Matrix effect on local structure surrounding Yb$^{3+}$ and spontaneous emission probability in oxide glasses

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Received 2 August 2001; revised 30 November 2001; accepted 30 November 2001

Abstract

Extended X-ray absorption fine structure measurements have been performed on Yb$^{3+}$ in silicate, borate, phosphate, and gallate glasses in order to investigate the local structures surrounding Yb$^{3+}$. The local structures of Yb$^{3+}$ ions in silicate, borate, and phosphate glasses were similar to those of Er$^{3+}$ ions. Yb$^{3+}$ ions do not occupy the network structural sites, but sit around the terminal region of the network or the region between the networks in these glasses. On the other hand, Yb$^{3+}$ ions substitute the Ga$^{3+}$ sites in complex anion structural units of the K$_2$O–Ga$_2$O$_3$–Nb$_2$O$_5$ glasses. We classified the local structures surrounding Yb$^{3+}$ ions in oxide glasses into two types: the former and the latter are interstitial and substitutive types, respectively. The relationship between the spontaneous emission probability for $^2$F$_{5/2} \rightarrow ^2$F$_{7/2}$ transition of Yb$^{3+}$ and the local structure of Yb$^{3+}$ in oxide glasses are discussed in terms of these two types. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Extended X-ray absorption fine structure spectroscopy; Local structure; Yb$^{3+}$; Rare earth ions in oxide glasses; Spontaneous emission probability; III–V Compound type oxide glass; K$_2$O–Ga$_2$O$_3$–Nb$_2$O$_5$ glass

1. Introduction

Glasses have been used for matrices of rare earth ion doped solid-state lasers because they have many advantages over single crystals such as mass production at low cost and easiness of forming fibers. For evaluating the lasing properties of glasses containing rare earth ions, spontaneous emission probability is most important [1]. Over the past few decades, a considerable number of studies have been made regarding the compositional dependence of the spontaneous emission probabilities of rare earth ions doped glasses [2], which is calculated on the basis of Judd–Ofelt theory [3,4], in terms of the local structures surrounding the rare earth ions.

The local structures surrounding rare earth ions in glasses have been often estimated by the absorption and fluorescence spectroscopies [5,6], because it is difficult to analyze the local structure surrounding trace amount of rare earth ions in glasses using infrared (IR) and Raman spectroscopies. Instead of such spectroscopic measurements, the local structures of trace amounts of rare earth ion in glasses can be analyzed using extended X-ray absorption fine structure (EXAFS) measurements. It results from the local diffraction of excited photoelectrons. The strength of oscillation are functions of the back-scattering power of an atomic matrix, and the thermal and static disorder of atomic positions. In the previous report [7], the authors analyzed the local structure surrounding Er$^{3+}$ in silicate, borate, and phosphate glasses by EXAFS measurements, and revealed the compositional dependence of the spontaneous emission probability of the $^4$I$_{13/2} \rightarrow ^4$I$_{15/2}$ transition of Er$^{3+}$, which is utilized for the 1.5 μm amplifier, in terms of the average Er–O distance calculated by EXAFS analysis. In order to develop a new laser glass, the matrix glass composition must be optimized for rare earth ions. Therefore, it is necessary to investigate the local structure surrounding rare earth ions in glasses in detail by systematically varying the matrix glass compositions.

In this paper, the local structures surrounding Yb$^{3+}$ in oxide glasses are investigated on the basis of EXAFS measurements. The relationship between the spontaneous emission probability for the $^2$F$_{5/2} \rightarrow ^2$F$_{7/2}$ transition of Yb$^{3+}$, which is prospective as a high power laser for nuclear fusion instead of Nd$^{3+}$ [8], and the matrix glass composition in terms of the local structures surrounding Yb$^{3+}$ are discussed.
Table 1

| Glass matrix compositions |
|---------------------------|
| Matrix glass composition (mol%) |
| Silicate                  |
| xNa$_2$O–(100 – x)SiO$_2$ (x = 10, 20, 30, 40) |
| 40R$_2$O–60SiO$_2$ (R = Li, Na, K) |
| Borate                    |
| xNa$_2$O–(100 – x)B$_2$O$_5$ (x = 10, 15, 20, 25, 30, 35) |
| Phosphate                 |
| xNa$_2$O–(90 – x)P$_2$O$_5$–10Al$_2$O$_3$ (x = 25, 30, 35, 40) |
| 30R$_2$O–60P$_2$O$_5$–10Al$_2$O$_3$ (R = Li, Na, K) |
| Gallate                   |
| 30K$_2$O–70Ga$_2$O$_3$ |
| 40K$_2$O–(60 – x)Ga$_2$O$_3$–xNb$_2$O$_5$ (x = 20, 30) |

2. Experimental procedure

2.1. Glass preparation

The matrix glass compositions investigated in this work are listed in Table 1. Glasses were prepared using special-grade reagents (99.9–99.99%) in 15 g batches. Each batch mixed with 2 mol% Yb$_2$O$_3$ was melted in a platinum or alumina crucible at given temperatures in air for 2 h. Each molten glass was poured onto a stainless-steel mold, and annealed for 1 h above glass transition temperature. The method for glass preparation was described in detail elsewhere [9]. Annealed samples were ground up to less than 3 μm using an alumina mortar and pestle for EXAFS measurements.

2.2. EXAFS measurements

Yb L$_{III}$-edge X-ray absorption spectra were measured in absorption and fluorescence modes at room temperature using a laboratory-type X-ray spectrometer (Model R-EXAFS 2000, Rigaku, Tokyo, Japan) that consisted an X-ray generator with a rotating Mo target and LaB$_6$, electron gun, a Ge (311) curved crystal monochromator, and detectors. The voltage and current of X-ray source were 24 kV and 230 mA, respectively. Incident, transmitted, and fluorescent X-ray intensities were monitored with an ionization chamber filled with argon gas, scintillation counter, and a solid-state detector, respectively. Powder samples were mounted uniformly on an adhesive tape. A number of such layers were measured in order to adjust the absorption edge/background ratio approximately to 0.001–0.01. The sampling range, points, and time were 9680–9830 eV, 520 points per sample, and 300 s per point, respectively. An Yb L$_{III}$-edge X-ray absorption spectrum of the crystalline Yb$_2$O$_3$ was also measured as a standard by the same way in order to calibrate the EXAFS spectra of samples. Moreover, a Ga K-edge X-ray absorption spectra of the gallate matrix glasses were measured to investigate these glass structures. The method for EXAFS data analysis was described in detail elsewhere [7].

3. Results and discussion

3.1. Matrix effect on local structure surrounding Yb$^{3+}$ ion in oxide glasses

Fig. 1 shows the radial distribution functions of Yb$^{3+}$ in silicate, borate, phosphate, and gallate glasses, as representative examples. The peaks of the radial distribution functions corresponding to the first and second neighboring ions could be identified because the positions did not change with the variation in k-space for the EXAFS analysis.

The peak positions and intensities, and spectral profiles of the radial distribution functions corresponding to the first and second neighboring ions did not change with the Na$_2$O content in the Na$_2$O–SiO$_2$ glasses, but depended on that in the Na$_2$O–B$_2$O$_3$ glasses. The peak positions, intensity and spectral profiles of the radial distribution functions corresponding to the first and second neighboring ions did not change with the content and type of alkali ions in the phosphate glasses. These compositional dependence of local structural parameters and radial distribution functions of Yb$^{3+}$ in silicate, borate, and phosphate glasses are similar to those of Er$^{3+}$ [7]: Yb$^{3+}$ ions coordinate to non-bridging...
oxygen ion sites, where alkali or alkaline earth ions terminate the network structure of silicate glasses. In borate glasses, the local structure surrounding Yb\(^{3+}\) ions is altered by the structural change of the borate anion. Yb\(^{3+}\) ions coordinate to non-bridging oxygen ion sites and BO\(_4\) structural units in the cases with and without the formation of non-bridging oxygen, respectively. The former is similar to the case in silicate glasses. Yb\(^{3+}\) ions selectively coordinate to the P=O site regardless of the glass composition variation.

Fig. 1(d) shows that the band of the radial distribution function for the second neighboring ion is located in the range of 2.5–4.0 Å with the two peaks around 2.7 and 3.5 Å. It is supported that the two different types of second neighboring ions would sit close to the Yb\(^{3+}\) ions in contrast to silicate, borate, and phosphate glasses. It is well known that Si\(^{4+}\), B\(^{3+}\), and P\(^{5+}\) are typical network formers and their glass structures. On the other hand, the structure of gallate glasses has not been fully understood because only a few papers have been published on that [10]. Therefore, we measured the Ga K-edge X-ray absorption spectra of K\(_2\)O–Ga\(_2\)O\(_3\)–Nb\(_2\)O\(_5\) matrix glasses in order to investigate the glass structure, which is necessary to discuss the local structure surrounding Yb\(^{3+}\) in these glasses.

Fig. 2 shows the radial distribution functions of Ga\(^{3+}\) in the 30K\(_2\)O–70Ga\(_2\)O\(_3\) and 40K\(_2\)O–30Ga\(_2\)O\(_3\)–30Nb\(_2\)O\(_5\) glasses, and that in the crystalline GaNbO\(_4\) as a reference. It is observed that the peak positions of the first (O\(^2−\)) and second neighboring ion were approximately 1.5 and 3.0 Å in the 30K\(_2\)O–70Ga\(_2\)O\(_3\) glass, respectively. The calculated oxygen coordination number of Ga\(^{3+}\) is 4.80. Approximately, the same fractions of the oxygen four- and six-coordinated Ga\(^{3+}\) may exist in the 30K\(_2\)O–70Ga\(_2\)O\(_3\) glass, which is consistent with the IR measurements [11]. The radial distribution functions varied with the addition of Nb\(_2\)O\(_5\) in the gallate glass: the radial distribution function for the O\(^2−\) is broad, and the peaks corresponding the second neighboring ions appear near 2.3 Å and around 2.8–3.5 Å in the 40K\(_2\)O–30Ga\(_2\)O\(_3\)–30Nb\(_2\)O\(_5\) glass. The calculated oxygen coordination number of Ga\(^{3+}\) in the 40K\(_2\)O–30Ga\(_2\)O\(_3\)–30Nb\(_2\)O\(_5\) glass is 6.28. Almost all Ga\(^{3+}\) would exist in the oxygen six-coordinated state in the 40K\(_2\)O–30Ga\(_2\)O\(_3\)–30Nb\(_2\)O\(_5\) glass. This result implies that a new anion structure would form in the gallate glasses due to the addition of Nb\(_2\)O\(_5\). The radial distribution function of Ga\(^{3+}\) in the crystalline GaNbO\(_4\) exhibits the peak near 1.6 Å due to the O\(^2−\). The oxygen coordination number of Ga\(^{3+}\) in the crystalline GaNbO\(_4\) that has rutile structure is 6 (see Fig. 3). The band corresponding to the second neighboring ions has three peaks around 2.4, 2.9 and 3.8 Å because the second neighboring ions are Ga\(^{3+}\) and Nb\(^{5+}\) in the crystalline GaNbO\(_4\) that has rutile structure. The oxygen coordination number and the distribution function of Ga\(^{3+}\), especially the spectral profile of second neighboring ion, in the 40K\(_2\)O–30Ga\(_2\)O\(_3\)–30Nb\(_2\)O\(_5\) glass are similar to those of the crystalline GaNbO\(_4\). Thus, it is concluded that the K\(_2\)O–Ga\(_2\)O\(_3\)–Nb\(_2\)O\(_5\) glasses have the rutile-like mixed anions structure of Ga\(^{3+}\) and Nb\(^{5+}\), and we call them the III–V compound type oxide glass.

Now that we have obtained the structure of gallate glasses, we are able to discuss the local structure of Yb\(^{3+}\) ion in K\(_2\)O–Ga\(_2\)O\(_3\)–Nb\(_2\)O\(_5\) glasses. The distribution function of Ga\(^{3+}\) would be similar to that of Yb\(^{3+}\) in the 40K\(_2\)O–30Ga\(_2\)O\(_3\)–30Nb\(_2\)O\(_5\) glass comparing Fig. 1(d) with Fig. 2: the band for the second neighboring ions has two peaks and is close to that of Yb\(^{3+}\) in 40K\(_2\)O–30Ga\(_2\)O\(_3\)–30Nb\(_2\)O\(_5\) glass in contrast to silicate, borate and phosphate glasses. The calculated oxygen coordination numbers of Ga\(^{3+}\) and Yb\(^{3+}\) in the 40K\(_2\)O–30Ga\(_2\)O\(_3\)–30Nb\(_2\)O\(_5\) glass are 6.28 and 6.01, respectively, on the basis of EXAFS analysis. Because Ga\(^{3+}\) and Yb\(^{3+}\) ions have the same valence state, and theionic radius of Ga\(^{3+}\) (76.0 pm) resembles that of Yb\(^{3+}\) (100.8 pm), they would have the same oxygen coordination number. 6. Therefore, it is considered that Yb\(^{3+}\) ions substitute the Ga\(^{3+}\) sites in the III–V compound type structural units. Fig. 3 schematically shows the local structure of Yb\(^{3+}\) ions in the K\(_2\)O–Ga\(_2\)O\(_3\)–Nb\(_2\)O\(_5\) glasses determined by the EXAFS analysis. Thus, Yb\(^{3+}\) ions sit close to the second neighboring ions (i.e.
3.2. Classification of local structure surrounding Yb$^{3+}$ ion in oxide glasses

From the results of EXAFS analyses, it is concluded that Yb$^{3+}$ ions coordinate to non-bridging oxygen ion sites, BO$_4$ structural units, and P=O sites in silicate, borate, and phosphate glasses, respectively. Yb$^{3+}$ ions do not occupy the network structural sites, but sit around the terminal region of the network or the region between the networks, because the typical network formers such as Si$^{4+}$, B$^{3+}$, and P$^{5+}$ have oxygen coordination numbers of 3 or 4, and Si–O, B–O and P–O bondings are strong. Fig. 4(a) schematically shows the local structure surrounding Yb$^{3+}$ ions in oxide glasses with typical network formers. Yb$^{3+}$ ions exist at a kind of interstitial site among large anion structural groups constituting a network, and we define such a local structure as ‘interstitial type’. On the other hand, the network of K$_2$O–Ga$_2$O$_3$–Nb$_2$O$_5$ matrix glasses consists of the structural units of the rutile-like III–V compound, GaNbO$_4$, of Ga$_2$O$_3$ and Nb$_2$O$_5$, though these oxides alone cannot form glass. Yb$^{3+}$ ions substitute the Ga$^{3+}$ sites in the glass network region, because Yb$^{3+}$ and Ga$^{3+}$ ions have the same valence state, +3, and oxygen coordination number. 6. Fig. 4(b) schematically shows the local structure surrounding Yb$^{3+}$ ions in the III–V compound type oxide glass. Yb$^{3+}$ ions exist in anion structural groups constituting a network, and we define such a local structure as ‘substitutive type’. Consequently, the local structure surrounding rare earth ions in the oxide glasses is classified into two types: interstitial type and substitutive type, as mentioned earlier.

3.3. Correlation between the local structure surrounding Yb$^{3+}$ ion and spontaneous emission probability of Yb$^{3+}$

We revealed the local structure surrounding Yb$^{3+}$, and classified the local structure surrounding rare earth ions in silicate, borate, phosphate, and gallate glasses. The spontaneous emission probabilities for f–f transitions of Yb$^{3+}$ ions in oxide glasses should be affected by the local structure surrounding Yb$^{3+}$ ions. Next, we will discuss the relationship between the local structure surrounding Yb$^{3+}$ and spontaneous emission probability for $^2F_{5/2}$ $\rightarrow$ $^2F_{7/2}$ transition of Yb$^{3+}$, A coefficient, which is utilized for the nuclear fusion laser [8], in silicate, borate, phosphate, and gallate glasses.

Fig. 5 shows the compositional dependence of A coefficient of silicate, borate, phosphate, and gallate glasses. These data were cited by the previous works [12]. In silicate, borate, and phosphate glasses, the A coefficient indicates around 1000 s$^{-1}$. On the other hand, the A coefficient of K$_2$O–Ga$_2$O$_3$–Nb$_2$O$_5$ glass samples show values about 2.5 times higher than those of silicate, borate, and phosphate glass samples. This suggests that the substitutive type of Yb$^{3+}$ shows A coefficient higher than the interstitial type of Yb$^{3+}$.

The spontaneous emission probability for $^2F_{5/2}$ $\rightarrow$ $^2F_{7/2}$ transition of Yb$^{3+}$, A coefficient is given by the following equation based on Judd–Ofelt theory [3,4]

$$A[(S,L)J : (S',L',J')] = \frac{64\pi^4 e^2}{3\hbar(2J+1)\lambda_p^3} \sum_{i=2,4,6} \Omega_i \left|\langle S,L,J || U^{(i)} || (S',L',J') \rangle\right|^2$$

(1)

where e and $\hbar$ have their customary meanings, S, L, J are the quantum numbers, $\lambda_p$ is the fluorescence wavelength, n is the refractive index at $\lambda_p$, $U^{(i)}$ is an eigenvalue so-called the reduced matrix elements of unit tensor operators, which is independent of the glass composition and determined by the f–f transitions, and $\Omega_i$ is a coefficient, which depends on the glass compositions. From Eq. (1), the factors affecting the compositional dependence of A coefficient are $[n(n^2 + 2)^2/9]$ and $\sum \Omega_i \left|\langle U^{(i)} \rangle\right|^2$ terms. The values of $[n(n^2 + 2)^2/9]$ term in silicate, borate, and phosphate glass samples and gallate glass samples are 2.86–3.22 and 4.26–4.81, respectively [12]. Therefore, A coefficients of gallate samples would show higher value than those of silicate, borate, and phosphate glass samples. However, refractive index would not be a main factor for determining A coefficient.
because the \( [n(n^2 + 2)^2/9] \) term of gallate glasses is only 1.5 times higher than that of silicate, borate, and phosphate glasses.

The \( \sum \Omega_i \|U^{(i)}\|^2 \) term is affected by the sum of the product of \( \Omega_i \) and \( \|U^{(i)}\|^2 \). Previous studies [13–15] regarding the product of \( \Omega_i \) and \( \|U^{(i)}\|^2 \) in oxide glasses concluded that \( \Omega_2 \|U^{(2)}\|^2 \) relates to the asymmetry in the local structure surrounding rare earth ions, and \( \Omega_6 \|U^{(6)}\|^2 \) relates to the covalency of rare earth ion and oxygen ion bonding. Taking two types of compositional dependence into account, the contribution rate of the \( \|U^{(i)}\|^2 \) eigenvalue \( 16 \) for the A coefficient are calculated: \( \|U^{(3)}\|^2 = 10\% \), \( \|U^{(4)}\|^2 = 30\% \), and \( \|U^{(6)}\|^2 = 60\% \). In the previous reports [7], the authors found that a correlation between the spontaneous emission probability for \( ^{2}F_{3/2} \rightarrow ^{2}F_{1/2} \) transition of Er\(^{3+} \), which is mainly determined by the \( \Omega_6 \|U^{(6)}\|^2 \) term, and the average Er–O distance calculated by EXAFS analysis. It shows the maximum value near the optimum Er–O distance 2.3 Å (\( = 1.03 + 1.26 \) Å), which is estimated from the ionic radii of Er\(^{3+} \) (1.03 Å) and O\(^{2-} \) (1.26 Å). On the other hand, there is no correlation between the A coefficient and the average Yb–O distance. Therefore, it is assumed that the \( \Omega_2 \|U^{(2)}\|^2 \) and \( \Omega_6 \|U^{(6)}\|^2 \) terms would not be effective for the A coefficient of K\(_2\)O–Ga\(_2\)O\(_3\)–Nb\(_2\)O\(_5\) glasses, even though the contribution rate of the \( \|U^{(2)}\|^2 \) and \( \|U^{(6)}\|^2 \) is higher than that of \( \|U^{(4)}\|^2 \). This consideration based on the EXAFS analysis agrees with the previous studies [12] that the main factor for determining the A coefficient is \( \Omega_2 \|U^{(2)}\|^2 \) term and not \( \Omega_4 \|U^{(4)}\|^2 \) and \( \Omega_6 \|U^{(6)}\|^2 \) terms.

Next, we pay attention to the effect of \( \Omega_2 \|U^{(2)}\|^2 \) term, which relates to the asymmetry in the local structure surrounding rare earth ions. As shown in Fig. 5, the A coefficients of Yb\(^{3+} \) show lower values in silicate, borate, and phosphate glasses, in which the local structure surrounding Yb\(^{3+} \) ions is of interstitial type. It is assumed that the asymmetry in the local structure surrounding interstitial type of Yb\(^{3+} \) ions would not change by varying the glass systems or compositions in silicate, borate, and phosphate glasses, because Yb\(^{3+} \) sits around regions between the glass networks as shown in Fig. 4(a). Therefore, it is considered that the A coefficients of Yb\(^{3+} \) show lower values in these glasses due to a smaller matrix effect on the \( \Omega_2 \|U^{(2)}\|^2 \) term. On the other hand, the A coefficients of Yb\(^{3+} \) show higher values in the K\(_2\)O–Ga\(_2\)O\(_3\)–Nb\(_2\)O\(_5\) glasses. As shown in Figs. 3 and 4(b), Yb\(^{3+} \) ions substitute the Ga\(^{3+} \) sites in the glass network region, and the geometric position of oxygen ions and balance of electric field surrounding Yb\(^{3+} \) ion is disordered because of different charged ions, Ga\(^{3+} \) and Nb\(^{5+} \), close to Yb\(^{3+} \). It is suggested that the substitutive type of Yb\(^{3+} \) have a large effect on the \( \Omega_2 \|U^{(2)}\|^2 \) term, thereby the energetic effect of disorders of geometric position and electric field surrounding Yb\(^{3+} \). Thus, A coefficients show the higher values in K\(_2\)O–Ga\(_2\)O\(_3\)–Nb\(_2\)O\(_5\) glasses.

The compositional dependence of the A coefficient is influenced mainly by the asymmetry in the local structure surrounding Yb\(^{3+} \) and not by the refractive index of the matrix glass or the covalency of Yb–O bonding. Next, we discuss about a parameter for the asymmetry in the local structure surrounding Yb\(^{3+} \) ions in oxide glasses in order to investigate the matrix effect on the A coefficient of Yb\(^{3+} \) ions. The factors affecting the A coefficient of Yb\(^{3+} \) in oxide glasses are disorders in geometric position and electric field surrounding Yb\(^{3+} \). We postulate an empirical disorder parameter \( D \), which expresses the degree of local structural asymmetry surrounding Yb\(^{3+} \) ion and is calculated from the radial distribution function as shown in Fig. 1, in terms of O\(^{2-} \) state as geometric disorder, and position and mixing state of second neighboring ion as electric disorder

\[
D = \Delta W \frac{\chi_{2nd}}{r_{Yb-2nd}X} \quad (0.5 \leq X \leq 1)
\]

where \( \Delta W \) is the half bandwidth of O\(^{2-} \) band, \( \chi_{2nd} \) is the electronegativity of the second neighboring ion, \( r_{Yb-2nd} \) is the distance between Yb\(^{3+} \) and second neighboring ions, and \( X \) is the proportion of the mixing state of second neighboring ions calculated by the peak intensity ratio of second ions. In Eq. (2), the first and the second terms denote the disorders of geometric position and electric field, respectively. For example, \( D \) is 0.14 in the 40Na\(_2\)O–60SiO\(_2\) glass: \( \Delta W \), \( \chi_{Na} \), and \( r_{Yb-Na} \) are 0.54 Å, 0.9 and 3.4 Å, respectively, and \( X \) = 1 because the radial distribution function shows only one peak for second neighboring ion. The silicate, borate, and phosphate glass samples have \( X \) = 1. \( D \) is 0.73 in the 40K\(_2\)O–30Ga\(_2\)O\(_3\)–30Nb\(_2\)O\(_5\) glass: \( \Delta W \), \( \chi_{Ga} \) and \( r_{Yb-Ga} \) are 0.72 Å, 1.6 and 2.7 Å, respectively, and \( X \) = 0.58 calculated by the radial distribution function of the two peak intensities for second neighboring ions. Fig. 6 shows the relationship between A coefficient and an empirical disorder parameter, \( D \) for Yb\(^{3+} \) in oxide glasses indicating that empirical disorder parameter \( D \) is a dominant factor for A coefficient. Finally, it is concluded that the main factor for the improvement of A coefficient in the K\(_2\)O–Ga\(_2\)O\(_3\)–Nb\(_2\)O\(_5\) glasses.

![Fig. 6. Relationship between spontaneous emission probability, A, for the \(^{2}F_{3/2} \rightarrow ^{2}F_{1/2} \) transition and empirical disorder parameter, D, of Yb\(^{3+} \) in oxide glasses. Line is drawn to guide the eye.](image-url)
glasses would be the synergistic effect of disorders of geometric position and electric field due to the substitutive type of the local structure surrounding Yb$^{3+}$.

4. Conclusion

The local structure surrounding Yb$^{3+}$ ions in silicate, borate, phosphate, and gallate glasses were investigated by EXAFS analysis. Yb$^{3+}$ ions do not occupy the network structural sites, but sit around the terminal region of the network or the region between the networks in silicate, borate, and phosphate glasses. On the other hand, Yb$^{3+}$ ions substitute the Ga$^{3+}$ sites in complex anion structural units of Ga$_2$O$_3$–Nb$_2$O$_5$, which form the networks of the III–V compound type in the K$_2$O–Ga$_2$O$_3$–Nb$_2$O$_5$ glasses. We classified the local structure surrounding Yb$^{3+}$ in oxide glasses into two types; the former and the latter are interstitial and substitutive types, respectively. The relationship between the spontaneous emission probability for $^2$F$_{9/2} \rightarrow ^2$F$_{7/2}$ transition of Yb$^{3+}$, A coefficient, and the local structure of Yb$^{3+}$ in oxide glasses is discussed in terms of these two types of Yb$^{3+}$. The A coefficient of substitutive type of Yb$^{3+}$ in K$_2$O–Ga$_2$O$_3$–Nb$_2$O$_5$ glasses show higher value than that of interstitial type of Yb$^{3+}$ in silicate, borate, and phosphate glasses. The matrix effect on the improvement of A coefficient in the K$_2$O–Ga$_2$O$_3$–Nb$_2$O$_5$ glasses can be explained by the synergetic effect of disorders of geometric position and electric field in the local structure surrounding Yb$^{3+}$ ions due to the substitutive type of the local structure surrounding Yb$^{3+}$.

Acknowledgements

This work was supported by Grand-in Aid for Scientific Research (A) No. 11305055 from Japan Society for the Promotion of Science. Thanks are due to Yuuki Moriyama and Keisuke Ogata for their assistance in preparing glass samples and analyzing EXAFS spectra.

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