Structural and luminescence properties of yellow $Y_3Al_50_{12}$:Ce^{3+} thin film phosphors prepared by Pulsed Laser Deposition

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Abstract. Recently oxide phosphors have gained much attention because of the variety of materials available and chemical stability as compared to sulfide phosphors. $Y_3Al_5O_{12}$:Ce^{3+} (YAG) crystal is an excellent host material which is able to compatibly accept divalent and/or trivalent activators from both rare earth and transition metal groups. It is well known that YAG is a highly efficient yellow phosphor. However, these phosphors in the form of thin films have not yet been fully realized due to technical difficulties. We prepared thin film type YAG phosphors on silicon (110) substrate using a pulsed laser deposition technique. The luminescent and structural properties of thin film phosphors were monitored as a function of key processing parameter which is the deposition temperature. The surface morphology of the grown thin films was strongly affected by the growth temperature. Electron diffraction spectroscopy confirms the presence of the Y, Al, O, and Si. Even though we could not obtain homogenous phases, by optimizing processing parameters, thin films with large homogenous areas and a high photoluminescence could be produced. XRD measurements revealed $Y_3Al_5O_{12}$ structure when grown at temperatures from room temperature to 750°C, however, other phases such as $Y_4Al_2O_9$ and $YAlO_3$ are observed as impurities. The PL results, which are in good agreement with the XRD data, showed that $Y_3Al_5O_{12}$ phase was relatively dominant in the film deposited at 750 ºC, so emission spectra is strong at around 570 nm.

1. Introduction

Inorganic luminescence materials are crystalline compounds that absorbed energy and subsequently emit this absorbed energy as visible light [1]. Yttrium Aluminium Garnet ($Y_3Al_50_{12}$:Ce^{3+}, YAG) has emerged as an excellent host material which is able to compatibly accept trivalent activator from both rare earth (Ce, Eu, Tb) and transition metal groups (Cr). The transition ions substitute the Al^{3+} positions while the rare earth ions substitute the Y^{3+} positions in the YAG crystal dodecahedron lattice sites. $Y_3Al_50_{12}$ has been widely studied for their applications as solid-state lasers due its high resistance to irradiation damage [2] and high thermal conductivity which allows a rapid removal of wasted heat due to inefficient excitation in the medium and enables the laser to produce a continuous beam of high quality [3]. YAG is an ideal substrate material for robust dielectric optical components, lens ducts [4], prisms and mirrors. YAG is also favoured for its high optical transmission, its durable properties better than glass or fused silica and its uniform refractive index. The YAG phosphor powders are also widely used as phosphors in cathode-ray tubes, field emission vacuum fluorescent and electroluminescent display devices [5].

Recently, by combining a blue InGaN LED with yellow Ce-doped YAG phosphore, different groups have successfully demonstrated white light emitting diodes (LEDs) [6-8]. The production of white light was made possible by the phosphore conversion from the LED to emission of a longer wavelength. The yellow emitting phosphore converts a major fraction of the blue excitation light from the LED chip into yellow light, and when both combined white light is produce. Bando *et al.* [9] and Muller-Mach *et el.* [10] have incorporated a phosphore/epoxy hybrid with a reflector cup containing a LED chip for phosphore conversion. The phosphore particles are randomly oriented and interdispersed in the cured epoxy. One of the bottleneck problems of the phosphore/epoxy hybrid system is the difficulty of achieving uniform emission of white light from the LED. In order to overcome the challenges of using mixtures of phosphore powders and epoxies thin film phosphore has been used [11,12].

In this study, YAG phosphore thin films were prepared by pulsed laser deposition (PLD), and the effects of the PLD process parameters on the structural and luminescent properties of YAG thin films were investigated.

2. Experimental Procedure

Most of the previous studies on YAG phosphore thin films used the commercial available powders for the preparation of their target, however, in this study we have synthesized the phosphore powder ourselves and pressed the target for the preparation of the thin films. For the preparation of the phosphore powder we have used the sol-combustion synthesis. In sol-combustion synthesis experiments, the Y_2O_3–Al_2O_3 mixed with nominal compositions were dissolved into a minimum amount of distilled water. The resulting solution was transferred into a crucible, which was then introduced into a muffle furnace maintained at 500 ^oC for 5-6 minutes. The voluminous and foamy combustion ash was easily milled to obtain the final $YAl_5O_{12}:Ce^{3+}$ phosphor powders. The powders were uniaxial compressed into a O13mm pellets under 500Kgc/m2. It could be noted that the compression procedure to make a pellet might be important for preparing $YAl_5O_{12}:Ce^{3+}$ powders by sol-combustion process. The properly mixed pellet was subject to oven calcination in air at 1000 ^oC for 2 hours. The $Y_3Al_50_{12}:Ce^{3+}$ thin film phosphors were grown on a Si (110) substrate by Nd: YAG (266 nm) pulse laser deposition (PLD). Process parameters such as gas pressure and substrate temperature were varied to observe the corresponding effects. XRD patterns of as-synthesized the resulting films were recorded on an x-ray diffractometer with Cu K_α = 1.5406 Å, which was operated at 40 kV voltage and 40 mA anode current. Data were collected in 2θ values from 20° to 80°. The morphologies and sizes of the particles were examined using a PHI 700 Nano Scanning Auger Microprobe (Nano SAM) and a Shimadzu model ZU SSX – 550 Superscan scanning electron microscope (SEM), coupled with an energy dispersive x-ray spectrometer (EDS). Photoluminescence (PL) measurements were performed at room temperature on a Cary Eclipse fluorescence spectrophotometer (Model: LS 55) with a built-in 150 W xenon lamp as the excitation source and a grating to select a suitable wavelength for excitation.

3. Results

The YAG phase formation under different substrate temperatures were obtained by XRD and the results are shown in figure 1. Samples prepared at room temperature (Figure 1(a)) are found to show intermediate phase of $Y_4Al_2O_9$ (YAM, JCPD Card No. 34-368). For samples prepared at 500ºC, the diffraction pattern of YAM, $YAlO_3$ (YAP, JCPD Card No. 33-41), and YAG (JCPDS No. 33-0040). Further increase in temperature to 750 °C resulted in the appearance of additional peaks related to YAG. It is evident from the XRD spectra that depositions at higher temperature lead to increase in the diffraction peaks which correspond to YAG phase. This clearly suggests that as the deposition temperature increases the degree of crystallization of YAG crystals also increases.

Figure 2 shows the morphology of $Y_3Al_50_{12}:Ce^{3+}$ thin film phosphors prepared at different substrate temperatures. From Figure 2(a) it can be seen that, under room temperature deposition $Y_3Al_50_{12}:Ce^{3+}$ films appear relatively rough with large spherical micro particles on the surface deposited on a smother background. The spherical particles on the surface appear to decrease in size as substrate temperature increase to 500 °C as shown in Figure 2(b). Otherwise there are no significant morphological differences between films deposited at room temperature and 500 °C. At higher substrate deposition temperature of 750 °C the spherical particles on the surface becomes irregular in shape and larger in size (Figure 2(c)). These irregular structures confirm the starting of partial crystallization of $Y_3Al_50_{12}:Ce^{3+}$ thin films phosphors. Figure 3 shows a representative EDS spectrum of the $Y_3Al_50_{12}:Ce^{3+}$ thin film. There appeared no other emissions apart from Y, O, Al, and Si in the EDS spectra of the samples. The non-existence of doped rare earth active Ce^{3+} ions in the samples is clear indication that these materials are in very little quantity in the films.

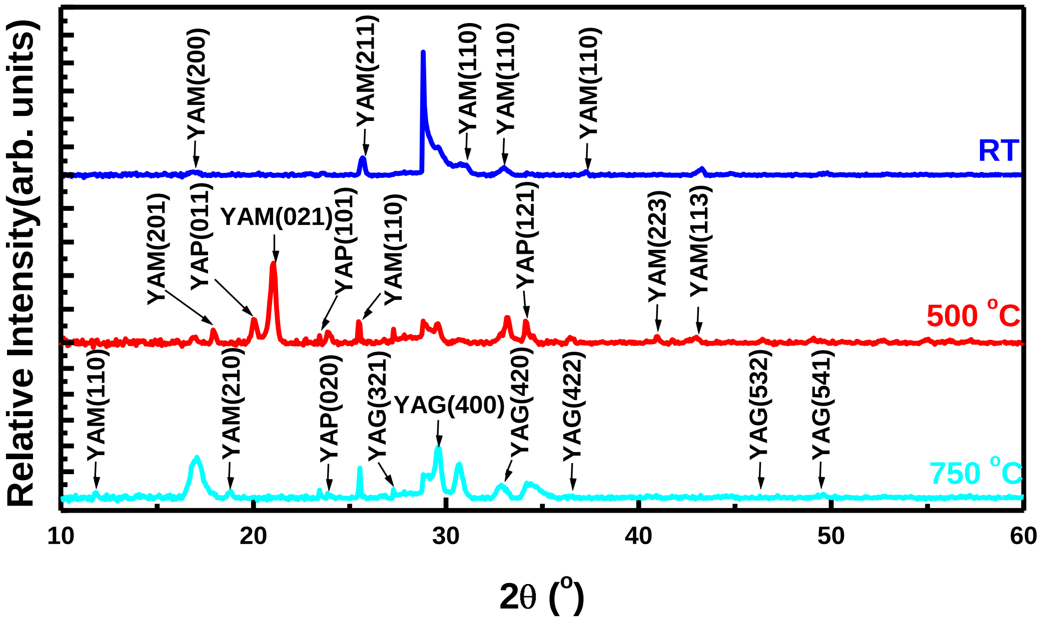


Fig. 1. XRD pattern of $Y_3Al_50_{12}:Ce^{3+}$ thin films deposited at different substrate temperatures.

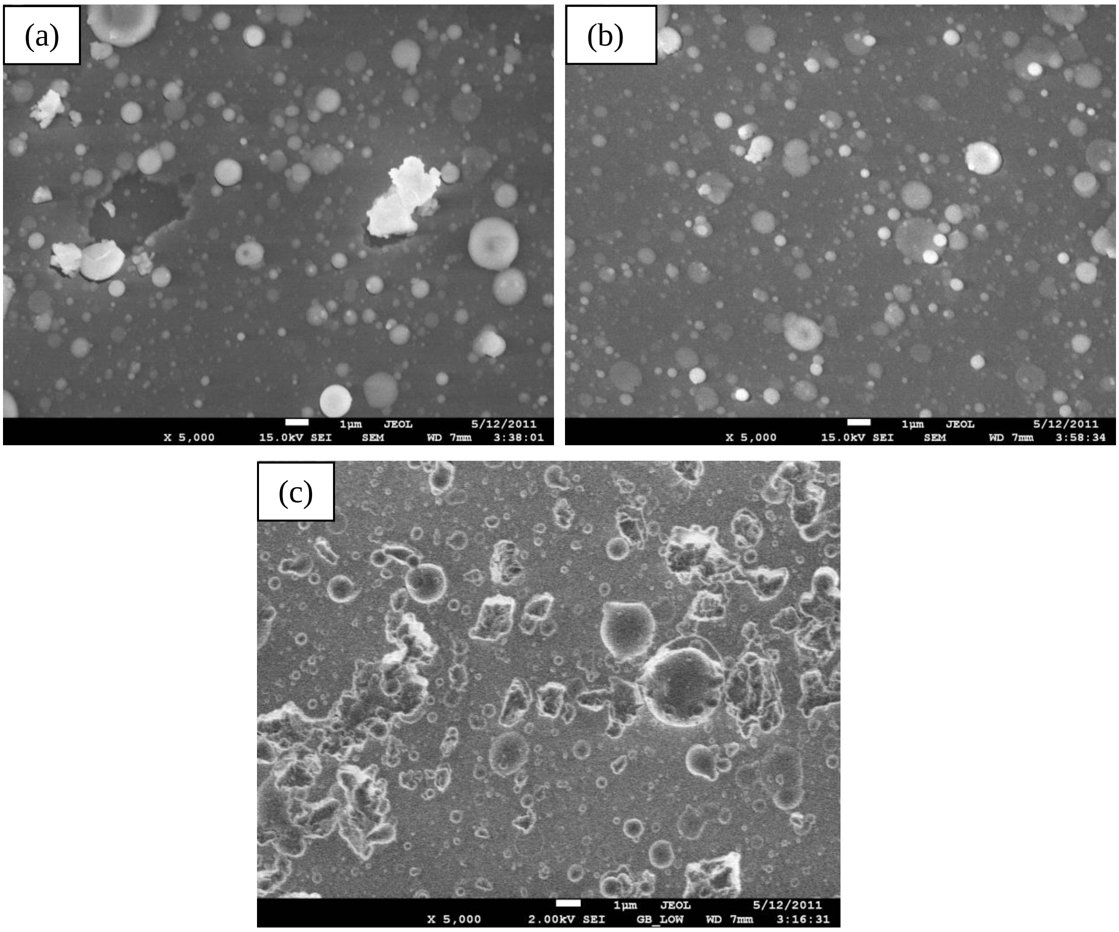
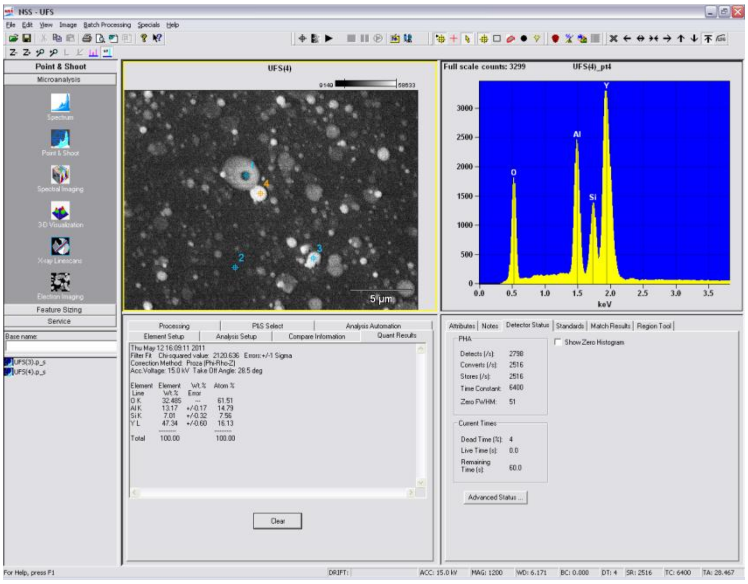


Fig. 2. SEM images of $Y_3Al_50_{12}$:Ce^{3+} thin films deposited at (a) room temperature, (b) 500 ºC, (c) 700 ºC.



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Thu May 12 16:09:11 2011
Filter Fit   Chi-squared value:  2120.636   Errors:+/-1 Sigma
Correction Method:  Proza (Phi-Rho-Z)
Acc.Voltage: 15.0 kV  Take Off Angle: 28.5 deg

Element  Element    Wt.%    Atom %
 Line      Wt.%     Error
O K       32.485     ---     61.51
Al K      13.17    +/-0.17   14.79
Si K       7.01    +/-0.32    7.56
Y L       47.34    +/-0.60   16.13
          ------             ------
Total    100.00             100.00
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PHA
Detects (/s): 2798
Converts (/s): 2516
Stores (/s): 2516
Time Constant: 6400
Zero FWHM: 51

☐ Show Zero Histogram

Current Times
Dead Time (%): 4
Live Time (s): 0.0
Remaining Time (s): 60.0

ACC: 15.0 kV MAG: 1200 WD: 6.171 BC: 0.000 DT: 4 SR: 2516 TC: 6400 TA: 28.467

Fig. 3. A representative EDS spectrum of the $Y_3Al_50_{12}$:Ce^{3+} thin film.

Figure 4 depicts the photoluminescence spectra of $Y_3Al_5O_{12}$:Ce^{3+} thin film phosphors prepared at different temperatures. All samples show a broad emission peaks in the range 400 – 700 nm. It can be seen from the spectra that the emission intensity enhanced with the increase in substrate temperature. A maximum PL intensity was obtained at 570 nm for films deposited at substrate temperature of 750 ^{o}C. The luminescence band is characteristic emission of $5d^1 \rightarrow 4f^1$ transitions of triply charged cerium ions [13-15], commonly in either in the ultraviolet or visible region spectral region. Generally, emission intensity increase with increase in degree of crystallinity. As mentioned earlier, the diffraction peak corresponding to the YAG phase increased with increasing in substrate temperature. Therefore, the increase in emission intensity with increase in substrate temperature could be due to the improved YAG crystallinity. The luminescent band value appears to slightly red shift with an increase in deposition temperature. As the deposition temperature increases, the crystal field splitting of 5d energy levels of the Ce^{3+} ion becomes larger (due to improved YAG phases), and the energy difference between the lowest 5d sublevel and the ground state of 4f configuration of Ce^{3+} become smaller. Therefore, emission band shifts to a longer wavelength (red shift).

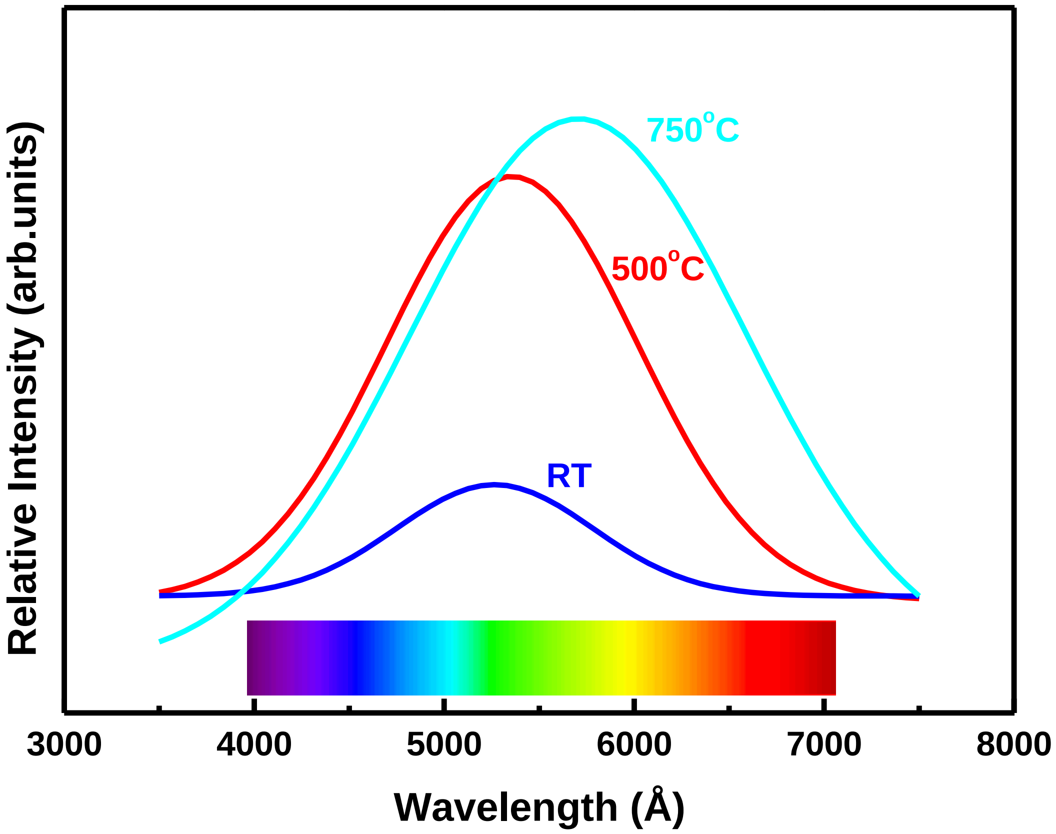

Fig. 4. Photoluminescence spectra of $Y_3Al_5O_{12}$:Ce^{3+} thin films deposited at different substrate temperatures.

4. Conclusions

$Y_3Al_50_{12}$:Ce^{3+} (YAG) thin film phosphors were synthesized by pulsed laser deposition technique. The effect of substrate temperature on the structural and luminescent properties of $Y_3Al_50_{12}$:Ce^{3+} thin films were studied. It is found that as the substrate temperature during deposition increases from room temperature to 750 ºC the degree of YAG phases increased. The intensity and maximum of the Ce^{3+} emission were found to change with the increase in substrate temperature.

Acknowledgements

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