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Formation of $LiNbO_3$ crystals at the surface of TeO_2-based glass by YAG laser-induced crystallization

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Abstract

Lithium niobate $LiNbO_3$ crystals were formed at the surface of CuO (1 mol%)-doped $25Li_2O$–$25Nb_2O_5$–$50TeO_2$ glass (mol%) by heat-assisted (150 °C) continuous-wave Nd:YAG laser irradiations with a wavelength of $\lambda = 1064$ nm. Nd:YAG laser energies absorbed by Cu^{2+} ions (d–d transitions) were converted to the lattice vibrations of surrounding Cu^{2+} ions (nonradiative relaxations), giving the increase in the temperature of the laser irradiated local region. The formation of $LiNbO_3$ crystals was confirmed from micro-Raman scattering spectra. For the line patterned by a laser scanning with a power of 0.59 W and a speed of 6 μm/s, the possibility of a *c*-axis orientation of $LiNbO_3$ crystals along the laser scanning direction was proposed. The present study demonstrates that the combination of Cu^{2+} and Nd:YAG laser with $\lambda = 1064$ nm, i.e. transition metal atom heat processing, is effective in inducting $LiNbO_3$ crystals in TeO_2-based glasses.

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1. Introduction

Laser-induced crystallization in glass has received much attention, because functional crystals are designed in a spatially selected part of a given glass [1–5]. A phenomenon taking place during laser irradiation in glass depends on a combination of laser (wavelength, power, irradiation time) and glass material (system, composition, thermal stability). Recently, Honma et al. [6] proposed a technique called "transition metal atom heat (TMAH) processing" for laser-induced crystallization in glass, in which a continuous-wave (cw) Nd:yttrium aluminum garnet (YAG) laser with a wavelength of $\lambda = 1064$ nm is irradiated to glasses containing transition metal (TM) ions such as Ni^{2+} and Cu^{2+}. Irradiated lasers are absorbed by TM ions through d–d transitions, and absorbed energies are converted to thermal energies through nonradiative relaxation process (electron–phonon couplings). And thus surroundings of TM ions are heated locally, consequently inducing crystallization in glass. Using this TMAH processing, highly oriented single-like crystal lines consisting of nonlinear optical $Ba_2TiGe_2O_8$ or $Ba_2TiSi_2O_8$ crystals have been patterned at the surface of BaO–TiO_2–GeO_2 or SiO_2 glasses by just scanning lasers [6].

$LiNbO_3$ is one of the most important ferroelectrics and has been used in various devices such as surface acoustic wave devices and waveguides in integrated optics due to its excellent electro-optical, pyroelectrical, piezoelectrical and photorefractive properties [7,8]. Usually $LiNbO_3$-related devices have been fabricated using $LiNbO_3$ single crystals. Patterning of $LiNbO_3$ single crystal lines at the glass surface is of interest, and if possible, various technical applications would be expected in electro-optic and photonic devices.

Crystallizations of $LiNbO_3$ in glasses by using heat treatment methods in an electric furnace have been reported so far [9–13], and recently laser-induced crystallizations of $LiNbO_3$ have been tried [14,15]. There has been, however, no report on the patterning of crystal lines with $LiNbO_3$ in glass. In this study, we focus our attention on the patterning of $LiNbO_3$ crystal lines at the surface of Li_2O–Nb_2O_5–TeO_2 glass using laser-induced crystallization technique, i.e., TMAH processing. We succeeded in writing $LiNbO_3$ crystal lines and examined the

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orientation of $LiNbO_3$ crystals in the lines from measurements of polarized micro-Raman scattering spectra.

2. Experimental

In this study, we used a glass with the composition of $25Li_2O$–$25Nb_2O_5$–$50TeO_2$ (mol%). Komatsu et al. [9] reported that $LiNbO_3$ crystals are formed in some Li_2O–Nb_2O_5–TeO_2 glasses such as $25Li_2O$–$25Nb_2O_5$–$50TeO_2$ using a conventional heat treatment method in an electric furnace. Furthermore, Shankar and Varma [13] examined the crystallization behaviour of Li_2O–Nb_2O_5–TeO_2 glasses in detailed and reported that $LiNbO_3$ microcrystallites were directly precipitated at the surface of $25Li_2O$–$25Nb_2O_5$–$50TeO_2$ glass by a single step heat treatment and transparent surface crystallized glasses exhibit second order optical nonlinearities and polar characteristics. In the laser-induced crystallization of TMAH processing, we need to include small amounts of TM ions in glass, and Cu^{2+} was selected in this study. The amount of 1 mol% CuO was added to $25Li_2O$–$25Nb_2O_5$–$50TeO_2$ glass.

The glass was prepared using a conventional melt quenching method. Commercial powders of reagent grade CuO, $LiCO_3$, Nb_2O_5, and TeO_2 were mixed and melted in a platinum crucible at 1050 °C for 1 h in an electric furnace. The melts were poured onto an iron plate and pressed to a thickness of ~1.5 mm with another iron plate. The glass transition, T_g, crystallization onset, T_x, and crystallization peak, T_p, temperatures were determined using a differential thermal analysis (DTA) at a heating rate of 10 K/min. Optical absorption spectrum was taken in the wavelength of 250–2000 nm on a Shimadzu UV-3150 spectrometer. The crystalline phases present in the crystallized samples were identified by X-ray diffraction (XRD) analyses (Cu Kα radiation) at room temperature.

The glasses were mechanically polished to a mirror finish with CeO_2 powders. A cw Nd:YAG laser with $\lambda = 1064$ nm was irradiated to the glass surface using an objective lens (20 magnification). The glasses were put on the stage and mechanically moved during laser irradiation to construct crystal lines. The morphology of crystal lines was observed with polarization optical and confocal scanning laser microscopes. Micro-Raman scattering spectra at room temperature for crystal lines were taken in the wavenumber (Raman shift) of 300–1200 cm^{-1} with a laser microscope (Tokyo Instruments Co., Nanofinder) operated at Ar^+ (488 nm) laser.

3. Results and discussion

The glassy state of the melt-quenched sample with the composition of $25Li_2O$–$25Nb_2O_5$–$50TeO_2$–$1CuO$ (mol ratio) (designated here as the base glass) was confirmed from XRD analyses, which showed only a halo pattern typical for amorphous materials. In the DTA pattern for the base glass, an endothermic peak due to the glass transition and an exothermic peak due to the crystallization were observed, giving the values of $T_g = 416$, $T_x = 495$ °C, and $T_p = 515$ °C. These values are almost the same as those ($T_g = 418$ °C and $T_x = 494$ °C) for $25Li_2O$–$25Nb_2O_5$–$50TeO_2$ glass

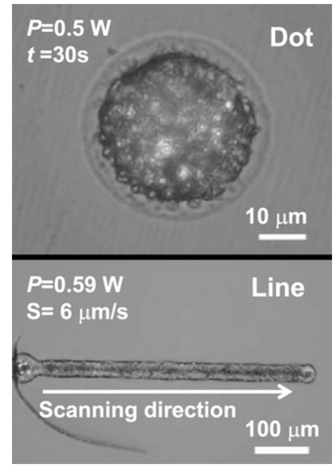

Fig. 1. Polarization optical micrographs for the dot obtained by Nd:YAG laser irradiations with a laser power of $P = 0.5$ W and an irradiation time of $t = 30$ s and for the line obtained by laser irradiations with $P = 0.59$ W and a scanning speed of $S = 6$ μm/s at the glass surface.

with no CuO reported by Komatsu et al. [9]. A broad and asymmetrical peak centered near 800 nm was observed in the optical absorption spectrum of the base glass. It is well known that Cu^{2+} ions with the electronic configuration of $3d^9$ in glass give a strong and broad absorption peak at around 800 nm, and this peak is assigned to the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition in Cu^{2+} ions in octahedral sites with strong tetragonal distortions [16,17]. The absorption coefficient, α, at 1064 nm was $\alpha = 6.0$ cm^{-1}. The glass was heat treated at 495 °C for 1 h in an electric furnace, and the formation of $LiNbO_3$ crystals was confirmed from XRD measurements, similar to $25Li_2O$–$25Nb_2O_5$–$50TeO_2$ glass without CuO [9,13].

The polarization optical micrographs for the dot obtained by laser irradiations with a laser power of $P = 0.5$ W and an irradiation time of $t = 30$ s and for the line obtained by laser irradiations with $P = 0.59$ W and a scanning speed of $S = 6$ μm/s are shown in Fig. 1. It is seen that structural changes are induced in the laser irradiated regions. The micro-Raman scattering spectra at room temperature for these dot and line are shown in Fig. 2 together with the spectrum for the base glass itself without any laser irradiations. Many sharp peaks are observed for the dot, indicating the crystallization in the laser irradiated region. The Raman scattering spectra for $LiNbO_3$ crystals have been reported so far [18–21]. The peaks at 272, 329, 365, 431, and 581 cm^{-1} for the dot shown in Fig. 2 are due to the bending and stretching modes of NbO_6 octahedra [18–21]. The peak at ~869 cm^{-1} would be associated to a deformation of NbO_6 octahedron [20,21]. The Raman scattering spectra shown in Fig. 2, therefore, indicate the formation of $LiNbO_3$ crystals by Nd:YAG laser irradiations in $25Li_2O$–$25Nb_2O_5$–$50TeO_2$–$1CuO$ glass. On the other hand, the peaks for the line are broad, and it is considered that the line would consist of a mixture of $LiNbO_3$ crystals and glassy phase. For both samples of the dot and line, second harmonic generations (SHGs) were confirmed in SHG microscope observations [22], indicating that $LiNbO_3$ crystals formed in the dot and line are nonlinear optical crystals.