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Photoreduction of Solid Europium Chloride in KBr by Visible Two-photon Excitation

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Solid $EuCl_3 \cdot 6H_2O$ in KBr disk was irradiated by visible laser light ranging from 455 nm to 475 nm condensed by lens and the time-resolved emission spectra were measured. Reduction of Eu^{3+} and emission from Eu^{2+} were observed by simultaneous two-photon absorption in solid sample.

We have studied photochemical reactions of lanthanide compounds induced by irradiation at f-d or charge transfer absorption and measured emission spectra from f-f transitions to investigate element-selective photochemical reactions induced by multiphoton excitation.[1)] Two-photon excitation of Eu^{2+} ions in CaF_2, SrF_2 and alkali halide crystals has been studied [2-6)] to investigate the aggregation kinetics of Eu^{2+} in single crystals. Two-photon luminescence excitation spectra of Eu^{3+} in CaF_2 and YAG were measured.[7,8)] We have reported that Eu^{3+} was reduced to form excited Eu^{2+} and the emission from Eu^{2+} ($4f^65d \rightarrow 4f^7$; 420 nm) was observed by irradiating $EuCl_3 \cdot 6H_2O$ in KBr sample with ultraviolet light (308 nm).[1)] In this letter, we report that Eu^{3+} is also reduced to form Eu^{2+} by two-photon excitation with visible laser light.

We employed the pulsed laser for irradiation; the dye-laser (FL3002 Lambda Physik; coumarin-2-dye) pumped with excimer-laser (EMG201MSC Lambda Physik pulse-width; 20 ns). The direct output beam of the laser was of 2 mm diameter and its energy was 0.3-3.2 mJ/pulse depending on wavelength. For detection, a diode array multichannel detector (SMA Princeton Instruments) and a photomultiplier (R928 Hamamatu) connected to a fast transient digitizer (7812HB Tektronix) were employed.

$EuCl_3 \cdot 6H_2O$ 0.04 g was ground and mixed with KBr 0.10 g, and then pressed to form a disk with 1 cm diameter. When the sample was irradiated by several pulses of the intense laser light, it became damaged by ablation. The sample disk was rotated (1 rotation/s) continuously to be irradiated on the new surface.

By irradiating solid $EuCl_3 \cdot 6H_2O$ in KBr with visible light beam (455-475 nm) without focusing, one-photon excitations and emissions assigned to f-f transitions of Eu^{3+} (520-640 nm) were observed. In order to observe multiphoton absorption, the sample was irradiated by visible laser light condensed by lens; the intensity of the

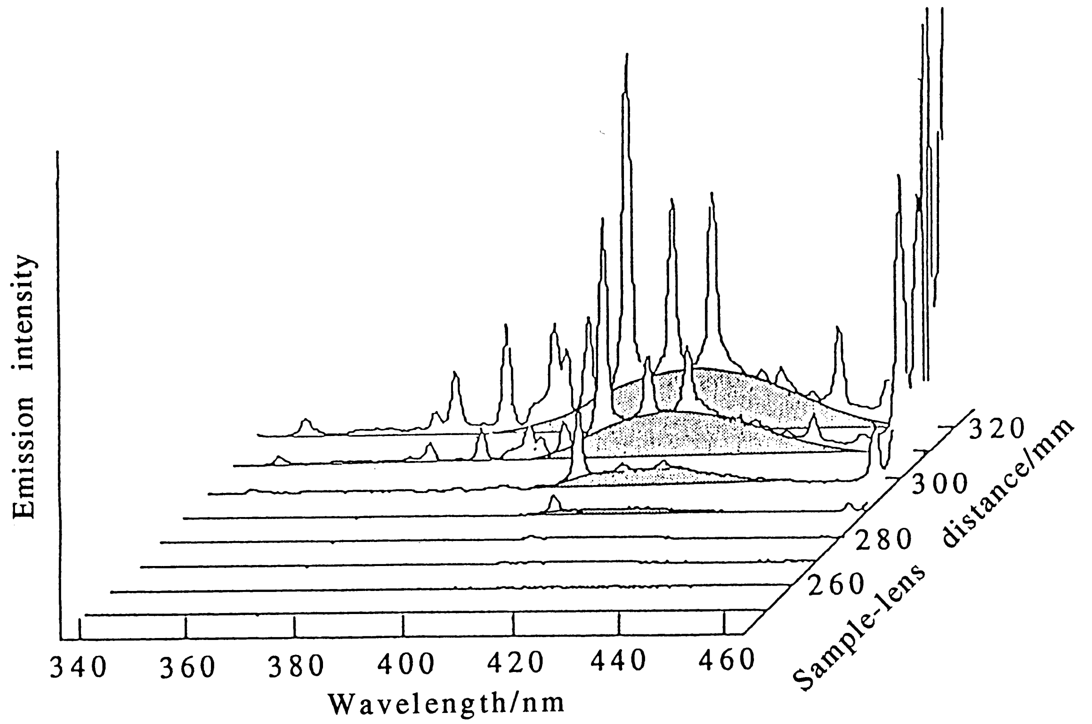

Fig. 1. The emission spectra of $EuCl_3 \cdot 6H_2O$ in KBr irradiated by 465 nm laser light with varying distance between sample and convex lens (f=330 mm); measured at 2 μs (gate time: 100 ns) after the laser irradiation. The marked area corresponds to the emission of Eu^{2+}.

irradiating light was adjusted by varying the distance (x) between lens and sample. We employed the convex lens (f=330 mm) for focusing onto $EuCl_3.6H_2O$ in KBr and detected the emissions (Fig. 1). The emission assigned to f-f transition of Eu^{3+} (520-640 nm) was observed by excitation of weaker light (x < 250 mm). When the distance between lens and sample was close to the focal distance (x ≥ 250 mm), the broad emission at 420 nm, assigned to the emission of Eu^{2+} ($4f^65d \rightarrow 4f^7$), was observed. This emission was also observed by irradiation at 308 nm.[1] In our previous report, it was proved that $EuCl_3 \cdot 6H_2O$ in KBr disk was photoreduced by 308 nm laser light to form excited Eu^{2+} and the emission from excited Eu^{2+} was observed directly after reduction of Eu^{3+}. Eu^{2+} was not stabilized in the KBr disk sample and was oxidized rapidly to form Eu^{3+}. Here, it is demonstrated that the visible multiphoton excitation also induces the emission from Eu^{2+} following the reduction of Eu^{3+}. When the distance between lens and sample was very close to the focus (x ≥ 290 mm), the sharp emission lines were observed. These emissions were assigned to atomic spectra of Eu and K. A pure KBr disk and a pure $EuCl_3 \cdot 6H_2O$ disk were also irradiated by condensed light. Emissions assigned to atomic spectra of K (KI; 344.6, 344.7, 404.4, 404.7 nm)

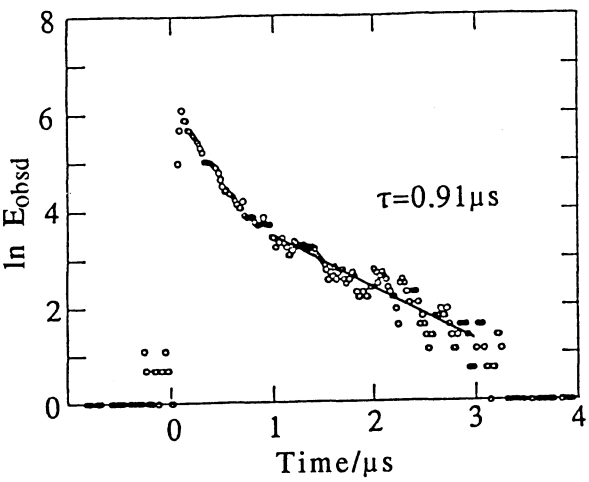

Fig. 2. The emission intensity at 416 nm from $EuCl_3 \cdot 6H_2O$ in KBr irradiated by condensed 465 nm laser light (solid line indicates the decay curve of lifetime of 0.91 μs).

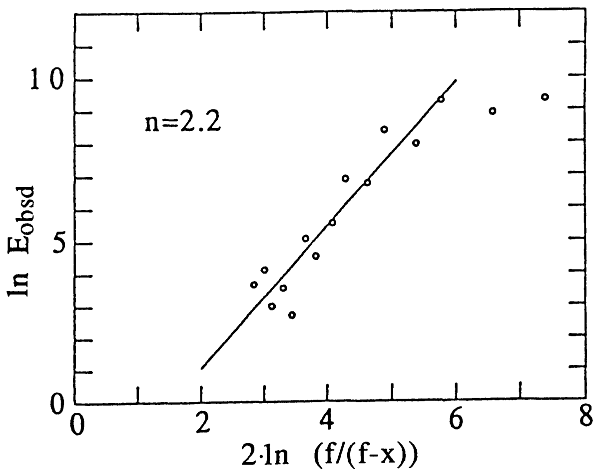

Fig. 3. The emission intensity (E_{obsd}) at 416 nm from $EuCl_3 \cdot 6H_2O$ in KBr which is dependent on the distance (x) between lens and sample (irradiated by condensed 465 nm laser light; f=330 mm).

and Eu (EuI; 459.4, 462.7, 466.2 nm and EuII; 382.0, 390.7, 393.1, 397.2, 413.0, 420.5 nm) were observed. The broad emission centered at 420 nm was not observed in these pure samples. The solid sample was sputtered by ablation and the vaporized atoms or molecules were further excited to emit atomic spectra. Also was found the continuum spectrum with short lifetime due to the plasma state produced by laser ablation.

Time dependence of these emissions was measured by photomultiplier. Emission at 416 nm which is assigned to Eu^{2+} ($4f^65d \rightarrow 4f^7$) had the lifetime of 0.9 μs. This was obtained from the decay curve shown in Fig. 2 after the fast component due to the continuum emission of the plasma state. This is in good accordance with the lifetime of 1.0 μs of the emission caused by the 308 nm irradiation.[1] Time dependence of the emission intensities at 459.4 nm (EuI) and 404.4 nm (KI) was quite different from that of 416 nm (Eu^{2+}). The emission due to the plasma state disappeared rapidly (< 0.2 μs), and the atomic spectra grew slightly (≈ 1 μs) and then decayed slowly (1-2 μs).

As the diameter of laser beam at sample surface is adjusted by lens, the relationship between observed intensity and the distance is indicated as $E_{obsd}=k \cdot I_0^n \cdot (f/(f-x))^{2n}$,where E_{obsd} is observed intensity of emission, I_0 is the intensity of direct output of laser-light, f is the focal distance of the lens, x is the distance between sample and lens, k is the constant and n is the number of the photon needed to induce the emission. The laser intensity at sample is $I_0 \cdot (f/(f-x))^2$. We could determine the number n from the relationship between E_{obsd} and x. It can be seen that the emission from Eu^{2+} is induced with two photons (n=2) from the experimental results (Fig. 3), and that the excited Eu^{2+} is produced directly after the photoreduction of Eu^{3+}. The atomic emissions of Eu or K were analysed to have larger number of photons (about n=3). The emission from Eu^{2+} was observed with light not too strong to cause ablation (250 ≤ x ≤ 270 mm).

It was also examined that the emission from Eu^{2+} depended on the wavelength of irradiation light. Considering the emission from Eu^{2+} is caused by two-photon absorption, the observed emission intensity was normalized with the laser intensity (Fig. 4). The stronger emission was observed with the shorter wavelength. While Eu^{3+} has the absorption at 465 nm corresponding to $^7F_0 \rightarrow {}^5D_2$ transition, the emission caused by 465 nm irradiation was not stronger compared to other wavelengths examined. Therefore, the two-photon excitation observed in the present study may be a simultaneous transition having no intermediate stable level.

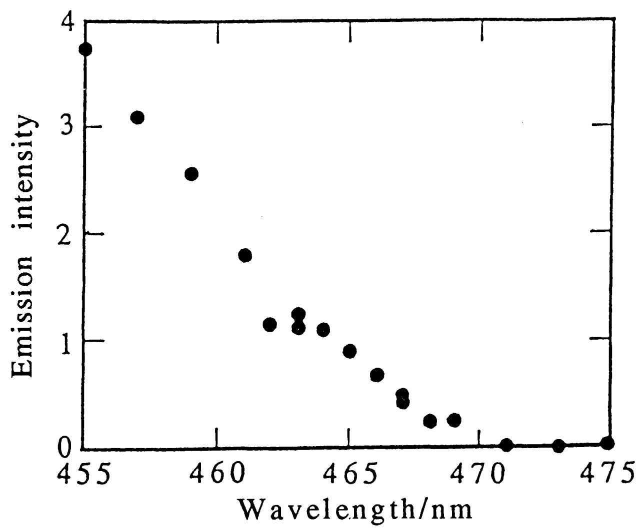

Fig. 4. The emission intensity of Eu^{2+} at 416nm depending on laser wavelength (455-475 nm); the distance between lens (f=330 mm) and sample is 280 mm.

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