学 位 論 文 の 要 約

論文題目　Unique Luminescence Properties Based on Electronic Structure and Local Environment in Mixed-Anion Compounds
(複合アニオン化合物における電子構造と局所配位環境がもたらす特異な光物性)

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要約

In this dissertation, it was investigated how the unique electronic structure and local environment of various mixed-anion compounds affect the properties of the luminescence centers through spectroscopic methods, and the luminescent properties of some oxynitrides and oxyhalides were characterized in a complex manner by combining spectroscopy with other techniques such as crystal structure analysis and *ab initio* calculations.

In Chapter 1, as the general introduction, the mixed-anion phosphors focused on as the novel functional materials are overviewed. Although the type of luminescence is determined by the cation species acting as the activator, the luminescence properties depend on the electronic structure and coordination environment, which can be controlled by the coordinating anion species. In the research on luminescent materials, anion-based material design is a useful strategy. Some studies about the mixed-anion phosphors following these concepts are introduced. The purposes and contents of the studies in this dissertation are briefly explained.

In Chapter 2, the fundamentals of luminescence phenomena discussed in this dissertation, related to the 5d-4f, 4f-4f transitions, charge transfer (CT) transition, and exciton states, are overviewed briefly. As the character of the host materials providing unique luminescence properties, the point groups in crystals and the band structure are introduced. Especially, the band structure for the luminescence materials activated by lanthanoid ions is described by the vacuum referred binding energy (VRBE) diagram, which is very useful to predict the luminescence properties and discuss the luminescence mechanisms.

In Chapter3, the Eu^{3+}-doped $YSiO_2N$ oxynitride was fabricated, and its luminescent properties were investigated. The $YSiO_2N:Eu^{3+}$ sample was excited efficiently by near-UV light (280–360 nm) and showed very intense red luminescence assigned to the Eu^{3+} 4f-4f transitions. Compared with prepared Eu^{3+}-doped oxide samples (α-$CaSiO_3:Eu^{3+}$, α-$Y_2Si_2O_7:Eu^{3+}$, and γ-$Y_2Si_2O_7:Eu^{3+}$), in $YSiO_2N:Eu^{3+}$, there were two major different luminescent features: the CT excitation band got redshifted by more than 9500 cm^{-1} because the energy of the valence band

(VB) top got increased due to the N 2p orbitals; the spectral intensity of the $^5D_0 \rightarrow {}^7F_2$ transition peaking at 626 nm got stronger because the Eu^{3+} occupied asymmetric Y^{3+} sites due to partial substitution of O^{2-} by N^{3-}. From the Judd-Ofelt analysis, the $YSiO_2N:Eu^{3+}$ sample had the much larger Judd-Ofelt intensity parameter, Ω_2, which depends on site-asymmetry, than other oxide samples. The fluorescence lifetime was estimated experimentally to be 0.664 ms, which was shorter than the radiative lifetime based on the Judd-Ofelt analysis of 1.32 ms. The experimental quantum yield of 32.3 % was lower than the calculated internal quantum efficiency of 50.3%. For development of red phosphors activated by Eu^{3+} for LEDs applications, Eu^{3+}-doped mixed-anion compounds have a significant potential to improve the main parameters of white LEDs.

In Chapter 4, the Eu^{3+} luminescence properties in oxynitride coordination environments for $YSiO_2N$ were thoroughly investigated in terms of the site-selective and time-resolved spectroscopy with the precise crystallographical data. The single-crystal X-ray and the time-of-flight neutron diffraction successfully identified the crystal structure of $YSiO_2N$ as the monoclinic lattice with the space group *C2/c*. In this lattice, all Eu^{3+} ions are incorporated in the $[YO_6N_2]$ dodecahedra, classified into two groups with centrosymmetry; C_n and C_i sites. Eu^{3+} ions at the C_n and C_i sites showed a completely different radiative rate for the electric dipole transition, resulting in the 27 times enhanced $^5D_0 \rightarrow {}^7F_2$ luminescence and the 8.4 times shorter luminescence lifetime by lacking an inversion center. The temperature dependence of the luminescence lifetime for the Eu^{3+} ions in C_i sites revealed that the thermally induced deviation from centrosymmetry increases the radiative rate with the Judd-Ofelt intensity parameter Ω_t increasing. Despite the significant difference in the radiative rate, the ligands-Eu^{3+} CT states were affected scarcely by site symmetry but severely by anion species. The *ab initio* calculation results and the photoluminescence excitation (PLE) spectra suggested that the thermal quenching of the Eu^{3+}: $^5D_0$ luminescence occurs *via* the CT states between N^{3-} and Eu^{3+} ions. The results indicate that not only the mixed-anion coordination but also the local structure that induces some distortion is necessary for the improvement of Eu^{3+} luminescence. The $YSiO_2N:Eu^{3+}$ provides a new possibility for developing the near-UV excitable narrow-band red phosphors with partial N^{3-} coordination.

In Chapter 5, the photoluminescence (PL) properties of the Eu^{2+}-doped $YSiO_2N$ sample at low temperatures were investigated in detail. The X-ray absorption spectroscopy revealed that almost half Eu ions in the sample were reduced into a divalent state through the high-temperature synthesis under the inert atmosphere. The as-made sample, including Eu^{2+} ions, showed the deep-red to near-infrared (NIR) luminescence at low temperatures below 300 K. Compared with typical Eu^{2+}: 5d-4f luminescence, this luminescence was anomalous in terms of

the following points; an abnormally large bandwidth (4061 cm^{-1}) and Stokes shift (5677 cm^{-1}) even at 4 K, deep-red to NIR luminescence peaking at 756 nm, and a complicated thermal quenching behavior. These features indicated that the anomalous luminescence in the YSiO$_2$N:Eu$^{2+/3+}$ sample is related to the Eu^{2+}-trapped exciton states. The VRBE diagram suggested that the typical Eu^{2+}: 5d → 4f luminescence was not observed because all the Eu^{2+}: 5d excited levels degenerated with the host conduction band (CB). The configurational coordinate diagram explained the anomalous luminescence from the Eu^{2+}-trapped exciton states (Eu^{3+} + e^-) which were located just below the CB bottom, by taking the lattice relaxation into account. This study provides new insight into the Eu^{2+}-trapped exciton luminescence in Y sites to obtain the deep-red to NIR luminescence, leading to new candidates for NIR applications, such as lighting, sensing, and bio-imaging devices.

In Chapter 6, luminescence properties of Ce^{3+} ions in the monoclinic YSiO$_2$N host were investigated at the wide temperature range of 4–600 K. The PL spectra showed the minor luminescence component besides the typical Ce^{3+} luminescence, depending on excitation wavelengths. The time-resolved spectroscopy revealed that the minor luminescence center took the distribution of luminescence lifetime of 34–58 ns, which is typical for Ce^{3+}: 5d → 4f transition. The results suggested that the minor luminescence was assigned to the Ce^{3+} luminescence in some Y^{3+} sites with intrinsic anion defects. By taking the contribution of this minor Ce^{3+} luminescence into account, Ce^{3+} luminescence in the [YO$_6$N$_2$] dodecahedra was characterized. Despite the site-symmetry, Ce^{3+} ions in the five nonequivalent Y sites showed almost the same properties and were not identified due to the structural similarity of the [YO$_6$N$_2$] dodecahedra. The temperature dependence of luminescence lifetimes provided the activation energy for thermal quenching of 0.272 eV. All the 5d ← 4f excitation bands of Ce^{3+} ions in the [YO$_6$N$_2$] dodecahedra were observed with the vacuum-UV spectroscopy, leading to the crystal field splitting of 1.69 eV and centroid energy of 4.11 eV.

In Chapter 7, the Ce^{3+} persistent luminescence (PersL) in the YSiO$_2$N host was successfully enhanced by co-doping Sm^{3+} and Tm^{3+} ions, as predicted by the semi-empirical VRBE diagram. The VRBE diagram of the YSiO2N host was constructed with the experimentally obtained parameters, including the host exciton creation energy, the CT energy for Eu^{3+}, and the centroid shift of Ce^{3+} 5d levels, leading to the optimal co-dopant lanthanoid ions, Sm^{3+} and Tm^{3+}, to obtain Ce^{3+} PersL at ambient temperature. The electron trap depths for Tm^{3+} and Sm^{3+} ions were estimated to be 0.726 and 1.04 eV, respectively. The prepared YSiO$_2$N:Ce^{3+}-Ln^{3+} (Ln = Sm or Tm) samples enhanced the Ce^{3+} blue PersL at 30 s after the excitation ceased by 2–3 times. The thermoluminescence (TL) glow curves of the Ln^{3+} co-doped

samples showed additional glow peaks related to *Ln*-traps and enhanced the TL intensity related to intrinsic defects. The TL glow curve analyses with the initial rise method combined with the thermal cleaning and trap density methods revealed that the *Ln*-traps located below the CB have a distribution with ~0.25 eV width, whose centers were similar to the predicted trap depth by the constructed VRBE diagram.

In Chapter 8, the influence of the anion variation on Eu^{3+}: ^5D_J luminescence in the isostructural YO*X* (*X* = Cl or Br) hosts, yet with the different coordination environment, was investigated from the spectroscopic perspective. For Eu^{3+} ions in the YOCl host incorporated in the nine-fold monocapped square antiprism polyhedra $[YO_4Cl_5]$ with noncentrosymmetric C_{4v} symmetry, the Judd-Ofelt Ω_2 parameter of the YOCl:Eu^{3+} **was 8.81×10^{-20} cm²**, comparable to the Eu^{3+}-doped oxides Y_2O_3 or YVO_4. The Ω_4 parameter also took a large value, 11.4×10^{-20} cm². On the other hand, the YOBr host consisted of the eight-fold distorted square antiprism $[YO_4Br_4]$ with C_{4v} 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 the YOBr:Eu^{3+} was relatively small, 2.72×10^{-20} cm², because of the structural similarity to the eight-fold regular square antiprism with D_4 symmetry. The Ω_4 parameter was also significantly large, 13.1×10^{-20} cm², due to the strongly covalent environment $[Eu^{3+}O_4Br_4]$. The CT band energies E^{CT} for the YOCl:Eu^{3+} and YOBr:Eu^{3+} were estimated to be 38163 cm⁻¹ and 36686 cm⁻¹, respectively. The smaller E^{CT} for the YOBr:Eu^{3+} resulted in the low thermal activation energy of the $^5D_0$ luminescence quenching. The difference in the relaxation processes of excited electrons between the CT and 4f-4f transitions made the precise assignment of complicated spectral structures possible. The large offset of the CT states in the configuration coordinate diagram for the YO*X*: Eu^{3+} caused thermally unstable and inefficient Eu^{3+} luminescence with the CT transition. It was revealed that the Judd-Ofelt intensity parameters Ω_t are significantly affected by the geometry of coordination polyhedra and the bonding character between Eu^{3+} ions and coordinating anions. The mixed-anion materials with the regular square antiprism-like local geometry have the great potential to show the intense $^5D_0 \rightarrow {}^7F_4$ luminescence located at ~700 nm, which is desirable as a fluorescence probe in biological applications.

In Chapter 9, the square pyramidal $[WO_5]^{4-}$ cluster in the oxychloride $Ca_3WO_5Cl_2$ showed the cyan CT luminescence between W 5d and O 2p orbitals. Compared with the blue CT luminescence of the $[WO_6]^{6-}$ octahedron in the oxide Ca_3WO_6, this cyan CT luminescence showed the higher absorption and lower luminescence energies. Because these characteristics of the $[WO_5]^{4-}$ square pyramid were not explained by the simple molecular orbital diagram for O_h symmetry, the *ab initio* calculations with the discrete-variational Xα (DV-Xα) and DV multi-

electron (DVME) methods were performed to discuss the luminescence properties of the $Ca_3WO_5Cl_2$. Both the one- and multi-electron calculations revealed that the $[WO_5]^{4-}$ square pyramid took the larger CT energy due to not the crystal field splitting but the Madelung potential related to the existence of Cl^- ions in a lattice. However, since the *ab initio* molecular orbital and configuration interaction calculation cannot take the structural relaxation of the excited states into account, the redshift of the CT luminescence for the $[WO_5]^{4-}$ cluster could not be understood by these *ab initio* calculation results. Supposing that the CT excited states of the $[WO_5]^{4-}$ cluster took the larger offset in the qualitative configurational coordinate diagram, the redshift and the lower quenching temperature of the CT luminescence for the $[WO_5]^{4-}$ square pyramid were accounted for. The results in this study are expected to promote research on the CT luminescence of tungstates in a variety of material groups including mixed-anion compounds.

In Chapter 10, for the expansion of the possibility of the prospective dosimetric material, Ce^{3+} and Li^+ co-doped MgB_4O_7, the glass-ceramic (GC) samples of $MgB_4O_7:Ce^{3+}-Li^+$ were successfully synthesized by ceramming a magnesium borate glass with the composition of $25MgO-72B_2O_3-3Li_2O-0.3Ce^{3+}$ at 600, 650, 700, 750, 800, and 850 °C. It was confirmed by X-ray diffraction that the obtained GC samples had the MgB_4O_7 crystals as the main phase with a small amount of impurity $Mg_2B_2O_5$ phase. The GC samples showed a typical blue PL band due to the Ce^{3+} 5d → 4f transition under UV illumination, whose peak was redshifted from the peak in the as-made glass. For the GC samples, the Ce^{3+} radioluminescence bands under X-ray irradiation were narrower than the PL bands because the Ce^{3+} ions in the MgB_4O_7 phase were selectively excited. In the TL glow curves after β-ray irradiation, the GC samples showed two TL glow peaks at ~100 °C and ~220 °C. Due to the presence of the shallow electron traps, the fading of TL and optically stimulated luminescence (OSL) took place. Considering the fading ratio of the OSL intensity stimulated by a blue LED, GC750 and GC800 showed good stability for the radiation dose storage. These results show that GC750 and GC800 have the potential to be an excellent material for dosimetry if the influence of shallow traps can be reduced either during the synthesis process or by application of a pre-heating before the OSL readout.