Photoluminescence and structural similarity of crystals with oxide–fluoride stacking structure and oxyfluoride glass

Kenji SHINOZAKI¹,2,†, Sohei SUKENAGA³ and Koji OHARA⁴

¹National Institute of Advanced Industrial Science and Technology (AIST), 1–8–31 Midorigaoka, Ikeda, Osaka 563–8577, Japan
²PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332–0012, Japan
³Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2–1–1 Katahira, Aoba-ku, Sendai 980–8577, Japan
⁴Diffraction and Scattering Division, Center for Synchrotron Radiation Research, Japan Synchrotron Radiation Research Institute (JASRI), 1–1–1 Kouto, Sayo, Hyogo 679–5198, Japan

In this study, we developed a highly efficient photoluminescent glass from the design of a short–medium range structure and the photoluminescence (PL) of a fluoroborate glass. We investigated PL and the structures of BaMgBO₃F ceramics and the B₂O₃-added composition of glasses and glass-ceramics. The glass showed higher quantum yield (QY) than ceramic samples, i.e., the QY was 95 % for glass and 51 % for ceramics, by a 395 nm excitation. The glass can contain a large amount of emission centers with small concentration quenching, and 15 % Eu-doped glass exhibited higher PL intensity and QY than commercial Y₂O₃:Eu³⁺ phosphor. The origin of a high QY and small concentration quenching were investigated by the structural analysis. The glass structure was investigated using ¹⁹F- and ¹¹B-magic-angle spinning nuclear magnetic resonance, extended X-ray absorption fine structure Ba K-edge, and high-energy X-ray diffraction. Moreover, the glass structure was simulated by molecular dynamics. It was found that the glass had a structural similarity with BaMgBO₃F crystal in the short-range order of B and Ba. The glass had a clear selectivity that B preferred to bind to O and Ba preferred to bind to F. The glass also exhibited unique medium-range ordering. Two types of Ba–Ba displacements were observed, which could be attributed to in-plane and out-plane layered displacements of the corresponding crystal, with the stacking structure of oxide–fluoride layers indicated by the radial distribution. The glass showed anion segregation, also similar to the layer-stacking structure of BaMgBO₃F. This made the low phonon sites coordinated with F compatible with the asymmetric sites derived from the oxide network segregation, resulting in high PL efficiency. The study results can contribute to the use of rare-earth ion-doped glasses in various applications such as laser and optical amplification, white light emitting diode (LED) lighting, and sensing technologies.

Key-words : Glass structure, Oxyfluorides, Photoluminescence, PDF analysis, Microsegregation

[Received August 6, 2020; Accepted September 25, 2020]
RE$^{3+}$-doped fluoride nanocrystals have been proposed. They show excellent PL, and owing to their high moldability and mass productivity, transparent glass-based phosphors are candidates not only as laser devices, but also as lighting and display devices such as LEDs. Although their emission intensity is usually lower than that of glass-ceramics, some precursor glasses show similar emission spectra. Qiu et al. proposed oxyfluoride glasses with 30CaF$_2$-20Al$_2$O$_3$-50SiO$_2$ form spherical fluoride-rich phase separation, and Er$^{3+}$-doped glass and glass-ceramics showed similar upconversion spectra because of the structural similarity of RE environment. Shinozaki et al. have reported that a large amount of MgF$_2$-added BaO-MgO-B$_2$O$_3$ glass shows similar upconversion spectra between glass and BaF$_2$ glass-ceramics, and shows prominent small nanocrystallization due to rapid nucleation. These studies indicate that the RE sites in oxyfluoride glasses are similar to the corresponding crystal phase and vice versa. Some oxyfluoride crystals have a layered structure of ionic fluoride and covalent oxide layers; in particular, the fluoroborate system is well-known. Fluoroborate crystals have been investigated as optical nonlinear crystals and phosphors, e.g., BaAlBO$_3$F and BaMgBO$_3$F. BaMgBO$_3$F is composed from the oxide layer of BO$_3$ and the fluoride layer of Ba–F, where F connects to Mg. Shinozaki et al. have reported a spectroscopic and short-range structural similarity of BaAlBO$_3$F crystal and its corresponding composition of glass. They also have reported that a large amount of MgF$_2$-added BaO–B$_2$O$_3$ glass exhibits a short-range structure similar to that of BaMgBO$_3$F using magic-angle spinning (MAS) nuclear magnetic resonance (NMR) and Raman scattering spectroscopy, where BaMgBO$_3$F exhibits higher emission characteristics. High emission characteristics can be expected when the structural similarity between glasses and crystals is utilized. However, the medium-range structure has not been elucidated. In this study, the medium-range structure of fluoroborate glass was investigated using high-energy X-ray diffraction (HEXRD). Furthermore, molecular dynamics (MD) was implemented to obtain glass structure. MD enables us to obtain the arrangement of a cation and anions, which is difficult to investigate experimentally in a multicomponent glass. In this work, we focus on the structure of fluoroborate glass prepared by vitrification of BaMgBO$_3$F crystal with small additives for glass formation using the melt-quenching process.

2. Experimental

2.1 Sample preparation and characterization

Eu$_x$Ba$_{1-y}$MgBO$_3$F ($y = 0$–0.5) ceramic samples were prepared under the conditions described in the previous literature. B$_2$O$_3$ was added to ceramic powders to achieve the nominal compositions of yEuF$_3$–(18.25 – y)BaF$_2$–18.25BaO–36.5MgO–27B$_2$O$_3$ ($y = 0$–18.25, \(\text{mol}\%\)). Then, the mixture was melted at 1373 K for 20 min in a platinum crucible in an ambient atmosphere. The melts were poured onto a brass plate and pressed to a thickness of \(\sim 1\) mm using another brass plate. The glass plates were mechanically polished using colloidal silica. Removal of F during melting was examined using the lanthanum alizarin complexone method. The density of the samples was determined using the Archimedes method. The glass transition temperature, \(T_g\), and the crystallization peak, \(T_c\), were determined using the differential thermal analyses (DTA) at a heating rate of 10 K/min in ambient atmosphere. The glass sample was heat-treated at the crystallization temperature, and the crystal phase in the samples was examined using XRD. The PL spectrum and internal quantum yields (QY) of the samples were evaluated at 297 K using a quantum efficiency measurement system (Otsuka Electronics QE-1100), which is composed of a spectrophotometer with an integral sphere. The samples were ground to a fine powder, and the cells were filled with the powder of exactly the same mass. Duration curves of PL for Eu$^{3+}$-doped samples were corrected by Spectrofluorophotometer (Hitachi High-Technologies, FL-7100) at 297 K.

The glass structure of the undoped sample was investigated using MAS NMR and HEXRD. $^{11}$B-MAS NMR spectroscopy was performed on a JEOL ECA-800 spectrometer (18.8 T, 800 MHz) using a 3.2 mm probe (JEOL, Tokyo, Japan) with ZrO$_2$ rotors, at a spinning speed of 20 kHz. $^{19}$Fluorine MAS NMR spectroscopy was performed on a JEOL ECA-600 spectrometer (14.3 T, 600 MHz) using an F-less 1 mm MAS probe (JEOL) with ZrO$_2$ rotors, at spinning speeds of 55–65 kHz. $^{11}$B- and $^{19}$F-MAS NMR signals were collected using a single pulse experiment with a small tip angle ($^{11}$B: 18 degree, $^{19}$F: 30 degree). $^{11}$B NMR spectra were referenced to a saturated H$_2$BO$_3$ solution at –19.49 ppm and $^{19}$F NMR spectra were referenced to CF$_3$COOH at –76.55 ppm. Ba K-edge X-ray absorption fine structure (EXAFS) spectroscopy was conducted at the BL14B2 beamline at SPring-8 (Hyogo, Japan). The samples were prepared by mixing glass and ceramic powders with boron nitride to an optimum concentration of the target ion. All data were collected in the standard transmission mode using an ion chamber detector at 298 K. The data analysis was performed using Athena, and the EXAFS spectra were theoretically fitted using the first shell model with an analysis package of FEFF6 embedded in Artemis. The phase-shifted radial distances and the coordination number were evaluated after the fitting.

For evaluating the short-to-medium-range ordering, HEXRD measurements were carried out for $Q$ values ranging from 0.16 to 25.00 Å$^{-1}$ ($Q = 4\pi \sin \theta / \lambda$, \(\lambda\): X-ray wavelength and \(2\theta\): diffraction angle) in the transmission mode using a two-axis diffractometer at HEXRD beamline BL04B2 at SPring-8 (Hyogo, Japan). Monochromatized high-energy X-rays with an energy of 113 eV were obtained with a Si(333) crystal monochromator. A sample with a thickness of 1 mm was measured at 297 K. The total data accumulation time was 5.5 h. The HEXRD intensity was reduced to the total interference function, multiplied by $Q$ and the Loach function, and Fourier-transformed into the pair correlation function, $g(r)$, using the conventional method.
2.2 MD simulation

MD was used to simulate the glass structure. Starting structures were obtained using an package of LAMMPS originally developed at Sandia National Laboratories, the United States.25,26) The initial configuration of \( N = 7884 \) particles (972Ba, 972Mg, 1404B, 3564O, and 972F) was obtained in the cell of \( 47.0514 \) Å to obtain the same experimental density as glass (\( d = 4.0 \text{ g/cm}^3 \)), and simulated by classical MD with a potential using the compressible ion model reported in.27) This potential allows to produce a reasonable structure for many glass systems including borates.28) Canonical ensemble to generate the glass structure was used for simulation of melting at 1500 K for 10 ns and cooling to 300 K at a cooling rate of 1 K/ps, and then held for 1 ns with a time step of 0.5 fs. The radial distribution function was calculated using the holding process at 300 K. The obtained configuration was visualized using a software of VESTA 3.29).

3. Results and discussion

Transparent glasses from a precursor glass of Eu\(_x\)Ba\(_{1-x}\)MgBO\(_3\)F with \( x = 0 \)–0.5, which can be rewritten as \( y\text{EuF}_3(18.25-y)\text{BaF}_2-18.25\text{BaO}-36.5\text{MgO}-27\text{B}_2\text{O}_3 \) (in mol \%) were prepared. Many fluoroborates lose several tens of percent of F during melting.30) From the chemical analysis, the loss of F was less than 1 \% for the nominal composition. Recently, Shinozaki et al. have reported that the presence of Mg\(_{2+}\) in fluoroborates forms Mg–F–Ba and Mg–F–Mg bonds and F taken into the glass network, and this suppresses the evaporation of F.31) The glasses showed glass transition temperature \( (T_g) \) at 446 °C and the crystallization peak \( (T_p) \) at 505 °C in the DTA curve. The XRD pattern of the sample is shown in Fig. 1. The glass shows an amorphous halo pattern, and after heat treatment, a single phase of BaMgBO\(_3\)F was precipitated. The BaMgBO\(_3\)F crystal used as the raw material of the glass was re-precipitated in nanosize by heat treatment. In many oxyfluoride glasses, fluoride crystals are precipitated by heat treatment.31) For example, CaF\(_2\) nanocrystals are precipitated in CaF\(_2\)–Al\(_2\)O\(_3\)–SiO\(_2\) glass.32)

By contrast, in this oxyfluoride glass, oxyfluoride crystals were crystallized by heat treatment. It is suggested that the formation of oxyfluoride crystals in the glass is superior to fluoride formation in terms of free energy or crystallization rate. It has been pointed out that the precipitated crystal phase and the precursor glass structure are related. For example, in a silicate system, there is a relationship that the linkage unit of the precipitated crystalline phase is similar to the precursor glass.7)

The PL spectra of the precursor Eu\(_{0.05}\)Ba\(_{0.95}\)MgBO\(_3\)F ceramics and its related composition of glass and glass-ceramics are shown in Fig. 2(a). The glass has higher PL intensity than the corresponding crystal phase. The \( ^7\text{D}_0 \rightarrow ^7\text{F}_1 \) emission is nearly independent of the host matrix owing to the magnetic-dipole transition, and \( ^5\text{D}_0 \rightarrow ^5\text{F}_2 \) emission is hypersensitive to its local structure owing to the electric-dipole transition.33) The integral intensity was evaluated by peak fitting and the ratio of \( R = (D_2 \rightarrow F_3)/(D_1 \rightarrow F_1) \), which relates with the Eu\(^{3+}\) site symmetry parameter. Fluoride glasses take a symmetric coordination owing to nondirectional nature of ionic bonding, e.g., \( R = 1.0 \) for \( 1\text{EuF}_3-60\text{ZrF}_4-33\text{BaF}_2-6\text{LaF}_3 \) glass,34) and oxide glasses show a relatively large value owing to the directionality of covalent bonding, e.g., \( R = 3.40 \) for 0.5Eu\(_2\)O\(_3\)–25Li\(_2\)O–74.5B\(_2\)O\(_3\) glass.35) The ratios \( R \) were \( R = 3.6 \) for the BaMgBO\(_3\)F:Eu ceramic sample, \( R = 3.4 \) for the glass, and \( R = 3.6 \) for the glass-ceramics. The glass has a slightly smaller \( R \) than the crystal. This indicates that local asymmetry of Eu\(^{3+}\) in the glass is smaller than that in the BaMgBO\(_3\)F crystals and glass-ceramics. The internal QYs of the glass and BaMgBO\(_3\)F crystals are shown in inset of Fig. 2(b). The internal QY for the glass is 95 \%, which is higher than that of the BaMgBO\(_3\)F:Eu\(^{3+}\) crystals. Shinozaki et al. have reported the impact of codoping of alkali ion in the Ba site and enhancement of the internal QY up to 82 \% by Li\(^{+}\) co-doping owing to charge compensation. The glass-ceramics also showed high QY, but smaller than that of the precursor glass. Generally, glass crystallization is attempted to increase the QY and PL intensity of glass, but it has been revealed that glass has higher QY and PL intensity compared with those of crystal. It should be noted that vitrification enhances the QY and PL intensity. Vitrification removed grain boundaries, defects, and charge compensation, which are likely to be the origins of non-radiative transitions, defect-derived absorption, and scattering centers that suppress the QY and absorption efficiency. The QY, lifetime of glass, and starting material ceramics for different amounts of Eu\(^{3+}\) content are shown in Fig. 2(c). Here, single-phase ceramics could not be obtained for \( x > 0.1 \). Glasses with \( x > 0.1 \) were made from the mixed-phase of BaMgBO\(_3\)F and an unknown phase starting materials. In both samples, the QY and lifetime decreased with increasing amounts of Eu\(^{3+}\) content owing to concentration quenching, however, the decrease in both the quantum efficiency and lifetime were smaller for glass than for ceramics. In the Ca\(_{1-2x}\)(Eu,Na)\(_x\)WO\(_4\) crystal, the
quantum efficiency was over 90% and the lifetime was 0.8 ms when 5% of the Ca site was replaced by Eu; however, they decreased considerably to 50% and 0.3 ms owing to concentration quenching when 12% of the Ca site was replaced.36) The glass obtained in this work showed a high quantum efficiency of 58% and almost constant lifetimes of 2.3 to 2.1 ms even after 50% Eu substitution of the Ba site. This low concentration quenching enabled a large amount of Eu to be added, while maintaining a high quantum efficiency. A comparison of the glass and a commercial Y2O3:Eu³⁺ crystal powder is shown in Fig. 2(d). The integral PL intensity of the glass powder excited by 395 nm was three times higher than that of the commercial Y2O3:Eu³⁺ powder owing to a high QY and large Eu content. Such high QY value and high PL intensity of RE in glasses have not been reported to the best of our knowledge. As transparent bulk phosphors can be easily synthesized and can be molded, the glass phosphor is expected to be used for lighting applications with UV-LED chip excitation. The structure of the glass exhibiting this emission characteristic was examined in detail as follows.

The low concentration quenching is related to the glass structure. To investigate the short-range structure of the glass, ¹⁹F- and ¹¹B-MAS NMR spectra and EXAFS for K-edge of Ba of the glass were measured. In Fig. 3(a), the peaks at 80 and 130 ppm appeared in ¹⁹F-MAS NMR. It has been reported that the chemical shifts of F in local structures of F-Mg, F-Ba, and F-B appeared at 194.8, 15, and 24 ppm, respectively.37),38) Scholz et al. prepared BaF₂-MgF₂ crystalline compounds, and their chemical shifts were at 80.7 and 87.9 ppm for FMgBa₃, −161.3 ppm for FMg₂Ba₄, and −169.9 ppm for FMg₃Ba₅.39) The first peak at −80 ppm is close to that of FMgBa₃ and the second peak at −130 ppm is between that of FMgBa₃ and

![Graphs and images from the document]

**Fig. 2.** (a) PL spectra. The spectra are normalized by integrated intensity of $^{7}D_{0} \rightarrow {}^{7}F_{1}$ transition. (b) QY in the visible range by the excitation of 395 nm for the precursor Eu₀.₀₅Ba₀.₉₅MgBO₃F ceramics and related composition of glass and glass-ceramics. (c) QY and lifetime of the glasses and ceramic samples with varying amount of Eu³⁺ for Ba³⁺ site. (d) Comparison of the glass obtained from the precursor composition of Eu₀.₁₅Ba₀.₈₅MgBO₃F and commercial powder of Y₂O₃:Eu.
This indicates that F in the glass is surrounded by both Ba and Mg, and not bound to B. The absence of a signal corresponding to F–B in the glass indicates that the chemical affinity of F– and B\(^{2+}\) is poor, and F has a significant selectivity for the neighboring cation. F in the BaMgBO\(_4\)F crystal is surrounded by three Ba\(^{2+}\) ions for in-plane (\(a\)-\(b\) axis) and two Mg\(^{2+}\) ions for out-plane (\(c\)-axis), and not bound to B as well. In Fig. 3(b), the \(^{11}\)B-MAS NMR spectrum shows peaks at 2 and 18 ppm, and the peaks are attributed to BO\(_3\) and BO\(_4\) units, respectively.\(^ {40}\) From the area of the peaks, 90.2% of B takes the BO\(_3\) unit and 9.8% takes the BO\(_4\) unit. As the BaMgBO\(_4\)F crystal consists of BO\(_3\), B has a similar environment in the glass and crystal. The coordination number of boron depends on the amount of alkaline ions in alkaline earth borate glasses. In the \(x\)Mg\(_2\)Ba\(_3\)O\(_7\)F system, the borate network is largely broken by the addition of alkaline earth ions; therefore, it is not able to contain considerable amount of alkaline earth ions for out-plane (\(b\)-axis) of the BaMgBO\(_4\)F crystal; i.e., 1.981 Å for Mg–O, 2.068 Å for Mg–F, 2.68–2.77 Å for Ba–O, 2.71–2.78 Å for Ba–F, 3.8–4.0 Å for Ba–Ba in out-plane (\(c\)-axis), and 4.6–4.7 Å for Ba–Ba in in-plane (\(a, b\)-axis) of the BaMgBO\(_4\)F crystal. The crystal structure and the displacements between Ba–Ba are shown in Fig. 4(c). It is notable that the glass has two types of Ba–Ba displacements equivalent to in-plane and out-plane Ba–Ba displacements. This indicates that the glass exhibits directionality, rather than a random structure. The modeling of Ba–Ba in the glass is FMg\(_2\)Ba\(_3\). This indicates that F in the glass is surrounded by both Ba and Mg, and not bound to B. The absence of a signal corresponding to F–B in the glass indicates that the chemical affinity of F– and B\(^{2+}\) is poor, and F has a significant selectivity for the neighboring cation. F in the BaMgBO\(_4\)F crystal is surrounded by three Ba\(^{2+}\) ions for in-plane (\(a\)-\(b\) axis) and two Mg\(^{2+}\) ions for out-plane (\(c\)-axis), and not bound to B as well. In Fig. 3(b), the \(^{11}\)B-MAS NMR spectrum shows peaks at 2 and 18 ppm, and the peaks are attributed to BO\(_3\) and BO\(_4\) units, respectively.\(^ {40}\) From the area of the peaks, 90.2% of B takes the BO\(_3\) unit and 9.8% takes the BO\(_4\) unit. As the BaMgBO\(_4\)F crystal consists of BO\(_3\), B has a similar environment in the glass and crystal. The coordination number of boron depends on the amount of alkaline ions in alkaline earth borate glasses. In the \(x\)Mg\(_2\)Ba\(_3\)O\(_7\)F system, the borate network is largely broken by the addition of alkaline earth ions; therefore, it is not able to contain considerable amount of alkaline earth ions for out-plane (\(b\)-axis) of the BaMgBO\(_4\)F crystal; i.e., 1.981 Å for Mg–O, 2.068 Å for Mg–F, 2.68–2.77 Å for Ba–O, 2.71–2.78 Å for Ba–F, 3.8–4.0 Å for Ba–Ba in out-plane (\(c\)-axis), and 4.6–4.7 Å for Ba–Ba in in-plane (\(a, b\)-axis) of the BaMgBO\(_4\)F crystal. The crystal structure and the displacements between Ba–Ba are shown in Fig. 4(c). It is notable that the glass has two types of Ba–Ba displacements equivalent to in-plane and out-plane Ba–Ba displacements. This indicates that the glass exhibits directionality, rather than a random structure. The modeling of Ba–Ba in the glass is
produced by RMC. Ba has the largest X-ray scattering factor in the glass composition, and the results largely reflect the distribution of Ba. On the other hand, the difference of scattering factor for X-ray of F and O are small and the scattering factor of B are small, therefore, there distribution could not obtain from only HEXRD.

The glass structure simulated using MD and the crystal structure of BaMgBO$_3$F are shown in Fig. 5, and the evaluated $g(r)$ for each ion are shown in Fig. 6. The coordination number ($N$) of the anions for each cation was evaluated, and $N_{Ba} = 3.7$ for B was obtained. The coordination numbers of B was higher than experimental data obtained using $^{11}$B-MAS NMR. The average anion ratio F/(O + F) of the first neighbor of B was 0.0, therefore; B preferably bound to O and hardly bound to F. The average anion ratio F/(O + F) of the first neighbor of Mg was 0.50. Mg bound to both O and F without strong preference. The average anion ratio F/(O + F) of the first neighbor of Ba was 0.60. The value is larger than a nominal anion ratio in the glass of 0.22. In other words, F strongly prefers to bind to Ba and not to B, and O is vice versa. The significant selectivity would be owing to the electronegativity ($X$) of cations. The value of electronegativity by the Allen scale is 0.881 for Ba, 1.293 for Mg, 2.051 for B, 3.61 for O, and 4.193 for F. As Ba has small electronegativity, Ba$^{2+}$ ion strongly attracts to F$^-$ ion. By contrast, the electronegativity of B$^{3+}$ is relatively close to that of O, and B–O bonding is possible with covalency. In a majority of fluoroborate crystals, B directly binds to O and does not form a bond with F. This also indicates that the B–O unit
is stable. This indicates that the chemical affinity of B and F is relatively poor. This agrees with the result of the $^{19}$F-NMR spectrum. The selectivity was not significant in Mg because its electronegativity is intermediate between Ba and B. This bonding selectivity forms a unique glass structural property; oxide BO$_3$ units form oxide aggregation and Ba–F species segregations. The corresponding crystal of BaMgBO$_3$F forms a stacking structure of BO$_3$–MgO$_4$, and Ba–F planes between them [Fig. 5(b)]. This layer-stacking structure corresponds to the two distances of the in-plane and out-plane of Ba–Ba. Similarly, oxide and fluoride segregation structure in the glass was observed in Fig. 5(a). magnesium borate units forms oxide segregation, and Ba–F forms fluoride segregation. The glass has a unique structure in which the layered structure of crystals is randomized, which indicates that the glass also has a layered-like structure as BaMgBO$_3$F. Greaves proposed a modified random network model of the oxide glass structure in which modifier cations in glass form microsegregation. In oxyfluoride glass, those with significantly different polarities have the property of easy aggregation. For example, it has been clarified using an MD simulation that a droplet phase separation having a composition similar to that of fluoride crystal emerges in a silicate-based oxyfluoride glass. In the oxyfluoride silicate case, the formation of spherical fluoride aggregation has been reported. However, the fluoroborate glass examined in this study is likely to have a channel or layer-like fluoride segregation structure. The RE site is surrounded by low-phonon energy F, as suggested by a decrease in the $R$-value in PL spectra. Although the coordination environment of fluoride significantly reduces the $R$-value due to the non-directional ionic bonding nature, the $R$ of the glasses in this study was as large as that of typical oxide glasses. The phonon energy of the Eu site was reduced by fluorine coordination, and the oxide segregation with directional covalent bonds distorted the coordination environment, making it asymmetric. The segregation structure also improved the dispersion of Eu sites and suppressed the concentration quenching. Less prone to concentration quenching in the glass is owing to the long distance between RE sites resulting from the low dimensional ordering of the glass structure. The glass can contain large amounts of Eu$^{3+}$ ions, while maintaining a high quantum efficiency. Therefore, a high internal quantum efficiency and high rare-earth content enable a high PL intensity. We succeeded in designing a segregated structure of anions similar to the corresponding composition of the fluoroborate crystal. Unlike crystals, glass does not require charge compensation and there is no grain boundary nor any defects. In addition, a large amount of emission centers can be doped with small concentration quenching. Further, such a segregated structure can be useful for various functionalities such as ion conduction and dielectric properties.

4. Conclusion

PL and structure of BaMgBO$_3$F corresponding composition of glass were investigated. The glass showed higher QY than ceramic samples (95 % for glass, 51 % for ceramics). The structures of the glass and BaMgBO$_3$F are similar; i.e., B mainly forms BO$_3$ units and Ba coordinates $\sim$9 anions, same as the crystal. Two types of Ba–Ba displacements were observed, which can be attributed to in-plane layered sites and out-plane layered sites indicated by the radial distribution. The glass has a clear selectivity that B prefers to bind to O and Ba prefers to bind to F owing to smaller chemical affinity. Owing to that, the glass shows union segregation, similar to the layer-stacking structure of BaMgBO$_3$F. Generally, when a large amount of F is coordinated, the asymmetry of the RE site becomes small, and the emission characteristics deteriorate. However, it is considered that this glass exhibits high emission characteristics because it has a high amount of fluoride coordination with low phonon energy and asymmetric local structure owing to segregation of oxides. The study results can contribute to the use of RE ion-doped glasses in various applications such as laser and optical amplification, white LED lighting, and sensing technologies.

Acknowledgements

The synchrotron radiation experiments were performed at BL04B2 and BL14B2 at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2016B1823 and 2017B1008). This work was supported by JSPS KAKENHI Grant No. 19K15663.

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