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Spectral variation of $Y_3Al_5O_{12}:Ce^{3+}$ nanophosphors and their optical simulation

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ABSTRACT

Yellow $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) nanophosphors were prepared through a high-energy planetary milling of the bulk phosphor: two groups of D50 = 200 nm and 500 nm. They showed the drastic narrowing of excitation peaks with blue-shifting of emission bands, indicative of smaller spectral overlap and Stokes shift, compared with the bulk. It was explained by their significant quenching of all Raman scattering modes, implying the restriction of electron-phonon couplings caused by their defects. The optical simulations of white LEDs based on the nanophosphor's mixture with $K_2SiF_6:Mn^{4+}$ red phosphor showed a higher color rendering index for their smaller concentrations.

1. Introduction

Phosphor-converted white light-emitting diodes (pc-WLEDs) are considered to be good general lighting devices due to high efficiency (~ conversion efficiency of ~ 39%, and power efficiency of 123 lm/W), long lifetime, and low applied voltage [1]. In this commercial pc-WLEDs for solid-state lighting (SSL), the most commonly used green-yellow and red phosphors are (Y, Lu)$_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) and (Sr, Ca)$AlSiN_3:Eu^{2+}$ compounds, respectively. The combination of the blue light from InGaN chip and the mixture of yellow-green and red luminescence from the phosphors generates a warm white light with color temperature of 3000 K and color rendering index of 85. The main energy loss channels in the pc-WLEDs consists of the blue chip (e.g., lower electrical, internal, and external efficiencies), and the phosphors (e.g., lower quantum efficiency, larger Stokes shift, and higher scattering/reabsorption rate). The overall green-yellow phosphor conversion efficiency is reported to be ~ 80%, which is higher than that of the red phosphor of 67%. It is due to higher Stokes efficiency of the green phosphor (84%) than that of the red phosphor (74%). In order to enhance the conversion efficiency, the one way is to minimize the Stoke loss, which arises from the difference in energy between the absorbed and emitted photons of the phosphor. The less Stokes loss is expected to be achieved by the red shift in absorption spectrum or the blue shift in emission spectrum (method 1). The phosphor conversion efficiency is also limited by the multiple scattering and reabsorption phenomena of lights emitted from phosphor particles. Since the light scattering effect of a particle is proportional to the sixth power of the particle diameter, the decreasing of phosphor size is one of the solutions for enhancing the conversion efficiency (method 2). Since the reabsorption of emitted light results from the spectral overlap between absorption and emission spectra, their spectral narrowing can reduce the spectral overlap so as to prevent the reabsorption (method 3). To sum up, the nanophosphors would be expected to be most suitable to tune the emission and excitation spectra so as to enhance the conversion efficiency through three above-mentioned methods [2]. The blue shift of emission spectrum (method 1) and the narrowing of excitation spectrum (method 3) were observed in some nanophosphors [3–8]. Despite many unique spectral results on the nanophosphors, there are a few spectral analysis given in literatures; some literatures attribute the spectral variations to the change in crystal field strength caused by surface strains in the nanophosphors [3,4,6,8], and others ignore them or skip their explanations [5,7]. Although the spectral changes in emission and excitation spectra are mainly influenced by the phonon interaction with electron or photon, there are a few information on the phonon effect on the spectral variations in the nanophosphors; the simulated emission spectra of YAG:Ce nanophosphors show that the size-dependent electron-phonon coupling strength is in a decreasing order from the bulk material to the nanophosphors of much smaller sizes [9].

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The aim of this letter is to understand spectral variations in both emission and excitation spectra of YAG:Ce nanophosphors in terms of electron-phonon interactions through Raman spectrum. Two classes of nanophosphors with average size of D50 = 207 nm and 520 nm were was prepared through a high-energy planetary milling of YAG:Ce^{3+} bulk phosphor. The drastic narrowing of excitation spectra together with blushifting of emission spectra for the nanophosphors was observed. Also the significant quenching of all Raman scattering modes for the nanophosphors was found, indicating the reduction in the electron-phonon coupling effect. It is also notable for the nanophosphors that the lower temperature dependence of PL spectrum was shown compared with the bulk phosphor. Finally, we performed optical simulations of white LEDs based on the nanophosphors, and compared their luminous efficiency and color rendering index as a function of phosphor conversion efficiency and phosphor concentration.

2. Experimental details

The commercial YAG:Ce^{3+} bulk phosphor (R sample, Lstone company, Korea) as a reference, and two different sizes of nanophosphors with average sizes of 207 nm (S sample) and 520 nm (L sample) were used for this study. The nanophosphors was prepared through a high-energy planetary milling of the commercial YAG:Ce^{3+} bulk phosphor. For nanomilling, the bulk phosphors were mixed with deionized water solvent and dispersant agent (BYK-180) together with spherical ZrO_2 balls with diameters of 800 and 300 μm. The mixtures were milled to the nanoscale at 400 rpm for 8 hours by a planetary miller (FRITSCH, Planetary Mono Mill). The final nanoparticles were obtained by separating the milled phosphors with 500 rpm centrifugation and then 220 and 550 nm syringe filtration. The samples were identified through X-ray diffraction technique (XRD, Rigaku ULTIMA4) scanning from 20° to 80° with 2θ step of 0.02°. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were obtained using a fluorescence spectrometer (Hitachi F-4500, Japan). Quantum efficiencies of all samples were recorded using an integrating sphere attached to the DARSA PRO-5200 fluorescence spectrophotometer (PSI Corporation, Korea). Raman spectra were measured by H-PeakSeeker Pro-785 Raman systems with 300 mW InGaAs line laser with 785 nm excitation wavelength. All samples for Raman measurement were pelletized by pressing, and they showed a similar diffuse reflectivity (about 50 % ± 5%) at Raman excitation wavelength of 785 nm. The particle sizes of the R/L and S samples were identified using a field-emission scanning electron microscope (FE-SEM; Vega II LSU, Tescan, USA Inc.) and a high-resolution transmission electron microscope (FE-TEM, JEM-2100F, JEOL, Japan), respectively. Nanoparticle size distribution was measured with a particle size analyzer (PSA, NANOTRAC WAVE, Microtrac, USA).

3. Results and discussion

Fig. 1 shows XRD patterns of YAG:Ce nanophosphors. All the reflections were indexed as a general garnet compound $Y_3[Al]_2(Al)_3O_{12}$ (JCPDS Card No. 73–1370) with a body-centered cubic structure (space group of Ia-3d (#230) and point group of O_h) [10]. The Y ions occupy the 24(c) sites eight-coordinated in dodecahedra. There are two different sites for the Al ions: octahedrally coordinated [Al] cations occupying the 16(a) sites with an octahedral point symmetry (C_{3i}), and tetrahedrally coordinated (Al) cations occupying the 24(d) sites with a tetrahedral point symmetry (S_4). No significant characteristic peaks for monoclinic and cubic ZrO_2 as a contaminant crushed during the ball milling process were observed. With decreasing particle sizes, XRD patterns showed more background noises along with broadening, and eventually the smallest sample showed the lower signal, and broadened-overlapped pattern. It can be described by the effect of crystal size and imperfections.

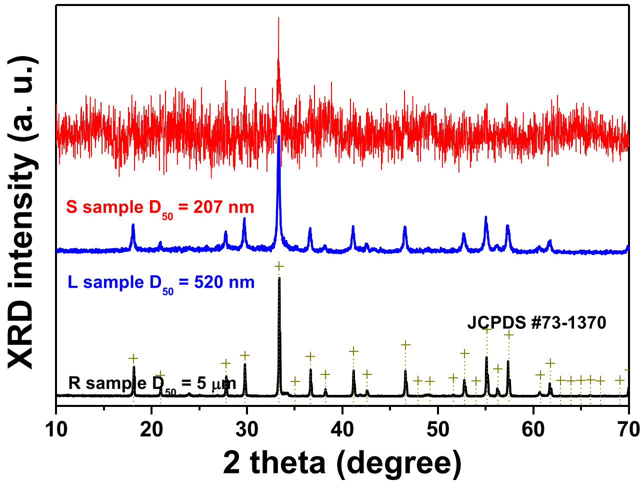

Fig. 1. XRD patterns of YAG:Ce nanophosphors.

Fig. 2 shows particle size analysis data and TEM/FE-SEM images. Particle size distribution of S and L samples showed in 100 – 400 nm range and 400 – 750 nm, and their mean particle sizes (D50) were 207 nm and 520 nm, respectively. It is notable for S samples that although they were prepared through a high-energy planetary milling and expected to be irregular and edged shape, they showed the spherical morphology. It can be explained by grounding effect of the sharped edges during the high-energy ball milling. TEM images with various magnifications showed various sizes from 50 nm up to 250 nm. Also we confirmed the presence of the amorphous phase on the surface of the smallest sample in the TEM image as indicated.

Fig. 3(a) shows Raman spectra of YAG:Ce nanophosphors at room temperature. Raman spectrum of YAG crystal consists of 25 single-phonon modes ($3A_{1g} + 8E_g + 14T_{2g}$) and their overtone and combination modes [11]. All Raman peaks observed in our experiment are assigned. In one-phonon mode, all Raman peak positions

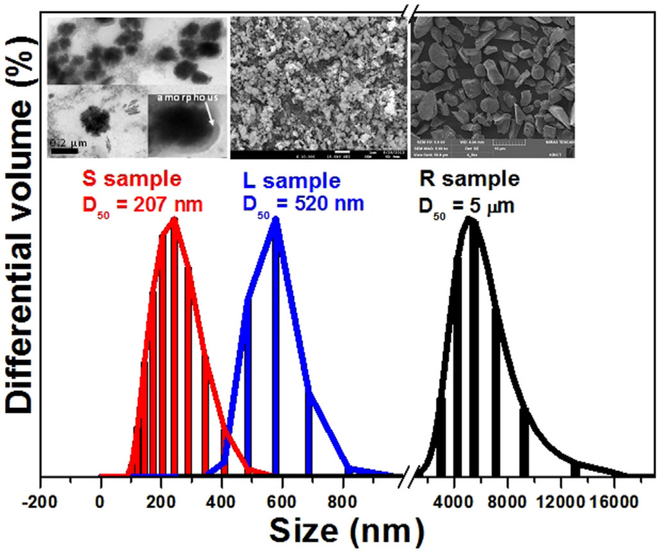

Fig. 2. PSA spectra and TEM/FE-SEM images of YAG:Ce nanophosphors.