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Review article

Laser patterning and characterization of optical active crystals in glasses

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ABSTRACT

This paper reports the recent progress in the laser patterning of optical active crystals such as $BaAlBO_3F_2$ and β-BaB_2O_4 in glasses. In the laser-induced crystallization using continuous-wave lasers such as Yb:YVO_4 fiber lasers (wavelength: 1080 nm), a steep temperature gradient is created in the laser-irradiated region, and highly oriented crystal lines are patterned at the glass surface. The quality and orientation of crystals patterned are characterized from the azimuthal dependence of second harmonic intensities, polarized micro-Raman scattering spectra, and transmission electron microscope observations. Two-dimensional planar crystals with high orientations are patterned by applying laser irradiations with large overlapping. The patterning of crystals in the inside of glass fibers is also possible by moving gradually laser focal point from the surface into the inside. The progress in the crystal patterning with desired morphologies and high orientations provides a high potential for optical active device applications.

Contents

1. Introduction

Glasses having high transparency, high chemical durability, and excellent thermal properties are key materials in microelectronics, optics, and optical fiber technology. As glass, however, has a random atomic arrangement with an inversion symmetry in its structure, generation of active functional properties such as second-order optical nonlinearity or ferroelectricity arising from anisotropic atomic arrangements cannot be expected in glass in principle. This has generally brought glass materials only to passive usages like optical glass fibers, while second-order optical nonlinearity or ferroelectricity is the property absolutely required to active applications such as electro-optic switching and wavelength conversion. One of the effective methods for fabrication of active glasses is to develop new functional glass-crystal hybrid materials, i.e., functional glass-ceramics or crystallized glasses. 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. So far, many optically transparent crystallized glasses containing active crystals have been reported. For instance, transparent

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surface crystallized glasses consisting of $Ba_2TiGe_2O_8$ crystals have been found to exhibit large second-order optical nonlinearities (i.e., ~20 pm/V) comparable to that of $LiNbO_3$ single crystals [1].

Laser-induced crystallization in glass has also received much attention, because in which active crystals are patterned only in spatially selected part [2–5]. Patterning of active crystals in glasses will have a high potential for practical applications in various active devices. Because glass has the thermodynamically non-equilibrium (metastable) state, all kinds of glasses tend to crystallize under the supply of sufficient energy and time giving atomic rearrangements. It is, therefore, very important not only to pattern optical active crystals but also to design crystals with desired morphologies such as high orientations just like single crystal or nano-scaled crystals. The phenomenon taking place during laser irradiations depends on the combination of the laser type and materials type (system, composition, thermal stability against crystallization). Indeed, different lasers such as continuous-wave (cw) Nd:YAG laser, femtosecond pulsed laser, and CO_2 laser have been applied to various glasses in order to induce structural modifications in glasses.

The present authors group proposed a laser irradiation technique for the patterning of active crystals at the glass surface, i.e., rare-earth atom heat (REAH) processing and transition metal atom heat (TMAH) processing [6–9], in which conventional lasers such as cw Nd:YAG lasers with a wavelength of λ = 1064 nm have been used for glasses containing rare-earth (RE) ions such as Sm^{3+} and Dy^{3+} and transition metal (TM) ions such as Ni^{2+} and Cu^{2+}. Using this technique, the present authors' group has succeeded in patterning optical active crystals such as $LiNbO_3$, β-BaB_2O_4, β′-$Sm_2(MoO_4)_3$, and (Sr,Ba)Nb_2O_6, which are summarized in Table 1 [5–54]. The data on the laser patterning of crystals reported by other research groups have been also summarized in Table 2 [55–76].

In this paper, we review the recent progress in the laser patterning of optical active crystals, in particular, focusing on the orientation of crystals. The features and mechanism of the laser-induced crystallization are also discussed, in which the importance of steep temperature gradient in the laser-irradiated region is emphasized.

2. Laser-induced crystallization technique and characterization

The principle of laser-induced crystallization techniques proposed by the present authors' group is described briefly. In REAH and TMAH processing [2–9], cw lasers such as Yb:YVO_4 lasers with λ = 1080 nm are irradiated onto glasses with some amounts of RE ions and TM ions. As RE ions and TM ions in glasses have absorption bands at around 1080 nm, some amounts of lasers are absorbed by RE ions through *f*–*f* transitions and TM ions through *d*–*d* transitions. As the main relaxation mechanism in these transitions is non-radiative, the laser energy absorbed by RE or TM ions is transferred to the lattice system (lattice vibrations) through electron-phonon coupling and the surrounding of RE or TM ions is heated. Consequently, if the temperature of the laser-irradiated region becomes higher than the glass transition or crystallization temperatures of a given glass, crystallization is induced. As the heat dissipation from the laser-irradiated region to the surrounding glass medium is expected to occur rapidly, it would be necessary to irradiate laser continuously to maintain high temperatures (greater than the crystallization temperature) and thus use cw type lasers for laser-induced crystallization in glass.

Typical methods for the patterning of crystal lines and their characterization are as follows. Laser beam is focused on the glass surface using objective lens (magnification 20–60) and sample stage is automatically moved during laser irradiations to construct line patterns. Crystal lines patterned by laser irradiations are examined with polarization optical microscope (POM) and confocal scanning laser microscope (CSLM) observations. Second harmonic (SH) intensity from crystal lines is measured by using a fundamental wave of Q-switched pulse Nd:YAG laser with λ = 1064 nm as a laser source, in which linearly polarized fundamental laser beams are introduced into crystal lines, and the azimuthal dependence of SH signals is measured by rotating the sample against incident lasers. Linearly polarized micro-Raman-scattering spectra at room temperature for crystal lines are measured with a laser microscope operated at Ar^+ laser (λ = 488 nm). The quality and orientation of crystals present in laser-patterned lines are also examined from transmission electron microscope (TEM) observations combined with a focused ion beam (FIB) method.

Table 1
Crystals patterned by irradiations of cw lasers (Nd:YAG with λ = 1064 nm, Yb:YVO_4 with λ = 1080 nm) in glasses reported by the present authors' group [6–54].

Glass system	Crystals	Features	Ref.
Sm_2O_3–BaO–TeO_2	$Sm_2Te_6O_{15}$	Dot, line	[6,10]
Li_2O–SiO_2	$Li_2Si_2O_5$	Line: orientation	[11]
Sm_2O_3–BaO–B_2O_3	β-BaB_2O_4	Line: single crystal Planar crystals	[8,12–14]
Li_2O–Nb_2O_5–SiO_2, B_2O_3, TeO_2	$LiNbO_3$	Line: high orientationPlanar crystals	[15–19]
Na_2O–Nb_2O_5–SiO_2–Al_2O_3	$NaNbO_3$	Line	[20]
K_2O–Nb_2O_5–B_2O_3–Al_2O_3, SiO_2	$KNbO_3$	Line	[21,22]
Sm_2O_3–Bi_2O_3–B_2O_3	$Sm_xBi_{1-x}BO_3$	Bending line	[7,23–26]
Gd_2O_3–Bi_2O_3–B_2O_3	$Gd_xBi_{1-x}BO_3$	Line	[27]
RE_2O_3–MoO_3–B_2O_3(RE: Sm, Gd, Tb, Dy)	β′-$RE_2(MoO_4)_3$	Line: high orientationPlanar crystals	[28–35]
Li_2O–FeO–Nb_2O_5–P_2O_5	$LiFePO_4$	Line: high orientation	[36]
Li_2O–Fe_2O_3–Nb_2O_5–P_2O_5	$Li_3Fe_2(PO_4)_3$	Line	[37]
Sm_2O_3–SrO–BaO–Nb_2O_5–B_2O_3	$Sr_xBa_{1-x}Nb_2O_6$	Line	[38,39]
BaO–TiO_2–GeO_2	$Ba_2TiGe_2O_8$	Line: chemical etching	[9,40–43]
BaO–TiO_2–SiO_2	$Ba_2TiSi_2O_8$	Line: high orientation	[9,43]
BaO–TiO_2–B_2O_3	$Ba_3Ti_3O_6(BO_3)_2$	Line	[44]
K_2O–Sm_2O_3–P_2O_5	$KSm(PO_3)_4$	Line	[45]
ZnO–B_2O_3–SiO_2–Sm_2O_3	ZnO	Line	[46]
La_2O_3–SrO–MnO_2–B_2O_3	$La_{0.7}Sr_{0.3}MnO_3$	Line	[47]
LaF_3–Na_2O–Al_2O_3–SiO_2	LaF_3	Nanocrystals	[48,49]
CaF_2–NaF–CaO–Al_2O_3–SiO_2	CaF_2	Nanocrystals	[48,50–53]
BaF_2–Al_2O_3–B_2O_3	$BaAlBO_3F_2$	Line: single crystal	[54]