Photoreduction and Emission of Solid Europium(III) Chloride in KBr by Laser Irradiation at 308 nm

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The emission and transient absorption spectra of solid europium irradiated with laser light at 308 nm were measured. $EuCl_3 \cdot 6H_2O$ in a KBr disk was photoreduced to form excited Eu^{2+}, and the emission from excited Eu^{2+} was observed directly after a reduction of Eu^{3+}. Since Eu^{2+} was not stabilized in the KBr disk sample, it oxidized rapidly to form Eu^{3+}. From a discussion concerning the temperature dependence of the rate constants of the reduction and deexcitation, it is shown that the reduction rate increases at higher temperature.

We studied the lifetimes of the excited states of the f-f transitions and photochemical reactions of lanthanide compounds induced by f-d or charge transfer transitions in order to investigate element selective photochemical reactions of lanthanide elements by multiphotoexcitation of f-f transitions. The lanthanide elements have complicated optical spectra because of the 4f shell; their absorption and fluorescence properties have been studied by many workers.[1,2] Europium has unique properties in that it is exceptionally stable in the divalent state (besides the trivalent state), while most lanthanide elements are stable only in the trivalent state in solution.

The photochemical separation of lanthanide elements in solution has been studied by some workers. Since most of the lanthanide elements are stable in the trivalent state in a solution system, separation is initiated by stabilizing divalent lanthanides in solution. Eu^{2+} produced by photoreduction is stabilized using either SO_4^{2-}[3] or 18-crown-6 ether[4] for the separation.

The optical absorption, emission and Zeeman splittings have been studied for Eu^{2+} substituted in NaCl, KCl, and KBr crystals.[5,6] Divalent europium was prepared by chemical reduction, and was then doped in alkali halide crystals.

We report here on laser irradiation (308 nm) of solid trivalent europium chloride $EuCl_3 \cdot 6H_2O$ in KBr which was used to investigate the photoreduction of Eu^{3+} in a solid system and discuss the emission of Eu^{2+}. This emission from Eu^{2+} in a solid sample may be a useful method to detect two-step excitation through f-f levels.

Experimental

We employed the XeCl excimer-laser (Lambda Physik EMG201MSC) for the irradiation of ultra-violet light at 308 nm (output energy: 400 mJ pulse^{-1}, pulse width: 20 ns). The emissions at the desired delayed time after laser pulse irradiation were measured by a diode array multichannel detector (Princeton Instruments SMA) with a 120 nm wavelength width and a 50 ns detection time width. These signals were integrated several hundred times in order to obtain a time-resolved emission spectrum. We also employed a photomultiplier (Hamamatu R928), a monochromator (ISA HR-320) and a fast transient digitizer (Tektronix 7912HB) to detect a single emission signal at the wavelength induced by pulse irradiation.

For the detection of the transient absorption, the probe light from a pulsed high-pressure xenon flash lamp (Tokyo Instruments XF-150) traversed the sample at right angles to the excitation laser light. The transient absorbance at various wavelengths was measured with a photomultiplier placed in the analyzing beam behind the sample disk. In order to eliminate the emission of a sample by laser irradiation, the emission signal obtained without probing light was subtracted from the observed signal of the transmitted probe light with laser irradiation. The transient absorbance was calculated from this signal and the reference signal of probe light without laser irradiation. We employed a spectrometer (JASCO Ubest-30) to measure the standard UV-visible absorption spectra.

As a sample disk, $EuCl_3 \cdot 6H_2O$ was ground and mixed with KBr, and then pressed to form a 1 cm diameter disk. Thick samples ($EuCl_3 \cdot 6H_2O$:0.04 g, KBr:0.10 g) for emission measurements and thin samples ($EuCl_3 \cdot 6H_2O$:0.005 g, KBr: 0.10 g) used to transmit probe light for absorption measurements were employed. The laser light was slightly focussed by a convex lens (f=150 mm) and laser spot at the sample disk was 0.1 cm^2.

Results and Discussion

The time-resolved emission spectra induced by 308 nm irradiation was observed by an SMA detector (Figs. 1 and 2), accumulating the signals for 300 pulses for each spectrum. The change in the intensity of these signals at a wavelength were fitted by a single exponential curve in order to obtain the emission lifetimes. $EuCl_3$ has a broad absorption band assigned to either f-d or a charge-transfer band in the ultraviolet region. Upon irradiation of 308 nm light, a broad absorption band was excited, followed by deexcitation to a lower f-f transition level; sharp emissions from Eu^{3+} (assigned to the f-f transition) were observed (Fig. 1). These spectra were consistent with the emissions observed after a direct excitation of the f-f transition of Eu^{3+} ($^7F_0 \rightarrow {}^5D_2$) at 465 nm. The lifetimes of these transition, $^5D_1 \rightarrow {}^7F_j$ and $^5D_0 \rightarrow {}^7F_j$, are 6.9 and 120 μs,

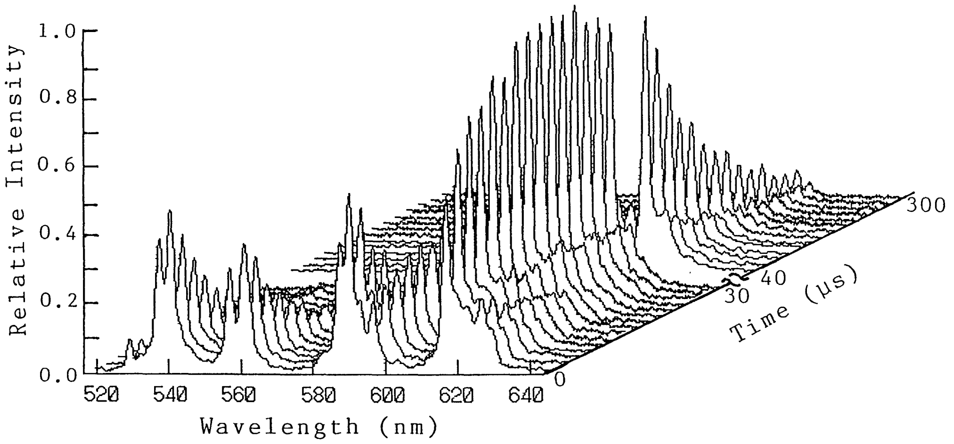

Fig. 1. The time-resolved emission spectra assigned to f-f transitions ($^5D_1$, $^5D_0 \rightarrow {}^7F_j$) of $EuCl_3 \cdot 6H_3O$ in KBr disk irradiated by 308 nm laser light.

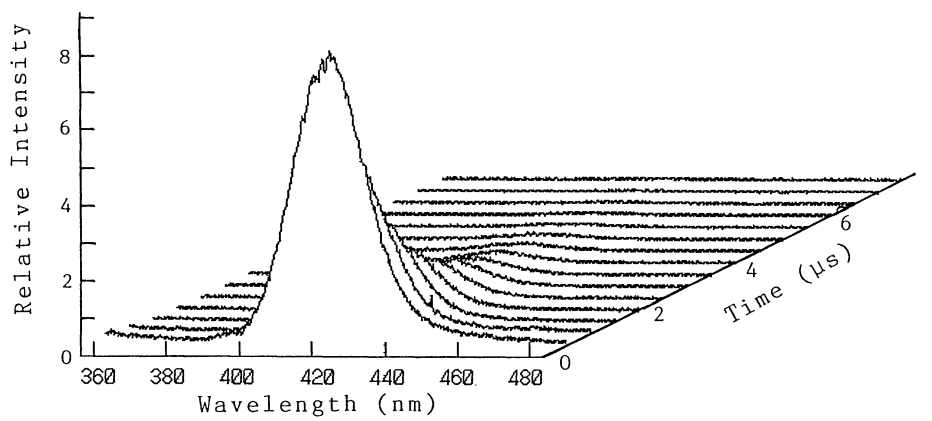

Fig. 2. The time-resolved emission spectra assigned to transition in Eu^{2+} ($4f^65d \rightarrow 4f^7$) by irradiating $EuCl_3 \cdot 6H_3O$ in KBr disk with 308 nm laser light.

respectively, and are the same as those obtained from 465 nm excitation. Besides the emission from f-f transitions, a broad intense emission band at 420 nm assigned to the transition of Eu^{2+} ($4f^65d \rightarrow 4f^7$) was observed (Fig. 2). The measured lifetime from this time-resolved emission spectra was 1.0 μs. When a disk sample of pure $EuCl_3 \cdot 6H_2O$ without KBr was irradiated by 308 nm laser light, the emissions due to the f-f transitions of Eu^{3+} were merely observed and the emission at 420 nm from Eu^{2+} was not observed. It thus seems that the KBr matrix temporarily donates an electrons to reduce $EuCl_3 \cdot 6H_2O$ in the KBr disk upon laser irradiation, and that the absorbed photon energy is transferred for both the reduction and fluorescence of the f-f transitions.

The standard absorption spectra of the disk sample was measured both before and after photoirradiation, and no change due to the production of Eu^{2+} was observed. Thus, photoreduced Eu^{2+} may not be stabilized in a KBr disk sample for a long time (the measuring time was shorter than 3 min). Also, the intensity of 420 nm emission during pulse-irradiation did not change, measured by accumulating the number of pulse-irradiations with a photomultiplier. Thus, photoreduced Eu^{2+} was not integrated but was oxidized to form Eu^{3+} rapidly, since electrons might not disperse or stabilize in a solid system. The reduction of Eu^{3+} and emission from Eu^{2+} was observed in a single 20 ns pulse.

The transient absorbance of Eu^{2+} produced by photoreduction was observed by a photomultiplier and transient digitizer at some wavelengths at room temperature (Fig. 3). The lifetimes of these signals were (1.0±0.2) μs, the same as for emission from Eu^{2+} at 420 nm. The produced Eu^{2+} may therefore be oxidized rapidly after deexcitation to the ground state. The intensity spectrum of this transient absorption signal is demonstrated in Fig. 4. This absorption spectrum corresponds to the absorption spectrum of Eu^{2+} given in the literature;[5,6] absorption was

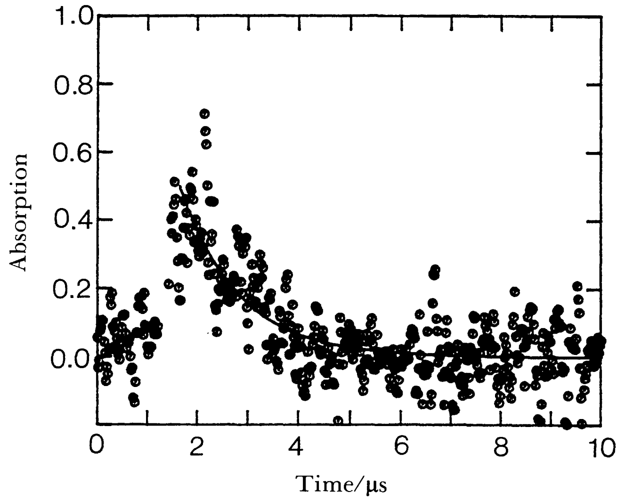

Fig. 3. The transient absorption at 340 nm of $EuCl_3 \cdot 6H_3O$ in KBr disk irradiated by 308 nm laser light.

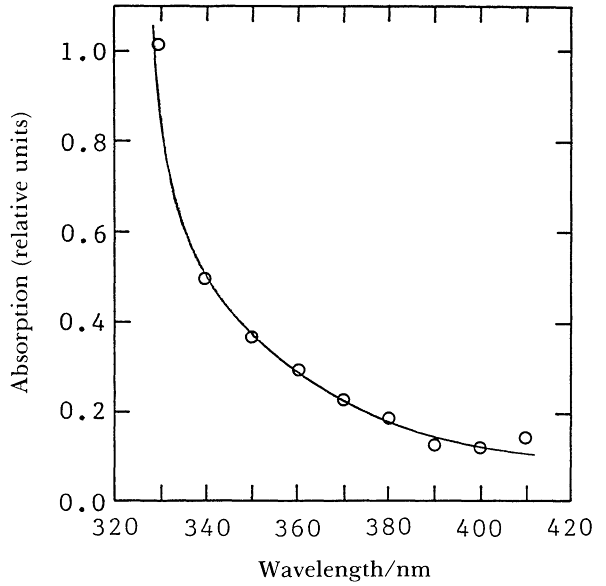

Fig. 4. The trasient absorption spectrum of $EuCl_3 \cdot 6H_2O$ in KBr disk irradiated by 308 nm laser light.

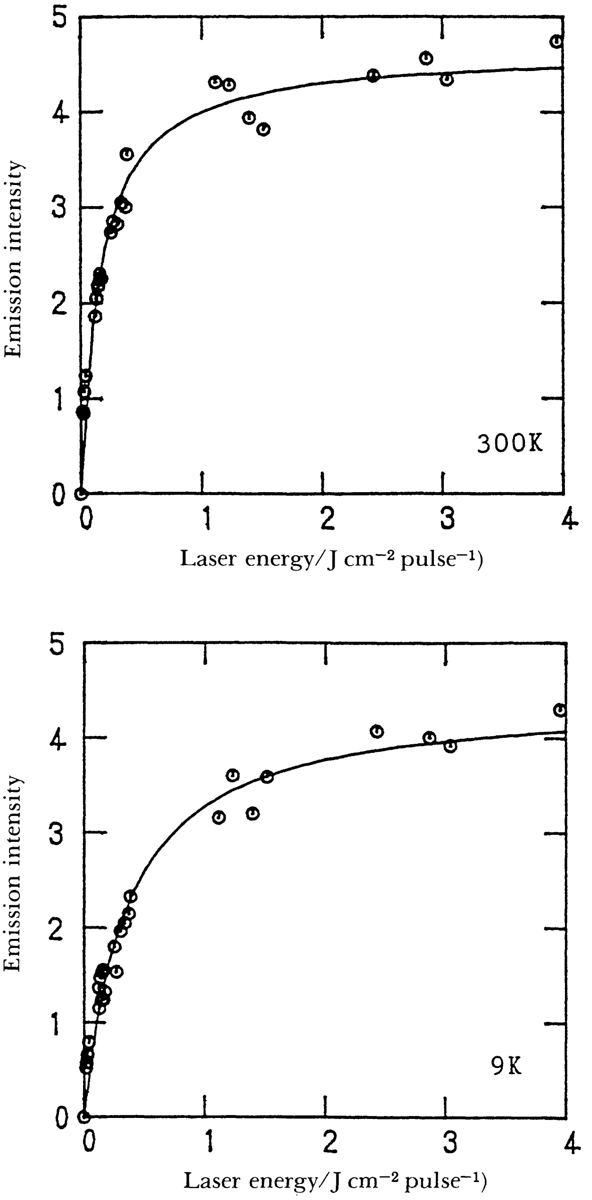

Fig. 5. The emission intensity at 420 nm and the irradiating laser energy (308 nm) of $EuCl_3 \cdot 6H_2O$ in KBr disk at 300 K and 9 K.

observed at shorter wavelengths than 410 nm, having maximum near 320 nm.

The production mechanism of excited Eu^{2+} that radiates fluorescence at 420 nm may estimated in two ways: 1) the excited Eu^{2+} is produced directly after the photoreduction of Eu^{3+} or 2) the ground state of Eu^{2+} produced by the photoreduction of Eu^{3+} is further excited. To examine which process actually takes place, we observed the relation between the laser energy and the emission intensity. The laser energy was varied by means of beam splitters and the emissions at 420 nm were detected by a photomultiplier at various laser intensities and temperatures. From the relationship between the laser energy and the emission intensity of Eu^{2+} (Fig. 5), the number of photons that induce emission from Eu^{2+} could be determined. From Fig. 5 a linear relation between the laser energy and the emission intensity of Eu^{2+} was observed at a lower laser energy, less than 0.5 J cm^{-2}-pulse^{-1}. Therefore, the reduction of Eu^{3+} and the emission of Eu^{2+} were induced by one photon absorption. At higher laser energy, the emission intensity saturates because of the rate constants of excitation and that deexcitations of Eu^{3+} become parallel.

To understand the relationship between the laser energy and the emission intensity of Eu^{2+}, we assumed a simplified energy diagram of reactions and emissions of this system, as demonstrated in Fig. 6. The levels are designated as follows: Level 1 is the ground state of Eu^{3+}; 2 is the excited f-d or charge-transfer state of Eu^{3+}; 3 is the fluorescence level of Eu^{3+}; 5 is the excited and fluorescence level of Eu^{2+}, assigned to $4f^65d$; and 4 is the ground state of Eu^{2+}, assigned to $4f^7$.

The mathematical treatment of the kinetics is simplified by assuming the existence of a steady state, as discussed by Maiman.[7] The transition probabilities are also indicated in Fig. 6: I is the irradiation laser energy; σ is the absorption cross section of Eu^{3+}; k_{21} is the radiationless deexcitation probability; k_{23} and k_{31} are the transition probabilities for radiationless and radiative deexcitation in Eu^{3+} transitions; k_{25} is the transition probability for reduction to the excited level of Eu^{2+} ($4f^65d$); k_{54} is the transition probability for the fluorescence of the excited level to the ground level of Eu^{2+}; and k_{41} is the transition probability of oxidation from the ground level of Eu^{2+} to Eu^{3+}. The real energetic scheme of f-f transition in Eu^{3+} may be complicated by many levels of f-f transitions: level 3, k_{23}, k_{31}, and k_{21} should separated into some components to illustrate actual emission spectra of f-f transition in Eu^{3+}. In order to discuss the emission of Eu^{2+} we simplified the f-f transitions, as shown in Fig. 6.

In terms of this model, the steady-state rate equations are:

$$\begin{aligned} dN_2/dt &= I\sigma N_1-(k_{21}+k_{23}+k_{25})N_2=0, \\ dN_3/dt &= k_{23}N_2-k_{31}N_3=0, \\ dN_4/dt &= k_{54}N_5-k_{41}N_4=0, \\ dN_5/dt &= k_{25}N_2-k_{54}N_5=0, \end{aligned}$$

and

$$N_0=N_1+N_2+N_3+N_4+N_5,$$

where N_i is the population of the ith state and N_0 is the total concentration.

I and N_5 correspond to the laser energy and the emission intensity of Eu^{2+}, respectively. The steady-state solution to this set of equations is given by

$$N_5=(k_{25}N_0/(k_{54}A))/(k_2/(A\sigma I)+1),$$

where $k_2=k_{21}+k_{23}+k_{25}$ and $A=1+k_{23}/k_{31}+k_{23}/k_{41}+k_{25}/k_{54}$. The observed data were fitted by a computer least-square method which varied two parameters: $a=k_{25}N_0/(k_{54}A)$ and $b=k_2/(A\sigma)$. Here, a represents the emission intensity at the saturated region, and b represents the gradient of the curve at the region in which the emission intensity and laser energy have a linear relationship. The fitted curves are also indicated in Fig. 5; this model explains these data very well.

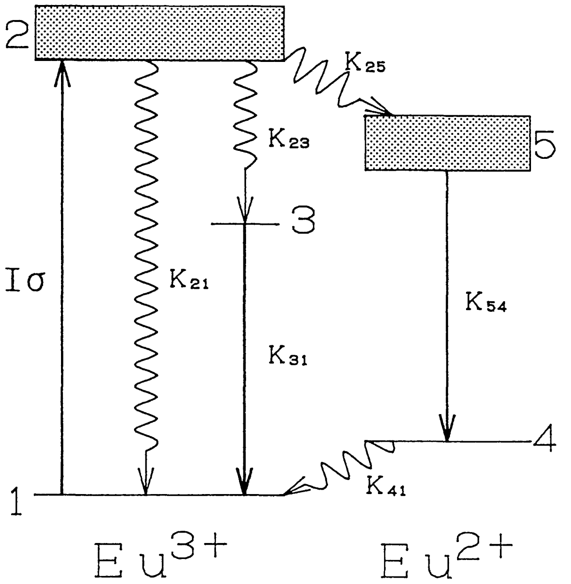

Fig. 6. The energy diagram of the system.

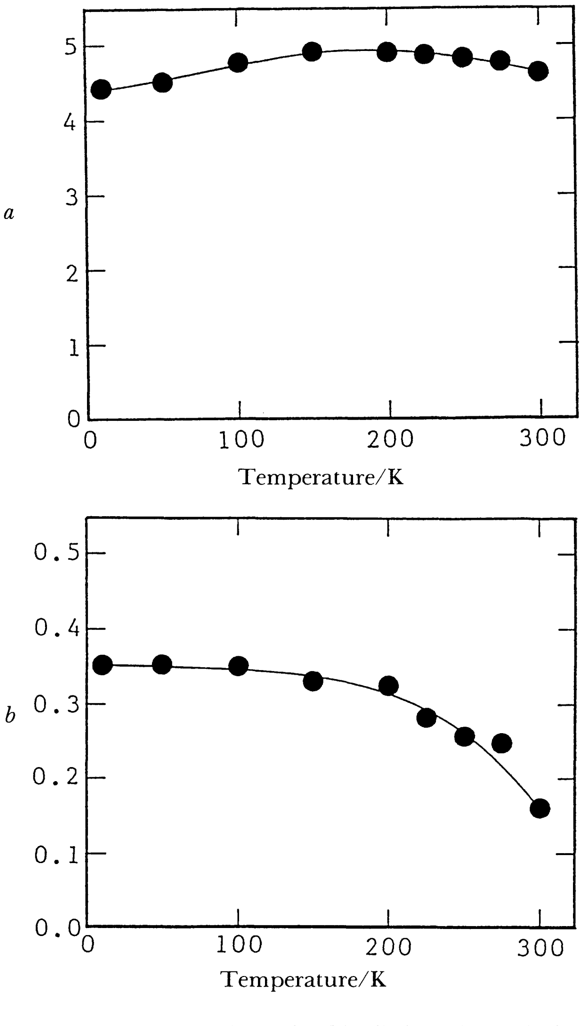

Fig. 7. The a and b obtained by fitting of the relation between the emission intensity at 420 nm and the laser energy of various temperature.

This relation was observed in various temperatures from 300 K to 9 K and the spectrum at each temperature was fitted by the formula. The lifetime of this emission at 420 nm was (1.0±0.2) μs and was independent of both the excitation intensity and temperature. The rate constants of the reduction or some transitions may be influenced by the temperature, and the relation between irradiation intensity and emission intensity may change upon varying the temperature. The obtained a and b in the temperature range 9 K to 300 K are given in Fig. 7. While a has little temperature dependence, b become smaller at higher temperature.

Considering the value k_{54} ($10^6\ \mathrm{s}^{-1}$), N_0 and σ are constant and independent of the temperature; the value $a/b=k_{25}N_0\sigma/(k_2k_{54})$ indicates the k_{25}/k_2 which corresponds to the rate of reduction to the total deexcitation process in excited Eu^{3+}. Though the absolute value could not be obtained from this measurement, the relative rate was obtained. From the temperature dependence of a/b, the probability to reduce excited Eu^{3+} became larger at higher temperatures.

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