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# Reduction of $\text{Sm}^{3+}$ to $\text{Sm}^{2+}$ by an Intense Femtosecond Laser Pulse in Solution

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Samarium 3+ ions in methanol were found to be reduced to the corresponding 2+ ions upon irradiation with intense femtosecond laser pulses. The reduction was observed at both pulses with central wavelengths of 403 nm converted from an 800 fs fundamental pulse and 800 nm with a duration of 43 fs. When the laser wavelength was tuned to the 4f–4f absorption at 403 nm corresponding to the  ${}^6\text{P}_{3/2} \leftarrow {}^6\text{H}_{5/2}$  transition, the reduction occurred by multiphoton absorption, presumably due to reaching the deep charge transfer state. In the case of excitation by 800 nm pulses of the fundamental wavelength of the Ti:sapphire laser, the reduction is considered to occur via solvent ionization followed by electron capture by  $\text{Sm}^{3+}$ . The product  $\text{Sm}^{2+}$  was detected by its fluorescence, which was observed for the first time in solution and showed a broad spectrum peak around 750 nm with a quantum yield of 0.050 in methanol in the presence of 15-crown-5-ether.

## 1. Introduction

Lanthanide and actinide ions undergo redox reactions upon irradiation with UV light,  $\gamma$ -rays, and, as observed recently, ultrashort laser pulses in solution<sup>1–10</sup> and in the solid phase.<sup>11–18</sup> The lanthanide ions have 4f–4f (ff) transitions in UV–vis–IR regions with atomic-like line spectra because f-orbital electrons have high electron densities near the nuclei and have weak interactions with the surrounding solvent. As a result, the 4f electronic excited states show low reaction activities; in fact, no photoredox reaction has been reported from the lowest emissive states in the 4f electronic excited state in solution. Some of the lanthanide ions have a charge transfer (CT) state in the deep UV region, and the CT state is photochemically active.  $\text{Ce}^{3+}$ ,  $\text{Eu}^{3+}$ , and  $\text{Sm}^{3+}$  show redox reactions to become  $\text{Ce}^{4+}$ ,  $\text{Eu}^{2+}$ , and  $\text{Sm}^{2+}$  in solution by one-photon UV light irradiation.<sup>1,9,10</sup> Until the present, there have been three methods to induce the photoreaction of  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ . The first one is excitation to the CT state by one-photon absorption, and the reaction quantum yields are determined to be relatively high (0.1–0.9) dependent on the solvent and the excitation wavelengths.<sup>2,3</sup> The photoreactive CT state could be reached by two sequentially absorbed photons via an excited state through the ff transitions. The idea of two-photon chemistry for the redox reactions was proposed in 1979.<sup>9</sup> The multiphoton reaction is the second method, the first example of which in solution was  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ .<sup>4,5</sup> The first laser light was tuned to one of the ff transitions  ${}^5\text{L}_6 \leftarrow {}^7\text{F}_0$  (394 nm), and the second and/or third photon was pumped up to the CT states using nano- and picosecond laser pulses. One of the important findings is that a short duration pulse excitation dramatically improves the reaction efficiency. A new reaction scheme as a third method was recently achieved by focused femtosecond laser pulses at a nonresonant wave-

length.<sup>6</sup> The scheme is explained in terms of a reduction to  $\text{Eu}^{2+}$  in response to solvent ionization, followed by electron capture by  $\text{Eu}^{3+}$ .

Several questions have emerged from the reduction of  $\text{Eu}^{3+}$  by laser pulses with a short duration. (i) Some other lanthanide ions should show similar reactions. What are they, and what are the physical and chemical requirements to induce the two- or three-photon redox reactions? (ii) Why is the femtosecond pulse effective? The lowest emissive state of  $\text{Eu}^{3+}$  has a lifetime longer than 100  $\mu\text{s}$ . The efficient reaction in response to short duration pulses suggests that the intermediate is not the emissive state. (iii) Two-photon excitation should be sufficient to reach the reactive CT state when the laser wavelength is around 400 nm. However, the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reaction by a short duration pulse seemed to require three photons. (iv) Solvent ionization easily occurs in the case of femtosecond pulse excitation. The electron is captured by  $\text{Eu}^{3+}$ , and  $\text{Eu}^{2+}$  is produced. How can we distinguish the multiphoton reaction via a resonant level from the solvent ionization followed by  $\text{Eu}^{2+}$  formation? (v) The resonant level can be reached by two-photon absorption of 800 nm pulses. Could several photons reach the CT level leading to  $\text{Eu}^{2+}$ ?

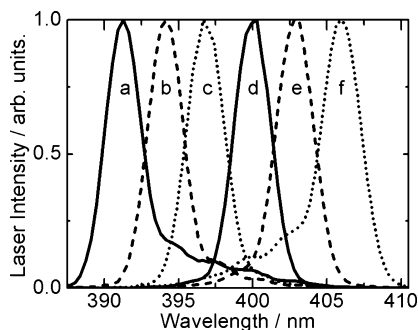
As an answer to the first question, we studied the  $\text{Sm}^{3+} \rightarrow \text{Sm}^{2+}$  reduction. The same three routes of one-UV-photon excitation, resonant multiphoton excitation, and solvent ionization are expected; in fact, the formation of  $\text{Sm}^{2+}$  followed by CT band one-photon excitation has been observed in the presence of crown ether.<sup>7,8</sup> We report herein the formation of  $\text{Sm}^{2+}$  in solution by the second and third routes in response to irradiation with femtosecond pulses at two different wavelengths. Excitation of the resonance of the ff transition at 403 nm is found to produce  $\text{Sm}^{2+}$  in solution via multiphoton absorption. The excitation by pulses at a laser wavelength of 800 nm, which corresponds to an isolated resonance of the system with regard to the electronic transitions, results in the formation of  $\text{Sm}^{2+}$ . An important finding is that  $\text{Sm}^{2+}$  emits fluorescence in methanol solution with reasonable quantum yields in the

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**Figure 1.** Spectra of the second harmonics of a Ti:sapphire laser. The second harmonic wavelengths were tuned by changing the relative crystal angle  $-9$  to  $+6^\circ$ ; correspondingly, the central wavelengths were changed from (a) ( $-9^\circ$ , 391 nm), (b) ( $-6^\circ$ , 394), (c) ( $-3^\circ$ , 397), (d) ( $0^\circ$ , 400), (e) ( $3^\circ$ , 403), and (f) ( $6^\circ$ , 406).

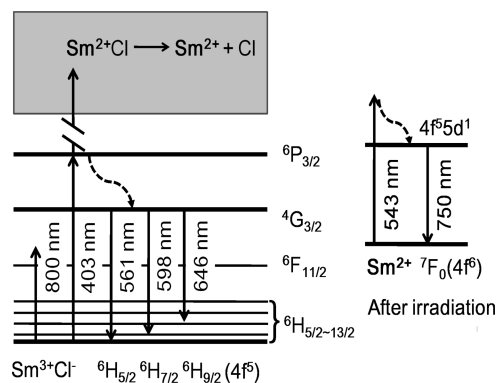
presence of crown ether. The fluorescence makes detection of the  $\text{Sm}^{2+}$  product easy and reliable. A discussion of the above questions and the influence of crown ether on the fluorescence properties of  $\text{Sm}^{2+}$  fluorescence are presented herein.

The photochemical reactions of lanthanide ions with ff transitions in solution are interesting both from a technological perspective and with regard to practical application.  $\text{Ln}^{3+}$  can be selectively excited because of the narrow ff absorption spectra. The redox reactions via the 4f excited state by the second photon could be utilized for purification and separation. These reactions would occur for actinide ions with 5f electrons and are expected to be utilized for nuclear reprocessing.<sup>5,9</sup>

## 2. Experimental Section

A linearly polarized femtosecond laser pulse with a central wavelength of 800 nm was delivered from a Ti:sapphire laser system Alpha 100/XS, Thales Laser, at a repetition rate of 100 Hz. The energy was reduced to less than 0.5 mJ/pulse. The transform-limited pulse had a duration of 43 fs. The pulse width was measured with a single-shot autocorrelator (Thales, TAIGA), and the total pulse energy was measured with a power meter (Gentec eo, PS-310B).

The second harmonics were generated by passing through a 0.1 cm BBO crystal. The spectra of the harmonics are shown in Figure 1. The central wavelength was tuned by changing the crystal angle  $\varphi$  from  $-9$  to  $+6^\circ$ , maintaining the angle  $\theta$  fixed, where the output at 400 nm was the maximum; correspondingly, the second harmonic wavelengths were changed from 391 to 406 nm. The band widths of fwhm of the second harmonics were approximately 3 nm with a shape slightly distorted from the Gaussian at 400 nm. When the central wavelengths were 391 or 406 nm, the spectra broadened to the long or short wavelength sides, respectively. The pulse duration of the 800 nm pulse was intentionally elongated by a programmable dispersive filter (AOPDF, Dazzler, Fastlite) to a 800 fs positively chirped and temporally trapezoidal pulse before converting it to the second harmonic. A plano-convex lens with a focal length of 100 mm was used to focus the laser beam into a sample cell located at the focal point. The focused diameter was assumed to be 60  $\mu\text{m}$  in diameter, which was based on the hole size on solid samples ( $\text{C}_{60}$ ) created by irradiation with the laser system using 800 nm pulses. The cell contained 0.16  $\text{cm}^3$   $\text{Sm}^{3+}$  solution in a 2 (width)  $\times$  4 (depth)  $\times$  20 (height)  $\text{mm}^3$  quartz cell. The  $\text{Sm}^{2+}$  product was detected by its fluorescence in a direction perpendicular to the incident laser after femtosecond laser 30000 shots irradiation, using an exciting light source of a green 543.5 nm He–Ne laser (05LPL MELLES GRIOT). A spectrophoto-



**Figure 2.** Reaction schemes of  $\text{Sm}^{3+}$  to  $\text{Sm}^{2+}$  for the case of resonant excitation (403 nm) and the monitoring scheme of products of  $\text{Sm}^{2+}$  after femtosecond pulse irradiation using their fluorescence. The upward arrows indicate excitation of the laser wavelengths, and downward ones are emission peaks of  $\text{Sm}^{3+}$  and  $\text{Sm}^{2+}$  ions. The dotted curves indicate internal conversion to the emission states. The upper gray area is the charge transfer state, where  $\text{Sm}^{3+}$  is thought to be reduced to  $\text{Sm}^{2+}$ . A green 543.5 nm He–Ne laser is used to excite the  $\text{Sm}^{2+}$ .

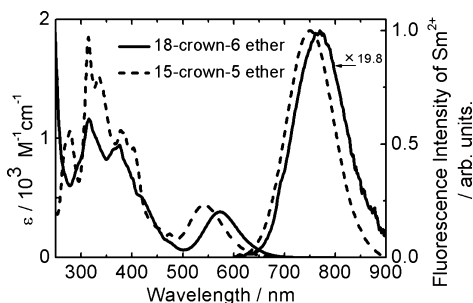
meter (USB2000, Ocean Optics, uncorrected) was used to measure the fluorescence with a typical spectral resolution of a few nanometers. The  $\text{Sm}^{2+}$  concentrations after laser irradiation were estimated by the absorption, assuming a molar extinction coefficient absorption coefficient of 400  $\text{M}^{-1} \text{cm}^{-1}$  at the peak of 545 nm.<sup>19</sup>

A KrF laser (248 nm, EMG201, Lambda Physik) was used to prepare  $\text{Sm}^{2+}$  ions in solution for fluorescence studies. Fluorescence spectra were measured with a spectrofluorometer (JASCO FP-6600, corrected), and the lifetimes were measured using a nitrogen laser (KEN810 Ushyo, pulse duration of  $<1$  ns).  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  (Aldrich, 99.99%), methanol (Nacalai, fluorescent grade), 18-crown-6-ether (18C6), 15-crown-5-ether (15C5) (Tokyo Kasei,  $>97\%$ ), and 12-crown-4-ether (12C4) (Tokyo Kasei,  $>97\%$ ) were used without further purification. The solution was degassed to avoid the oxidation of  $\text{Sm}^{2+}$  by dissolved oxygen.

## 3. Results

**3.1. Laser Excitation Schemes of  $\text{Sm}^{3+}$  and  $\text{Sm}^{2+}$  Fluorescence.** The energy levels of  $\text{Sm}^{3+}$  and  $\text{Sm}^{2+}$  and the excitation wavelengths are shown in Figure 2. The energy gap between the luminescence level of  $^4\text{G}_{3/2}$  and the ground state of  $^6\text{H}_{5/2}$  is approximately 17 800  $\text{cm}^{-1}$  (561 nm in  $\text{H}_2\text{O}$ ), and the highest nonemissive state of  $^6\text{F}_{11/2}$  is 10 600  $\text{cm}^{-1}$  (942 nm in glass) above the ground state; spectral shifts of several nanometers can be seen in different media.<sup>20,21</sup> The fundamental wavelength of 800 nm of a Ti:sapphire laser cannot match any excited electronic levels of  $\text{Sm}^{3+}$  ion and is therefore referred to herein as a nonresonant wavelength of the system. The second harmonics of a Ti:sapphire laser can be tuned by tilting the BBO crystal to the 403 nm transition, which is the central wavelength of the ff transitions of  $\text{Sm}^{3+}$  ion with the highest molar extinction coefficient of 3.3  $\text{M}^{-1} \text{cm}^{-1}$  in the visible region in solution. Several levels overlap at the wavelength, and the most probable candidate is the  $^6\text{P}_{3/2} \rightarrow ^6\text{H}_{5/2}$  transition.<sup>17</sup>  $\text{Sm}^{3+}\text{Cl}^-$  is assumed for the CT band from chloride ion to the metal ion and shows an absorption peak at 220 nm starting at 265 nm.<sup>22</sup> The ground state of  $\text{Sm}^{2+}$  in acidic solution is approximately 1.55 eV above the ground state of the  $\text{Sm}^{3+}$ .

The fluorescence of  $\text{Sm}^{2+}$  in solution is reported for the first time in this paper and is assignable to the broad  $5d \rightarrow 4f$  transition.  $\text{Sm}^{2+}$  solution was prepared by the irradiation



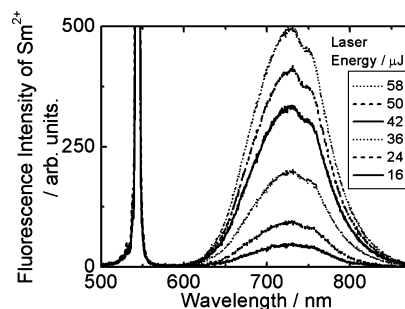
**Figure 3.** Absorption (the first absorption band around 550 nm) and fluorescence spectra (around 750 nm) of  $\text{Sm}^{2+}$  in methanol in the presence of 0.1 M 15-crown-5-ether and 18-crown-6-ether. Fluorescence quantum yields are 0.050 and 0.00083, respectively.

of 0.01 M  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  with 0.1 M 15C5 in methanol with a KrF laser operated at a 50 mJ/pulse, 10 Hz for 10 min. The irradiation wavelength at 248 nm corresponds to the long wavelength edge of the charge transfer band peak at 220 nm.  $\text{Sm}^{2+}$  formation by this method was visually recognized by the color change from colorless to pink in the case of the 15C5 system, and a formation quantum yield of 0.23 has been reported by some of the present authors for the case of a 18C6 system.<sup>8</sup> The absorption spectra of  $\text{Sm}^{2+}$  are available in the literature.<sup>18,19</sup>  $\gamma$ -Ray irradiation and chemical preparation can create divalent lanthanide ions, including  $\text{Sm}^{2+}$ , in solids<sup>18</sup> and in solution,<sup>19</sup> respectively.

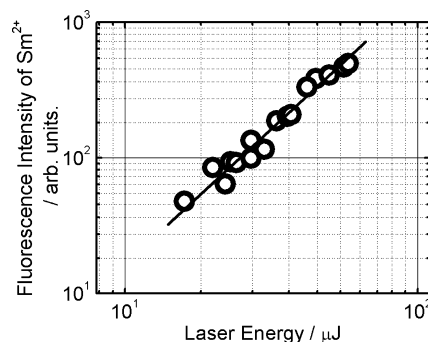
Under the assumption that the molar extinction coefficient of  $400 \text{ M}^{-1} \text{ cm}^{-1}$  at 545 nm in the present system is the same as that at 555 nm in tetrahydrofuran of chemically prepared  $\text{Sm}^{2+}$ ,<sup>19</sup> the concentrations were evaluated to be on the order of  $1 \times 10^{-3} \text{ M}$  for the case shown in Figure 3. The origin of the  $\text{Sm}^{2+}$  fluorescence peaks around 750 nm appears to be the  $5d \rightarrow 4f$  transition, with the fluorescence being the mirror image of the broad absorption bands around 550 nm.  $\text{Sm}^{2+}$  fluorescence quantum yields are 0.050 with a lifetime of  $4.1 \mu\text{s}$  in the presence of 15C5 and 0.00083 with a lifetime of 15 ns in the presence of 18C6. The low radiative transition rates can be derived for  $\text{Sm}^{2+}$  fluorescence and are discussed later. No absorption change nor emission were observed in the crown ether-free solution by irradiation with a 248 nm laser. New absorption due to  $\text{Sm}^{2+}$  and the emission were just barely recognized in the presence of 12C4. Fluorescence of  $\text{Sm}^{2+}$  in solid has been reported elsewhere,<sup>11–17</sup> and the  $\text{Sm}^{2+} \text{ ff } ^5\text{D}_0 \rightarrow ^7\text{F}_n$  transitions are seen at 685, 700, and 725 nm with sharp spectral features. A broad band peak at 700 nm is seen in the background of the ff spiky spectra and can be assigned to the  $5d \rightarrow 4f$  fluorescence.<sup>16</sup> As in Figure 3, there is no spiky fluorescence peak; i.e., no detectable intensity due to  $\text{Sm}^{2+} \text{ ff } ^5\text{D}_0 \rightarrow ^7\text{F}_n$  transition was seen in the 700 nm region, probably due to the low fluorescence quantum yields of the ff  $\text{Sm}^{2+}$  transition in solution.

It has been known that the  $4f \rightarrow 5d$  absorption and  $5d \rightarrow 4f$  fluorescence properties are affected by media for some lanthanide ions like  $\text{Ce}^{4+}$  and  $\text{Eu}^{2+}$ .<sup>23,24</sup>  $\text{Eu}^{2+}$  salts and the solution can be treated under normal ambient conditions, and the fluorescence properties have been studied comprehensively in a variety of solvents with/without various crown ethers.<sup>23</sup> The  $\text{Eu}^{2+}$  absorption and fluorescence properties in solution are a good criterion, and those of  $\text{Sm}^{2+}$  are discussed later.

**3.2.  $\text{Sm}^{2+}$  Formation by Femtosecond Pulse Excitation with a Resonant Wavelength of 403 nm.** Methanol solutions of  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  with 15C5 were irradiated by a pulse at a central wavelength of 403 nm corresponding to the ff transition of  $^6\text{P}_{3/2}$



**Figure 4.** Fluorescence after irradiating methanol solution of 0.04 M  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  with 0.2 M 15-crown-5-ether. Samples were irradiated by pulses at a central wavelength of 403 nm corresponding to the transition of  $^6\text{P}_{3/2} \leftarrow ^6\text{H}_{5/2}$  with an 800 fs pulse at 100 Hz for 5 min with laser energy from 0 to 58  $\mu\text{J}/\text{pulse}$ . The broad emission is due to the  $\text{Sm}^{2+}$  fluorescence. Signals at 543.5 nm are scattered lights of a monitoring He–Ne laser.

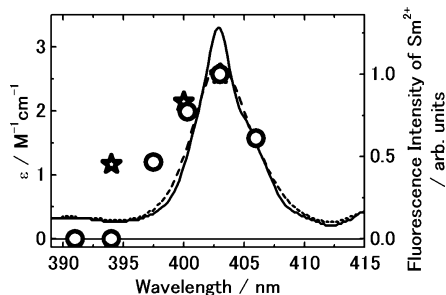


**Figure 5.**  $\text{Sm}^{2+}$  fluorescence intensity increases nonlinearly with increases in the irradiation energy with a 403 nm 800 fs pulse in the pulse energy range from 16–63  $\mu\text{J}/\text{pulse}$ . The solid line of the log–log plots has a slope of 2.0.

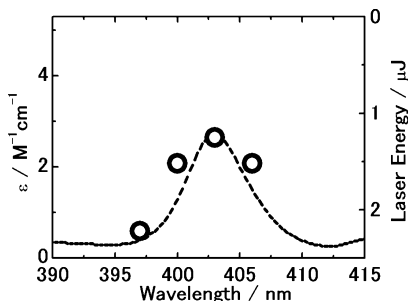
$\leftarrow ^6\text{H}_{5/2}$ . The irradiation pulses were the second harmonics of the fundamental pulses of 800 nm with a duration of positively chirped 800 fs and had laser energies from 0 to 58  $\mu\text{J}/\text{pulse}$ . The pulse duration of the second harmonics was not measured, but we call it an 800 nm pulse here. If the second harmonics were obtained from 600 or 200 fs duration fundamental pulses, we call them 600 and 200 fs pulses, respectively. After irradiation at 100 Hz for 5 min, the samples were irradiated using a green 543.5 nm He–Ne laser, and broad emissions around 725 nm were detected, as shown in Figure 4. The emission is slightly different from that in Figure 2, simply because of the uncorrected spectrometer system. Figure 4 shows the  $\text{Sm}^{2+}$  fluorescence intensities increasing with increases in the irradiating laser energy. The  $\text{Sm}^{2+}$  fluorescence intensity increases nonlinearly with increases in the irradiation energy, and Figure 5 shows that the solid line of the log–log plots has a slope of 2.0. In the case of reduction from  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$ , three-photon absorption and the back one-photon reduction are assumed to be involved.<sup>5</sup> The same scheme could be applied for the samarium ion reactions.

The fluorescence intensities of  $\text{Sm}^{2+}$  after the 800 fs pulse irradiation were measured at several excitation wavelengths, where the pulse energy was kept as low as 3  $\mu\text{J}/\text{pulse}$ . The long duration pulse and low irradiation pulse energy would have prevented solvent ionization or filament formation accompanied by electron ejection. The fluorescence intensity of  $\text{Sm}^{2+}$  was the highest at 403 nm, which is the central wavelength of the ff absorption, was reduced to 1/2 at 396 nm, as shown in Figure 6, and then was reduced to practically zero at 391 and 394 nm. The wavelength dependence corresponds to an action spectrum





**Figure 6.** Influence of excitation wavelengths on the  $\text{Sm}^{2+}$  fluorescence intensity for a 800 fs pulse with a pulse energy of 3  $\mu\text{J}/\text{pulse}$  (○) and a 600 fs pulse with a pulse energy of 25  $\mu\text{J}/\text{pulse}$  (☆). The  $\text{Sm}^{2+}$  fluorescence intensities are normalized at the peak 403 nm. The solid line is the absorption spectrum around 403 nm of the  $\text{Sm}^{3+}$  ion of 0.04 M  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  with 0.2 M 15-crown-5-ether with 1 nm resolution and the dotted line with 3-nm resolution.

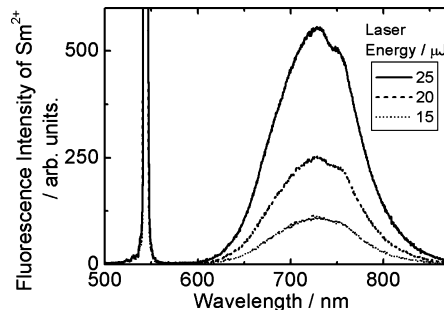


**Figure 7.** Threshold energies of the excitation pulse for the  $\text{Sm}^{2+}$  formation were plotted at four wavelengths (○), and the absorption spectrum of the 403 nm transition with a spectral resolution of 3 nm. The vertical scale is the laser energy from the top of 0.0 down to 2.5  $\mu\text{J}$ .

and approximately follows the absorption spectrum. We can conclude that the photoconversion to  $\text{Sm}^{2+}$  occurs via the ff transition. Considering the lack of reaction by one-photon excitation at this wavelength and the slope of 2.0 of the  $\text{Sm}^{2+}$  fluorescence intensity vs the laser energy in Figure 5, we can conclude that the 403 nm levels work as intermediates of the multiphoton reaction.

The excitation pulses have approximately 3 nm widths (fwhm), as shown in Figure 1, and they are approximately half the width of the ff transition; therefore, the excitation spectra were compared with the spectrum with 3 nm resolution, which is shown as the dotted line in Figures 6 and 7. The action spectrum with 3  $\mu\text{J}/\text{pulse}$  has some deviation from the absorption spectrum. These broad and/or asymmetrical spectral characters of the excitation pulses could explain the deviation. A 391 nm pulse has a broad tail extending to the long wavelength side, while a 406 nm pulse has a broad tail extending to the short wavelength side. For 600 and 200 fs pulses with an energy of 25  $\mu\text{J}/\text{pulse}$ , fluorescence intensities of  $\text{Sm}^{2+}$  were observed to some extent even at an off-resonant wavelength of 394 nm, where no fluorescence due to  $\text{Sm}^{2+}$  formation for an 800 fs pulse with 3  $\mu\text{J}/\text{pulse}$ , as plotted in Figure 6 with stars for the 600 fs pulse. A certain amount of  $\text{Sm}^{2+}$  was presumably produced by the electron capture mechanism.

In Figure 7, the laser energies are plotted at four wavelengths where the  $\text{Sm}^{2+}$  fluorescence reached a certain fixed fluorescence intensity, which was 0.5 in arbitrary units in Figure 5 and was just discernible above the background. It is clearly indicated that the reduction to  $\text{Sm}^{2+}$  is efficient when the excitation pulse is tuned to the ff transition. These experiments support the conclusions deduced from the wavelength dependencies at the fixed irradiation intensity in Figure 6.



**Figure 8.** Samples were irradiated with pulses at 100 Hz for 5 min with an 800 nm nonresonant wavelength of the system with a pulse duration of 43 fs. The fluorescence was detected by excitation with a green 543.5 nm He–Ne laser after irradiating methanol solution of 0.04 M  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  with 0.2 M 15-crown-5-ether. The broad emission around 725 nm is due to  $\text{Sm}^{2+}$  fluorescence.

**3.3.  $\text{Sm}^{2+}$  Formation by Femtosecond Pulse Excitation with a Nonresonant Wavelength of 800 nm.** A solution with 0.04 M  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  with 0.2 M 15C5 in methanol was irradiated by femtosecond pulses with a pulse duration of 43 fs under a nonresonant wavelength of 800 nm, which can be regarded as an isolated resonance of the electronic transitions of the system seen in Figure 2. The formation of  $\text{Sm}^{2+}$  was detected by its fluorescence observed with a green He–Ne laser after 800 nm pulse irradiation, as shown in Figure 8. The broad emission around 725 nm (uncorrected) can safely be assigned to  $\text{Sm}^{2+}$  fluorescence. The  $\text{Sm}^{2+}$  fluorescence intensities after irradiation by 800 nm laser pulses increased with increases in the irradiation laser energy up to 25  $\mu\text{J}/\text{pulse}$ .

The white laser was visible when the reduction occurred, as we have observed with the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction under nonresonant excitation conditions.<sup>6</sup> Many filaments are presumably formed because the critical power for the filament formation in methanol is reported to be 0.42  $\mu\text{J}$  for 38 fs pulses focused with a lens having a 33 cm focal length.<sup>23</sup> Bubbles were also seen during the irradiation, indicating the reverse reaction concomitant with hydrogen molecule formation.

#### 4. Discussion

Several questions have arisen regarding multiphoton reductions since the discovery of  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ : (i) Do other lanthanide ions show similar reactions? (ii) Why is the femtosecond pulse effective? (iii) Is this a three-photon reaction? Two photons should be enough to reach the reactive CT state. (iv) Solvent ionization easily occurs by femtosecond excitation. Is there any influence on the resonant multiphoton reaction? (v) The resonant level can be reached by two-photon absorption of 800 nm pulses. Could several photons reach the CT level leading to  $\text{Sm}^{2+}$ ? We discuss these questions herein as well as the role of crown ether on the low radiative rate constants of  $\text{Sm}^{2+}$  fluorescence, and the bubble formation during the reduction.

**4.1. Some Other Lanthanide Ions Should Show Similar Reactions.** What are these reactions, and what are the physical and chemical requirements for inducing two- or three-photon redox reactions? The common oxidation state of lanthanide (Ln) ions in solution is 3+, and  $\text{Ln}^{3+}$  in solution is very stable; however, some lanthanide ions can exist as 2+ or 4+ oxidation states. Those unstable oxidation states should be principally realized with some drastic chemical procedures and/or external energy input techniques. Photoexcitation is the simplest method, and  $\text{Ce}^{4+}$ ,  $\text{Eu}^{2+}$ , and  $\text{Sm}^{3+}$  are actually transformed from  $\text{Ln}^{3+}$  by appropriate UV light excitation.<sup>1,9,10</sup> The reactive excited states are charge transfer (CT) states for the cases of Eu and

Sm ions and f–d transitions for the Ce ion. These excited states can be reached by two- and/or three-photon excitations; therefore, multiphoton reactions have been predicted<sup>9</sup> and have been realized for the Eu ion,<sup>4,5</sup> and now the Sm ion in this study. Yb<sup>2+</sup>, Tm<sup>2+</sup>, Dy<sup>2+</sup>, and Nd<sup>2+</sup> have been known in tetrahydrofuran.<sup>19</sup> Relatively small differences in their oxidation potentials to form Tb<sup>4+</sup> and Pr<sup>4+</sup> from their parent Ln<sup>3+</sup>.<sup>9</sup> These lanthanide ions may be the next targets for multiphoton reactions. The existence of 2+ and 4+ oxidation states would be ascribed to the extra stability associated with the formation of stable empty 4f<sup>0</sup> (Ce<sup>4+</sup>), half-filled 4f<sup>7</sup> (Eu<sup>2+</sup>), and filled 4f<sup>14</sup> (Yb<sup>2+</sup>) subshells.

**4.2. Why Are the Short Pulses Used for the Resonant Excitation at 403 nm Followed by Sm<sup>2+</sup> Formation?** The intermediate state is assumed to be the 403 nm state (<sup>6</sup>P<sub>3/2</sub>) and not the lowest emissive state, the <sup>4</sup>G<sub>3/2</sub> state. (Figure 2) This assumption is based on the results of the multiphoton reduction of Eu<sup>3+</sup> to Eu<sup>2+</sup>. In the Eu<sup>3+</sup> → Eu<sup>2+</sup> reaction system, the reduction efficiency was found to be 10<sup>-1</sup> using short pulses (250 fs and 2 ps), which was a dramatic improvement from 10<sup>-5</sup> observed with the 20 ns duration pulses. We have therefore concluded that the lifetime of the intermediate would be picoseconds in the case of short pulse excitations and that the intermediate state is the <sup>5</sup>L<sub>6</sub> level. The lowest emissive state of <sup>5</sup>D<sub>0</sub>, where the lifetime is 110 μs, can be an intermediate state for multiphoton excitation, while the reaction efficiency is on the order of 10<sup>-5</sup>. For the case of Sm<sup>3+</sup>, the <sup>6</sup>P<sub>3/2</sub> state would have a short lifetime and can be an efficient intermediate state. This state quickly relaxes to the lowest emissive state, the <sup>4</sup>G<sub>3/2</sub> state, which has a lifetime of 4.5 μs in methanol.<sup>28</sup> An experiment by nanosecond laser excitation would clarify whether or not the <sup>4</sup>G<sub>3/2</sub> state is a highly efficient intermediate of the redox reaction.

**4.3. Is the Third Photon Involved, Though Apparently Only a Two-Photon Reaction Occurs?** The laser energy dependence with the quadratic dependence shows an apparent two-photon reaction. We needed to take into account a one-photon back-reaction of Eu<sup>2+</sup> → Eu<sup>3+</sup> in the case of the multiphoton Eu<sup>2+</sup> → Eu<sup>3+</sup> reaction. The Sm<sup>2+</sup> → Sm<sup>3+</sup> photoreaction has been observed,<sup>29</sup> and 403 nm light can excite the Sm<sup>2+</sup>; therefore, the Sm<sup>3+</sup> reduction probably involve three photons. The CT state that is ultimately reached, where the excited species separate to Sm<sup>2+</sup> and the oxidized counterion or solvent molecular cation, has not been clarified in this paper. If a two-photon reaction occurs via the <sup>4</sup>G<sub>3/2</sub> level, the CT state is 5.29 eV (234 nm) from the ground state of <sup>6</sup>H<sub>5/2</sub>, while if three photons are required through the intermediate of the <sup>6</sup>P<sub>3/2</sub> state, the CT level is 9.22 eV (134 nm) from the ground state. Any multiphoton processes can reach the deep UV CT levels, where the reduction would be induced by one-photon UV excitation.

**4.4. Multiphoton Reaction via the Resonant Level with 403 nm Pulses Avoiding Solvent Ionization Followed by Electron Capture.** The action spectrum of Sm<sup>2+</sup> formation at a fixed irradiation energy of 3 μJ in Figure 6 and the threshold intensities at the four wavelengths in Figure 7 indicate a resonance effect via real 403 nm transitions, primarily due to <sup>6</sup>P<sub>3/2</sub> ← <sup>6</sup>H<sub>5/2</sub>. The nonresonant excitation mechanism, solvent ionization, and the capture of electrons by Sm<sup>3+</sup> would not contribute to the production of Sm<sup>2+</sup> in the cases of 403 nm excitation in Figures 6 and 7, where the excitation energies are lower than 3 μJ/pulse. In fact, no white-light laser was visually observed in the 800 fs pulse experiments. The intensities in the present experiments would have been approximately 1 order of magnitude smaller than that of the white-light laser threshold

in the 800 nm experiments. The intensities in the present reduction experiments are estimated to have been 1.3 × 10<sup>11</sup> W cm<sup>-2</sup> at 3 μJ/pulse in Figure 6 and below 1 × 10<sup>11</sup> W cm<sup>-2</sup> in Figure 7, using a diameter of 60 μm. The white-light laser threshold energy has been reported to be 0.42 μJ for a 38 fs pulse in methanol,<sup>23</sup> corresponding to (3.5–14) × 10<sup>12</sup> W cm<sup>-2</sup> assuming beam sizes 10–20 μm in diameter. Multiphoton absorption experiments for organic molecules in solution have been done under similar focusing optics using 795 nm with 40 fs in this laboratory. The input laser intensity could be lower than 1 × 10<sup>13</sup> W cm<sup>-2</sup>, in other words, white-light laser was not observed in the case of a few organic solvents, including acetonitrile.<sup>26</sup>

The third mechanism, i.e., solvent ionization and reduction, would contribute to the formation of Sm<sup>2+</sup> under irradiation energies higher than 25 μJ/pulse for a 600 fs pulse. Still, the second mechanism, i.e., multiphoton absorption and reduction, would be major, because the conversion efficiency to Sm<sup>2+</sup> is the highest in the 403 nm Sm<sup>3+</sup> ff transition region, as partly shown Figure 6. The solvent ionization and reduction mechanism should show no wavelength dependence because filament formation would be independent of wavelength in 391–406 nm under the assumption that the linear and nonlinear indices remain unchanged.

**4.5. Could Several Photons Reach the CT Level by 800 nm Pulses and Lead to Sm<sup>3+</sup> Formation?** Sm<sup>3+</sup> ions can be excited by two-photon absorption upon irradiation with 800 nm fundamental pulses. Lanthanide ions can be excited by two-photon absorption and show their inherent luminescence.<sup>30</sup> The transitions between f orbitals are forbidden in a one-photon process; however, the ff transitions are allowed with two photons. The intermediate state of <sup>6</sup>P<sub>3/2</sub> can be pumped by two-photon absorption processes. The fundamental pulse at 800 nm has a broad spectrum width of approximately 30 nm; therefore, the <sup>6</sup>P<sub>3/2</sub> ← <sup>6</sup>H<sub>5/2</sub> transition at 403 nm can be excited by a two-photon process. Further, one- or two-photon excitation of the <sup>6</sup>P<sub>3/2</sub> state could reach the charge transfer state leading to Sm<sup>2+</sup>. We could not assign or extract this process because there was no indication of Sm<sup>2+</sup> under the intensities where no white-light laser emits. When the laser energy was 3 μJ/pulse with a duration of 43 fs (2.5 × 10<sup>12</sup> W cm<sup>-2</sup>), the intensity was high enough to induce two-photon absorption. Neither the Sm<sup>2+</sup> signal nor white-light laser were observed. The conversion efficiency from Sm<sup>3+</sup> to Sm<sup>2+</sup> by this mechanism would be lower than with the present detection system. In successful two-photon experiments,<sup>30</sup> no changes have been found in the emission intensity upon prolonged illumination for the case of Eu<sup>3+</sup> at an intensity of 3.2 × 10<sup>10</sup> W cm<sup>-2</sup>.

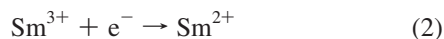
Whenever femtosecond white-light laser was generated during the irradiation, Eu<sup>2+</sup> fluorescence was observed afterward, as for an Eu<sup>3+</sup> system.<sup>6</sup> Filament formation and white-light lasers in methanol concomitant with electron ejection have been discussed elsewhere.<sup>25,27</sup> In the 800 nm and 43 fs laser irradiation in Figure 8, the intensity of 1.3 × 10<sup>13</sup> W cm<sup>-2</sup> at the lowest laser energy of 15 μJ was nearly equal to or above the white-light laser threshold of (3.5–14) × 10<sup>12</sup> W cm<sup>-2</sup>. In fact, white-light laser was visually observed on a white paper put in the rear of the sample cell. The process of two-photon excitation followed by further excitation to the CT state leading to Sm<sup>2+</sup> could be possible. The generation of a white-light laser and the formation of electrons makes it impossible to extract this multiphoton process. It may be notable that the efficiency of the *n*-photon (*n* = 2–5) excitation was not nonlinearly enhanced but deviated from the *n*th order relation and was getting

**TABLE 1: Fluorescence Quantum Yield ( $\phi$ ), Lifetime ( $\tau$ ), Radiative Rate Constant ( $k_f$ ), and Nonradiative Rate Constant ( $k_n$ ) in Methanol**

complex	$\phi$	$\tau/\text{ns}$	$k_f/10^6 \text{ s}^{-1}$	$k_n/10^6 \text{ s}^{-1}$	ref
$\text{Eu}^{2+}$ -15C5	0.24	830	0.29	0.9	23
$\text{Eu}^{2+}$ -18C6	0.067	200	0.33	4.6	23
$\text{EuCl}_2$	0.00036	2.1	0.21	590	23
$\text{Sm}^{2+}$ -15C5	0.050	4100	0.0012	0.24	this work
$\text{Sm}^{2+}$ -18C6	0.00083	15	0.055	67	this work

saturation in the region of laser intensities where white-light laser emits for the cases of organic compounds.<sup>26</sup> The trend of saturation instead of a nonlinear increase in multiphoton absorption can be explained in terms of a limitation of the peak intensity. The limitation (intensity clamping) occurs in the region of laser intensities where white-light laser emits.<sup>25,27</sup>

To relate the  $\text{Sm}^{2+}$  formation to the white-light laser and electron ejection, the  $\text{Sm}^{2+}$  formation mechanisms are estimated as below.



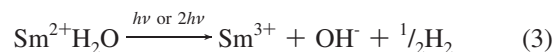
In solid samples,  $\text{Sm}^{2+}$  is created from  $\text{Sm}^{3+}$  by infrared femtosecond laser irradiation.<sup>11–17</sup>  $\text{Sm}^{2+}$  can be identified by its color change from colorless to a somewhat orange absorption at 200–600 nm and a new fluorescence around 700 nm assignable to  $\text{Sm}^{2+}$ . It has been suggested that an electron is ejected from the medium and that  $\text{Sm}^{3+}$  ions act as electron-trapping centers.  $\text{Sm}^{3+}$  can be reduced to  $\text{Sm}^{2+}$  in glasses by irradiation with  $\gamma$ -rays of  $^{60}\text{Co}$ .<sup>18</sup> The active electrons and holes are created in the solids, and some of the electrons are trapped by  $\text{Sm}^{3+}$ , leading to  $\text{Sm}^{2+}$ . In the present study we observed chemical reactions occurring with a 800 nm pulse in solution similar to those observed in solids irradiated by femtosecond pulses and by  $\gamma$ -rays.

**4.6. Influence of Crown Ether on the Fluorescence Properties of  $\text{Sm}^{2+}$ .** The  $\text{Sm}^{3+}$  to  $\text{Sm}^{2+}$  photoreduction by UV (248 nm) laser light was demonstrated by Donohue,<sup>7</sup> and this reaction proceeds by a one-photon process.<sup>8</sup> 18C6 was used as a stabilizer for the product  $\text{Sm}^{2+}$  in those experiments.<sup>7,8</sup> In fact, the color changes due to  $\text{Sm}^{2+}$  formation were observed only in the samples to which crown ether had been added. Fortunately, it is found in this paper that the  $\text{Sm}^{2+}$  complex system emits fluorescence. The fluorescence makes detection of the  $\text{Sm}^{2+}$  product easy and reliable. The structures of  $\text{Sm}^{2+}$ –15C5 and 18C6 complexes would be similar to those of  $\text{Eu}^{2+}$ –crown ether complexes, which have been estimated on the basis of NMR analysis of  $\text{Sr}^{2+}$  complexes.<sup>23</sup> The  $\text{Eu}^{2+}$  is covered by three 15C5 in the complex and shielded from the surrounding solvents, or  $\text{Eu}^{2+}$  is captured in the hole of 18C6 and the top and bottom are exposed to solvent molecules. The diameters of  $\text{Eu}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Sm}^{2+}$  are similar, i.e., 250, 252, and 254 pm;<sup>23</sup> therefore, the same structures for the  $\text{Sr}^{2+}$  complexes can hold for the  $\text{Sm}^{2+}$ –crown ether complexes.

The fluorescence properties of  $\text{Sm}^{2+}$  crown ether complexes were found to be similar to those of  $\text{Eu}^{2+}$  complexes, although with some different features. The  $\text{Eu}^{2+}$  complexes have been thoroughly studied, and some of their properties are listed in Table 1. Dramatic enhancement of the fluorescence quantum yields ( $\phi$ ) for  $\text{Eu}^{2+}$  complexes by crown ethers has been reported;

the highest yield is 0.24 for the  $\text{Eu}^{2+}$ –15C5 complex and 0.067 for the  $\text{Eu}^{2+}$ –18C6 complex, while it is only 0.000 36 for  $\text{EuCl}_2$  crown ether-free in methanol (Table 1). This trend has been explained in terms of an increase in the radiationless rate constant  $k_n$  while maintaining constant  $k_f$ . The same tendency but a rigorous change has been observed for  $\text{Sm}^{2+}$  complexes; the highest yield ( $\phi$ ) is 0.050 for the  $\text{Sm}^{2+}$ –15C5 complex and only 0.000 83 in the 18C6 complex. A distinct difference for  $\text{Sm}^{2+}$  complexes is the low values of  $k_f$  and a large change (about 50 times) in the radiative rate constant  $k_f$ , in addition to a large change of  $k_n$ , indicating that the electronic structure in the fluorescent state could be largely changed by the surrounding molecules. There are a few tens of nanometer shifts in the absorption and fluorescence peaks between 15C5 and 18C6 complexes of  $\text{Eu}^{2+}$  and  $\text{Sm}^{2+}$ , but there are no clear signs of such peculiar behavior in the rate constants for  $\text{Sm}^{2+}$  complexes.

**4.7. Bubble Formation.** Bubbles were seen during the irradiation for both 800 and 403 nm excitations. The bubbles can be assumed to be due to  $\text{H}_2$  formation, as it is known that photoexcited  $\text{Sm}^{2+}$  is very active and efficiently converted to  $\text{Sm}^{3+}$ , accompanied by reductions of solvents and/or coordinated  $\text{H}_2\text{O}$  with the evolution of  $\text{H}_2$ .<sup>29</sup> In the present experiments for the resonance excitation at 403 nm,  $\text{Sm}^{2+}$  is directly excited and is expected to form  $\text{Sm}^{3+}$ .  $\text{Sm}^{2+}$  would be excited by two-photon absorption in the case of the 800 nm pulse, and the excited  $\text{Sm}^{2+}$  reacts with the solvents.



Although  $\text{Sm}^{2+}$  was partially protected by crown ether from solvent molecules in the present experiments, some water molecules would still be coordinated and reduced by the excited  $\text{Sm}^{2+}$ , and finally converted to hydrogen molecules, as in (3).

## 5. Conclusions

Samarium 3+ ions in methanol were found to be reduced to the corresponding 2+ ions upon irradiation with intense femtosecond laser pulses. This is the second example of lanthanide(3+) ion reduction, after the first example of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$ , occurring in response to a short pulse excitation. Both lanthanide ions can be reduced in three ways: CT excitation by UV light by one-photon absorption; resonance excitation by pico- and subpicosecond pulses by multiphoton excitation; and the 3+ ion trapping electron, which is ejected in a filament accompanying the white laser with a femtosecond laser at nonresonant wavelength with respect to the ff transition of the systems. According to the stability and electrochemical potentials from the 3+ ion to the 2+ ion conversion, some other lanthanide ions will probably show the same reactions with the same three methods. One of the secure targets is  $\text{Yb}^{3+} \rightarrow \text{Yb}^{2+}$ .

During the course of the Sm ion study, the fluorescence of  $\text{Sm}^{2+}$  was observed in solution for the first time. These absorption and emission properties interestingly depend on the added crown ethers, and the features are similar but more enhanced compared to those of  $\text{Eu}^{2+}$ .

Three of the five questions raised in the Introduction remain unresolved. (ii) Why is the femtosecond pulse effective? The  $^6\text{P}_{3/2}$  state would have a short lifetime and can be an efficient intermediate state. How does the lowest emissive state, the  $^4\text{G}_{3/2}$  state, work? It has a lifetime of 4.5  $\mu\text{s}$  in methanol. (iii) The reactive CT state seemed to shift to higher energy. The nature of the reactive CT states reached by two- or three-photon

absorption has not been clear. (v) Could several photons reach the CT level by 800 nm pulses and lead to  $\text{Eu}^{2+}$  and/or  $\text{Sm}^{2+}$  formation? The mechanisms related to questions ii and iii would likely be solved by using tunable femto- and nanosecond double pulse excitation. Question v could be solved by a careful study in the region of laser intensities where no white-light laser emits.

In future research regarding redox control in lanthanide ions, these reactions could be utilized for purification and separation.<sup>5,9</sup> The differences of the redox potentials in actinide ions between  $\text{Ac}^{n+}$  and  $\text{Ac}^{m+}$  ( $m = n - 1, n + 1$ ) are often smaller than those between  $\text{Sm}^{3+}$  and  $\text{Sm}^{2+}$ . Therefore, actinide ions with 5f electrons are expected to show similar reactions and to be utilized for nuclear reprocessing.

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