

Upconversion luminescence properties of $\text{Y}_2\text{O}_3\text{:Er,Yb}$ colloid prepared by laser ablation in liquid

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The upconversion luminescence of $\text{Y}_2\text{O}_3\text{:Er,Yb}$ nanoparticles was observed by an optical microscope, and in-situ measurement of the upconversion spectra in a single particle level was performed. The nanoparticles were prepared by laser ablation in liquid. The target material was synthesized by a precipitation method and sintered at 1250 °C. The particle size of the prepared nanoparticles was a few hundred nm. In the upconversion spectra, the red luminescence ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) of the nanoparticles was stronger than their green luminescence ($^2\text{H}_{11/2}/^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$), while the red luminescence of the target material was weaker than its green luminescence. Because nanoparticles have a large specific surface area, the groups with high phonon energy on the surface accelerate the nonradiative relaxation of the red luminescence process. Fragmentation of target material by laser ablation in liquid led to the increase in the ratio of red to green luminescence.

Key words: Nanoparticle, upconversion, Y_2O_3 , laser ablation, femtosecond laser.

Introduction

In recent years, rare-earth-doped fluorescent nanomaterials have attracted much attention due to their unique optical properties and various potential applications. Upconversion nanoparticles are fluorescent materials that emit visible light during the irradiation of near-infrared light [1]. In human cells, the absorbance of light in wavelengths between 650 and 1000 nm is low [2]; this region is called the ‘optical transmission window’. Upconversion nanoparticles, such as $\text{Y}_2\text{O}_3\text{:Er,Yb}$, can be excited and emit light in this region; therefore, these nanoparticles are attractive for use as markers for bioimaging and cancer therapy [3, 4]. Organic dyes, quantum dots and fluorescent proteins have also been used in bioimaging. They are powerful tools that can help explain the transfer pathways of medicines and identify the positions of lesions in living systems. The traditional bioimaging methods suffer from many problems such as autofluorescence and the damage to living cells, which can be solved by using up conversion nanoparticles for bioimaging instead [5]. Autofluorescence is the phenomenon whereby the background emission of living cells is increased by the irradiation of the excitation light during the bioimaging of the specific cell. Autofluorescence is one of the major challenges in bioimaging, but it can be reduced with near-infrared excitation. Cancer therapy is another

area where the use of upconversion nanoparticles is very attractive. Photodynamic therapy is an especially promising method of cancer therapy because it is less invasive than other methods. In this therapy method, a sensitizer is administered to living cells, which are then irradiated with visible light. This irradiation generates active oxygen, which leads to tumor cell death. If upconversion nanoparticles are administered to cells in combination with a sensitizer, such as talaporfin sodium, then near-infrared irradiation can be used from outside of human body and large tumor cells can be killed because of the large penetration depth of the near-infrared light [6].

There are various nanoparticle preparation methods, which can roughly be divided into gas-phase [7, 8] and liquid-phase methods [9]. Colloidal solutions of nanoparticles prepared by liquid-phase methods are suitable for biomedical applications. One of these methods is laser ablation in liquid, which creates nanoparticles in liquid by irradiating a target with a pulsed laser beam [10-14]. Laser ablation in gas or vacuum has been studied by many researchers who fabricated various functionalized thin films on a substrate [15]. Recently, many researchers have begun studying laser ablation in liquid. Laser ablation in liquid has many advantages: the nanoparticles are formed easily; the nanoparticles are collected with high efficiency; and the formation of nanoparticles in high pressure plasma is interesting from an academic point of view. Usually the laser ablation target in liquid is a metal, such as gold or silver, because of their stability. The dependency of various parameters such as wavelength,

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energy density and solvent on the properties of prepared nanoparticles has been researched. However, there are a few reports about fluorescent materials prepared by laser ablation in liquid.

In this study, we fabricated a $\text{Y}_2\text{O}_3\text{:Er,Yb}$ colloidal solution by laser ablation in liquid. An optical microscope was used to observe the luminescence of the upconversion nanoparticles. A spectrometer was used to record the spectra of the nanoparticles, and it was found that their spectra were different from that of the target material. We concluded that this discrepancy was related to the multiphonon relaxation in the red luminescence process.

Experiments

The target was synthesized by a normal precipitation method [16]. Yttrium nitrate $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, erbium nitrate $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and ytterbium nitrate $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were ultrasonically dissolved in DI water. An ammonium solution (28%) was added to this solution and then stirred for 2 hours. The solution was then aged for 24 hours to obtain a precipitate at room temperature. This solution was separated with centrifugation (5000 rpm, 10 minutes, DI water: 3 times, ethanol: 1 time) to obtain the sample powder. This powder was dried in a vacuum oven at 60 °C for 12 hours. This powder was then heated at 900 °C in an electric furnace. The powder was pressurized to obtain the target filling rate of 90%. The pellet was sintered at 1250 °C for 4 hours. The molar concentration of Er was 1%, and that of Yb was 10% in $\text{Y}_2\text{O}_3\text{:Er,Yb}$.

The $\text{Y}_2\text{O}_3\text{:Er,Yb}$ target was irradiated with a focused pulse laser beam in DI water for 30 minutes. The laser was a second harmonic generation Nd: YAG (wavelength: 532 nm, pulse width: 13 ns, repetition rate: 10 Hz). The focus length of the lens was 80 mm. The energy density on the surface of the target was 1.06 J/cm².

The composition of the sample was characterized with an X-ray diffractometer (XRD, PANalytical, X'pert-MPD-OEC). Photoluminescence (PL) spectra and upconversion spectra of the target material were measured by a fluorescence spectrophotometer (Hitachi High-Technologies Co. F-7000) at room temperature. A xenon lamp and laser diode (LD, 980 nm, 300 mW) were used as excitation sources for the photoluminescence and upconversion spectra measurements. To observe the upconversion spectra of the nanoparticles directly, a system with an optical microscope and a femtosecond laser (Spectra Physics, Tsunami, pulse width: 80 fs, repetition rate: 80 MHz) was used. To observe the nanoparticles, the upconversion colloidal solution was dropped onto a quartz glass slide and dried in air. The luminescence image of the nanoparticles was acquired by a CCD camera, and a spectrum of each nanoparticle was measured by the spectrometer simultaneously by cutting the excitation laser beam with a filter. The particle size and morphology were

observed by scanning electron microscopy (SEM, Hitachi High-Technologies, S-4800). For the SEM measurements, the upconversion colloidal solution was dropped on a carbon membrane on a copper grid and the solvent was removed by drying in a vacuum oven.

Results and discussion

The XRD pattern of the target material and powder diffraction file (PDF) data of Y_2O_3 (01-071-0049) with Miller indices are shown in Fig. 1. The peak height and angle of this XRD pattern corresponds to the PDF data of Y_2O_3 . Therefore, Y_2O_3 was successfully synthesized as the target material.

We investigated the optical properties of the bulk upconversion materials. Fig. 2(a) shows the PL spectra of the target material with an excitation wavelength of 380 nm (26,300 cm⁻¹). In the case of UV excitation, green luminescence ($^2\text{H}_{11/2}/^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) was dominantly observed. No red luminescence ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) was observed.

Fig. 2(b) shows the upconversion spectra of the target material excited by a laser diode with a wavelength of 980 nm (10,200 cm⁻¹). In the case of near-infrared excitation, green and red luminescence were both observed in the upconversion spectrum, which was similar to previous studies [16]. The intensity ratio of green luminescence to red luminescence was more than 1. In the case of the bulk material, this phenomenon was frequently observed.

Fig. 3(a) shows the upconversion spectra of the target material when excited by a femtosecond laser with a wavelength of 793 nm (12,600 cm⁻¹). The PL intensity

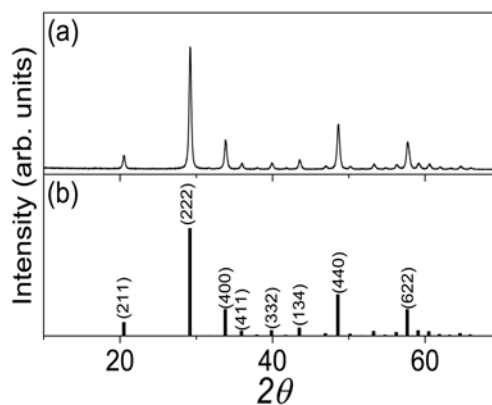


Fig. 1. (a) XRD pattern of target material, (b) PDF data of Y_2O_3 .

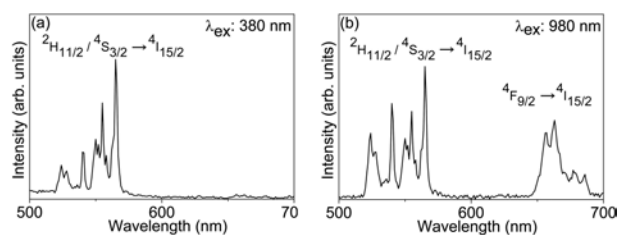


Fig. 2. (a) PL spectra of target material and (b) Upconversion spectra of target material.

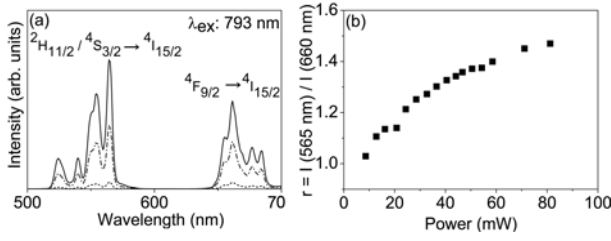


Fig. 3. (a) Upconversion spectra of target material. Laser power: solid line 81 mW, chain line 44 mW, dotted line 9 mW and (b) Intensity ratio of green luminescence (565 nm) to red luminescence (660 nm) as a function of excitation power.

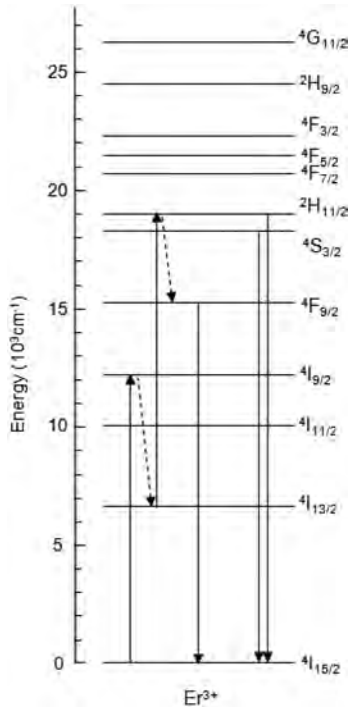


Fig. 4. Energy level diagram of Er^{3+} .

significantly depends on the excitation wavelength of the femtosecond laser and was highest at 793 nm around 800 nm. The upconversion spectrum of the femtosecond laser (793 nm) was almost the same as that of LD (980 nm) as shown in Fig. 2(a). No appreciable wavelength shift was observed. The intensity ratio of green luminescence to red luminescence as a function of excitation power is shown in Fig. 3(b). An increase in excitation power causes an increase in this ratio. A similar tendency was observed previously because higher excitation power increased the population of higher green levels ($^2H_{11/2}/^4S_{3/2}$) [17].

Fig. 4 shows an energy level diagram of Er^{3+} . The mechanism of luminescence by excitation around 800 nm is as follows [18]:

Green:

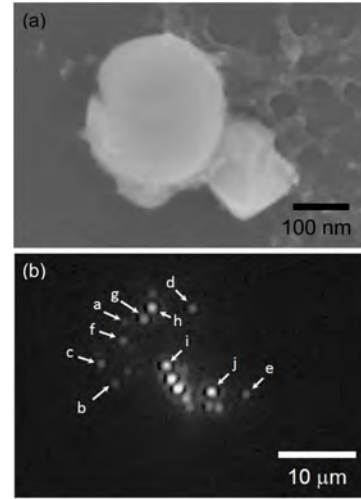
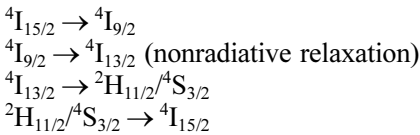


Fig. 5. (a) SEM image of $Y_2O_3:Er,Yb$ nanoparticles and (b) optical microscope image of $Y_2O_3:Er,Yb$ nanoparticles with excitation from a femtosecond laser.

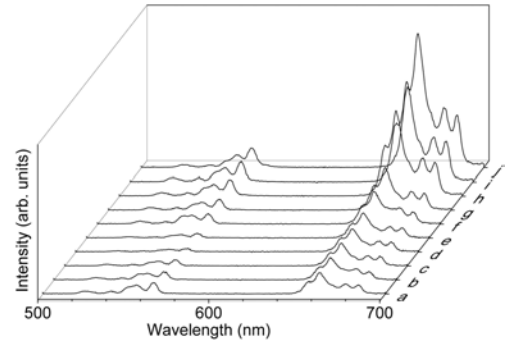


Fig. 6. Upconversion spectra of each $Y_2O_3:Er,Yb$ nanoparticle as shown in Figure 5 (b).

Red:

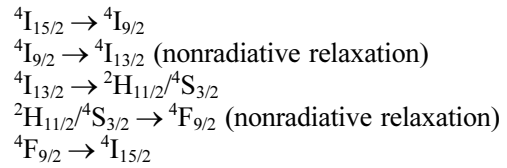


Fig. 5(a) shows an SEM image of the $Y_2O_3:Er,Yb$ nanoparticles. Most of the nanoparticles had a spherical shape, although there were a few that had a polyhedral shape, and a particle size of a few hundred nm. Additionally, the nanoparticles showed some slight aggregation. The optical microscope image of the $Y_2O_3:Er,Yb$ nanoparticles is shown in Fig. 5(b). Nanoparticles on a quartz glass slide were excited by a focused femtosecond laser beam. Each luminescence size was significantly larger than the size of a nanoparticle because of the scattering of light. There was a large deviation in the luminescence intensity for each nanoparticle, which could be due to the difference of crystallinity, size and/or surface defects of each nanoparticle. The upconversion spectra of each nanoparticle are shown in Fig. 6; these spectra were

collected by usage of an aperture to eliminate the luminescence of the other nanoparticles. Compared to the upconversion spectra of the target material, as shown in Fig. 3(a), the intensity ratio of green luminescence (565 nm) to red luminescence (660 nm) in the nanoparticles was significantly smaller, with a value of 0.27 ± 0.12 . This tendency has been reported previously [18, 19]. Fragmentation by laser ablation in liquid would lead to a decrease in the intensity ratio of green luminescence to red luminescence, according to the following explanation [18, 19]. As mentioned above, the nonradiative relaxation processes of large energy gaps ($^4\text{I}_{9/2} \rightarrow ^4\text{I}_{13/2}$, $^2\text{H}_{11/2}/^4\text{S}_{3/2} \rightarrow ^4\text{F}_{9/2}$) are included in the red luminescence process. In general, nonradiative relaxation processes prevent luminescence. Therefore, the red luminescence (660 nm) was decreased in the bulk material. The rate of phonon emission, w , is expressed by the following equation [20]:

$$w \propto \exp\left(-k \frac{\Delta E}{h\nu_{\max}}\right),$$

where E is energy gap to the nearest lower level and $h\nu_{\max}$ is maximum energy of phonon. Nanoparticles have a large specific surface area, and functional groups such as OH^- and CO_3^{2-} , which have high vibrational modes, tend to adhere to this surface [18, 21, 22]. This adhesion increases $h\nu_{\max}$ and increases the rate of phonon emission. Therefore, the nonradiative relaxation processes ($^4\text{I}_{9/2} \rightarrow ^4\text{I}_{13/2}$, $^2\text{H}_{11/2}/^4\text{S}_{3/2} \rightarrow ^4\text{F}_{9/2}$) would be bridged, and the population of $^4\text{F}_{9/2}$ would increase, leading to an increase in the observed red luminescence. The penetration depth of red luminescence (660 nm) in human cells is larger than that of green luminescence (565 nm). This property is useful for biomedical applications because of the need for low autofluorescence and no damage to cells. The upconversion nanoparticles prepared by laser ablation in liquid, which strongly emitted red luminescence, would be suitable for these applications.

Conclusions

$\text{Y}_2\text{O}_3:\text{Er},\text{Yb}$ upconversion nanoparticles were prepared by laser ablation in liquid. The spectra of each nanoparticle were investigated by a femtosecond laser system with an optical microscope. In these spectra, the intensity of the red luminescence (660 nm) was stronger than that of the green luminescence (565 nm). Nonradiative transitions in the red luminescence process would effectively be bridged by an increase in the multiphonon relaxation through surface groups. These nanoparticles could be useful for biomedical applications.

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