Correlation between the basicity and optical property of Er³⁺ ion in oxide glasses

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Abstract

A number of glasses in various glass systems, such as B_2O_3 -, SiO₂- and TeO₂-based glass glasses, were prepared to examine the 1.5 µm absorption bandwidth $\Delta\lambda_a$ of Er^{3+} ions. According to the theory, the 1.5 µm bandwidth of Er^{3+} ions is dominated by the refractive index *n* and Judd-Ofelt parameter Ω_6 . However, a significant correlation was found only between Ω_6 and $\Delta\lambda_a$. It has been also proposed that the bandwidth was dominated by the optical basicity Λ , which could be theoretically estimated from glass composition. As expected, significant correlation was confirmed in each glass system, and correlation common to all the glass systems was, however, not found between $\Delta\lambda_a$ and Λ . Then, the relationship against O1s binding energy was In B_2O_3 - and SiO₂-based glasses, a common correlation was observed, and in TeO₂-based glasses, however, the data points were located at the different region from the correlation curve for B_2O_3 - and SiO₂-based glasses. It was finally concluded from phonon sideband spectra that the peculiarity in TeO₂-based glasses was attributable to the unique structure around Er^{3+} ions in TeO₂-based glasses.

1. Introduction

Recently, high-speed and large-capacity telecommunication system is needed to satisfy the demand expansion of the internet traffic. Wavelength division multiplexing (WDM) system is the most likely candidate to meet the increasing demand. Er-doped fiber amplifier (EDFA) has been commonly used for the communication at 1.5 μ m band, and in the case of silica (SiO₂)-based amplifiers, however, the amplification wavelength range is only about 30 nm. If the amplification bandwidth is expanded, more signals are transmitted through the extended communication band. Therefore, host materials providing wider amplification bandwidth have been searched strenuously. It is known that the fluorescence characteristic of Er³⁺ ions depends on refractive index of host matrixes, chemical bonding character of Er–O bonds and the variety of coordination environment around Er³⁺ ions. In the case of using tellurite (TeO₂)-based glasses, the amplification bandwidth attained to about 80 nm at 1.5 μ m band [1], which was due to the higher refractive index of TeO₂-based glasses than SiO₂-based glasses. Chemical bonding character of Er–O bonds depends on the basicity of host matrixes, but little is known on the correlation between the fluorescence characteristic of Er³⁺ ions and basicity. Sugimoto and Tanabe [2] have confirmed the correlation in various glasses, where the acidic glasses showed broader emission. In their study, however, the glass composition was not changed systematically.

Then, in this study, the composition has been modified systematically in the various glass systems, that is, borate, silicate and tellurite glasses, investigating the correlation between the glass basicity and optical property. In the present study, the bandwidth of absorption was evaluated instead of emission. Furthermore, the glass basicity was estimated both from theory and experiment. Finally, the influence of local structures was also discussed.

2. Experimental

TeO₂-, B₂O₃- and SiO₂-based glasses were prepared, and the glass composition is given in Table I. Concentration of Er_2O_3 is 1.0 mol% in TeO₂-based glasses, and 0.5 mol% in B₂O₃- and SiO₂-based glasses. All glasses were prepared from reagent grade powders of TeO₂, B₂O₃, SiO₂, Bi₂O₃, La₂O₃, TiO₂, Er_2O_3 , Eu_2O_3 , Li_2CO_3 , Na₂CO₃ and K₂CO₃. The glass batches of 10 g for TeO₂-based glasses and 5 g for B₂O₃- and SiO₂-based glasses were mixed in a mortar for 15 min, and were melted in a Au or Pt crucible with an electric furnace in air at 800 ~ 900 °C for TeO₂-based glasses, at 1100 °C for B₂O₃-based glasses, and at 1500 ~ 1650 °C for SiO₂-based glasses. After melting for 30 ~ 90 min, the melts were quenched. The quenched materials were annealed for 60 min near the glass transition temperatures. The obtained glasses were polished to obtain optical surfaces.

Table I. Composition of the glasses prepared in this study.		
Abbreviation	Glass composition (mol%)	
LiLaTe+Er	$xLi_2O(30-x)La_2O_3(70TeO_2+1.0Er_2O_3)$	x =17.5, 20, 22.5, 25, 27.5, 30
BTiTe+Er	$20B_2O_3 \cdot xTiO_2 \cdot (80-x)TeO_2 + 1.0Er_2O_3$	x = 0, 5, 10, 15
BTe+Er	$xB_2O_3 \cdot (100-x)TeO_2 + 1.0Er_2O_3$	x = 15, 20, 25, 30
KTe+Er	$xK_2O(100-x)TeO_2+1.0Er_2O_3$	x = 10, 12.5 15, 17.5, 20
LiB+Er	xLi ₂ O·(100-x)B ₂ O ₃ +0.5Er ₂ O ₃	x = 10, 15, 20, 25, 30, 35
NaB+Er	xNa ₂ O·(100-x)B ₂ O ₃ +0.5Er ₂ O ₃	x = 10, 15, 20, 25, 30, 35
KB+Er	xK ₂ O·(100-x)B ₂ O ₃ +0.5Er ₂ O ₃	x = 10, 15, 20, 25, 30, 35
BiB+Er	xBi ₂ O ₃ ·(100-x)B ₂ O ₃ +0.5Er ₂ O ₃	x = 30, 40, 50, 60, 65
NaSi+Er	xNa ₂ O·(100-x)SiO ₂ +0.5Er ₂ O ₃	x = 15, 20, 25, 30, 33.3, 40, 45, 50
LaBTe+Er	$xLa_2O_3 \cdot xB_2O_3 \cdot (100-2x)TeO_2 + Er_2O_3$	x = 5, 10, 15, 20
LaWTe+Er	$10La_2O_3 \cdot xWO_3 \cdot (90-x)TeO_2 + Er_2O_3$	x = 10, 20, 30, 40,50
BiWTe1+Er	$xBi_2O_3 \cdot (40-x)WO_3 \cdot 60TeO_2 + Er_2O_3$	x = 5, 7.5, 10, 12.5, 15
BiWTe2+Er	$xBi_2O_3 \cdot 2xWO_3 \cdot (100-3x)TeO_2 + Er_2O_3$	x = 5, 10, 15, 20, 25
WTe+Er	$xWO_3 \cdot (100-x)TeO_2 + Er_2O_3$	x = 10, 15, 20, 25, 30
NaZnTe	$xNa_2O\cdot(30-x)ZnO\cdot70TeO_2+Er_2O_3$	x = 0, 5, 10, 15, 20
KWTe+Er	$(40-x)K_2O\cdot xWO_3\cdot 60TeO_2+Er_2O_3$	x = 15, 20, 25, 30, 35
BiBTe1+Er	$xBi_2O_3 \cdot xB_2O_3 \cdot (100-2x)TeO_2 + Er_2O_3$	x = 10, 20, 30, 40, 50
BiBTe2+Er	$xBi_2O_3 \cdot 2xB_2O_3 \cdot (100-3x)TeO_2 + Er_2O_3$	x = 5, 10, 15, 20, 25, 30, 33

The absorption spectra were measured with a UV/VIS/NIR spectrophotometer (JASCO, V-570) in the wavelength range of 1200 ~ 1800 nm, obtaining absorption cross-section at 1.5 μ m band, and the absorption spectra at 400 ~ 1100 nm were also measured for the Judd-Ofelt analysis. The Judd-Ofelt parameters of Er³⁺ ions were calculated by using the absorption cross-sections of the five intense bands (${}^{4}F_{7/2}$, ${}^{2}H_{11/2} + {}^{4}S_{3/2}$, ${}^{4}F_{9/2}$, ${}^{4}I_{11/2}$, ${}^{4}I_{13/2}$) in 400 ~ 1100 nm, the concentration of Er³⁺ ions obtained from density of the glasses, the refractive index of glass matrix at 1548 nm and the thickness of the samples. The density was measured by an Archimedes method. The refractive index was measured with a prism coupler method (Metricon, Model 2010). Phonon sideband (PSB) spectra were measured by using the glass samples doped with Eu³⁺ ions instead of Er³⁺ ions, investigating the local structure around rare earth ions.

X-ray photoelectron spectroscopy (XPS) was applied to estimate the basicity of the glasses. The binding

energy of O1s signal was used as a measure of basicity [3]. In XPS measurements, a monochromatic Al-K α radiation (h ν = 1486.6 eV) was irradiated to the fresh surfaces obtained by fracturing the rod-shaped glass samples in an ultra high vacuum ($\approx 5 \times 10^{-7}$ Pa).

Theoretical basicity was calculated from the equation of optical basicity (Λ) proposed by Duffy and Ingram [4].

$$\Lambda = \sum_{i} \frac{z_i r_i}{2\gamma_i} \qquad \gamma_i = 1.36(\chi_i - 0.26) \tag{1}$$

where z_i is the oxidation number of the cation *i*, and r_i is the ionic ratio with respect to the total number of oxides. γ_i is the basicity moderating parameter and is given from the Pauling electronegativity χ_i .

3. Results and Discussion

3.1 Absorption Cross Section

Absorption cross section, σ_a , was calculated by the following Equation 2.

$$\sigma_{a} = \frac{\ln 10 \cdot A}{lc} \tag{2}$$

where A is the absorbance, l is the thickness of sample, c is the concentration of Er^{3+} ions.

Figures $1(a) \sim 1(d)$ show the absorption cross sections at 1.5 µm band due to the transition of Er^{3+} : ${}^{4}I_{15/2} \rightarrow {}^{4}I_{13/2}$ in KTe+Er, WTe+Er, KB+Er, and NaSi+Er glasses, respectively. The magnitude of absorption cross sections decreases as K₂O content increases in KTe+Er and KB+Er glasses. In KB+Er glasses, furthermore, the two peaks at around 1480 and 1510 nm shift to the longer wavelength side with increasing K₂O content. In WTe+Er and NaSi+Er glasses, however, the intensity and position of the peak hardly change despite the compositional change.



Figure 1: Absorption cross sections at 1.5 μm band of (a) KTe+Er, xK₂O·(100–x)TeO₂+1.0Er₂O₃, (b) WTe+Er, xWO₃· (100–x) TeO₂+Er₂O₃, (c) KB+Er, xK₂O·(100–x)B₂O₃+0.5Er₂O₃, and (d) NaSi+Er, xNa₂O·(100–x)SiO₂+0.5Er₂O₃ glasses.



Figure 1: (continuation)

<u>3.2 Correlation between Effective Absorption Linewidth and Judd-Ofelt *Ω*₆ **Parameter**</u>

The Er^{3+} emission at 1.5 µm as well as absorption consists of two components associated with the magnetic dipole (MD) transitions which give the narrow component and the electric dipole (ED) transitions which are observed as the broad component. According to the Judd-Ofelt theory [5,6], radiative decay rate, *A*, is related with the line strength, *S*, as the following Equation 3.

$$A_{J'J} = \frac{64\pi^4 e^2}{3h(2J'+1)\lambda^3} \{ \frac{n(n^2+2)^2}{9} S_{ED} + n^3 S_{MD} \}$$
(3)

where *e* is the elementary charge, *h* is the Planck constant, *n* is the refractive index of host matrix, S_{ED} and S_{MD} indicate the line strengths of electric and magnetic dipole transitions, respectively. It could be seen that the larger refractive index the larger A and the contribution of S_{ED} . As for Er^{3+} ion, the line strength S_{ED} of ${}^{4}I_{15/2} \rightarrow {}^{4}I_{13/2}$ transition is described by the Judd-Ofelt parameters Ω as follows.

$$S_{\rm ED}[{}^{4}\mathrm{I}_{13/2}; {}^{4}\mathrm{I}_{15/2}] = 0.019\,\Omega_{2} + 0.118\,\Omega_{4} + 1.462\,\Omega_{6} \tag{4}$$

From Eq. 4, the Judd-Ofelt Ω_6 parameter is the dominant factor for S_{ED} among three Ω_t parameters. It is therefore suggested from Eqs. 3 and 4 that the increase of *n* and Ω_6 result in larger contribution of the broad ED component in total transitions. It is also known that the Ω_6 parameter represents the degree of hybridization between Er 4f–5d orbitals, and hence it is associated with the covalency of Er–O bonds. This is explained as follows. Er6s orbital shields Er4f from Er5d, and Er–O bond is formed by overlapping Er6s–O2p orbitals. Hence, the Er6s shielding power becomes greater and Ω_6 parameter decreases when the Er–O bond covalency increases and more electrons populate Er6s orbital.

As mentioned above, Ω_6 is the dominant factor for S_{ED} , and hence it is expected that Ω_6 has a correlation with emission linewidth. According to McCumber theory [7], the connection between the cross sections of emission and absorption is indicated by Equation 5.

$$\sigma_e(\nu) = \sigma_a \exp[(\varepsilon - h\nu)/kT]$$
(5)

As expected from Eq. 5, emission linewidth is evaluated by absorption linewidth. In this study, emission linewidth was indirectly evaluated by absorption linewidth, and the effective absorption linewidth, $\Delta \lambda_a$, was adopted instead of the full width at half maximum (FWHM). As shown in Equation 6, $\Delta \lambda_a$ is obtained by dividing the peak area by the peak height, which is based on the rectangular approximation of the absorption peak.

$$\Delta \lambda_{a} = \frac{\int_{1.2\mu m}^{1.8\mu m} \sigma_{a}(\lambda) d\lambda}{\sigma_{a_{max}}}$$
(6)

As shown in Figures 2 ~ 4, $\Delta \lambda_a$ are plotted against Ω_6 , A and *n* to explore the dominant factor. The strongest correlation is confirmed between $\Delta \lambda_a$ and Ω_6 (Fig. 2), indicating that Ω_6 is the predominant factor determining the amplification bandwidth. However, to obtain Ω_6 , various measurements are needed. If Ω_6 parameter were predicted without any experiment, it would be quite useful for the material design of broad bandwidth amplifiers.



Figure 2: Correlation between effective absorption linewidth $\Delta \lambda_a$ and Ω_6 parameter.



Figure 3: Correlation between effective absorption linewidth $\Delta \lambda_a$ and radiative decay rate, A.



Figure 4: Correlation between effective absorption linewidth $\Delta \lambda_a$ and refractive index *n*.

3.3 Relationship between Effective Absorption Linewidth and Basicity of Glass

As above mentioned, Ω_6 parameter is associated with the Er–O bond covalency and basicity of glass matrix. In the glasses with higher basicity, more electrons on oxide ions are donated to the neighboring cations, and Er³⁺ ions receive more electrons through Er6s–O2p orbital. Consequently, the hybridization between Er 4f–5d orbitals is restricted, resulting in the decrease in Ω_6 parameter. Then, the correlation

between the basicity of glass and the absorption linewidth was examined.

Optical basicity, Λ , was calculated from Eq. 1, and the effective absorption linewidth, $\Delta\lambda_a$, was plotted against Λ . As shown in Figure 5, $\Delta\lambda_a$ decreases linearly with increasing Λ in B₂O₃- and TeO₂ based glasses, and the slope is, however, different between the glass systems. In SiO₂-based glasses, $\Delta\lambda_a$ is almost constant even though the substantial change is clearly seen in Λ . This is probably due to the preferential site occupation of Er³⁺ ions. The calculated value of optical basicity Λ represents the average basicity of a glass matrix and does not represent the basicity of the specific oxide ions surrounding Er³⁺ ions. There remains another reason for the poor correlation that the glass basicity is inappropriately estimated. As shown in Eq. 1, the optical basicity Λ is calculated from electronegativity. It is known however that electronegativity is not a universal constant but a variable which changes depending on the chemical bonding character.



Figure 5: Correlation between effective absorption linewidth $\Delta \lambda_a$ and optical basicity Λ .

Then, the correlation with the experimental O1s binding energy was examined. Nanba et al. [3] proposed that O1s binding energy was available as a measure of basicity of oxide glass. It is well known that the chemical shift of the core orbitals is associated with the change of atomic charge. For example, in the oxide ions with higher basicity, electron population is also high in their outer shell levels. In such case, electrons in the core levels are directed away from the nuclei to reduce the shielding power, resulting in the chemical shift to the lower binding energy side. Figure 6 shows the relationship between $\Delta \lambda_a$ and O1s binding energy, where the data points for SiO₂-based glasses indicate the O1s binding energy of non-bridging oxygen (NBO) because Er^{3+} ions in SiO₂-based glasses are preferentially surrounded by NBOs [8]. The O1s signals in other glasses consisted of symmetric one component, and hence the average binding energy was plotted. As shown in Fig. 9, the O1s binding energy of TeO₂-based glasses is lower than that of B₂O₃-based glasses, indicating the higher basicity of oxide ions in TeO₂-based glasses than B₂O₃-based glasses. In Fig. 5, however, the data points for these glasses are in almost the same basicity region. As pointed out by Nanba et al. [3], the optical basicity of TeO₂-based glasses seems to be estimated lower than it is. As shown in Fig. 6, a common correlation between $\Delta \lambda_a$ and O1s

binding energy is applicable to B_2O_3 - and SiO_2 -based glasses, and another correlation is recognized in TeO₂-based glasses. Local environment around Er^{3+} ions in TeO₂-based glasses may be different from the other glasses.



Figure 6: Correlation between effective absorption linewidth $\Delta \lambda_a$ and O1s binding energy. The data points for NaSi+Er glass are the O1s binding energy of non-bridging oxygen.

3.4 Influence of local structure around Er³⁺ ions

Figure 7 shows the PSB spectra of KTe+Eu and WTe+Eu glasses, and the assignments of the peaks are shown in Table II. A broad peak at $660 \sim 750 \text{ cm}^{-1}$ is commonly confirmed in these glasses, which is formed by overlapping the peaks attributed to the Te–O bonds in TeO₄ trigonal bi-pyramid and TeO₃ trigonal pyramid. It is noted that the compositional change in the PSB spectra is quite small as compared with the change in Raman spectra (not shown). The slight variation in the PSB spectra was also seen in the other TeO₂-based glasses. It is consequently concluded that each rare earth ions are preferentially surrounded by TeO_n units in TeO₂-based glasses.

Figure 8 shows the PSB spectra of KB+Eu glass, and the peak assignments are shown in Table III. The peaks at 800 ~ 1100 cm⁻¹ are attributed to the various borate groups, and the peaks above 1300 cm⁻¹ are assigned to bridging and non-bridging B–O bonds [11]. As compared with the TeO₂-based glasses (Fig. 7), the change in the PSB spectra is significant, indicating that the local structure around rare earth ions also changes in borate glasses. It is also noted that the PSB intensity around 1400 cm⁻¹ remarkably increases at x > 30 mol%, which is due to the preferential coordination of NBOs in borate glasses [8]. In Fig. 6, two plot points associatd with arrows indicate the KB+Er glasses at x = 30 and 35 mol%. The O1s binding energy of these glasses plotted in Fig. 6 is the average value, and hence if Er³⁺ ions are preferentially surrounded by NBOs, the average O1s binding energy of oxide ions around Er³⁺ ions should be less than the average of whole oxide ions in the glasses, which is probably close to the binding energy of the NBO component in NaSi+Er glasses shown in Fig. 6.

As also seen in Fig. 6, the TeO₂-based glasses and NBOs in the SiO₂-based glasses indicate almost the same O1s binding energy, whereas $\Delta \lambda_a$ in the TeO₂-based glasses is much larger than that in the SiO₂-based glasses. As mentioned, Er^{3+} ions are preferentially surrounded by TeO_n units in the

TeO₂-based glasses. However, O1s XPS signal in the TeO₂-based glasses consists of only one component, indicating that electrons in the TeO₂-based glasses are delocalized through Te–O bonds with higher π -bonding character. It is therefore supposed that the electronic states of oxide ions in the TeO₂-based glasses are equivalent, and the plot points in Fig. 6 express the actual binding energy of oxide ions in TeO_n units. Despite the similarity in O1s binding energy between oxide ions in TeO_n units and NBOs in silicate glasses, the TeO₂-based glasses indicate larger Ω_6 values than the SiO₂-based glasses (Fig. 2). As above described, when more electrons are donated to Er6s orbital from oxide ions, Ω_6 becomes smaller. The basicity, that is, the electron donation power of oxide ions in TeO_n units and NBOs in silicate glasses seems to be the same. If the number of oxide ions surrounding an Er³⁺ ion is different between the TeO₂-based glasses than SiO₂-based glasses, the comparatively-larger Ω_6 values in the TeO₂-based glasses than SiO₂-based glasses, the comparatively-larger Ω_6 values in the TeO₂-based glasses are explainable.



Figure 7: PSB spectra of (a) KTe+Eu: $xK_2O \cdot (100-x)TeO_2+1.0Eu_2O_3$ and (b) WTe+Eu: $xWO_3 \cdot (100-x)TeO_2+Eu_2O_3$ glasses. PET is the pure electron transition of Eu: ${}^7F_0 \rightarrow {}^5D_2$.

Table II. Assignments of the bands present in PSB spectra [9, 10].		
Peak position /cm ⁻¹	Assignment	
460	Te–O bonds in TeO ₄	
660	Te–O bonds in TeO ₄	
750	Te– O^{-} bonds in Te O_{3}	
840	W–O bonds	
930	W=O bonds	



Figure 8: Phonon sideband spectra of $KB+Eu: xK_2O\cdot(100-x)B_2O_3+0.5Eu_2O_3$ glasses.

Table III. Assignments of the bands present in PSB spectra [11].		
Peak position /cm ⁻¹	Assignment	
770	tetraborate groups	
805	boroxol rings	
880	tetraborate groups	
900~1000	diborate groups	
1050	tetraborate groups	
1120	diborate groups	
1350 ~ 1400	B–O bonds	
1420 ~ 1550	$B-O^{-}$ bonds	

Both the theoretical basicity and the experimental O1s binding energy are basically representative of the nature of matrix glasses, and the Ω_6 value is, however, dominated directly by the local structure around rare earth ions. Some explanatory variable other than basicity and O1s binding energy, which is sensitive to the local structure around rare earth ions, is required for the prediction of optical properties of rare earth ions in glass.

4. Conclusion

A number of glasses in various glass systems were prepared to examine the 1.5 μ m absorption bandwidth $\Delta \lambda_a$ of Er^{3+} ions. According to the theory, the broad components in the absorption spectra are associated to the electric dipole transitions, which are intensified with the increase in refractive index *n* and Judd-Ofelt parameter Ω_6 . As expected, a good correlation was confirmed between $\Delta \lambda_a$ and Ω_6 , and between $\Delta \lambda_a$ and *n*, however, no significant correlation was recognized. Ω_6 is the parameter representing the degree of hybridization between Er 4f–5d orbitals, and Er6s orbital prevents the hybridization to reduce Ω_6 . The basicity of glass matrixes is interpreted as the power of electron donation, and hence it had been expected that a good relationship would be found between $\Delta\lambda_a$ and optical basicity Λ . In each glass system, a correlation was actually confirmed, and among the whole systems, however, a common correlation was not recognized between $\Delta\lambda_a$ and optical basicity Λ . Then, the correlation between $\Delta\lambda_a$ and experimental O1s binding energy was investigated. In B₂O₃- and SiO₂-based glasses, a common correlation was found, and in TeO₂-based glasses, however, the data points were distributed at the different region. It was found from PSB spectra that rare earth ions in TeO₂-based glasses were preferentially surrounded by TeO_n units. It was supposed from the XPS and PSB analyses that the coordination structure of rare earth ions in TeO₂-based glasses was different from those in B₂O₃- and SiO₂-based glasses. It was finally concluded that some local-structure-sensitive explanatory variable other than basicity and O1s binding energy was required for the precise prediction of optical properties of rare earth ions.

5. References

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