Photonic Crystallized Structures in Glass

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Recent studies on creation of photonic crystallized structures in glass will be described in this review. Concept for photonic crystallized glass and several interesting topics in related with the subject will be presented as following: 1) The largest second-order optical nonlinearity in thermally crystallized BaTiGeO₅ (BTG) glass has been obtained ever reported. 2) Novel processing of ultraviolet laser-induced nano-crystallization has been developed, and single-crystalline patterning by CW–YAG laser irradiation through the atomic heating has been investigated and demonstrated for the first time in glass-based materials with second-order optical nonlinearity. 3) Origin of permanent second-harmonic generation (SHG) in GeO₂–SiO₂ crystallized glass films has been found and clarified. In addition, a new technique for enhancement of the permanent SHG by means of modification on defects state has been demonstrated.

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1. Introduction

The modification and manipulation of microscopic structures on materials have attracted considerable interest for future industries including several applications of electronics, photonics, bioengineering, and so on. For typical examples, so many efforts and valuable challenges have been performed for fabrication of nanostructured patterns and devices, especially using materials of Si semiconductors and other materials.

Although glasses such as silica (SiO₂) and others, exclusively used as an optical fiber for communication network, are very key materials for photonic applications, few attentions have been paid until recently in terms of nano- and micro-scale structures in glass materials. For example of research on nanotechnology in glass, it has been reported that a nanometer-scale phase separation induced by ArF excimer laser irradiation was found in Ge-doped SiO₂ glass films, and the photochemical effect was investigated as an origin of large photo-induced refractive index change. In these days, several attempts of optically processing by using femtosecond laser pulses have been demonstrated for creations of laser-induced microscopic structures such as optical waveguides, three-dimensional optical storage, Bragg gratings, and movement of bubble in silica glasses.

Glass is the material that has the inversion symmetry, therefore, glass should not have in principle second-order optical nonlinearity, \( \chi^{(2)} \). This has brought the glass materials only to passive usages like fibers in optical transmission of photonic networks, while second-order optical nonlinearity is the property absolutely required to active applications, i.e., electro-optic (EO) switching and modulation, wavelength conversion etc., in signal processing of photonic information technology. So far, active devices and components, which require the second-order optical nonlinearity, have been realized with organic and inorganic crystal materials.

Although, as mentioned previously, nowadays there must be a huge trend of laser-induced micro-structuring in glass, most of them would lead to a sort of hetero glass-structures in glass. Therefore, functions appeared in such structured glasses may still be limited in glass-based properties. On the other hand, approaching on micro-structuring with non-glass phase by laser architectures to induce more active functions to the glass is now just becoming a surge. By taking account of putting active functions like a second-order optical nonlinearity to the glass, micro-structuring of crystalline phase with the nonlinearity in glass, so to call hetero functional-structures, should be one of the best solutions for photonic active materials used in the next advanced glass-fiber realm. In this review, our challenges for crystalline-structures with second-order optical nonlinearity induced in glass materials are described. A concept for photonic crystallized structures in glass will be presented at first, and then three topics will be introduced, 1) a large second-order optical nonlinearity in thermally crystallized Ba₃TiGeO₅ (BTG) glass, 2) laser-induced nano-crystallization and single-crystal patterning by laser irradiation, and 3) permanent second-order optical nonlinearity in crystallized GeO₂–SiO₂ glass films. In this article, the subject 3) presented here as the most recent topic will be reported in detail, and a lot of references will be selected for the other topics.

2. Concept of photonic crystallized structures in glass

As described previously, glass with an amorphous structure is the material that has the inversion symmetry, therefore glass should not exhibit, in principle, the second-order optical nonlinearity, \( \chi^{(2)} \). Although ultraviolet (UV) and thermal poling have been reported to be one of the most efficient ways to induce the second-order optical nonlinearity in SiO₂-related glasses and films, the poled glasses show a degradation of the induced nonlinearity even at room temperature. It has been reported on crystallization with nano- and/or micro-scale particles in these poled glasses, and become well-understanding of its important role for obtaining large and stable induced second-order optical nonlinearity in the glass. Matsumoto et al. suggested that the XRD peaks measured at around 2θ = 22° should directly decide an amplitude of the induced third-order optical nonlinearity, \( \chi^{(3)} \), so that induced \( \chi^{(2)} \) may increase with increasing of \( \chi^{(3)} \), through the relation of effective \( \chi^{(2)} = 3E_{sc}\chi^{(3)} \), where \( E_{sc} \) is a space-charge electric field built-in into the poled glass. Therefore, decay of the effective \( \chi^{(2)} \) in poled glass should be occurred by decrease of \( E_{sc} \) through a return process of electrons to the home-site even at room temperature.

Permanent property of functions in materials must be the most important subject for real application use, certainly it must be more critical than amplitude matter of the effect. It is possible to give a solution to such a long-term stability of the nonlinearity induced in glass. As a pioneer work in nonlinear
optical glasses, findings and developments of transparent crystallized glasses with second-order optical nonlinearity have been reported.\textsuperscript{15–17} The $\chi^{(2)}$ induced in the crystallized glass is stable and permanent at room temperature, therefore, it is one of the best ways to obtain the photonic glasses with active functions based on second-order optical nonlinearity. In design and fabrication of these photonic crystallized glasses for optical application use, there should be several requirements with careful considerations for texture and composition in the glass as described below:

1) Fabrication of nano-scale crystallization or single-domain crystallization, i.e., single crystal, is performed to use the crystallized glass in optical transparent application.

2) Crystalline directions of each domain must be oriented to cause effectively a macroscopic second-order optical nonlinearity.

In addition with 1) and 2) for texture design and processing,

3) Composition consideration in glass is required for a large second-order optical nonlinearity in crystallized glass.

Conceptual pictures of these photonic crystallized glasses are shown in Fig. 1-a) and -b) for the case of space selective crystallization. As shown in Fig. 1-b), photonic crystallized structures in glass are defined that crystalline agents with microscopic second-order optical nonlinearity could be created and oriented in localized area of glasses. The ordered crystalline region would work as optical waveguides and dots with a large macroscopic second-order optical nonlinearity in contrast with the ordinary crystallized glass in Fig. 1-a). Those structures in photonic crystallized glass can exhibit the ability of change (tunable) of refractive index through the nonlinearity, which are quite similar role to single crystal materials for optical signal processing, but much better matching properties for connection and introduction to current infrastructure of “glass” fiber network, because of glass-made materials/devices. In addition, higher applicability could be exhibited to create some structures with complicated periodicity such as domain inversion for quasi-phase matching of second-harmonic generation (SHG). It seems to be lower potential to fabricate the periodic textures in these extrinsic ordered structures on glasses than those by re-construction in intrinsic ordered-structure materials (single crystals).

In addition, for the process of optical integrated circuits (ICs) on thin film substrates, a strong advantage of this concept can be supposed that simple and low-cost process for design and fabrication in optical ICs would be applied by making glass films in the initial stage (producing of difficult crystal films is not necessary), and then following of laser-induced ordered crystallization in localized area, where active waveguides with crystal-like functions are required for signal processing. Because of easy connections to the other glass components, such glass-based active devices are more preferred to introduce into the glass fiber network rather than crystal-based ones.

In this concept, it should be pointed out that thermal affairs, such as movements of ions/atoms and ordering reconstructions of them to crystalline phases, are the most dominant for the crystallization in glass. Therefore, we focus on thermal processing for crystallization, even in laser irradiations an excimer laser with ultraviolet (UV) wavelength for phonon stimulating and CW Nd:YAG laser for excitation of ions as atomic heater in glass were used in our experiments. These thermal approaching ways in our study are quite unique for micro-structuring in glass at the moment, on the contrary to a major trend in the use of ultra short-pulsed laser system.

3. Challenges for photonic crystallized glass

3.1 Large second-order optical nonlinearity in Ba$_2$TiGe$_2$O$_6$ (BTG) crystallized glass

Ba$_2$TiGe$_2$O$_6$ crystal with fesnoite-type structure has been known to exhibit strong ferroelastic properties, but not investigated to show any nonlinear optical properties. It was reported by Takahashi et al.\textsuperscript{18} that a transparent crystallized glass with composition of 30BaO-15TiO$_2$-55GeO$_2$ (BTG-55) in mol% was successfully obtained by taking account of stoichiometric glass-crystalline phases. In stoichiometric composition of crystallized glass, induced optical properties, especially second-order optical nonlinearity may not be decreased by solid solution of “impurity phases” to desired “pure” crystalline phase.\textsuperscript{19} It could be expected to obtain one of the ideal nonlinearities of crystal origin in stoichiometric crystallized glass.

Surface crystallization with approximately 10 $\mu$m thickness and strongly oriented X-ray diffraction (XRD) peaks were observed in crystallized BTG-55 heat-treated at 720°C for 3 h. Figure 2 shows a SEM image for cross-section and XRD patterns of BTG-55 in an inserted figure. Amplitude of second-order optical nonlinearity, $d$-coefficient for SHG, was quantitatively measured by the Maker fringe method, and a typical result (SHF fringe patterns) is presented in Fig. 3. From the fitting to measured pattern, $d$-coefficient in crystallized BTG-55 can be estimated to be 22 pm/V.\textsuperscript{20} This value is almost comparable to $d_{33}$ in LiNbO$_3$ crystal ($\sim 28$ pm/V), and the largest

![Fig. 1. Conceptual pictures of crystallized glasses, a) ordinary crystallized glass and b) photonic crystallized structure in glass.](image-url)
in crystallized glasses ever reported.

Two important factors for successfully obtaining of the largest second-order optical nonlinearity in BTG-55 crystallized glass are stated. One is the performance of stoichiometric composition in crystallized glass as described above, and the other is the orientation texture along to the polarization direction organized by surface crystallization mechanism.\(^{23}\) It is clearly seen in inset of Fig. 2 that surface crystallized region is oriented to c-axis of crystalline phase, which is the most prior direction for crystal growth. That orientation is caused by larger amount of nucleation and faster growth in c-axis direction for competing geometrical selection according to theory of three-dimensional crystal growth. Furthermore, in this BTG-55, its polarization is along to the c-axis. Therefore, ordered structure for highly efficient macroscopic second-order optical nonlinearity is automatically organized in the crystallized BTG-55. As conclusive remarks, two requirements, (2) and (3), declared in previous chapter for “Concept of photonic crystallized glass” are well satisfied in this case.

3.2 Laser-induced crystallization in glass

a) Laser-induced nano-crystallization in tellurite glasses

Tellurite (TeO\(_2\)) glasses are well-known to be a promising material for photonics use, such as nonlinear optical switches for signal processing\(^{23}\) and erbium-doped fiber amplifiers, which is strongly expected to support or replace the currently used fiber amplifier of silica for advanced wavelength division multiplexing (WDM) system.\(^{24}\) Shioya et al.\(^{15}\) succeeded in fabricating transparent crystallization of the tellurite glass system, K\(_2\)O–Nb\(_2\)O\(_5–\)TeO\(_2\), by heat treatments and confirmed that the transparent crystallized glass containing a crystalline phase with a diameter of around 40 nm was fabricated. Kim et al.\(^{16}\) reported the first finding of second harmonic generation (SHG) in the crystallized glasses of the tellurite glass system. In addition, we recently discovered a large photo-induced index change and crystallization by laser irradiations in this tellurite glass system.\(^{24,25}\) These significant experimental results stimulate us to try fabrications of a possible structure in tellurite glasses constructed by photo-induced nano-scale crystalline phase bringing important optical functions as described above.

A simple and easy way to create a nano-scale structure has been proposed, and demonstrated a fabrication of periodic grating structure consisting of nano-crystalline particles using laser-induced nano-crystallization in tellurite-based glasses.

Glass samples with the composition of 15K\(_2\)O–15Nb\(_2\)O\(_5–\)70TeO\(_2\) (mol\%) were prepared using a conventional melt-quenching method. UV-irradiation was performed by a pulsed XeCl laser operating at 308 nm and laser intensity of 100 mJ/cm\(^2\) for a pulse. Laser-induced 1D and 2D gratings were fabricated using a phase mask, which was designed with 400 nm pitch for 308 nm UV-irradiation. Figure 4 shows a SEM image of 1D ordering of nano-crystalline particles induced by UV laser irradiations.\(^{26}\) It can be seen that nano-particles with around 50 nm diameter are positioned in a line, and a periodic structure consisting of crystalline particles and glassy phases is fabricated. In addition, change of refractive index, \(\Delta n\), was induced by UV-irradiation, and the value of \(\Delta n/n\) is more than 5%, and this is at least one-order of magnitude larger than that of UV irradiated silica glass. SH emission and its polarization dependence from the nano-structure were confirmed, and it is suggested that each nano-particle may have the same orientation in crystalline phase.

Although origin and optical properties in this unique nanostructure are not fully understood yet, such a crystalline-glassy periodic structure could be expected to give a novel nano-photonic circuit using near-field optical transmission.

b) Single-crystalline patterning by YAG laser irradiation

Recently, Honma et al. reported that crystalline waveguides with strong SHG in Sm-doped Bi\(_2\)O\(_3–\)B\(_2\)O\(_3\) glasses were successfully fabricated by CW Nd:YAG laser irradiation.\(^{26–28}\) It has been found that Sm ions with f-f transitions (\(^{4}S\(_{9/2} \rightarrow \)\(^{6}H\(_{15/2}\)\)) absorb photon energy at 1.06 \(\mu\)m, and release it as thermal energy through the non-radiate relaxation.\(^{27}\) This is a sort of "laser-excited atomic heater in glass", and using this novel atomic technology, it is quite possible to create local laser-induced crystallization in glass.

Figure 5 presents crystalline waveguides fabricated by CW–YAG laser scanning in Sm-doped glasses. Using SHG microscopy, SH emission was confirmed and rotation-angle dependence of SHG intensity was obviously measured. These
results strongly suggest that induced crystalline waveguides are in the state of single-domain crystalline phase, i.e., single crystal. We have successfully obtained several kinds of single-crystalline patterning, for example RO-Sm$_2$O$_3$-TeO$_2$ (R: Mg, Ba), Sm$_2$O$_3$-Bi$_2$O$_3$-B$_2$O$_3$, Sm$_2$O$_3$-BaO-B$_2$O$_3$ (β-BBO), and Sm$_2$O$_3$-BaO-TiO$_2$-GeO$_2$, thus this novel process can be widely used for a lot of glass system.

In the single-crystalline patterning of β-BBO, c-axis of the crystalline phase, which is the prior direction of crystal growth, is always set to be parallel with laser scanning direction. In that case, the polarization of β-BBO is normal to the waveguides, in contrast with the case of surface crystallized BTG-55. Crystallized glasses for both β-BBO and BTG-55 are very useful for nonlinear optical waveguides with EO and SHG functions. Because a degenerate for decision of negative or positive in polarization to relation with prior to crystal growth is still remaining in laser-induced single-crystal patterning, it seems to be possible to fabricate periodic structure of domain inversion by means of control on polarity of polarization (poling) during laser-induced crystal growth.

3.3 Permanent second-order optical nonlinearity in crystallized silica glass films

Silica (SiO$_2$)-related glasses are the promising materials for future advanced photonic applications. Nowadays conventional optical fibers consisting of Ge-doped SiO$_2$ (Ge:SiO$_2$) glasses, for instance, have been widely used for optical information network and photonic sensing systems.

Recently, crystallization behaviors in Ge:SiO$_2$ glasses have been investigated in cases of both fiber preforms and thin films, fabricated by vapor-phase axial deposition (VAD) and chemical vapor-phase deposition (CVD) methods, respectively. A SHG emission caused directly from the crystalline particles in thermally crystallized CVD films (no poling) were successfully found by means of SHG microscopic technique. This result indicates that the intrinsic $\chi^2$, i.e. not caused by the effective origin, in the Ge:SiO$_2$ glasses can be induced by thermally crystallization, and in addition, such a permanent induced effect must be important and useful for long-term reliability of non-linear glass devices in actual photonic applications.

Ge:SiO$_2$ glass films with composition of xGeO$_2$·(1-x)SiO$_2$, x = 15, 20, 29, 30, and 33 in mol% were fabricated by chemical vapor-phase deposition (CVD) method. CVD glass films with thickness of approximately 2-5 μm were deposited on pure SiO$_2$ substrates. Glass samples with CVD Ge:SiO$_2$ films were cut to the dimension of 10 x 10 mm with a thickness of 1 mm.

Heating for crystallization were performed at 1150-1200°C for 1-3 h in air to obtain transparent crystallized glass films. XRD patterns were measured in the crystallized glass films to confirm induced crystalline phases, and optical surface observation, using both polarization optical microscope and SHG microscope, were investigated. A SHG microscopy is reported as an interesting technique to obtain periodic structures of polarization, such as domain inversion structure in nonlinear single-crystal materials. SHG microscopic measurements were performed by the use of Q-switched Nd:YAG laser with 1.06 μm wavelength as a fundamental light source. The SHG microscopy (SHGM) in this study was set to be suitable for observation of crystallized glasses, which are, in general, not uniform and space-localized appearances of crystalline particles. A YAG laser beam with diameter of about 10 mm was introduced to illuminated samples, then transparent fundamental and induced SHG emissions ($\lambda = 532$ nm) were measured, although fundamental one must be isolated by a cut-off filter before reaching to CCD image detection. A typical condition of Q-switched Nd:YAG laser was 125 mJ/cm$^2$ pulse in laser energy, 10 pps in pulse repetition, and 10 nsec in pulse width.

Measured XRD patterns for Ge:SiO$_2$ films are exactly the same as those previously reported for UV-poled glass with 15GeO$_2$-85SiO$_2$ composition. Measured XRD pattern in crystallized films much more resembles the one of α-cristobalite in SiO$_2$ than any other SiO$_2$ crystalline phases and GeO$_2$ phases. The intensity of XRD peak at around 22° in Fig. 6 is remarkably large compared to the other XRD peaks, and this means that the orientation of crystalline particles are more or less aligned to a unique direction, probably that normal to the surface.

XRD pattern from 2θ = 21.0° to 23.0° of crystallized glass films is expanded in Fig. 7. The XRD peak has a complicated form consisting of at least three components between 21.5° and 22.2°, and the peak was deconvoluted into three Gaussian components as shown in the figure. Peak components were assigned as 2θ = 22.0°, 21.8°, and 21.6°, for “peak 1”, “2”, and “3”, respectively. The fine structure of XRD peaks at around 22° is also measured in UV-poled glasses and VAD bulk crystallized glasses. In particular, the intensity of XRD peak in UV-poled glass, corresponding to “peak 3” in this paper, was pointed out to be responsible for the SHG induced by the poling.

Peak positions for (111) of β-cristobalite and (101) of α-
cristobalite are presented in Fig. 7 as reference. It is clearly indicated that combined XRD peak in crystallized Ge:SiO$_2$ films is positioned between $\alpha$- and $\beta$-cristobalite phases.

Measured photograph of SHGM for a crystallized CVD film with 30GeO$_2$–70SiO$_2$ heat-treated at 1130°C for 8 h in air is presented in Fig. 8-a) and a photograph taken under polarization microscope of cross-polarizers configuration is shown in Fig. 8-b). It was intentionally performed that image area for Fig. 8-a) was positioned to be exactly the same as that for Fig. 8-b). In a photograph of Fig. 8-b), two kinds of crystalline particles with approximately 40 nm diameter were observed in surface of crystallized films. One is accompanied by optical retardation, the other not.

In Fig. 8-a) of SHGM, obvious SHG emissions ($\lambda=532$ nm) are appeared from some crystalline particles and it can be found in comparison with Fig. 8-b) (cross-polarizers configuration of polarization microscope) that SHG emissions are caused by the crystalline particles only with a strong optical retardation. Other crystalline particles without SHG emission are not accompanied by the retardation. Laser intensity of the fundamental beam was not uniformed in the area of SHGM, so that, around the center region may be the most emphasized because of distribution on fundamental beam intensity. Several snake lines are noticed in Fig. 8-a) and -b). Those are cracking lines introduced by the crystallization process with large particle size.

We also tried the experiment of surface etching in crystallized CVD films, which could modify the XRD patterns as reported by Matsumoto et al.\textsuperscript{11} In our experiment, after polishing the surface less than approximately 1 $\mu$m, the original complex shape of XRD patterns at around 22° changes to a single peak positioned at close to “peak 1” as shown in Fig. 9. At that stage, as the most interesting behavior, SHG emissions disappeared attending with vanishment of “peak 1” by removal of surface. In addition, optical retardation observed in Fig. 8-b) was fade-out with increasing surface polishing. Photographs of SHGM and cross-polarizers configuration are presented in Fig. 10-a) and -b), respectively. Image area is exactly the same also in this case, and all crystalline particles, which are observed in Fig. 8-b) before surface polishing, still exist after polishing. Vanishing of optical retardation from crystalline particles is indicated in Fig. 10-b), and degradation of SHG is exhibited in Fig. 10-a).

After the polishing, we found an enhancement of polishing especially in boundary area between crystalline particles and glassy surroundings, and that is the same aspect in Fig. 4 of reference.\textsuperscript{12} For overall discussion of these results presented.

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**Fig. 7.** Photographs of surface on crystallized glass films obtained under a) SHG microscope, and b) optical polarization microscope (cross-polarizers).

**Fig. 8.** XRD patterns for before and after surface polishing in crystallized CVD glass films with 30GeO$_2$–70SiO$_2$ composition treated at 1130°C for 8 h in air.

**Fig. 9.** Aspects after surface polishing, a) SHGM, and b) optical microscope (cross-polarizers), for the same area in Fig. 7-a) and -b).
here, a residual stress between crystalline and glassy phases should be considered, because of two evidences for it, i.e. 1) optical retardation in crystalline particles and 2) enhancement of etching in boundary regions after surface polishing. Since the α- and β-cristobalite have the inversion symmetry, both crystalline phases are not SHG-active, therefore, it is strongly suggested that SHG-active crystalline particles have stress-distorted β-cristobalite phase ("peak 3"), pseudo-β-cristobalite, created by thermally crystallization. On this assumption, the most plausible explanation of SHG disappearance from the particles by surface polishing is the release of residual stress by means of surface etching. We should state the reason for existence of the β-cristobalite phase even at room temperature, which is, in general, stable in higher temperature range (−250°C). Two possible reasons may be considered, one is due to partially solid solution of GeO2 into SiO2 cristobalite and the other, also in this case, a residual stress that should be introduced to crystalline particles and glassy regions including the boundary area. During the process of thermal crystallization, 1) difference of thermal expansion between crystalline and glassy phases, and/or 2) compaction due to crystallization might be the major origins for introduction of the residual stress. In Fig. 9, 20 position of the largest peak after polishing is slightly shifted to higher degree of 2θ, compared to "peak 1" before polishing. It means that after surface polishing, crystalline phase released from stress is having smaller lattice constant that than before polishing. By taking account of this fact, it is suggested that the residual stress must apply stretching force to the crystalline particles, in other words, induced crystalline particles are in the state of low pressure environment. It is known that β-cristobalite is more stable phase in low pressure situation than α-cristobalite.

Based on this finding on Ge:SiO2 crystallized glass films, a new attempt for larger SHG was demonstrated by modification of defect conditions in the CVD glass films for crystallization. Figure 11 shows a change of absorption spectra in Ge:SiO2 CVD films with a composition of 33GeO2-67SiO2 as a function of annealing temperature below 800°C in air. Several defects such as Ge-related oxygen-deficient vacancies (GODV) peaked at around 5.1 eV have been reported in this glass system.29) Although, here, we do not go into the detail of defect origin, it is clearly seen in Fig. 11 that absorption coefficient of spectra is drastically decreased with increasing the degree of annealing temperature. In this annealing, any XRD signals for crystallization were not observed in Ge:SiO2 CVD films, and thus almost all kinds of defect are reduced by the annealing below 800°C for 30 min.

Crystallization was then performed as the same heating condition, 1200°C for 2 h, for all annealing temperatures. Measured XRD patterns are presented in Fig. 12, and XRD pattern with non-annealing (as-deposition) is also stated in the figure for comparison. It can be found that remarkable enhancement of "peak 3", which is an indicator for induced nonlinearity caused by crystallization, is successfully achieved by annealing treated before crystallization. Increase of SHG-active pseudo-β-cristobalite may suppose due to decrease of free volume in glass structure by means of decrease of defects before crystallization.

4. Conclusion

We review recent research works on micro-structuring with second-order optical nonlinearity in glass materials. Concept and definition of photonic crystallized structures in glasses were proposed, and important subjects to create the photonic crystallized glass were made in statement. Several recent topics were introduced as follows: 1) The largest second-order optical nonlinearity, almost comparable to LiNbO3 crystals, in thermally crystallized Ba2TiGeO8 (BTG) glass has been obtained ever reported. 2) Novel laser-induced nano-crystallization in tellurite glasses has been developed and single-crystal patternning by CW YAG laser irradiation as the atomic heating has been demonstrated for the first time in glass-based materials with second-order optical nonlinearity. 3) Origin of permanent second-harmonic generation (SHG) in GeO2-SiO2 crystallized glass films has been found and clarified. By the use of SHG microscopic technique, it has been successfully found that SHG emissions with 532 nm wavelength, corresponding to a fundamental Q-switched Nd:YAG laser with 1.06 µm, are clearly depending on stress-induced crystalline phase in thermally crystallized Ge-doped SiO2 glass films. β-cristobalite-like phase, stress-distorted phase with SHG-active, were suggested for the origin of crystalline particles with SHG emissions. In addition, a new technique for enhancement of β-cristobalite-like with SHG was demonstrated by using a modification of defects condition in the glass. In addition, a new technique for enhancement of the permanent SHG by means of modification on defects state has been demonstrated.

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