Laser-induced crystallization in glass is a new crystallization technique of glass materials. This article reports the progress in the patterning of nonlinear optical crystal lines on the glass surface by laser irradiation techniques. Two techniques for the patterning of crystal lines have been developed, i.e., rare-earth atom heat processing and transition metal atom heat processing, in which continuous-wave lasers such as Nd:YAG laser (wavelength: $\lambda = 1064$ nm) are irradiated onto the glasses containing rare-earth ions such as Sm$^{3+}$ and Dy$^{3+}$ or transition metal ions. We introduced these atomic laser heating techniques for the patterning of nonlinear optical crystal lines on the glass surface by laser irradiation techniques. Two techniques for the patterning of crystal lines in glasses might be, therefore, called “Rare-earth atom heat processing” and “Transition metal atom heat processing.”

1. Introduction

Glass is the key materials in microelectronics, optics, and optical fiber technologies because of their high transparency, high chemical durability and good thermal stability. However, glass has the inversion symmetry, and therefore, glass should not generate the second order optical nonlinearity, $\chi^{(2)}$. This has generally brought glass materials only to passive usages like optical glass fibers, while second-order optical nonlinearity is the property absolutely required to active applications such as electrooptic switching and wavelength conversion by second-harmonic generation (SHG). Active devices, which require the second-order optical nonlinearity, have been realized by the use of organic and inorganic crystal materials. The study about introducing second ordered optical nonlinearity in glass materials has been reported.[1]-[4] Transparent crystallized glasses, i.e., composites of crystalline and glassy phases, also give permanent second order optical nonlinearities. For instance, Komatsu et al.[5,6] developed transparent TeO$_2$-based crystallized glasses consisting of nonlinear optical nanocrystals. Other crystallized glasses with typical nonlinear optical crystals for optics such as LiNbO$_3$ (LN), $\beta$-BaB$_2$O$_4$ ($\beta$-BBO), SrBi$_2$Ta$_2$O$_9$, LaBGeO$_5$ (LBGO), Ba$_2$TiGe$_2$O$_8$ (BTG) and Ba$_2$TiSi$_2$O$_8$ (BTS) have been prepared.[7]-[12] Especially Takahashi et al.[13] fabricated transparent surface crystallized glasses consisting of c-axis oriented BTG crystals and found that they show the large second order optical nonlinearity ($d_{31} \sim 22$ pm/V) comparable to that of LiNbO$_3$ single crystal.

If we chose crystallized glass for the second order optical nonlinear application, we must pay attention to control transparency as well as orientation of crystal to introduce large optical nonlinearity. Usually, crystallized glasses are fabricated using well-controlled heat treatments in an electric furnace, and desired crystals are formed at the surface or in the interior of glass. In this kind of heat treatment method, it is generally difficult to induce crystallization in spatially selected regions. Furthermore when we make surface oriented crystallized glass, uni-axis orientation perpendicular to the glass surface occur, however we could not control the orientation in surface. It is of interest and of importance to develop glass/crystal hybrid materials, in which functional crystals are induced in a desired part in a given glass matrix. Such hybrid materials will have a high potential for practical applications in various active devices.

On the other hand, laser irradiation to glass has been regarded as a process for spatially selected structural modification and/or crystallization in glass.[13]-[18] A periodic structure consisting of arrangements of ordered nano crystals has been fabricated in TeO$_2$ based glasses through XeCl eximer laser (wavelength $\lambda = 308$ nm) irradiation by Fujiwara et al.[15]-[18] It seems that laser modification technique is necessary to fabricate periodic structure such as quasi phase matching structure and/or Bragg gratings structure for a use of optical wave-guides.

By the way, involving absorption of electromagnetic radiation in a solid, there is a subsequent complementary evolution of heat. This heat results from the non-radiative relaxation of the excitation. It is known that photoluminescence phenomena of transition metal or rare-earth ion doped glass involve non-radiative relaxation process. The study of non-radiative relaxation in solids is focused to develop laser material from 1960’s. To develop laser host materials with good quantum efficiency, it is very important how to quantitively and eliminate non-radiative factor in these materials. Photo thermal spectroscopy[19] and Photo acoustic spectroscopy[20] methods are typical quantitative method of non-radiative relaxation. However nobody took any notice on local processing or local crystallization in tiny region of glass by using of non-radiative relaxation process.

The author’s group[21,35,38,42,44]-[46] 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. This technique for the writing of crystal dots and lines in glasses might be, therefore, called “Rare-earth atom heat...
processing” (REAH). By using REAH technique, present authors have succeeded in patterning of single crystal lines consisting of nonlinear optical crystals in some glasses.

Recently, the present author’s group also proposed a transition metal atom (such as V^{3+}, V^{4+}, Fe^{2+}, Ni^{2+}, Cu^{2+}) heat processing technique (TMAH), instead of REAH processing.\(^{39)-(41),(45)-(48),(57)\) 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+}. In this paper, we review the crystal line patterning in glasses fabricated by REAH and TMAH processing. Especially, we discuss about the morphology and second harmonic generation of crystal lines consisting of nonlinear optical crystals.

2. Mechanism of laser-induced local heating

Sato et al. examined the laser-induced crystallization behavior by samarium atom heat processing technique at first.\(^{21)}\) They confirmed the formation of Sm_{2}Te_{6}O_{15} micro-crystalline dots on 10Sm_{2}O_{3}–10BaO–80TeO_{2} glass and proposed the crystallization mechanism as follows: Since Sm^{3+} has an absorption band around 1064 nm as shown in Fig. 1(a), some amounts of cw Nd:YAG laser are absorbed by Sm^{3+} in glass through f–f transitions (\(^{6}F_{9/2} \rightarrow ^{4}H_{5/2}\)), consequently inducing thermal effects through continuous electron-phonon coupling. We found the same behavior in dysprosium (Dy^{3+}) containing glasses, and recently Gupta et al.\(^{43)}\) 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_{2}O_{3}–La_{2}O_{3}–B_{2}O_{3}–GeO_{2} glass. Nd^{3+} has the absorption band around 800 nm and shows the non-radiative relaxation inducing thermal effects. Using REAH processing, we examined the patterning of crystalline dots or lines in various glasses. Especially, we reported the formation of single crystal lines consisting of nonlinear optical BiBO_{3}\(^{26)}\) and \(\beta\)-BaB_{2}O_{4} (\(\beta\)-BBO)\(^{30)}\) crystals in Sm_{2}O_{3}–Bi_{2}O_{3}–B_{2}O_{3} and Sm_{2}O_{3}(Dy_{2}O_{3})–BaO–B_{2}O_{3} glasses. Furthermore, Ihara et al.\(^{29)}\) 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).

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 prerequisite to prepare glasses with some amounts (approximately more than 8 mol% at \(P = 1.0\) W) of Sm_{2}O_{3}, meaning some limitations of the application of REAH processing for the writing of crystal lines in glass. It is well known that transition metal ions such as V^{4+}, Fe^{2+} and Ni^{2+} in glass give rise to absorption bands in the visible and near infrared spectral regions. For instance, Fig. 1(b) shows the optical absorption spectra at room temperature for 1 mol% NiO containing BaO–TiO_{2}–GeO_{2} glass. The absorption bands around 300–600 and 750–1400 nm are attributed to \(^{3}A_{2} \rightarrow ^{3}T_{1}\) and \(^{3}A_{2} \rightarrow ^{3}T_{2}\) transition in six-fold Ni^{2+} ions.\(^{49)}\) The absorption coefficients, \(\alpha\), at 1064 nm are \(\alpha = 6.0\) cm\(^{-1}\) for 1NiO–33.3BaO–16.7TiO_{2}–50GeO_{2} glass. This absorption coefficient is comparable to those for 10Sm_{2}O_{3}–40BaO–50B_{2}O_{3} glasses (\(\alpha = 4.5\) cm\(^{-1}\)), and it is found that YAG laser irradiated spots in NiO-doped glasses can be crystallize. A glass with the composition of 33.3BaO–16.7TiO_{2}–50GeO_{2} has the values of glass transition of 670°C and crystallization of 780°C. It is, therefore, considered that the temperature of the YAG laser irradiated region in NiO doped glass would raise at least up to around 780°C. And present author’s group also confirmed laser-induced crystallizations in Fe^{2+}, V^{3+}, V^{4+} and Cu^{2+} containing glasses by YAG laser irradiation.\(^{39)-(41)}\)

3. Writing of crystal line and its morphology

As mentioned above, single-crystal or tailored crystallized patterns by REAH and TMAH processing are easily fabricated. For instance, the polarized optical micrographs for the sample obtained by Nd:YAG laser irradiations in 10Sm_{2}O_{3}–35Bi_{2}O_{3}–55B_{2}O_{3} glass are shown in Fig. 2, where Nd:YAG laser power with \(P = 0.6–0.8\) W and scanning speeds with \(S = 10\) μm/s was.
irradiated on the glass surface. In the laser power of $P = 0.6$ W, it was found from the micro-Raman scattering spectrum that the line is not crystal, but glass, indicating the formation of refractive index change. In $P = 0.66$ W, a homogenous crystal line with a uniform width of $\sim 5 \mu m$ was clearly patterned. When the laser power is higher than 0.8 W, crystals with a rough morphology grow, as shown in Fig. 2.

The $\beta$-BBO single crystal formation in Sm$_2$O$_3$–BaO–B$_2$O$_3$ glasses by X-ray diffraction analysis and polarization micro Raman scattering spectra. $\beta$-BBO crystallized pattern has the $c$-axis orientation along to the laser scanning direction in REAH processing. The direction of BiBO$_3$ orientation, i.e., uni-axial growth, is decided by self-organization even though the scanning direction changes drastically. $\beta$'-Gd$_2$(MoO$_4$)$_3$ (designate as GMO) is a well known ferroelastic and ferroelectric crystals. By using laser irradiation technique GMO line patterns exhibits unique morphology as shown in Fig. 3. Laser scanning formed self-organized periodical domain structure. It is, therefore, obvious that there are an optimal glass composition and laser irradiation conditions to obtain single crystal patterns for each target crystal.

On the other hand, niobate based crystals such as lithium niobate LiNbO$_3$ (LN) and strontium barium niobate Sr$_{1-x}$Ba$_x$Nb$_2$O$_6$ (SBN) are important ferroelectrics, and they have been used in various devices such as surface acoustic wave devices and phase modulator waveguides in integrated optics due to their excellent electro-optical, pyroelectrical, piezoelectrical and photorefractive properties. In SBN glass ceramics, we succeeded the fabrication of laser-induced crystallization and transparent glass ceramics, in which has electro optical effect. It is, therefore, of particular interest and of importance to develop glasses crystallizing LN or SBN and to pattern their crystals in glasses. We succeeded the writing of crystal lines consisting of LN on the surface of Li$_2$O–Nb$_2$O$_5$–SiO$_2$–B$_2$O$_3$ glass with an addition of CuO or Sm$_2$O$_3$ as absorbents of laser light. Figure 4 shows the polarized optical micrographs for the lines obtained by laser irradiations on the glass surface with a suitable condition in the glasses. The optimal conditions of laser power and scanning speed are also shown in the figure. The structural modifications with a width of 2–5 $\mu m$ giving a smooth retardation are clearly observed. There are clear polarization dependences in Fig. 4. To identify the crystalline phase in laser written lines, we examined the electron backscattered diffraction (EBSD) measurements. Figure 5 is a high-resolution SEM image and EBSD patterns of the laser written patterns on Cu–LNS glass. It is clearly observed kikuchi lines on a laser inducing point because of the crystallization by laser irradiations. By analyzing the EBSD pattern, the crystalline phase was identified as LiNbO$_3$ crystal. By using the EBSD technique the crystal orientation can be determined as c- (mostly) or a-axis growth by collecting inverse pole figure map around the laser written region.

![Fig. 3. Polarized optical micrograph for the $\beta$-Gd$_2$(MoO$_4$)$_3$ crystal patterns obtained by Yb-fiber laser irradiations with a laser power of $P = 1.2$ W and a laser scanning speeds of $S = 5 \mu m/s$ in 35mO$_2$–18.25Gd$_2$O$_3$–63.75MoO$_3$–15B$_2$O$_3$ glass.](image)

![Fig. 4. Polarized optical micrographs of the laser written LiNbO$_3$ patterns on (a) 0.5CuO–0.3Er$_2$O$_3$–40Li$_2$O–32Nb$_2$O$_5$–28SiO$_2$ glass and (b) 5Sm$_2$O$_3$–35Li$_2$O–30Nb$_2$O$_5$–20SiO$_2$–15B$_2$O$_3$ glass.](image)

![Fig. 5. SEM image and electron backscattered diffraction (EBSD) pattern of LiNbO$_3$ crystal line on 0.5CuO–0.3Er$_2$O$_3$–40Li$_2$O–32Nb$_2$O$_5$–28SiO$_2$ glass.](image)
We obtained the results of c-axis growth along with the scanning direction by means of polarized micro-Raman scattering spectroscopy.46) The results of EBSD47) would support the c-axis growth obtained in the Raman study as shown in Fig. 6 and second harmonic intensity measurements as shown in Fig. 7.46) Some readers may worry about the loss of optical transmission due to transition metal ion presence. But most of doped Cu2+ ions easily precipitate on glass surface as Cu metal by reduced heat treatment.48) In the growth of LN single crystals, the preferred growth directions are a and c directions. In the writing of β-BBO and Ba2TiX2O8 (X = Ge and Si) by laser irradiations, we obtained only c-axis grown lines. The growth directions of laser-induced lines are related with anisotropic atom packing giving the anisotropic growth rate. β-BBO and Ba2TiX2O8 are having layered crystal structures and hence the degree of the anisotropy of atom packing between a and c axes is very high. On the other hand, LN crystal doesn’t have any layered structures. Therefore, it is considered that LN crystals exhibit a and c axis preferred growths in the line writing by laser irradiations.

4. Crystal growth kinetics by laser scanning

Many studies on the crystallization behaviors in Li2O–2SiO2 glasses have been reported so far, and nucleation and crystal growth rates of Li2Si2O5 crystals in the crystallization in electric furnaces have been clarified as a function of heat treatment temperature.50)–56) It is, therefore, of interest to pattern Li2Si2O5 crystal lines by laser irradiations and to clarify crystal growth behaviors in the laser-induced crystallization for Li2O–2SiO2 glasses.57) The composition of base glass Li2O–2SiO2 corresponds to that of the Li2Si2O5 crystalline phase, and CuO is added as absorbent for irradiated lasers. The compositions of the glasses examined in this study are xCuO–33.3Li2O–66.7SiO2 with x = 0, 1, and 2 (in the molar ratio). The glasses were prepared by a conventional melt quenching method.

The fiber lasers with λ = 1080 nm were irradiated onto the surface of 1CuO-doped glass, in which the laser power \( P \) was 2.1–2.3 W and the laser scanning speed \( S \) was 2–32 \( \mu \)m/s. The polarized optical micrographs for the samples obtained by laser irradiations are shown in Fig. 8. The morphological changes with a width of ~5 \( \mu \)m are clearly observed. Except the line patterned...
by the laser irradiations with $P = 2.3 \text{ W}$ and $S = 2 \mu \text{m/s}$ in Fig. 8, each line shows a homogeneous color’s distribution along the scanning direction, indicating that a stable structural change is taking place under a given laser irradiation condition.

For $1\text{CuO–33.3Li}_2\text{O–66.7SiO}_2$ and $2\text{CuO–33.3Li}_2\text{O–66.7SiO}_2$ glass, laser irradiation experiments at various laser powers and scanning speeds were carried out, and the formation of $\text{Li}_2\text{Si}_2\text{O}_5$ crystals was examined from micro-Raman scattering spectrum measurements. The values of crystal growth rate $U_{\text{crystal}}$ determined from these experiments are summarized in Fig. 9. For $2\text{CuO}$-doped glass, $\text{Li}_2\text{Si}_2\text{O}_5$ crystals are induced by small laser powers compared with $1\text{CuO}$-doped glass. It is considered that the temperature of the laser-irradiated region increases with increasing $\text{Cu}^{2+}$ content and laser powers, and thus the results shown in Fig. 9 would be reasonable. It should be pointed out that plate-shape glass samples were fractured under the laser irradiation conditions with the scanning speeds of over $S = 50 \mu \text{m/s}$. Since the laser irradiation gives a rapid heating and rapid cooling, plate-shape glasses would be fractured due to laser-induced thermal stresses. The values of $U_{\text{crystal}}$ in the present study are, therefore, ranging from 1 to $40 \mu \text{m/s}$.

Burger and Weinberg summarized the data of the isothermal crystal growth rates of $\text{Li}_2\text{Si}_2\text{O}_5$ at various temperatures in $\text{Li}_2\text{O–2SiO}_2$ glasses reported by many researchers. We reproduced the data summarized by them in Fig. 10 in this paper and marked the values of $U_{\text{crystal}} = 1–40 \mu \text{m/s}$ obtained in the present study with a solid line circle. Although in laser induced crystal growth we have to consider non-isothermal process due to local thermal gradient. However the influence would be smaller in lower scanning speeds. It is seen that the values of $U_{\text{crystal}} = 1–40 \mu \text{m/s}$ correspond to the isothermal crystal growth rates at the temperature range of 650–850°C. It is noted that these temperatures are considerably high compared with the values of the glass transition ($T_g = 450–454^\circ \text{C}$) and crystallization peak ($T_p = 586–651^\circ \text{C}$) temperatures in the $\text{CuO}$-doped $33.3\text{Li}_2\text{O–63.7SiO}_2$ glasses examined in this study. It is expected that in such high temperatures of 650–850°C nucleation rates of $\text{Li}_2\text{Si}_2\text{O}_5$ crystals would be small. Furthermore, as seen in Fig. 9, the values of $U_{\text{crystal}} = 1–40 \mu \text{m/s}$ are located at the side being close to the maximum isothermal crystal growth rate $U_{\text{max}}$. This might be one reason for the successful patterning of homogeneous crystal lines consisting of oriented $\text{Li}_2\text{Si}_2\text{O}_5$ crystals in the laser irradiations for $\text{CuO}$-doped $33.3\text{Li}_2\text{O–66.7SiO}_2$ glasses.

5. Conclusion

It was clarified from the azimuthal dependence of second harmonic intensities, polarized micro-Raman scattering spectra and electron back scattering pattern that crystals in the lines are highly oriented along the laser scanning direction, i.e., the patterning of single-like crystal lines. The laser-induced crystallization technique would open a new door for the fabrication processing of light control optical devices.

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References

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