

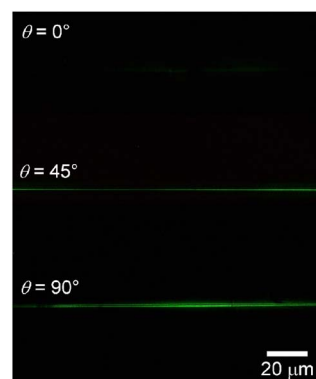


FIG. 4. (Color online) Second harmonic wave images from a crystal line written by YAG laser irradiation in Fe_2O_3 (0.3 mol %)-doped BTG50 glass obtained by heat treatment ($670^\circ C$, 1 h) in 7% H_2 -93% Ar mixed gas atmosphere. θ is the angle of the crystal line against linearly polarized incident laser.

that the technique developed in this study is called “transition metal atom heat processing.” Since the doping amount of TM ions is small, this technique will be widely applicable to other glass systems.

In conclusion, a technique for the writing of crystal lines in glasses was developed, in which continuous-wave Nd:YAG laser (wavelength: $\lambda=1064$ nm) was irradiated to the glasses containing TM ions. The crystal lines consisting of nonlinear optical fersnoite-type $Ba_2TiGe_2O_8$ and $Ba_2TiSi_2O_8$ crystals were patterned in NiO-, Fe_2O_3 -, and V_2O_5 -doped (0.3–1 mol %) BaO-TiO₂-GeO₂ and BaO-TiO₂-SiO₂ glasses. It was found that the absorption and nonradiative relaxation process in the $d-d$ transitions of TM ions are effective for YAG laser-induced heating. The technique developed in this study was proposed to be called “transition metal atom heat processing.”

This work was supported from Ministry of Internal Affairs and Communications Strategic Information and Communications R&D Promotion Programs (SCOPE), Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, Culture and Technology, Japan, and by the 21st Century Center of Excellence (COE) Program in Nagoya University of Technology.

- ¹K. O. Hill, B. Malo, F. Bilodeau, D. C. Johnson, and J. Albert, *Appl. Phys. Lett.* **62**, 1035 (1993).
- ²T. Fujiwara, R. Ogawa, Y. Takahashi, Y. Benino, T. Komatsu, and J. Nishii, *Phys. Chem. Glasses* **43C**, 213 (2002).
- ³R. Sato, Y. Benino, T. Fujiwara, and T. Komatsu, *J. Non-Cryst. Solids* **289**, 228 (2001).
- ⁴T. Honma, Y. Benino, T. Fujiwara, T. Komatsu, and R. Sato, *Appl. Phys. Lett.* **82**, 892 (2003).
- ⁵T. Honma, Y. Benino, T. Fujiwara, T. Komatsu, and R. Sato, *Appl. Phys. Lett.* **83**, 2796 (2003).
- ⁶M. Abe, Y. Benino, T. Fujiwara, R. Sato, and T. Komatsu, *J. Appl. Phys.* **97**, 123516 (2005).
- ⁷N. Chayapiwut, T. Honma, Y. Benino, T. Fujiwara, and T. Komatsu, *J. Solid State Chem.* **178**, 3507 (2005).
- ⁸R. Ihara, T. Honma, Y. Benino, T. Fujiwara, R. Sato, and T. Komatsu, *Solid State Commun.* **136**, 273 (2005).
- ⁹Y. Takahashi, Y. Benino, T. Fujiwara, and T. Komatsu, *Appl. Phys. Lett.* **81**, 223 (2002).
- ¹⁰Y. Takahashi, Y. Benino, T. Fujiwara, and T. Komatsu, *J. Appl. Phys.* **95**, 3503 (2004).
- ¹¹J. S. Berkes and W. B. White, *Phys. Chem. Glasses* **7**, 191 (1966).
- ¹²Th. G. Mayerhofer and H. H. Dunken, *Vib. Spectrosc.* **25**, 185 (2001).
- ¹³W. Johnstone, *J. Am. Ceram. Soc.* **48**, 608 (1965).
- ¹⁴C. R. Bamford, *Phys. Chem. Glasses* **4**, 173 (1962).