

The Fabrication and Characterization of YAG:Ce³⁺ Nano-Particles

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Nano-particles of YAG (Y₃Al₅O₁₂): Ce³⁺ were obtained by sintering YAG precursor. The precursor was obtained by co-precipitation method from aluminum, yttrium and cerium nitrates using ammonium hydrogen carbonate as precipitant. YAG:Ce³⁺ crystals were obtained by sintering the precursors at 1000°C. It was confirmed by TEM that the crystalline size was about 50 nm. The photoluminescence (PL) spectra were measured by using Xe lamp as the excitation light. The emission is due to the transition between 5d-4f energy levels. The thin film including YAG: Ce³⁺ crystal was fabricated by layer-by-layer sequential adsorption method. It was found that the nano-particles were uniformly distributed in the multilayer thin films.

Key words: layer-by-layer, nano-particles, photoluminescence, YAG, Ce³⁺

1. INTRODUCTION

Recently, functional devices using nano particles are drawing attentions because of its new characteristics [1]. There are many reports on the film fabricated by nano particles, however, most of them are using dry process for the film fabrication and few of them are concerning the wet process.

It is known that layer-by-layer sequential adsorption method of polyelectrolytes, which fabricated ultra-thin films by dipping the substrate successively in each polyelectrolytes solution (polyanion or polycation), is one of the promising techniques among the wet processes for ultra-thin organic films [2-3]. Using this method, it is able to fabricate nano-particles/polymer hybrid thin films. Recently, we reported the new film fabrication method using the layer-by-layer sequential adsorption technique for fabricating ultra thin film containing ferrite nano particles [4].

In this study, yttrium aluminum garnet (YAG, Y₃Al₅O₁₂) nano particles are newly introduced into the layer-by-layer thin film with some polymers.

The doped single crystals of YAG are widely used in laser and

cathode ray tube (CRT) applications because they are thermally stable. The resolution of image on a CRT display is related closely to the particle size of phosphors. In general smaller particles are favorable for higher resolution. And nano-particle is favorable for the fabrication of thin film by wet process. The commercial method for YAG powder is a solid-state reaction [5-7] between the component oxides which requires repeated mechanical mixing and extensive heat treatment at high temperature (1700°C). The particle-size prepared by this method is large for the fabrication of thin film by wet process. Therefore, we prepared nano-scale YAG phosphors by wet-chemical method such as co-precipitation method [8]. And we prepared uniform thin film involving YAG phosphors by the layer-by-layer sequential adsorption method.

2. EXPERIMENTAL

Nano-particles of YAG: Ce³⁺ were fabricated by co-precipitation method [8]. We used Y(NO₃)₃ · 6H₂O (99.9%:SOEKAWA CHEMICALS), Al(NO₃)₃ · 9H₂O (99.9%:WAKO) and Ce(NO₃)₃ · 6H₂O (99.9%:WAKO). As

precipitant, we used ammonium hydrogen carbonate (NH₄HCO₃; WAKO). Aqueous solution was prepared by dissolving the nitrate salts in distilled water. The concentration of the solution was 0.15M for Al³⁺, 0.09M for Y³⁺, and 0.5–5mol% (0.5%, 0.75%, 1%, 1.5%, 2%, 5%) for Ce³⁺. The concentration of ammonium hydrogen carbonate (AHC) solution was selected as 1.5M and was made by dissolving AHC into distilled water.

It is known that precipitation method is the normal-strike method (adding precipitant solution to the salt solution) or the reverse-strike method (adding salt solution to the precipitant solution) [9-10]. The reverse-strike method was used in this study. In co-precipitation method, the precursor precipitate was produced by adding the nitrate salt solution at speed of 3ml/min into the AHC solution at room temperature. The precipitate was filtrated, washed for several times with distilled water, rinsed with ethanol. The precipitate was dried at 100°C in vacuum for 1hour. Then the precursor was calcined at 1000°C for 1.5 hours.

Thin films were produced by layer-by-layer sequential adsorption method [2-3]. The scheme is shown in Fig.1. This method utilized electrostatic attraction between the materials that had opposite electronic charge (Fig.1 (a)). Since it is known that nano-particles have a little electrical charge, it is able to fabricate nano-particles/polymer hybrid film by this method (Fig.1(b)). We used poly allylamine hydrochloride (PAH) as the polycation and poly acrylic acid (PAA) as the polyanion. In Fig.2, structural formulas of PAH and PAA are shown. YAG nano-particles were used as the cation. The Substrate of Si wafer was used. The surface of the substrate was treated with KOH solution to be hydrophilic. The concentration of PAH, PAA solution was adjusted to 10⁻²M. YAG solution was prepared by dispersing YAG nano-particles:30mg (the concentration of Ce³⁺ was 1.0mol%) in distilled water. YAG (in PAH) solution was prepared by dispersing YAG nano-particles : 30mg (the concentration of Ce³⁺ was 1.0mol%) in PAH solution. The pH of each solution was adjusted to 2.0 with HCl aqueous solution. We prepared the films of YAG (in PAH)/PAA and YAG/PAA. This process had four steps; (1) the substrate was immersed in YAG (in PAH) solution or YAG solution;(2) rinsed in water twice; (3) immersed in polyanion (PAA); (4) rinsed in water twice. These processes were carried out by using the automatic dipping machine we have developed [11]. The cross-sequential images of thin films and the images of YAG nano-particles were observed by a transmission electron microscope (TEM). The

photoluminescence (PL) spectrum of YAG nano-particles was measured using Xe lamp as excitation light at room temperature. Furthermore, the PL excitation (PLE) spectrum was measured.

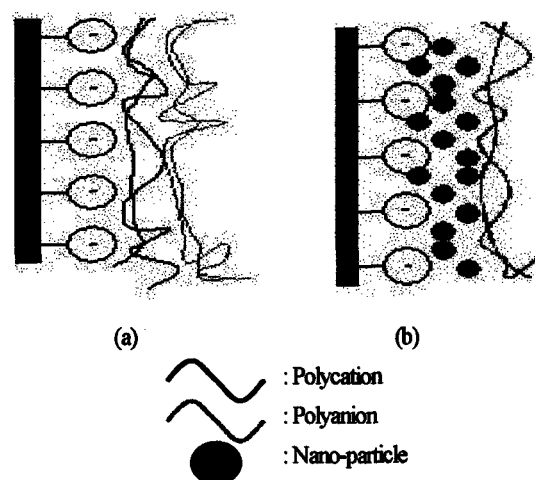


Fig.1: Layer-by-layer sequential adsorption process

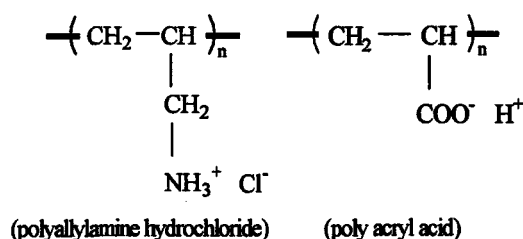


Fig.2: Structural formulas of polyelectrolytes

3. RESULTS AND DISCUSSION

The PL Spectrum of YAG nano-particles (Ce³⁺: 1mol%) was shown in Fig.3. The emission is due to 5d-4f energy levels. The maximum PL intensity was observed at 527.4nm.

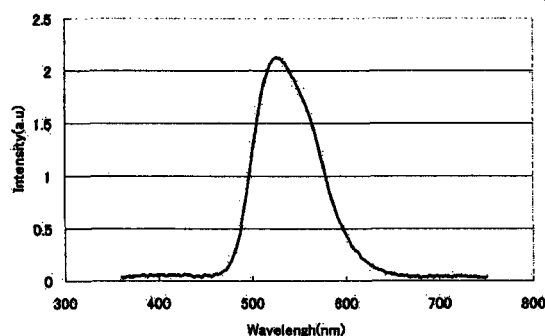


Fig.3: PL spectrum of YAG nano-particles

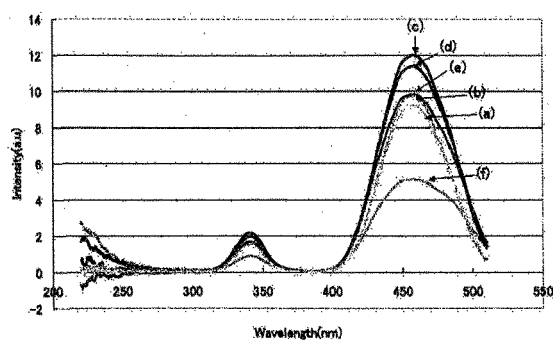


Fig. 4: PLE spectrum of YAG nano-particles
(a); 0.5mol%, (b); 0.75mol%, (c); 1mol%,
(d); 1.5mol%, (e); 2mol%, (f); 5mol%: Ce^{3+}

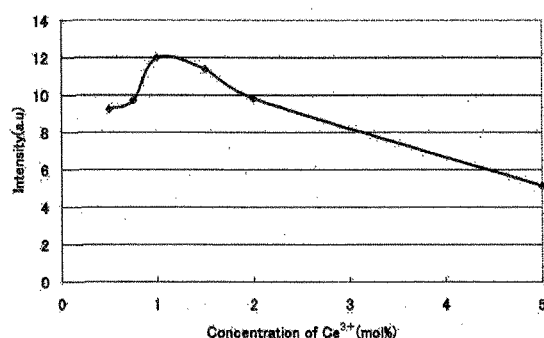


Fig. 5: Dependence of PL intensity on
the concentration of Ce^{3+}

The PLE spectrum of YAG nano-particles is shown in Fig. 4. Dependence of PL intensity on the concentration of Ce^{3+} is shown in Fig. 5. Fig. 5 shows that the maximum PL intensity was observed when the concentration of Ce^{3+} was 1mol%. The PL intensity decreased as the increase in the concentration of Ce^{3+} when the molar concentration exceeded more than 1mol%.

The results indicate that the concentration quenching was observed when the concentration was between 1mol% and 5mol%. In Fig. 4 and 5, it was found that the proper concentration of Ce^{3+} was 1mol% and the appropriate wavelength of the excitation was 457.8nm. Generally, the intensity of nano-scale phosphor is smaller than that of the micro-scale one. Therefore further study is required for the fabrication of the high quality nano-scale phosphor.

The TEM images of YAG nano-particles (Ce^{3+} : 1mol%) are shown in Fig. 6 (a) and (b). Fig. 6 shows YAG nano-particles agglomerate. It was found the particle size was around 50nm. The cross-sectional images of the thin films are shown in Fig. 7 and 8.

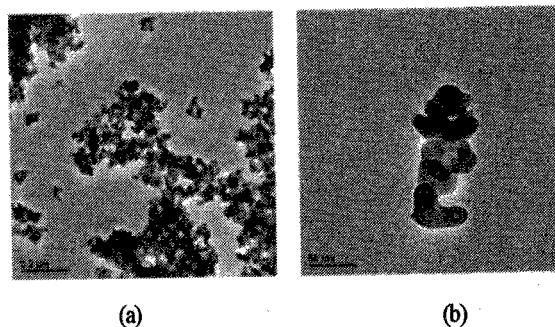


Fig. 6: TEM images of YAG nano-particles

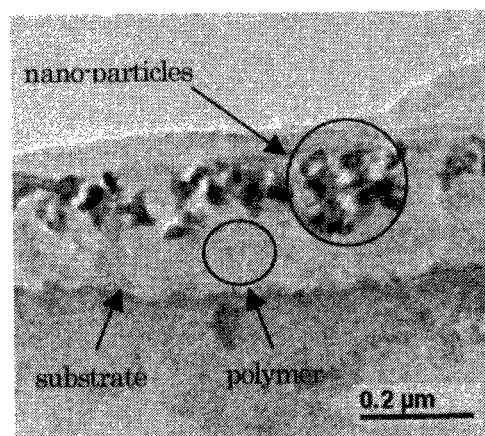


Fig. 7: Cross-sectional TEM image of
(YAG (in PAH)/PAA) layer-by-layer self-assembled film

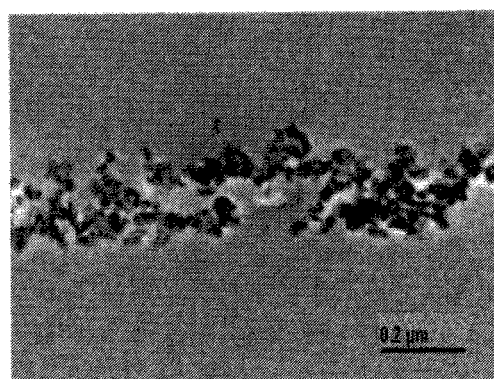


Fig. 8: Cross-sectional TEM image of
(YAG/PAA) layer-by-layer self assembled film

In Fig. 7, the thickness of this film was estimated to 200~250nm. The two images of Fig. 7 and Fig. 8 clearly show that the number of YAG nano-particles (Ce^{3+} : 1mol%) is larger in (YAG/PAA) film than (YAG (in PAH)/PAA) film. Few nano-particles were adsorbed at the surface of the substrate. The reason of the difference between (YAG (in PAH)/PAA) and (YAG/PAA) is as follows. In the case of the former, since YAG nano-particles in (YAG (in PAH)/PAA) film were mixed completely in polymer (PAH) chain, PAH with YAG nano-particles adsorbed PAA, whereas in the latter, since YAG

nano-particles in (YAG/PAA) film directly adsorbed PAA, the number of YAG nano-particles was larger than (YAG (in PAH)/PAA) film. The result of Fig.7 indicates that when the electrical charge of YAG was weak the surface charge of the substrate was weak. It is very difficult for the YAG particles to be transferred on the substrate until sufficient PAH/PAA layers were self-assembled. In Fig.8, it was found that YAG nano particles were distributed in thin film by layer-by-layer adsorption method. In Fig.8, YAG nano-particles were agglomerated and were not densely distributed in the film. It is assumed that this phenomenon is due to the weak adsorption force between YAG and PAA as weak acid group with carboxyl group.

4. CONCLUSIONS

YAG:Ce³⁺ nano-particles were prepared by co-precipitation method. The particle size was estimated to be around 50nm from the image of TEM. The maximum PL intensity was observed at 527.4nm. The proper concentration of Ce³⁺ was 1mol%. The proper excitation wavelength was 457.8 nm for the nano-particles. The (YAG(in PAH)/PAA), (YAG/PAA) and thin films were prepared by layer-by-layer sequential adsorption method. It is found that YAG nano-particles were distributed in thin film by this method.

5. ACKNOWLEDGMENT

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6. REFERENCE

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