Local Structure around Er$^{3+}$ Ions in Sol-Gel Derived GeO$_2$ Glasses

Kazuhiro YAMAMOTO, Kazuo KOJIMA, Katsumi HANDA, Noriyuki WADA* and Kazuhiko OZUTSUMI

Department of Applied Chemistry, Ritsumeikan University, 1-1-1, Nojiigahasi, Kusatsu-shi, Shiga 525-8577
*SR Center, Ritsumeikan University, 1-1-1, Nojiigahasi, Kusatsu-shi, Shiga 525-8577
**Department of Materials Science and Engineering, Suzuki National College of Technology, Shiroko-cho, Suzuki-ku, Mie 510-0294

Vibrational, Er $L_{	ext{III}}$-edge X-ray absorption fine structure (XAFS), and upconversion fluorescence spectra have been measured for sol-gel derived xEr$_2$O$_3$·(100−x)GeO$_2$ (x = 1−10) glasses. Raman spectra indicated that with increasing the Er$_2$O$_3$ content, the bridging angle of the Ge–O–Ge linkage was distorted and non-bridging oxygen atoms (NBOs) were generated. Infrared absorption spectra of the glasses showed that the amount of the residual OH group increased with increasing the Er$_2$O$_3$ content. XAFS analysis showed the argumentation of both the coordination number ($N_{\text{Er–O}}$) and the Debye–Waller factor ($\sigma_{\text{exc}}$) with increasing the Er$_2$O$_3$ content. This argumentation is probably due to the coordination of NBOs, OH group, and bridging oxygen atoms (BOs) to the Er$^{3+}$ ion. XAFS analysis for the glasses gives no evidence of clustering of Er$^{3+}$ ions as reported previously. Quenching of Er$^{3+}$ upconversion fluorescence in the glasses with high Er$_2$O$_3$ content is considered to be caused mainly by the coordinated OH group.

Received September 25, 2003; Accepted March 23, 2004

Key-words: Sol-gel method, GeO$_2$ glass, Erbium, Raman spectrum, XAFS, Upconversion fluorescence

1. Introduction

Heavy-metal oxide glasses such as germanate, gallate, and tellurite glasses have been widely used as host materials for rare-earth (RE) ions, because these glasses have relatively low phonon energies so that doped RE ions show high optical activities as frequency upconverters, lasers, and amplifiers.1−7

Sol-gel derived glasses can be obtained at relatively lower temperatures than melt derived ones, and are more homogeneous because a three-dimensional glasslike network grows well in a liquid medium.8 In general, the rigid covalent lattice of the GeO$_2$ glass makes it difficult to incorporate RE ions into the glass structure.9 However, the sol-gel process is usually able to prepare glasses with higher dopant concentrations. Indeed, there have been many reports on sol-gel derived glasses doped with RE ions.

It is considered that emission properties of RE ions in glasses are affected by the local structure around RE ions, because clustering of RE ions and the existence of the OH group cause the non-radiative relaxation. In order to investigate a relationship between emission properties and the local structure around RE ions, several techniques have been applied, for example fluorescence line narrowing,10,11 12 NMR,13 MD,14 X-ray absorption fine structure (XAFS),15,16 and so on. Especially, XAFS technique is very useful since it can extract direct structural information around selected atoms in amorphous materials.

We have already reported the sol-gel derived germanate glasses doped with RE ions.21−25 However, structural information around Er$^{3+}$ ions doped in the sol-gel derived GeO$_2$ glasses has not been obtained yet.

In the present work, we have investigated the local structure around Er$^{3+}$ ions doped in the sol-gel derived GeO$_2$ glasses using vibrational and synchrotron radiation Er $L_{	ext{III}}$-edge XAFS spectroscopy. Visible upconversion fluorescence spectra were also measured.

2. Experimental

2.1 Sample preparation

Tetraethoxysilane (Kojundo, 99.999%), tris-acetylatedonoirbium (Soekawa, 99.5%), butanol, distilled water, and acetic acid were used as starting materials to prepare xEr$_2$O$_3$·(100−x)GeO$_2$ (x = 1−10) glasses. Sol solutions were kept at 70°C for 1 week, and then dried at 100°C for 1 week. Obtained dried gels were heated to 640°C at a heating rate of 5°C/h and kept at 640°C for 1 h. Further details for sample preparation have been described elsewhere.21−25 The obtained samples, except for that of x = 10, were polished for optical measurements. The size of the obtained sample with x = 10 was too small to carry out optical measurements. Glasses of yNa$_2$O·(100−y)GeO$_2$ (y = 0 and 10) were prepared by the ordinary melt-quenching method for the purpose of the comparative study of Raman spectra.

2.2 Measurements of Raman, upconversion fluorescence, and IR spectra, and thermogravimetry

A Raman spectrometer NR 1800 (JASCO) and a CCD detector which was cooled at liquid nitrogen temperature were used to measure Raman and upconversion fluorescence spectra. Emission line of 488.0 nm of an Ar$^+$ laser (Spectra Physics, 100 mW) and that of 647.1 nm of a Kr$^+$ laser (COHERENT INNOVA, 230 mW) were employed as excitation sources for Raman spectra (Stokes side) and upconversion fluorescence (anti-Stokes side), respectively. The polished glass samples were set with 90° scattering geometry.

IR absorption spectra of glass samples were measured in the
range of 4600–400 cm\(^{-1}\) with a Shimadzu FTIR-8600 instrument by the ordinary KBr method. In order to estimate the \(\text{H}_2\text{O}\) content in the glass, thermogravimetry (TG) was carried out with a Shimadzu DTG-60H instrument at a heating rate of 5°C/min for the sample with \(x=10\). The sample for the TG measurement was crushed into powders in an \(\text{N}_2\)-purged glove box to prevent the sample from moisture.

2.3 XAFS measurement

The glass samples were crushed to powders with an agate mortar and a pestle, and then dispersed on scotch tape. Some of these tapes were superposed to adjust the amount of the sample for measuring XAFS spectra. As a standard sample was employed an \(\text{Er}_2\text{O}_3\) crystal, where 6 oxygen atoms are coordinated to an erbium atom and the mean interatomic distance of Er–O is 2.272 ± 0.02 pm.\(^{30}\) XAFS spectra at the Er \(L_{\text{III}}\)-edge were recorded in a transmission mode with a beamline BL-4 at SR Center of Ritsumeikan University. A superconducting compact storage ring AURORA (525 MeV, 300 mA) was used as an X-ray synchrotron radiation source. The beamline BL-4 consists of a double-crystal monochromator and several types of detectors. In the present work, Ge (220) crystals (2\(\theta=4.00\) ± 0.10°) were employed to monochromatize white X-ray emitted from AURORA. Incident and transmitted X-ray beam intensities were detected by each ionization chamber filled with \(\text{N}_2\) (50%)–Ar (50%) gas.

The data analysis was carried out by a standard procedure.\(^{26}\) A background absorption was estimated by a Victoreen-type function and subtracted from a measured XAFS spectrum. The threshold energy (\(E_0\)) was determined to be the energy at an inflection point around the Er \(L_{\text{III}}\)-edge absorption, and the obtained energy data were converted into the photoelectron wave vector, \(k\), by the following equation:

\[
k = \sqrt{\frac{2en}{h}(E - E_0)},
\]

where \(m\) is the electron mass, \(h\) is the Planck’s constant, and \(E\) is the measured photon energy. In order to extract an experimental extended X-ray absorption fine structure (EXAFS) oscillation, \(\chi(k)\exp\), a polynomial function assumed for an X-ray absorption due to an isolated erbium atom was subtracted from the above background-absorption-subtracted XAFS spectrum. The radial structure function (RSF) was obtained by the Fourier transform of \(\chi(k)\exp\) weighted by \(k^3\chi(k)\exp\), as follows:

\[
F(\chi) = \frac{1}{\sqrt{2\pi}} \int_{k_{\text{min}}}^{k_{\text{max}}} W(k) k^3 \chi(k)\exp e^{-2\pi i k \chi} dk,
\]

where \(W(k)\) is a Hanning-type window function and the values of \(k_{\text{min}}\) and \(k_{\text{max}}\) are about 2.3 × 10\(^{-2}\) and 8.9 × 10\(^{-2}\) pm\(^{-1}\), respectively.

Least-squares fitting was carried out using the following theoretical EXAFS formula, \(\chi(k)\text{theo}\):

\[
\chi(k)\text{theo} = \sum_j N_j F_j(k, \sigma_j) e^{-2\sigma_j^2 k^2} e^{-2\omega j/k} \sin(2\chi \sigma_j + \delta_j(k)),
\]

where \(N_j\) is the coordination number, \(\sigma_j\) is the Debye–Waller factor which is composed of thermal vibration and structural disorder, \(r_j\) is the interatomic distance, \(j\) means the \(j\)th shell from the X-ray absorbing atom, \(\lambda(k)\) is the electron mean free path, and \(F_j(k, \sigma_j)\) and \(\delta_j(k)\) are McKale’s backscattering amplitude of photoelectron and the phase-shift function, respectively.\(^{27}\) The \(F_j(k, \sigma_j)\) and \(\delta_j(k)\) values in \(\chi(k)\text{theo}\) were modified for the standard sample of \(\text{Er}_2\text{O}_3\). Then, these modified values were used in order to obtain the EXAFS parameters, \(N_j\), \(r_j\), and \(\sigma_j\), for glass samples.

3. Results

Figure 1 shows Raman spectra of \(x\text{Er}_2\text{O}_3\cdot(100−x)\text{GeO}_2\) and \(y\text{Na}_2\text{O}\cdot(100−y)\text{GeO}_2\) glasses. For \(x\text{Er}_2\text{O}_3\cdot(100−x)\text{GeO}_2\) glasses, the rise in the base line on the high frequency side (900 cm\(^{-1}\)~) came from the tail of the fluorescence due to the electronic transition from \(2^3\text{H}_4\text{I}/2\) to \(2^1\text{H}_4\text{I}/2\) of the \(\text{Er}^{3+}\) ion. Dominant peaks and broad features were observed in the range 350–650 cm\(^{-1}\), and relatively weak peaks around 865 and 980 cm\(^{-1}\). With increasing the \(\text{Er}_2\text{O}_3\) content, the dominant peak around 430 cm\(^{-1}\) became slightly broad, and broad features around 533 and 603 cm\(^{-1}\) relatively strong. In the samples of \(x≥3\), a weak peak around 980 cm\(^{-1}\) vanished away, and another peak around 865 cm\(^{-1}\) gradually grew up. For the sample of \(x=7\), a new peak could be observed around 765 cm\(^{-1}\).

Figure 2 shows IR spectra in the range 4000–2500 cm\(^{-1}\). A main absorption band around 3450 cm\(^{-1}\) were observed for the samples of \(x≥3\), and its intensity became strong with increasing the \(\text{Er}_2\text{O}_3\) content.

Figure 3 shows a TG curve of 10\(\text{Er}_2\text{O}_3\cdot90\text{GeO}_2\) glass. The total weight loss is 4.7%, which leads to the glass composition of 7.4\(\text{Er}_2\text{O}_3\cdot66.2\text{GeO}_2\cdot26.4\text{H}_2\text{O}\).

Figure 4 gives normalized X-ray absorption near-edge structure (XANES) spectra of \(x\text{Er}_2\text{O}_3\cdot(100−x)\text{GeO}_2\) glasses. A peak located around 8375 eV is assigned to the transition from \(^{2}S_{1/2}\) to \(^{2}D_{3/2}\) of the \(\text{Er}^{3+}\) ion.\(^{28}\) With increasing the \(\text{Er}_2\text{O}_3\) content, this peak shifted slightly to the higher energy side, and the width of the peak was broadened.

Figure 5 shows \(k^3\chi(k)\exp\) oscillations which are extracted from Er \(L_{\text{III}}\)-edge XAFS spectra of the \(x\text{Er}_2\text{O}_3\cdot(100−x)\text{GeO}_2\) glasses and the \(\text{Er}_2\text{O}_3\) crystal. The EXAFS oscillations of the glass samples are similar to each other, and show smooth sine curves, which is characteristic of amorphous materials. On the other hand, the EXAFS oscillation of the \(\text{Er}_2\text{O}_3\) crystal is not a smooth sine curve because of the contribution from a second shell composed of erbium atoms.

Figure 6 shows RSFs given by the Fourier transform of the curves shown in Fig. 5 without phase shift correction. A first peak around 2.0 × 10\(^5\) pm and a second peak around 3.5 × 10\(^5\) pm.
Fig. 2. IR spectra of sol-gel derived $x\text{Er}_2\text{O}_3\cdot(100-x)\text{GeO}_2$ glasses.

Fig. 3. TG curve of the 10Er$_2$O$_3$·90GeO$_2$ glass.

Fig. 4. Normalized Er $L_{III}$-edge XANES spectra for $x\text{Er}_2\text{O}_3\cdot(100-x)\text{GeO}_2$ glasses.

Fig. 5. Extracted EXAFS oscillations, $k^2\chi(k)_{\exp}$, for $x\text{Er}_2\text{O}_3\cdot(100-x)\text{GeO}_2$ glasses and standard sample.

Fig. 6. RSFs obtained by Fourier transform of the $k^2\chi(k)_{\exp}$ shown in Fig. 5 without phase shift correction.

pm observed in the Er$_2$O$_3$ crystal are corresponding to the interactions of Er–O and Er–Er, respectively. First peaks in the glass samples were located at almost the same position as the Er$_2$O$_3$ crystal. For the glass samples, no second peak can be observed, indicating that the local order in the second shell range is almost lost in these samples. In order to obtain detailed structural parameters concerning the Er–O interaction, i.e. $N_{\text{Er–O}}$, $r_{\text{Er–O}}$, and $\sigma_{\text{Er–O}}$, inverse Fourier transform and least-squares fitting were carried out for the first peaks shown in Fig. 6.

Results of fitting and obtained parameter values are shown in Fig. 7 and Table 1, respectively. The errors for the interatomic distance and coordination number are $\pm 0.01 \times 10^2$ pm and $\pm 0.8$, respectively. The obtained values of $N_{\text{Er–O}}$ and $r_{\text{Er–O}}$ are plotted as a function of the Er$_2$O$_3$ content in Fig. 8. With
Fig. 7. Fitting results for first peaks shown in Fig. 6. Solid and dotted lines represent inverse Fourier transformed and least-squares fitting values, respectively.

Fig. 8. Variations in the coordination number of Er (●) and the interatomic distance of Er–O (●) for xErO$_3$·(100–x)GeO$_2$ glasses.

Table 1. Coordination Number $N_{\text{Er-O}}$, Interatomic Distance $r_{\text{Er-O}}$, and Debye-Waller Factor $\sigma_{\text{Er-O}}$ of Sol–Gel Derived xErO$_3$·(100–x)GeO$_2$ Glasses Obtained by the Least-Squares Fitting. The Errors for the Interatomic Distance and Coordination Number are ±0.01 x 10$^2$ pm and ±0.8, respectively.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$N_{\text{Er-O}}$</th>
<th>$r_{\text{Er-O}}/10^2$ pm</th>
<th>$\sigma_{\text{Er-O}}/10^3$ pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>8.1</td>
<td>2.30</td>
<td>0.126</td>
</tr>
<tr>
<td>7</td>
<td>7.5</td>
<td>2.31</td>
<td>0.121</td>
</tr>
<tr>
<td>4</td>
<td>7.0</td>
<td>2.33</td>
<td>0.122</td>
</tr>
<tr>
<td>3</td>
<td>6.8</td>
<td>2.34</td>
<td>0.112</td>
</tr>
<tr>
<td>2</td>
<td>6.7</td>
<td>2.34</td>
<td>0.110</td>
</tr>
<tr>
<td>1</td>
<td>6.1</td>
<td>2.35</td>
<td>0.100</td>
</tr>
</tbody>
</table>

Increasing the Er$_2$O$_3$ content, the value of $N_{\text{Er-O}}$ increased from about 6 up to 8, while the value of $r_{\text{Er-O}}$ decreased. The value of $\sigma_{\text{Er-O}}$ also increased with the increase in the Er$_2$O$_3$ content (Table 1).

Figure 9 shows Er$^{3+}$ upconversion fluorescence spectra of the xEr$_2$O$_3$·(100–x)GeO$_2$ glasses. In the samples with $x \leq 4$, upconversion fluorescence was clearly observed around 526 and 548 nm, which were due to the transitions of $^3H_{11/2} \rightarrow ^1I_{15/2}$ and $^5S_{3/2} \rightarrow ^1I_{15/2}$, respectively. The upconversion fluorescence was the strongest in the sample of $x=1$ and weakened rapidly with increasing $x$, and finally it vanished completely in the sample of $x=7$. Therefore, it is thought that the optical quenching begins for the sample of $x=2$. Moreover, there is a possibility that it begins at $x$ of less than 1.

4. Discussion

In Fig. 1 the dominant peak around 430 cm$^{-1}$ is assigned to the symmetric stretching vibration of the Ge–O–Ge linkage, and slightly shifts to higher frequency side with increasing the Er$_2$O$_3$ content. This shift is due to the decrease in the Ge–O–Ge bridging angle from 133° for a pure GeO$_2$ glass where [GeO$_2$] is a structural unit of forming the glass network. Martino et al. suggested that the weak peaks around 533 and 603 cm$^{-1}$ in alkali germanate glasses corresponded to the peaks of 575 and 620 cm$^{-1}$ observed in alkali silicate glasses, respectively. In alkali silicate glasses, these peaks are the mixture of bending and stretching modes of the Si–O–Si linkage, which are the characteristic modes depending on the bridging angle. In a calculation, they have been expected to become strong and shift to the higher frequency side with decreasing the bond angle of the Si–O–Si linkage. Therefore, both the shift of the peak around 430 cm$^{-1}$ and the growth of the peaks around 533 and 603 cm$^{-1}$ in Fig. 1 are considered to indicate the distortion of the bridging angle of the Ge–O–Ge linkage with increasing the Er$_2$O$_3$ content.

In Fig. 1 the weak peaks around 865 and 980 cm$^{-1}$ for the glasses of $x=1$, 2 and $y=0$ are assigned to the transverse-optic (TO) and longitudinal-optic (LO) component of the
asymmetric stretching mode of the Ge–O–Ge linkage, respectively.$^{29,31}$ As observed in Fig. 1, in alkali germanate glasses, when the alkali oxide content increased, both peaks shifted to the lower frequency sides with their relative intensities being almost constant.$^{29-31}$ Therefore, it has been considered that the growth of only the peak around 865 cm$^{-1}$ was practically caused by the generation of the non-bridging oxygen atoms (NBOs), the peak being attributed to the symmetric stretching mode of Ge–O– in the structural Q$^3$ unit of [GeO$_2$O$_x$]$^{-1}$, where the subscript 3 means the number of the bridging oxygen atoms (BOs).$^{30,31,38}$ In the present work, in the samples of $x \geq 3$ the 980 cm$^{-1}$ LO component vanishes, therefore the growth of the peak around 865 cm$^{-1}$ is considered to be due to the symmetric stretching mode of Ge–O– in the Q$^3$ unit. In addition, the peak around 765 cm$^{-1}$ for the sample of $x=7$ can be assigned to the symmetric stretching mode of Ge–O– in the Q$^2$ unit. Therefore, with increasing the Er$_2$O$_3$ content, the Q$^2$ and Q$^3$ units began to be generated in the samples of $x=3$ and 7, respectively. These facts lead to the possibility that the Er$^{3+}$ ions are coordinated by both the BOs and NBOs in the high Er$_2$O$_3$ content ($x \geq 3$) glasses, while mainly by the BOs in the low Er$_2$O$_3$ content ($x \leq 2$) glasses. However, considering that NBOs have been reported to be generated in alkali germanate glasses even in the low alkali oxide content, and their amounts have increased with increasing the alkali oxide content, small amounts of NBOs that are undetectable by Raman spectroscopy may possibly be produced in the low Er$_2$O$_3$ content ($x \leq 2$) glasses and coordinated to Er$^{3+}$ ions in the present study.

It is well known that alkali germanate glasses changes their local structure due to the introduction of oxygen atoms by alkali oxide; the conversion of the Ge atom coordinated by 4 oxygen atoms into that coordinated by 6 oxygen atoms with increasing the alkali oxide content. On the other hand, in the Bi$_2$O$_3$–GeO$_2$ glasses, it has been reported that any six-coordinated Ge atoms were not generated by the addition of Bi$_2$O$_3$, and Bi$^{3+}$ ions broke the glass-forming network of Ge–O–Ge to produce NBOs.$^{36}$ Bi$^{3+}$ and Er$^{3+}$ ions have the same electric charges, and similar ionic radius of 1.17 and 1.03 x 10$^{-10}$ pm, respectively. Therefore, it is expected that the behavior of forming NBOs without producing six-coordinated Ge atoms in the glass is similar.

By the way, as for the glass-forming ability, Bi$^{3+}$ ions have been reported to be condition glass former where a lone pair of electrons, $6s^2$, played an important role.$^{37,38}$ However, Er$^{3+}$ ions don’t possess such a lone pair of electrons, so that Er$^{3+}$ ions may not be condition glass former unlike Bi$^{3+}$ ions.

In addition, for the glass of $x = 10$ in Fig. 1, since the peak of 865 cm$^{-1}$ assigned to NBO is not observed, it is considered that the oxygen atoms introduced by Na$_2$O may be consumed only for the formation of six-coordinated Ge atoms. On the other hand, in the glasses of $x$Er$_2$O$_3$–(100–$x$)Ge$_2$O$_3$, since the 865 cm$^{-1}$ peak is found for the glass with $x = 3$, the oxygen atoms supplied by Er$_2$O$_3$ is considered to be utilized only to form NBOs.

In order to discuss the amount of NBOs, we assume that all oxygen atoms introduced by the addition of Er$_2$O$_3$ are coordinated to the Ge atoms, then the proportion of NBOs to all oxygen atoms is evaluated to be 22% and the number of the Ge atoms bonded to an oxygen atom is estimated to be 1.78 for the sample of $x=7$. This number of 1.78 is almost corresponding to that of the 25Na$_2$O–75GeO$_2$ glass reported by Ueno et al.$^{39}$ However, the Raman intensity ratio of the Q$^3$ peak to the peak around 430 cm$^{-1}$ for the 7Er$_2$O$_3$–93GeO$_2$ glass shown in Fig. 1 is weak compared to that of the 25Na$_2$O–75GeO$_2$ glass.$^{34}$ This discrepancy is probably caused by the Q$^2$ unit which was generated in the 7Er$_2$O$_3$–93GeO$_2$ glass, but hardly produced in the Na$_2$O–GeO$_2$ glasses with the Na$_2$O content of less than 25 mol%.$^{29-31,34}$ Therefore, the amount of NBOs in the 7Er$_2$O$_3$–93GeO$_2$ glass may be the same order as that in the 25Na$_2$O–75GeO$_2$ glass. We may have another reason to explain the above difference in the Raman intensity ratio; if clustering of Er$^{3+}$ ions occurs in the 7Er$_2$O$_3$–93GeO$_2$ glass, then oxygen atoms supplied by the addition of Er$_2$O$_3$ may be consumed by forming the Er–O–Er bonding, resulting in the decrease in the amount of NBOs.

On the other hand, it is also possible to assign the peak around 765 cm$^{-1}$ in Fig. 1 to the stretching vibration of OH in Ge–OH$^{40}$ besides the symmetric stretching mode of Ge–O– in the Q$^3$ unit described above. It is considered that the glass samples with the high Er$_2$O$_3$ content include more OH groups than those with the low Er$_2$O$_3$ content. Indeed, as shown in Fig. 2, the absorption band around 3450 cm$^{-1}$ due to the fundamental O–H stretching vibration of the Ge–OH group$^{41}$ became strong with increasing the Er$_2$O$_3$ content.

In Fig. 6, no peaks due to the correlation of the Er–Er in the second shell region were observed for the glass samples. It is thought that particularly in the high Er$_2$O$_3$ content, the formation of the cluster of the Er$^{3+}$ ions would occur. It has been reported that EXAFS gives no direct evidence for the existence of the cluster of RE ions.$^{15-20}$ In the present work, we obtained the similar result.

As shown in Fig. 8, with increasing the Er$_2$O$_3$ content, the value of $r_{E-E}$ decreased from about 6 to 8, and that of $r_{E-O}$ decreased from 2.35 to 2.30 x 10$^{-10}$ pm. In general, increasing the coordination number leads to the augmentation of the interatomic distance. However, in the present work, we obtained an opposite tendency. The value of 2.30 x 10$^{-10}$ pm is quite close to the sum of the ionic radius for the Er$^{3+}$ (1.03 x 10$^{-10}$ pm) and O$^-$ (1.26 x 10$^{-10}$ pm) ions, and at this time $r_{E-O} = 8.1$ does not contradict the Shannon’s radius-ratio rule; the rule needs more than 0.732 of the ratio of Er$^{3+}$/O$^-$ for the 8 coordination, and Er$^{3+}$/O$^-$ = 0.817 satisfies this condition. Murata et al. reported the values of $r_{E-O}$ and $r_{E-E}$ in different oxide glass hosts examined by the XAFS technique.$^{16}$ In their report, the values of $r_{E-O}$ and $r_{E-E}$ are, respectively, 2.26 x 10$^{-10}$ pm and 6.1 for 40Li$_2$O–60SiO$_2$ glass host, 2.24 x 10$^{-10}$ pm and 6.5 for 40Na$_2$O–60SiO$_2$ glass host, and 2.23 x 10$^{-10}$ pm and 7.2 for 40K$_2$O–60SiO$_2$ glass host.$^{16}$ Moreover, for alkali borate glasses, the values of $r_{E-O}$ and $r_{E-E}$ are, respectively, 2.30 x 10$^{-10}$ pm and 6.0 for 30Li$_2$O–70B$_2$O$_3$ glass host, 2.26 x 10$^{-10}$ pm and 6.3 for 30Na$_2$O–70B$_2$O$_3$ glass host, and 2.25 x 10$^{-10}$ pm and 7.3 for 30K$_2$O–70B$_2$O$_3$ glass host.$^{16}$ These results indicate the tendency of decreasing the value of $r_{E-O}$ with increasing of that of $r_{E-E}$, depending on the kind of the alkali cation. On the other hand, d’Acapito et al. reported that in 81.7P$_2$O$_5$–9.2Al$_2$O$_3$–5.1Li$_2$O–2.0B$_2$O$_3$ glass host, the value of $r_{E-O}$ increases from 2.233 to 2.246 x 10$^{-10}$ pm with increasing the value of $r_{E-E}$ from 6.8 to 7.6, and that in SiO$_2$/TiO$_2$ thin films, the values of $r_{E-O}$ and $r_{E-E}$ are 2.245–2.277 x 10$^{-10}$ pm and 6.1–6.8, respectively.$^{18}$ Peters et al. reported that the values of $r_{E-O}$ and $r_{E-E}$ are, respectively, 2.22 x 10$^{-10}$ pm and 6.6–6.8 for multicomponent glass host, 2.18–2.22 x 10$^{-10}$ pm and 6.1–6.4 for aluminosilicate glass hosts, 2.23 x 10$^{-10}$ pm and 7.5 for fluorosilicate glass hosts, and 2.23–2.25 x 10$^{-10}$ pm and 7.2–7.5 for phosphate glass hosts.$^{19,20}$ The results of d’Acapito et al. and Peters et al. indicate the tendency of decreasing the value of $r_{E-O}$ with decreasing that of $r_{E-E}$. 

The reason for increasing the value of \( N_{\text{Er-O}} \) is considered to be that NBOs and OH groups, both of which were generated with the increase in the \( \text{Er}_2 \text{O}_3 \) content as discussed above in the Raman and IR spectra, and BOs are bonded to the \( \text{Er}^{3+} \) ions. Murata et al.\(^{10} \) have reported that the \( \text{Er}^{2+} \) ions were coordinated to the NBO site in the sodium borate glasses, when the NBOs were generated in the glasses with the \( \text{Na}_2 \text{O} \) content of over 29 mol\%. It is also considered that the residual OH groups are bonded to the \( \text{Er}^{3+} \) ions. Therefore, \( \text{Er}^{3+} \) ions are considered to be coordinated with NBOs, OH groups, and BOs in high \( \text{Er}_2 \text{O}_3 \) content glasses. This consideration is agreed with broadening of the first peaks observed in the XANES spectra, which will be mentioned below. On the other hand, in the low \( \text{Er}_2 \text{O}_3 \) content, the value of \( N_{\text{Er-O}} \) is about 6, and the \( r_{\text{Er-O}} \) value of 2.35 \( \times \) 10\(^{-8} \) pm is longer than that for the high \( \text{Er}_2 \text{O}_3 \) content. This is thought to arise from somewhat loose bonding between the \( \text{Er}^{3+} \) ion and BO in the glasses with the low \( \text{Er}_2 \text{O}_3 \) content.

As seen in Table 1, the Debye–Waller factor increases with increasing the \( \text{Er}_2 \text{O}_3 \) content. This means that when the \( \text{Er}_2 \text{O}_3 \) content is small, the \( \text{Er}^{3+} \) ions can distribute homogeneously in the glass structure, but when it is large, various environments resulting from the distortion of bridging angle of the Ge–O–Ge linkage and three kinds of bonding species (NBOs, OH groups, and BOs) lead to the reduction in the symmetry around the \( \text{Er}^{3+} \) ions, resulting in the augmentation in the Debye–Waller factor.

In Fig. 4, the first peak shows the tendency to broaden with increasing the \( \text{Er}_2 \text{O}_3 \) content. In general, XANES spectra reveal the electronic states and the three-dimensional configuration of an X-ray absorbing atom. Therefore, it is thought that this broadening indicates both the existence of the various environments and the lowering of the symmetry around the \( \text{Er}^{3+} \) ions.

In Fig. 9, the upconversion fluorescence intensity decreases with increasing the \( \text{Er}_2 \text{O}_3 \) content. This is probably because the residual OH groups make the upconversion fluorescence weaken by the non-radiative relaxation.

Concerning the clustering of the \( \text{Er}^{3+} \) ions, the evidence is not obtained in Fig. 6 as described above. However, small amounts of the clustering of \( \text{Er}^{3+} \) ions (Er–O–Er) that cannot be detected in the XAFS technique may exist in the glass. Moreover, longer-range interactions between the \( \text{Er}^{3+} \) ions that are also undetectable by the XAFS method have been suggested to exist in the glasses.\(^{15} - ^{20} \) Therefore, there is a possibility that such clustering and interactions are another reason for the decrease in the upconversion intensity with increasing the \( \text{Er}_2 \text{O}_3 \).

5. Conclusions

The measurements of vibrational, Er \( L_{\text{IR}} \)-edge XAFS, and upconversion fluorescence spectra have been carried out for the sol–gel derived \( x \text{Er}_2 \text{O}_3 \cdot (100-x) \text{Ge}_2 \text{O}_3 \) (\( x = 1 \sim 10 \)) glasses. The results of Raman spectra showed that the increase in the \( \text{Er}_2 \text{O}_3 \) content caused both the distortion of the bridging angle of the Ge–O–Ge linkage and the generation of the \( Q^2 \) and \( Q^2 \) units with NBOs. It was considered that some NBOs were coordinated to the \( \text{Er}^{3+} \) ions. Moreover, the amount of the residual OH group increased in the glasses with increasing the \( \text{Er}_2 \text{O}_3 \) content, which was confirmed by IR absorption spectra. The results of XAFS analysis showed that in the glasses with high \( \text{Er}_2 \text{O}_3 \) content, \( \text{Er}^{3+} \) ions were coordinated by 8 oxygen atoms with short interatomic distance \( r_{\text{Er-O}} \), while in the glasses with low \( \text{Er}_2 \text{O}_3 \) content, 6 oxygen atoms were coordinated to the \( \text{Er}^{3+} \) ion with long interatomic distance. This high coordination number of 8 may be due to the coordination of the NBOs, OH group, and BOs to the \( \text{Er}^{3+} \) ions in the glasses with high \( \text{Er}_2 \text{O}_3 \) content, and the long interatomic distance mainly due to somewhat loose Er–BO bonding in the glasses with low \( \text{Er}_2 \text{O}_3 \) content. The Debye–Waller factor increased with increasing the \( \text{Er}_2 \text{O}_3 \) content, which was caused by the reduction in the symmetry around the \( \text{Er}^{3+} \) ions due to the distortion of the bridging angle of the Ge–O–Ge linkage and the bonding of three kinds of species (NBOs, OH groups, and BOs) to the \( \text{Er}^{3+} \) ions. The \( \text{Er}^{3+} \) upconversion fluorescence of the glasses was considered to be weak by the residual OH group with increasing the \( \text{Er}_2 \text{O}_3 \) content. Clustering of the \( \text{Er}^{3+} \) ions could not be detected in the present XAFS study, but long-range interactions between \( \text{Er}^{3+} \) ions as well as small amounts of clustering might prefer to occur.

Acknowledgements

This work was partly supported by a grant from Nippon Sheet Glass Foundation.

References


