Journal of Alloys and Compounds 408–412 (2006) 757–760

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Photochemistry of $SmCl_3$ and $SmBr_3$ in air-saturated methanol solution

Mitsuhiro Kusaba*, Yoshiaki Tsunawaki

Department of Electrical Engineering and Electronics, Osaka Sangyo University, 3-1-1 Nakagaito, Daito, Osaka 574-8530, Japan

Received 30 July 2004; received in revised form 16 December 2004; accepted 13 January 2005

Abstract

Photochemistry of Sm^{3+} has been studied by means of the nanosecond laser flash photolysis using a KrF excimer laser with the oscillation wavelength of 248 nm. Samples were an air-saturated methanol solution of $SmCl_3$ and that of $SmBr_3$. It is found that the photoreduction of Sm^{3+} to Sm^{2+} is induced in the methanol solution of $SmCl_3$ and the photoreduction yield at 100 ns after the laser irradiation and the lifetime of Sm^{2+} are estimated to be 0.29 ± 0.06 and 5.2 ± 0.7 μs, respectively. In the photolysis of the methanol solution of $SmBr_3$, a solvated electron, e_{sol}^- and Br_2^- were formed.

Keywords: Light absorption; Time-resolved optical spectroscopies; Laser processing; Photoreduction of Sm^{3+}

1. Introduction

Lanthanide ions in solution have broad and sharp absorption bands in the UV and near UV to near IR spectral regions, respectively [1]. The former bands are called charge-transfer (CT) or 5d ← 4f transition bands. The latter ones are due to inner f-shell transitions (f′ ← f transitions). Although a single photon in the visible region excites the f′ ← f transition of these ions, only luminescence is observed and no photoredox reaction can be practically induced. The direct excitation of the CT or 5d ← 4f transition bands has been found to induce the photoredox reactions of some lanthanide ions including Ce^{3+}, Eu^{3+} and Sm^{3+} [1–4]. It is, furthermore, known that the photoreduction of Eu^{3+} is taken place via an f′ ← f transition band by the multi-photon excitation using a dye laser [5] and a Ti:sapphire laser [6].

Although the photoreduction of Sm^{3+} to Sm^{2+} in solid has been investigated [7], there are few reports on the photoreduction in solution because the photoproduct, Sm^{2+}, is unstable in the solution. In previous works [4,8,9], the sample added a macrocyclic ether, 18-crown-6, to the degassed methanol solution in order to stabilize Sm^{2+} was employed. In the degassed solution, when the laser was irradiated to Sm^{3+}, the color of the solution changed to brown depending on the shot number of the laser. The photoproduct was identified as Sm^{2+} by measuring the absorption spectrum of the irradiated sample [4,8,9]. Although the photoreduction of Sm^{3+} to Sm^{2+} in the air-saturated solution has not been observed, to clear its photoreduction will provide useful information for the development of new organic synthesis process. In this work, the transient absorption spectra for air-saturated methanol solutions of $SmCl_3$ and $SmBr_3$ have been measured by means of the nanosecond laser flash photolysis using a KrF excimer laser with the oscillation wavelength of 248 nm. It is found that the photoreduction of Sm^{3+} to Sm^{2+} is induced in air-saturated solution of $SmCl_3$ and a solvated electron, e_{sol}^- and Br_2^- are formed in that of $SmBr_3$ by the laser irradiation.

2. Experimental

A KrF excimer laser (COMPex 102, Lambda Physik; 248 nm, 26 ns of full width at half maximum, 200 mJ/pulse) was used in order to excite Sm^{3+}, and a pulse Xe lamp (XF-80-60, Tokyo Instruments; ca. 10 μs pulse during) was used as a monitoring light. The monitoring light beam was passed through a sample cell (10 mm × 10 mm × 45 mm).

---

* Corresponding author. Tel.: +81 72 875 3001; fax: +81 72 870 8189.
E-mail address: kusaba@elec.osaka-sandai.ac.jp (M. Kusaba).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.01.087

The output signal was obtained with a monochromator (H-10UV, Jobin Yvon)/photomultiplier (R636-10, Hamamatsu) system and was measured with a digital storage oscilloscope (TDS380/P, Tektronix). The laser fluence was measured with a Joule meter (ED-500, Gentec) and was adjusted by the optical filter cell containing an ethanol solution of naphthalene. The area of the laser irradiation was 0.5 cm × 3.0 cm. The observation of the transient species was carried out in the region close to the cell surface. The flash photolysis measurements were carried out at room temperature.

Samples were an air-saturated methanol solution of $SmCl_3{\cdot}6H_2O$ (99.5%, Wako) and that of $SmBr_3{\cdot}6H_2O$ (99.9%, Aldrich). The absorption spectra of these samples were measured by a spectrophotometer (U-3500, Hitachi). The photoreduction yield of Sm^{3+} to Sm^{2+} can be determined by comparing the absorbance of Sm^{2+} with that of a reference sample under the same irradiation conditions [9]. The molar extinction coefficients of Sm^{2+} in the methanol was assumed to be the same as that in aqueous solution, i.e. 400 $M^{-1}\,cm^{-1}$ at 570 nm [10]. The reference sample was naphthalene in degassed cyclohexane solution. The $T_n \leftarrow T_1$ absorption bands of naphthalene is known to have the extinction coefficient of 24100 $M^{-1}\,cm^{-1}$ at 414 nm with the yield of 0.75 [11,12]. The peak wavelength of triplet spectrum of naphthalene is influenced by ambient temperature. In fact, the peak of the absorption spectrum under the experimental 295 K was observed at 412 nm.

3. Results and discussion

The absorption spectra of the methanol solutions of $SmCl_3$ and that of $SmBr_3$ were observed in the UV region as shown with the full and the dotted line in Fig. 1, respectively. The CT bands of lanthanide ions have been discussed in detail [13]. These spectra are identified as the CT bands from the halogen, Cl^- and Br^-, orbital to the f-orbital of Sm^{3+} and the peaks of the CT bands for the methanol solution of $SmCl_3$ and $SmBr_3$ are at 220 nm with the molar extinction coefficient of 550.8 $M^{-1}\,cm^{-1}$ and at 245 nm with that of 196.9 $M^{-1}\,cm^{-1}$, respectively. These absorption bands suggest that a KrF excimer laser can be employed as the light source to excite the bands.

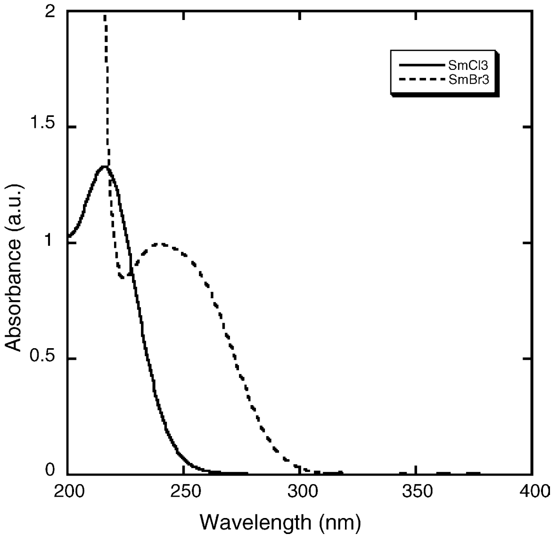

Fig. 1. Absorption spectra of the methanol solution of $SmCl_3$ (full line) and that of $SmBr_3$ (dotted line). The charge-transfer bands from Cl^- to Sm^{3+} and from Br^- to Sm^{3+} appear below 310 nm.

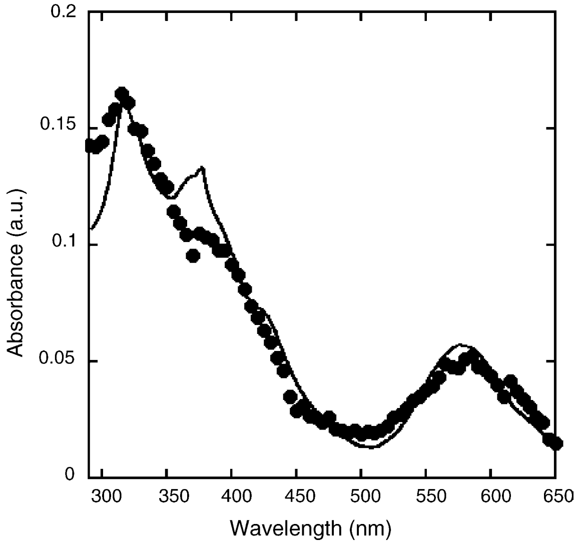

Fig. 2. Transient absorption spectra of Sm^{2+}. The filled circles shows the transient absorption spectrum at 100 ns after the laser irradiation of the sample of $SmCl_3$. The full line is the absorption spectrum of Sm^{2+} in methanol solution.

The transient absorption spectrum when the sample of $SmCl_3$ was irradiated by the laser is shown in Fig. 2. The filled circles and the full line show the transient absorption spectrum at 100 ns after the laser irradiation and the absorption spectrum of Sm^{2+} with 18-crown-6 in degassed methanol solution, respectively. Although the absorption spectrum of Sm^{2+} in air-saturated solution has not been reported, the peaks at 310, 380 and 580 nm in the transient absorption spectrum were in agreement with the peaks of the absorption spectrum of Sm^{2+} with 18-crown-6. The slight difference between two spectra will be due to the interaction between the d-orbital of Sm^{2+} and the crown ether, 18-crown-6. Linearity between the transient absorbance of Sm^{2+} versus the laser fluence was constant, i.e. the slope of the logarithmic plots of the two values was 1.0. The linear dependence of the concentration of Sm^{2+} on the laser fluence indicates that the photoreduction of Sm^{3+} to Sm^{2+} in air-saturated solution occurs via a one-photon process. The photoreduction yields of Sm^{3+} to Sm^{2+} at 100 ns after the laser irradiation were determined to be 0.29 ± 0.06. The time profile of the absorbance at 580 nm of Sm^{2+} in the methanol solution after the laser irradiation is shown in Fig. 3. The lifetime of Sm^{2+} in the air-saturated methanol was estimated to be 5.2 ± 0.7 μs.

Fig. 4 shows the transient absorption spectrum at 100 ns after the laser irradiation to the methanol solution

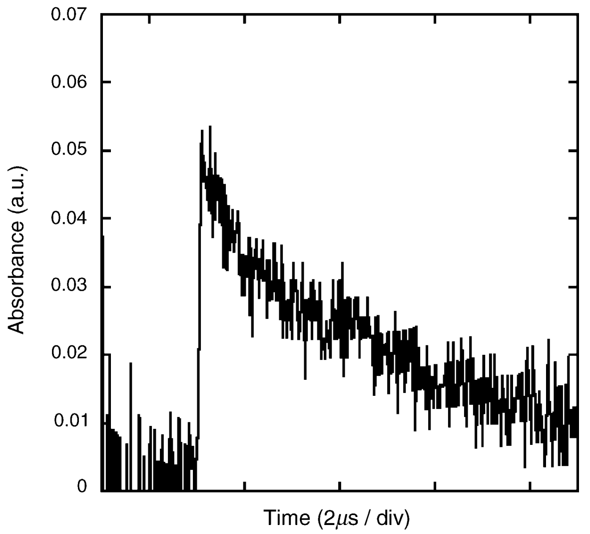

Fig. 3. Time profile of absorbance at 570 nm of Sm^{2+} in the methanol solution after the laser irradiation.

of $SmBr_3$. This absorption spectrum was not in agreement with the absorption spectrum of Sm^{2+} and had two absorption peaks at 360 and 720 nm in the spectral region between 300 and 800 nm. It is well known that a solvated electron, e_{sol}^- and Br_2^- have the absorption peaks at 720 nm ($\varepsilon = 1.85 \times 10^4\,M^{-1}\,cm^{-1}$) and 360 nm ($\varepsilon = 1.2 \times 10^4\,M^{-1}\,cm^{-1}$), respectively [14].

The photoreaction process of $SmCl_3$ and $SmBr_3$ in methanol can be explained as follows. In the case of $SmCl_3$ in methanol, as soon as a photon is absorbed in the CT band due to the CT transition from Cl^- to Sm^{3+}, a geminate pair $(Sm^{2+}–Cl)^*$ is formed and dissociates to $Sm^{2+} + {}^{\bullet}Cl$. These processes are shown as follows.

$$Sm^{3+}–Cl^- + h\nu \rightarrow (Sm^{2+}–Cl)^*, \quad (1)$$

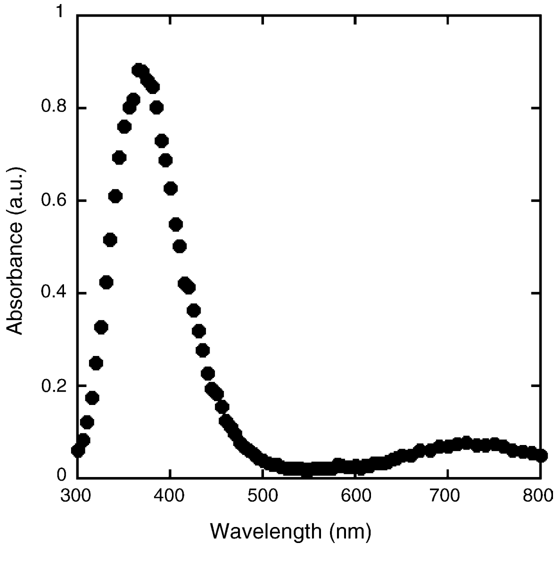

Fig. 4. Transient absorption spectrum of the solvated electron e_{sol}^- (720 nm) and Br_2^- (360 nm). The filled circle shows the transient absorption spectrum at 100 ns after the laser irradiation of the sample of $SmBr_3$.

$$(Sm^{2+}–Cl)^* \rightarrow Sm^{2+} + {}^{\bullet}Cl. \quad (2)$$

The photoredution yield of Sm^{3+} to Sm^{2+} will be determined by the efficiencies of dissociation and geminate recombination of the excited species $(Sm^{2+}–Cl)^*$. Reaction between the oxidized ligand (${}^{\bullet}Cl$) and the neighboring solvent competes with the geminate recombination. The formed Sm^{2+} is unstable in the air-saturated solution because the Sm^{2+} reacts efficiently with the resolved oxygen and the lifetime of the Sm^{2+} is $5.2 \pm 0.7\,\mu s$.

On the other hand, when the $SmBr_3$ in methanol was irradiated by the laser, the reaction shown as follows will occur. Immediately after the CT band of Br^- to Sm^{3+} is excited, the geminate pair $(Sm^{2+}–Br)^*$, is not formed but the excited Br^- $(Br^-)^*$, is formed and a solvated electron, e_{sol}^- is ejected and the broad band with the peak at 720 nm appears;

$$Sm^{3+}–Br^- + h\nu \rightarrow Sm^{3+} + (Br^-)^*, \quad (3)$$

$$(Br^-)^* \rightarrow {}^{\bullet}Br + e_{sol}^-. \quad (4)$$

${}^{\bullet}Br$ radical produced simultaneously with a solvated electron react with the neighboring Br^- and Br_2^- is formed and the absorption peak of the Br_2^- appears at 360 nm.

$${}^{\bullet}Br + Br^- \rightarrow Br_2^-. \quad (5)$$

Halogen ions such as Br^- and Cl^- have charge-transfer to solvent (CTTS) spectra and the solvated electron is formed by pumping the CTTS bands. The CT band of Br^- to Sm^{3+} is not overlapped with the CTTS bands of Br^- because the CTTS bands of Br^- appears in the spectral region below 225 nm. Therefore, the CTTS band cannot be directly excited by KrF excimer laser with the oscillation wavelength of 248 nm. The formation of the solvated electron, e_{sol}^- and Br_2^- will suggest that new photoreaction mechanisms exist on the reaction process via the CT band excitation. Although the reason for observed difference between Cl^- and Br^- does not clear at the present time, the difference reaction may be affected by the electronegativity of ligands. Because the absorption peak of CT band relates to the electronegativity [13].

4. Conclusions

The transient absorption spectra for the air-saturated methanol solutions of $SmCl_3$ and $SmBr_3$ have been measured by means of the nanosecond laser flash photolysis using a KrF excimer laser with the oscillation wavelength of 248 nm. It is found that the photoreduction of Sm^{3+} to Sm^{2+} is induced in air-saturated solution of $SmCl_3$ and the photoreduction yield at 100 ns after the laser irradiation and the lifetime of Sm^{2+} are estimated to be 0.29 ± 0.06 and $5.2 \pm 0.7\,\mu s$, respectively. In the photolysis of the methanol solution of $SmBr_3$, a solvated electron and Br_2^- were formed. The dependence of the photoreaction of Sm^{3+} on the counter ions will suggest that new photoreaction mechanisms exist on the reaction process via the CT band excitation.

Acknowledgement

We thank Mr. Y. Tsujisawa for his assistance with this work.

References

[1] T. Donohue, in: C.B. Moore (Ed.), Chemical and Biochemical Applications of Lasers, vol. 5, Academic Press, New York, 1980, pp. 239–273.

[2] M. Kusaba, N. Nakashima, W. Kawamura, Y. Izawa, C. Yamanaka, Chem. Phys. Lett. 197 (1992) 136–140.

[3] M. Kusaba, N. Nakashima, W. Kawamura, Y. Izawa, C. Yamanaka, J. Alloys Compd. 192 (1993) 284–286.

[4] M. Kusaba, Y. Tsunawaki, N. Nakashima, J. Photochem. Photobiol. A: Chem. 104 (1997) 35–37.

[5] M. Kusaba, N. Nakashima, Y. Izawa, C. Yamanaka, W. Kawamura, Chem. Phys. Lett. 221 (1994) 407–411.

[6] N. Nakashima, S. Nakamura, S. Sakabe, H. Schillinger, Y. Hamanaka, C. Yamanaka, M. Kusaba, N. Ishihara, Y. Izawa, J. Phys. Chem. A 103 (1999) 3910–3916.

[7] J. Qui, K. Miura, T. Suzuki, T. Mitsuyu, K. Hirao, Appl. Phys. Lett. 74 (1999) 10–12.

[8] T. Donohue, in: G.L. McCarthy, J.J. Phyne, H.B. Silber (Eds.), The Rare Earths in Modern Science and Technology, vol. 3, Plenum, New York, 1983, pp. 223–226.

[9] M. Kusaba, Y. Tsunawaki, N. Nakashima, Mater. Sci. Forum 315–317 (1999) 211–215.

[10] A.N. Kamenskaya, Russ. J. Inorg. Chem. 29 (1984) 251–258.

[11] J.C. Scaiano, Handbook of Organic Photochemistry, vol. 1, CRC Press, Boca Raton, FL, 1989.

[12] I. Carmichael, W.P. Helman, G.L. Hug, J. Phys. Chem. Ref. Data 16 (1987) 239–260.

[13] B. Keller, K. Bukietynska, B. Jezowska-Trzebiatowska, Bull. Acad. Pol. Sci. Ser. Sci. Chim. 24 (1976) 763–769.

[14] A. Iwata, N. Nakashima, M. Kusaba, Y. Izawa, C. Yamanaka, Chem. Phys. Lett. 207 (1993) 137–142.