

Second Edition

PHOSPHOR HANDBOOK

Edited by

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chapter two — section seven

Fundamentals of luminescence

Eiichiro Nakazawa

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2.7 Transient characteristics of luminescence

This section focuses on transient luminescent phenomena, that is, time-dependent emission processes such as luminescence after-glow (phosphorescence), thermally stimulated emission (thermal glow), photo (infrared)-stimulated emission, and photoquenching. All of these phenomena are related to a quasistable state in a luminescent center or an electron or hole trap.

2.7.1 Decay of luminescence

Light emission that persists after the cessation of excitation is called *after-glow*. Following the terminology born in the old days, luminescence is divided into fluorescence and phosphorescence according to the duration time of the after-glow. The length of the duration time required to distinguish the two is not clearly defined. In luminescence phenomena in inorganic materials, the after-glow that can be perceived by the human eye, namely that persisting for longer than 0.1 s after cessation of excitation, is usually called phosphorescence. Fluorescence implies light emission during excitation. Therefore, fluorescence is the process in which the emission decay is ruled by the lifetime (<10 ms) of the emitting state of a luminescence center, while the phosphorescence process is ruled by a quasistable state of a center or a trap.

In organic molecules, fluorescence and phosphorescence are distinguished by a quite different definition. The two are distinguished by whether the transition to emit light is

allowed or forbidden by spin selection rules. Light emission due to an allowed transition is called *fluorescence*, while that due to a forbidden transition, usually showing a long after-glow, is called *phosphorescence* (see 2.5).

2.7.1.1 Decay of fluorescence

The decay process of the luminescence intensity $I(t)$ after the termination of excitation at $t = 0$ is generally represented by an exponential function of the elapsed time after the excitation.

$$I(t) = I_0 \exp(-t/\tau) \quad (120)$$

where τ is the decay time constant of the emission. It should be noted that the emission decay curve of nonlocalized centers, donor-acceptor pairs for example, is not always represented in the exponential form of Eq. 120. (See 2.4.)

If one denotes the number of excited luminescence centers in a unit volume by n^* , and the radiative and nonradiative transition probabilities by W_R and W_{NR} , respectively, then the rate equation for n^* is:

$$\frac{dn^*}{dt} = -(W_R + W_{NR})n^* \quad (121)$$

and the solution of this equation is:

$$n^*(t) = n_0^* \exp[-(W_R + W_{NR})t] \quad (122)$$

Here, n_0^* is the value at $t = 0$, that is, at the end-point of excitation or, in other words, at the start point of the after-glow.

Therefore, the lifetime of the center, which corresponds to the elapsed time for n^* to be decreased by the factor of e^{-1} of n_0^* , is $(W_R + W_{NR})^{-1}$. Since the emission intensity is proportional to n^* , the decay time of the after-glow in Eq. 120 is equal to the lifetime of the center:

$$\tau = (W_R + W_{NR})^{-1} \quad (123)$$

and the luminescence efficiency of the center is given by:

$$\eta = \frac{W_R}{W_R + W_{NR}} \quad (124)$$

The radiative transition probability W_R of an emitting state is the summation of the spontaneous emission probability $A_{m \rightarrow n}$ from the state m to all the final states n , (see Eq. 29)

$$W_R = \sum_n A_{m \rightarrow n} = \sum_n \frac{1}{\tau_{mn}} \quad (125)$$

chapter three — section three

Principal phosphor materials and their optical properties

Tsuyoshi Kano

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3.3 Luminescence of rare earth ions¹⁻³

3.3.1 Electronic configuration

The rare-earth elements usually comprise 17 elements consisting of the 15 lanthanides from La (atomic number 57) to Lu (atomic number 71), of Sc (atomic number 21), and of Y (atomic number 39). The electronic configurations of trivalent rare-earth ions in the ground states are shown in Table 12. As shown in the table, Sc³⁺ is equivalent to Ar, Y³⁺ to Kr, and La³⁺ to Xe in electronic configuration. The lanthanides from Ce³⁺ to Lu³⁺ have one to fourteen 4f electrons added to their inner shell configuration, which is equivalent to Xe. Ions with no 4f electrons, i.e., Sc³⁺, Y³⁺, La³⁺, and Lu³⁺, have no electronic energy levels that can induce excitation and luminescence processes in or near the visible region. In contrast, the ions from Ce³⁺ to Yb³⁺, which have partially filled 4f orbitals, have energy levels characteristic of each ion and show a variety of luminescence properties around the visible region.¹⁻³ Many of these ions can be used as luminescent ions in phosphors, mostly by replacing Y³⁺, Gd³⁺, La³⁺, and Lu³⁺ in various compound crystals.

The azimuthal quantum number (*l*) of 4f orbitals is 3, giving rise to 7 (= 2*l* + 1) orbitals, each of which can accommodate two electrons. In the ground state, electrons are distributed so as to provide the maximum combined spin angular momentum (*S*). The spin angular momentum *S* is further combined with the orbital angular momentum (*L*) to give the total angular momentum (*J*) as follows;

$$J = L - S, \text{ when the number of } 4f \text{ electrons is smaller than } 7$$

$$J = L + S, \text{ when the number of } 4f \text{ electrons is larger than } 7$$

An electronic state is indicated by notation ^{2S+1}L_{*J*}, where *L* represents *S*, *P*, *D*, *F*, *G*, *H*, *I*, *K*, *L*, *M*, ..., corresponding to *L* = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, ..., respectively. More accurately, an actual electronic state is expressed as an intermediate coupling state, which can be described as a mixed state of several ^{2S+1}L_{*J*} states^{2,4} combined by spin-orbit interaction. For qualitative discussions, however, the principal *L* state can be taken to represent the actual

Table 12 Electronic Configurations of Trivalent Rare-Earth Ions in the Ground State

Atomic number	Ions	Corresponding element	4f electrons	S Σs	L Σl	J Σ(L+S)
21	Sc ³⁺	Ar		0	0	0
39	Y ³⁺	Kr		0	0	0
57	La ³⁺			0	0	0
58	Ce ³⁺	Xe	↑	1/2	3	5/2
59	Pr ³⁺	Xe	↑ ↑	1	5	4
60	Nd ³⁺	Xe	↑ ↑ ↑	3/2	6	9/2
61	Pm ³⁺	Xe	↑ ↑ ↑ ↑	2	6	4
62	Sm ³⁺	Xe	↑ ↑ ↑ ↑ ↑	5/2	5	5/2
63	Eu ³⁺	Xe	↑ ↑ ↑ ↑ ↑ ↑	3	3	0
64	Gd ³⁺	Xe	↑ ↑ ↑ ↑ ↑ ↑ ↑	7/2	0	7/2
65	Tb ³⁺	Xe	↑↓ ↑ ↑ ↑ ↑ ↑ ↑	3	3	6
66	Dy ³⁺	Xe	↑↓ ↑↓ ↑ ↑ ↑ ↑ ↑ ↑	5/2	5	15/2
67	Ho ³⁺	Xe	↑↓ ↑↓ ↑↓ ↑ ↑ ↑ ↑ ↑	2	6	8
68	Er ³⁺	Xe	↑↓ ↑↓ ↑↓ ↑↓ ↑ ↑ ↑ ↑	3/2	6	15/2
69	Tm ³⁺	Xe	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑ ↑ ↑	1	5	6
70	Yb ³⁺	Xe	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑ ↑	1/2	3	7/2
71	Lu ³⁺	Xe	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	0	0	0

state. The mixing due to spin-orbit interaction is small for the levels near ground states, while it is considerable for excited states that have neighboring states with similar J numbers. The effect of mixing is relatively small on the energy of levels, but can be large on their optical transition probabilities.

3.3.2 Electronic processes leading to luminescence

3.3.2.1 4f energy levels and relaxation

The 4f electronic energy levels of lanthanide ions are characteristic of each ion. The levels are not affected much by the environment because 4f electrons are shielded from external electric fields by the outer $5s^2$ and $5p^6$ electrons. This feature is in strong contrast with transition metal ions, whose 3d electrons, located in an outer orbit, are heavily affected by the environmental or crystal electric field. The characteristic energy levels of 4f electrons of trivalent lanthanide ions have been precisely investigated by Dieke and co-workers.⁵ The results are shown in Figure 22, which is known as a Dieke diagram.⁵ The levels were determined experimentally by considering the optical spectra of individual ions incorporated in LaCl_3 crystals; this diagram is applicable to ions in almost any environment because the maximum variation of the energy levels is, at most, of the order of several hundred cm^{-1} .

Each level designated by the number J in Figure 22 is split into a number of sublevels by the Stark effect due to the crystal field. The number of split sublevels is, at most, $(2J + 1)$ or $(J + 1/2)$ for J of integer or J of half-integer, respectively. The number of levels is determined by the symmetry of the crystal field surrounding the rare-earth ion. The width of each level shown in Figure 22 indicates the range of splittings within each component.

Light-emitting levels are indicated by semicircles below the energy levels. Most of the emitting levels are separated from the next lower level by at least $2 \times 10^3 \text{ cm}^{-1}$ or more. This is because the excited states relax via two competitive paths: one is by light emission and the other by phonon emission. The rate of phonon emission, w , depends on the number of phonons emitted simultaneously to bridge the energy gap and is expressed as:

$$w \propto \exp(-k\Delta E/h\nu_{\max}), \quad (24)$$

where ΔE is the energy gap to the nearest lower level and $h\nu_{\max}$ is the maximum energy of phonons coupled to the emitting states. The phonon emission rate, w , decreases rapidly with an increase in ΔE , so that the competitive light emission or radiative process becomes dominant.⁶ Thus, the well-known high luminescence efficiencies for $^5D_0$ of Eu^{3+} and $^5D_4$ of Tb^{3+} are based on the large energy gap of more than 10^4 cm^{-1} that needs to be bridged to the next lower level of these ions. The above formula implies that large values of $h\nu_{\max}$ also quench light emission. This is demonstrated by the fact that luminescence of Eu^{3+} in aqueous solution is almost quenched, but begins to appear if H_2O is replaced by D_2O .⁷

Luminescence originating from electronic transitions between 4f levels is predominantly due to electric dipole or magnetic dipole interactions. Electric dipole f - f transitions in free 4f ions are parity-forbidden, but become partially allowed by mixing with orbitals having different parity because of an odd crystal field component. The selection rule in this case is $|\Delta J| \leq 6$, (except for $0 \rightarrow 0$, $0 \rightarrow 1$, $0 \rightarrow 3$, $0 \rightarrow 5$). Typical examples of this mechanism are demonstrated by the luminescence from the ^5D_J states of Eu^{3+} ; the intensity of these transitions depends strongly on the site symmetry in a host crystal (See Section 3.3.3.7 Eu^{3+}). Magnetic dipole f - f transitions are not affected much by the site symmetry because they are parity-allowed. The J selection rule in this case is $\Delta J = 0, \pm 1$ (except for $0 \rightarrow 0$).

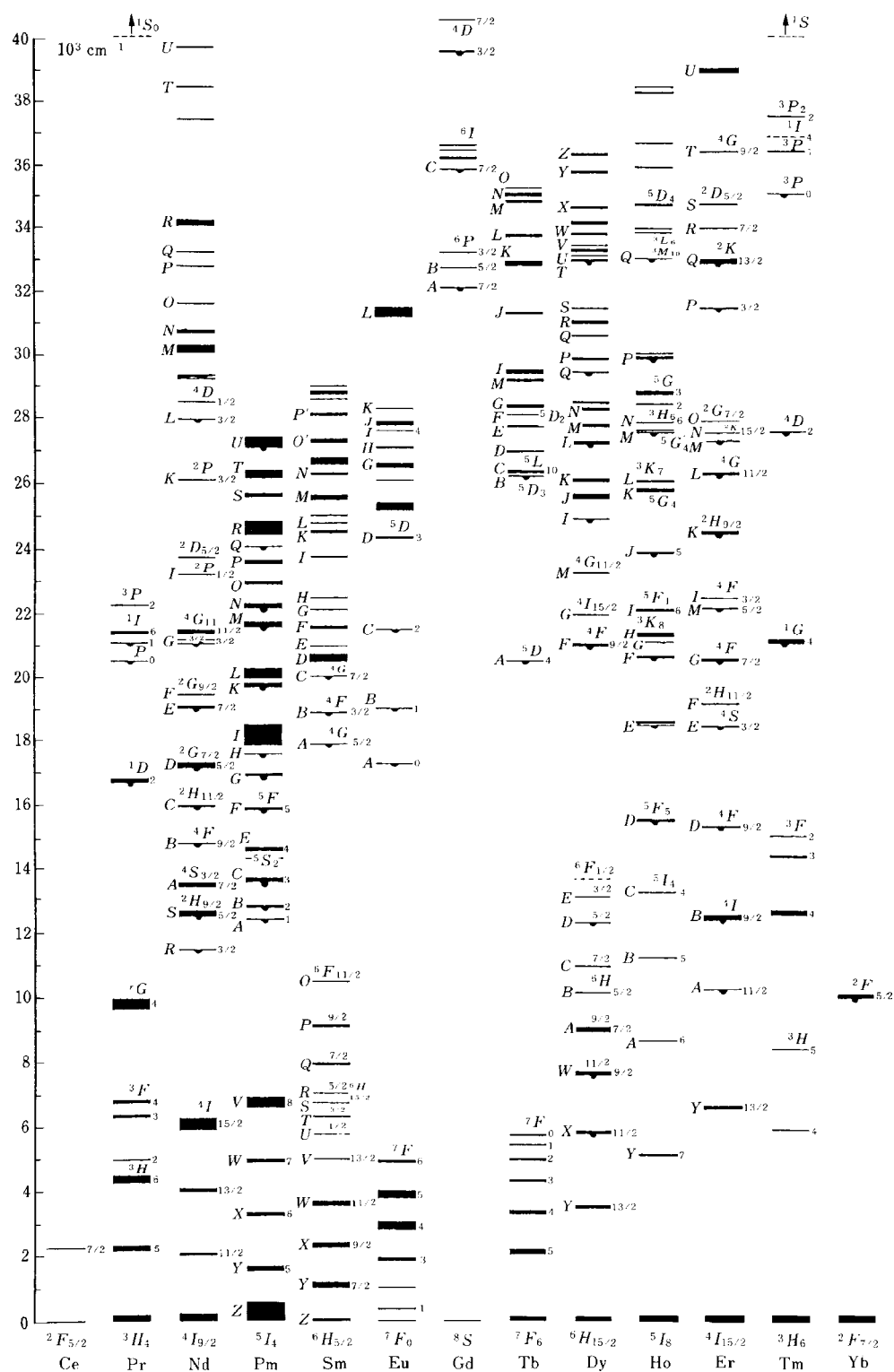


Figure 22 Energy levels of trivalent lanthanide ions. (From Dieke, G.H., *Spectra and Energy Levels of Rare Earth Ions in Crystals*, Interscience, 1968; *American Institute of Physics Handbook*, 3rd edition, McGraw-Hill, 1972, 7-25. With permission.)

Oscillator strengths are of the order of 10^{-5} to 10^{-8} for partially allowed electric dipole transitions, and 10^{-8} for magnetic dipole transitions.

The electric dipole transition probability between $4f$ levels can be calculated using the Judd-Ofelt theory.^{8,9} This theory assumes closure of the wavefunctions mixed to a $4f$ orbital and takes an average for the energy separation between the allowed states and the $4f$ levels. In spite of such approximations, the theory gives satisfactory agreement with observed values in many cases. The points of the calculation are sketched out as follows.

The absorption coefficient, $k(\lambda)$, is experimentally determined; here, $k(\lambda) = \ln(I/I_0)/a$, where I_0 is intensity of incident light, I is intensity of transmitted light, and a is sample thickness. By using the value of $k(\lambda)$, the line strength S is given by the following formula.

$$\int k(\lambda) d\lambda = \frac{8\pi^3 e^2 \lambda \rho}{3ch(2J+1)} \cdot \frac{1}{n} \cdot \frac{(n^2+2)^2}{9} \cdot s \quad (25)$$

where ρ is the density of the lanthanide ion and n is the refractive index. The parameters Ω_2 , Ω_4 , and Ω_6 , giving the light emission probability, are included in S and are determined by a least square fit of:

$$s = \sum_{t=2,4,6} \Omega_t \left| \langle (S, L) J \parallel U^{(t)} \parallel (S', L') J' \rangle \right|^2 \quad (26)$$

Here, $\langle (S, L) J \parallel U^{(t)} \parallel (S', L') J' \rangle$ ($t = 2, 4, 6$) are reduced matrix elements characteristic of individual ions and available as a table.⁸ Using the parameters Ω_2 , Ω_4 , and Ω_6 for specific host material, the light emission probability, A , between the levels of interest is calculated as follows:

$$A = \frac{64\pi^4 e^2}{3h(2J'+1)\lambda^3} \cdot n \cdot \frac{(n^2+2)^2}{9} \cdot s' \quad (27)$$

$$S' = \Omega_2 [U^{(2)}]^2 + \Omega_4 [U^{(4)}]^2 + \Omega_6 [U^{(6)}]^2$$

The theory contains some assumptions not strictly valid in actual cases, but still provides useful theoretical explanations for the nature of the luminescence spectra, as well as the excited-state lifetime, of lanthanide ions.^{2,10}

Luminescence spectra of various trivalent lanthanide ions in YVO_4 (or YPO_4) are shown in Figure 23.¹² The luminescence and excitation spectra in Y_2O_3 are shown in Figure 24.¹³ The luminescence spectra are composed of groups of several sharp lines. Each group corresponds to a transition between an excited and ground state designated by the total angular momentum, J . The assignment of the transition corresponding to each group of lines can be made on the basis of the energy level diagram shown in Figure 22. The excitation spectra generally consist of sharp lines due to the $4f-4f$ transition and of broad bands due to the $4f-5d$ transition and/or charge-transfer processes. Excited states giving rise to these broad excitation bands will be discussed in the next subsection.

The lifetimes of the luminescence due to $4f \rightarrow 4f$ transitions are mostly in the range of milliseconds because of the forbidden character of the luminescence transition.¹¹ For luminescence due to a spin-allowed transition between levels having equal spin multiplicity (e.g., $^3P_0 \rightarrow ^3H_J$ of Pr^{3+}), a relatively short lifetime of $\sim 10^{-5}$ s is observed.

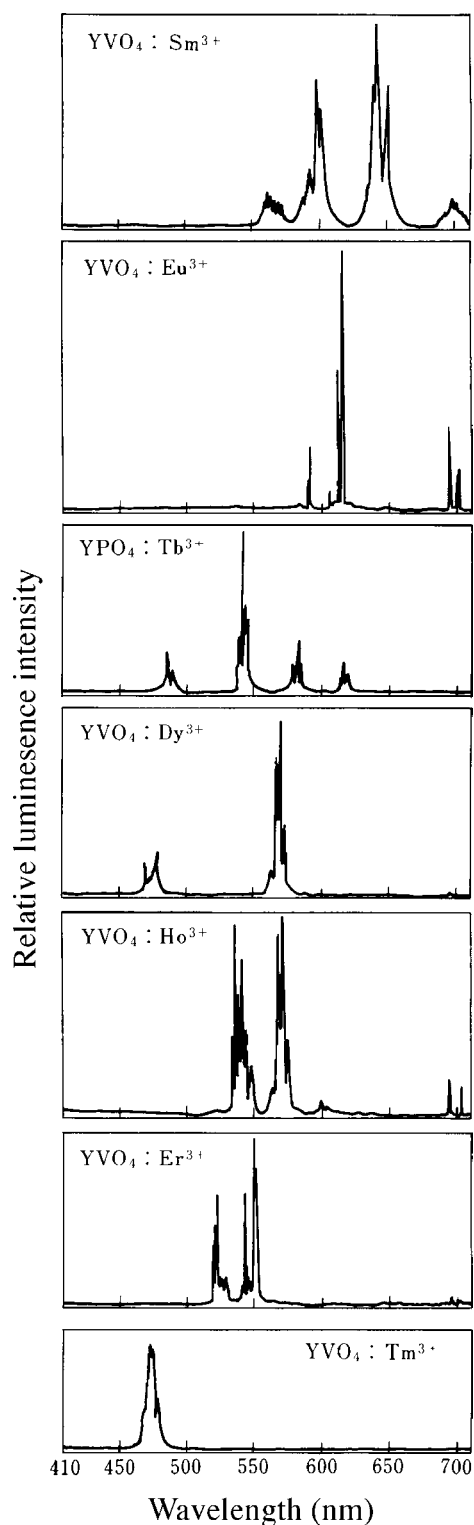


Figure 23 Emission spectra of various trivalent rare-earth ions in YVO₄ or YPO₄ hosts under cathode-ray excitation. (From Pallila, F.C., *Electrochem. Technol.*, 6, 39, 1968. With permission.)

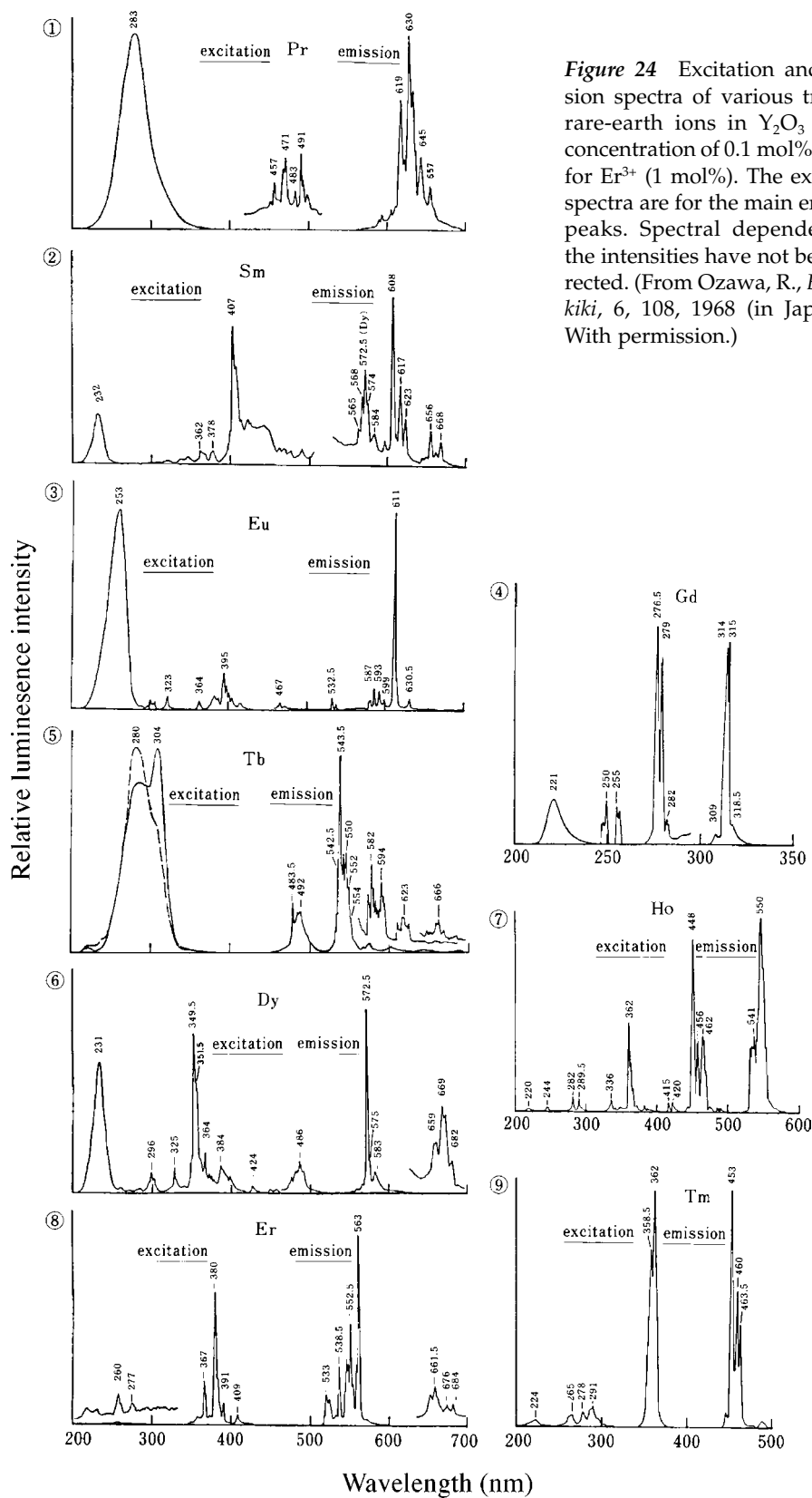


Figure 24 Excitation and emission spectra of various trivalent rare-earth ions in Y_2O_3 with a concentration of 0.1 mol%, except for Er^{3+} (1 mol%). The excitation spectra are for the main emission peaks. Spectral dependence of the intensities have not been corrected. (From Ozawa, R., *Bunseki-kiki*, 6, 108, 1968 (in Japanese). With permission.)

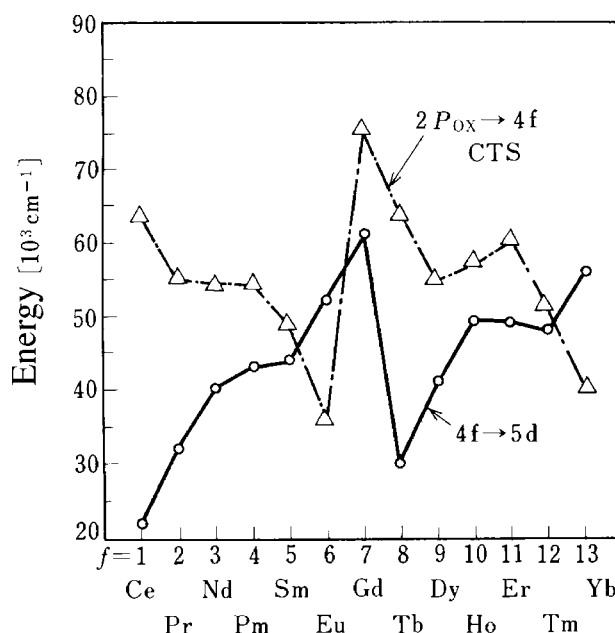


Figure 25 Energies for $4f \rightarrow 5d$ and CTS transitions of trivalent rare-earth ions. (From Hoshina, T., *Luminescence of Rare Earth Ions*, Sony Research Center Rep., 1983 (in Japanese). With permission.)

3.3.2.2 $4f^{n-1} 5d^1$ states and charge-transfer states (CTS)

In the energy region spanned by $4f$ levels, one finds two additional kinds of electronic states with different characters from those levels. They are the $4f^{n-1}5d^1$ states and the charge-transfer states (CTS). In the former, one of the $4f$ electron(s) is transferred to a $5d$ orbital and, in the latter case, electrons in the neighboring anions are transferred to a $4f$ orbital. Both of these processes are allowed and result in strong optical absorptions. They are observed as broadband excitation spectra around 300 nm, as is shown in Figure 24. Optical absorptions due to $f-d$ transitions are found for Pr^{3+} and Tb^{3+} ; those due to a charge-transfer transition are found in Eu^{3+} . The broad-band excitation spectra around 230 nm for Sm^{3+} , Dy^{3+} , and Gd^{3+} are due to host absorptions.

The energies of the $4f^{n-1}5d^1$ and CTSs are more dependent on their environments than the energies of $4f$ states, but the relative order of energies of these states are found to be the same for the whole series of rare-earth ions in any host materials. The transition energies from the ground states to these states are shown in Figure 25.^{2,14} These energies are obtained by determining the values of parameters so as to agree with absorption spectra of trivalent rare-earth oxides. As shown in the figure, $4f-5d$ transitions in Ce^{3+} , Pr^{3+} , Tb^{3+} , and CTS absorptions in Eu^{3+} and Yb^{3+} have energies less than $\text{ca. } 40 \times 10^3 \text{ cm}^{-1}$. They can, therefore, interact with $4f$ levels, leading to $f \rightarrow f$ emissions. In case the energy levels of these states are lower than those of $4f$ levels, direct luminescence transitions from these levels are found, such as $5d \rightarrow 4f$ transitions in Ce^{3+} , Pr^{3+} , and Eu^{2+} . Spectra of this luminescence vary as a result of crystal field splitting in host crystals (Section 3.3.3). Luminescence due to the transition from CTS has also been reported for Yb^{3+} (See Section 3.3.3.18).

By comparing chemical properties of trivalent rare-earth ions with Figure 25, one can conclude that those ions that are easily oxidized to the tetravalent state have lower $4f \rightarrow 5d$ transition energies, while those that are easily reducible to the divalent state have lower CTS transition energies. It has also been confirmed that $4f^0$, $4f^7$, and $4f^{14}$ electronic configurations are relatively stable.

3.3.2.3 Divalent and tetravalent cations

In appropriate host crystals with divalent constituent ions such as Ca^{2+} , Sr^{2+} , or Ba^{2+} , Sm^{2+} , Eu^{2+} , and Yb^{2+} are stable and can luminesce. The electronic configurations of these ions are the same as those of Eu^{3+} , Gd^{3+} , and Lu^{3+} , respectively. The excited states of the divalent ions, however, are lowered compared with those of the corresponding trivalent ions, because the divalent ions have smaller nuclear charges. The lower $4f-5d$ transition energy reflects their chemical property of being easily ionized into the trivalent state. All trivalent ions, from La^{3+} to Yb^{3+} , can be reduced to the divalent state by γ -ray irradiation when doped in CaF_2 .¹⁵

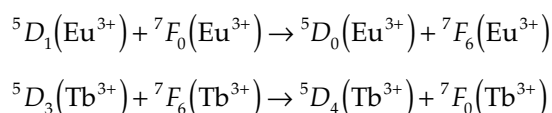
The electronic configurations of the tetravalent cations, Ce^{4+} , Pr^{4+} , and Tb^{4+} are the same as those of trivalent ions La^{3+} , Ce^{3+} , and Gd^{3+} , respectively. Their CTS energy is low, in accordance with the fact that they are easily reduced. When Ce, Pr, or Tb ions are doped in compound oxide crystals of Zr, Ce, Hf, or Th, the resulting powders show a variety of body colors, probably due to the CTS absorption band.¹⁶ Luminescence from these CTSs has not been reported.

3.3.2.4 Energy transfer

The excitation residing in an ion can migrate to another ion of the same species that is in the ground state as a result of resonant energy transfer when they are located close to each other. The ionic separation where the luminescence and energy transfer probabilities become comparable is in the vicinity of several Angstroms. Energy migration processes increase the probability that the optical excitation is trapped at defects or impurity sites, enhancing nonradiative relaxation. This causes concentration quenching, because an increase in the activator concentration encourages such nonradiative processes. As a result, that excitation energy diffuses from ion to ion before it is trapped and leads to emission. On the other hand, a decrease in the activator concentration decreases the energy stored by the ions. Consequently, there is an optimum in the activator concentration, typically 1 to 5 mol% for trivalent rare-earth ions, resulting from the trade-off of the above two factors. In some compounds such as $\text{NdP}_5\text{O}_{14}$, the lattice sites occupied by Nd are separated from each other by a relatively large distance (5.6 Å), and a high luminescence efficiency is achieved even when all the sites are occupied by activator ions (Nd). Such phosphors are called *stoichiometric phosphors*.

The energy transfer between different ion species can take place when they have closely matched energy levels. The energy transfer results either in the enhancement (e.g., $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$) or in the quenching (e.g., $\text{Eu}^{3+} \rightarrow \text{Nd}^{3+}$) of emission. The effects of impurities on the luminescence intensities of lanthanide ions in Y_2O_3 are shown in Figure 26. Energy transfer between $4f$ levels has been shown to originate from the electric dipole-electric quadrupole interaction using glass samples.¹⁷

The luminescence spectra of Eu^{3+} , as well as that of Tb^{3+} , have strong dependence on the concentration. This is because at higher concentrations, the higher emitting levels, $^5D_1$ of Eu^{3+} and $^5D_3$ of Tb^{3+} , transfer their energies to neighboring ions of the same species by the following cross-relaxations; that is:



The energy transfer from a host crystal to activators leads to host-excited luminescence. The type of charge carriers to be captured by the doped ions, either electrons or holes, determines the nature of the valence changes in the ions. For a $\text{Y}_2\text{O}_2\text{S}$ host, Tb^{3+} and Pr^{3+}

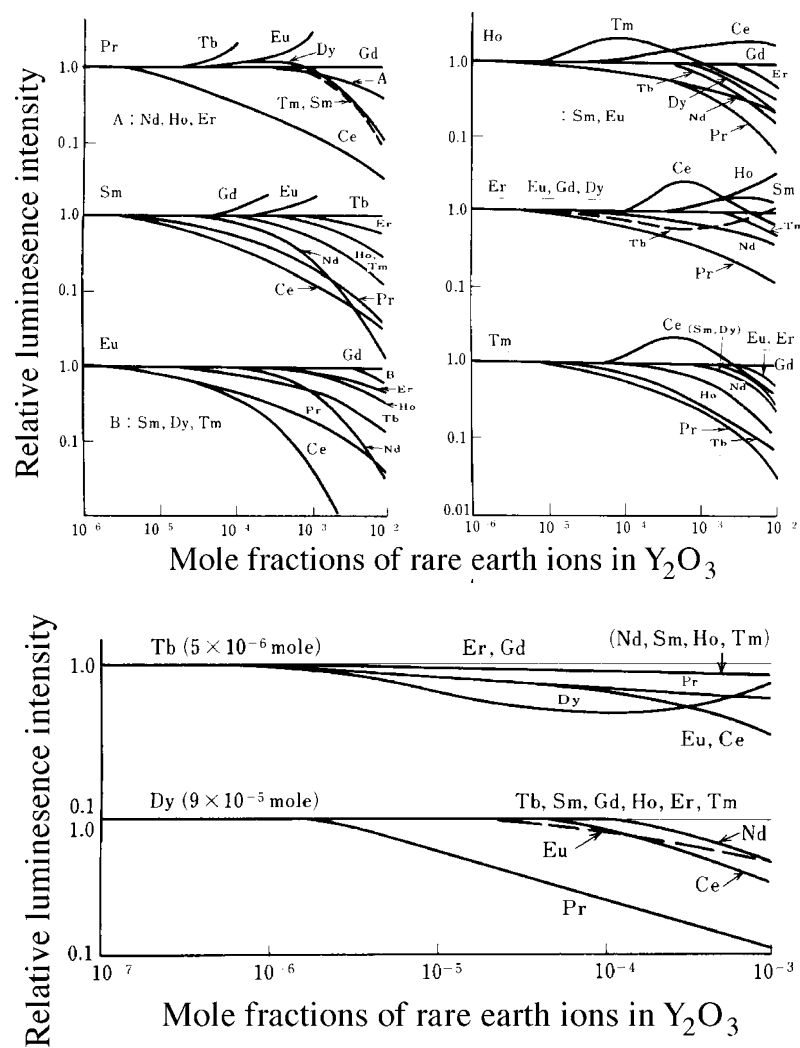


Figure 26 Decrease of luminescence intensities of trivalent rare-earth ions in Y_2O_3 due to the addition of other rare-earth ions. The concentration of ions is 10^{-3} mol% except for Tb and Dy (see the figure). (From Ozawa, R., *Bunseki-kiki*, 6, 108, 1968 (in Japanese). With permission.)

will act as hole traps, while Eu^{3+} will act as an electron trap at the initial stage of host excitation. In the next stage, these ions will capture an opposite charge and produce excitation of $4f$ levels.¹⁸⁻²⁰ A similar model has also been applied to $Y_3Al_5O_{12}:Ce^{3+}, Eu^{3+}, Tb^{3+}$.²¹ Energy transfer from an excited oxy-anion complex to lanthanide ions is responsible for the luminescence observed in $CaWO_4:Sm^{3+}$,²² $YVO_4:Eu^{3+}$,^{23,24} and $Y_2WO_6:Eu^{3+}$.²⁵

3.3.3 Luminescence of specific ions

3.3.3.1 Ce^{3+}

Among the lanthanide ions, the $4f \rightarrow 5d$ transition energy is the lowest in Ce^{3+} , but the energy gap from the $5d^1$ states to the nearest level ($^2F_{7/2}$) below is so large that the $5d$ level serves as an efficient light-emitting state. The luminescence photon energy depends strongly on the structure of the host crystal through the crystal-field splitting of the $5d$ state, as shown in [Figure 27](#)²⁶ (see also Reference 27 and the discussion in [Section 3.3.3.8](#)

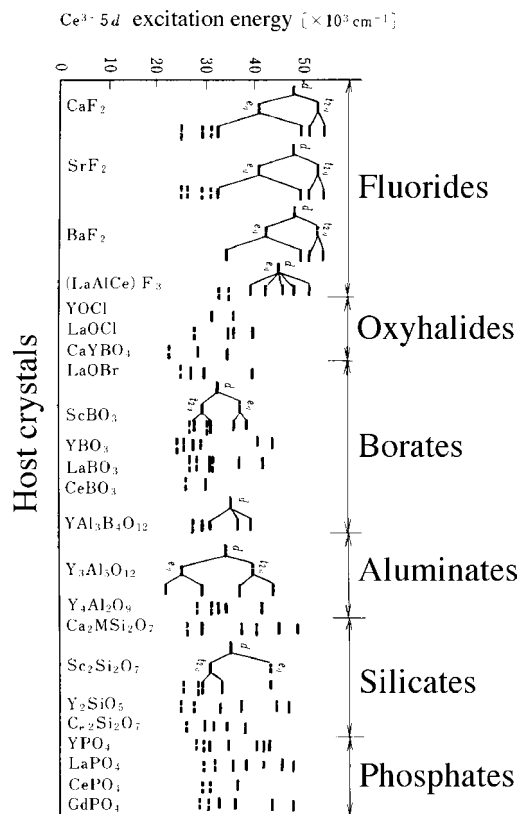


Figure 27 Energies of 5d excited levels of Ce³⁺ in various host crystals. (From Narita, K. and Taya, A., *Tech. Digest, Phosphor Res. Soc. 147th Meeting, 1979* (in Japanese). With permission.)

on Eu²⁺ described below) and varies from near-ultraviolet to the green region. Typical luminescence spectra of some Ce³⁺-activated phosphors are shown in Figure 28.²⁸ The two emission peaks are due to the two terminating levels, ²F_{5/2} and ²F_{7/2}, of the 4f configuration of Ce³⁺.

The decay time of the Ce³⁺ emission is 10⁻⁷ to 10⁻⁸ s, the shortest in observed lanthanide ions. This is due to two reasons: the *d* → *f* transition is both parity-allowed and spin-allowed since 5*d*¹ and 4*f*¹ states are spin doublets.²⁹ By virtue of the short decay time, Y₂SiO₅:Ce³⁺ and YAlO₃:Ce³⁺ are used for flying spot scanners or beam-index type cathode-ray tubes. (See Sections III.6.2.3.3 and 6.2.1.6.) Also, Ce³⁺ is often used for the sensitization of Tb³⁺ luminescence in such hosts as CeMgAl₁₁O₁₉³⁰ (See Section III.5.3.1).

3.3.3.2 Pr³⁺

Luminescence of Pr³⁺ consists of many multiplets, as follows: ~515 nm (³P₀ → ³H₄), ~670 nm (³P₀ → ³F₂), ~770 nm (³P₀ → ³F₄), ~630 nm (¹D₂ → ³H₆), ~410 nm (¹S₀ → ¹I₆), and ultraviolet (5*d* → 4*f*) transitions. The relative intensities of the peaks depend on the host crystals. As an example, the emission spectrum of Y₂O₂S:Pr³⁺ is shown in Figure 29. The radiative decay time of the ³P₀ → ³H₄ or ³F₄ emission is ~10⁻⁵ s, which is the shortest lifetime observed in 4*f* → 4*f* transitions. For example, in Y₂O₂S host, decay times until 1/10 initial intensity are 6.7 μs for Pr³⁺, 2.7 ms for Tb³⁺, and 0.86 ms for Eu³⁺.² The short decay time of Pr³⁺ is ascribed to the spin-allowed character of the transition. Since the short decay time is fit for fast information processing, Gd₂O₂S(F):Pr³⁺, Ce³⁺ ceramic has been developed for an X-ray detector in X-ray computed tomography.³¹

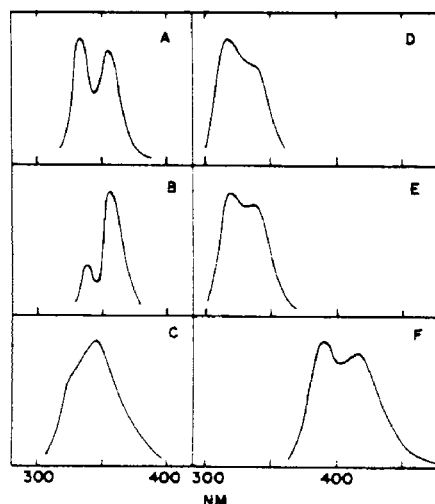


Figure 28 Emission spectra and excitation wavelengths of Ce^{3+} in various hosts. (A) YPO_4 , 254-nm excitation; (B) YPO_4 , 324-nm excitation; (C) GdPO_4 , 280-nm excitation; (D) LaPO_4 , 254-nm excitation; (E) LaPO_4 , 280-nm excitation; (F) YBO_3 , 254-nm excitation. (From Butler, K.H., *Fluorescent Lamp Phosphors, Technology and Theory*, The Pennsylvania State University Press, 1980, 261. With permission.)

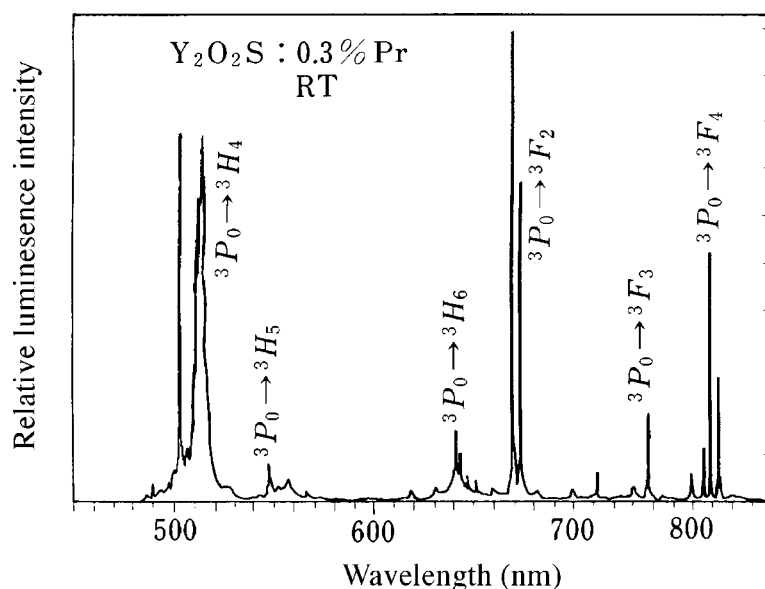


Figure 29 Emission spectrum of $\text{Y}_2\text{O}_2\text{S}:\text{Pr}^{3+}$ (0.3%) at room temperature. (From Hoshina, T., *Luminescence of Rare Earth Ions*, Sony Research Center Rep., 1983 (in Japanese). With permission.)

The quantum efficiency of more than 1 was reported for Pr^{3+} luminescence when excited by 185-nm light.^{32,33} The excitation-relaxation process takes the following paths: $^3\text{H}_4 \rightarrow ^1\text{S}_0$ (excitation by 185 nm), $^1\text{S}_0 \rightarrow ^1\text{I}_6$ (405-nm emission), $^1\text{I}_6 \rightarrow ^3\text{P}_0$ (phonon emission), $^3\text{P}_0 \rightarrow ^3\text{H}_4$ (484.3-nm emission), $^3\text{P}_0 \rightarrow ^3\text{H}_5$ (531.9 nm emission), $^3\text{P}_0 \rightarrow ^3\text{H}_6$, $^3\text{F}_2$ (610.3-nm emission), and $^3\text{P}_0 \rightarrow ^3\text{F}_3$, $^3\text{F}_4$ (704 nm emission). The sum of the visible light emissions in the above processes was estimated to have a quantum efficiency of 1.4.³³ In some fluoride crystals, the $4f^15d^1$ state was found to be lower than $^1\text{S}_0$, resulting in broad-band UV luminescence (see Figure 30).

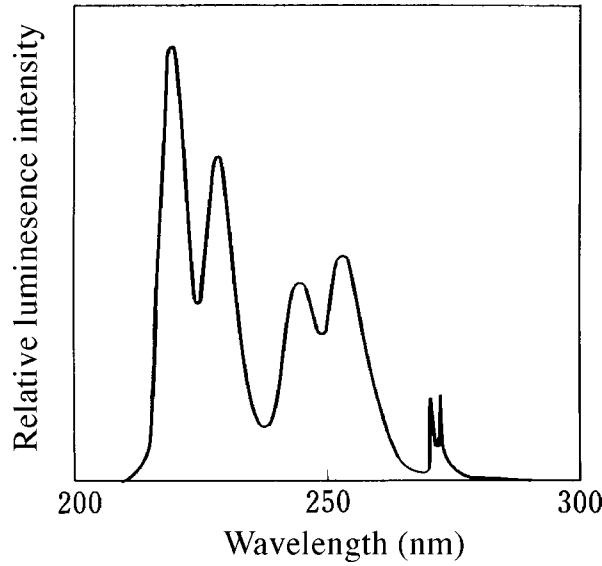


Figure 30 Emission spectrum of LiYF₄:Pr³⁺ (1%) using 185-nm excitation. (From Piper, W.W., Deluca, J.A., and Ham, F.S., *J. Luminesc.*, 8, 344, 1974. With permission.)

3.3.3.3 Nd³⁺

The four lower-lying levels of Nd³⁺ provide a condition favorable to the formation of population inversion. For this reason, Nd³⁺ is used as the active ion in many high-power, solid-state lasers (at 1.06 μm wavelength); the most common hosts are Y₃Al₅O₁₂ single crystals (yttrium aluminum garnet, YAG) or glass. The relative emission intensity of Nd³⁺ in Y₃Al₅O₁₂ has been found to be as follows³⁴:

${}^4F_{3/2} \rightarrow {}^4I_{9/2}$	(0.87–0.95 μm)	: 0.25
${}^4F_{3/2} \rightarrow {}^4I_{11/2}$	(1.05–1.12 μm)	: 0.60
${}^4F_{3/2} \rightarrow {}^4I_{13/2}$	(~ 1.34 μm)	: 0.15
${}^4F_{5_{3/2}} \rightarrow {}^4I_{9/2}$	and others ($\tau = 230 \mu\text{s}$)	: ~ 0.010

3.3.3.4 Nd⁴⁺

Luminescence in the regions ~415, 515, 550, and ~705 nm has been reported in Cs₃NdF₇:Nd⁴⁺.³⁵

3.3.3.5 Sm³⁺

Red luminescence at ~610 nm (${}^4G_{5/2} \rightarrow {}^6H_{7/2}$) and ~650 nm (${}^4G_{5/2} \rightarrow {}^6H_{9/2}$) is observed in Sm³⁺. High luminescence efficiency in Sm³⁺, however, has not been reported. Sm³⁺ acts as an auxiliary activator in photostimulable SrS:Eu²⁺ (Mn²⁺ or Ce³⁺) phosphors. Under excitation, Sm³⁺ captures an electron, changing to Sm²⁺, which in turn produces an excitation band peaking at 1.0 μm .^{36,37} (See 3.6.)

3.3.3.6 Sm²⁺

The $4f^55d^1$ level of Sm²⁺ is located below its $4f$ levels in CaF₂, resulting in band luminescence due to the $5d \rightarrow 4f$ transition (728.6 nm, $\tau \sim \mu\text{s}$). In SrF₂ and BaF₂, on the other hand, a line spectrum due to the $4f \rightarrow 4f^5 D_0 \rightarrow {}^7F_1$ transition has been observed (696 nm, $\tau \sim \mu\text{s}$).³⁸

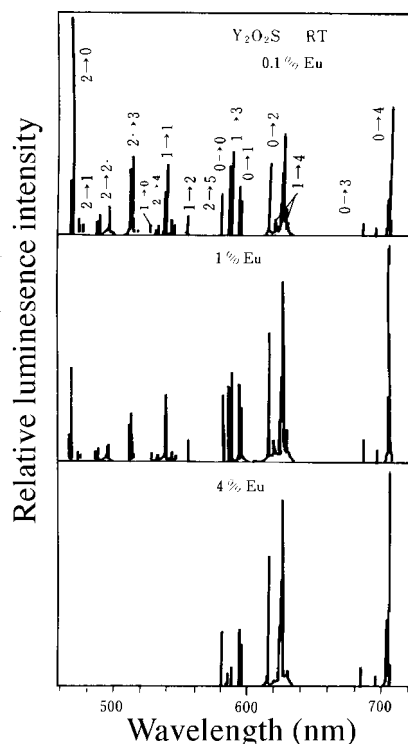


Figure 31 Eu^{3+} concentration dependence of the emission spectrum of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$. (From Hoshina, T., *Luminescence of Rare Earth Ions*, Sony Research Center Rep., 1983 (in Japanese). With permission.)

Also, in BaFCl , line emission at 550 to 850 nm due again to $^5D_{0,1} \rightarrow ^7F_{0-4}$ transitions has been reported.³⁹

3.3.3.7 Eu^{3+}

A number of luminescence lines due to $^5D_J \rightarrow ^7F_J$ of Eu^{3+} in $\text{Y}_2\text{O}_2\text{S}$ are shown in Figure 31. As can be seen, the emissions from $^5D_2$ and $^5D_1$ are quenched, with an increase in the Eu^{3+} concentration due to a cross-relaxation process, ($^5D_J \rightarrow ^5D_0$) $\rightarrow$ ($^7F_0 \rightarrow ^7F_J$), as discussed in Section 3.3.2.4. The emission in the vicinity of 600 nm is due to the magnetic dipole transition $^5D_0 \rightarrow ^7F_1$, which is insensitive to the site symmetry. The emission around 610–630 nm is due to the electric dipole transition of $^5D_0 \rightarrow ^7F_2$, induced by the lack of inversion symmetry at the Eu^{3+} site, and is much stronger than that of the transition to the $^7F_1$ state. Luminescent Eu^{3+} ions in commercial red phosphors such as YVO_4 , Y_2O_3 and $\text{Y}_2\text{O}_2\text{S}$, occupy the sites that have no inversion symmetry. The strong emission due to the electric dipole transition is utilized for practical applications. (See 5.3.2 and 6.2.1.) If the Eu^{3+} site has inversion symmetry, as in $\text{Ba}_2\text{GdNbO}_5$, NaLuO_2 ,⁴⁰ and InBO_3 ,⁴¹ the electric dipole emission is weak, and the magnetic dipole transition becomes relatively stronger and dominates, as is shown in Figure 32.

The spectral luminous efficacy as sensed by the eye has its maximum at 555 nm. In the red region, this sensitivity drops rapidly as one moves toward longer wavelengths. Therefore, red luminescence composed of narrow spectra appear brighter to the human eye than various broad red luminescences having the same red chromaticity and emission energy. For the red emission of color TV to be used in the NTSC system, the red chromaticity standard has been fixed at the coordinates $x = 0.67$, $y = 0.33$; in 1955, the ideal emission spectra were proposed as a narrow band around 610 nm, before the development of Eu^{3+}

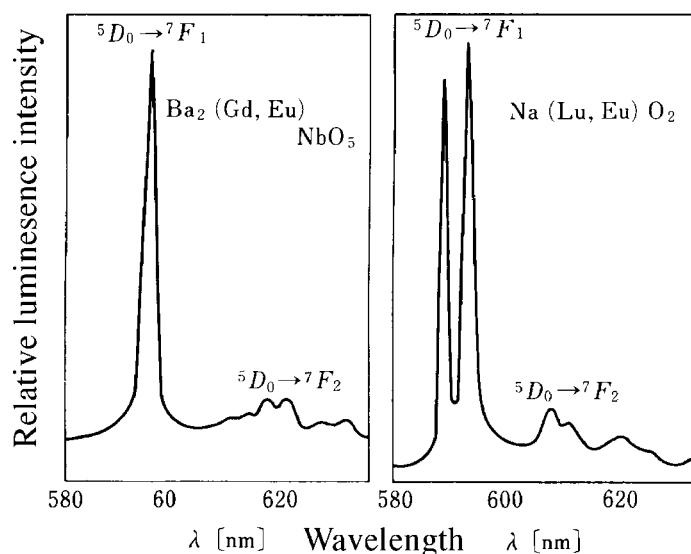


Figure 32 Emission spectra of Eu^{3+} from the sites having the inversion symmetry. (From Blasse, G. and Bril, A., *Philips Tech. Rev.*, 31, 304, 1970. With permission.)

phosphors.⁴² This proposal was dramatically fulfilled for the first time in 1964 by newly developed $\text{YVO}_4\text{:Eu}^{3+}$.⁴³ Since then, Eu^{3+} phosphors have completely replaced broad-band emitting Mn^{2+} phosphors or $(\text{Zn,Cd})\text{S;Ag}$, which were predominantly in use at that time. Just after the introduction of $\text{YVO}_4\text{:Eu}^{3+}$, another Eu^{3+} -activated phosphor, $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$, was developed⁴⁴ and is in current use due to its better energy efficiency as well as its stability during recycling in the screening process of CRT production. The possibility of further improvement can occur in materials with single-line emission, as in $\text{Y}_2(\text{WO}_4)_3\text{:Eu}^{3+}$.⁴⁵ Use of narrow-band luminescence is also advantageous in three-band fluorescent lamp applications, where both brightness and color reproducibility are required. For high color rendering lamps, $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ has been used as the red-emitting component.

The sequence of excitation, relaxation, and emission processes in $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ is explained by the configurational coordinate model shown in Figure 33.⁴⁶ The excitation of Eu^{3+} takes place from the bottom of the ${}^7F_0$ curve, rising along the straight vertical line, until it crosses the charge-transfer state (CTS). Relaxation occurs along the CTS curve. Near the bottom of the CTS curve, the excitation is transferred to ${}^5D_J$ states. Relaxation to the bottom of the ${}^5D_J$ states is followed by light emission downward to ${}^7F_J$ states. This model can explain the following experimental findings. (1) No luminescence is found from ${}^5D_3$ in $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$. (2) The luminescence efficiency is higher for phosphors with higher CTS energy.⁴⁷ (3) The quenching temperature of the luminescence from ${}^5D_J$ is higher as J (0,1,2,3) decreases. The excited 4f states may dissociate into an electron-hole pair. This model is supported by the observation that the excitation through the ${}^7F_0 \rightarrow {}^5D_2$ transition of $\text{La}_2\text{O}_3\text{:Eu}^{3+}$ causes energy storage that can be converted to luminescence by heating. The luminescence is the result of the recombination of a thermally released hole with an Eu^{2+} ion.^{48,49}

By taking a model where CTS is a combination of $4f^7$ electrons plus a hole, one finds that the resulting spin multiplicities should be 7 and 9. It is the former state that affects optical properties related to the ${}^7F_J$ state by spin-restricted covalency.⁵⁰ The intensity ratio of the luminescence from ${}^5D_0 \rightarrow {}^7F_2$ and from ${}^5D_0 \rightarrow {}^7F_1$ decreases with increasing CTS energy sequentially as ScVO_4 , YVO_4 , ScPO_4 , and YPO_4 , all of which have the same type of zircon structure.⁵¹ The above intensity ratio is small in $\text{YF}_3\text{:Eu}^{3+}$, even though Eu^{3+} occupies a site without inversion symmetry.⁵² It is to be noted that CTSs in fluorides have

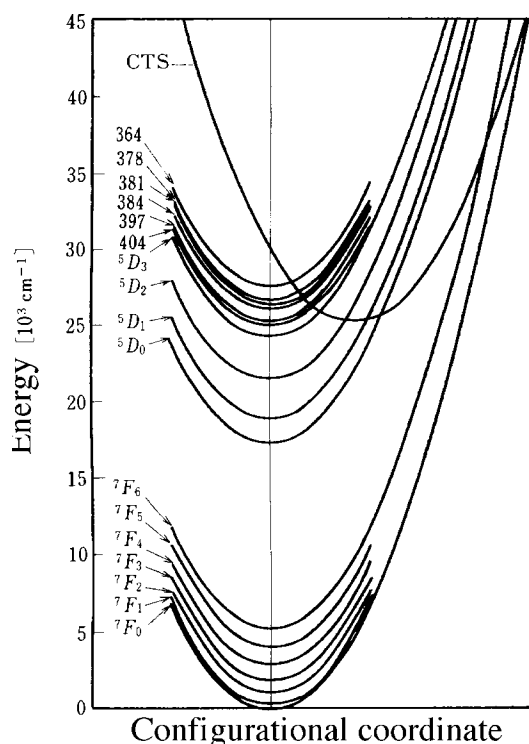


Figure 33 Configurational coordinate model of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$. (From Struck, C.W. and Fonger, W.H., *J. Luminesc.*, 1/2, 456, 1970. With permission.)

higher energies than those in oxides. These results suggest that higher CTS energies reduce the strength of the electric dipole transition $^5D_0 \rightarrow ^7F_2$ in Eu^{3+} .

3.3.3.8 Eu^{2+}

The electronic configuration of Eu^{2+} is $4f^7$ and is identical to that of Gd^{3+} . The lowest excited state of $4f$ levels is located at about $28 \times 10^3 \text{ cm}^{-1}$ and is higher than the $4f^6 5d^1$ level in most crystals, so that Eu^{2+} usually gives broad-band emission due to $f-d$ transitions. The wavelength positions of the emission bands depend very much on hosts, changing from the near-UV to the red. This dependence is interpreted as due to the crystal field splitting of the $5d$ level, as shown schematically in Figure 34.⁵³ With increasing crystal field strength, the emission bands shift to longer wavelength. The luminescence peak energy of the $5d-4f$ transitions of Eu^{2+} and Ce^{3+} are affected most by crystal parameters denoting electron-electron repulsion; on this basis, a good fit of the energies can be obtained.²⁷

The near-UV luminescence of Eu^{2+} in $(\text{Sr,Mg})_2\text{P}_2\text{O}_7$ is used for lamps in copying machines using photosensitive diazo dyes. The blue luminescence in $\text{BaMgAl}_{10}\text{O}_{17}$ is used for three-band fluorescent lamps. (See Figure 35.)⁵⁴ $\text{Ba}(\text{F,Br}):\text{Eu}^{2+}$ showing violet luminescence is used for X-ray detection through photostimulation⁵⁵ (see 7.5). Red luminescence is observed in Eu^{2+} -activated CaS^{36} ; the crystal field is stronger in sulfides than in fluorides and oxides.

The lifetime of the Eu^{2+} luminescence is 10^{-5} – 10^{-6} s, which is relatively long for an allowed transition. This can be explained as follows. The ground state of $4f^7$ is ^8S , and the multiplicity of the excited state $4f^6 5d^1$ is 6 or 8; the sextet portion of the excited state contributes to the spin-forbidden character of the transition.²⁹

Sharp-line luminescence at $\sim 360 \text{ nm}$ due to an $f-f$ transition and having a lifetime of milliseconds is observed when the crystal field is weak so that the lowest excited state of

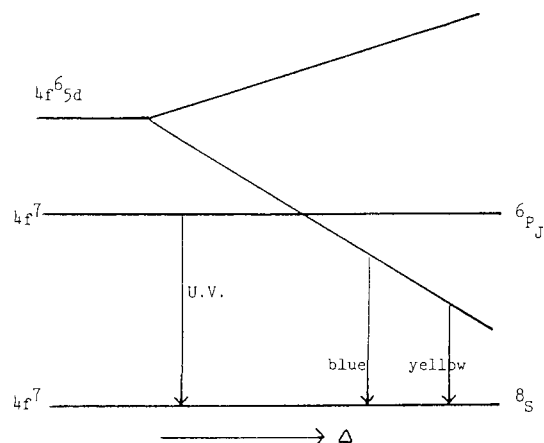


Figure 34 Schematic diagram of the energies of $4f^7$ and $4f^65d^1$ levels in Eu^{2+} influenced by crystal field Δ . (From Blasse, G., Material science of the luminescence of inorganic solids, in *Luminescence of Inorganic Solids*, DiBartolo, B., Plenum Press, 1978, 457. With permission.)

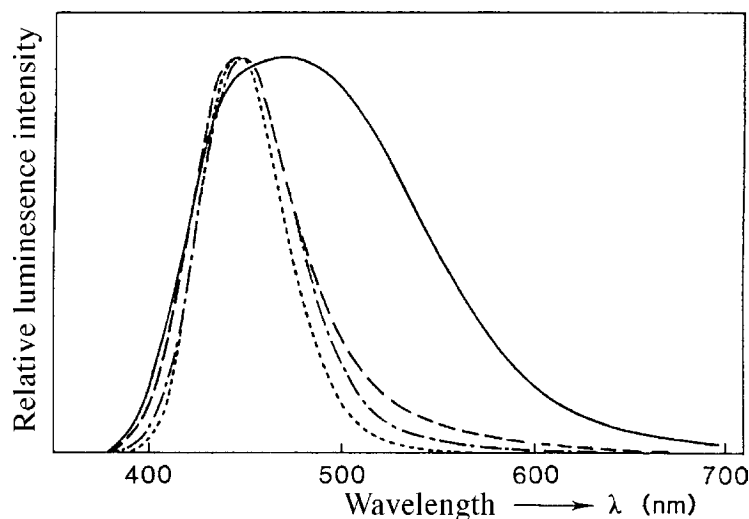


Figure 35 Emission spectra of Eu^{2+} in $\text{BaMgAl}_{10}\text{O}_{17}$ and related compounds using 254-nm excitation at 300K. ----: $\text{Ba}_{0.95}\text{Eu}_{0.05}\text{MgAl}_{10}\text{O}_{17}$, - · - · -: $\text{Ba}_{0.825}\text{Eu}_{0.05}\text{Mg}_{0.5}\text{Al}_{10.5}\text{O}_{17.125}$, — — —: $\text{Ba}_{0.75}\text{Eu}_{0.05}\text{Mg}_{0.2}\text{Al}_{10.8}\text{O}_{17.2}$, — — —: $\text{Ba}_{0.70}\text{Eu}_{0.05}\text{Al}_{11}\text{O}_{17.25}$. (From Smets, B.M.J. and Verlijsdonk, J.G., *Mater. Res. Bull.*, 21, 1305, 1986. With permission.)

$4f^7(^6P_J)$ is lower than the $4f^65d^1$ state, as illustrated in Figure 34. The host crystals reported to produce UV luminescence are BaAlF_5 , SrAlF_5 ⁵⁶ (see Figure 36), $\text{BaMg}(\text{SO}_4)_2$,⁵⁷ $\text{SrBe}_2\text{Si}_2\text{O}_7$,⁵⁸ and $\text{Sr}(\text{F,Cl})$.⁵⁹

3.3.3.9 Gd^{3+}

The lowest excited $4f$ level of Gd^{3+} ($^6P_{7/2}$) gives rise to sharp-line luminescence at $\sim 315 \text{ nm}$ ⁶⁰ and can sensitize the luminescence of other rare-earth ions.⁶¹ The energy levels of the CTS and the $4f^65d^1$ states are the highest among rare-earth ions, so that Gd^{3+} causes no quenching in other rare-earth ions. As a consequence, Gd^{3+} serves, as Y^{3+} does, as a good constituent cation in host crystals to be substituted by luminescent rare-earth ions. For X-ray phosphors, Gd^{3+} is better suited as a constituent than Y^{3+} since it has a higher absorption cross-section due to its larger atomic number.

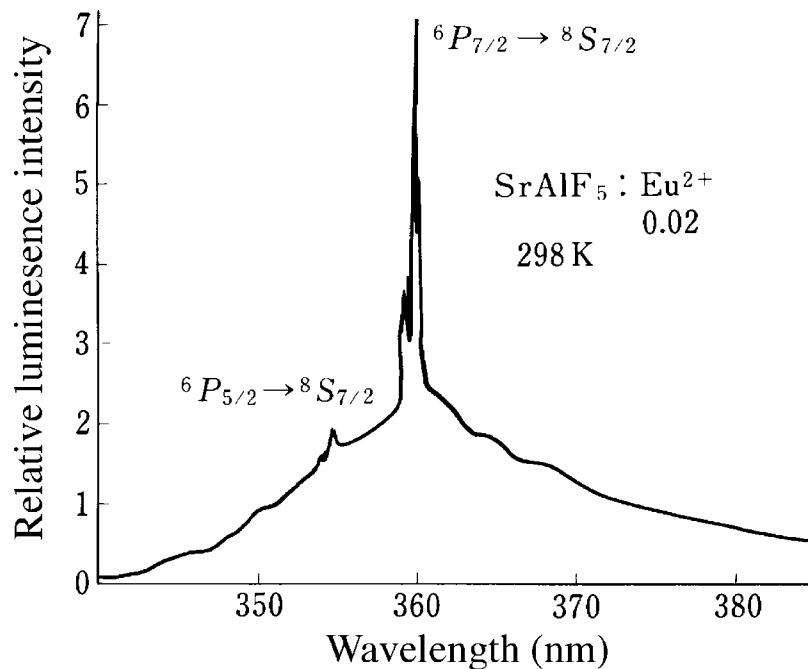


Figure 36 Emission spectrum at 298K of $\text{SrAlF}_5:\text{Eu}^{2+}$ using 254-nm excitation. (From Hews, R.A. and Hoffman, M.V., *J. Luminesc.*, 3, 261, 1970. With permission.)

3.3.3.10 Tb^{3+}

Luminescence spectra consisting of many lines due to $^5D_J \rightarrow ^7F_J$ are observed for Tb^{3+} . As an example, the spectra of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ are shown in Figure 37, in which the Tb^{3+} concentration varies over a wide range. The intensity of the emissions from $^5D_3$ decreases with increasing Tb^{3+} concentration due to cross-relaxation, as discussed in Section 3.3.2.4. Among the emission lines from the $^5D_4$ state, the $^5D_4 \rightarrow ^7F_5$ emission line at approximately 550 nm is the strongest in nearly all host crystals when the Tb^{3+} concentration is a few mol% or higher. The reason is that this transition has the largest probability for both electric-dipole and magnetic-dipole induced transitions.² The Tb^{3+} emission has a broad excitation band in the wavelength region 220 to 300 nm originating from the $4f^8 \rightarrow 4f^75d^1$ transition.

The chromaticity due to the Tb^{3+} emission has been estimated by calculation of the various transition probabilities.⁶² The spectral region around 550 nm is nearly at the peak in the spectral luminous efficacy; in this region, therefore, the brightness depends only slightly on the wavelength and the spectral width. Thus, the narrow spectral width of the Tb^{3+} emission is not so advantageous in cathode-ray tube applications as compared with the case of red Eu^{3+} emission previously described.

The intensity ratio of the emission from $^5D_3$ to that from $^5D_4$ depends not only on the Tb^{3+} concentration, but also on the host material. In borate hosts such as ScBO_3 , InBO_3 , and LuBO_3 , the relative intensity of $^5D_3$ emission is much weaker than in other hosts, such as phosphates, silicates, and aluminates.² Figure 38 shows emission spectra of a series of $\text{Ln}_2\text{O}_3:\text{Tb}^{3+}(0.1\%)$ ($\text{Ln} = \text{La}, \text{Gd}, \text{Y}, \text{and Lu}$) materials having the same crystal structure.² It is seen that the relative intensity of the $^5D_3$ emission increases dramatically as one progresses from $\text{La} \rightarrow \text{Gd} \rightarrow \text{Y} \rightarrow \text{Lu}$, with the ionic radii becoming smaller.

In addition to the Tb^{3+} concentration, one needs to consider two additional factors that help determine the ratio of $^5D_3$ to $^5D_4$ intensity. One is the maximum energy of phonons that causes phonon-induced relaxation, as discussed in Section 3.3.2.1; if the maximum phonon

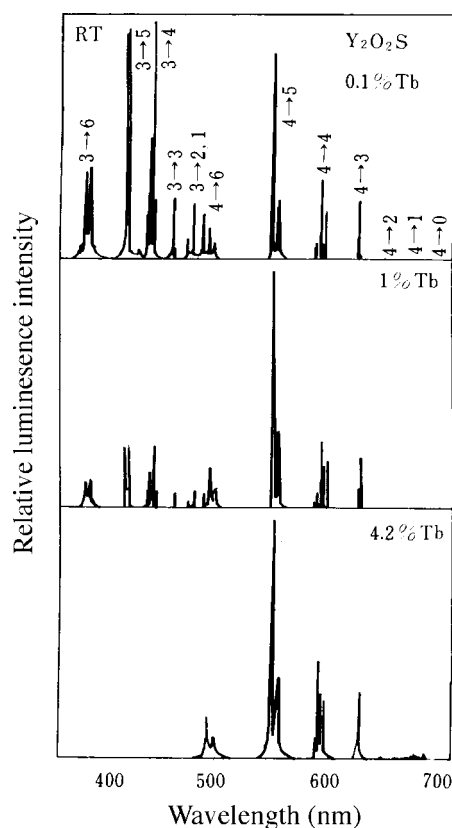


Figure 37 Tb^{3+} concentration dependence of emission spectra of $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ at room temperature. (From Hoshina, T., *Luminescence of Rare Earth Ions*, Sony Research Center Rep., 1983 (in Japanese). With permission.)

energy is large, the ratio of $^5\text{D}_3$ to $^5\text{D}_4$ intensity becomes small. The luminescence of Tb^{3+} in borate hosts is explained by this factor. The other factor is the energy position of the $4f^75d^1$ level relative to $4f^8$ levels, which can be discussed in terms of the configurational coordinate model. In this model, the potential curve of $4f^75d^1$ can be drawn just like the CTS in [Figure 33](#). If the minimum of the $4f^75d^1$ curve is fairly low in energy and the Frank-Condon shift is fairly large, there is a possibility that an electron excited to the $4f^75d^1$ level can relax directly to the $^5\text{D}_4$, bypassing the $^5\text{D}_3$ and thus producing only $^5\text{D}_4$ luminescence.² The net effect of these two factors on the spectra of $\text{Ln}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ in [Figure 38](#) is not known quantitatively.

YVO_4 is a good host material for various Ln^{3+} ions, as shown in [Figure 23](#). However, Tb^{3+} does not luminesce in this host. A nonradiative transition via a charge-transfer state of $\text{Tb}^{4+}\text{-O}^{2-}\text{-V}^{4+}$ has been proposed as a cause.⁶³ The transition energy to this proposed state is considered to be relatively low because both the energies of conversion from Tb^{3+} to Tb^{4+} and that from V^{5+} to V^{4+} are low. The Frank-Condon shift in the transition would be so large that the proposed state would provide a nonradiative relaxation path from excited Tb^{3+} to the ground state.

Tb^{3+} -activated green phosphors are used in practice in three-band fluorescent lamps (see [5.3.2](#)), projection TV tubes ([6.2.1.5](#)), and X-ray intensifying screens ([7.1](#)).

3.3.3.11 Dy^{3+} ^{64,65}

The luminescence lines of Dy^{3+} are in the 470 to 500-nm region due to the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ transition, and in the 570 to 600-nm region due to the $^6\text{F}_{15/2} \rightarrow ^6\text{F}_{11/2}$ transition. The color

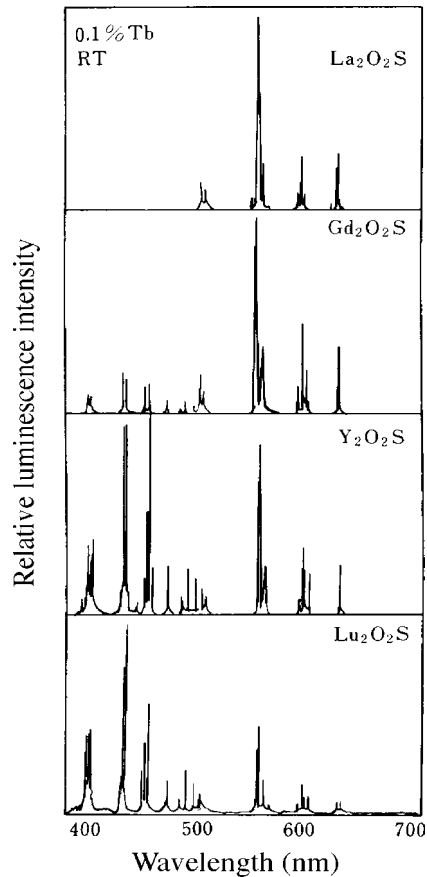


Figure 38 Emission spectra of $\text{Ln}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ (0.1%) (Ln = La, Gd, Y, and Lu) at room temperature. (From Hoshina, T., *Luminescence of Rare Earth Ions*, Sony Research Center Rep., 1983 (in Japanese). With permission.)

of the luminescence is close to white. In $\text{Y}(\text{P,V})\text{O}_4$, the relative intensity of the latter decreases with increasing P concentration. This can be understood if one considers that the $\Delta J = 2$ transition probability decreases with a decrease in the polarity of the neighboring ions as in the case of the $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} . The energy of the CTS and $4f^85d^1$ is relatively large so that direct UV excitation of Dy^{3+} is not effective. The excitation via host complex ions by energy transfer can however be effective. The quantum efficiency of UV-excited (250–270 nm) luminescence of $\text{YVO}_4:\text{Dy}^{3+}$ has been reported to be as high as 65%.

3.3.3.12 Dy^{2+} ⁶⁶

Luminescence of Dy^{2+} has been reported to consist of line spectra at 2.3–2.7 μm at 77K and 4.2K in CaF_2 , SrF_2 , and BaF_2 . Dy^{2+} in these hosts was prepared by the reduction of Dy^{3+} through γ -ray irradiation.

3.3.3.13 Dy^{4+} ⁶⁷

Luminescence lines of $\text{Cs}_3\text{DyF}_7:\text{Dy}^{4+}$ at 525 nm due to $^5D_4 \rightarrow ^7F_5$ transition and at 630 nm due to $^5D_4 \rightarrow ^7F_3$ transition have been reported.

3.3.3.14 Ho^{3+}

Efficient luminescence of Ho^{3+} has rarely been found due to the crowded energy level diagram of this ion. In LaCl_3 , cross-relaxation between $(^5S_2 \rightarrow ^5I_4) \leftrightarrow (^5I_8 \rightarrow ^5I_7)$ at an

interionic distance of 7.5 Å has been reported.⁶⁸ A green luminescence due to the $^5F_4, ^5S_2 \rightarrow ^5I_8$ transition has been reported in an infrared-to-visible up-conversion phosphor, $\text{LiYF}_4:\text{Yb}^{3+}, \text{Ho}^{3+}$.⁶⁹

3.3.3.15 Ho^{2+}

Infrared luminescence of Ho^{2+} in CaF_2 appearing around 1.8 μm at 77K has been reported.⁷⁰

3.3.3.16 Er^{3+}

Green luminescence due to the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} has been reported in infrared-to-visible up-conversion phosphors, such as $\text{LaF}_3:\text{Yb}^{3+}, \text{Er}^{3+}$,⁷¹ and $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$.⁷² (See 12.1). This luminescence was also reported in ZnS ,⁷³ Y_2O_3 ,⁷⁴ and $\text{Y}_2\text{O}_2\text{S}$.⁷⁵ The emission color is a well-saturated green.

Er^{3+} ions embedded in an optical fiber (several hundreds ppm) function as an optical amplifier for 1.55- μm semiconductor laser light. Population inversion is realized between lower sublevels of $^4I_{13/2}$ and upper sublevels of $^4I_{15/2}$. This technology has been developed for optical amplification in the long-distance optical fiber communication systems.⁷⁶

3.3.3.17 Tm^{3+}

The blue luminescence of Tm^{3+} due to the $^1G_4 \rightarrow ^3H_6$ transition has been reported in ZnS ,⁷⁷ as well as in infrared-to-visible up-conversion phosphors sensitized by Yb^{3+} such as $\text{YF}_3:\text{Tm}^{3+}, \text{Yb}^{3+}$.⁷⁸ Electroluminescent $\text{ZnS}:\text{TmF}_3$ has also been investigated as the blue component of multicolor displays.⁷⁹ The efficiency of the blue luminescence of Tm^{3+} is low, and is limited by the competitive infrared luminescence, which has a high efficiency.

3.3.3.18 Yb^{3+}

The infrared absorption band of Yb^{3+} at about 1 μm due to the $^5F_{5/2} \rightarrow ^5F_{7/2}$ transition is utilized for Er^{3+} -doped infrared-to-visible up-conversion phosphors as a sensitizer (See 12.1).^{71,72} The CTS energy of Yb^{3+} ions is low next to the lowest of Eu^{3+} among the trivalent lanthanide ions (see Figure 25). Yb^{3+} has no 4f energy levels interacting with CTS, so that luminescence due to the direct transition from CTS to the 4f levels can occur. This luminescence has been observed in phosphate⁸⁰ and oxysulfide hosts.⁸¹ Figure 39 shows the excitation and emission spectra of $\text{Y}_2\text{O}_2\text{S}:\text{Yb}^{3+}$ and $\text{La}_2\text{O}_2\text{S}:\text{Yb}^{3+}$.⁸¹ As seen in Figure 33, CTS is characterized by a fairly large Frank-Condon shift. As a result, the emission spectra are composed of two fairly broad bands terminating in $^2F_{5/2}$ and $^2F_{7/2}$, as shown in Figure 39.

3.3.3.19 Yb^{2+}

The emission and absorption of Yb^{2+} due to the $4f^{14} \leftrightarrow 4f^{13}5d^1$ transition have been reported.⁸² Emission peaks are at 432 nm in $\text{Sr}_3(\text{PO}_4)_2$ (see Figure 40), 505 nm in $\text{Ca}_2\text{PO}_4\text{Cl}$, 560 nm in $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$, and 624 nm in $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$. The lifetimes of the emissions are between $1\text{--}6 \times 10^{-5}$ s.

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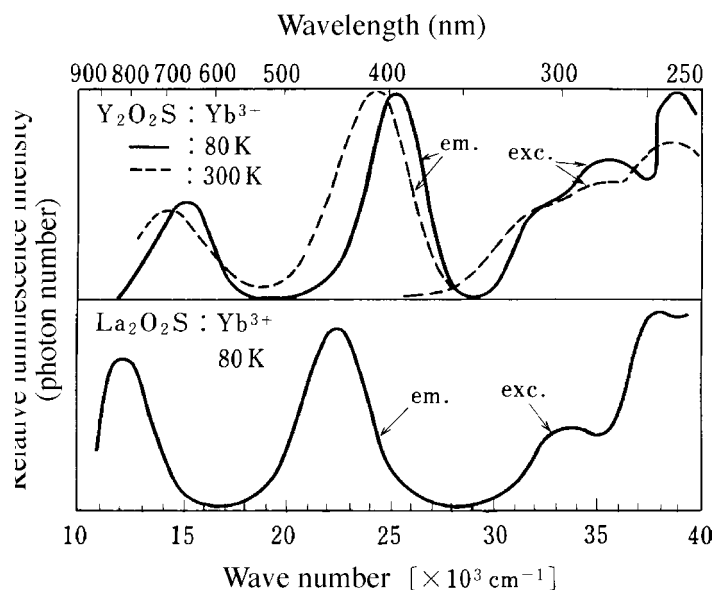


Figure 39 Excitation and emission spectra of $\text{Y}_2\text{O}_2\text{S}:\text{Yb}^{3+}$ and $\text{La}_2\text{O}_2\text{S}:\text{Yb}^{3+}$. (From Nakazawa, E., *J. Luminesc.*, 18/19, 272, 1979. With permission.)

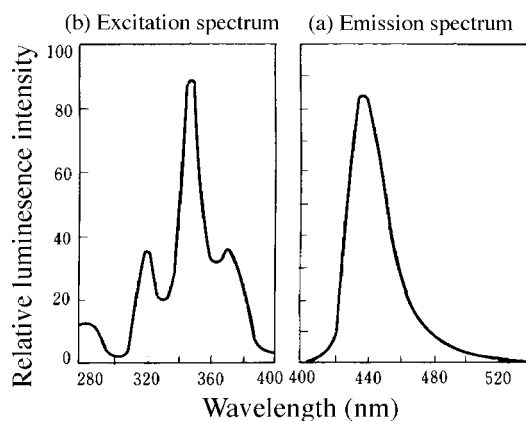


Figure 40 Emission (a) and excitation (b) spectra of $\text{Sr}_3(\text{PO}_4)_2:\text{Yb}^{2+}$ at liquid nitrogen temperature. (From Palilla, F.C., O'Reilly, R.E., and Abbruscato, V.J., *J. Electrochem. Soc.*, 117, 87, 1970. With permission.)

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