Relationship between the local structure and spontaneous emission probability of Er\(^{3+}\) in silicate, borate, and phosphate glasses

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Received 11 August 2000; accepted 2 September 2000

Abstract

Extended X-ray absorption fine structure (EXAFS) measurements have been performed on Er\(^{3+}\) in order to investigate the local structure surrounding the Er\(^{3+}\). Er\(^{3+}\) 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 Er\(^{3+}\) ions is altered by the structural change of the borate anion. Er\(^{3+}\) 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. Er\(^{3+}\) ions selectively coordinate to the P\(_2\)O site regardless of the glass composition variation. A correlation was observed between the spontaneous emission probability for \(^{4I_{13/2}} \rightarrow ^{4I_{15/2}}\) transition of Er\(^{3+}\) and the average Er±O distance calculated by EXAFS analysis. It shows the maximum value near 2.32 Å, and we conclude that the overlapping radial integral of the 4f and 5d orbitals of Er\(^{3+}\) would be the largest at the optimum Er\(^{3+}\)±O\(^2-\) distance 2.3 Å. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Local structure; Covalency of Er–O bonding; Extended X-ray absorption fine structure spectroscopy; Spontaneous emission probability; Rare earth ions in oxide glasses

1. Introduction

Glass lasers containing rare earth ions as active ions have been put to practical uses such as nuclear fusion and optical fiber amplifiers [1]. They are developed evaluating the stimulated emission cross section, fluorescent lifetime, and radiative quantum efficiency, which are calculated based on spontaneous emission probability [2]. Therefore, the spontaneous emission probability of rare earth ions in oxide glasses is one of the indispensable properties for designing laser glasses.

As previously pointed out [3–13], the compositional dependence of the spontaneous emission probability of rare earth ions doped oxide glasses, which is calculated on the basis of the Judd–Ofelt theory [14,15], relates to the local structures surrounding rare earth ions. Thus, it is important to reveal the local structures surrounding rare earth ions in oxide glasses in order to design new glass lasers. The local structures of trace amounts of rare earth ion in oxide glasses have been analyzed using extended X-ray absorption fine structure (EXAFS) measurements [16–18]. EXAFS is a powerful tool for obtaining information about the surroundings of rare earth ion in glasses that do not possess a long range order, because EXAFS results from the local diffraction of excited photoelectrons, and the strength of oscillation are functions of the back-scattering power of an atomic matrix, and the thermal and static disorder of atomic positions. However, few studies have tried to examine the local structure of rare earth ions in oxide glasses systematically varying the matrix glass compositions.

The purpose of this work is to investigate the effect of composition on the local structure of Er\(^{3+}\) in silicate, borate, and phosphate glasses based on EXAFS analysis. We discuss the relationship between the spontaneous emission probability of the \(^{4I_{13/2}} \rightarrow ^{4I_{15/2}}\) transition of Er\(^{3+}\), which is utilized for the 1.5 µm amplifier, and the local structure surrounding Er\(^{3+}\).

2. Experimental procedure

2.1. Glass preparation

The matrix glass compositions are listed in Table 1. Glasses were prepared using special-grade reagents.

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PII: S1468-6996(00)00014-0
2.2. EXAFS measurements

Er LIII-edge X-ray absorption spectra were measured by a transmission mode at room temperature using a laboratory-type X-ray spectrometer (Model R-EXAFS 2000, Rigaku, Tokyo, Japan), which consists of an X-ray generator with a rotating Mo target and LaB6 electron gun, a Ge (220) curved crystal monochromator, and detectors. The voltage and current of X-ray source were 17 kV and 120 mA, respectively. Incident and transmitted X-ray intensities were monitored uniformly on an argon gas filled ionization chamber and a scintillation counter. 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 0.5–1.5. The sampling range, points, and time were 8200–9250 eV, 520 points per one sample, and 100 s per one point, respectively. An Er LIII-edge X-ray absorption spectrum of the crystalline Er2O3 was also measured as a standard by the same way in order to calibrate the EXAFS spectra of samples.

An EXAFS data analysis was performed using the software package (rex2) developed by Rigaku, as follows. Fig. 1 shows the EXAFS function, χ(k), of Er3+ in a silicate glass, as an example. The EXAFS function, χ(k), was obtained normalizing the spectrum that was obtained by subtracting the background from the measured X-ray absorption spectrum. The background was estimated using Victoreen’s equation [19]. Normalization was carried out using the McMaster coefficient [20]. The normalized spectrum was converted to the photo energy, E, to the photoelectron wavevector, k, via

\[ k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}, \]

(1)

where m and ℏ have their ordinary meanings, E is the energy of the incident X-ray beam, and E0 is the threshold energy for production of a photoelectron. E0 was determined by the inflection point of the Er LIII-edge measured for the crystalline Er2O3. The radial distribution function, ρ(r’), was obtained by Fourier transformation of the EXAFS function, kχ(k), in the k-space range of 3.8–10.5 Å⁻¹. r’ is related to the true distance r by a “phase shift” α = r – r’. The average Er–O distance and the geometrical position of the O²⁻ ions surrounding the Er³⁺ ion were estimated qualitatively from the peak position, intensity, and profile of the radial distribution function, ρ(k) of the O²⁻ ion in the radial distribution function was fitted to the EXAFS basic equation [21]

\[ \chi(k) = \frac{N}{kr^2} \cdot B(k) \cdot \exp(-2\alpha^2k^2) \cdot \exp[-2r/\lambda(k)] \cdot \sin[2kr + \phi(k)] \]

(2)

by the least-square method in order to determine the local structure parameters, such as the average Er–O distance, rEr–O, the oxygen coordination number, N, of Er³⁺ and the Debye–Waller factor, σ. The back-scattering factor, B(k), and the phase shift, ϕ(k), calculated by McCale et al. [22] were used. The mean free path, λ, of the photoelectron

### Table 1

| Matrix glass composition (mol%) | rEr–O (Å) | N | σ (Å) | A (s⁻¹) |
|---------------------------------|-----------|---|-------|---------|
| Silicate                        |           |   |       |         |
| 40Li2O–60SiO2                   | 2.26      | 6.1| 0.056 | 88.4    |
| 10Na2O–90B2O3                   | 2.24      | 6.1| 0.073 | 60.1    |
| 20Na2O–80SiO2                   | 2.24      | 6.5| 0.054 | 59.9    |
| 30Na2O–70SiO2                   | 2.24      | 6.6| 0.060 | 58.8    |
| 40Na2O–60SiO2                   | 2.24      | 6.5| 0.052 | 66.0    |
| 40K2O–60SiO2                    | 2.23      | 7.2| 0.056 | 59.3    |
| 40CaO–60SiO2                    | 2.26      | 6.1| 0.062 | 116.9   |
| 40SrO–60SiO2                    | 2.26      | 6.0| 0.060 | 103.3   |
| Borate                          |           |   |       |         |
| 30Li2O–92B2O3                   | 2.35      | 8.4| 0.092 | 128.0   |
| 30Li2O–70B2O3                   | 2.30      | 6.0| 0.092 | 138.7   |
| 10Na2O–90B2O3                   | 2.34      | 8.6| 0.074 | 144.0   |
| 15Na2O–85B2O3                   | 2.33      | 8.4| 0.086 | 143.6   |
| 20Na2O–80B2O3                   | 2.30      | 7.5| 0.092 | 141.0   |
| 25Na2O–75B2O3                   | 2.27      | 6.2| 0.104 | 123.9   |
| 30Na2O–70B2O3                   | 2.26      | 6.3| 0.092 | 108.1   |
| 35Na2O–65B2O3                   | 2.25      | 6.1| 0.086 | 94.7    |
| 30K2O–70B2O3                    | 2.25      | 7.3| 0.092 | 71.8    |
| 30CaO–70B2O3                    | 2.31      | 7.2| 0.080 | 157.3   |
| 30SrO–70B2O3                    | 2.30      | 7.0| 0.076 | 148.4   |
| Phosphate                       |           |   |       |         |
| 30Li2O–60P2O5–10Al2O3           | 2.26      | 7.4| 0.084 | 101.2   |
| 25Na2O–65P2O5–10Al2O3           | 2.26      | 7.7| 0.074 | 117.6   |
| 30Na2O–60P2O5–10Al2O3           | 2.26      | 7.7| 0.082 | 118.1   |
| 35Na2O–55P2O5–10Al2O3           | 2.26      | 7.5| 0.084 | 123.7   |
| 40Na2O–50P2O5–10Al2O3           | 2.25      | 7.3| 0.084 | 107.9   |
| 30K2O–60P2O5–10Al2O3            | 2.26      | 7.4| 0.084 | 117.7   |

(99.9–99.99%) in 15 g batches. Each batch, with 2 mol% Er2O3 mixed, was melted in a platinum or alumina crucible at the given temperatures, in air, for 2 h. Each molten glass was poured onto a stainless steel mold, and annealed for 1 h above a glass transition temperature. The method for glass preparation was described in detail elsewhere [10]. Annealed samples were ground up to less than 3 μm using an alumina mortar and pestle for EXAFS measurements.

Fig. 1. EXAFS function χ(k) vs k after background removal, normalization, and E to k conversion in Er³⁺ doped 30Na2O–70SiO2 glass.
was obtained from EXAFS data measured for the crystalline Er$_2$O$_3$.

3. Results and discussion

3.1. Compositional dependence of the local structure surrounding the Er$^{3+}$ ion

Table 1 lists the $r_{\text{Er}-\text{O}}$, $N$, and $\sigma$ in silicate, borate, and phosphate glasses. We determined the coordination site of surrounding the Er$^{3+}$ ions in the binary alkali or alkaline earth silicate glass systems were measured. Fig. 2(a) and (b) shows the radial distribution functions of the Er$^{3+}$ ion in the Na$_2$O–SiO$_2$ and 40R$_2$O–60SiO$_2$ (R = Li, Na, K) glasses, respectively. 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. In this case, the peak positions of the first (O$^{2-}$) and second neighboring ion were approximately 1.9 and 3.3 Å, respectively. In contrast, the radial distribution functions varied with the type of the alkali ions in the 40R$_2$O–60SiO$_2$ (R = Li, Na, K) glasses. The peak position of O$^{2-}$, which is related to the average Er–O distance, decreased and the peak intensity of O$^{2-}$ increased in the order of R = Li$^+$, Na$^+$, and K$^+$. The peak position of the second neighboring ion did not change, but peak intensity increased in the order of R = Li$^+$, Na$^+$, and K$^+$. This means that the radial distribution function of the second neighboring ion depends not on the content but type of alkali metal oxide.

Greaves [23] proposed the modified random network model for the structure of silicate glass. According to this model, the network structure that the SiO$_4$ tetrahedrons are connected in three-dimensionally and randomly at the corners and/or edges is cut non-uniformly, and the regions that consist mainly of bridging oxygens and of non-bridging oxygen ions are both formed by adding network modifiers such as Na$_2$O in silicate glasses. From the results of EXAFS analysis, it is considered that Er$^{3+}$ ions coordinate the region of non-bridging oxygen ions because the second neighboring ion of Er$^{3+}$ is an alkali ion in silicate glasses. Fig. 3 schematically shows the local structure of Er$^{3+}$ ions in silicate glasses based on the EXAFS analysis. Thus, the local structure surrounding Er$^{3+}$ in silicate glasses would change not with the variation of the alkali metal oxide content, but with their species, because Er$^{3+}$ ion coordinates the non-bridging oxygen region in which there is an abundance of alkali ions.

3.1.2. Borate glasses

The Er L$_{III}$-edge EXAFS in the binary alkali or alkaline earth borate glass systems were measured. Fig. 4 shows the radial distribution function of Er$^{3+}$ ion in the Na$_2$O–B$_2$O$_3$ glasses. The radial distribution function for the O$^{2-}$ ion shows a peak near 1.9 Å. In contrast to Er$^{3+}$ doped silicate glasses, this peak position, which is related to the average distance of Er–O, decreased on increasing Na$_2$O content; however, the intensity and width exhibit the minimum and maximum, respectively, at 25 mol% of Na$_2$O. The maximum of peak width at 25 mol% of Na$_2$O suggests that the geometrical position of O$^{2-}$ ions surrounding Er$^{3+}$ is the most disordered. The radial distribution function for the second neighboring ion could not be identified because the intensities were too low. From this result, it is supposed that the second neighboring ions surrounding Er$^{3+}$ are extremely disordered.

It is well known that the oxygen coordination number of
boron changes from three to four on increasing alkali or alkaline earth metal oxide content in borate glasses [24]. Several kinds of anion structural groups, which consist of BO$_3$ and BO$_4$, coexist in alkali borate glasses. The number of the type of anion structural groups would reach the maximum at 25 mol% of Na$_2$O in the Na$_2$O±B$_2$O$_3$ glass system. It is assumed that Er$^{3+}$ would sit next to the anion structure of boron because the structural change of borate glass corresponds to the variation of the geometrical position of the O$_2^{2-}$ ions surrounding Er$^{3+}$ with glass composition. Fig. 5 schematically shows the local structure of Er$^{3+}$ ions in the borate glasses based on the EXAFS analysis. Oxygen ions introduced by the addition of Na$_2$O into the borate glass are first consumed for the change of coordination number from BO$_3$ to BO$_4$, and the non-bridging oxygen ions are not formed below 29 mol% of Na$_2$O [24]. As shown in Fig. 5, Er$^{3+}$ would coordinate only to the negatively charged BO$_4$ site in the glass composition range where non-bridging oxygen ions are not formed. Therefore, it is considered that the local structure surrounding Er$^{3+}$ in borate glasses is influenced by the structural change of borate anions. On the other hand, Er$^{3+}$ would coordinate to the non-bridging oxygen ion site in the glass composition range where non-bridging oxygen ions are formed. In this case, the local structure surrounding Er$^{3+}$ in borate glasses would be similar to that in silicate glasses, which is shown in Fig. 3.

3.1.3. Phosphate glasses

The Er L$_{III}$-edge EXAFS in the alkali phosphate glasses containing 10 mol% Al$_2$O$_3$ were measured. Fig. 6 (a) and (b) shows the radial distribution function of Er$^{3+}$ ion in the Na$_2$O–P$_2$O$_5$–Al$_2$O$_3$ and 30R$_2$O–60P$_2$O$_5$–10Al$_2$O$_3$ (R = Li, Na, K) glasses. The peak positions, intensities and spectral profiles of the radial distribution functions corresponding to the first (O$_2^{2-}$) and second neighboring ions did not change with the content and type of alkali ions. The peak positions of the O$_2^{2-}$ ion and the second neighboring ion were approximately 1.9 and 3.5 Å, respectively. The distance between Er$^{3+}$ and the second neighboring ion agree with the Er–P distance (3.56 Å) in the ErP$_5$O$_{14}$ compound [25]. Therefore, the second neighboring ion of Er$^{3+}$ ion is identified as P$_5^{5+}$ ion in the phosphate glasses. Fig. 7 schematically shows the local structure of Er$^{3+}$ ions in the phosphate glasses based on the EXAFS analysis. The phosphate glass structure is formed by the connection of PO$_4$ tetrahedral units in which some of the P$_5^{5+}$ and O$_2^{2-}$ bonds are the P–O double bond or P–O bond [26]. It is considered that Er$^{3+}$ ions selectively coordinate to certain sites breaking the P–O or P–O bond, and thus, the local structure surrounding Er$^{3+}$ is independent of glass composition in phosphate glasses.

3.2. Compositional dependence of spontaneous emission probability

We revealed the local structure surrounding Er$^{3+}$ in silicate, borate, and phosphate glasses. The spontaneous emission probabilities for f–f transitions of Er$^{3+}$ ions in oxide glasses...
was the most disordered at 25 mol% of Na$_2$O. It is supposed that the $A$ coefficient is not influenced by the disorder of oxygen coordination surrounding Er$^{3+}$ ions. Therefore, the compositional dependence of the $A$ coefficient would be related to the variation of the coordination site of Er$^{3+}$ ion that is brought about by the structural changes of the borate anion.

In phosphate glasses, the $A$ coefficient is independent of the glass composition (in the range of 101.2–123.7 s$^{-1}$) because Er$^{3+}$ ions selectively coordinate to a P=O site that is independent of glass composition. The site selectivity for Nd$^{3+}$, Ti$^{3+}$, and Cr$^{3+}$ was also reported in similar phosphate glasses [10,27,28]. We successfully performed a direct observation of the site selectivity between Er$^{3+}$ and the P=O bond using EXAFS measurement.

The relationship between the $A$ coefficient and local structural parameters calculated by EXAFS analysis is discussed in detail below. Fig. 8(a)–(c) shows the relationships between the $A$ coefficient and properties like the average distance of Er–O, $r_{\text{Er-O}}$, oxygen coordination number, $N$, of Er$^{3+}$ ion, and the Debye–Waller factor, $\sigma$, in silicate, borate, and phosphate glasses. The $A$ coefficient exhibits the maximum near 2.32 Å as shown in Fig. 8(a). It is considered that the $A$ coefficient would be influenced by the chemical bonding of Er–O because $r_{\text{Er-O}}$ is the parameter that reflects the condition of the chemical bonding of Er–O.

The $A$ coefficient shows the minimum around $N$ of seven as shown in Fig. 8(b). In general, the ideal oxygen coordination numbers of Er$^{3+}$ ions are supposed to be six or eight. The coordination number of seven means that both ErO$_6$ and ErO$_8$ would exist, or one of the oxygen sites would shift from those of the actual ErO$_6$ or ErO$_8$ because $N$ calculated by the EXAFS analysis is the average value. As a result, it is supposed that the $A$ coefficient would decrease when mixing ErO$_6$ and ErO$_8$, or shifting the oxygen site from the ideal six- or eight-coordination sites around Er ions. In other words, the $A$ coefficient might be maximized if Er ions have the ideal ErO$_6$ or ErO$_8$ coordinations.

There is no correlation between the $A$ coefficient and $\sigma$ as shown in Fig. 8(c). It is assumed that the $A$ coefficient is independent of the symmetry of the local structure surrounding Er$^{3+}$ ions because $\sigma$ is the parameter that represents the geometrically disordered position of oxygen.

The spontaneous emission probability of an electric-dipole transition is given by the following equation based on the Judd–Ofelt theory [14,15]

$$A[(S,L,J) : (S',L',J')] = \frac{64\pi^4 e^2}{3h(2J + 1)\lambda_p} \times \left[ \frac{n(n^2 + 2)^2}{9} \right] \sum_{\nu=2,4,6} \Omega_{\nu} |(S,L,J)| |U^{(\nu)}(S',L',J')|^2$$

where $S$, $L$, and $J$ are the quantum numbers, $\lambda_p$ the emission wavelength, $n$ the refractive index at $\lambda_p$, $U^{(\nu)}$ are

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**Fig. 8. Relationship between spontaneous emission probability, $A$, for the $^4I_{15/2} \rightarrow ^4I_{13/2}$ transition of Er$^{3+}$ and (a) average Er–O distance, $r_{\text{Er-O}}$, (b) oxygen coordination number, $N$, of Er$^{3+}$ ion, and (c) the Debye–Waller factor, $\sigma$, in silicate, borate, and phosphate glasses. Lines are drawn to guide the eye.**

glasses should be affected by the local structure surrounding Er$^{3+}$ ions. Next, we will discuss the relationship between the spontaneous emission probability for the $^4I_{15/2} \rightarrow ^4I_{13/2}$ transition of Er$^{3+}$, the $A$ coefficient, which is utilized for the 1.5 μm optical fiber amplifier, and the local structure surrounding Er$^{3+}$ in silicate, borate, and phosphate glasses.

Table 1 also lists the $A$ coefficient. These data were cited by the previous works [11]. In silicate glasses, the $A$ coefficient changes little (from 58.8 to 66.0 s$^{-1}$) with the Na$_2$O content, although it significantly changes (from 66.0 to 116.9 s$^{-1}$) with the type of alkali metal oxide. The compositional dependence of the $A$ coefficient agrees well with the results of EXAFS analysis that showed that the local structure of Er$^{3+}$ ions in silicate glasses changed not with the Na$_2$O content, but with the type of alkali metal oxide.

In borate glasses, the $A$ coefficient decreases from 144.0 to 94.7 s$^{-1}$ on increasing the Na$_2$O content. It was found that the oxygen coordination of Er$^{3+}$ in the Na$_2$O–B$_2$O$_3$ glasses

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eigenvalues, the so-called reduced matrix elements of unit tensor operators, which are independent of the glass compositions and determined by the $f$–$f$ transitions, and $\Omega_t$ are coefficients, which depend on the glass composition. From Eq. (3), the factors affecting the compositional dependence of the $A$ coefficient would be the $[n(n^2 + 2)^2/9]$ and $\sum \Omega_t \langle \langle U^{(t)} \rangle \rangle^2$ terms. The value of the $[n(n^2 + 2)^2/9]$ term changes little (1.943–2.172) because the variation of $n$ with glass composition is 1.477–1.556. In this study. Therefore, the value of the $[n(n^2 + 2)^2/9]$ term is not a dominant factor for determining the $A$ coefficient, and can be regarded as a constant. On the other hand, the $\sum \Omega_t \langle \langle U^{(t)} \rangle \rangle^2$ term is affected by the sum of the product of coefficients, which depend on the glass composition. From structural changes around Er ions. On the other hand, allowed by the mixing of the 4f $N$ $1$ $u$ $1$ $s$ $l$ $f$ $r$ $f$ $l$ $f$ $s$ $l$ $f$ term is a main factor concerning the electronic structure of the Er$^{3+}$ ion within the 4f$^N$ configuration. This overlapping radial integral is affected by the covalency of the Er$^{3+}$ and $O^2-$ bonding. The coefficient $\Omega_{t}$ is important because the $A$ coefficient is dominantly by the $\langle \langle U^{(t)} \rangle \rangle^2$ term.

It is estimated from the ionic radii of Er$^{3+}$ (1.03 Å) and $O^2-$ (1.26 Å) that the optimum Er–O distance would be 2.3 Å (1.03 + 1.26 Å) [30]. Therefore, it is assumed that the Er–O distance is close to the optimum Er–O distance of 2.3 Å, and then the overlapping radial integral of the 4f and the 5d orbitals of Er$^{3+}$ reaches the maximum, and thus, the A coefficient of Er$^{3+}$:4$I_{13/2} \rightarrow 4$I$_{15/2}$ shows the maximum value.

4. Conclusions

The local structure surrounding Er$^{3+}$ ions in silicate, borate, and phosphate glasses was investigated by EXAFS analysis. Er$^{3+}$ ions coordinate to the non-bridging oxygen ion site where alkali or alkaline earth ions terminate the network structure of silicate glasses. In borate glasses, Er$^{3+}$ ions coordinate to the anion structural units of BO$_4$ in the range that the non-bridging oxygen is not formed. On the other hand, in the range that the non-bridging oxygen is formed, Er$^{3+}$ ions coordinates to the non-bridging oxygen ion site, which is similar to the case of silicate glasses. Er$^{3+}$ ions selectively coordinate to the P=O site. A correlation was found between the A coefficient of Er$^{3+}$:4$I_{13/2} \rightarrow 4$I$_{15/2}$ and the average Er–O distance calculated by EXAFS analysis. The A coefficient shows the maximum near the average Er–O distance of 2.32 Å. The Er–O distance is close to the optimum Er–O distance 2.3 Å, and then the overlapping radial integral of the 4f and the 5d orbitals of Er$^{3+}$ increases, and thus, the A coefficient shows the maximum value near 2.32 Å.

Acknowledgements

Thanks are due to Dr Isao Tanaka and Dr Kazuyoshi Ogasawara at Kyoto University for valuable comments concerning the electronic structure of the Er$^{3+}$ ion in oxide glasses. This work was supported by Grand-in Aid for Scientific Research (A) No. 11305055 from Japan Society for the Promotion of Science.

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