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Design of crystallization of oxyfluoride glasses based on the local structure of fluorine

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This article reviews the development of new oxyfluoride glass-ceramics designed from the viewpoint of the local fluorine structure and crystallization process. Oxyfluoride glasses often form fluoride crystals, but formation of oxyfluoride glasses with a large fraction of fluorine is rare. We successfully fabricated oxyfluoride crystals of BaAlBO₃F₂ in glass-ceramics through heat-treatment by controlling the local structure of fluorine. The glass showed highly efficient photoluminescence with Eu³⁺-doping up to 97%. A reason for this is the high fluorine content and structural similarity to the crystal. Laser-induced crystallization was performed on Ni²⁺-doped glass as a heating source, and lines composed of a single crystal were fabricated. Birefringence images and transmission electron microscope observations indicate that the growth of highly c-axis oriented BaAlBO₃F₂ crystals follows the laser scanning direction even if it changes. Notably, the direction of the c-axis of BaAlBO₃F₂ crystals changes gradually at crossing and bending points. The model of “self-organized homo-epitaxial growth” is proposed for orientations of single crystal line with crossing and bending shapes.

Key-words : Oxyfluoride glass, Glass-ceramics, Fluoride nanocrystals, Crystal morphology, Crystal orientation

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1. Introduction

Glasses are key materials in optical fields owing to their advantages of high transparency, formability, hardness, and chemical and thermal durability. Crystalization of glass has been investigated as a technique to improve their properties and functionality such as photoluminescence (PL), second order optical nonlinearity, ferroelectricity, chemical and thermal durability. Crystallization of various glass-ceramics such as SiO₂ and B₂O₃ have relatively high covalency; on the other hand, fluorides have high ionicity. This difference of polarization creates poor chemical affinity, which greatly impacts glass crystallization (morphology and phase), phase separation behavior, and a metastable phase and high temperature phase form, which cannot be obtained by conventional ceramic synthesis processes such as solid-state reactions.¹,¹⁴,¹⁵ A previous study reported the synthesis of a high-temperature hexagonal SrAl₂O₄ phase: Eu²⁺, Dy³⁺, which is typically a monoclinic phase as a typical afterglow material formed by crystallization of supercooling melt and crystal.¹⁶

In recent years, as a new approach for controlling glass crystallization, laser irradiation has received considerable attention as a new tool for controlling the crystallization process by a spatially selected and rapid heating rate, i.e., laser-induced crystallization.¹,¹⁷⁻²⁰ This enables the fabrication of designed micro-architecture such as waveguides in glass. Furthermore, this is a new challenge for the design of crystal growth steps. In laser-induced crystallization, a spatially limited region is locally heated, creating a steep temperature gradient that is then moved along the laser scanning direction. Besides the heat treatment conditions, the glass structure and chemical composition are also important for controlling the size and morphology of crystals formed in glass-ceramics. Especially in the oxyfluoride system, glass network formers such as SiO₂ and B₂O₃ have relatively high covalency; on the other hand, fluorides have high ionicity. This difference of polarization creates poor chemical affinity, which greatly impacts glass crystallization (morphology and phase), phase separation behavior, and
properties. For example, the luminescence of RE depends on the local structure and type of the most neighbor anions. A thorough understanding of the local structure of fluorine, the middle structure of oxyfluoride glasses, and the crystallization process is key for developing new glasses and glass-ceramics with improved functionality.

2. Nanocrystallization mechanism in aluminosilicate-based oxyfluorides

Transparent oxyfluoride nanocrystallized glasses with fluoride nanocrystals have been key aspects of glass phosphors since the report of Wang and Ohwaki in 1993. After synthesizing PbF2 nanocrystallized glass, many oxyfluoride glass-ceramics have been reported, such as CdF3, BaF2, SrF2, CaF2, LaF3, and NaYF4. Most studies have been based on the aluminosilicate system except for those on PbF2 and CdF3 systems. Rüssel and coworkers proposed that the size distribution of BaF2 nanocrystallized glass is very small due to the SiO2-rich shell surrounding the fluoride nanocrystals, which suppresses diffusion of crystal components (Ba2+ and F−).

Fluorine in oxyfluoride glasses breaks the polymerized network of SiO2 by forming Si–F bonds, resulting in a notable decrease of the glass transition temperature and viscosity. Shinozaki et al. reported that the glass transition temperature of the glass matrix increases with increasing heat-treatment temperature, indicating that crystallization is drastically suppressed when the glass transition temperature reaches the heat-treatment temperature.

The normal crystal growth model based on classic nucleation theory provides the following expression for the kinetics of crystal growth rate, $U$:

$$U \propto \left( D'' \text{ or } \frac{1}{\eta''} \right) \left[ 1 - \exp \left( -\frac{\Delta G_v}{kT} \right) \right]$$

where $D''$ and $\eta''$ are the diffusion coefficient and viscosity at the interface between the liquid (matrix) and crystal, respectively, $\Delta G_v$ is the difference in free energy between the glassy and crystalline phase, $k$ is the Boltzmann constant, and $T$ is the temperature. Cristallization increases the viscosity (\(\eta''\)), which decreases the crystal growth rate ($U$). Therefore, a remarkable change of viscosity by fluorine removal due to crystallization is necessary for nanocrystallization in such a mechanism; therefore, transparent glass-ceramics with fluoride nanocrystals have been reported only for the aluminosilicate system, PbF2, or the CdF3-containing system to the best of the author’s knowledge. Some exceptions exist, such as the study that formed BaF2 nanocrystals in borate glass by controlling fluoride migration using additives, where the authors proposed that the drastic change of viscosity caused by fluorine removal effects not only the crystals morphology but also the dispersion state of nanocrystals. Figure 1 shows a transmission electron microscope (TEM) image of a thin foil fabricated at the surface of transparent glass-ceramics in 25CaF2–5CaO–20Al2O3–50SiO2 by a focused ion beam (FIB) sample preparation method. It was demonstrated that CaF2 nanocrystals are not present at the surface to ~150 nm in bulk glass-ceramics obtained solely by heat treatment at 700°C for 3 h in an electric furnace. Some fluorine evaporates from the sample surface during heating, resulting in an increase of the glass transition temperature, i.e., decreased mobility of ions and increased crystallization temperature around the surface.

Generally, crystallization can be classified as follows: crystallization only at the surface (surface crystallization) or crystallization of both the surface and interior (volume crystallization). The dispersion state of the oxyfluoride glass-ceramics is unique in that crystallization only occurs in the interior. From nanoindentation measurements, it was found that a surface with no CaF2 nanocrystals has a higher indentation elastic modulus and hardness than a surface with CaF2 nanocrystals. Control of fluorine dispersion is important for surface properties such as mechanical properties and chemical durability.

3. Glass structure, PL, and crystallization of novel fluoroborate glasses

Control of the local structure and connectivity of fluorine is key to controlling the crystal phase and morphology. The author has previously focused on the alumina, zinc, or magnesia-doped barium fluoroborate system. B2O3 has one of the highest covalencies and BaF2 has high ionicity; therefore, their chemical affinity is poor. The electron-negativity of Al, Zn, and Mg lies between B and Ba, so the mixing state of ions is largely affected by the addition of these chemicals. Here, previous research on the structure, optical properties, and crystallization of 50BaF2–xAl2O3–(50 – x)B2O3 (x = 0, 10, 20, and 25) is discussed. The amount of fluorine in the glasses was F/(F + O) = 0.4, and fluorine evaporation was barely observed in a 25Al2O3 sample. It was found that, at the F1s X-ray photoelectron spectroscopy (XPS) spectra, the peak shifted towards higher binding energy (B.E.) with the addition of Al2O3 [see Fig. 2(a)]. This indicates that the electrostatic interactions between fluorine and surrounding cations changed with the addition of Al2O3. The value of binding energy in the glass with no Al2O3, i.e., B.E. = 684 eV, was similar to that of Ba–F bonds in BaF2, indicating the
formation of Ba–F bonding. The value of the binding energy of fluorine in the glass with 25Al2O3 was similar to that of fluoroaluminate glass and AlF3. These results suggest the formation of Al–F–Ba (n) and Al–F–Al bonds in 50BaF2–25Al2O3–25B2O3 glass with a disappearing F–Ba bond. In other words, fluorine clearly selects connecting cations. The O1s XPS spectra for the glasses and the results of single peak fitting are also shown in Fig. 2(b), indicating single peaks and almost the same peak position (B.E. = 531 eV). The peak positions with a single component in O1s peaks indicate that the glasses are composed of bridging oxygens; non-bridging oxygen is not formed despite the addition of a large amount of BaF2. XPS and Raman scattering spectra indicate that the addition of Al2O3 enable BO4, BO3F, and BO2F units to transform into BO3 units with the formation of Al(O,F)x units (x = 4–6); i.e., the formation of BO3F and AlO3F2 can be explained by the following reaction;

\[
\text{BO}_{3/2} + \text{Ba}_{1/2}F \rightarrow \text{[BO}_3F]^- + \text{Ba}^+ \\
2[\text{BO}_3F]^- + \text{Ba}_{1/2}F \rightarrow \text{2BO}_{3/2} + [\text{AlO}_3F_2]_2^- + \text{Ba}^{2+}
\]

where the bridging oxygen is not broken in the reaction.

Further change of the Al unit can occur; however, structural information on the Al environment is currently unknown. Further study is required on aspects such as 27Al-NMR.

The glass contains a large amount of fluorine, which lowers the phonon energy, resulting in a non-radiative relaxation process low in PL and a similar structure of the glass to that of BaAlBO3F2. Fluoride crystals and some oxyfluoride crystals show highly efficient PL. BaAlBO3F2 crystals show highly efficient PL with rare earth doping, indicating that the glass would also have highly efficient PL. The PL spectra at \( \lambda_{\text{ex}} = 396 \text{ nm} \) for Eu3+ in 50BaF2–xAl2O3–(50 – x)B2O3 glasses is also shown in Fig. 3.

X-ray diffraction (XRD) patterns for the samples heat-treated at the crystallization peak temperature are shown.
in Fig. 4. It is found that no Al2O3 sample forms BaF2 (cubic), yet β-BaB2O4 are formed and the 25Al2O3 sample forms oxyfluoride BaAlBO3F2 crystals. Fluoride-containing glasses often lead to the formation of fluoride crystals through their crystallization.8) Stamboulis et al.31) proposed that the addition of fluorine into 2SiO2:Al2O3·(2-x)CaO·xCaF2 glasses results in the formation of F–Ca(n) bonds at low fluorine contents and both F–Ca(n) and Al–F–Ca(n) bonds at higher fluorine contents. Consequently, CaF2 nanocrystals are easily formed due to the reaction of 2Ca–F → CaF2 + Ca2+ during heat treatment. On the other hand, the 50BaF2–25Al2O3–25B2O3 glass forms BaAlBO3F2 after heat-treatment at the crystallization peak temperature.26,27) These glass-ceramics have some interesting features; for example, Okada et al. reported that BaAlBO3F2 glass-ceramics not only exhibit good PL properties, but also good optical PL and dosimetry properties with the addition of RE.32,33) It is considered that a large amount of F–Ba (n) bonds are formed in the glass with no Al2O3 (1Er2O3·50BaF2·50B2O3); therefore, BaF2 crystals are formed during crystallization. On the other hand, 25Al2O3 glass is considered to contain Al–F–Ba (n) bonds, and BaAlBO3F2 crystals might be formed after heat treatment instead of BaF2. It should be noted that the structure of the glass is similar to that of BaAlBO3F2 crystals; i.e., three coordinated borate and bipyramidal AlO4F2 units, where three oxygen ions form a layer and two fluoride ions form the top and bottom of the unit, forming an oxygen layer of BO3–AlO3 and fluoride with barium ions between the layer. The addition of Al2O3 clearly has a significant effect on the structure and crystallization behavior of 1Er2O3·50BaF2·xAl2O3·(50–x)B2O3 (x = 0–25) glasses.

4. Single crystal growth of oxyfluoride crystal by laser-induced crystallization of glass

In order to fabricate waveguide architecture on a glass surface, the laser-induced technique has been proposed. Komatsu group has succeeded in generating highly oriented or single crystal architecture on a glass surface by NIR laser irradiation, typically using a YAG:Nd (1064 nm) or YVO4:Yb (1080 nm) laser on RE- or transition metal-(TM) doped glass. The RE and TM act as a heating source. The details of this technique are described in a review paper.20) To fabricate a waveguide laser, fluoride single crystal architecture would be effective; however, as discussed above, the crystal growth of fluoride is spontaneously terminated by increasing the viscosity around the crystal. Kanno et al. applied laser-induced crystallization on CaF2 containing aluminosilicate glass, but the formed crystal was nanosized.24) Another study used B2O3 to decrease the viscosity around the fluoride crystal in order to increase the size of CaF2 crystal, and then the crystal size increased with addition of B2O3, but the formed crystal was still ~100 nm.35) Oxyfluorides typically form fluoride crystals because of poor chemical affinity between fluoride modifiers and oxide glass formers. However, in 50BaF2–25Al2O3–25B2O3 glass, BaAlBO3F2 forms due to structural similarity. Furthermore, it should be emphasized that the formation of oxyfluoride crystals containing a large fraction of fluorine has not been reported to the best of my knowledge. BaAlBO3F2 (BABF) is an attractive material for demonstrating the high-efficiency second harmonic generation (SHG) laser, especially in high power and ultraviolet (UV) regions, because the crystal has approximately twice the SHG efficiency of KH2PO4 (KDP), a deep UV absorption edge, and high thresholds for laser-induced damage.36–39) As the crystal also has highly efficient PL with RE doping, such a waveguide would be applicable for waveguide laser devices.

For the patterning of BaAlBO3F2 crystals by laser irradiation, 3NiO-doped 50BaF2–25Al2O3–25B2O3 (mol) was used. Laser energy absorbed by Ni2+ ions is transferred to thermal energy due to non-radiative relaxation in Ni2+ ions; consequently, spatially selected crystallization is induced. A nonlinear optical BaAlBO3F2 crystal has a hexagonal structure (lattice constant a = 0.48770 nm and c = 0.93824 nm) and a birefringence value of ∆n = 0.046 at 532 nm [Δn = n0 (1.6346) − n0 (1.5890)].30) The author and coworkers used the birefringence imaging technique to examine crystal orientation in laser-patterned lines.40–42) The birefringence images obtained by the Abrio IM imaging system for the fabricated crystal line are shown in Fig. 5. For the line patterned with P = 1.1 W, a light blue color was observed for the whole of the line. The color indicates the direction of birefringence and the brightness indicates the size of the retardation; i.e., the light blue color indicates that the slow axis, i.e., the direction of high refractive index in the line, is perpendicular (i.e., 90°) to the direction of line growth. The homogeneous color of the line fabricated at P = 1.1 W suggests that the quality and
Micro-PL spectra for the line fabricated using the same technique as for the Er2O3-doped sample, the glass-ceramics, and the base glass are shown in Fig. 6. Emissions corresponding to the f-f transitions of \( ^2H_{11/2} \rightarrow ^4I_{15/2} \), \( ^4S_{3/2} \rightarrow ^4I_{13/2} \), and \( ^4F_{9/2} \rightarrow ^4I_{15/2} \) of Er\(^{3+}\) ions are observed. A peak attributed to \( ^4S_{3/2} \rightarrow ^4I_{15/2} \) at \( \sim 540 \text{ nm} \) is clearly observed for the line part and the glass-ceramics but is not clear for the base glass. The appearance of the sharp peak at \( \sim 540 \text{ nm} \) in the line, known as the hypersensitive transition, indicates the site environment of Er\(^{3+}\) ions compared with the glass part, suggesting that Er\(^{3+}\) ions are incorporated into BaAlBO\(_3\)F\(_2\) crystals. In order to observe the orientation of BaAlBO\(_3\)F\(_2\) crystals in the line by TEM, the line part was processed to thin foil shapes using the FIB method, i.e., (a) a cross-section of the line and (b) a parallel-section of the center of the line. The scanning electron microscope (SEM) image of the thin foil preparation in the line is shown in Fig. 7. A bright-field image for the thin foils (a) and (b) is shown in Fig. 8. The foil of (a) shows a bell-shaped crystal on a glass surface \( \sim 2 \mu\text{m} \) height and \( \sim 2 \mu\text{m} \) width. The selected area electron diffraction (SAED) patterns in the area of a circle with a diameter of 1 \( \mu\text{m} \) at the center of the crystal line are shown in the inset of Fig. 8. The dark part in the inner region indicates the crystal and the bright region is the amorphous phase. Clear diffraction spots were observed without any rings, demonstrating that the lines consists of a single crystal. The diffraction patterns for the cross-section thin foil (a) and the parallel-section thin foil (b) are attributed to diffraction from the zone axis of [0001] and [1100] of the BaAlBO\(_3\)F\(_2\) crystal, respectively. A high-resolution TEM image of the thin foil (b) is shown in Fig. 8(c). The lattice of the BaAlBO\(_3\)F\(_2\) crystal is observed. Distances of the lattice in the scanning direction are assigned to [0001] and those in the direction toward the surface are [1100]. Therefore, these results indicate that the BaAlBO\(_3\)F\(_2\) crystal present in the line consists of a single crystal. Furthermore, it indicates that the direction of crystal growth along the laser scanning direction is the c-axis, i.e. the BO\(_3\)–AlO\(_3\) oxide layer stacking direction, and the [1100] axis toward the surface direction.

5. Artificially controlled orientation in single crystals grew on a glass surface

With laser-induced crystallization, it is possible to fabricate a bending shaped line. This is interesting from the perspectives of both fundamental science and practical applications. For practical device applications such as optical waveguides, it is important to establish the technique of laser-induced crystallization, which enables the
fabrication of desirable two-dimensional line patterns to integrate the optical circuit. As for basic crystallization science, crystal growth in bended and branch shapes would not occur spontaneously in the liquid phase and probably only occur through artificial crystallization in solids. Owing to the unique nature of glass crystallization induced by this technique, crystal growth in the solid phase and bended and branch crystal growth shapes are made possible. To clarify the orientation behavior and mechanism of crystal growth for BaAlBO3F2 in the laser-induced crystallization of glasses, we conducted unique experiments researching the patterning of crossing crystal lines.

We conducted the laser patterning with a crossed shape in the glass. First, a straight line of BaAlBO3F2 single crystals was patterned by laser irradiation with \( P = 1.10 \) W and \( S = 8 \) \( \mu m/s \) in the glass, then the second laser irradiation with \( P = 1.05 \) W and \( S = 6 \) \( \mu m/s \) was performed against the first line at an angle of 90° (perpendicular). Here, the second laser irradiation does not induce crystallization. The birefringence images for the crossed lines are shown in Fig. 9(a). The birefringence measurements reveal the following results: (1) before line crossing, the second laser irradiation does not induce crystallization (no birefringence); (2) after line crossing, crystal patterns are highly oriented is induced (homogeneous reddish line). This model is illustrated in Fig. 9(c). The second laser patterned line also consists of BaAlBO3F2 crystals, same as the first crystal line. If BaAlBO3F2 maintains the preferential crystal growth direction (i.e., the \( c \)-axis) even in the second crystal line, it is expected that the color of the second crystal line would be blue for the whole line. However, the crystal growth direction was along the \( a \)-axis in the laser scanning direction. In the case of the second line patterned in same laser power as fist line, the crystal orientation along \( c \)-axis for laser scanning direction drastically changes and grow along \( a \)-axis after crossing point [see Fig. 9(b)].

Considering the crystal growth mechanism in the crossed line experiments designed in this study, the first crystal line at the crossing point acts as a nucleation site for the second crystal line. Furthermore, the lattice constants of the BaAlBO3F2 crystal with a hexagonal structure are \( a = 0.48770 \) nm and \( c = 0.93824 \) nm; thus, a lattice mismatch is expected. The lattice mismatch for the combination of \([1100]//[0001]\) provides an extremely large lattice mismatch of \( f = 48\% \), where the lattice mismatch is defined as \( f = (A - B)/B \), and A and B are the lattice constants of host and guest crystals. Conversely, the combination of \([1100]//[1100]\) has no mismatch. Therefore, it would be difficult to have epitaxial growth with the combination of \([1100]//[0001]\) because of the large strain arising from the large lattice mismatch. As glass is in a thermodynamic non-equilibrium state, it always tends to transfer into the thermodynamic equilibrium state to decrease the free energy in the system. This explains the formation of thermally metastable crystals. Even if the growth direction of crystals is not the most energetically favorable direction, crystallization itself is thermodynamically desired in glass. This explains why the initial crystal
growth direction of BaAlBO3F2 in the crossing line is the non-favorable α-axis direction (instead of the favorable c-axis direction). In the part beyond a distance of approximately 200 μm, its direction changes to the c-axis because it is the preferable crystal growth direction.

The relationship describing the crystal growth direction at the crossing point between the first and second crystal lines is expressed as a combination of [1/100]/[1/100]. That is, “homo-epitaxial crystal growth” is established in the crossing lines at the crossing point patterned by laser irradiation. A schematic illustration for the crystal growth direction at the crossing line is shown in Fig. 6. To the best of our knowledge, the crystal growth behavior observed in this study has never been observed in normal crystal growth experiments performed in an electric furnace with homogeneous heating. Similar experiments on the crossing of crystal lines with different angles of 30° and 60° were also conducted and the birefringence images are shown in Fig. 10. It is found that highly oriented BaAlBO3F2 crystals are formed in the second lines after crossing, even for crossing angles of 30 and 60°, indicating that the first crystal line at the crossing point acts as a nucleation site for the second line. Furthermore, the color of the second crystal lines at and near the crossing point is a homogeneous light blue, but its color changes gradually and continuously to green and yellowish green. For the crossing angle of 30°, a rotation angle of 30° is required to establish the preferential crystal growth direction along the laser scanning direction, which is shown schematically in Fig. 10. The second crystal line, with an angle of 30°, rotates along
the laser scanning direction, then the crystal growth direction changes to along the c-axis. Homo-epitaxial crystal growth is also established in the crossing crystal lines with angles of 30 and 60°. BaAlBO3F2 is composed of AlO3F2 trigonal bipyramids and [BO3]3 triangles are alternately arranged in a trigonal pattern and connected via common oxygen corners to generate a two-dimensional infinite [AlBO3F2] layer parallel to the ab-plane. Ba2+ ions are located between these layers to balance the charge and also to hold the layers together through coordination with oxygen and fluoride atoms. These structural features might enable a gradual change in the stacking state of two-dimensional [AlBO3F2] layers in laser-patterned BaAlBO3F2 crystal lines, i.e., the gradual rotation of [AlBO3F2] layers and thus of the c-axis. Next, BaAlBO3F2 crystal lines were patterned with spiral shapes and examined their orientation behavior. The spiral line with different curvatures was patterned, and the birefringence image obtained for the spiral line is shown in Fig. 11. The orientation gradually changes and is regularly along the c-axis in the scanning direction. These results indicate that BaAlBO3F2 crystals are highly oriented even in the spiral line. On the basis of the results shown in Fig. 11, it is concluded that the direction of the c-axis of BaAlBO3F2 crystals changes gradually along the laser scanning direction. This indicates that a single crystal changes orientation gradually. When the scanning direction changes sharply, the change in orientation is delayed because of the large lattice mismatch. However, the orientation also gradually changes to the preferred crystal growth direction. In laser-induced crystallization, the diffusion of ions and structural units to the crystal growth front is regulated by the laser scanning direction, i.e., almost from one direction. According to Eq. (1), the crystal growth rate depends on the diffusion coefficient and viscosity at the interface. To maximize the crystallization growth rate, crystals prefer to orient along the fastest growing direction. As demonstrated in this study, a straight line grew along the c-axis toward the laser scanning direction. Crystals prefer to maintain their preferential crystal growth direction, which is energetically more stable. When the laser scanning direction changes, the glass is still crystallized because of the decrease in the free energy of the system due to the crystallization of glass. However, at the same time, crystals must grow under the conditions of minimum strain energy when changing their atomic arrangements toward the laser scanning direction. This explains why the crystal growth direction changes gradually when the scanning direction changes gradually. Finally, it is emphasized that laser-induced crystallization, in which the region and direction of crystal growth are restricted artificially to a narrow space, can provide new crystal growth engineering, such as the self-organized homo-epitaxial growth proposed in this study.

6. Conclusions

Glasses with a 50BaF2–xAl2O3–(50 – x)B2O3 composition, which contain a high fraction of fluoride [F/(F + O) = 0.4], were prepared by the conventional melt-quenching technique. The local structure of fluorine changes and becomes more connective with the addition of Al2O3. 25Al2O3-doped glass shows structural similarity and forms BaAlBO3F2 after heat-treatment, where the formation of oxyfluoride crystals in glass is rare. The glass shows highly efficient PL with Eu3+-doping up to 97%. Laser-induced crystallization was performed on Ni 2O3-50BaF2–25Al2O3–25B2O3 glass.40) Glasses with different curvatures were patterned, and the birefringence image obtained for the spiral line is shown in Fig. 11. The orientation gradually changes and is regularly along the c-axis in the scanning direction. These results indicate that BaAlBO3F2 crystals are highly oriented even in the spiral line. On the basis of the results shown in Fig. 11, it is concluded that the direction of the c-axis of BaAlBO3F2 crystals changes gradually along the laser scanning direction. This indicates that a single crystal changes orientation gradually. When the scanning direction changes sharply, the change in orientation is delayed because of the large lattice mismatch. However, the scanning direction changes gradually because the lattice mismatch is small; therefore, the orientation also gradually changes to the preferred crystal growth direction. In laser-induced crystallization, a steep temperature gradient is created in the laser-irradiated local region; such a steep temperature gradient moves along the laser scanning direction, consequently providing crystal patterning with high orientation. The crystal growth rate is described in Eq. (1). In laser-induced crystallization, the diffusion of ions and structural units to the crystal growth front is regulated by the laser scanning direction, i.e., almost from one direction to another.

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