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Order/Disorder Hybrid Structures in Photonic Glass Materials

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Abstract. Investigations for space-selected structure ordering from nano-particles to single-crystal patterning in glasses will be described. Transparent crystallization in glass must be the best material solution to obtain novel functional glasses with a permanent second-order optical nonlinearity. We focus on the new functions created by structure ordering in glass by means of laser micro-fabrication for space-selected crystallization. Two topics in our recent experimental results of space-selected structure ordering in glass will be presented as follows: 1) Single crystalline patterning by *atom heat laser processing* in Sm-doped glasses for optical waveguides with second-order optical nonlinearity, 2) structure ordering of domains in crystallized glass fibers for possible photonic fiber-type devices with active signal processing.

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 nano-structured textures, patterns, and devices, especially for materials of Si semiconductors and other elements [1,2].

Although glasses such as silica (SiO_2) 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, it has been reported that a nanometer-scale phase separation induced by ArF excimer laser irradiation was found in Ge-doped SiO_2 glass films, and the photochemical effect was investigated as an origin of large photo-induced refractive index change [3]. In these days, several attempts of optically processing by using ultra-short pulsed (~femtosecond) laser have been demonstrated for productions of laser-induced microscopic structures such as optical waveguides [4], three-dimensional optical storage [5], Bragg gratings [6], and movement of bubble [7] in silica and silica-related 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 micro-fabrications 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 *structure ordering for photonic functional* *glass*, should be one of the best solutions for photonic active materials used in the next advanced glass-fiber realm. In this review paper, our challenges for space-selected 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 two recent topics will be introduced, 1) single crystalline patterning by *atomic heat laser processing* in Sm-doped glasses for optical waveguides with second-order optical nonlinearity, 2) structure ordering of oriented domains in crystallized glass fibers for possible photonic fiber-type devices with active functions.

Concept of Order/Disorder Structures

Functional Structures in Crystallized Glasses. 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) [8] and thermal [9] poling have been reported to be one of the most efficient way to induce the second-order optical nonlinearity in SiO_2-related glasses, fibers, and films, the poled glasses show a degradation of the induced nonlinearity even at room temperature, ~280 days [10]. It has been reported on crystallization with nano- and/or micro-scale particles in these poled glasses [11,12], and become well-understanding of its important role for obtaining large and stable induced second-order optical nonlinearity in the glass.

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 [13,14]. The $\chi^{(2)}$ appeared 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 [15]:

(1) Fabrication of nano-scale crystallization or single-domain crystallization, i.e., single crystal, is useful for optical transparent applications.
(2) Crystalline directions of each domain must be oriented to cause a macroscopic second-order optical nonlinearity effectively.

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 functional structures in glasses are shown in Fig. 1-a) and -b) for the case of space-selected crystallization. Usual nano-crystallization in glass is shown in Fig. 1-a), where nano-crystallites created by thermal excitations are stated in random orientation. 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 nano-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 photonic ICs would be applied by making glass films in the initial stage (difficult producing of crystalline 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 structure ordering of them to crystalline phases, are the most dominant subject 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 laser micro-structuring in glass at the moment, on the contrary to a major trend in the use of ultra short-pulsed laser system.

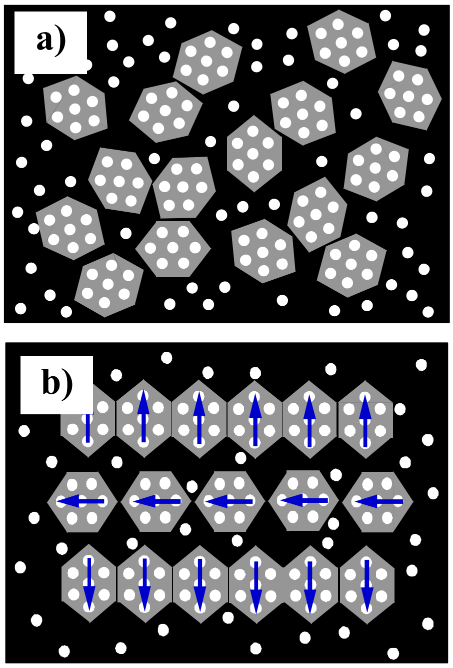

Fig. 1 Textures of nano-crystallized glass, a) usual crystallization in random orientation, b) space-selected crystallization with tailored orientation.

Atomic Laser Heating for Crystalline Patterning. Recently, Honma et al. reported that crystalline waveguides with strong second-harmonic generation (SHG) in Sm-doped Bi_2O_3-B_2O_3 and BaO-B_2O_3 glasses were successfully fabricated by CW Nd:YAG laser irradiation [16,17]. It has been found that Sm ions with f-f transitions, from $^6H_{5/2}$ to $^6F_{9/2}$, absorb photon energy at 1064 nm, and release it as thermal energy through the non-radiative relaxation. This is a sort of "*atomic laser heating in glass*", and using this novel technique, it is quite possible to create space-selected crystallization and patterning in glass.

SH observations of crystal-line patterns fabricated by scanning of CW-YAG laser in Sm-doped glasses have been performed. Typical conditions for laser scanning are 0.6-0.9 W of laser power and 10 μm/sec of scan speed at the wavelength of 1064 nm. Using SHG microscopy, SH emission from the lines was confirmed and rotation-angle dependence of SHG intensity was obviously measured. Optical waveguides for integrated circuits should have complicated line patterns rather than such straight lines. Recently, we succeeded to fabricate angled and curved crystalline patterning in several glass systems [18].

Crystallized Glass Fibres and SHG Observations. Glasses with a composition of $15K_2O$-$15Nb_2O_5$-$70TeO_2$ (in mol%) and 30BaO-$15TiO_2$-$55GeO_2$ (in mol%) were prepared by conventional melt-quenching method. It has been reported that BaO-TiO_2-GeO_2 (BTG) crystallized glass exhibits a large second-order optical nonlinearity, which is almost comparable to that in $LiNbO_3$ crystal materials [19]. The glasses were formed in rod shape with a dimension of 3-6 mm diameter x 30-60 mm length as a preform for fibre drawings. Transparent glass fibres with around 200-350 μm diameter were formed, and typical drawing speed is 4 m/min, and heating temperature of the fibre preform is 640°C in fibre drawing process of tellurite glasses. There was no observation of roughness and/or defects in side surface of the fibre, which may be often caused by lower drawing speed because of crystallization in the glass.

Crystallization process for nano-scale crystallites by two step heating technique was applied to the tellurite glass fibres. The first step at 375°C for 5 h was performed for the nucleation, and then second one at 425°C for 1 h for crystal growth. After these treatments, nano-crystallized glass fibres keeping with high transparency were successfully fabricated. In addition, we performed SHG measurements for both glass systems. Oriented domain structure in crystallized glass fibers with BTG compositions due to surface crystallization mechanism was clarified and strong SHG was observed [20].

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