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Compositional dependence of Judd-Ofelt parameters of Er^{3+} ions in alkali-metal borate glasses

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The Judd-Ofelt intensity parameters, Ω_t ($t=2,4,6$) for f-f transitions of Er^{3+} ions doped in B_2O_3-R_2O (R=Na,K) glasses were determined from optical-absorption measurements, and their compositional dependence was investigated systematically. The values of Ω_2 exhibited a maximum around 25 mol % R_2O, while those of Ω_4 and Ω_6 decreased monotonically with an increase in R_2O content. The compositional dependences of $\Omega_{4,6}$ were consistent with those of the isomer shift in ^{151}Eu Mössbauer spectroscopy, which gives information about the 6s-electron density of Eu^{3+} ions. The variation of Ω_2 against R_2O content was related to the change in asymmetry of the rare-earth ligand due to the structural mixing of borate groups, while those of $\Omega_{4,6}$ were related to the local basicity of rare-earth sites in the glass.

I. INTRODUCTION

The radiative quantum efficiency of a rare-earth ion in glasses is of interest in designing laser glasses utilizing its particular emission. The properties of laser glasses are characterized by the absorption and emission probabilities, which are influenced by the ligand field of rare-earth ions as well as the nonradiative properties.

Among various rare-earth ions, Er^{3+} is one of the most popular ones since its laser oscillation is utilized as a fiber amplifier of doped silica at 1.55 μm.[1] Moreover, it exhibits three fluorescences, blue, green, and red, in visible region and the green-upconversion emission at 0.55 μm has been observed in oxide glasses by infrared III-V diode laser (LD) pumping.[2] These transitions can be enhanced by increasing the probability of a particular transition, which is a function of ligand field of rare-earth ions.

The Judd-Ofelt (JO) theory[3,4] is a most useful theory in estimating the probability of the forced electric dipole transitions of rare-earth ions in various environments. For example, it has been applied to design the Nd-containing laser glasses utilizing $^4F_{3/2}\rightarrow{}^4I_{11/2}$ emission in silicate and phosphate glasses.[5-8]

In the JO theory, three parameters Ω_2, Ω_4, and Ω_6 appear and they can be determined experimentally from the measurements of absorption spectra and refractive index of host material. From these parameters, several important optical properties, i.e., the radiative transition probability, the oscillator strength, the branching ratio, and the spontaneous emission probability can be evaluated. In glass, however, the relationship between these parameters and the structure of the rare-earth sites has not been elucidated yet owing to its unknown random structure. From the practical point of view, in order to increase the laser or upconversion efficiency, it is important to clarify the relation between the glass composition and the Ω_t parameters and to gain a higher transition probability of a particular fluorescence or excited-state absorption. In the present work, the intensity parameters were determined for Er^{3+} ions in alkali-metal borate glasses. Since the structures of alkali-metal borate glasses have been studied by many researchers,[9,10] it is possible to evaluate the relationship between the Ω_t parameters and the sites of rare-earth ions.

II. THEORY

According to the JO theory,[11] the electric dipole transitions between two states of $4f^N$ configuration of rare-earth ions, which are forbidden when ions are free, become allowed in the crystal field by mixing into the $4f^N$ configuration another configuration having opposite parity. Judd[3] considered that the configurations possible to be mixed into $4f^N$ are those of the type $4f^{N-1}nl^1$ ($n\geq5$, $l\neq3$), for example $4f^{N-1}5d^1$. The matrix elements of the electric dipole operator are calculated by considering the crystal field as a first-order perturbation. This calculation is simplified by setting the following four approximations. First, the states of $4f^N$ configurations are taken as linear combinations of Russell-Saunders coupled states (intermediate coupled states); second, all the components of the ground level are assumed to be equally populated; third, the energy of the states of configurations mixed into $4f^N$ configurations is assumed to be much larger than that of $4f^N$ configuration; and fourth, the local field approximation. Finally, the line strength for the electric dipole transition between an initial J manifold $|(S,L)J\rangle$ and a final J manifold $|(S',L')J'\rangle$ is obtained by[11]

$$S^{\mathrm{ed}}[(S,L)J;(S',L')J'] = \sum_{t=2,4,6} \Omega_t |\langle (S,L)J||U^{(t)}||(S',L')J'\rangle|^2 , \quad (1)$$

where three terms $\langle \| U^{(t)} \| \rangle$ are the reduced matrix elements of the unit tensor operators calculated in the intermediate-coupling approximation, and the coefficients Ω_2, Ω_4, and Ω_6 are the intensity parameters which contain the effects of the crystal-field terms, radial integrals of an electron, and so on.

The line strengths for both electric and magnetic dipole transitions[12] are related to the integrated absorbance and are given by[13]

$$\int_{\text{band}} k(\lambda)d\lambda = \frac{8\pi^3 e^2 \bar{\lambda} \rho}{3ch(2J+1)n^2}(\chi_{\text{ed}} S^{\text{ed}} + \chi_{\text{md}} S^{\text{md}}) \ , \qquad (2)$$

where $k(\lambda)$ is the absorption coefficient, $\bar{\lambda}$ is the mean wavelength of the absorption band, ρ is the concentration of the rare-earth ion, c is the speed of light, h is Planck's constant, e is the elementary charge, and the χ terms correct the effective field at a well-localized center in a medium of isotropic refractive index n and are given by $\chi_{\text{ed}} = n(n^2+2)^2/9$ for electric dipole transitions and $\chi_{\text{md}} = n^3$ for magnetic dipole transitions. Since the reduced matrix elements $\langle \| U^{(t)} \| \rangle$ are constant characteristic to each transition, three parameters Ω_t can be obtained experimentally from the line strengths of at least three bands.

III. EXPERIMENTAL PROCEDURE

A. Sample preparation

The glasses were prepared from reagent-grade powders of B_2O_3, Na_2CO_3, K_2CO_3, and Er_2O_3 (99.9%). 10-g batches of the composition of $(100-x)B_2O_3 \cdot xNa_2O \cdot 0.3Er_2O_3$ ($x=10$, 15, 20, 25, 30, 35) and $(100-x)B_2O_3 \cdot xK_2O \cdot 0.3Er_2O_3$ ($x=10$, 15, 20, 25, 30) were mixed in an alumina mortar, and melted at 1100 °C in a platinum crucible for 30 min. The melt was poured into a carbon mold and cooled in air and subsequently annealed near the glass transition temperature of each glass for 30 min. For the absorption measurement, the glass obtained was cut and polished with diamond paste into a thickness of 3–6 mm.

B. Determination of the Ω_t parameters

Absorption spectra were measured at room temperature with a Simadzu UV-2200 Recording Spectrophotometer in the range of 190–900 nm. Within this range only the $^2K_{15/2} \leftarrow {}^4I_{15/2}$ transition contains the magnetic dipole contribution, but this contribution is negligibly little for this transition. So the magnetic dipole transition can be ignored to calculate the Ω_t parameters. The values of integrated absorbance and the mean wavelength of six absorption bands listed in Table I were calculated after subtracting the base line of the spectrum. This base-line subtraction most affects the accuracy of the band integration and thus the accuracy of the Ω_t parameters in this calculation. To obtain the Er^{3+} concentration in a unit volume, the density of the samples were measured by Archimedes' method at room temperature using kerosene as the immersing liquid and SiO_2 glass as a standard. The refractive indices of glasses at the Na D line were measured at room temperature using an ERMA Abbe refractometer. The refractive indices were assumed to be constant since the wavelength dispersions of the alkali-metal borate glasses are too small to be taken into account in the present wavelength range. Since the numerical values of the reduced matrix elements of the unit tensor operator of Er^{3+} ions have been calculated and reported by Weber[13] and Carnall, Fields, and Rajnak,[14] the phenomenonological parameters Ω_2, Ω_4, and Ω_6 were determined by the method of least-squares fitting by using Eqs. (1) and (2) with these values listed in Table I. In order to evaluate the validity of the intensity parameters obtained by the fitting, the root-mean-square values (δ_{rms}) were calculated by

$$\delta_{\text{rms}} = \left[\frac{\sum (S_c - S_m)^2}{\sum S_m^2} \right]^{1/2} , \qquad (3)$$

where S_m and S_c are the measured and the calculated line strengths, respectively, and summation is taken over all the bands used to calculate the Ω parameters.

TABLE I. The reduced matrix elements of $U^{(t)}$ and typical mean wavelengths $\bar{\lambda}$ for the Er^{3+} transition used in this study (Refs. 13 and 14).

$(S,L)J$	$(S',L')J'$	$(U^{(2)})^2$	$(U^{(4)})^2$	$(U^{(6)})^2$	Band	$\bar{\lambda}$ (nm)
$^4I_{15/2}$	$^4I_{13/2}$	0.0188	0.1176	1.4617		1520
	$^4F_{9/2}$	0	0.5655	0.4651	1	652
	$^4S_{3/2}$	0	0	0.2285	2	521
	$^2H_{11/2}$	0.7056	0.4109	0.0870		
	$^4F_{7/2}$	0	0.1467	0.6273	3	487
	$^4F_{5/2}$	0	0	0.2237	4	450
	$^4F_{3/2}$	0	0	0.1204		
	$^2H_{9/2}$	0	0.078	0.17	5	407
	$^2G_{11/2}$	0.9178	0.5271	0.1197	6	378
	$^2G_{9/2}$	0	0.2416	0.1235		
	$^2K_{15/2}$	0.0219	0.0041	0.0758		
	$^2G_{7/2}$	0	0.0174	0.1163		

IV. RESULTS

The absorption spectra of Er^{3+} in sodium borate and potassium borate glasses are shown in Figs. 1(a) and 1(b), respectively. The absorption spectra are normalized from the optical density by the sample thickness and also by the Er^{3+} concentration. The absorption cross sections of $^4G_{11/2} \leftarrow {}^4I_{15/2}$ and $^2H_{11/2} \leftarrow {}^4I_{15/2}$ transitions exhibit a maximum at 25 mol % R_2O, and other transition monotonically decrease with increasing R_2O content in both borate glasses.

The intensity parameters Ω_t obtained from the fitting are listed in Table II and their compositional dependences are plotted in Figs. 2(a) and 2(b) for the Na_2O and K_2O systems, respectively. They exhibit similar trends against R_2O content in both systems. The value of Ω_2 shows a maximum around 25 mol % R_2O in both borate glasses. On the other hand, the values of Ω_4 and Ω_6 decrease monotonically with an increase in alkali-metal content. The compositional dependence of Ω_t parameters for the potassium borate glasses is larger than those for the sodium borate glasses.

V. DISCUSSION

A. Compositional variation of Ω_2

According to the results in Fig. 2, Ω_2 was very sensitive to the environment in which rare-earth ions exist. It is well known that most of the physical properties of alkali-metal borate glasses exhibit a maximum (or minimum) around 20–30 mol % of the alkali-metal content, which has been related to the structural change.[9] The value of Ω_2 obtained also exhibits a maximum around 25 mol % of the alkali-metal content. Therefore, this maximum of Ω_2 can be related to the structural change of the sites of rare-earth ions.

It has been reported that Ω_2 is closely related to the hypersensitive transitions,[11] i.e., the larger the hypersensitive transition is, the larger the value of Ω_2 is. In the case of the Er^{3+} ion, the transitions of ${}^2H_{11/2} \leftarrow {}^4I_{15/2}$ and ${}^4G_{11/2} \leftarrow {}^4I_{15/2}$ are the hypersensitive ones for which $\langle \| U^{(2)} \| \rangle$ is large. Jørgensen and Judd[15] reported that the hypersensitivity of certain lines in the spectra of rare-earth ions has its origin in the inhomogeneity of the environment of rare-earth ions, and the most striking effect would be expected for highly polarized and asymmetric environment around rare-earth ions. Consequently, in the alkali-metal borate glass containing 25-mol % alkali content, Er^{3+} ions are considered to exist at the most largely polarized and asymmetric sites. Although the local structure at the sites of rare-earth ions cannot be deduced from these parameters, the polarity and asymmetry of the rare-earth sites may be estimated. In

TABLE II. Values of n_D^{20}, ρ, and Ω_t parameters of samples. BNx: $(100-x)B_2O_3 \cdot xNa_2O \cdot 0.3Er_2O_3$; Bk$x$: $(100-x)B_2O_3 \cdot xK_2O_3 \cdot 0.3Er_2O_3$.

Sample	n_D^{20} (−)	ρ (10^{20} cm^{-3})	Ω_2 (10^{-20} cm^2)	Ω_4	Ω_6	δ_{rms} (%)
BN10	1.492	1.058	3.21	1.98	1.39	1.38
BN15	1.500	1.122	3.87	1.81	1.37	2.45
BN20	1.504	1.155	5.49	1.84	1.18	3.21
BN25	1.512	1.208	6.11	1.66	0.99	3.58
BN30	1.520	1.247	6.09	1.63	0.76	4.82
BN35	1.520	1.270	5.12	1.13	0.60	4.10
BK10	1.488	1.016	3.33	1.97	1.54	1.30
BK15	1.490	1.026	3.90	1.84	1.46	0.56
BK20	1.490	1.030	5.66	2.00	1.31	3.13
BK25	1.494	1.043	7.31	1.70	0.87	3.68
BK30	1.500	1.056	5.98	1.06	0.45	5.76

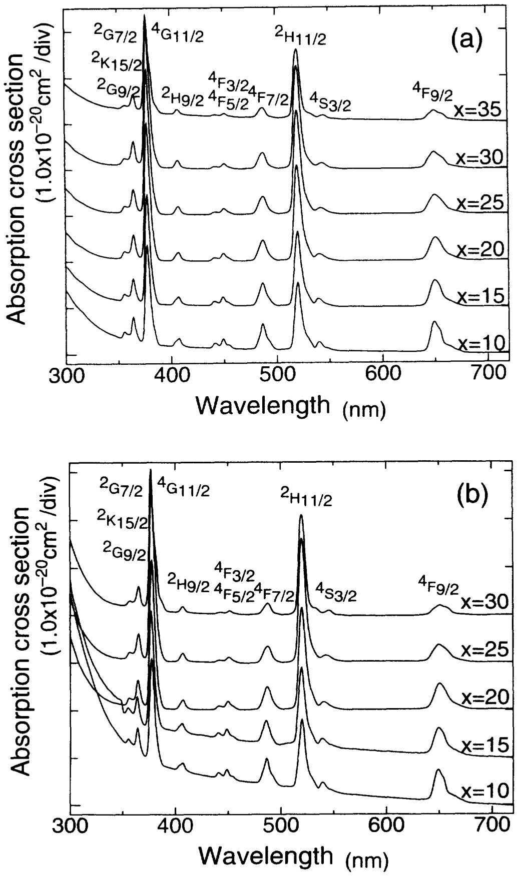

FIG. 1. Variations of absorption spectra of (a) $(100-x)B_2O_3 \cdot xNa_2O \cdot 0.3Er_2O_3$ and (b) $(100-x)B_2O_3 \cdot xK_2O_3 \cdot Er_2O_3$ glasses.

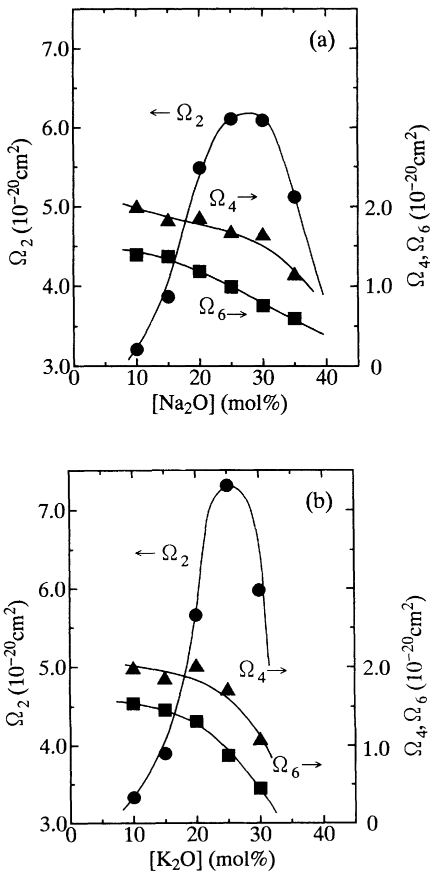

FIG. 2. Compositional dependence of Ω_t parameters of Er^{3+} in (a) B_2O_3-Na_2O glasses and (b) B_2O_3-K_2O_3 glasses.

alkali-metal borate glasses, as shown in Fig. 3, there exist several kinds of structural groups.[9,16] With increasing R_2O content, the amount of boroxyl ring (B_3O_3, Coordination Number, CN of all boron atoms is 3, B^{III}) decreases and that of tetraborate groups ($B_8O_{16}{}^{8-}$, $6B^{III}+2B^{IV}$) increases. At about 20 mol % R_2O, the amount of tetraborate becomes maximum and that of diborate group ($B_4O_9{}^{4-}$ $2B^{III}+2B^{IV}$) begins to appear. The diborate group reaches maximum at about 33 mol % R_2O, beyond which the nonbridging oxygen appears. Thus, the structure of alkali-metal borate glasses is always a mixture of multiple kinds of borate groups. Therefore, the local structure around rare-earth ions in glasses should be influenced by the fraction of borate groups in the glasses. In the previous study on the local structure of Eu^{3+} in sodium borate glasses, the measurement of phonon sideband (PSB) spectra succeeded to clarify the local structure of the rare-earth ions.[10] The PSB spectra associated with the ${}^5D_2 \leftarrow {}^7F_0$ transition were observed in the excitation spectra monitoring the ${}^5D_0 \rightarrow {}^5F_2$ emission at 612 nm. In Fig. 4, the electron-phonon coupling strength of several modes obtained from the analysis of PSB spectra are plotted for boroxol rings, tetraborate and diborate groups as a function of Na_2O content. The coupling strength g of each mode is considered to be proportional to the fraction of groups present around rare-earth ions. Also shown by the dotted lines are the number of groups per formula unit obtained by NMR,[9,16] which show similar trends against R_2O content. Especially, the structural units of borate groups around rare-earth ions are substantially mixed at about 25 mol % R_2O. Thus, the structure surrounding rare-earth ions are considered to be highly distorted and polarized around 25 mol % R_2O. This situation is also reflected on the alkali-metal dependence of Ω_2 for Eu^{3+} in sodium borate glasses.[17] Since only the $\Omega_2\langle \| U^{(2)} \| \rangle^2$ term affects the line strength of the ${}^5D_0 \rightarrow {}^7F_2$ transition, and the ${}^5D_0 \rightarrow {}^7F_1$ transition is a magnetic-dipole one, the intensity ratio of $({}^5D_0 \rightarrow {}^7F_2)/({}^5D_0 \rightarrow {}^7F_1)$, R is a measure of Ω_2 for Eu^{3+} ligand field. R shows a maximum around 25 mol % Na_2O, which is consistent with the present results for Er^{3+} ions.

B. Compositional variation of Ω_4 and Ω_6

It is reported experimentally that values of Ω_4 and Ω_6 are less sensitive to the environment of Er^{3+} ions than that of Ω_2.[11] In fact, $\Omega_{4,6}$ measured in this study were insensitive to the structure change of glass. If values of Ω_4 and Ω_6 were affected by the glass structure, as is the case of Ω_2, they should have exhibited a maximum or a minimum and would not have varied monotonically with the amount of R_2O. According to the theory, the values of Ω_t may be represented simply by[11]

$$\Omega_t = (2t+1)\sum_{p,s} |A_{sp}|^2 \Xi^2(s,t)(2s+1)^{-1} , \qquad (4)$$

where A_{sp} are sets of constants and are functions of the structure of the hosts, and $\Xi(s,t)$ are given by[3]

$$\Xi_{(s,t)} = 2\sum_{n,l}(2f+1)(2l+1)(-1)^{f+l} \times \begin{Bmatrix} 1 t s \\ f l f \end{Bmatrix} \begin{pmatrix} f 1 l \\ 000 \end{pmatrix} \begin{pmatrix} l s f \\ 000 \end{pmatrix} \times \frac{\langle 4f|r|nl\rangle\langle nl|r^s|4f\rangle}{\Delta E(\psi)} , \qquad (5)$$

where $\Delta E(\psi)$ is the energy difference between the $4f^N$ configuration and the mixed $4f^{N-1}nl^1$ configuration, in this case $4f^{N-1}5d^1$, and $\langle nl|r^k|n'l'\rangle$ is an abbreviation for

$$\int_0^\infty R(nl) r^k R(n'l') dr ,$$

and R/r is the radial part of the appropriate one-electron wave function. If values of Ω_4 and Ω_6 are not affected by the host structure surrounding rare-earth ions, they are affected by $\Xi(s,t)$ more than A_{sp}. From the tendency of Ω_4 and Ω_6 in Fig. 2 and Eq. (4), $\Xi(s,t)$ were found to decrease with increasing alkali-metal content. To account for this, two reasons may be possible: an increase in energy gap between the $4f^N$ configuration and the next excited configuration $4f^{N-1}nl^1$, $\Delta E(\psi)$, or a decrease in radial integral, $\langle 4f|r^k|nl\rangle$, with increasing alkali-metal content. Both of the changes may be brought in by the increase of the electron density on oxygen ions, i.e., the basicity of the glass.[18] With an increase in the basicity of the glass, the energy of the $4f^{N-1}nl^1$ configuration becomes high and the electron density of the mixed nl or-

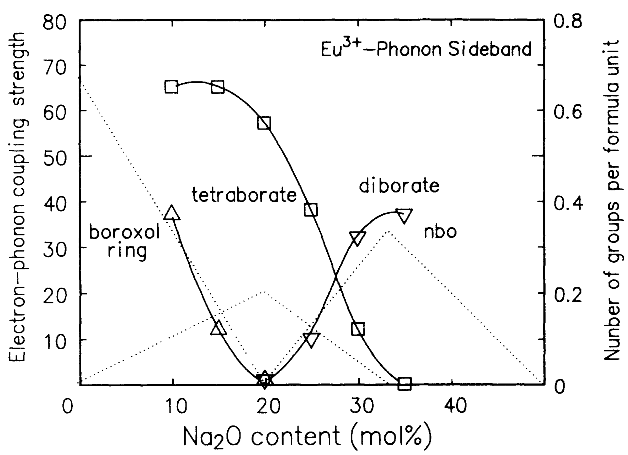

FIG. 4. Compositional variations of electron-phonon coupling strength of borate groups. The dotted line shows the number of groups per formula unit (Ref. 9).

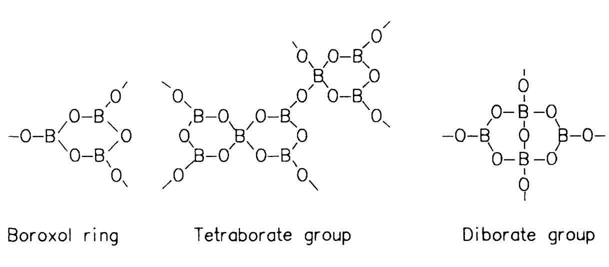

FIG. 3. Structure of borate groups (Ref. 16).

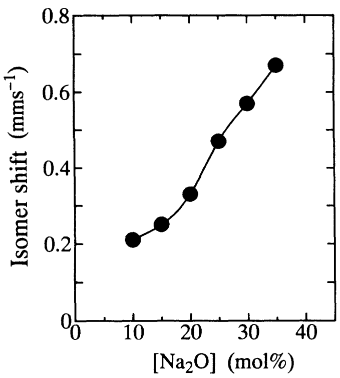

FIG. 5. Compositional dependence of isomer shift for $^{151}Eu^{3+}$ in sodium borate glasses (Ref. 19).

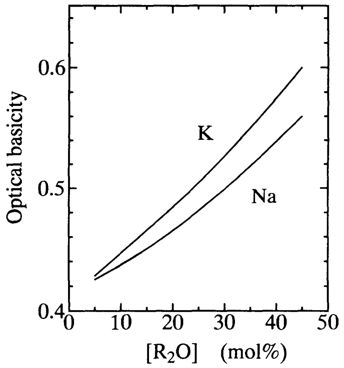

FIG. 6. Compositional dependence of calculated optical basicity for B_2O_3-R_2O_3 glasses (R =Na,K).

bital becomes small because of the repulsion between electrons of the mixed nl orbital and those of the 6s orbital whose density increases with an increase in basicity. Consequently, $\Delta E(\psi)$ becomes large and $\langle 4f|r^k|nl\rangle$ becomes small with an increase of the basicity. The increase of 6s-electron density of the rare-earth ions with an increase of the alkali-metal content is supported by the compositional dependence of the isomer shift ($\Delta_{\rm IS}$) in ^{151}Eu Mössbauer spectroscopy,[19] which is shown in Fig. 5. The $\Delta_{\rm IS}$ value of Eu^{3+} is related to the electron density at the nucleus and is given by[20]

$$\Delta_{\rm IS}=C\{|\Psi a(0)|^2-|\Psi s(0)|^2\}\ , \qquad (6)$$

where C is a constant related to the radius ratio of excited to ground nuclear states and is positive for ^{151}Eu nuclei.[21] Thus, the lower $\Delta_{\rm IS}$ can be attributed to a lower electron density at the ^{151}Eu nucleus, $|\Psi(0)|^2$, owing to a decreased covalency of Eu—O bond.[22]

Since only the s-electron density contributes to the $|\Psi(0)|^2$, the outer 6s orbital should take the same trend with that at the nucleus. As shown in Fig. 5, the value of $\Delta_{\rm IS}$ of the Eu^{3+} ions in B_2O_3-Na_2O glass increased monotonically with an increase in Na_2O content.[19] This suggests the 6s-electron density increased with an increase in alkali-metal content and supports our estimation of electronic states of rare-earth ions in this borate glass.

C. Difference between Na_2O and K_2O systems

As shown in Fig. 2, the compositional dependence of the Ω_t parameters of Er^{3+} in the B_2O_3-K_2O system is larger than that of the B_2O_3-Na_2O system. This result can be ascribed to the difference in ionic radius and electronegativity between K and Na. The compositional dependence of the optical-basicity calculated with the equations by Duffy and Ingram[18] is shown in Fig. 6. Because the electronegativity of K ($x_{\rm K}$=0.91) is smaller than that of Na ($x_{\rm Na}$=1.01),[23] the compositional change in basicity of the glass becomes larger for the K_2O system since B_2O_3 is an acidic oxide ($x_{\rm B}$=2.50). Consequently, the change in the local environment of the B_2O_3-K_2O system with alkali-metal content is more drastic than that of B_2O_3-Na_2O due to larger electron densities on oxygen ions, and so the Ω_t parameters.

VI. CONCLUSIONS

The Ω_2 parameter of alkali-metal borate glass, which has a relation to the hypersensitive transitions, exhibits a maximum around 25 mol % R_2O. This compositional dependence of Ω_2 is closely related to the structural change of the sites of rare-earth ions; higher polarization and asymmetry of the rare-earth ligand due to the structural mixing of various borate groups. On the other hand, the Ω_4 and Ω_6 parameters decrease monotonically. This tendency indicates that Ω_4 and Ω_6 are not directly related to the ligand symmetry of rare-earth ions but to the electron density on the oxide ion, i.e., the basicity of the glass.

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