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ABSTRACT

The photoluminescence spectra and luminescence lifetimes of Eu^{3+} -doped oxyhalides, YOX: Eu^{3+} (X = Cl or Br), and their temperature dependence on different halide species of mixed-anion coordinations were investigated and analyzed. In terms of the ionic and covalent nature of bonding, Eu^{3+} ions form different coordination polyhedra in the isostructural YOCl and YOBr hosts: a ninefold $[Eu^{3+}O_4Cl_5]$ and an eightfold $[Eu^{3+}O_4Br_4]$ polyhedra. The Judd–Ofelt Ω_2 parameter for YOCl: Eu^{3+} takes a very large value (=8.81 × 10⁻²⁰ cm²) due to the ninefold polyhedron with $C_{4\nu}$ symmetry. On the other hand, despite the same $C_{4\nu}$ symmetry, YOBr: Eu^{3+} shows a very small Ω_2 parameter for YOX: Eu^{3+} are much larger than those for other Eu^{3+} -doped oxides, possibly related to the covalency of halide anions, Cl^- and Br^- , showing an intense luminescence band (${}^5D_0 \rightarrow {}^7F_4$) at around 700 nm. The Eu^{3+} ions in these YOX hosts were excitable by charge transfer bands in 270–280 nm regions. The relaxation pathways from the charge transfer states to the initial states for luminescence are discussed, using the configuration coordinate diagrams with the spectroscopic characterization.

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I. INTRODUCTION

Red luminescent materials activated with trivalent europium ions, Eu³⁺, have been investigated for various applications,^{1,2} such as cathode ray tubes,^{3–5} fluorescent tubes,^{6–8} white light-emitting diodes (wLEDs),^{9–11} displays,^{12,13} and anti-counterfeiting paints for banknotes.¹⁴ The Eu³⁺ luminescence is attractive due to the following three reasons: the sharp luminescence lines attributed to the 4f-4f transition with a small effect of the electron–phonon coupling, the hypersensitivity of the ${}^5D_0 \rightarrow {}^7F_2$ transition depending crucially on a local environment around Eu³⁺, and the efficient charge transfer (CT) excitation from ligands. The enormous amount of inorganic compounds has been considered to obtain an intense Eu³⁺ orange–red luminescence with high luminous efficacy for radiation (lm W⁻¹). Mono-anion materials, including oxides, nitrides, halides, and sulfides, have been regarded as the widely used host compounds of inorganic phosphors, because it is relatively easy to prepare and analyze their crystalline phases and compositions. Nowadays, mixed-anion compounds attract the attention of material scientists because of the possibility of developing new functional materials from these.¹⁵ When a Eu³⁺ ion is surrounded by multiple types of anions with different characteristics (e.g., electronegativity, polarizability, ionic radius, and valence state), its luminescent properties can be significantly affected by increasing the local asymmetry and enhancing the crystal field splitting.¹⁵ According to the Judd–Ofelt theory, which quantitatively evaluates the transition probabilities of lanthanoid ions, ^{16–18} a Eu^{3+ 5}D₀ \rightarrow ⁷F₂ luminescence of around 620 nm is sensitive to the asymmetry of the local environment, following which an enhancement in the Eu³⁺ red luminescence in the mixed-anion coordination is expected.

In this study, we focus on compounds with oxyhalide coordination, represented by the chemical composition of YOX (X = Cl or Br), to investigate the influence on Eu³⁺ luminescence. The YOX is

one of the matlockites containing rare-earth elements. Matlockite is the name of the mineral with the composition PbClF, whose layered structure has a tetragonal unit cell with the space group P4/nmm (No. 129).¹⁹ In both YOCl and YOBr, the Y³⁺ sites have a monocapped square antiprism with $C_{4\nu}$ symmetry accommodating trivalent lanthanoid ions Ln^{3+} without any charge compensation. This local structure has only two symmetrical operations, a fourfold rotation axis C_4 and a mirror plane σ_{ν} , with no inversion center in the $C_{4\nu}$ sites. In addition, Ln^{3+} ions are surrounded by both X^- and O^{2-} , possibly leading to further distortion in the local field and an enhancement in the transition probabilities.

In a few previous studies,^{20–22} a strong Eu³⁺ luminescence in the YOX hosts was observed and discussed. First, Blasse reported some essential characteristics of Eu³⁺ luminescence in a series of *REOX* hosts (*RE* = Y, Gd, La, and *X* = Cl, Br), such as the relative PL intensity and quantum yields with a cation and anion variation.²⁰ He concluded that the choice of *X*⁻ significantly affected the crystal field around a Eu³⁺ ion and the spectral energy distribution of Eu³⁺ 4*f*-4*f* luminescence. Subsequently, Hölsä calculated the crystal field parameters for YOCI:Eu³⁺ and YOBr:Eu³⁺ based on spectroscopy and simulated the energy diagrams for Eu³⁺ with the Stark splitting.^{21,22} While the Judd–Ofelt intensity parameters Ω_t are a powerful tool to predict the radiative decay rates and relative intensities of the electric dipole transition, there have been no reports on detailed analyses of lanthanoid ions in these oxyhalide compounds based on the Judd–Ofelt theory.

In this work, the effect of an oxyhalide ligand field on Eu³⁺ luminescence was characterized based on the Judd–Ofelt theory.^{16–18} Here, Eu³⁺ concentration is fixed to be 0.5%, which is lower than that in Blasse's (5%) and Hölsä's (1%) studies,^{20–22} to investigate the intrinsic properties of isolated Eu³⁺ ions. The estimated Judd–Ofelt intensity parameters Ω_t (t = 2, 4, and 6) of the Eu³⁺: ⁵D₀ \rightarrow ⁷F_{2,4,6} luminescence reveal that the existence of chloride Cl⁻ and bromide Br⁻ ions causes different spectral shapes and a variation in the relative PL intensity. In addition, spectroscopic characterization at various temperatures gives essential information about the relaxation process of the Eu³⁺: ⁵D₀ state and its quenching process. This insight into the relaxation mechanism of the Eu³⁺ 4f and Eu³⁺- X^- CT excited states helps us develop a novel red-emitting phosphor activated with Eu³⁺.

II. EXPERIMENTAL PROCEDURE

The Eu³⁺-doped oxyhalide samples, YOX:Eu³⁺ (X = Cl or Br), were fabricated through the synthesis procedures described below. The oxychloride powder sample doped with 0.5 mol. % Eu³⁺, Y_{0.995}Eu_{0.005}OCl, was prepared by oxidation of a chloride compound. The starting chemicals of YCl₃ · 6H₂O (99.9%) and Eu₂O₃ (99.99%) were weighed and mixed homogenously with an alumina mortar. The mixture was calcinated at 500 °C for 6 h in the air atmosphere. The oxybromide powder sample doped with 0.5 mol. % Eu³⁺, Y_{0.995}Eu_{0.005}OBr, was synthesized through bromination of an oxide compound. The starting chemicals of Y₂O₃ (99.99%) and Eu₂O₃ (99.99%) were weighed and mixed not be sample doped with 0.5 mol. % Eu³⁺, Y_{0.995}Eu_{0.005}OBr, was synthesized through bromination of an oxide compound. The starting chemicals of Y₂O₃ (99.99%) and Eu₂O₃ (99.99%) were weighed and mixed not be and mixed not be only on the starting chemicals of Y₂O₃ (99.99%) and Eu₂O₃ (90.99%) were weighed and mixed not be mixture and sintered at 500 °C for 2 h under N₂ gas flow. Since the prepared oxyhalide samples easily reacted with moisture, they were kept in a

glovebox filled with high purity Ar gas. For luminescence properties' measurements, the powder form samples were sealed in a quartz tube with an inner diameter of 6 mm under a vacuum.

Synchrotron x-ray diffraction (SXRD) data of the YOX:Eu³⁺ samples were obtained at 300 K on a monochromated incident beam at the BL02B2 JASRI beamline ($\lambda = 0.413269$ Å) of Spring-8. The sample in powder form was put in a Lindeman capillary tube with an inner diameter of 0.1 mm. The sealed capillary was rotated during measurements to suppress the effect of preferential orientation. The obtained SXRD patterns were analyzed with the Rietveld method using the RIETAN program.²³ For the Rietveld refinement, the atomic positions and the isotropic displacement parameter U_{iso} for Eu incorporated in Y sites are restricted to be the same as those of Y.

Photoluminescence excitation (PLE) spectra were measured with a setup consisting of a Xe short arc lamp (OPM2-502XQ, Ushio Inc.), double monochromators (SP-300i, Acton Research Corp.), and a photomultiplier tube (R3896, Hamamatsu Photonics). The sample was cooled down to 4 K by a closed-cycle He gas cryogenic refrigerator (CRT-A020-SE00, Ulvac Cryogenics). The PLE spectra were calibrated by the spectrum of the Xe lamp (excitation light source) detected by a Si standard photodiode (S1337-1010BQ, Bunkoukeiki Co. Ltd.).

For photoluminescence (PL) measurements, luminescence was detected by a photomultiplier tube (R10699, Hamamatsu Photonics) equipped with a monochromator (SP-2300i, Princeton Instruments). The monochromatic excitation light was obtained by the double monochromator system with the Xe lamp, which is the same as the PLE measurements.

The temperature-dependent PL spectra excited with a near-UV LED (UV17-0399-B, DOWA Electronics Materials Co., Ltd., $\lambda = 280$ nm) were detected by a CCD spectrometer (USB-2000+, Ocean Optics) connected with an optical fiber. The sample was attached in a liquid nitrogen cryostat (Helitran LT3, Advanced Research Systems) to control its temperatures from 100 to 800 K. The obtained PL spectra were calibrated by the spectrum of a deuterium-tungsten halogen light source (DH-2000, Ocean Optics).

The luminescence decay curves were investigated at various temperatures (100–800 K) with a luminescence lifetime spectrometer equipped with a Xe flashlamp (Quantaurus-Tau-C11367, Hamamatsu Photonics). The sample temperature was controlled by the liquid nitrogen cryostat.

III. RESULTS

A. Structural analysis of matlockite-type YOX (X = Cl or Br)

The SXRD data of the YOX: Eu^{3+} samples were collected to identify the crystalline phase and refine the lattice parameters. The diffraction patterns shown in Fig. 1 indicate that the single phases of matlockite-type YOCl and YOBr crystals were successfully prepared. The Rietveld refinement of these SXRD patterns was performed based on the tetragonal structure (space group: *P4/nmm*, No. 129). The refined lattice parameters of a tetragonal unit cell are a = b = 3.90018(5) Å and c = 6.5919(2) Å for the YOCl: Eu^{3+} and a = b = 3.83931(8) Å and c = 8.2622(5) Å for the YOBr: Eu^{3+} . Other crystallographic parameters obtained by



FIG. 1. SXRD patterns of the (a) YOCI:Eu³⁺ and (b) YOBr:Eu³⁺ samples at room temperature ($\lambda = 0.413269$ Å). The observed and calculated intensities and difference plots are shown by red + marks, solid blue lines, and solid gray lines, respectively. Green tick marks indicate calculated Bragg peak positions based on a matlockite-type tetragonal structure belonging to the space group *P4/nmm*. Reliability factors: $R_{wp} = 6.201\%$, $R_p = 4.788\%$, and $R_e = 2.383\%$ for the YOCI:Eu³⁺ and $R_{wp} = 6.106\%$, $R_p = 4.550\%$, and $R_e = 2.844\%$ for the YOBr:Eu³⁺.

the Rietveld refinement are provided in Tables S-I and S-II in the supplementary material. The output reliability factors R_{wp} (YOCl) and R_{wp} (YOBr) were 6.201% and 6.106%, respectively, indicating a good agreement between the observed and fitted patterns. The layered crystal structures of YOCl and YOBr along the a-axis are depicted in Fig. 2(a). Comparing the lattice parameters between YOCl and YOBr, the unit cell varies anisotropically by substituting

small Cl⁻ (1.81 Å) with large Br⁻ (1.96 Å)²⁵ in the matlockite structure. Along the in-plane direction [100] and [010], the lattice constant *a* and *b* of the YOBr:Eu³⁺ were slightly smaller by 0.060 87(9) Å (only -1.56%) than that of the YOCl:Eu³⁺. In contrast, the lattice constant *c* of the YOBr:Eu³⁺ is considerably larger than that of the YOCl:Eu³⁺, which was unexpected from the ionic radius difference.

The distances between two [X-Y-O-Y-X] sheets were refined to be 1.669(3) Å for the YOCl:Eu $^{3+}$ and 2.774(2) Å for the YOBr: Eu^{3+} , respectively. In terms of the local structure around Y^{3+} ions in the YOX hosts, the critical difference is the bond length between Y^3 ⁺ and X^- ions across the two sheets. Local environments around Y^{3+} in YOX hosts are picked up and shown in Fig. 2(b). Here, X⁻ ions in the same and adjacent [X-Y-O-Y-X] sheets are labeled as $X_{\rm I}$ and $X_{\rm II}$, respectively. Based on the refined structure of the YOCl:Eu³⁺, the distance from Y^{3+} to Cl_{I}^{-} and Cl_{II}^{-} are 3.0735(10) and 3.026(3) Å, resulting in the ninefold monocapped square antiprism [YO₄Cl₅]. In contrast, the bond lengths between Y^{3+} and Br⁻ in the refined YOBr:Eu³⁺ structure are 3.1658(13) Å for $Y^{3+}-Br_{T}^{-}$ and 4.403(3) Å for $Y^{3+}-Br_{II}^-$. The length of $Y^{3+}-Br_{I}^-$ bonding is longer by 0.0923(16) Å than that of Y^{3+} -Cl_I bonding, as expected due to the larger ionic radius of Br⁻. The Y³⁺-Br_{II} bonding is relatively long because the two [Br-Y-O-Y-Br] sheets are well separated. The significant difference in the bond length between Y³⁺- Br_{I}^{-} and $Y^{3+}-Br_{II}^{-}$ leads to the eightfold distorted square antiprism [YO₄Br₄]. This eightfold coordination polyhedron is also considered in other lanthanoid oxybromide compounds with the matlockite structure.²⁰ The different coordination number of the Y³⁺ sites in the YOX hosts possibly contributes to the luminescent properties of accommodated lanthanoid ions, whereas both local structures belong to the same point group $C_{4\nu}$.

B. Charge transfer excited states of Eu³⁺ in oxyhalide YOX

The prepared YOX:Eu³⁺ samples showed red luminescence under UV light illumination (see Fig. S-1 in the supplementary material). Figure 3 shows the PLE spectra of the YOX:Eu³⁺ samples at 4 K monitored with Eu³⁺ luminescence over 600 nm. In both spectra of the YOX:Eu³⁺, the excitation lines and bands are classified into three categories: the Eu³⁺ 4*f*-4*f* transition, the CT transition from ligands, and the defects-related absorption.

The sharp lines are assigned to the 4*f*-4*f* transition of Eu³⁺: from ⁷F₀ to ⁵D₁ (~19 000 cm⁻¹ = ~526 nm), ⁵D₂ (~21 500 cm⁻¹ = ~465 nm), ⁵L₆ (~25 300 cm⁻¹ = ~395 nm), ⁵D₄ (~27 600 cm⁻¹ = ~362 nm), and ⁵H₆ (31 300 cm⁻¹ = ~319 nm) states. Many sharp lines in the range of 26 000–27 400 cm⁻¹ are due to the convolution of the ⁵L_{*j*}, ⁵G_{*j*} \leftarrow ⁷F₀ transitions.^{21,22}

The broad and asymmetric excitation bands located over $31\,000 \,\mathrm{cm}^{-1}$ are attributed to the CT transition from coordinating anions (X^- or O^{2-}) to Eu^{3+} ions. Since the CT transition is Laporte-allowed,² PLE intensities of the CT bands are much more intense than that of Eu^{3+} 4*f*-4*f* excitation lines. The YOCI:Eu³⁺ exhibited stronger CT bands than the YOBr:Eu³⁺. The centroid energies of asymmetric CT bands ($E^{\rm CT}$) are estimated to be 38 163 cm⁻¹ for the YOCI:Eu³⁺ and 36 686 cm⁻¹ for the YOBr:Eu³⁺



FIG. 2. (a) Crystal structure of YOX (X = CI or Br) along the a-axis. The solid black line indicates a tetragonal unit cell. The distance between the two [X-Y-O-Y-X] sheets is shown. (b) Local structures of a ninefold [YO₄Cl₅] and an eightfold [YO₄Br₄] polyhedron. The crystal structures were depicted with the VESTA program.²⁴

YOBr



YOC

FIG. 3. PLE spectra of the YOX:Eu³⁺ samples at 4 K, monitored with Eu³⁺ 4*f*-4*f* luminescence over 600 nm. The PLE intensities are normalized by the integrated area of the ${}^{5}D_{1} \leftarrow {}^{7}F_{0}$ magnetic dipole transition, whose line strength is insensitive to the local environment around Eu³⁺ ions. PLE intensity of the YOCI:Eu³⁺ over 30 000 cm⁻¹ is divided by five.

by Gaussian fitting (the detailed procedure is provided in Fig. S-2 in the supplementary material).

A very weak excitation band was observed below the CT excitation bands attributed to the defects-related absorption of intrinsic vacancies of the host oxyhalides.

C. Assignment of Eu³⁺ 4*f*-4*f* luminescence

Figure 4(a) shows the PL spectra of the YOX: Eu^{3+} samples at 4 K under CT excitation ($\lambda_{ex} = 280 \text{ nm}$). Characteristic Eu³⁺: ⁵D₀ luminescence lines were observed in the range from 580 to 850 nm. The number of the ${}^{5}D_{0}$ luminescence lines in the $C_{4\nu}$ symmetry and the energy diagram of Eu^{3+} 4f levels for the YOX hosts were calculated by Forsberg²⁶ and Hölsä and Porcher,^{21,22} respectively. Thus, the ⁵D₀ luminescence lines were assigned, listed in Tables S-III and S-IV in the supplementary material. In the range of 16 900–17 100 cm⁻¹, the luminescence lines of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ magnetic dipole (MD) transition are overlapped with those of the ${}^{5}D_{1} \rightarrow {}^{7}F_{3}$ electric dipole (ED) transition from the higher excited state. The complicated structure due to the severe overlap makes the correct assignment difficult. In order to distinguish the ⁵D₀ luminescence from a small contribution of the ⁵D₁ luminescence, the PL spectra of the YOX:Eu³⁺ samples were measured at 4 K, excited by the different excitation pathways: the CT transition $(\lambda_{ex} = 280 \text{ nm})$ and the ${}^{5}\text{L}_{6} \leftarrow {}^{7}\text{F}_{0}$ transition $(\lambda_{ex} = 395 \text{ nm})$. The enlarged PL spectra in the range of 16650-17300 cm⁻¹ for the $YOX:Eu^{3+}$ samples are shown in Fig. 4(b), where the PL intensities are normalized with the integrated area of the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition peaking at 17 195 cm⁻¹ for the YOCI:Eu³⁺ and 17 203 cm⁻¹ for the YOBr: Eu^{3+} . The population of the ${}^{5}D_{0}$ and ${}^{5}D_{1}$ levels was changed by two different excitation routes, the CT and 4f-4f transition, because of the different relaxation processes. As the branching ratio and the relevant spectral shape of the ${}^{5}D_{0}$ and ${}^{5}D_{1}$ luminescence



FIG. 4. (A) PL spectra of the YOX:Eu³⁺ samples at 4 K, excited by the CT transition (λ_{ex} = 280 nm). The PL intensities are normalized by the integrated area of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ magnetic dipole transition, whose line strength does not depend on the local environment around Eu³⁺ ions. Below 13 600 cm⁻¹ ($\lambda > -735$ nm), the spectra were obtained with a low spectral resolution and displayed with the PL intensity enlarged 100 times. (b) and (c) Enlarged PL spectra at 4 K with different excitation wavelengths, 280 nm (shown in solid lines, CT transition) and 395 nm (shown in broken lines, ${}^{5}L_{6} \leftarrow {}^{7}F_{0}$ transition). The PL intensities are normalized by the integrated area of the (b) ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ and (c) ${}^{5}D_{1} \rightarrow {}^{7}F_{1}$ transitions.

are not affected by excitation processes, the PL lines with the consistent relative intensity indicate the precise assignment of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ luminescence in the normalized PL spectra. The two luminescence lines peaking at 16757 and 16946 cm⁻¹ for the YOCl:Eu³⁺ and 16752 and 16976 cm⁻¹ for the YOBr:Eu³⁺ are assigned to the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ MD transition.

Figure 4(c) displays the enlarged spectra at 4 K in the range from 17 300 cm⁻¹ (= ~578 nm) to 19 800 cm⁻¹ (= ~505 nm). As reported by Hölsä and Porcher,^{21,22} many luminescence lines attributed to the Eu³⁺ 4*f*-4*f* transition from the higher excited states ⁵D₁ and ⁵D₂ were observed. The ⁵D₂ luminescence is drastically enhanced under the 4*f*-4*f* excitation at 395 nm, compared with the CT excitation. These different intensity ratios between the ⁵D₁ \rightarrow ⁷F_{*J*</sup> and ⁵D₂ \rightarrow ⁷F_{*J*</sup> transitions enable us to assign the complicated luminescence structures. The enhancement of the ⁵D₂ luminescence intensity was significant in the YOBr:Eu³⁺. The assignment of each luminescence line is listed in Table S-V in the supplementary material and represented in Fig. 4(c). All the assigned luminescence lines corresponded with the assignment in the previous reports by Hölsä and Porcher.^{21,22}}}

D. Temperature dependence of Eu^{3+} : ${}^{5}D_{0}$ luminescence in YOX

The PL spectra of the YOX:Eu³⁺ samples were measured at various temperatures (T = 100-800 K) with the excitation by the CT transition ($\lambda_{ex} = 280$ nm). Figures 5(a) and 5(b) show the measured spectra in the region of the principal radiative transitions of Eu³⁺ (${}^{5}D_{0} \rightarrow {}^{7}F_{0-4}$). In Fig. 5(c), the integrated PL intensities in the range of 14 000–15 000 cm⁻¹ (${}^{5}D_{0} \rightarrow {}^{7}F_{4}$) are plotted against temperature to eliminate the influence of the ${}^{5}D_{1}$ luminescence. For both oxyhalide samples, the Eu³⁺ luminescence intensity was decreased monotonously from 100 K. The temperature profile of the Eu³⁺: ${}^{5}D_{0}$ luminescence does not correspond to the typical single barrier quenching curve described in the Boltzmann distribution.

Temperature dependence of luminescence lifetime is a good indicator to discuss thermal quenching behavior of the Eu³⁺: ${}^{5}D_{0}$ luminescence without the effect of the possibly temperature-dependent absorption coefficient. Figure 6(a) and 6(b) show the luminescence decay curves of the YOX:Eu³⁺ samples at various temperatures (T = 100-800 K) excited by the CT transition ($\lambda_{ex} = 280$ nm). In contrast to the temperature-dependent PL intensity, the slope of the decay curves was almost unchanged up to ~600 K and then increased. All the decay curves slightly deviated from the single-exponential profile, fitted by a second-order exponential function, described as

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2),$$
(1)

where A_1 and A_2 are the amplitudes of each decay component and τ_1 and τ_2 are the luminescence lifetime at each temperature. In general, the Eu³⁺: ⁵D₀ luminescence shows the single-exponential decay profile. However, in the YOX:Eu³⁺ samples, the decay curves could not be fitted with a single-exponential function, indicating the existence of a slight energy transfer (ET) process. As the purpose is to discuss the possible quenching process, the average luminescence lifetime of the ⁵D₀ state at each temperature τ_f (*T*) was estimated by the following equation:

$$\tau_{\rm f}(T) = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}.$$
 (2)

The average lifetimes at each temperature from 100 to 800 K are plotted against temperature and shown in Fig. 6(c). These profiles were fitted with the typical quenching curves following the single barrier quenching model described as²⁷

$$\tau_{\rm f}(T) = \frac{1}{\Gamma_v + \Gamma_0 \exp(-E_a/kT)},\tag{3}$$



FIG. 5. PL spectra of the YOX:Eu³⁺ samples at various temperatures (T = 100-800 K) excited with a near-UV LED ($\lambda_{ex} = 280$ nm). (c) Temperature-dependent integrated PL intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ transition.



FIG. 6. (a) and (b) Luminescence decay curves of the YOX: Eu^{3+} samples at various temperatures (T = 100-800 K) excited by the CT transition ($\lambda_{ex} = 280$ nm). (c) Temperature dependence of luminescence lifetimes estimated by a second-ordered exponential function [Eq. (1)]. The plots were fitted by the single barrier quenching curves, as shown in Eq. (3). The fitted curves over 800 K are represented in broken lines.

where Γ_{ν} is the radiative transition rate for Eu³⁺: ⁵D₀ luminescence, Γ_0 is the attempt rate of the nonradiative process, E_a is the activation energy of thermal quenching, k is the Boltzmann constant (= 0.695 cm⁻¹·K⁻¹), and T is the temperature. Since the nonradiative term $\Gamma_0 \exp(-E_a/kT)$ is negligible at low temperatures, the Γ_{ν} value is described by the reciprocal number of the luminescence lifetime at low temperature, τ_0 . The RMS errors for the fitting are relatively small. The obtained parameters, Γ_{ν} , τ_0 , Γ_0 , E_a , and the quenching temperature $T_{50\%}$, are listed in Table I. At $T_{50\%}$, the lifetime is half of the τ_0 , where the Γ_{ν} and the nonradiative term become equal.

IV. DISCUSSION

A. Difference in local environment with multiple anions

In order to characterize a luminescence center ion, deep insight into the local environment is inevitable. First, we discuss the geometrical and chemical environments of the Y^{3+} sites where impurity lanthanoid ions are incorporated. As mentioned in Sec. III A, the YOCl and YOBr are isostructural yet with the different coordination environment: the ninefold monocapped square antiprism polyhedron [YO₄Cl₅] and the eightfold distorted square antiprism polyhedron [YO₄Br₄]. Both polyhedra have the $C_{4\nu}$

TABLE I. Obtained values by the single barrier quenching curve fitting. The output is the radiative transition rate for Eu³⁺: ⁵D₀ luminescence Γ_{ν_1} the luminescence lifetime at low temperature τ_0 , the attempt rate of the nonradiative process Γ_0 , the thermal activation energy E_a , and the quenching temperature $T_{50\%}$.

	$\Gamma_{v} (10^{3} \mathrm{s}^{-1})$	τ_0 (ms)	$\Gamma_0 (10^9 {\rm s}^{-1})$	$E_{\rm a} ({\rm cm}^{-1})$	T _{50%} (K)
YOCl:Eu ³⁺	1.021	0.979	75.4	8870	704
YOBr:Eu ³⁺	0.664	1.51	1.17	7833	783

symmetry despite the different coordination numbers. Considering only the geometry of anion polyhedra around Y^{3+} , the eightfold [YO₄Br₄] polyhedron is similar to the regular square antiprism with the D_4 symmetry. In fact, the [YO₄Br₄] polyhedron loses the twofold rotation axis and belongs to the $C_{4\nu}$ symmetry.

The critical difference in shapes of the coordination polyhedron is derived from the distance between two [X-Y-O-Y-X] sheets: 1.669(3) Å for the YOCI:Eu³⁺ and 2.774(2) Å for the YOBr: Eu³⁺. In analogy to the isostructural BiOX (X = F, Cl, Br, and I), the two sheets are held together by Coulomb interaction between Y³⁺ and X⁻ and nonbonding van der Waals interaction along the [001] direction.^{28–30} These bonding and nonbonding interactions are cooperative. For the YOCl host, the ionicity of the interaction between Y³⁺ and Cl_{II}⁻ in the neighboring two sheets is strong because of the high electronegativity of Cl. On the contrary, the ionicity of the bonding between Y³⁺ and Br⁻ is weak due to the long bond length stemming from a large ionic radius of Br⁻ and the low electronegativity of Br. The nonbonding van der Waals interaction, which is comparatively weak, is dominant between the two [Br-Y-O-Y-Br] sheets, consequently as the considerable distance as 2.774(2) Å.

B. Judd-Ofelt analysis based on PL spectra

We perform the Judd–Ofelt analysis of the PL spectra shown in Fig. 4(a) with the static model.^{11,18,38} The detailed procedure is provided in Sec. S-III in the supplementary material. The calculated values are listed in Table II. The histogram representing the comparison of the calculated Judd–Ofelt intensity parameters Ω_t (t = 2, 4, and 6) is depicted in Fig. 7(a). For the comparison, the reported Ω_t parameters in some inorganic compounds are listed in Table III. The branching ratios of the ⁵D₀ luminescence for the YOX hosts are shown in Fig. 7(b) and Table IV.

The validity of the Judd–Ofelt analysis is evaluated by comparing the results of the luminescence decay measurements.

TABLE II.	Calculated v	alues based c	on the Judd-	Ofelt analysis.	The output is the	e Judd–Ofelt int	ensity param	eters Ω_t (t = 2,	4, and 6),	the spontaneous	emission rates of	the
${}^{5}D_{0} \rightarrow {}^{7}F_{J}$	MD and ED	transition A _R (⁷	F _J) (J = 1, 2,	4, and 6), and	the radiative life	time τ_R for Eu ³⁺	ions in the `	YOCI and YOBr	hosts.	·		

	$\Omega_2 \ (10^{-20} \text{cm}^2)$	$\Omega_4~(10^{-20}\text{cm}^2)$	$\Omega_6 \ (10^{-20} \text{cm}^2)$	$A_{\rm R}(^{7}{\rm F}_{1}) (10^{2}{\rm s}^{-1})$	$A_{\rm R}(^{7}{\rm F_2}) (10^2 {\rm s}^{-1})$	$A_{\rm R}(^{7}{\rm F}_{4}) (10^{2}{\rm s}^{-1})$	$A_{\rm R}(^{7}{\rm F_{6}}) (10^{2}{\rm s^{-1}})$	$\tau_{\rm R}~({\rm ms})$
YOCI	8.81	11.4	0.982	1.10	6.49 2.00	4.09	0.0223	0.821
TOBI	2.72	15.1	2.00	1.11	2.00	4.04	0.0620	1.19

The calculated spontaneous emission rates $A_{\rm R}$ show a similar trend to the Γ_{ν} values determined by the luminescence decay curves. For the YOCI:Eu³⁺, the Γ_{ν} (=1.02 × 10³ s⁻¹) is greater than for the YOBr:Eu³⁺ (=6.64 × 10² s⁻¹), which corresponds to the larger $A_{\rm R}$ for the ED transition in the YOCI:Eu³⁺. However, both Eu³⁺-doped oxyhalides YOX have some differences between the experimental lifetime τ_0 and the calculated lifetime $\tau_{\rm R}$ values. The $A_{\rm R}$ also depends on the refractive index of the host material. Thus, the difference can be caused by the error of the refractive index used for the calculation.

It is considered that the Ω_2 parameter correlates with the site asymmetry around Eu^{3+,39} The Ω_2 parameter of the YOCI:Eu³⁺ takes 8.81×10^{-20} cm², comparable to that of Y_2O_3 :Eu³⁺ $(9.86 \times 10^{-20} \text{ cm}^2)^{40}$ or YVO₄:Eu³⁺ $(7.49 \times 10^{-20} \text{ cm}^2)^{37}$ which are known to be phosphors with a high Ω_2 parameter (Table III). It is due to the noncentrosymmetric ninefold [Eu³⁺O₄Cl₅] structure with the $C_{4\nu}$ symmetry. For the YOBr:Eu³⁺, despite the same site symmetry $C_{4\nu}$, the Ω_2 parameter is $2.72 \times 10^{-20} \text{ cm}^2$, which is less than one-third of the YOCI:Eu³⁺. As mentioned in Sec. IV A, the main difference in the local environment around Eu³⁺ ions between the YOCI and YOBr is the coordination number of halide ions. In the YOBr host, Eu³⁺ ions occupy the eightfold distorted square antiprism structure [Eu³⁺O₄Br₄], whose geometry is similar to a regular square antiprism with the D_4 symmetry. According to



FIG. 7. (a) Histogram of calculated Judd–Ofelt intensity parameters Ω_t (t=2, 4, and 6) for the YOX:Eu³⁺ samples, based on the PL spectra shown in Fig. 4(a). (b) Histogram of the branching ratios of ${}^5D_0 \rightarrow {}^7F_J$ (J=0-6) transition for Eu³⁺ ions in the YOX hosts.

Judd, the hypersensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ED transition described by the Ω_{2} parameter is observed remarkably not in the D_{4} but in the $C_{4\nu}$ symmetry.⁴¹ For the eightfold [Eu³⁺O₄Br₄] polyhedron, the pseudo- D_{4} character may cause a significant Ω_{2} difference between the YOCl and YOBr hosts with coordination number decreasing although the actual symmetry is $C_{4\nu}$. It is found that the Ω_{2} parameter correlated with the asymmetry cannot be determined only by the site symmetry. The shape of a coordination polyhedron around Eu³⁺ should be considered to control the Ω_{2} parameter which determines the spontaneous emission rate of the hypersensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ED transition at 620–630 nm.

The Ω_4 and Ω_6 parameters are considered to show a similar trend to the variation of the local environment.^{18,39} A few previous studies reported that the $\Omega_{4,6}$ parameters correlate with covalency of a $Ln^{3+}-O^{2-}$ bonding.^{42,43} Table III shows the tendency for the inorganic crystalline materials in the magnitude of the Ω_4 parameters. The Ω_4 parameters for the YOX:Eu³⁺ samples are considerably large (11.4 × 10⁻²⁰ cm² for the YOCI:Eu³⁺ and 13.1 × 10⁻²⁰ cm² for the YOB:Eu³⁺). Both the Ω_4 and Ω_6 parameters for the YOB:Eu³⁺ are larger than those for the isostructural YOCI:Eu³⁺. Considering the electronegativity of anions, chlorine and bromine have the smaller Pauling electronegativities χ_p [$\chi_p(Cl) = 3.16$ and $\chi_p(Br) = 2.96$] than oxygen [$\chi_p(O) = 3.44$].⁴⁴ Thus, the YOX can be regarded as more covalent host materials compared with many oxides. In the case of a comparison between the isostructural YOCI:Eu³⁺ and YOBr:Eu³⁺, the Y³⁺-Br⁻ bonding is more covalent than the Y³⁺-Cl⁻ bonding. In fact, the results of the Ω_4 and Ω_6

TABLE III. Calculated Judd–Ofelt intensity parameters Ω_{ℓ} (*t*=2, 4, and 6) for a variety of Eu³⁺-doped crystalline materials in order of the Ω_4 parameters.

Host compounds	$\Omega_2 \ (10^{-20} \text{cm}^2)$	$\Omega_4 \ (10^{-20} cm^2)$	$\Omega_6 \ (10^{-20} \mathrm{cm}^2)$
YOBr (this work)	2.72	13.1	2.66
YOCl (this work)	8.81	11.4	0.982
$Y_2O_2S^{31}$	13.0	10.2	
α -Y ₂ Si ₂ O ₇ ¹¹	3.95	7.22	
YAlO ₃ ³²	2.66	6.33	0.8
YSiO ₂ N ¹¹	7.58	3.41	
α -CaSiO ₃ ¹¹	3.69	2.79	
CaF_2^{33}	0.73	2.53	
$Y_2O_3^{34}$	9.86	2.23	< 0.32
$\mathrm{Gd}_2\mathrm{O}_3^{35}$	15.6	1.42	
$Lu_2O_3^{35}$	12.2	1.2	
LaF_3^{36}	1.19	1.16	0.39
YVO_4^{37}	7.49	0.47	
YPO4 ³⁷	0.78	0.38	

TABLE IV. Branching ratios (%) of the Eu³⁺: ${}^5D_0 \to {}^7F_J$ (J = 0–6) transition in the YOCI and YOBr hosts.

	${}^{5}D_{0} \rightarrow {}^{7}F_{J}$									
_	J = 0	J = 1	<i>J</i> = 2	<i>J</i> = 3	J = 4	<i>J</i> = 5	<i>J</i> = 6			
YOCl YOBr	2.05 0.860	9.02 13.2	53.3 23.8	1.51 5.46	33.6 55.2	0.322 0.748	0.183 0.738			

parameters for the YOX:Eu³⁺ followed this tendency of covalency. Especially, the coordination of covalent Br contributes to the significant $\Omega_{4,6}$ parameters in the YOBr:Eu³⁺. The large Ω_4 is also confirmed in the covalent host Y_2O_2S (= 10.2×10^{-20} cm²). Although Eu³⁺-doped oxides show various Ω_4 values with the compositional and structural differences, all the values are smaller than those of the covalent YOX and Y_2O_2S hosts. Fluorides show the small Ω_4 values due to the large electronegativity of fluorine [$\chi_p(F) = 3.98$].⁴⁴ The vanadates and phosphates, which form the oxide tetrahedron unit with strong bonding and give less covalency to Eu³⁺, have very small values. These results support that the $\Omega_{4,6}$ parameters are correlated with the bonding character between Eu³⁺ and coordinating anions.

Compared with other Eu³⁺-doped phosphors, the YOX:Eu³⁺ takes a considerably large Ω_4 value by the covalent properties of halide anions. Moreover, the Ω_2 parameter is controlled by the shape of anion polyhedron, which cannot be described only by the site symmetry in the YOX:Eu³⁺. Those results will give us information to design the luminescence spectral distribution. Remarkably, the YOBr:Eu³⁺ exhibits a high branching ratio of the ${}^5D_0 \rightarrow {}^7F_4$ transition over 50% due to both small Ω_2 and large Ω_4 parameters in a unique Y³⁺ site. The ${}^5D_0 \rightarrow {}^7F_4$ luminescence is located at 680–710 nm, where the transmittance of bio-tissues is high, and the sensitivity of a Si detecter is high (the so-called first biological window).^{45,46} The Eu³⁺-doped covalent oxybromide with the intense ${}^5D_0 \rightarrow {}^7F_4$ luminescence is expected as a candidate for bio-imaging phosphor with the first biological window.

C. Relaxation dynamics of excited states in YOX:Eu³⁺

In this section, we discuss the dynamics of the excited states for Eu³⁺ ions in the YOX hosts. As shown in Sec. III D, Eu³⁺ luminescence in the YOX hosts quenches at high temperatures (>600 K). First, we consider the validity of the single barrier quenching model used for the fitting in Fig. 6(c). There are two possible quenching processes for Eu³⁺: ⁵D₀ luminescence: the multiphonon relaxation (MPR) and the thermal activation via the CT states. The MPR rate to the lower ⁷F₆ level can be low because the energy difference is as large as ~12 300 cm⁻¹ and the maximum phonon energy of the YOX hosts is only ~600 cm⁻¹ due to the vibrational mode of the Y–O bonding.⁴⁷ Therefore, the possible thermal quenching process is the thermal activation via the CT states with a single potential barrier. The relaxation process from the ⁵D₀ to the ⁷F_f ground states through the CT states is a typical quenching process.⁴⁸ Dorenbos reported that there is a clear trend between the quenching temperature and the CT energy position. From this trend, the lower CT energy leads to the lower quenching temperature. In the PLE spectra (Figs. 3 and S-2 in the supplementary material), the CT energy related to the Eu³⁺-X⁻ CT states are determined to be 38 163 cm⁻¹ for the YOCl:Eu³⁺ and 36 686 cm⁻¹ for the YOBr:Eu³⁺. The results that the larger thermal activation energy of the YOCl:Eu³⁺ ($E_a = 8870 \text{ cm}^{-1}$), compared with the YOBr:Eu³⁺ ($E_a = 7833 \text{ cm}^{-1}$), corresponds to the prediction from the quenching model through the CT states.

In Fig. 4(c), the ${}^{5}D_{1}$ and ${}^{5}D_{2}$ luminescence intensity ratio considerably depends on excitation pathways. The principal relaxation process after the 4f-4f excitation is the MPR from one excited 4f level to the next lower level. Once Eu³⁺ ions are excited through the ${}^{5}L_{6} \leftarrow {}^{7}F_{0}$ transition, they relax down into ${}^{5}D_{J}$ levels with several phonons emission because of the small energy difference between two adjacent 4f levels (${}^{5}L_{6}-{}^{5}D_{3}$: 1500 cm⁻¹, ${}^{5}D_{3}-{}^{5}D_{2}$: 2400 cm⁻¹, ${}^{5}D_{2}-{}^{5}D_{1}$:2500 cm⁻¹, and ${}^{5}D_{1}-{}^{5}D_{0}$: 1700 cm⁻¹).⁴⁹ On the other hand, the weak ${}^{5}D_{1}$ and ${}^{5}D_{2}$ luminescence with respect to the ${}^{5}D_{0}$ luminescence under the CT excitation [Fig. 4(a)] can be explained by the weak feeding process from the CT to the ${}^{5}D_{1,2}$ states and the strong feeding process to the ${}^{5}D_{0}$ state. Based on these results, the activation energy to the ${}^{5}D_{0}$ state is smaller than that to the ${}^{5}D_{1}$ and ${}^{5}D_{2}$ states. Nevertheless, the very weak ${}^{5}D_{1}$ and ${}^{5}D_{2}$ luminescence even at low temperature is due to a small contribution of the tunneling effect.

Although the ${}^{5}D_{0}$ luminescence is not quenched up to ~600 K from the lifetime analysis, the PL intensity of the Eu ${}^{3+}$: ${}^{5}D_{0}$ luminescence in the YOX hosts monotonously decreases from 100 K with temperature [Fig. 5(c)]. As mentioned above, the excited Eu ${}^{3+}$ ions with the CT transition relax to the minimum of the potential curve and then relax to the ${}^{5}D_{0}$ initial state of the radiative transition. If all of the population of CT states relax to the ${}^{5}D_{0}$ state, the temperature dependence of PL intensity follows that of PL lifetime. The observed difference between the temperature dependence of PL and lifetime can be caused by the temperature dependence of the feeding process. It is assumed that the CT states have another relaxation route via an intersection with the ${}^{7}F_{6}$ state. Therefore, the monotonous decreasing PL intensity is observed even in the temperature range where the ${}^{5}D_{0}$ lifetime is unchanged.

In order to explain the obtained results, the conventional coordinate diagrams (CCD) of the YOX:Eu³⁺ are constructed and shown in Fig. 8. R_0 represents the equilibrium position of a Eu³⁺ ion to a ligand. The offset of the 4f states does not change because the Eu³⁺-ligands distances are almost the same between the ground and excited states. In contrast, the offset of the CT parabolas is very large.^{48,50} We assumed that the parabolas for the CT states have the same curvature as that for the 4f states. The bottom energy of the CT and the offset value are not determined quantitatively by the obtained results. On the other hand, based on the results of the tunneling process from the CT to the ⁵D_{1,2} states, the relaxation process from the CT to the ${}^{5}D_{0}$ and ${}^{7}F_{I}$ states, and the activation energy from the ⁵D₀ to the CT states, the bottom of the CT parabolas should be located above the ${}^{5}D_{2}$ level (~21 500 cm⁻¹) and between two parabolas of the ${}^{5}D_{0}$ and ${}^{7}F_{6}$ states, as shown in Fig. 8. It is clear that the CT states play a crucial role in the dynamics of the excitation process. The large offset of the CT states in the YOX: Eu^{3+} is disadvantageous to the relaxation from the CT to ${}^{5}D_{0}$ states for the efficient and thermally stable ${}^{5}D_{0}$ luminescence. Tailoring the small lattice relaxation following the CT excitation is also



FIG. 8. Configuration coordinate diagram of $Eu^{3+} 4f^6$ levels and $Eu^{3+}X^-$ charge transfer states for the YOX: Eu^{3+} . Arrows depicted in the diagram represent the pathways of excitation, luminescence, and relaxation processes.

essential to develop the novel Eu³⁺-activated phosphors with high efficiency and thermal stability. In this CCD, the values of $Sh\omega$ (S, \hbar , and ω are the Huang–Rhys factor, the Dirack constant, and the phonon energy, respectively,) are 12 271 cm⁻¹ for the YOCI:Eu³⁺ and 11 995 cm⁻¹ for the YOBr:Eu³⁺. Since Eu³⁺ do not show CT luminescence, the Sh ω cannot be determined directly from the Stokes shift ($2S\hbar\omega$). In contrast, the Yb³⁺-doped materials can show CT luminescence, and the $S\hbar\omega$ values are reported between 3000 and 8750 cm⁻¹.⁴⁶ Considering the phonon energy of the Y–X and the comparison with the values for Yb³⁺ CT luminescence, the $S\hbar\omega$ values for the YOX:Eu³⁺ are large. It is not clear at the present that the obtained large Sh ω in YOX:Eu³⁺ is reasonable or not. To determine the precise position of the CT parabolas, further investigation for the dynamics of the excited states related to the CT states in Eu³⁺-doped materials is necessary.

V. CONCLUSION

The influence of anion variation on Eu^{3+} : ${}^5\text{D}_J$ luminescence in isostructural YOX (X = Cl or Br) hosts, but with a different coordination environment, was investigated from a spectroscopic perspective.

For Eu³⁺ ions in the YOCl host incorporated into the ninefold monocapped square antiprism polyhedra [YO₄Cl₅] with the noncentrosymmetric $C_{4\nu}$ symmetry, the Judd–Ofelt Ω_2 parameter of YOCl:Eu³⁺ is 8.81 × 10⁻²⁰ cm², which is comparable with the Eu³⁺-doped oxides Y₂O₃ or YVO₄. The Ω_4 parameter also takes a large value of 11.4 × 10⁻²⁰ cm². On the other hand, the YOBr host consists of an eightfold distorted square antiprism [YO₄Br₄] with $C_{4\nu}$ symmetry due to the large separation of two [Br-Y-O-Y-Br] sheets attributed to the covalency of Br. The Ω_2 parameter of YOBr:Eu³⁺ is 2.72×10^{-20} cm², which is relatively small because of its structural similarity to the eightfold regular square antiprism with D_4 symmetry. The Ω_4 parameter is 13.1×10^{-20} cm², which is significantly large due to the strongly covalent environment [Eu³⁺O₄Br₄]. The charge transfer band energies E^{CT} for YOCL:Eu³⁺ and

The charge transfer band energies E^{CT} for YOCl:Eu³⁺ and YOBr:Eu³⁺ are estimated to be 38 163 and 36 686 cm⁻¹, respectively. The smaller E^{CT} for YOBr:Eu³⁺ results in a low thermal activation energy of ⁵D₀ luminescence quenching. The difference in the relaxation processes of excited electrons between the charge transfer and the 4*f*-4*f* transitions makes a precise assignment of complicated spectral structures possible. The large offset of the charge transfer states in the configuration coordinate diagram for YOX: Eu³⁺ causes thermally unstable and inefficient Eu³⁺ luminescence with the charge transfer transition.

This work reveals that the Judd–Ofelt intensity parameters Ω_t are significantly affected by the geometry of coordination polyhedra and the bonding character between Eu³⁺ ions and coordinating anions. The mixed-anion host materials with the regular square antiprism like local geometry have great potential to show an intense ${}^5D_0 \rightarrow {}^7F_4$ located at ~700 nm, which is desirable as a fluorescence probe in biological applications.

SUPPLEMENTARY MATERIAL

See the supplementary material that contain pictures of the samples, Gaussian fitting for the PLE spectra, additional details on refined crystallographic parameters, lists of the assignment of Eu³⁺ 4f-4f luminescence, and the detailed procedure of the Judd–Ofelt analysis.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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