Research Article

Preparation of SiO₂-Capped Sr₂MgSi₂O₇:Eu,Dy Nanoparticles with Laser Ablation in Liquid

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The effect of SiO₂ capping on the optical properties of nanoparticles was investigated. The photoluminescence (PL) intensity was successfully improved by SiO₂-capping. Sr₂MgSi₂O₇:Eu,Dy nanoparticles were prepared by laser ablation in liquid. The SiO₂ capping was performed using the Stöber method with ultrasonication. The TEM images indicated that the Sr₂MgSi₂O₇:Eu,Dy nanocrystal was capped with amorphous SiO₂, and the shape of the completely capped nanoparticle was an elliptical nanorod, which aggregated after a long SiO₂ capping reaction time. The peak wavelength and the shape of the PL spectra were not changed by the pelletization and the laser ablation in liquid. The PL intensity of SiO₂ capped nanoparticles was significantly increased. Nonradiative relaxation via surface defects and energy transfer to water molecules decrease the PL intensity. These phenomena accelerate in the case of nanoparticles. SiO₂ capping would prevent these phenomena and improve the optical properties of nanoparticles. The combination of laser ablation in liquid and the chemical reaction is important to expand the applications of this method in various research fields.

1. Introduction

Extensive studies have recently been conducted regarding laser ablation in liquid because of the high purity and simplicity of preparing a colloidal solution. Laser ablation in liquid is a method used to prepare nanoparticles in solution by irradiating a target material in a liquid with a focused pulse laser beam. Many researchers have studied laser ablation in the gas phase or under vacuum since the development of the laser in the 1960s [1]. Laser ablation in liquid has generally been applied to the preparation of metal nanoparticles such as gold and silver, and this technique has significantly improved during the 2000s [2–9]. The nanoparticles prepared using this method were collected with high efficiency. Recently, this method was used not only for metal but also for organic materials [5, 8, 10] and ceramics [8, 11]. Some researchers have applied the technique of laser ablation in liquid to phosphor materials because the resulting nanoparticles have

unique optical properties and various potential applications [12].

If a phosphor material is reduced to nanosize, its optical properties decline [13, 14]. This decline occurs because specific surface area related to surface defects is increased. The surface defects increase the occurrence of nonradiative relaxation. Surface capping of a nanoparticle is an effective method for improving the optical properties of the nanoparticles. The photoluminescence was increased by capping nanoparticles with organic or inorganic materials [13, 15–19]. The capping layer passivates the surface defects that reduce the optical properties. SiO₂ capping is a promising method for the passivation of nanoparticles because of its low toxicity, high hydrophilic properties, optical transparency, and ease of synthesis. Many methods can be used to cap nanoparticles with SiO₂ such as the sol-gel method [20], the precipitation method [21], the microemulsion method [22, 23], the diffusion flame method [24, 25], and the supercritical method [26, 27]. The sol-gel method is widely

used for capping because of the low temperature process, results in high uniformity, and can be used in the synthesis of dense ceramics [20]. The sol-gel method includes the following two-step reaction:

The rate of each reaction depends on the pH [28]. The rate of the hydrolysis reaction is accelerated under both acidic and basic conditions but not at a neutral pH, whereas the rate of the condensation reaction is accelerated in the range from pH 6 to pH 14. The Stöber method forms SiO_2 nanoparticles and/or SiO_2 capping layers and is classified as a sol-gel synthesis that uses a basic catalyst such as ammonia. [29]. The SiO_2 particle size is controlled by the pH, the concentration of the reagents, and the reaction time.

In this study, SiO_2 -capped $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu,Dy}$ nanoparticles prepared using laser ablation in liquid were investigated. In general, the optical properties of the phosphor material are degraded by reducing the particles to nanosize. Capping is a useful way to improve the optical properties. We applied the Stöber method to the nanoparticles prepared using laser ablation in liquid. Laser ablation in liquid in conjunction with a chemical reaction would be useful for various applications.

2. Experimental Methods

The powder of $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu,Dy}$ was purchased from Mitsubishi Chemical. Ethanol (fluorescence analysis grade), tetraethyl orthosilicate (TEOS), ammonia water, and 1-propanol were purchased from Kanto Chemical. These reagents were used without further purification.

Laser ablation in liquid was used for the preparation of nanoparticles. $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu,Dy}$ powder was pressed into a mold to obtain a pellet with a filling rate of 60%. The pellet was sintered in a furnace under an argon atmosphere at 1100°C for 1 hour. The pellet to be used as a target was placed in a cell under an argon atmosphere, and ethanol was poured into the cell. The target was irradiated with pulsed laser beam (JDS Uniphase, Model 210, THG, wavelength: 355 nm, pulse width: 50 ns, repetition rate: 7 kHz, power: 2 W) for 6 hours. A lens with a focal length of 90 mm was used to focus the laser beam onto the top surface of the target. The distance between the top of the target and the surface of the ethanol was 7 mm. The solution was evaporated after the laser ablation in liquid to obtain the nanoparticle powder.

The SiO_2 capping was performed using the Stöber method. The nanoparticle powder (5 mg) was redispersed in ethanol (150 μL) using ultrasonication at 20°C for 1.5 hours. TEOS (0.5 μL), ammonia water (2.0 μL), and deionized (DI) water (2.5 μL) were added to the solution for the surface modification, and ultrasonication was performed at 20°C . The duration of the ultrasonication was varied. 1-Propanol was added to the solution to terminate the reaction. A 2-step centrifugation (15000 rpm for

FIGURE 1: XRD spectra of (a) the raw material powder, (b) the target and (c) the nanoparticles prepared via laser ablation in liquid.

10 minutes, 6000 rpm for 10 minutes, CT15E, Hitachi Koki) and decantation were used to remove the unreacted reagent.

The nanoparticles were identified using an X-ray diffractometer (XRD, D8 Discover μHR , Bruker AXS). The nanoparticles were observed using a field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi High-Technologies) and a field-emission transmission electron microscope (FE-TEM, 200 kV, JEM-2010F, JEOL). An energy dispersive X-ray (EDX) analysis was performed at the same time. The photoluminescence (PL) spectra were measured using a fluorescence spectrophotometer (F-7000, Hitachi High-Technologies).

3. Results and Discussion

The XRD spectra of the raw material powder (a), the target (b), and the nanoparticles prepared using laser ablation in liquid (c) are shown in Figure 1. Peaks for $\text{Sr}_2\text{MgSi}_2\text{O}_7$ were observed in each spectrum. $\text{Sr}_2\text{MgSi}_2\text{O}_7$ possesses a tetragonal crystal structure characterized by $a = 7.9957$, $c = 5.1521 \text{ \AA}$ and the space group $\text{P4}_2\text{m}$ [30]. No transformation of $\text{Sr}_2\text{MgSi}_2\text{O}_7$ to another phase was observed during the sintering of the target and the laser ablation in liquid. Strontium formate was formed as a byproduct by the laser ablation in liquid, as shown in Figure 1(c). A similar phenomenon was observed in our previous study [14]. Carboxylic acid is formed as a result of the oxidation of alcohol. The reaction between the target material and solvent ethanol would form strontium formate. The reference intensity ratio

FIGURE 2: SEM images of nanoparticles with or without SiO_2 -capping. The reaction time of the SiO_2 capping: (a) 0 hours, (b) 1 hour, and (c) 4 hours.

FIGURE 3: TEM images of the nanoparticles with SiO_2 capping. The reaction time of the SiO_2 capping: (a) 1 hour and (b) 4 hours. (c) High-magnification TEM image of the SiO_2 capped nanoparticles. (d) Electron diffraction pattern of the SiO_2 -capped nanoparticles.

(RIR), which estimates the amount of the sample from the ratio of the peak intensity in the XRD pattern of the sample to that of corundum ($\alpha\text{-Al}_2\text{O}_3$), indicated that the ratio of $\text{Sr}_2\text{MgSi}_2\text{O}_7$ to $\text{Sr}(\text{HCOO})_2$ was 83 : 17.

The SEM images of nanoparticles with or without SiO_2 capping are shown in Figure 2. The reaction times for the Stöber method for SiO_2 capping were 0 (a), 1 (b), and 4 hours (c). The nanoparticles without SiO_2 capping aggregated and formed almost spherical particles, as shown in Figure 2(a). Flocculation of the nanoparticles may have occurred during the fabrication of the sample powder as a result of

evaporation. In contrast, the shape of the nanoparticles with SiO_2 capping in the initial stage (1 hour) was an elliptical nanorod growing one-dimensionally. After several hours, these nanorods aggregated and were tightly connected by SiO_2 capping. The shape of the SiO_2 synthesized using the Stöber method in the presence of $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu,Dy}$ nanoparticles, which was an elliptical nanorod, was different from that in the absence of $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu,Dy}$ nanoparticles, which was almost spherical. The formation of the elliptical nanorod would be related to the presence of the nanoparticles and the ultrasonication. Long-time ultrasonication

would accelerate the aggregation of nanoparticles, and they would be capped with SiO_2 .

Figures 3(a), 3(b), and 3(c) show TEM images of the nanoparticles with SiO_2 capping. Figure 3(d) shows the electron diffraction pattern of the SiO_2 capped nanoparticles. The reaction time of the SiO_2 capping in Figures 3(a), 3(c), and 3(d) was 1 hour and that in Figure 3(b) was 4 hours. Figures 3(a) and 3(b) depict phenomena in the SEM images similar to those shown in Figure 2. Lattice fringes were observed in the high-magnification TEM image of the SiO_2 -capped nanoparticles in Figure 3(c). The SiO_2 capping layer synthesized using the Stöber method was amorphous as a result of this process without heat treatment. Figure 3(c) indicates that crystalline $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu,Dy}$ nanoparticles were capped with amorphous SiO_2 . The primary particle size would be approximately 10 nm in dotted lines of Figure 3(c). Because the secondary particle size was a few ten nanometers, the particles formed via the laser ablation in liquid method were flocculated, as shown in Figure 2(a), and these particles were partially deagglomerated by ultrasonication, as shown in Figure 3(c). Figure 3(d) shows the electron diffraction pattern of the SiO_2 capped nanoparticles. The ring patterns indicated that these nanoparticles are polycrystalline. Figure 4 shows the EDX spectrum of the SiO_2 capped nanoparticles. The elements of the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ nanoparticles, the SiO_2 capping layer, and the copper grid were observed in the EDX spectrum. The atomic ratios of Si, Sr, and Mg in the SiO_2 -capped nanoparticles were 80.3, 12.0, and 7.7, respectively. The above data demonstrate that the nanoparticles were capped with SiO_2 .

Figure 5 shows the PL spectra of (a) the raw material powder, (b) the target, and (c) the nanoparticles prepared via laser ablation in liquid. The peak wavelength and shape of the spectra of the raw material powder, the target, and the nanoparticles were nearly identical. This result indicated that no transformation of the luminescent center or the host material by pelletization and laser ablation was observed. The target was rapidly heated to a high temperature as a result of the irradiation from the laser beam and then cooled. This process introduces possibilities for transformation such as a phase change. However, no major transformation was observed under these experimental conditions. In general, the emission wavelength and the broadening of a Eu^{2+} spectrum are sensitive to the host material as a result of f-d transitions [31]. The experimental results provided no evidence for a transformation of the host material. No observation of a peak that would be typical of the luminescence of Eu^{3+} suggested that oxidation of luminescent center (the transformation from Eu^{2+} to Eu^{3+}) did not occur. The PL spectra did not significantly change, although strontium formate was formed, as shown in Figure 1(c). In this study, a small amount of byproduct would not have a strong impact on the PL spectra.

The effect of SiO_2 capping on the PL intensity of the $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu,Dy}$ nanoparticles is shown in Figure 6. The reaction time of the SiO_2 capping varied from 0 to 4 hours. The peak intensity of the PL spectra increased as the reaction time increased. Figure 7 shows the peak intensity as a function of the reaction time. The peak intensity increased

FIGURE 4: EDX spectrum of the SiO_2 -capped nanoparticles.

FIGURE 5: PL spectra of (a) the raw material powder, (b) the target and (c) the nanoparticles prepared via laser ablation in liquid.

gradually up to 2 hours and increased significantly at approximately 4 hours. In general, many defects that reduce the PL intensity via nonradiative relaxation exist on the nanoparticle surface [13]. Water molecules, which possess a large vibrational energy, exist near the nanoparticles in the colloidal solution and also reduce the PL intensity via energy transfer to the water molecules [32]. Nanoparticles have a large specific area and, therefore, exert a profound effect resulting in a decrease in the PL intensity compared with the bulk material [13, 14]. Capping nanoparticles would passivate the surface defects and prevent the transfer of energy to the water molecules. Therefore, capping resulted in improved optical properties in previous studies [13, 15–19]. Capping nanoparticles with SiO_2 was nearly complete at 4 hours.

FIGURE 6: PL spectra of the nanoparticles with or without SiO₂ capping. The reaction time varied from 0 to 4 hours.

FIGURE 7: Peak intensity of the PL spectra as a function of the reaction time of the SiO₂ capping.

4. Conclusions

Sr₂MgSi₂O₇:Eu,Dy nanoparticles were prepared via laser ablation in liquid and were capped with SiO₂ using the Stöber method. The shape of the SiO₂-capped nanoparticles was an elliptical nanorod. The TEM images indicated that the Sr₂MgSi₂O₇:Eu,Dy nanocrystal was capped with an amorphous SiO₂ layer. The PL intensity of the SiO₂-capped nanoparticles increased with increasing SiO₂ capping reaction times. The nonradiative relaxation via surface defects and the energy transfer to the water molecules was reduced by SiO₂ capping.

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