

ENERGY TRANSFER PROCESS BETWEEN Ce^{3+} AND Tb^{3+} IN $LaOCl$ HOST

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ABSTRACT : Energy transfer process between Tb^{3+} and Ce^{3+} has been studied in $LaOCl$ host. The energy absorbed by Ce^{3+} transfers to Tb^{3+} which has levels emitting strong fluorescence. The probability of energy transfer depends strongly on the concentration or the distance of activator ions. While the energy transferred on Tb^{3+} emits from 5D_3 level at low concentration of Ce^{3+} , the energy goes back to Ce^{3+} (Back Transfer) and then emits from low levels of Ce^{3+} and Tb^{3+} at the high concentration. The Back Transfer process has been identified by the experiment with varying the concentration of the activator, Ce^{3+} . The relaxation is more effective if Ce^{3+} intermediates than if not.

요약 : $LaOCl$ 입자 물질에서 Ce^{3+} 와 Tb^{3+} 사이의 에너지 전달 과정을 연구하였다. Ce^{3+} 에서 흡수된 에너지는 강한 형광 방출 준위가 있는 Tb^{3+} 으로 에너지가 전달되었다. 에너지가 전달되는 확률은 활성제 이온의 농도 혹은 거리에 크게 의존하였다. 농도가 낮을 때는 Tb^{3+} 으로 전달된 에너지가 5D_3 준위에서 방출되었다. 그러나 높은 농도에서는 다시 Ce^{3+} 으로 에너지는 이동하고(역전달) 더 낮은 Ce^{3+} 혹은 Tb^{3+} 의 준위로부터 방출되었다. 역전달 현상은 Ce^{3+} 이온의 농도를 변화시키는 실험을 통하여 확인하였다. 이와 같이 Ce^{3+} 이 관여하면 매개하지 않은 경우보다 이완이 잘 일어났다.

Key words : Energy transfer, $LaOCl$, Cross relaxation, Fluorescence.

INTRODUCTION

Luminescence properties of rare-earth activated material have been studied by many investigators.¹⁻⁵ High operating efficiency and high color rendering property are required for application of luminescence material. The 3-band light emitting type fluorescence lamp⁶ utilizes a mixture of three kind of phosphors which emit light in blue, green and

red, each having a narrow band of the light emission. Tb^{3+} activated phosphor is known to be one of green-emitting materials and has been studied in various aspect for the improvement in the properties.⁷

The energy transfer mechanism from energy donor(a sensitizer) to energy acceptor(an activator) has become an important subject to be studied for phosphor development, because the light emitting

efficiency of the phosphor can be improved by adding a kind of ion as a sensitizer in the phosphor. Ce^{3+} ion was used as a sensitizer in several paper⁸⁻¹⁰ and the energy transfer mechanism between Ce^{3+} (a sensitizer) and Tb^{3+} (an activator) in various host has been studied.

Fluorescence quenching and enhancement mechanism can be explained mainly by ion-ion interaction and ion-lattice interaction. Dexter¹¹ studied a fluorescence quenching mechanism in inorganic phosphor and revealed that the concentration and temperature are important factor of fluorescence yield. The influence of energy transfer on fluorescence yield was studied by Inokuti, et. al.¹² by exchange mechanism between energy donor and acceptor.

In the case of HOST : Ce, Tb system, the energy absorbed by Ce^{3+} degrades to low state or transfers to 5D_3 of Tb^{3+} , of which energy emit fluorescence or relaxes to 5D_4 level. Even though several relaxation can be involved in these process, Cross Relaxation can give a main role for the process under the specific condition such as concentrations of activator and sensitizer.¹³⁻¹⁴ In these case, the relaxation rate is much higher than fluorescence emitting one. Green emission from 5D_4 level, accordingly, increases while 5D_3 blue emission quenches.

Among the several hosts, oxychloride has not yet used commercially but has been studied widely by spectroscopic methods because it is very useful for understanding the properties of lanthanide elements.¹⁵ The studies have been focused on the optimum condition for green emission under assumption that the energy transfer is one directional i. e., from donor to acceptor.

In the present paper, luminescence properties of LaOCl activated with terbium and cerium have been studied in detail. A new energy transfer process has also been studied with the optimum conditions for Tb^{3+} emission in green and blue.

EXPERIMENTAL

Apparatus : A 300 W Xenon arc lamp was used for excitation light source. The excitation wavelength was turned with a monochromator having 25 cm focal length. Sample holder is a brass button which have a shallow hole of 1mm depth and 1mm diameter in the center of its front face (Fig. 1(a)). The button is introduced in button holder (Fig. 1(b)) which can be optically aligned. The tuned light source through the excitation monochromator is focused on the sample face with a concave mirror. The illuminating area of the sample is about 0.5×2 mm. The fluorescence emitted from the sample goes through emission monochromator and PMT and Amplifier. The signals are collected on personal computer through digital interface (Stanford Research System Inc, SR465). The home-made emission monochromator has 1800gr/mm grating and 0.75m focal length, and its bandpass was adjusted to 0.5 nm which gives sufficient wavelength resolution for room temperature fluorescence. The block diagram of the system is shown in Fig. 2.

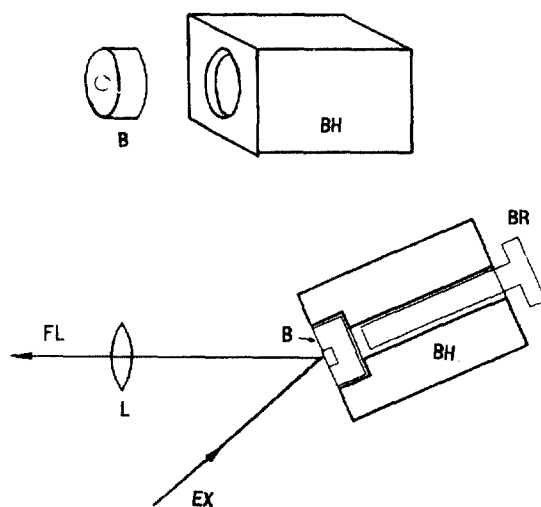


Fig. 1. Schematic diagram of sample button and button holder.

B: Brass sample button, BH: Button Holder,
BR: Button Remover, FL: Fluorescence, EX:
Excitation Light, L: Collimating Lens.

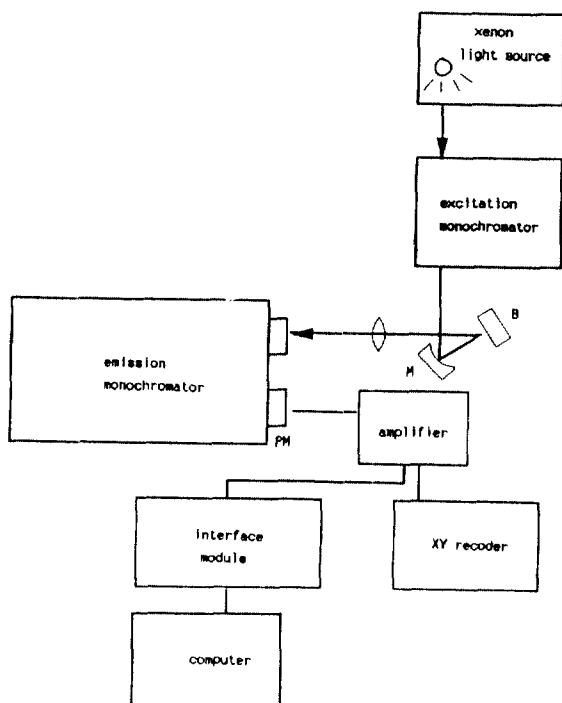


Fig. 2. Schematic diagram of the experimental setup.

B: sample button, M: concave mirror, PM: photomultiplier.

Reagents : Appropriate amounts of three lanthanide oxides (La_2O_3 , $(NH_4)_2Ce(NO_3)_6$ and Tb_4O_7 : 99.99%, Wako Pure Chemical Industry LTD) were dissolved in hydrochloric acid, respectively. The lanthanum solution was diluted to 0.1M and other two solutions to 0.01M as stock solution. These solutions were standardized by EDTA titration method.

Procedure : 20ml of each lanthanum solution was pipetted into a 100ml beaker and appropriate amount of the cerium solution was added in it to make cerium concentration of 0.0002mol%~1mol%. The mixture solution of lanthanum and terbium was prepared similarly with the above to make terbium concentration of 0.003mmol%~10M%. The mixture solution of three lanthanides was also prepared to make 0.1mol% terbium with 0.0002mol%~

1 mol% of cerium and 0.01mol% terbium with 0.002mol%~1mol% of cerium. Each mixture solution evaporated to dryness on hot plate. Adding a few ml of deionized water, the mixture evaporated again to dryness. This evaporation was repeated three times. The residue was ignited in a small porcelain crucible in a furnace at 600°C for 2 hours. The powder was ground in a agate mortar and was placed in a hole on the sample holder with the flat end of a glass rod.

RESULT AND DISCUSSIONS

Lanthanide chloride ($LnCl_3$) has been investigated frequently for spectroscopic property of lanthanide elements. It is well known¹⁶ that lanthanide chloride compounds are very hygroscopic and unstable in atmospheric environment but lanthanide oxychloride ($LnOCl$) is very stable. During the ignition, lanthanide chloride is oxidized and the displacement of oxygen in the compounds can be occurred. These reactions are strongly depended on ignition temperature. As shown in Fig. 3, if lanthanum chloride is ignited at 300°C, some of the compound are oxidized, and both of $LaCl_3$ and $LaOCl$ coexist. If the temperature goes up to 600°C, all of $LaCl_3$ convert to $LaOCl$. But $LaCl_3$ is oxidized fully to La_2O_3 at 1000°C. Therefore, the temperature should be kept below 1000°C to prevent full oxidation of $LaCl_3$ to La_2O_3 .

The spectra and the related energy levels of Tb^{3+} are shown in Fig. 4. When the sample is excited by 320nm, the transitions from 5D_3 to $^7F_{6,5,4,3}$ level are clearly resolved, and the strong threshold peak of the second order scattering on excitation monochromator appears at 640nm (Fig. 4(a)). The lower levels, $^7F_{2,1,0}$ are weak not to be found in the spectrum excited by 320nm, but can be resolved when excited by 305nm (Fig. 4(b)). The emission from 5D_3 level can not be found in the two spectra, because the emission should be found at shorter wavelength

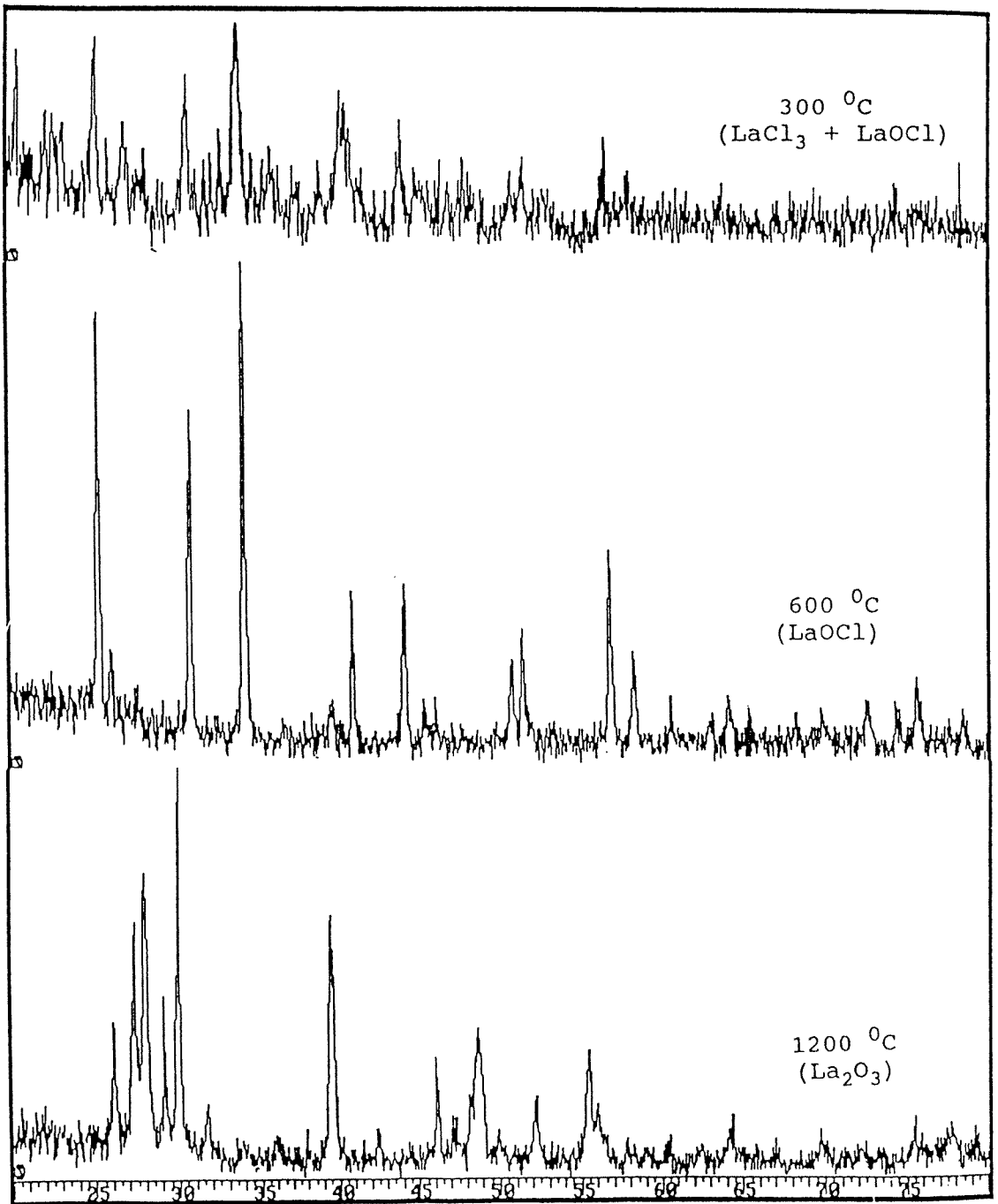


Fig. 3. X-ray powder diffraction pattern of LaCl_3 , LaOCl , La_2O_3 .

region and is also not intense.

It is well known that total emission of a luminescence compound is linearly dependent upon the

concentration of activator.¹³ For terbium-activated compound, excitation energy transfers to two energy levels of $^5\text{D}_3$ and $^5\text{D}_4$, mainly by internal con-

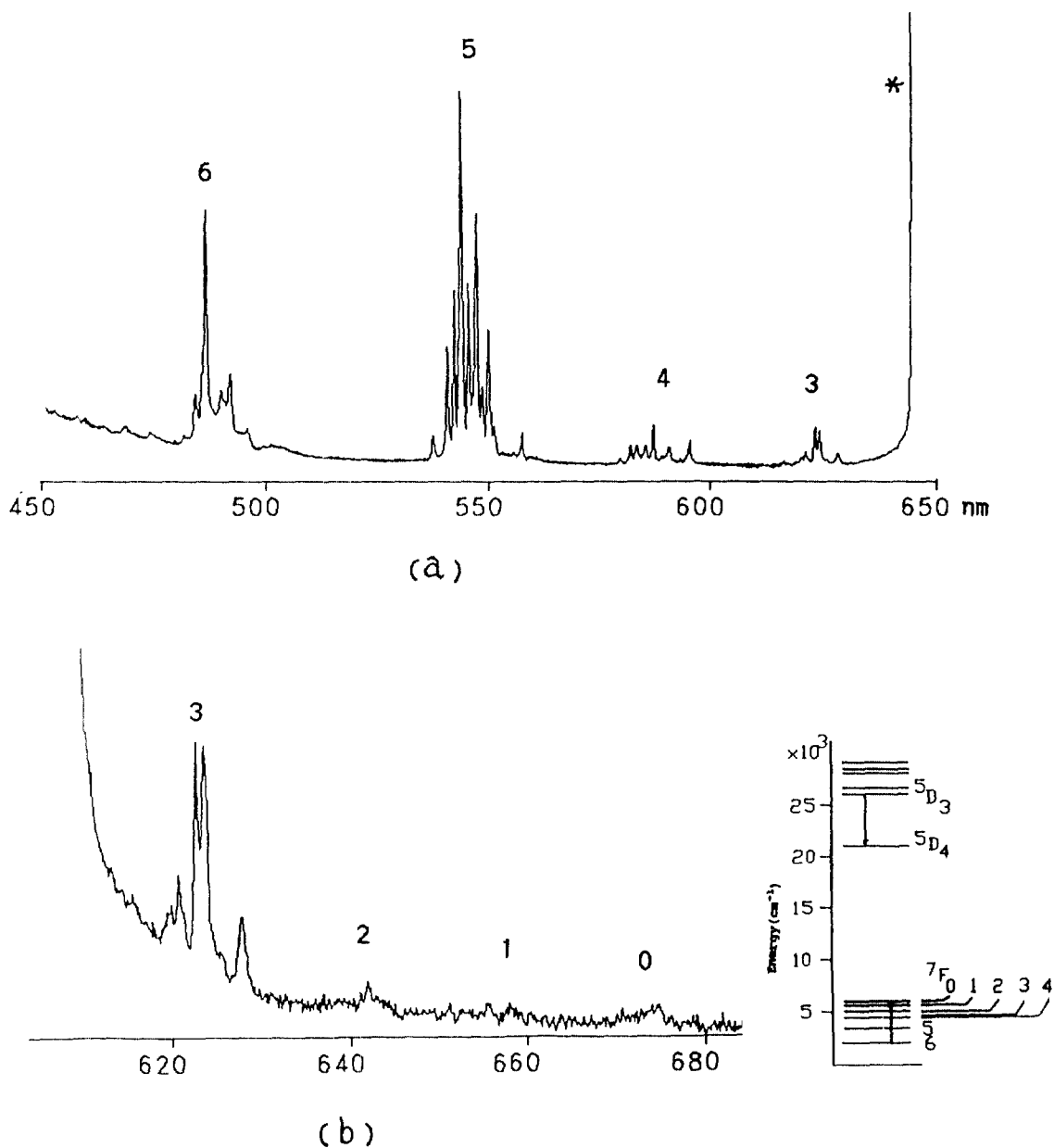


Fig. 4. Fluorescence spectra of Tb^{3+} originating from $5D_4$ level in $LaOCl: Tb^{3+} 0.1mol\%, Ce^{3+} 0.02mol\%$. Marks in Fig. are j value of $7F_j$.

* is second order scattering of excitation monochromator.

(a) excitation by 320nm.

(b) excitation by 305nm.

(c) Schematic representation of Tb^{3+} energy level.

version process, but most of the energy transfers to 5D_3 level. The emission, therefore, comes mainly from 5D_3 . As energy gap between 5D_3 and 5D_4 levels is similar to the width of the $^7D_{0-6}$ multiplet, the energy transfer can be permitted from 5D_3 to 5D_4 between ions. This process is called Cross Relaxation (indicated by arrows in *Fig. 4(c)*), which has close relation with the distance between terbium ions, the concentration. As the concentration increases, the probability that Cross Relaxation is permitted increases compared with the probability of internal conversion, resulted in increasing the rate of relaxation from 5D_3 to 5D_4 . This phenomenon is explained by the result shown in *Fig. 9(a)*. The emission intensity ratio of $^5D_3 / ^5D_4$ is decreasing as the concentration of Tb^{3+} is increasing. This phenomenon has been reported in the Tb^{3+} activate compounds.

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The excitation and emission spectra for Ce^{3+} in LaOCl are shown in *Fig. 5(a)* and (b). Although Ce^{3+} has $4f^1$ configuration and excited to $4f^05d$, two absorption bands are shown in the region between 250nm~350nm in *Fig. 5(a)* due to the crystal field

splitting of $4f^05d(^2D)$ state of Ce^{3+} . The transition of $4f$ to $6s$ or Charge Transfer State (CTS) exist at the higher energy region (about $40,000cm^{-1}$) and can not be found in the *Fig.*, because excitation source of xenon lamp used in this experiment can not cover this range. *Fig. 5(b)* shows a emission spectrum of LaOCl doped only Ce^{3+} in which have a broad peak in long ultra-violet region. As Ce^{3+} has $4f^1$ configuration, the ground state have doublet($^2F_{5/2}$ and $^2F_{7/2}$) and Ce^{3+} emission is due to a $5d \sim 4f$ transition which is an allowed electric dipole transition as quantum mechanical selection rule. The emission, therefore, should have two peaks. The broad peak can be resolved into two Gaussian shaped peaks at 400 and 420nm.

Fig. 6 shows two excitation spectra of LaOCl monitored at 543nm(the emission wavelength of the 5D_4 level of Tb^{3+}), one of which is doped only with Tb^{3+} and another is codoped with both of Tb^{3+} and Ce^{3+} . In the first spectrum obtained with LaOCl doped only with Tb^{3+} , three peaks are found at about 250, 350 and 370nm, among which the first peak is the peaks of high level of Tb^{3+} , the second is

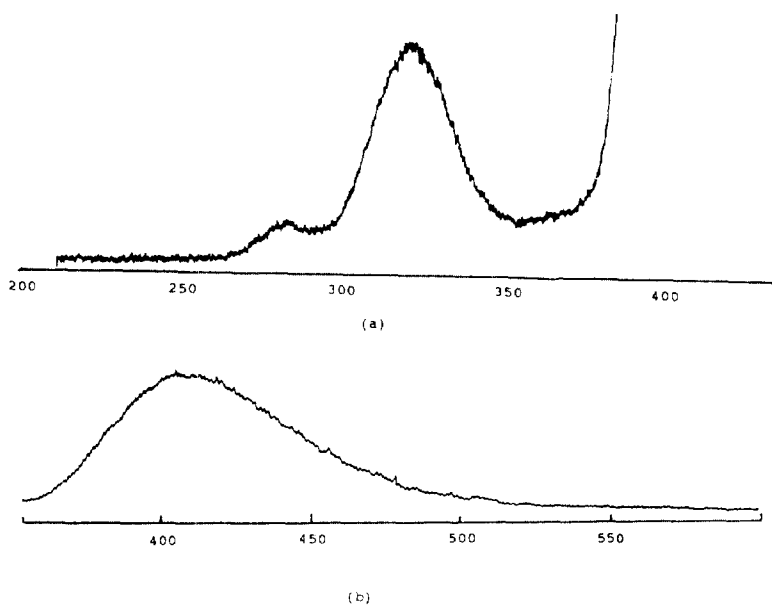


Fig. 5. Excitation spectrum(a) and emission spectrum(b) of Ce^{3+} in LaOCl, Ce=0.1mol%.

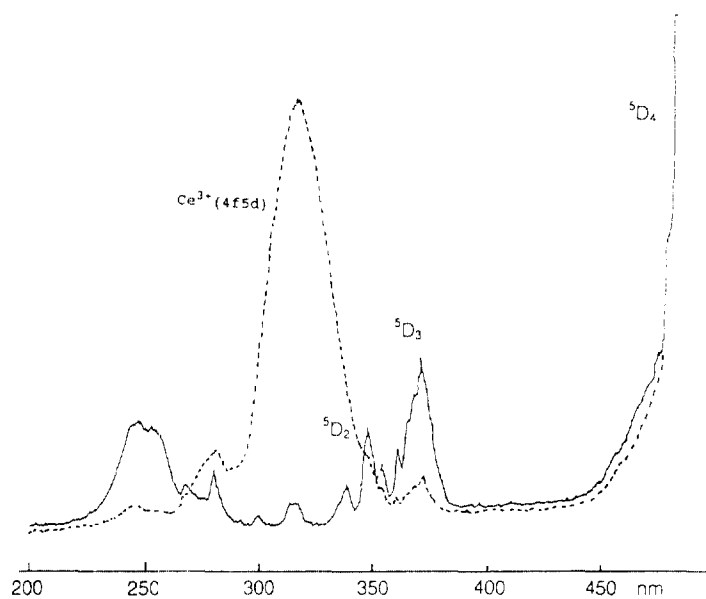


Fig. 6. Excitation spectra of $LaOCl: Tb, Ce$ monitored at 543nm.

hard line: excitation of $LaOCl: Tb, Tb=10mol\%, Ce=0mol\%$.

broken line: excitation of $LaOCl: Tb, Ce Tb=0.1mol\%, Ce=0.01mol\%$.

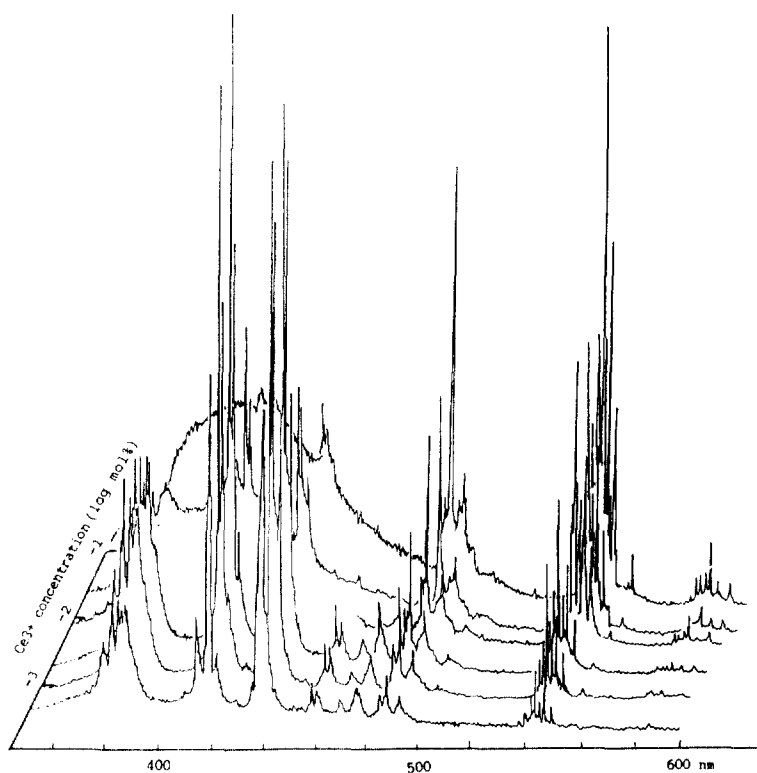


Fig. 7. The fluorescence spectra of the Tb^{3+}, Ce^{3+} in $LaOCl$. Excitation at 320nm, $Tb=0.1mol\%, Ce=0.1\sim 0.00025mol\%$.

one of 5D_2 and the third one of 5D_3 . But the peak can not be found at about 320nm, which is the excitation wavelength of Ce^{3+} . On the other hand, in the second one from codoped with Ce and Tb, the peak is found at 320nm, which is the biggest peak and the excitation peak of Ce^{3+} . It is explained from the above fact that at the existence of Ce, the most energy is used to the excitation of Ce^{3+} and the energy transfers to 5D_4 of Tb^{3+} .

The fluorescence spectra of LaOCl codoped with Tb^{3+} and Ce^{3+} are shown in Fig. 7 which is obtained with a fixed concentration of Tb^{3+} and increasing the concentration of Ce^{3+} from 0.00025 to 0.1mol%. The peaks are found at 385, 418, 440, 493, 545 and 585nm in all the spectrum, among which the first three peaks are emitted from 5D_3 of Tb and the last three from 5D_4 . As the sample is excited at 320nm of the main excitation wavelength of Ce^{3+} , all of the fluorescence peaks can be concluded to be originated from Ce^{3+} , not from Tb^{3+} . In addition, as the concentration of Ce^{3+} increases, the fluorescence peaks from 5D_3 level decrease but those from 5D_4 in-

crease. To understand more easily, these trends are shown in Fig. 8 for the fluorescence intensities of 5D_3 , and 5D_4 of Tb^{3+} and Ce^{3+} as a function of Ce concentration. The emission intensities of 5D_4 of Tb^{3+} and Ce^{3+} increase as the concentration increases. On the other hand, that of 5D_3 also increases at low concentration but decreases at the high concentration.

The intensity ratio of $^5D_3/^5D_4$ are shown for the samples doped only with Tb^{3+} (Fig. 9(a)) and codoped with Tb^{3+} and Ce^{3+} (Fig. 9(b)), in which the ratio

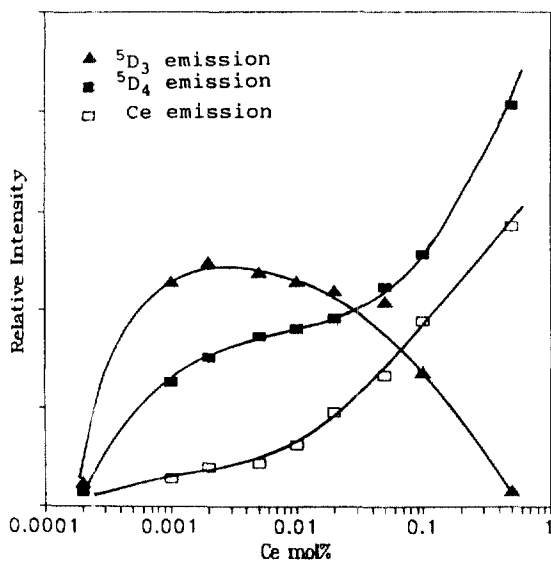
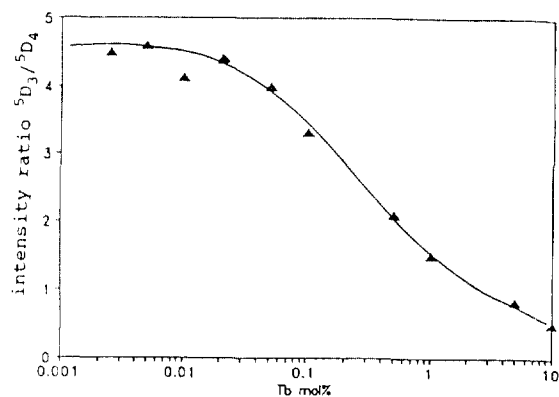
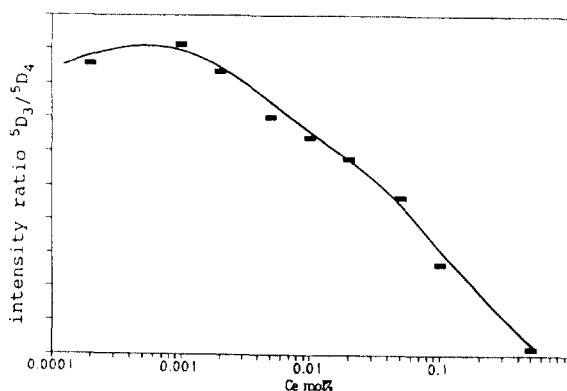


Fig. 8. Intensity of Tb^{3+} emission with Ce^{3+} concentration in LaOCl. Emissions of 5D_3 , 5D_4 and Ce were measured at 418, 545, 400nm respectively.



(a)



(b)

Fig. 9. Intensity ratio ($^5D_3/^5D_4$) vs. activator concentration.

(a) LaOCl: Tb, Tb = 0.002~10mol%

(b) LaOCl: Tb, Ce, Tb = 0.1mol%, Ce^{3+} = 0.005~0.5mol%

shows almost constant value but decreases at higher concentration of Tb³⁺ than 0.05mol% in the system doped with Tb³⁺, and increases at first time but decreases at higher concentration of Ce³⁺ than 0.005mol% in the codoped system. In the system doped only with Tb³⁺ as shown in Fig.9(a), the intensity ratio is almost constant but decreases at higher concentration of Tb³⁺ than 0.05mol%. This reduction can be explained to be caused by Cross Relaxation between Tb ions but does not give significant meaning at the low concentration. In the codoped system, in which the concentration of Tb³⁺ is fixed and that of Ce³⁺ is varied, the absolute intensity of ⁵D₃ and the ratio also increase but decrease, unexpectedly, at higher concentration of Ce³⁺ than 0.005mol% as shown in Fig.8 and 9(b). It has been well known that the absolute intensity and the ratio should not reduce by Cross Relaxation under the condition of a fixed concentration of Tb³⁺. It can be, therefore concluded that other energy loss mechanism for ⁵D₃ quenching should be involved except Cross Relaxation under the present experimental condition and that the excitation energy of ⁵D₃ of Tb³⁺ apparently move again (Back Transfer) to Ce³⁺ by Tb-Ce interaction.

This Back Transfer mechanism can be identified by the curvature of Ce³⁺ emission intensity curve in Fig. 8. The increasing rate of Ce³⁺ emission intensity increase at the concentration of 0.005mol%, at which the emission intensity of ⁵D₃ decrease. Otherwise, If there were only one directional transfer, the probability of energy loss would increase linearly with Ce concentration and the curve would be convex to upper. But in the present result in Fig. 8, the curve is convex to lower. This is another evidence of Back Transfer mechanism. The path of energy transfer is represented in Fig. 10 including Back Transfer, and in this mechanism Tb³⁺ may serve as a energy donor and an acceptor at different energy levels.

As conclusions, The excited energy absorbed by

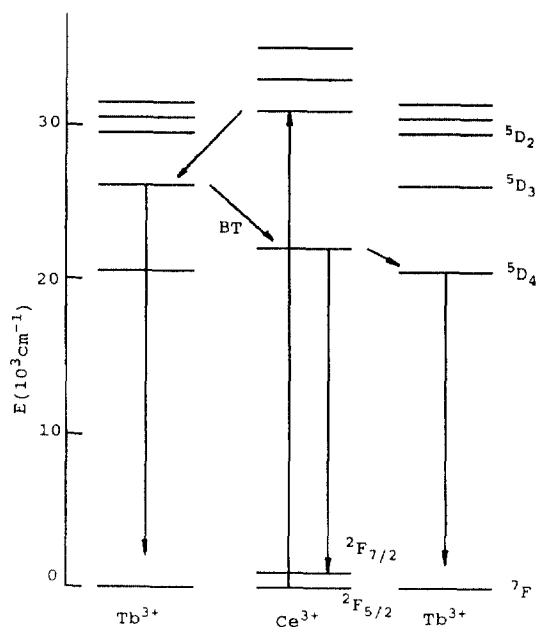


Fig. 10. Energy transfer scheme between Ce³⁺ and Tb³⁺ in LaOCl.

BT: back transfer process.

Ce³⁺ relaxes gradually and emits from itself or transfer to Tb³⁺ in the host codoped with Tb³⁺ and Ce³⁺. The transition from ⁵D₃ to ground state can be possible at low concentration of Ce³⁺, but the energy move to Ce³⁺ again (Back Transfer) and the intensity from ⁵D₃ therefore becomes weak. The energy Back-Transferred to low level of Ce³⁺ decays to ground state ²F_j of Ce³⁺ or moves to ⁵D₄ level of Tb³⁺. Therefore, the emission from ⁵D₃ increases as the emission from ⁵D₄ decrease. The relaxation of Tb³⁺ intermediated by Ce³⁺ is more effective than the cross relaxation of pure Tb³⁺

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