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Preparation of Long-Afterglow Colloidal Solution of $Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+} by Laser Ablation in Liquid

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Abstract

We have successfully prepared a novel nanoparticle solution of $Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+} with afterglow properties by means of laser ablation in liquid. This process also produced by-products of different kinds, depending on the liquid used. The amount of by-product and the size of the nanoparticles were controlled by the energy density of laser ablation. The amount of by-product was reduced by a decrease in the energy density, which also decreased the particle size of the nanoparticles. The PL spectrum of the nanoparticles was the same as that of the target materials used for laser ablation. The afterglow properties deteriorated with a decrease in particle size. We concluded that an increase in specific surface area caused by a decrease in particle size resulted in the decrease of luminescent intensity.

Keywords: laser ablation; nanoparticle; photoluminescence; afterglow.

1. Introduction

Extensive studies have recently been carried out on fluorescent nanoparticles due to their unique physical properties and variety of possible applications. When such nanoparticles are dispersed in a solution such as a colloid, they become useful in many research fields such as biotechnology, information security, and electronics. Until now, afterglow nanoparticles dispersed in solvent have not been fabricated. Afterglow nanoparticles emit without a continuous light excitation. In the case of normal fluorescence, luminescence is observed during excitation but is not observed after blocking the excitation. In the case of afterglow, however, luminescence is observed both during excitation as well as after the blocking of excitation. The first afterglow material, ZnS:Cu, was discovered in the eighteenth century. The decay time constant of the afterglow of this material is quite short. Long-afterglow material, such as $SrAl_2O_4$: Eu^{2+}, Dy^{3+}, was first discovered by Matuzawa in 1996 [1]. This aluminate material, which is water soluble, has a green luminescence that is attributed to the Eu^{2+} ion. Recently, a silicate system such as $Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+} was proposed as a water-insoluble afterglow material by many research groups [2-5]. The typical mechanism of afterglow involves the trapping of a carrier at the trap level that exists in afterglow material. For example, trapped electrons are excited to a conduction band at room temperature [1,6-10]. These excited electrons result in luminescence through the radiative transition of recombination between electrons and holes. In the case of $SrAl_2O_4$: Eu^{2+}, Dy^{3+}, it was suggested that holes were trapped at the Dy^{3+} level [2]. These afterglow materials are applied in many fields, such as in disaster relief evacuation signs that glow in the dark, power-saving of light sources, increased operability of watches or cell phones, and various forms of entertainment with lights that glow in the dark. One of our future plans is to use afterglow material as a marker for bioimaging if it is possible to be produced on a nanoscale. We think that this system can resolve the existing problem of autofluorescence faced in the application to bioimaging, namely that the excitation of markers would also excite fluorescent materials such as NADH and Tryptophan exist in living cells. Ideally, only the emission of a marker would be observed if afterglow nanoparticles were used as a marker and the excitation light were blocked. If there were no observation of the emission of living cells, this would resolve the problem of autofluorescence.

There are many methods to prepare nanoparticles; these are broadly divided into two categories: liquid phase preparation [11,12] and gas phase preparation [13,14]. In the case of liquid phase preparation, it is easy to disperse nanoparticles in a liquid such as a colloidal solution, which has bioaffinity, and the nanoparticles can be collected with high efficiency. Liquid phase preparation includes both a chemical method and a physical method. In the chemical method, it is difficult to prepare multielement nanoparticles such as $Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+}. While gas phase laser ablation has been used for various research purposes for a long time [15], laser ablation in liquid, which is classified as a physical method, has been investigated more recently [16-20]. Laser ablation in liquid also prepares nanoparticles due to its effect upon them. The target material in liquid is irradiated with a focused pulsed laser beam.

In this study, we fabricated a colloidal solution of afterglow nanoparticles for the first time using laser ablation in liquid, and we then investigated their optical properties. The resulting colloidal solution would be utilized for biomedical applications. We varied the solution and energy density of the laser beam and investigated its composition, by-product, and optical properties, which consist of photoluminescence and afterglow properties.

2. Experimental methods

Powdered $Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+} was procured from the Mitsubishi Chemical Corporation. Figure 1 shows a schematic of laser ablation in liquid. The target was placed in a cell that was filled with liquid and was then irradiated with a focused laser beam. The laser was a third-harmonic generation pulsed laser (JDS Uniphase Co. Model 210, wavelength: 355 nm, pulse width: 50 ns, energy: 0.5 mJ/pulse, repetition rate: 4 kHz). The focal length of the lens was 10 mm. The energy density of the irradiating laser beam was varied by changing the height of the target position. We fabricated the target by spark plasma sintering (SPS, SPS Syntex Inc. SPS-515S) because a compacted target only, was broken up when placed in liquid. Figure 2 shows a schematic of SPS. A sample folder was made of carbon. The sample powder was pressurized at 50 MPa and an electric current (540 A, 2.4 V) was passed through it. The sample was heated by Joule heat to 1100 °C and was then sintered for 10 min in an Ar atmosphere to prevent the transformation of the sample powder.

We characterized the composition of the prepared nanoparticles using an X-ray diffractometer (XRD, PANalytical B.V. X’pert-PRO-MRD). Centrifugation was utilized to obtain the sample powder. The particle size in liquid, which is an important factor in biological usage, was measured by dynamic light scattering (DLS, Sysmex Co. Zetasizer Nano). The optical properties (fluorescence and afterglow) were measured using a fluorescence spectrophotometer (Hitachi High-Technologies Co. F-7000).

3. Results and discussion

Figure 3 shows the target of $Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+}. The sample powders were pelletized by SPS. The filling rate of this target was 92%. The heating temperature during SPS was varied in the range from 1000 °C to 1300 °C. The target obtained at 1000 °C was not tenaciously bound together and was broken up in the liquid. The color of the target obtained at 1300 °C changed due to the transformation of the sample powder. In this study, the target was fabricated by SPS at 1100 °C.

Figure 4 shows XRD patterns of the sample before and after SPS. $Sr_2MgSi_2O_7$ is classified as an akermanite structure, in which two tetrahedral SiO_4 are connected at a common oxygen atom. The XRD patterns of both the sample powder before SPS and the target after SPS corresponded to the Powder Diffraction File data for $Sr_2MgSi_2O_7$ (PDF-4 10753217).

Figure 5 shows PL spectra of the sample before and after SPS at an excitation wavelength of 365 nm. The fluorescence of $Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+} can be attributed to Eu^{2+}, which was similar to another afterglow material $SrAl_2O_4$: Eu^{2+}, Dy^{3+}, while Dy^{3+} would generate trap levels related to the property of afterglow [1]. In general, the fluorescence of Eu^{2+} attributed to the transition from the $4f^65d^1$ level is a broad emission [21]. On the contrary, the fluorescence of Eu^{3+}, whose 4*f* electrons are shielded from external electric fields by the outer 5s and 5p electrons, is a sharp emission around 600 nm [21]. The peak shape and peak wavelength of the sample after SPS are the same as those of the sample before SPS. We therefore considered that the color centers of the Eu^{2+} ions were not transformed to Eu^{3+} ions by SPS. The host crystal $Sr_2MgSi_2O_7$ also was not transformed by SPS because no wavelength shift was observed in the PL spectra, which were sensitive to the host crystal.

We next investigated the dependency of the composition of the prepared nanoparticles on the kind of liquid subjected to laser ablation. Figure 6 shows XRD patterns of the target and of the nanoparticles prepared in two kinds of liquid at an energy density of 3.7 J/cm^2. The kind and amount of by-products that were formed by laser ablation in liquid depended on the kind of liquid used. The by-product formed in deionized (DI) water was strontium carbonate, which might have been synthesized by the reaction between strontium ion and carbon dioxide in DI water. The by-product formed in ethanol was strontium formate, which might have been synthesized by the reaction between strontium ion and ethanol. Table 1 shows the ratio of the afterglow nanoparticles ($Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+}) and the by-products ($SrCO_3$, $Sr(HCOO)_2$) in each liquid to the total prepared nanoparticles, as estimated by the Reference Intensity Ratio (RIR). RIR is a method of estimating the amount of sample by the ratio of peak intensity in the XRD pattern of the sample to corundum (α-Al_2O_3). At the same energy density, the amount of by-product in DI water (41%) was significantly smaller than it was in ethanol (76%). DI water was used as the liquid in the following experiments.

We next investigated the effect that the energy density of laser ablation in liquid had on the composition and size of the formed nanoparticles. Figure 7 shows XRD patterns of the nanoparticles at each energy density. These results indicate that afterglow nanoparticles with strontium carbonate as a by-product were formed at each energy density. The peaks around 25 degrees that are attributed to the by-product were reduced by a decrease in the energy density of the laser ablation in liquid. Figure 8 shows the ratio of the afterglow nanoparticles ($Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+}) and the by-product ($SrCO_3$) to the total prepared nanoparticles, as a function of the energy density. These results indicate that the ratio of by-product can be decreased by a decrease in the energy density. Figure 9 shows the particle size of the nanoparticles measured by DLS as a function of energy density. Particle size in liquid is measured by DLS because Brownian motion is utilized for this measurement. The size of the prepared nanoparticles was reduced by a decrease in the energy density of the laser ablation in liquid. In this study, nanoparticles with a size of 76 nm were obtained. For reference, the particle distribution at each energy density is given in the supplementary data.

Figure 10 shows the PL spectra of the target and afterglow nanoparticles at an excitation wavelength of 280 nm. No discrepancy was observed between the peak wavelength or shape of the PL spectra in the target and nanoparticles. These peaks are typical of the broad fluorescence spectra that are attributed to f-d transitions of Eu^{2+}. The wavelength of the fluorescence spectra of f-d transitions of Eu^{2+} is susceptible to the crystal field, while that of f-f transitions of Eu^{3+} is not affected because the 4f electrons are shielded by 5s and 5d electrons [21]. The typical fluorescence spectrum of Eu^{3+} is characterized by sharp red emissions. Therefore, the host crystal ($Sr_2MgSi_2O_7$) and color center (Eu^{2+}) would not be transformed by laser ablation in liquid.

Next, the afterglow properties of the nanoparticles were investigated. Figure 11 shows a decay curve of the afterglow nanoparticles, which indicates the afterglow intensity as a function of time following the blocking of excitation. The intensity of fluorescence spectrophotometer was measured every 50 ms. The afterglow intensity was normalized at starting time. As mentioned above, the particle size of nanoparticles prepared by laser ablation in liquid depends on the power density. The afterglow properties of nanoparticles with different particle size were compared. A decrease in particle size reduced the afterglow intensity and duration. As mentioned in the introduction, afterglow is attributed to the recombination of the trapped carriers. In the case of trapped electrons, the following eq. 3.1

is applied to the decay curve if the traps and color centers have nearly equal capture cross-sections [22]:

$$I(t) = I_0 \big/ (1 + \gamma t)^n \qquad (3.1)$$

$$\gamma = N / a n_t\,, \qquad (3.2)$$

where $I(t)$ is the afterglow intensity of the decay curve, I_0 is the initial afterglow intensity, t is time, N is the trap concentration, a is the probability per second that a trapped electron will be thermally excited into the conduction band, as given by the following eq. 3.3, and n_t is the number of electrons per unit volume in the trap level. If one trap is related to the afterglow, the type of decay is the second-order and the n value is 2. However, actual value of n is around 0.5 – 2 because traps with various energy levels exist in afterglow material. The afterglow property significantly depends on the n value as shown in eq. 3.1.

$$a = s \exp(-\varepsilon / kT)\,, \qquad (3.3)$$

where s is the frequency factor, ε is the energy between the conduction band and the trap level, k is the Bolztmann constant, and T is temperature. If t is far greater than $1/\gamma$, eq. 3.1 can be approximated by the following eq. 3.4:

$$I(t) \propto t^{-n}\,. \qquad (3.4)$$

Therefore, the afterglow intensity decayed significantly with an increase in the n value. The values of *n* at each energy density were found by the curve-fitting shown in Figure 11. The values of *n* at 3.7 J/cm^2 (average particle size: 710 nm), 1.6 J/cm^2 (235 nm) and 0.58 J/cm^2 (76 nm) were 0.59±0.0078 (correlation coefficient *r*: 0.995), 0.88±0.017 (*r*: 0.993) and 1.1±0.071 (*r*: 0.959), respectively. Figure 12 shows the value of *n* as a function of average particle size. A decrease in average particle size causes a decrease in both the afterglow intensity and duration because a large *n* value indicates significant decay of the afterglow. A decrease in particle size increases the specific surface area of the particles. This would increase the nonradiative transition through the energy levels of surface defects and the vibration of water molecules, which would in turn reduce the afterglow intensity and duration. Surface passivation by polymer and silica would be effective to prevent such a diminishment in afterglow properties.

4. Conclusions

Novel optical nanoparticles with afterglow properties dispersed in solvent were prepared by laser ablation in liquid. The composite of nanoparticles was controlled by the energy density of the laser ablation of the target material. By-product was reduced by a decrease in the energy density to 0.85 J/cm^2. The size of afterglow nanoparticles was also controlled by the energy density. We obtained afterglow nanoparticles whose average size ranged from 76 to 710 nm.

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Figure captions

Figure 1. Schematic of laser ablation in liquid.

Figure 2. Schematic of spark plasma sintering (SPS) system.

Figure 3. Pelletized target of $Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+}.

Figure 4. XRD patterns: (a) sample before SPS, and (b) sample after SPS.

Figure 5. PL spectra: (a) sample before SPS, and (b) sample after SPS.

Figure 6. XRD patterns of the nanoparticles prepared in two kinds of liquid at an energy

density of 3.7 J/cm^2: (a) target material, (b) nanoparticles prepared in DI water, and (c) nanoparticles prepared in ethanol.

Figure 7. XRD patterns of nanoparticles at each energy density: (a) 3.7 J/cm^2, (b) 2.4 J/cm^2, (c) 1.6 J/cm^2, (d) 1.1 J/cm^2, and (e) 0.85J/cm^2.

Figure 8. Ratio of compounds to the total prepared nanoparticles, as a function of energy density: (a) the afterglow nanoparticles ($Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+}), and (b) the by-product ($SrCO_3$).

Figure 9. Particle size of nanoparticles in liquid as a function of energy density.

Figure 10. PL spectra at an excitation wavelength of 280 nm: (a) target, and (b) afterglow nanoparticles.

Figure 11. Decay curve of afterglow nanoparticles (excitation wavelength: 280nm, emission wavelength: 465nm).

Figure 12. Value of *n* as a function of average particle size.

Supplementary data: Particle size distribution at each energy density measured by DLS is shown in Figure S1-5.