Field enhancement effect of small Ag particles on the fluorescence from Eu^{3+}-doped SiO_2 glass

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We have investigated the effects of nanometer-sized silver particles on the optical properties of Eu^{3+} ions in SiO_2 glass. Glass samples were prepared by the sol-gel method. The mean particle size and volume fraction of silver particles, which were estimated from UV-VIS absorption spectra using Mie-Drude theory modified by electron mean free path model, rapidly increased with the reduction time of Ag^+ up to ~3 min at 900 °C. The fluorescence from Eu^{3+} ions for the excitation by N_2 laser was greatly enhanced in the presence of silver particles of 4.3 nm size. Our experimental results suggest that the origin of enhanced fluorescence is from local field enhancement around Eu^{3+} ions, owing to the surface plasmon resonance of small silver particles. © *1999 American Institute of Physics.* [S0003-6951(99)01311-X]

Nanometer-sized ultrafine particles of metals and semiconductors have several intriguing properties including optical nonlinearity,[1,2] specific heat[3] and magnetism[4] which differ from those of their bulk states. In the past decade, these ultrafine particles have been studied extensively. There is a wide variety of fabrication methods of glasses containing ultrafine particles: melt quenching,[5,6] sol-gel,[7,8] ion implantation,[9,10] and sputtering.[11] Much attention has been paid to the study of optical properties of nanometer-sized particles dispersed in glass matrices from the viewpoint of scientific interest and their application. If such ultrafine particles can be uniformly dispersed in a solid matrix, the stability of the particles increases and the solid can be handled easily.

Recently, an active research has been focused on the optical properties of rare-earth ions in low dimensional semiconductors because of their potential application in optoelectronics devices.[12,13] It was suggested that excitation of rare-earth ions occurred through the recombination of photogenerated carriers confined in semiconductor nanocrystals and subsequent energy transfer to rare-earth ion in or near the nanocrystal. On the other hand, the observation of Raman scattering and fluorescence enhancements for molecules adsorbed on or close to a rough metallic surface[14,15] has encouraged the study of optical properties of composite materials, such as Eu^{3+}-doped glass containing small silver particles. In these systems, any significant influence of the metallic particles on the absorption and emission rates of the rare-earth ions should be primarily of electronic origin. Several theoretical approaches have been proposed to describe the absorption and decay rates of molecular species in the presence of rough metallic surfaces and particles.[16,17] The electromagnetic mechanism can be viewed as an additional interaction due to the high field gradients nearby the metallic particles, produced by plasmon excitations in the particles at the Mie resonance frequency. A basic interest in these composite materials is to see under what conditions the emission

yield, which is a balance between emission and decay rates, can be optimized. In this letter, we report the enhancement of fluorescence and the size dependence of Ag on the fluorescence from Eu^{3+}-doped SiO_2 glass containing small Ag particles.

We prepared Eu^{3+}-doped SiO_2 glass containing small Ag particles (Eu_2O_3:2 wt %, Ag:0.05 wt %) by the sol-gel method. $Si(OC_2H_5)_4$ was first partially hydrolyzed with a mixed solution of H_2O, C_2H_5OH, and HNO_3 with a molar ratio of 1:1:0.15 per mol of $Si(OC_2H_5)_4$. After the solution had been stirred for 1 h, a solution of $Eu(NO_3)_3 \cdot 6H_2O$ and $Ag(NO_3)$, which were ultrasonically dissolved in C_2H_5OH, was mixed with the solution. The resultant solution was hydrolyzed by adding the mixed solution of H_2O, C_2H_5OH, and HNO_3. In this second hydrolysis reaction, the molar ratio of H_2O, C_2H_5OH, and HNO_3 was maintained at 4:1:0.15 per mol of complex alkoxide. After being stirred for 15 min, the solution was poured into a polystyrene container and left covered for ~five days to form a stiff gel, and then dried without the cover for ~ten days at room temperature. The gels contain physically and chemically adsorbed water and organic compounds on the gel particle surfaces.

In order that the porous dried gels were transformed into nonporous glasses, the dried gels were heat treated for 2 h at 900 °C. Upon heating in air, these gels shrank due to dehydration condensation of the hydroxyl groups and sintering, which resulted in collapse of the pores. After cooling down to room temperature, the glasses were heat-treated under a flowing 20% H_2-80% N_2 mixed gas at 900 °C for 30 s-10 min (see the insertion in Fig. 1). The reduction atmosphere made the silver particles to be formed and to be grown in SiO_2 glass. Sample thicknesses were ~0.5 mm. The mean particle size and the volume fraction of Ag particles were estimated from UV-VIS absorption spectra using Mie-Drude theory which was reconstructed by Doremus.[18] Figure 1 shows the absorption spectra of our samples. Small Ag particle has a peak in the absorption spectrum around 394 nm due to a surface plasmon resonance of the spatially confined electrons in the Ag particle. It can been seen that, with in-

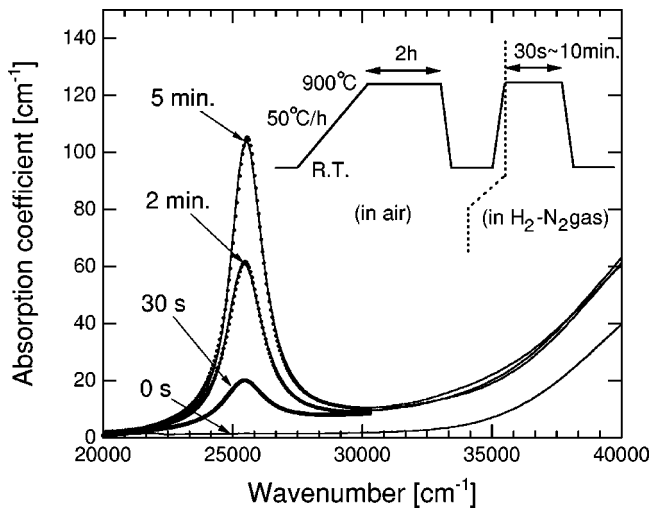[a] Electronic mail: hayatomo@mse.nitech.ac.jp

FIG. 1. Absorption spectra of Eu^{3+}, Ag^+-doped SiO_2 glass before and after the reduction process for Ag^+ in H_2-N_2 mixed gas at 900 °C. The peak around ~ 394 nm is caused by the surface plasmon resonance of small Ag particles (solid lines: experimental results, dotted lines: fitted curves).
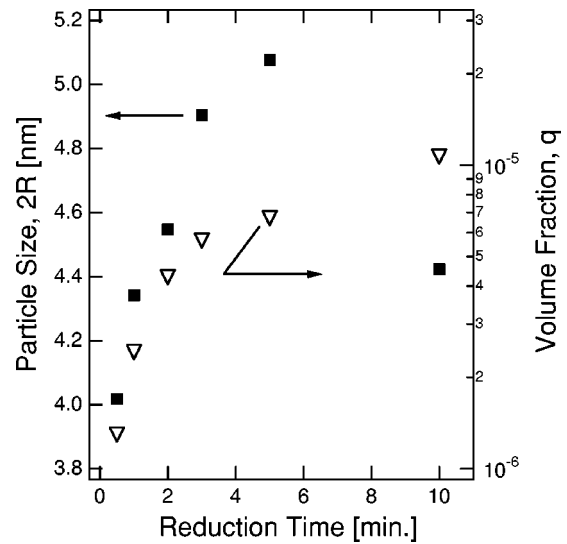

FIG. 2. Mean particle size, 2 R, and volume fraction, q, of small Ag particles, which were estimated from UV-VIS, absorption spectra using the Mie-Drude equation, as a function of the reduction time.

creasing reduction time, the intensity of the plasma oscillation peak increased.

Classical light scattering theory by Mie[19] and free electron theory by Drude[20] well explain the characteristic absorption peak due to the surface plasmon resonance. In the Mie equation the absorption coefficient is

$$\alpha(\omega) = \frac{9qn^3\omega}{c} \frac{\widetilde{\epsilon}_{m2}(\omega)}{[\widetilde{\epsilon}_{m1}(\omega) + 2n^2]^2 + \widetilde{\epsilon}_{m2}(\omega)^2}, \qquad (1)$$

where n, q, and $\widetilde{\epsilon}_m (= \widetilde{\epsilon}_{m1} + i\widetilde{\epsilon}_{m2})$ are the refractive index of host material, the volume fraction of metallic particles, and the dielectric function of the particle material. According to Drude's free electron theory, $\widetilde{\epsilon}_m$ is expressed by

$$\widetilde{\epsilon}_m(\omega) = 1 + i\frac{\omega_p^2 \tau}{\omega(1 - i\omega\tau)}, \qquad (2)$$

where τ is the relaxation time, and $\omega_p = (N_e e^2 / \epsilon_0 m)^{1/2}$ is the frequency of plasma oscillation (N_e, e, and m are the number, charge, and mass of electrons, respectively). Doyle[21] and Kreibig et al.[22] proposed that, for a spherical particle much smaller than the mean free path of the electrons in bulk material, l_∞, the collisions of the conduction electrons with the particle surfaces become important as an additional relaxation process and the effective mean free path, l, is restricted by the particle size, 2 R. Thus, the relaxation time τ can be substituted for the collision time

$$\tau_c = 2R/v_f, \qquad (3)$$

where $v_f (= 1.39 \times 10^8 \text{ cm/s})$ is the Fermi velocity. Eventually, we get from Eqs. (1) and (2), when $\omega\tau_c \gg 1$

$$\alpha(\omega) = \frac{9qn^3}{c(1 + 2n^2)} \frac{\omega^2\omega_r^2/\tau_c}{(\omega^2 - \omega_r^2)^2 + (\omega_r^2/\omega\tau_c)^2}, \qquad (4)$$

$$\omega_r^2 = \omega_p^2/(1 + 2n^2), \qquad (5)$$

where ω_r is the resonance frequency of the surface plasmon. Under this approximation, the full width at half maximum (FWHM) is given by $\Delta\omega_{1/2} \simeq 1/\tau_c$, thus we can obtain the following relationship:[23]

$$2R = v_f/\Delta\omega_{1/2}. \qquad (6)$$

The fitted results of surface plasmon peaks by the Mie-Drude Eq. (4) are included in Fig.1. Figure 2 shows the correlation of the estimated mean Ag particle size and the volume fraction with the reduction time. It can be seen that, up to 3 min, the particle size, 2 R, and the volume fraction, q, rapidly increased with increasing reduction time. On the contrary, at 10 min of the reduction time, the mean particle size decreased. This decrease in Ag particle size indicated a breakdown of the Mie-Drude theory, in which a shape size distribution and no interaction between particles were assumed.

Fluorescence spectra from Eu^{3+} in the samples were measured by an image-intensified charge coupled device (ICCD) spectrum system (InstaSpec™ V system, ORIEL Instruments). Both N_2 laser and Dye laser (Rhodamine 6G) were used as the excitation lights. The emission light was led to a monochromator through an optical fiber and detected by an ICCD camera. By adjusting the gate pulse width, T_w, for the ICCD camera to a larger width than the lifetime of the $^5D_0$ level, we could observe the fluorescence spectra of $^5D_0 \rightarrow {}^7F_{0,1,2,3}$, although in case of dye laser excitation it was not possible to separate the $^5D_0 \rightarrow {}^7F_0$ line from the excitation light. Moreover, when the gate pulse width and the delay time were adequately controlled, a time resolved fluorescence spectra could be measured. From the measurement under a condition of $T_w = 10 \mu s$ and delay step$=10 \mu s$, we observed the time evolution of $^5D_0 \rightarrow {}^7F_2$ emission. The lifetime of $^5D_0$ level was ~ 1.4 ms for all samples. Figure 3 shows the integrated fluorescence intensities of $^5D_0 \rightarrow {}^7F_2$ transition, calibrated by the sample thicknesses, for each excitation by N_2 laser (337 nm) and rhodamine 6 G dye laser (578 nm) as a function of the reduction time. When Eu^{3+} in the sample was excited by N_2 laser, the intensity had a maximum around 30 s of the reduction time. On the other hand, the fluorescence intensity for the excitation by the dye laser, I_{ex578}, gradually decreased as the reduction time increased. This decrease in fluorescence intensity of the $^5D_0 \rightarrow {}^7F_2$ transition corresponds to the decrease in the number of Eu^{3+} ions because the dye laser directly excites Eu^{3+} ions to the $^5D_0$
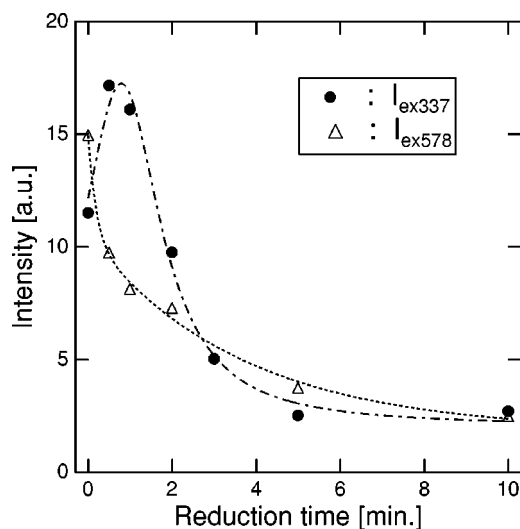
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FIG. 3. Fluorescence intensity of $^5D_0 \to {}^7F_2$ transition for each excitation by N_2 laser (337 nm) and Rhodamine 6 G dye laser (578 nm) as a function of the reduction time.

level. It is supposed that some of them were held in Ag particles as the impurities, and others were reduced to Eu^{2+} in the reduction process of Ag^+ ions. Here we take the ratio of I_{ex337} and I_{ex578}, $\bar{I} = I_{ex337}/I_{ex578}$, which is proportional to the fluorescence intensity per Eu^{3+} ion. It is found that the ratio $\bar{I}$ was twice greater than that in the absence of Ag particles. When the reduction time was longer than 1 min, the ratio decreased and such an enhancement was not observed, (see Table I).

Malta et al.[24] reported a diminution in fluorescence from Eu^{3+} in the presence of small Ag particles using melt glasses containing Eu^{3+} and small Ag particles, in which Ag par-

TABLE I. Size dependence of Ag on the fluorescence from Eu^{3+}-doped SiO_2 glass containing small Ag particles.

Reduction time (min)	Mean particle size (nm)	Fluorescence ($\bar{I} = I_{ex337}/I_{ex578}$)
0 (No Ag particles)	···	0.26
0.5	4.02	0.59
1	4.34	0.66
2	4.54	0.45
5	5.08	0.23
10	4.42	0.36

ticles were produced by x-ray irradiation. Furthermore, they attempted to interpret their results from their theoretical point of view,[25] and proposed two possible mechanisms: one is an energy transfer between Eu^{3+} and Ag particle. The other is a local field enhancement around Eu^{3+} ions. They insisted that whether the fluorescence from Eu^{3+} was diminished or enhanced was dependent on the size of Ag particles and the lifetime of upper level in Eu^{3+}. As mentioned above, the lifetime of the $^5D_0$ level was almost the same for all samples of the present investigation and the time response for a pulsed excitation of dye laser did not show any nonexponentiality. This implies that the most probable mechanism for the fluorescence enhancement in our results is the local field enhancement around Eu^{3+} ions, due to the induced surface plasmon resonance of small Ag particles.

[1] H. Hache, D. Ricard, C. Flytzanis, and U. Kreibig, Appl. Phys. A: Solids Surf. **47**, 347 (1988).
[2] K. Uchida, S. Kaneko, S. Omi, C. Hata, H. Tanji, Y. Asahara, A. J. Ikushima, T. Tokizaki, and A. Nakamura, J. Opt. Soc. Am. B **11**, 1236 (1994).
[3] G. R. Stewart, Phys. Rev. B **15**, 1143 (1977).
[4] C. Chaumont and J. C. Bernier, Solid State Commun. **48**, 357 (1983).
[5] S. D. Stookey, J. Am. Ceram. Soc. **32**, 246 (1949).
[6] R. D. Maurer, J. Appl. Phys. **29**, 1 (1958).
[7] J. Matsuoka, R. Naruse, H. Nasu, and K. Kamiya, J. Non-Cryst. Solids **218**, 151 (1997).
[8] I. Tanahashi and T. Mitsuyu, J. Non-Cryst. Solids **181**, 77 (1995).
[9] K. Fukumi, A. Chayahara, K. Kadono, T. Sakaguchi, Y. Horino, M. Miya, J. Hayakawa, and M. Satou, Jpn. J. Appl. Phys., Part 2 **30**, L742 (1991).
[10] G. W. Arnold and J. A. Borders, J. Appl. Phys. **48**, 1488 (1977).
[11] I. Tanahashi, Y. Manabe, and T. Tohda, J. Appl. Phys. **79**, 1244 (1996).
[12] J. H. Shin, G. N. van den Hoven, and A. Polman, Appl. Phys. Lett. **66**, 2379 (1995).
[13] M. Fujii, M. Yoshida, Y. Kanzawa, S. Hayashi, and K. Yamamoto, Appl. Phys. Lett. **71**, 1198 (1997).
[14] M. Fleischmann, P. J. Hendra, and A. J. McQuillan, Chem. Phys. Lett. **26**, 163 (1974).
[15] D. A. Weitz, S. Garoff, J. I. Gersten, and A. Nitzan, J. Chem. Phys. **78**, 5324 (1983).
[16] P. Das and H. Metiu, J. Phys. Chem. **89**, 4680 (1985).
[17] H. Chew, J. Chem. Phys. **87**, 1355 (1987).
[18] R. H. Doremus, J. Chem. Phys. **40**, 2389 (1964).
[19] M. Born and E. Wolf, *Principles of Optics*, 6th ed. (Pergamon, Oxford, 1980).
[20] C. Kittel, *Introduction of Solid State Physics*, 7th ed. (Wiley, New York, 1996).
[21] W. T. Doyle, Phys. Rev. **111**, 1067 (1958).
[22] U. Kreibig and C. v. Fragstein, Z. Phys. **224**, 307 (1969).
[23] G. W. Arnold, J. Appl. Phys. **46**, 4466 (1975).
[24] O. L. Malta, P. A. Santa-Cruz, G. F. de Sá, and F. Auzel, Chem. Phys. Lett. **116**, 396 (1985).
[25] O. L. Malta and M. A. Couto dos Santos, Chem. Phys. Lett. **174**, 13 (1990).