



Article Femtosecond Laser-Induced Self-Assembly of Ce³⁺-Doped YAG Nanocrystals

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Abstract: Direct three-dimensional laser writing of crystallization inside glass has been intensely studied as an attractive technique for fabricating photonic devices. In particular, polarization-dependent periodic nanostructures composed of the partial crystallization in glass can be self-assembled through focused irradiation of femtosecond pulses. Here, we report on the $Y_3Al_5O_{12}$ (YAG) crystal precipitation in nanoscale by femtosecond laser irradiation inside Al_2O_3 - Y_2O_3 glass. Furthermore, we focus on the white emission by Ce: YAG in which a part of Y^{3+} site was replaced by Ce³⁺, the effect on photoluminescence (PL) characteristics by changing of ligand field induced by nanostructure formation was observed.

Keywords: YAG glass; nanograting; photoluminescence; femtosecond laser; crystallization

1. Introduction

Glass-ceramic is one of the key materials in the field of materials engineering due to its excellent physical properties and ease of formability derived from glass. For example, the partial crystallization of glass composed of a Li₂O-SiO₂ system including sensitizer has been practically used as a photosensitive machinable glass [1,2]. A photo thermo-refractive glass is also a well-studied glass-ceramic candidate for a phase hologram [3]. The polychromatic properties of such glass are caused by the photochemical precipitation of Ag nanoparticles and the subsequent anisotropic crystal-growth of NaF nano-crystals [4]. To realize the high functionality of such glass-ceramics, the process control of both nucleation and crystal growth are critical. Meanwhile, progress in high-power ultrashort pulse lasers [5] has opened new frontiers in physics and technology of light-matter interactions [6], leading to innovative discovery ranging from laser surgery [7], integrated and fiber optics [8,9], optical data storage [10], 3D nanostructuring [11], glass decomposition [12], spatial control of element distribution [13], and nanoparticle synthesis [14], to non-reciprocal photosensitivity [15]. In particular, space-selective patterning of crystals in glasses through laser irradiation is an extremely attractive approach. Recently the patterning of crystallization with a high orientation has been achieved by scanning laser-irradiated local regions [16]. By the optimal combination between the laser-induced temperature gradient, crystal growth rate, and laser writing speed and direction [17,18], it is possible to space-selectively grow a single crystal [19,20], and to design a spatial nucleation site and control the crystal growth direction [21,22]. Structural changes based on heat accumulation generated by femtosecond laser pulses having a faster pulse repetition rate than the timescale of thermal diffusion is generally isotropic according to the temperature distribution [23]. Recently, we observed the self-assembly of a periodic nanostructure, in which a partially crystallized domain was aligned in a plane perpendicular to the laser polarization direction [24]. Based on the observation of periodic nanostructures induced inside

various materials, we have empirically classified such polarization-dependent periodic nanostructures as having one of the following three characteristics: (1) a structural deficiency including nanovoids [25], (2) a strained crystal structure [26], (3) a partial crystallization [27]. However, because conventional crystallization is promoted by cooling from molten state via symmetrical heat diffusion, it is difficult to control crystallization and orientation at the nanoscale. Cao et al. also reported that the oriented LiNbO₃-like crystals were precipitated by the femtosecond laser irradiation in Li₂O-Nb₂O₅-SiO₂ glass, leading to an angular dependence of SHG being obtained with the probe laser polarization [28]. They have explained that the main force for the well-defined texture formation composed of the nanocrystals with their polar axis oriented perpendicular to the femtosecond laser polarization would be the effect of the laser polarization on the anisotropic induced dipole. Poumellec et al. also proposed a new interpretation based on a space-charge built from ponderomotive force and stored in the dielectric inducing an asymmetric stress field [29]. They deduced that the driving force of the nanostructure exists before and drives the phase separation in lithium niobium silicate glass, leading to a self-organized nanostructure made of LiNbO₃ crystalline plates embedded in lamella-shaped frames of amorphous SiO_2 [30]. As LiNbO₃ is an anisotropic and ferroelectric crystal, the electric dipole is generally not parallel to the electromagnetic field, except when the laser polarization direction is along the principle axis. Indeed, the relative permittivities of a LiNbO₃ crystal with a negative uniaxial birefringence are $\epsilon_{11}^r = 83.3, \epsilon_{33}^r = 28.5$, respectively [31]. As a result, a non-zero torque forces the nanocrystal to rotate to the stable positions, where the polar axis is perpendicular to the writing laser polarization [32,33].

However, $Dy_3Al_5O_{12}$ garnet nanocrystals were successfully self-assembled in the plane perpendicular to the writing laser polarization [27], despite the fact that the crystal structure of garnet group represented by yttrium aluminum garnet ($Y_3Al_5O_{12}$ or YAG) is a typical isotropic cubic structure. Furthermore, the relative permittivity of $Dy_3Al_5O_{12}$ was reported to be 2.67 [34], which is more than one digit smaller than that of LiNbO₃. The formation mechanism of the bulk nanograting structure consisting of nanocrystals has still remained a mystery. Therefore, we focused on a precipitation of Ce-doped YAG nanocrystals in nanoscale by femtosecond laser irradiation inside Y_2O_3 -Al₂O₃ glass with the stoichiometric composition of YAG. Here a change in the photoluminescence (PL) properties from the emission center in which a part of Y^{3+} site was replaced by Ce³⁺ before and after femtosecond laser irradiation was investigated.

2. Materials and Methods

Commercially available reagents of aluminum oxide and yttrium oxide were homogeneously mixed to the composition of 62.5Al₂O₃-37.5Y₂O₃ in alumina mortar, and pressed into pellets. The pellets were sintered for 12 h at 1100 °C in air. The calcined pellets were crushed and then used as a preform for an aerodynamic levitation with CO_2 laser melting [35]. While being observed by a charge-coupled device (CCD) camera (KP-FD30, Hitachi Kokusai Electric, Tokyo, Japan), the calcined preforms of approximately 15 mg were levitated using a flow of dry air (N₂: 79% O₂: 21%) and melted through focusing of 100 W CO₂ laser via a ZnSe lens (f = 254 mm). To ensure the melting was homogeneous, the measured temperature by a radiation thermometer was maintained above the melting point for tens of seconds. After that, the melt was rapidly cooled by turning off the laser power, and a transparent spherical sample was obtained. Any bubbles that appeared on the samples obtained were melted again and eliminated, as these would otherwise interrupt laser propagation. Since the weight loss of a spherical sample before and after the CO_2 laser melting was less than 0.1%, no apparent compositional variation was considered to have been generated. The glass phase of the as-prepared samples was verified by Cu Ka X-ray diffraction (XRD, SmartLab, Rigaku, Tokyo, Japan). The glass-transition (T_g) and crystallization (T_x) temperatures for the as-prepared glass samples were determined by measurements using thermogravimetry and a differential thermal analyzer (TG-DTA, Thermoplus TG8120, Rigaku, Tokyo, Japan) at a heating rate of 10 °C/min. For reference, the prepared spherical glass sample was crystallized at crystallization temperature for 30 min. To discuss the luminescence properties, we also fabricated Ce-doped YAG glass (Ce-YAG glass) composed of 62.5Al₂O₃-36.1Y₂O₃-1.4CeO₂

by the same method. The excitation and emission spectra of the Ce-YAG glass samples before and after crystallization at 920 °C were also measured by spectrofluorometer (FluoroMax, Horiba-Jobin Yvon, Kyoto, Japan). The top and bottom parts of the spherical glass samples were polished in a parallel manner for later use in the femtosecond-laser irradiation experiments. Laser experiments were performed using a mode-locked regeneratively amplified Ti: sapphire laser system (RegA 9000, Coherent, Santa Clara, CA, USA) operating at 800 nm. The pulse duration was tuned ranging from 50 fs to 1 ps. The laser pulses were focused at 60 μ m below the sample surface using a microscope objective lens (LU Plan Fluor, 50 × 0.80 N.A., Nikon, Tokyo, Japan). The laser energy was controlled by a variable neutral density filter (typically $0.5 \sim 3.0 \mu$ J). To change the amount of accumulated heat, the pulse repetition rate was also modulated from 10 to 250 kHz. The focus spot was scanned in the plane perpendicular the laser propagation direction at 10 μ m/s by moving the glass sample by the XYZ translation stage. Simultaneously, an irradiated spot was observed using a CCD camera (CSDW2M60CM28, Toshiba-Teli, Tokyo, Japan). After laser irradiation, the modified regions in the glass samples were inspected using confocal fluorescence microscope (exciting laser wavelength: 532 nm). The structural changes in the glass were analyzed by a confocal Raman spectrometer excited by a diode-pumped solid-state (DPSS) laser with a wavelength of 532 nm (Nano Finder 30, Tokyo Instruments, Tokyo, Japan). After polishing the sample to the depth of the beam waist location, the polished sample surface was also inspected using a field-emission scanning electron microscope (FE-SEM) (JSM-7100F, JEOL, Tokyo, Japan) equipped with a cathodoluminescence (CL) spectrometer (iHR-320, Horiba, Kyoto, Japan).

3. Results

3.1. Photoluminescence Properties of Ce³⁺-Doped Yttrium Aluminum Garnet (YAG) Crystal and Glass

Figure 1 shows DTA curve and XRD patterns of the $62.5\text{Al}_2\text{O}_3$ - $37.5\text{Y}_2\text{O}_3$ glass sample prepared. The T_g and T_x for the as-prepared glass samples were 890 °C and 920 °C, respectively Figure 1a. Unlike the previously reported results [36,37], no apparent XRD sharp peak assigned to $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) crystal was observed for the as-made glass sample (Figure 1b). The XRD pattern for the sample after annealing at 920 °C for 30 min, clearly indicates that $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) crystal was deposited. The YAG crystal has a body-centered cubic garnet structure belonging to the space group Ia3d, where the Y occupies a dodecahedral site (24c), two of the five Al atoms occupy octahedral sites (16a), and the other three Al occupy tetrahedral sites (24d). The O atoms locate at one equivalent site (96h). In the crystal lattice of YAG, the Ce³⁺ which substitutes for Y³⁺ in the site of D₂ symmetry has 8 nearest neighbor oxygen atoms. The eightfold coordination of Ce³⁺ in the dodecahedral site can be described as a cubic coordination with an additional tetragonal distortion [38].



Figure 1. (a) Differential thermal analysis (DTA) curve and (b) X-ray diffraction (XRD) patterns of the prepared 62.5Al₂O₃-37.5Y₂O₃ glass sample. The XRD pattern for the ample after annealing at 920 °C for 30 min is also shown in (b).

Figure 2c shows excitation and emission spectra before and after crystallization of the Ce-YAG glass. Insets depict the photographs of the as-prepared Ce-YAG glass and the crystallized Ce-YAG glass, illuminated by visible or ultraviolet (UV) light (365 nm). The excitation-emission patterns before and after crystallization of the Ce-YAG glass are also shown in Figure 2a,b. Both of excitation and emission peak intensities for Ce-YAG glass greatly increased after the crystallization. Because the improved crystallinity generally results in the increase of emission intensity, the emission intensity can serve as an index of local crystallization induced by the femtosecond laser irradiation. Two broad excitation peaks were observed for Ce-YAG glass and Ce-YAG crystal. Although the peak position of a longer wavelength was almost the same as approximately 450 nm, the peak of a shorter wavelength was red shifted from 340 nm for crystal to 380 nm for glass. The electronic configuration of Ce^{3+} is [Xe]4f¹, the blue absorption and yellow emission of which are attributed to the transition between 4f to 5d. Although the 4f electron is shielded by the outer 5s and 5p orbitals, it is well known that the 5d electron is strongly influenced by the crystal field environment and the site symmetry, leading to large crystal field effects on the excited states. According to the ligand field theory, the 5d state will split into triplet $2T_{2g}$ states with higher energy and doublet $2E_g$ states with lower energy in the cubic field [39]. Since the ligand field strength in glass is generally weaker than that in crystals, the two excitation bands at 340-380 nm and 450 nm could be attributed to the $4f-5d_2$ and $4f-5d_1$ transitions, respectively [40]. An asymmetric broad emission ranging from 480 to 700 nm was observed for both Ce-YAG glass and Ce-YAG crystal. This emission consists of doublet sub-emissions assigned to the $5d_1 \rightarrow {}^2F_{7/2}$ and $5d_1 \rightarrow {}^2F_{5/2}$ transition, since the ground state of Ce^{3+} consists of ${}^2F_{7/2}$ and ${}^2F_{5/2}$ due to the spin-orbit interaction [41].



Figure 2. The excitation-emission contour maps (**a**) before and (**b**) after crystallization of the Ce-YAG (yttrium aluminum garnet) glass by annealing at 920 °C for 30 min. The excitation and emission spectra are also shown in (**c**). Insets depict the photographs of the as-prepared Ce-YAG glass and the crystallized Ce-YAG glass, illuminated by visible or ultraviolet (UV) light (365 nm).

3.2. Photo-Induced Local Crystallization

Although it was expected that a polarization-dependent periodic nanostructure could be induced by the irradiation of femtosecond laser pulses, as with the case of Al₂O₃-Dy₂O₃ glass, no apparent birefringence was observed under the polarization microscope in both of Ce-YAG glass and undoped YAG glass. To confirm the formation of nanograting structure, the polished sample in the plane perpendicular to the laser writing direction was inspected by a FE-SEM Figure 3a-c. Furthermore, to reveal the structural changes of the photo-induced regions in glass samples, the Raman spectra of the modified regions after laser irradiation were also measured as shown in Figure 3d. Backscattering electron images (BEIs) indicate that a periodic nanostructure with an orientation perpendicular to the laser polarization direction was clearly formed in the case of the pulse repetition rate of 10 kHz and 50 kHz. While, in the case of the pulse repetition rate of 250 kHz, a large melting region was formed as a result of heat accumulation. In this case, the nanograting structure was partially formed. Based on the reported thermal diffusivity (D_{th}) [42], the thermal diffusion length $(L \sim \sqrt{D_{\text{th}}t_{\text{int}}})$ during the interpulse time (t_{int}) was roughly estimated to be 20 µm, 9 µm, and 4 µm for 10 kHz, 50 kHz, and 250 kHz, respectively. Although the glass composition is almost same as the stoichiometric composition of $Y_3Al_5O_{12}$ crystal, the striped shades were observed in BEIs, owing to the difference in the density. The YAG crystal phase was periodically precipitated in the stripe-like bright contrast regions in BEIs, corresponding to the nanograting structure, which was similar to that reported in a previous study [27]. The periods of bright contrast regions in BEIs were calculated to be approximately 250 nm, even in the case a pulse repetition rate was changed. While, the width of bright contrast regions slightly decreased from approximately 130 nm to 90 nm with an increasing pulse repetition rate. Detailed investigations using a high-resolution transmission electron microscopy should be required. Although no apparent Raman peaks were observed in the initial undoped YAG glass samples, some characteristic sharp peaks were observed after laser irradiation. A comparison between the spectrum on the laser-modified region in undoped YAG glass and the reference spectra indicates that the YAG crystal was precipitated following laser irradiation. In particular, the appearance of the Raman peak assigned to YAG crystal were more remarkable for the higher pulse repetition rate. These results indicated that a nanograting structure is composed of YAG crystal precipitation.



Figure 3. (a) Schematic indicating the orientation of the laser propagation, polarization direction and writing direction. Symbols of $k_{\rm ph}$, *E* and *S* indicate the orientation of the laser propagation, polarization direction and writing direction, respectively. Backscattering electron images on the polished sample in the plane perpendicular to the laser traces written by the femtosecond laser pulses with (b) 10 kHz, (c) 50 kHz, and (d) 250 kHz. The laser parameters were as follows: 800 nm, 40 fs, 1.0 µJ, 10,000 pulse/µm, 0.80 NA. (e) Raman spectra of the prepared 62.5Al₂O₃-37.5Y₂O₃ glass samples before and after laser irradiation with various pulse repetition rate. The reference Raman spectrum of the Y₃Al₅O₁₂ crystal precipitated by annealing of undoped YAG glass is also shown.

3.3. Cathode Luminescence from Nanograting Structure

We have observed cathodoluminescence (CL) based on the spatial distribution of the Ce^{3+} emission in nanoscale crystallization. BEIs are on the polished sample in the plane perpendicular to the laser traces written by the femtosecond laser pulses with 50 kHz, and the CL intensity map on the same surface are shown in Figure 4a,b. The asymmetric broad emission ranging from 480 to 700 nm, assigned to the $5d_1 \rightarrow {}^2F_{7/2}$ and $5d_1 \rightarrow {}^2F_{5/2}$ transition, was observed at the crystallized region Figure 4c, which is similar to the PL spectrum. The emission intensity at the crystallized region exceeded more than 2 orders higher compared to that of the unirradiated region. This reason is due to the difference in the surrounding ligand field of Ce^{3+} between glass and ceramics [43]. Interestingly, the CL intensity inside the crystallized region was periodically oscillating according to the nanograting structure Figure 4d. The crystallized region was also inspected by a fluorescence polarization measurement using a confocal fluorescence microscope Figure 4e. Each polarization direction of the excitation light (532 nm) and the detection light (550 nm) was tuned by the polarizer, and set to be horizontal (H) or vertical (V) with respect to the nanograting structure orientation. In the measurements, the emission intensity of 550 nm excited by light with a wavelength of 532 nm was detected. The first and second characters in transverse axis denotes that the polarization direction of the excitation light and the detection light, e.g., "HV" shows the horizontally polarized excitation and the vertically polarized detection. The emission intensity increased when the polarization directions of the excitation light and the detection light are the same, i.e., HH and VV. Furthermore, the emission intensity for VV was higher than that for HH.



Figure 4. (a) Backscattering electron image (BEI) on the polished sample in the plane perpendicular to the laser traces written by the femtosecond laser pulses with 50 kHz. Symbols of *E* and k_{ph} indicate the writing laser polarization and propagation direction, respectively. Symbols of V and H indicate the direction relative to the nanograting structure orientation. (b) Cathodoluminescence (CL) intensity map at 550 nm on the same surface in (a). Green arrow indicates the measurement point of CL spectrum in (c). Dotted white line indicates the measurement position of CL intensity profile in (d). (e) Plots of the emission intensities using confocal fluorescence microscope. Each polarization direction of the excitation light and the detection light was set to be horizontal (H) or vertical (V) with respect to the nanograting structure orientation. The arrows in (d) are guides for the eyes.

3.4. Progress of Photoinduced Crystallization

We have also investigated the difference in the emission intensity of Ce^{3+} from the crystallized region induced by the femtosecond laser pulses with various repetition rates, pulse widths, and pulse energies Figure 5. In the measurements, a confocal fluorescence microscope was used. The crystallized region at 60 μ m below the sample surface was inspected by an objective lens (LU Plan Fluor, 50×0.80 N.A., Nikon, Tokyo, Japan). The pinhole size was set to be 100 μ m. The typical optical slice thickness is given by [44]:

$$A = \left\{ \left(\frac{0.88\lambda}{n - \sqrt{n^2 - NA^2}} \right)^2 + \left(\frac{\sqrt{2}nd}{NA} \right)^2 \right\}^{\frac{1}{2}}$$
(1)

here λ , *n*, *NA*, and *d* are the emission wavelength (~580 nm), the refractive index of air (~1), the numerical aperture, and the pinhole diameter, respectively. In addition, assuming the pinhole size is infinitely small, the lateral resolution is also given by [45]:



$$L = 0.51 \frac{\lambda}{NA} \tag{2}$$

Figure 5. (a) Photoluminescence (PL) spectra of the crystallized regions induced by the femtosecond laser pulses with various pulse repetition rates. The laser parameters were as follows: 800 nm, 40 fs, 1.0 μ J, 0.80 NA. For irradiating the same number of pulses per unit area, the writing speed was adjusted. (b) Pulse width dependence of the PL intensity in the crystallized region. The E_p or the P_p was set to be 1.0 μ J, 1.25 × 10⁷ W, respectively. (c) Pulse repetition rate dependence of the PL intensity as a function of the pulse energy. The pulse width was set to be 40 fs.

The values of *A* and *L* are calculated to be approximately 1.3 μ m and 0.4 μ m. Furthermore, considering a spherical aberration, the axial resolution can be roughly estimated to be 1.6 μ m. Since the length of the laser-modified region was at least 10 μ m for 250 kHz, we deduced that the PL intensity measured by our confocal setup can be an intercomparison. Although quantitative analysis of crystallinity in a local region from the PL intensity is difficult, to evaluate the crystallinity of the laser irradiated region qualitatively we obtained the PL intensity by the methods shown below.

The spectral mapping of Ce^{3+} emission ranging from 560 nm to 620 nm was performed in a plane involving the laser-modified region while varying the depth every 1 μ m to a total of 10 μ m. The maximum PL intensity in every spectra map was integrated 10 times. Finally, we deduced that the evaluated PL intensity is proportional to the crystallinity. In the experiments for estimating the pulse repetition rate dependence on the PL intensity, for irradiating the same number of pulses per unit area, the writing speed was adjusted. The PL intensity was evidently increased with increasing the pulse repetition rate, suggesting that the heat accumulation during laser irradiation effects on the crystal nucleation and/or growth Figure 5a. As shown in Figure 5b, the PL intensity decreased with increasing the pulse width under the same pulse energy (E_p) , in contrast, increased with increasing the pulse width under the same peak power (P_p) . From these results, it is suggested that the crystal nucleation is photoinduced in a supersaturated region where the electric field intensity exceeds a certain threshold. In the case of higher pulse repetition rate, the PL intensity linearly increased with increasing the E_p under the same pulse width of 40 fs Figure 5c. According to the increase of the pulse energy, the PL intensity was increased and then saturated regardless of the pulse repetition rate. These results suggested that the crystallinity becomes high in proportion to the pulse energy. However, in the case of low pulse repetition rate of 10 kHz, there was no significant change in the PL intensity with increase of the E_p up to 2.5 μ J, although the PL intensity was slightly higher than that for as-prepared Ce-YAG glass. For over 2.5 μ J, the PL intensity was increased to approximately the same level as that for the higher repetition rate. We deduced that the nuclei of YAG crystal before

growth were kept in a glass matrix in the case of the lower pulse energy and the pulse repetition rate due to smaller effect of the heat accumulation.

To make a comparison of the PL intensity induced by various pulse repetition rate in Figure 5a, the PL intensity ratios at 590 nm before and after the laser irradiation are listed in Table 1.

| Repetition Rate (kHz) | PL Intensity Ratio ¹ |
|-----------------------|---------------------------------|
| 10 | 6 |
| 50 | 38 |
| 250 | 198 |

Table 1. PL intensity ratios before and after the laser irradiation.

¹ The PL intensity at 590 nm from the modified region was normalized by that for the pristine Ce-YAG glass.

Table 1 shows the PL intensity ratio increased proportional to the pulse repetition rate. Furthermore, the fact that the PL intensity was almost the same value in the case of the pulse energy lower than 2.5 μ J at 10 kHz Figure 5c, indicates that an interpulse time of 100 μ s or less should be required for crystal growth. Therefore, we deduced that the increase of laser energy absorption followed by thermal accumulation during laser pulse irradiation caused the proportional increase of PL intensity. At the moment, it is difficult to estimate the timescale of nucleation process because the laser energy absorption increases with increasing pulse repetition rate [46]. To discuss the nucleation process, detailed experiments of a transient photoluminescence and absorption should be required.

3.5. Nucleation and Growth of YAG Nanocrystals

To confirm the growth of the photo-induced nuclei, thermal treatment was performed. The samples after the femtosecond laser irradiation with various pulse energies and pulse repetition rates were annealed at 300 °C, 500 °C, and 700 °C for 30 min. The measurements were repeated several times. The PL intensity ratios of the laser-modified region before and after thermal treatment are plotted in Figure 6. In the case of lower pulse repetition rate of 10 kHz and 50 kHz, the *R* value for every thermal treatment was increased, although the annealing temperature is quite a lot lower than T_g of 890 °C. On the other hand, no apparent change in the *R* value was observed in the case of 250 kHz pulse repetition rate. These results are suggested that the crystal nuclei were already grown during the irradiation of higher pulse repetition rate laser pulses.



Figure 6. (a) Plots of PL intensity of the laser-modified region as a function of the pulse energy after annealing at (a) 300 °C, (b) 500 °C, (c) 700 °C for 30 min. The PL intensity was normalized as the ratio of the intensity before and after thermal treatment ($R = I_{PL}^{anneal}/I_{PL}^{laser}$). Dotted line (R = 1) indicates there is no change in the PL intensity before and after thermal treatment.

4. Discussion

4.1. Polarization-Dependent Phenomena

The formation of the polarization-dependent subwavelength nanostructure composed of the partial crystallization was formed in few kinds of glass such as Al₂O₃-Dy₂O₃ glass [27], Li₂O-Nb₂O₅-SiO₂

glass [33], and La₂O₃-Ta₂O₅-Nb₂O₅ glass [47]. In the case of Li₂O-Nb₂O₅-SiO₂ glass, the induced LiNbO₃ is an anisotropic and ferroelectric crystal. In addition, although the structure of the $Ta_xO_v^{z+}$ crystal cluster is unknown, it is known that the Ta_2O_5 thin film exhibits a piezoelectric property [48]. On the other hand, $Dy_3Al_5O_{12}$ and $Y_3Al_5O_{12}$ belong to the garnet-type structure and is optically isotropic crystal with cubic symmetry. It is also known that the relative permittivity of Y₃Al₅O₁₂ is low (~11) [49] compared to LiNbO₃. In our experiments, polarization-dependent periodic nanostructures composed of the partially crystallized domain with garnet-type structure were successfully photo-induced by the femtosecond laser irradiation with the relatively low pulse repetition rate (Figure 3). The enhancement of PL and CL intensity of the Ce³⁺ activators due to large ligand field strength supports the local crystallization in nanograting structures Figure 4. Furthermore, it is known that the emission efficiency of Ce^{3+} doped $Gd_3Ga_5O_{12}$ crystal can be improved by applying pressure of several GPa [50]. This effect is interpreted in terms of two possible phenomena: (i) by pressure-induced electronic crossover of the excited 5d energy level of the Ce³⁺ with the conduction band bottom of the host crystal, and (ii) by decrease of electron-lattice coupling with increasing pressure, resulting in reduction of the Stokes shift and non-radiative transitions between the low vibrational levels of the 5d state and high vibrational levels of the ground 4f state. On the other hand, Ma et al. recently proposed a possible mechanoluminescence mechanism for Ce³⁺-doped YAG involving the phonon-assisted mechanical energy transfer processes [51]. Based on the demonstration of the mechanoluminescence degradation under a cyclic stress test, they reported that the electrons at the ground level of Ce^{3+} could be transferred to the excited levels with the assistance of the energy from the phonons in the matrix, which then recombined with the holes. In our case, Raman peaks of YAG were apparently increased with increasing pulse repetition rate, Figure 3e, suggesting the increase of crystallinity. We deduced that the effect induced by the crystal field environment is dominant compared to the phonon-assisted mechanical energy transfer model. Therefore, the crystallization and alignment in nanoscale will be interpreted in terms of not only a torque force provided by the anisotropic and ferroelectric properties of crystal, but also a pressure difference periodically induced by electron plasma within the laser focus. Based on the formation of a subwavelength periodic plasma-field structure consisting of the overcritical plasma layers perpendicular to the laser polarization [11,52], a periodic modulation of the pressure may also be produced. Meanwhile, it is known that the crystal nucleation rate is given by [53,54]:

$$J \propto J_0 \exp\left(-\frac{W*}{\kappa_{\rm B}T}\right), \ W^* = \frac{16\pi\sigma^3}{3\Delta P^2}$$
(3)

where I_0 , W^* , κ_B , T, σ , and ΔP are the prefactor, energy barrier to nucleation, the Boltzmann constant, temperature, surface tension of the nucleus, and pressure difference between in and out of the nucleus, respectively. This equation represents how the pressure difference reduces the energy barrier to nucleation, leading to an increase of the nucleation rate. Of course, the nucleation rate also increases with temperature. Assuming the electron pressure is proportional to the pressure difference, finally, crystallization could occur at a higher electron plasma density region. Assuming the electron pressure is proportional to the pressure difference, finally, crystallization could preferentially occur at a higher electron plasma density region. In general, based on the crystal field theory, the photoluminescence properties depend on the polarization direction as well as the stress axis relative to the crystallographic axis. However, this cannot explain the results of fluorescence polarization measurements Figure 4e, because the crystallized region in the nanograting structure is polycrystalline. Although the periodic stress field corresponding to the nanograting structure may be related to such polarization-dependent photoluminescence properties, more detailed investigations should be required. Although another interesting phenomenon inducing an asymmetric stress field caused by the ponderomotive force, which is proportional to the laser intensity gradient, was also observed [29], this force is not sensitive to the laser polarization direction.

4.2. Nucleation and Growth Mechanism for Photoinduced Crystallization

From the results in Figures 5 and 6, we consider the nucleation and growth mechanism to be as follows: firstly, the electric field intensity of a laser pulse affects the nucleation process, since the PL intensity increased with increasing in the peak power and the pulse width. Furthermore, the heat accumulation phenomenon during laser irradiation with high pulse repetition rate also affects the nucleation, particularly the size of crystal nucleus. Based on the classical nucleation theory [55], the growth rate of crystal nucleus can be given by:

$$\frac{dr}{dt} \propto \left(1 - \frac{r_c}{r}\right) \tag{4}$$

where r_c is the radius of critical nucleus. If the radius of the crystal nucleus induced by the laser irradiation is larger than r_c , the crystal nucleus will grow. Meanwhile, according to the time-temperature-transformation (T-T-T) curve for isothermal crystallization of quenched amorphous YAG [56], the progress in crystallinity for the sample after the laser irradiation at room temperature and the thermal treatment at 700 °C for 30 min is quite low. Furthermore, the *R* value was slightly increased with an increase of the annealing temperature, and decreased with an increase of the pulse repetition rate. These results suggested that the size of crystal nucleus for the higher pulse repetition rate becomes larger. In addition, even though the temperature of the photo-induced region in glass is speculated to be much higher than crystallization temperature, the *R* value was not very different to changing pulse energy. This may be related to the solid-state conversion of bulk solid glass to a crystal [57], determined by kinetics, not thermodynamic equilibrium.

5. Conclusions

We investigated femtosecond laser-induced crystallization in Ce^{3+} -doped YAG glass prepared using an aerodynamic levitation melting method. We observed the self-assembly of periodic nanostructure in which partially precipitated Y₃Al₅O₁₂ garnet structure was aligned in a plane perpendicular to the laser polarization direction. To grow YAG nanocrystals locally inside Ce^{3+} doped YAG glass by the irradiation of femtosecond laser pulses, thermal accumulation induced by an interpulse time of 100 µs or less should be required. We have proposed the formation mechanisms of periodic nano-crystallization in a plane perpendicular to the laser polarization. A periodic pressure difference induced by electron plasma within the laser focus could reduce the energy barrier to nucleation, leading to an increase of the nucleation rate. Such self-assembled nanostructure of Ce^{3+} -doped YAG nanocrystals will open the possibilities of a new type of light-emitting device.

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References

- 1. Zanotto, E.D. Metastable phases in lithium disilicate glasses. J. Non Cryst. Solids 1997, 219, 42–48. [CrossRef]
- 2. Stookey, S.D. Photosensitive Glass. Ind. Eng. Chem. 1949, 41, 856–861. [CrossRef]
- 3. Lumeau, J.; Glebova, L.; Golubkov, V.; Zanotto, E.D.; Glebov, L.B. Origin of crystallization-induced refractive index changes in photo-thermo-refractive glass. *Opt. Mater.* **2009**, *32*, 139–146. [CrossRef]
- Stookey, S.D.; Beall, G.H.; Pierson, J.E. Full-color photosensitive glass. J. Appl. Phys. 1978, 49, 5114–5123. [CrossRef]

- 5. Strickland, D.; Mourou, G. Compression of amplified chirped optical pulses. *Opt. Commun.* **1985**, *56*, 219–221. [CrossRef]
- Gattass, R.R.; Mazur, E. Femtosecond laser micromachining in transparent materials. *Nat. Photon.* 2008, 2, 219–225. [CrossRef]
- Tirlapur, U.K.; Konig, K. Cell biology—Targeted transfection by femtosecond laser. *Nature* 2002, 418, 290–291.
 [CrossRef]
- 8. Davis, K.M.; Miura, K.; Sugimoto, N.; Hirao, K. Writing waveguides in glass with a femtosecond laser. *Opt. Lett.* **1996**, *21*, 1729–1731. [CrossRef]
- 9. Haque, M.; Lee, K.K.C.; Ho, S.; Fernandes, L.A.; Herman, P.R. Chemical-assisted femtosecond laser writing of lab-in-fibers. *Lab Chip* 2014, 14, 3817–3829. [CrossRef]
- 10. Glezer, E.N.; Milosavljevic, M.; Huang, L.; Finlay, R.J.; Her, T.-H.; Callan, J.P.; Mazur, E. Three-dimensional optical storage inside transparent materials. *Opt. Lett.* **1996**, *21*, 2023–2025. [CrossRef]
- 11. Shimotsuma, Y.; Kazansky, P.G.; Qiu, J.; Hirao, K. Self-Organized Nanogratings in Glass Irradiated by Ultrashort Light Pulses. *Phys. Rev. Lett.* **2003**, *91*, 247405. [CrossRef] [PubMed]
- 12. Lancry, M.; Poumellec, B.; Canning, J.; Cook, K.; Poulin, J.-C.; Brisset, F. Ultrafast nanoporous silica formation driven by femtosecond laser irradiation. *Laser Photon. Rev.* **2013**, *7*, 953–962. [CrossRef]
- Sakakura, M.; Kurita, T.; Shimizu, M.; Yoshimura, K.; Shimotsuma, Y.; Fukuda, N.; Hirao, K.; Miura, K. Shape control of elemental distributions inside a glass by simultaneous femtosecond laser irradiation at multiple spots. *Opt. Lett.* 2013, *38*, 4939–4942. [CrossRef] [PubMed]
- 14. Qiu, J.; Jiang, X.; Zhu, C.; Shirai, M.; Si, J.; Jiang, N.; Hirao, P.K. Manipulation of Gold Nanoparticles inside Transparent Materials. *Angew. Chem. Int. Ed.* **2004**, *43*, 2230–2234. [CrossRef] [PubMed]
- 15. Yang, W.; Kazansky, P.G.; Svirko, Y.P. Non-reciprocal ultrafast laser writing. *Nat. Photon.* **2008**, *2*, 99–104. [CrossRef]
- 16. Komatsu, T.; Ihara, R.; Honma, T.; Benino, Y.; Sato, R.; Kim, H.; Fujiwara, T. Patterning of Non-Linear Optical Crystals in Glass by Laser-Induced Crystallization. *J. Am. Ceram. Soc.* **2007**, *90*, 699–705. [CrossRef]
- Komatsu, T.; Honma, T. Nucleation and Crystal Growth in Laser-Patterned Lines in Glasses. *Front. Mater.* 2016, 3, 32. [CrossRef]
- Stone, A.; Sakakura, M.; Shimotsuma, Y.; Miura, K.; Hirao, K.; Dierolf, V.; Jain, H. Femtosecond laser-writing of 3D crystal architecture in glass: Growth dynamics and morphological control. *Mater. Des.* 2018, 146, 228–238. [CrossRef]
- 19. Miura, K.; Qiu, J.; Mitsuyu, T.; Hirao, K. Space-selective growth of frequency-conversion crystals in glasses with ultrashort infrared laser pulses. *Opt. Lett.* **2000**, *25*, 408–410. [CrossRef]
- Stone, A.; Jain, H.; Dierolf, V.; Sakakura, M.; Shimotsuma, Y.; Miura, K.; Hirao, K.; Lapointe, J.; Kashyap, R. Direct laser-writing of ferroelectric single-crystal waveguide architectures in glass for 3D integrated optics. *Sci. Rep.* 2015, *5*, 10391. [CrossRef]
- 21. Ogawa, K.; Honma, T.; Komatsu, T. Birefringence imaging and orientation of laser patterned β-BaB₂O₄ crystals with bending and curved shapes in glass. *J. Solid State Chem.* **2013**, 207, 6–12. [CrossRef]
- 22. Xuan, H.; Fan, C.; Bertrand, P.; Liu, Q.; Zeng, H.; Brisset, F.; Chen, G.; Zhao, X.; Lancry, M. Size-controlled oriented crystallization in SiO₂-based glasses by femtosecond laser irradiation. *J. Opt. Soc. Am. B* 2014, *31*, 376–381. [CrossRef]
- Sakakura, M.; Shimizu, M.; Shimotsuma, Y.; Miura, K.; Hirao, K. Temperature distribution and modification mechanism inside glass with heat accumulation during 250 kHz irradiation of femtosecond laser pulses. *Appl. Phys. Lett.* 2008, 93, 231112. [CrossRef]
- 24. Mori, S. Nanogratings Embedded in Al₂O₃-Dy₂O₃ Glass by Femtosecond Laser Irradiation. *J. Laser Micro Nanoeng.* **2016**, *11*, 87–90. [CrossRef]
- Asai, T.; Shimotsuma, Y.; Kurita, T.; Murata, A.; Kubota, S.; Sakakura, M.; Miura, K.; Brisset, F.; Bertrand, P.; Lancry, M. Systematic Control of Structural Changes in GeO₂ Glass Induced by Femtosecond Laser Direct Writing. *J. Am. Ceram. Soc.* 2015, *98*, 1471–1477. [CrossRef]
- Mori, M.; Shimotsuma, Y.; Sei, T.; Sakakura, M.; Miura, K.; Udono, H. Tailoring thermoelectric properties of nanostructured crystal silicon fabricated by infrared femtosecond laser direct writing. *Phys. Status Solidi A* 2015, 212, 715–721. [CrossRef]
- 27. Shimotsuma, Y.; Mori, S.; Nakanishii, Y.; Kim, E.; Sakakura, M.; Miura, K. Self-assembled glass/crystal periodic nanostructure in Al₂O₃-Dy₂O₃ binary glass. *Appl. Phys. A* **2018**, 124, 82. [CrossRef]

- Cao, J.; Bertrand, P.; François, B.; Helbert, A.-L.; Lancry, M. Angular Dependence of the Second Harmonic Generation Induced by Femtosecond Laser Irradiation in Silica-Based Glasses: Variation with Writing Speed and Pulse Energy. *World J. Nano Sci. Eng.* 2015, *5*, 96–106. [CrossRef]
- 29. Bertrand, P.; Lancry, M.; Desmarchelier, R.; Hervé, E.; Brisset, F.; Poulin, J. Asymmetric Orientational Writing in glass with femtosecond laser irradiation. *Opt. Mater. Express* **2013**, *3*, 1586. [CrossRef]
- 30. Cao, J.; Poumellec, B.; Mazerolles, L.; Brisset, F.; Helbert, A.-L.; Surble, S.; He, X.; Lancry, M. Nanoscale phase separation in lithium niobium silicate glass by femtosecond laser irradiation. *J. Am. Ceram. Soc.* **2017**, *100*, 115–124. [CrossRef]
- Kushibiki, J.; Takanaga, I.; Arakawa, M.; Sannomiya, T. Accurate measurements of the acoustical physical constants of LiNbO₃ and LiTaO₃ single crystals. *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* 1999, 46, 1315–1323. [CrossRef] [PubMed]
- 32. Cao, J.; Bertrand, P.; Brisset, F.; Helbert, A.-L.; Lancry, M. Tunable angular-dependent second-harmonic generation in glass by controlling femtosecond laser polarization. *J. Opt. Soc. Am. B* 2016, *33*, 741. [CrossRef]
- Cao, J.; Lancry, M.; Brisset, F.; Mazerolles, L.; Saint-Martin, R.; Bertrand, P. Femtosecond Laser-Induced Crystallization in Glasses: Growth Dynamics for Orientable Nanostructure and Nanocrystallization. *Cryst. Growth Des.* 2019, 19, 2189–2205. [CrossRef]
- 34. Papagelis, K.; Ves, S. Vibrational properties of the rare earth aluminum garnets. J. Appl. Phys. 2003, 94, 6491. [CrossRef]
- 35. Yoshimoto, K.; Masuno, A.; Ueda, M.; Inoue, H.; Yamamoto, H.; Kawashima, T. Low phonon energies and wideband optical windows of La₂O₃-Ga₂O₃ glasses prepared using an aerodynamic levitation technique. *Sci. Rep.* **2017**, *7*, srep45600. [CrossRef] [PubMed]
- Alahraché, S.; Deschamps, M.; Lambert, J.; Suchomel, M.R.; Meneses, D.D.S.; Matzen, G.; Massiot, D.; Véron, E.; Allix, M. Crystallization of Y₂O₃–Al₂O₃ Rich Glasses: Synthesis of YAG Glass-Ceramics. *J. Phys. Chem. C* 2011, 115, 20499–20506. [CrossRef]
- 37. Lee, C.-H.; Jung, S.-K.; Yoda, S.; Cho, W.-S. Microstructure of rapidly quenched YAG-based glass–ceramics prepared by aerodynamic levitation. *Ceram. Int.* **2015**, *41*, 14475–14481. [CrossRef]
- 38. Chen, L.; Chen, X.; Liu, F.; Chen, H.; Wang, H.; Zhao, E.; Jiang, Y.; Chan, T.-S.; Wang, C.-H.; Zhang, W.; et al. Charge deformation and orbital hybridization: Intrinsic mechanisms on tunable chromaticity of Y₃Al₅O₁₂:Ce³⁺ luminescence by doping Gd³⁺ for warm white LEDs. *Sci. Rep.* **2015**, *5*, 11514. [CrossRef]
- Robbins, D.J. The Effects of Crystal Field and Temperature on the Photoluminescence Excitation Efficiency of Ce³⁺ in YAG. J. Electrochem. Soc. 1979, 126, 1550–1555. [CrossRef]
- 40. Ueda, J.; Tanabe, S. (INVITED) Review of luminescent properties of Ce³⁺-doped garnet phosphors: New insight into the effect of crystal and electronic structure. *Opt. Mater. X* **2019**, *1*, 100018. [CrossRef]
- 41. Jacobs, R.R.; Krupke, W.F.; Weber, M.J. Measurement of excited-state-absorption loss for Ce³⁺ in Y₃Al₅O₁₂ and implications for tunable 5d→4f rare-earth lasers. *Appl. Phys. Lett.* **1978**, *33*, 410–412. [CrossRef]
- 42. Sato, Y.; Taira, T. The studies of thermal conductivity in GdVO₄, YVO₄, and Y₃Al₅O₁₂ measured by quasi-one-dimensional flash method. *Opt. Express* **2006**, *14*, 10528. [CrossRef] [PubMed]
- Sontakke, A.D.; Ueda, J.; Xu, J.; Asami, K.; Katayama, M.; Inada, Y.; Tanabe, S. A Comparison on Ce³⁺ Luminescence in Borate Glass and YAG Ceramic: Understanding the Role of Host's Characteristics. *J. Phys. Chem. C* 2016, 120, 17683–17691. [CrossRef]
- Wilhelm, S.; Gröbler, B.; Gluch, M.; Heinz, H. Confocal Laser Scanning Microscopy Principles; ZEISS: Jena, German, 2003; Available online: http://zeiss-campus.magnet.fsu.edu/referencelibrary/pdfs/ ZeissConfocalPrinciples.pdf (accessed on 15 December 2020).
- 45. Wilson, T. Resolution and optical sectioning in the confocal microscope. *J. Microsc.* **2011**, 244, 113–121. [CrossRef] [PubMed]
- 46. Miyamoto, I.; Cvecek, K.; Schmidt, M. Evaluation of Nonlinear Absorptivity and Absorption Region in Fusion Welding of Glass using Ultrashort Laser Pulses. *Phys. Procedia* **2011**, *12*, 378–386. [CrossRef]
- Zhang, B.; Tan, D.; Liu, X.; Tong, L.; Kazansky, P.G.; Qiu, J. Self-Organized Periodic Crystallization in Unconventional Glass Created by an Ultrafast Laser for Optical Attenuation in the Broadband Near-Infrared Region. *Adv. Opt. Mater.* 2019, *7*, 19900593. [CrossRef]
- Audier, M.; Chenevier, B.; Roussel, H.; Vincent, L.; Pena, A.; Salaün, A.L. A very promising piezoelectric property of Ta₂O₅ thin films. II: Birefringence and piezoelectricity. *J. Solid State Chem.* 2011, 184, 2033–2040. [CrossRef]

- 49. Krupka, J.; Derzakowski, K.; Tobar, M.; Hartnett, J.G.; Geyer, R.G. Complex permittivity of some ultralow loss dielectric crystals at cryogenic temperatures. *Meas. Sci. Technol.* **1999**, *10*, 387–392. [CrossRef]
- 50. Kaminska, A.; Duzynska, A.; Berkowski, M.; Trushkin, S.; Suchocki, A. Pressure-induced luminescence of cerium-doped gadolinium gallium garnet crystal. *Phys. Rev. B* 2012, *85*, 155111. [CrossRef]
- 51. Ma, Z.; Zhou, J.; Zhang, J.; Zeng, S.; Zhou, H.; Smith, A.T.; Wang, W.; Sun, L.; Wang, Z. Mechanics-induced triple-mode anticounterfeiting and moving tactile sensing by simultaneously utilizing instantaneous and persistent mechanoluminescence. *Mater. Horizons* **2019**, *6*, 2003–2008. [CrossRef]
- 52. Gildenburg, V.B.; Pavlichenko, I.A. High contrast periodic plasma pattern formation during the laser-induced breakdown in transparent dielectric. *Phys. Plasmas* **2017**, *24*, 122306. [CrossRef]
- 53. Kelton, K. Crystal Nucleation in Liquids and Glasses. Solid State Physics 1991, 45, 75–177. [CrossRef]
- 54. Balibar, S.; Caupin, F. Nucleation of crystals from their liquid phase. *Comptes Rendus Phys.* **2006**, *7*, 988–999. [CrossRef]
- 55. Lifshitz, I.; Slyozov, V. The kinetics of precipitation from supersaturated solid solutions. *J. Phys. Chem. Solids* **1961**, *19*, 35–50. [CrossRef]
- Johnson, B.R.; Kriven, W.M. Crystallization kinetics of yttrium aluminum garnet (Y₃Al₅O₁₂). *J. Mater. Res.* 2001, *16*, 1795–1805. [CrossRef]
- 57. Savytskii, D.; Knorr, B.; Dierolf, V.; Jain, H. Demonstration of single crystal growth via solid-solid transformation of a glass. *Sci. Rep.* **2016**, *6*, 23324. [CrossRef] [PubMed]

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