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Preparation of Y_2O_3:Er,Yb nanoparticles by laser ablation in liquid

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ABSTRACT

We prepared a Y_2O_3:Er,Yb nanoparticles by laser ablation in liquid. The laser used the second harmonic generation Nd:YAG (532 nm). A preparation process and measurement of upconversion properties were performed by varying the range of the energy density of the laser. Images from scanning electron microscopy (SEM) indicated that two types of nanoparticles existed in the product of laser ablation in liquid. We concluded the following: one type of nanoparticles was prepared from the nucleation of materials in a plume and the other was prepared by fragmentation. In the photoluminescence spectra, green ($^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$) and red ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) fluorescence were observed using a 980 nm laser diode (LD) as the excitation source. We confirmed that the fluorescence intensity increased with increasing energy density of the laser. Thus, we concluded that the number of the nanoparticles increased as the energy density of the laser was increased.

1. Introduction

In recent years, rare-earth doped fluorescent materials have attracted much attention because of their unique optical properties and potential applications in the field of bio-imaging, color displays, and optical communications [1–5]. Articles on the upconversion fluorescent properties of rare-earth doped Y_2O_3 have been reported. The upconversion fluorescent materials are substances that emit visible light by irradiating near infrared as an exciting light [6–8]. Activators, such as Er^{3+}, Tm^{3+}, Ho^{3+}, and Pr^{3+}, function as the upconversion fluorescent materials [9–13]. Light of various colors is emitted depending on the rare-earth ions. Because Yb^{3+} has energy bands at 980 nm ($^2F_{5/2} \rightarrow {}^2F_{7/2}$), it is often used as an effective sensitizer. In particular, Y_2O_3 as a host material has the same crystal structure as Er_2O_3 and Yb_2O_3 [14–16]. Y_2O_3 includes a comparatively high refractive index, low phonon energy, and high chemical and thermal stability.

Thus far, the chemical synthetic methods, such as solid state, hydrothermal, coprecipitation, and sol–gel methods, are well-known for preparing the upconversion nanoparticles [17–22]. In these methods, however, nanoparticles are easily aggregated by heating processes. It has been difficult to prepare the finely dispersed nanoparticles, and new synthetic methods are needed. Additionally, nanoparticles have been prepared in the gas-phase. Laser ablation, such as pulse laser deposition (PLD), has often been studied by researchers who fabricate nanoparticles on various targets [23–25].

We focused on laser ablation in liquid. This technology is for preparing the colloidal solution by irradiating the targets with a pulsed laser beam in liquid. Laser ablation in liquid has many advantages: the nanoparticles are formed easily; the nanoparticles are collected with high efficiency compared with preparation in the gas phase; and pure colloidal solutions can be prepared, compared with general chemical synthesis methods. Recently, many researchers have studied laser ablation in liquid, and various materials have been irradiated with this technology. Cotton et al. prepared a colloidal solution by irradiating the metal targets with a laser [26]. Mafune et al. prepared Au nanoparticles in a surfactant [27,28]. Hosokawa et al. irradiated organic materials with laser ablation [29]. Koshizaki and co-workers prepared a colloidal solution containing ceramics using this technology [30]. However, no research has yet been performed to prepare the upconversion colloidal solution by laser ablation in liquid.

In this study, a Y_2O_3:Er,Yb colloidal solution was prepared by laser ablation in liquid. We used nanosecond laser pulses in the preparation of the nanoparticles. We investigated the relations between the particle size of the upconversion nanoparticles and the energy density of laser ablation in liquid. Subsequently, we evaluated the performance of the process by viewing the samples with a scanning electron microscope (SEM) and a transmission electron microscope (TEM). Additionally, the optical properties of the upconversion nanoparticles were measured with fluorescence spectrophotometer.

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2. Experimental methods

2.1. Preparation of the target

$Y(NO_3)_3{\cdot}6H_2O$ (99.99% Kanto Chemical Co., Inc.), $Er(NO_3)_3{\cdot}5H_2O$ (99.9% Mitsuwa's Pure Chemicals), $Yb(NO_3)_3{\cdot}5H_2O$ (99.9% Wako Pure Chemical Industries, Ltd.), and aqueous ammonia (28% Kanto Chemical Co., Inc.) were used as starting materials. We completely dissolved $Y(NO_3)_3{\cdot}6H_2O$ (11.1 mmol), $Er(NO_3)_3{\cdot}5H_2O$ (0.125 mmol) and $Yb(NO_3)_3{\cdot}5H_2O$ (1.25 mmol) with deionized water. Aqueous ammonia (11 mL) was added dropwise to this solution. The prepared solution was aged for 24 h. The precipitations were dried at 900 °C for 2 h. The dried powder was pressed into shapes and sintered at 1250 °C for 4 h. The targets were 9 mm in diameter and 3 mm in height.

An overview of the synthesis scheme is given by the following reaction steps:

$$RE(NO_3)_3 + 3NH_4OH \rightarrow RE(OH)_3 + 3NH_4NO_3 \quad (1)$$

$$2RE(OH)_3 \xrightarrow{900\,^{\circ}C} RE_2O_3 + 3H_2O \quad (2)$$

where RE indicates Y, Er, Yb.

2.2. Preparation of the colloidal solution

The Y_2O_3:Er,Yb colloidal solution was prepared by laser ablation in liquid. The target was placed on the bottom of the cell that was filled with 2 ml of deionized water. The Nd:YAG laser (Spectron Laser Systems Ltd., SL8585G) served as a light source for pulsed laser ablation and was operated with the second harmonic generation (wavelength: 532 nm) at a laser energy of 23.1 mJ/pulse and a repetition rate of 10 Hz. The average energy density of the laser was varied in the range of 0.20–1.61 J/cm^2. When we irradiated an alignment paper (Laser Create Corp) with laser, we calculate the average energy density from the spot size per pulse and the power of the laser. The pulse width was 13 ns when measured with a fast PIN photodiode and a digital oscilloscope. The target was irradiated with the laser for 30 min.

2.3. Characterizations

We characterized the composition of the synthesized target and the prepared nanoparticles with an X-ray diffractometer (XRD, PANalytical X'pert-PRO-MRD). The average particle size was measured by Dynamic Light Scattering (DLS, Sysmex Co. Zetasizer Nano). The laser source of the DLS was a He-Ne laser (633 nm). The configuration of the nanoparticles was observed by scanning electron microscopy (SEM, Hitachi High-Technologies Co. S-4800) and transmission electron microscopy (TEM, JEOL Ltd. JEM-1010BS). The colloidal solution of Y_2O_3:Er,Yb was placed onto the elastic carbon supporting film. A powder of the Y_2O_3:Er,Yb targets was placed on a microscope stage. The elemental analysis of the nanoparticles was performed by energy dispersive X-ray (TEM-EDX) spectroscopy. Under irradiation with a 980 nm laser diode (LD), upconversion properties were measured using a fluorescent spectrophotometer (Hitachi High-Technologies Co. F-7000).

3. Result and discussion

Fig. 1 shows the XRD patterns of Y_2O_3:Er,Yb in the synthesized targets and the prepared nanoparticles. The vertical bars below the patterns represent the standard diffraction data (ICDD-PDF-4 no. 01-079-1716). The synthesized targets and the prepared nanoparticles had a space group Ia3 of the C-type Y_2O_3 structure. These nanoparticles were prepared at an average energy density of

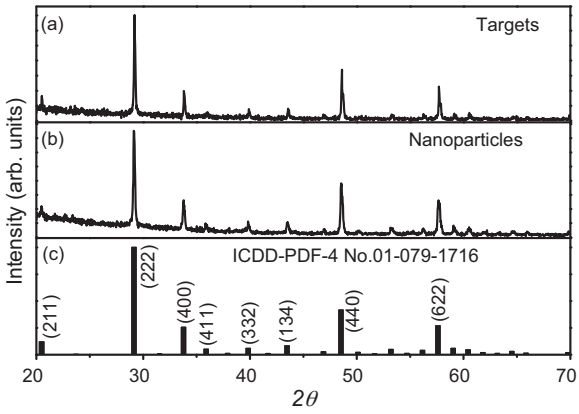

Fig. 1. XRD pattern of targets (a), nanoparticles (b) and ICDD-PDF-4 no. 01-079-1716 of Y_2O_3.

4.2 J/cm^2. We found that the crystal phase of the nanoparticles prepared by laser ablation in liquid was the same as that of the targets. No additional peaks representing other phases were observed.

Fig. 2 shows the particle size as a function of the average energy density in laser ablation in liquid. The particle size was measured with DLS. This particle size was calculated from the scattering intensity of the fluctuation, which is dependent on the Brownian motion of the particle. The size distribution of DLS is provided in Supporting information (SI1). We found that the particle size increased with the increasing energy density of the laser. Yoshimura et al. showed a similar tendency [31].

We observed the configuration of the nanoparticles with SEM. In SEM images, nanoparticles on the order of 10^1–10^2 nm were observed. Fig. 3 shows the SEM images of the synthesis targets and the nanoparticles prepared by laser ablation in liquid. Fig. 3(a) shows the SEM images of the targets. Many aggregated nanoparticles on the order of a 10^2 nm were observed. Fig. 3(b)–(d) shows the SEM images of the nanoparticles. The average energy density in Fig. 3(b)–(d) is 0.59, 1.06 and 1.61 J/cm^2, respectively. In 0.20 and 0.35 J/cm^2, the nanoparticles measuring on the scale of 10^2 nm nanometers were not observed. In the range between 0.59 and 1.61 J/cm^2, the nanoparticles on the scale of 10^2 nm were observed. During the preparation of the nanoparticles, the threshold average energy density ranged between 0.35 and 0.59 J/cm^2. We found that the particle size increased with increasing energy density of the laser in a similar manner as DLS. The nanoparticles were aggregated to each other. The size of the primary particles was nearly unchanged by the energy density. We found that the size and configurations of the nanoparticles measuring on the order of 10^2

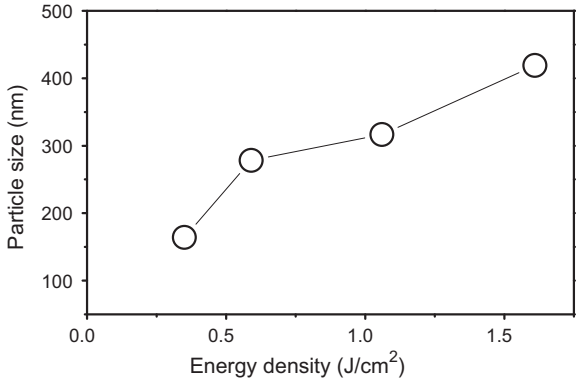

Fig. 2. Particle size as a function of the energy density for laser ablation in liquid.