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Preparation of YAG : Ce nanocrystals by an environmentally friendly wet process Effect of Ce^{3+} concentration on photoluminescent property

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Nanometre-sized yttrium aluminum garnet doped with Ce^{3+} (YAG : Ce) crystals were prepared at a low temperatures by use of an environmentally-friendly wet process, in which an alcohol-water mixture with metal salts is refluxed without any addition of surfactants or adsorbing ligands. All of the YAG : Ce particles with 0.1-10 mol% of Ce^{3+} ions were found to be nanocrystals. YAG : Ce nanocrystals emitted at a 532 nm wavelength with the excitation light at 454 nm. The highest quantum efficiency was achieved at a very small Ce^{3+} content of 0.3 mol %. The decay curve of the fluorescence consisted of the three exponential terms, and the average fluorescence lifetime was around 110 ns irrespective of the Ce^{3+} concentration.

Key words: YAG, Environmentally-friendly wet process, Nanocrystals, Quantum efficiency, Ce^{3+} concentration, Fluorescence lifetime.

Introduction

Yttrium aluminum garnet doped with cerium(III) ions (YAG : Ce) has attracted a great deal of attention because it can efficiently convert the blue light emitting diode radiation into a very broad yellow emission band, which provides a basis to produce white light emitting diodes and be applied for panel displays [1]. To improve the brightness and resolution of the displays, a considerable attention has been directed to develop phosphors with fine particles.

YAG : Ce phosphor has been mainly synthesized by a solid-state reaction. However, it is very difficult to obtain fine crystals by this method which requires a high temperature above 1,600 °C with a long heating time to attain single phase (YAG) [2]. To obtain ultra-fine and monophasic YAG powders at a relatively low temperature, many preparation process methods such as a co-precipitation method [3], combustion method [4], hydrothermal method [5] and sol-gel method [6] have been extensively investigated so far. On the other hand, we have developed a synthetic method for nanocrystalline metal oxide particles at low temperatures through an environmentally-friendly wet process, the so called NAC-FAS (Nanometre-sized Crystal Formation in an Alcoholic Solution) method, in which an alcohol-water mixture with metal salts is refluxed [7]. We have already reported that this method makes it possible to prepare YAG : Ce nanocrystals with a single phase at low temperatures [8].

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In this study, we investigated the effect of the Ce^{3+} concentration of YAG : Ce prepared by the NAC-FAS method on the crystal structure and the photoluminescent property.

Experimental Procedure

$YCl_3 \cdot 6H_2O$ (5.9×10^{-3} mol) and $AlCl_3 \cdot 6H_2O$ (9.5×10^{-3} mol) with a molar ratio of $YCl_3 : AlCl_3 = 3 : 5$ were dissolved in ethanol (100 ml), and then, various amounts of $CeCl_3 \cdot 7H_2O$ ($5.9 \times 10^{-6} - 5.9 \times 10^{-4}$ mol) was added to the above solution. To the solution, NaOH (4.6×10^{-2} mol) dissolved in ethanol (50 ml) was added dropwise under refluxing over 2 hours and then the refluxing was further continued for 1 hour. After cooling to room temperature, precipitates in the reaction mixture were isolated by centrifugal separation at a rotating rate of 13,000 rpm., washed with methanol, dried in a vacuum (0.5 mmHg (66.66 Pa), 20 °C) and heated at 400 °C for 1 hour. The solid was washed with distilled water and methanol, centrifuged at a rotating rate of 13,000 rpm., dried in a vacuum (0.5 mmHg (66.66 Pa), 20 °C) and finally heated at 850 °C for 1 hour to give YAG : Ce with various concentrations of Ce^{3+}.

The products as-obtained were characterized using powder X-ray diffraction (XRD: RIGAKU RINT 2400), transmission electron microscopy (TEM: JEOL JEM-3010), a visible-ultraviolet spectrophotometer (Hitachi U-4000), a fluorescence spectrometer (JASCO FP-6500) and a fluorescence lifetime spectrometer (HORIBA FluoroCuve).

Results and Discussion

Fig. 1 shows XRD patterns of YAG : Ce with various Ce

contents (Ce/Y = 0-10 mol%). From these results only YAG peaks were observed in all cases and any peak derived from by-products such as CeO_2 did not appear, the YAG : Ce particles were found to be obtained as a single phase. In Fig. 2 are presented the results of diffuse reflection spectra in the UV-vis region for YAG : Ce doped with various Ce contents (0-10 mol%). As a result, the absorbance at around 454 nm was found to increase monotonically up to 10 mol% Ce content. Together with the result of these spectra, the XRD results that YAG : Ce have the garnet structure irrespective of increasing the Ce content (Fig. 1) indicates that the dopant Ce^{3+} was completely incorporated into YAG crystals to form a garnet solid solution. YAG:Ce with various Ce contents (0.1-10 mol %) were also confirmed to be nanocrystals with a particle size of 40-70 nm in diameter for YAG (a) and 0.3 mol% Ce-doped YAG (b) as shown in Fig. 3.

Fig. 4 shows three dimensional fluorescence spectra of YAG : Ce nanocrystals with 0.3 mol% Ce. In this excitation range (360-550 nm) and emission range (450-720 nm), only one broad luminescent peak due to the 4f-5d transition of Ce^{3+} ions was observed for YAG : Ce. Fig. 5 shows the excitation (left) and emission (right) spectra to be excited at around 454 nm and emitted at 532 nm, respectively. Furthermore, external quantum efficiency and internal quantum efficiency of the photoluminescent emission for YAG : Ce is shown as a function of Ce concentration in Fig. 6. The quantum efficiency was recorded at an excitation

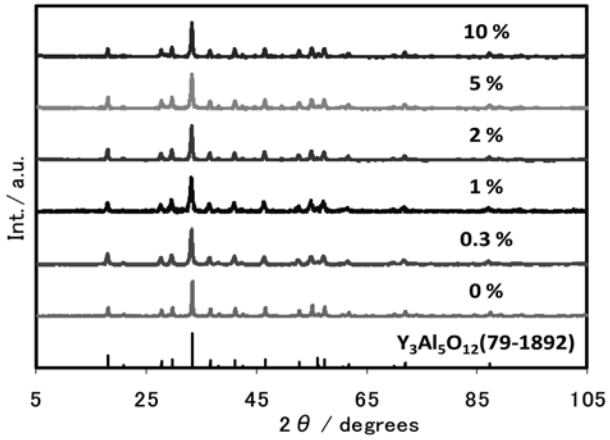

Fig. 1. XRD patterns of YAG : Ce^{3+}.

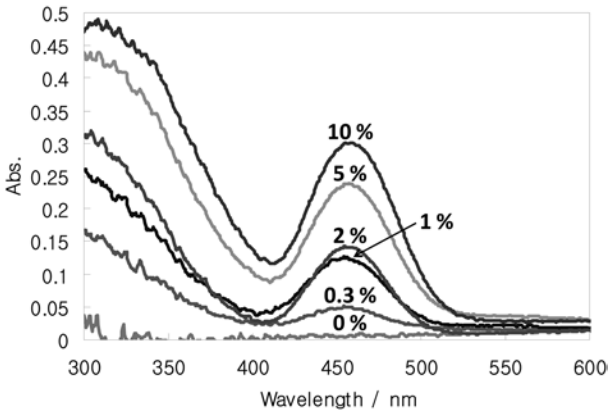

Fig. 2. UV-vis spectral patterns of YAG : Ce^{3+}.

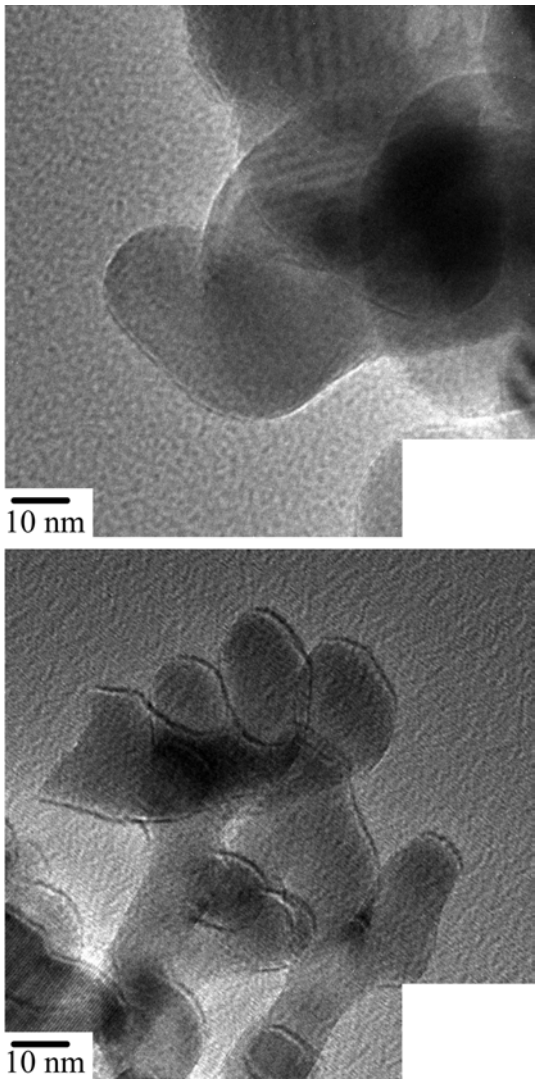

Fig. 3. TEM micrographs of YAG : Ce^{3+} at Ce = 0 mol% (a), 0.3 mol% (b).

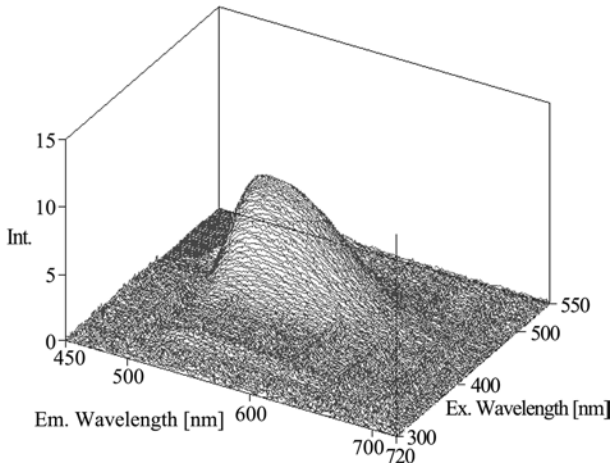

Fig. 4. 3D spectra of YAG : Ce^{3+} at Ce = 0.3 mol%.

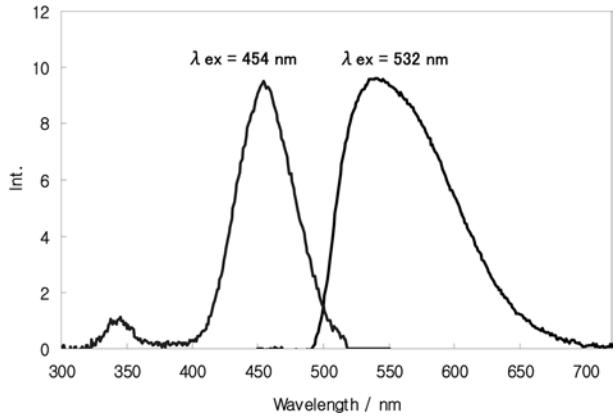

Fig. 5. Excitation and emission spectra of YAG : Ce^{3+} at Ce = 0.3 mol%.

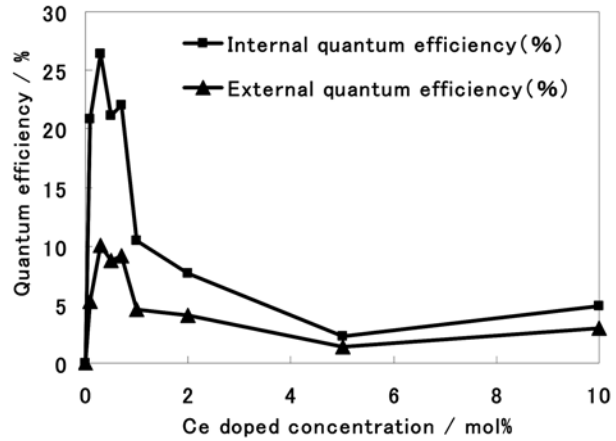

Fig. 6. External and internal quantum efficiency of YAG : Ce^{3+}.

wavelength of 453-457 nm and at an emission wavelength of 531-544 nm. The external quantum efficiency and the internal quantum efficiency showed a maximum efficiency of 10.1% and 26.4% at a Ce content of 0.3 mol%, respectively. As the absorption efficiency (30-60%) was increased with an increase of the Ce content through 0.1-10 mol% Ce , it is thought that the sharp rise in the quantum efficiency below 0.3 mol% Ce is mainly caused by increasing the Ce content, whereas the decrease above 0.3 mol% Ce is due to concentration quenching. Generally, the quantum efficiency of nanoscale phosphors is much smaller than that of the bulk because nanometre-sized particles have a high surface area, which induces more surface defects and/or distortion and easy oxidation of Ce^{3+} to Ce^{4+}. The internal quantum efficiency of YAG : Ce (Ce^{3+} : 1 mol%) nanophosphor prepared by a glycothermal method was reported to be 21.3% [9], indicating that our YAG : Ce nanocrystals have a much higher quantum efficiency (26.4%). Also, the prevention from oxidation of Ce^{3+} by refluxing in ethanol in the reaction conditions is thought to contribute to the high efficiency [7]. One of the reasons why the maximum efficiency can be achieved with a very small content of 0.3 mol% is the excellent dispersion of Ce^{3+} ions in YAG : Ce nanophosphors in this wet process.

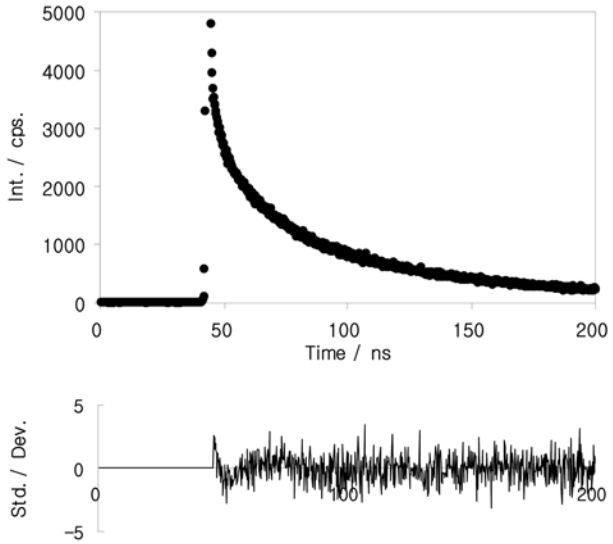

Fig. 7. The decay curve of luminescence of YAG : Ce^{3+}(2 mol%).

Table 1. Decay times of YAG:Ce^{3+}

	λex	λem	τ1 (ns)	τ2 (ns)	τ3 (ns)
YAG : Ce^{3+} (1 mol%)	450 nm	> 550	62.3 67.69%	177.5 22.24%	24.2 10.07%
YAG : Ce^{3+} (2 mol%)	450 nm	> 550	45.5 46.00%	129.3 46.94%	9.76 7.06%

Fig. 7 shows the luminescent decay curve of YAG : Ce (2 mol% Ce^{3+}) together with a standard/deviation diagram. The decay time curve contained three exponential terms with a medium decay time τ_1, a long decay time τ_2 and a short decay time τ_3 as shown in Table 1. The decay times τ_1 and τ_3 are comparable to those reported by Zhang *et al.*, suggesting that similar structural compositions to their YAG : Ce was also involved in our YAG : Ce [10]. The average fluorescence lifetime τ of YAG : Ce with 1 mol% Ce content and 2 mol% Ce content were 115 ns and 107 ns, respectively, which indicated the Ce concentration had little influence on the fluorescence lifetime.

Conclusions

YAG : Ce nanocrystals were obtained at a relatively low sintering temperature, 850 °C, by use of an environmentally-friendly wet process. When a very small Ce content (0.3 mol%) was us ed as dopant, a high maximum quantum efficiency was achieved. The average luminescence lifetime was around 110 ns irrespective of the Ce^{3+} ion concentration.

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