Effect of annealing on the structure of $Y_3(Al,Ga)_5O_{12}$:Tb thin films grown by PLD

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Abstract. $Y_3(Al,Ga)_5O_{12}$:Tb thin films were grown in an O_2 working atmosphere on Si (100) substrates using the pulsed laser deposition technique. The influence of different annealing times, on the optical, morphological and the structural properties of the films, was investigated. Atomic force microscopy showed an increase in grain size with an increase in annealing time. The photoluminecent (PL) emission spectrum presented similar characteristics for all different annealing times, and the emissions are described by the well-known $^5D_4$–^7F_J (J=6, 5, 4, 3…) transitions of the Tb^{3+} ion. The main PL emission peak was due to the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} and was measured at a wavelength of 544 nm with minor peaks at 489 nm ($^5D_4 \rightarrow {}^7F_6$), 561 nm ($^5D_4 \rightarrow {}^7F_4$) and 625 nm ($^5D_4 \rightarrow {}^7F_3$). A new excitation band located at around 200 nm was observed from all the annealed films which pointed to a change in the chemical environment, owing to the fact that, the 5d level depends strongly on the nature of the host due to a greater radial extension of the 5d orbital. A shift in the peak position to lower diffraction angles was also observed in the X-ray diffraction results compared to the pattern of the $Y_3(Al,Ga)_5O_{12}$:Tb powder and other thin films.

1. Introduction

Luminescent materials have received a worldwide technological interest for a broad range of everyday applications. Among them, Yttrium aluminium garnet material (YAG) activated with Tb^{3+} is one of the most heavy-duty phosphors which are widely used in display applications [1-3]. The brightness and saturation characteristics were improved by the replacement of a portion of Al with Ga in the YAG host to improve the saturation characteristics at higher electron beam density excitations [4,5]. On the other hand, this partial replacement of Al with Ga slightly increased the deterioration of luminescence efficiency under electron bombardment [1]. However, $Y_3(Al,Ga)_5O_{12}$:Tb phosphor powder, showed very good cathodoluminescent (CL) stability, during prolonged electron bombardment [2]. Most phosphor materials consist of multi-components and their luminescence efficiency is largely affected by the right stoichiometry and growth mode. One of the most important things in the deposition of a phosphor thin film is the stoichiometric transfer of target material to the substrate [6]. It is well known that the pulsed laser deposition (PLD) technique can produce a wide variety of complex compounds with controlled composition and properties. In this study, PLD $Y_3(Al,Ga)_5O_{12}$:Tb thin films were grown with a set of fixed processing conditions. Thermal heating

was used to improve the crystal quality and to decrease structural defects in the films. It is well known that, during the annealing process, dislocations, and other structural defects move in the material and adsorption/decomposition may occur at the surface, thus the structure and the stoichiometric ratio of the material may change [6]. As reported in the literature [3], the interdiffusion of atomic species between the Si substrate and $Y_3(Al,Ga)_5O_{12}$:Tb thin films were observed for post annealing at higher temperatures, which has an impact on the film's optical properties. A. Yousif *et. al.* [7] reported that annealing improved the photoluminescence (PL) intensities as well as the crystallinity of the $Y_3(Al,Ga)_5O_{12}$:Tb films, but changes in the surface topography was observed after the annealing process, which showed spherically grains covered with inhomogeneous distribution of Ga on the surface relative to the distribution of the deposited film. Another study on the annealing effect on the $Y_3(Al,Ga)_5O_{12}$:Tb film [8], showed that stress and aggravated cracking occurred during annealing, which left regions enriched with Si after annealing at the higher temperatures. In this work, we report on the effect of different annealing times on the optical, morphological and the structural properties of the $Y_3(Al,Ga)_5O_{12}$:Tb film annealed at 800 ^oC.

2. Experiment

The Si (100) wafers used as substrates were first cleaned as described elsewhere [3, 7]. The PLD technique was used for the preparation of the films. The deposition chamber was evacuated to a base pressure of 1.3×10^{-5} mbar and then backfilled with O_2 to a pressure of 5.3×10^{-2} mbar. The $Y_3(Al,Ga)_5O_{12}$:Tb target was ablated in the O_2 working atmosphere using a 266 nm Nd:YAG pulsed laser. The laser frequency, number of pulses, fluency, substrate temperature and target-to-substrate distance were fixed at 10 Hz, 20000, 0.767 J/cm^2, 300 ^oC and 4.5 cm, respectively. Some of the deposited thin films were annealed for 1 and 2 hrs at 800 ^oC in air. $Y_3(Al_x,Ga_y)_5O_{12}$:Tb was also synthesized by using an urea-nitrate solution combustion synthesis technique. $Y(NO_3)_3.4H_2O$, CON_2H_4 and $Ga(NO_3)_3.5H_2O$ were used as starting materials, which were dissolved in diluted water during stirring and heating to obtain a mixing aqueous homogenous precursor solution. The solution was placed in a furnace preheated at 500 °C. After the combustion process was completed, the obtained solid precursors were then ground and fired at 900 °C for 2 h in air to produce the final samples. X-ray diffraction (XRD) analysis was carried out using a Bruker AXS D8ADVANCE X-ray diffractometer. The PL properties of the films were measured using a Carry eclipse spectrophotometer at room temperature. The surface topography was examined using a Shimadzu SPM-9600 atomic force microscope (AFM).

3. Results and discussion

Figure 1(a) shows the XRD patterns of the powder, the as-deposited and the annealed $Y_3(Al,Ga)_5O_{12}$:Tb thin films. A small (420) diffraction peak at the same position for the powder was observed for the as-deposited film. The annealed films shows three diffraction peaks at 29.3^o, 32.7 ^{o}, and 35.9^o which correspond to the (400), (420) and (422) crystalline planes[2], respectively. Furthermore, an increase in the annealing time resulted in an increase in the intensity of the (420) diffraction peak as shown in Figure 1(a). Which clearly indicates that the crystallinity of the $Y_3(Al,Ga)_5O_{12}$:Tb film was enhanced with an increase in the annealing time. The estimated average crystallite size of the $Y_3(Al,Ga)_5O_{12}$:Tb was obtained by using Scherrer's equation [9] and was found to be ~ 23 nm and ~25 nm for the 1 and 2 hrs annealed films, respectively. Furthermore, a slight shift in the peak position to a lower diffraction angle was observed for the annealed films compared with the $Y_3(Al,Ga)_5O_{12}$:Tb commercial powder. Figure 1(b) represents the XRD patterns for the commercial and synthesised $Y_3(Al_x,Ga_y)O_{12}$:Tb powder with different Ga concentrations, which show a shift of the peaks to lower diffraction angles with an increase in the Ga concentration. This is due to the fact that the ionic radius of Ga^{3+}(0.062 nm) is larger than the ionic radius of Al^{3+} (0.053 nm) [10]. Therefore with an increase in Ga concentration a change in the host lattice is expected. Figure 2 demonstrates the effect of the Ga concentration on the lattice parameter, showing the host site with

a=12.27 Å, 12.16 Å and 12.06 Å for $Y_3Ga_5O_{12}$ [11], $Y_3Al_{2.1},Ga_{2.9}O_{12}$ [12] and $Y_3Al_{3.97},Ga_{1.03}O_{12}$, [13] respectively. As a result of an increase in the Ga concentration, the inter-planar spacing will increase and a shift towards lower angles in the diffraction peak will be observed as pointed out by Bragg's law. It can be concluded that, the shift towards the lower diffraction angles in the XRD patterns of the annealed films probably indicating that the films are enrichment with Ga compared with the as prepared film. The Auger electron spectroscopy elemental mapping of films showed some inhomogeneous distribution of Ga on the surface of the deposited films, indicating that some areas of the films were enriched with Ga [7].Ga with a very low melting point of 29.76 ^oC, maybe transferred as agglomerated clusters during the PLD process and with annealing treatment, start to interact with the rest of materials to form structures that are enrichment with Ga.

Figure 3(a-c) shows the AFM micrographs of the surface of the as-deposited and annealed $Y_3(Al,Ga)_5O_{12}$:Tb thin films. The regions evaluated show that the surface layer was uniform and the substrate was well covered with particles. The as-deposited films consist of a granular structure of grains with various grain sizes. Annealing at 800°C for 1 and 2 hrs induced changes in the root mean square (RMS) roughness and the surface topography. The RMS roughness changed from 16 nm to 21 and 30 nm respectively. The surface topography shows larger grain sizes compared with the as prepared film, due the fact that, grain growth takes place by diffusion when the temperature is high enough and or the heat treatment time is long enough [14].

Figure 4(a) shows the excitation and emission spectra, for the as prepared Tb^{3+} in $Y_3(Al_x,Ga_y)_5O_{12}$ host with different Ga and Al concentration. The emission lines were obtained for the excitation wavelength of 260, 267 and 272 nm for $Y_3Ga_5O_{12}$:Tb, $Y_3Al_3Ga_2O_{12}$:Tb and $Y_3Al_5O_{12}$:Tb respectively. Four main PL bands for both green and blue emission are clearly resolved which are associated with the f–f internal orbital transitions of Tb^{3+} ions. They are attributed to the well-known $^5D_4$–^7F_J (J=6, 5, 4, 3…) and $^5D_3$–^7F_J (J=6, 5, 4, 3…) transitions of the Tb^{3+} ions [2, 3], which present similar characteristics for the Tb in $Y_3(Al_x,Ga_y)_5O_{12}$ with different Al and Ga concentration. This is due to the fact that, the lanthanide elements (rare earth) have a partially filled inner $4f^n$ shell surrounded by completely filled outer $5s^2$ and $5p^6$ orbitals which shielded the sharp 4f-4f line emissions of the Tb^{3+} from the anionic environment. Therefore they are relatively independent of the host material and are determined by the energy transition between the 4f states only. On the other hand, the energy of the 5d levels depends strongly on the nature of the host due to a greater radial extension of the 5d orbital which can be seen in the excitation bands of as prepared powder with different Al and Ga concentrations.

Mayolet et al.[15] studied the $4f^75d$ configuration in $Y_3(Al_x,Ga_y)_5O_{12}$:Tb and they concluded that there are five excitation band energies (E_1, E_2, E_3, E_4 and E_5) which clearly depend strongly on different concentrations of Ga. Figures 5(b-d) are the excitation bands changes for different concentrations of Ga, as redrawn from Ref. [15]. Their results may be summarized as follows:

1. For a high Al composition: the E_l, E_2, E_3 and E_4, excitation bands, correspond to the excitation of the $4f^75d$ states of Tb^{3+} whereas, E_5 is hidden by the inter-band transition E_g in the host.
2. For a high Ga composition: E_l, E_2, $E_{3,4}$ (E_3, E_4 collapse) and E_5 (shoulder) correspond to the excitation of a $4f^8 \rightarrow 4f^75d$ transition of Tb^{3+} ions.

If the peak positions, as determined from the excitation spectra, are known for the different excitation bands, it may be used to explain the appearance of the new excitation band at 200 nm for the annealed films compared to as prepared film in Figure 5 (a), as indication that the annealed films were enrich with Ga. Figure 4(e) shows the E_5 excitation spectra of the $Y_3(Al_x,Ga_y)_5O_{12}$:Tb with different concentration of Ga as indicated, which clearly confirms the above statements.

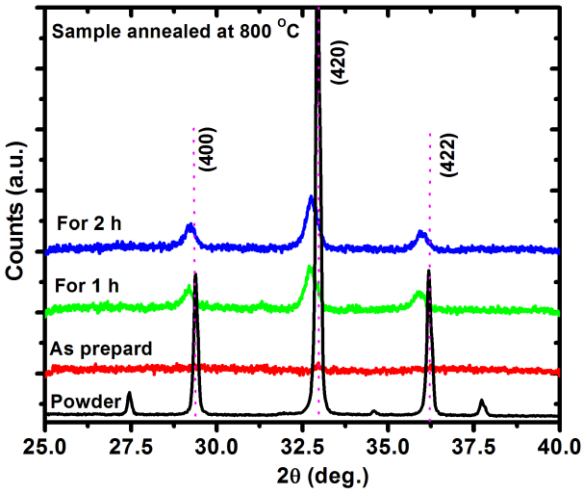

Figure 1 (a) XRD patterns of the $Y_3(Al,Ga)_5O_{12}$:Tb phosphor powder, and $Y_3(Al,Ga)_5O_{12}$:Tb films as prepared and annealed at 800 °C.

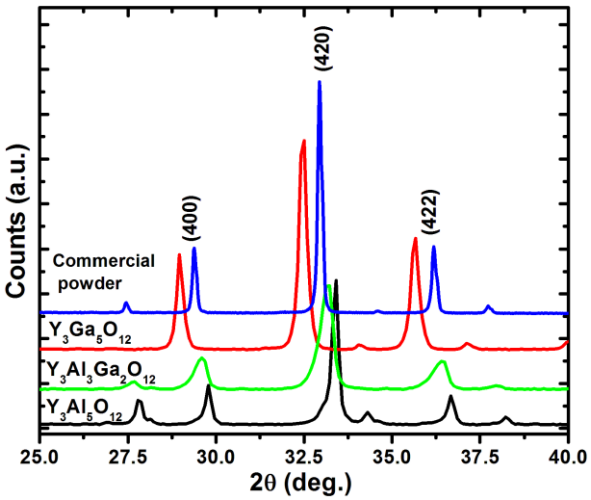

Figure 1 (b) XRD patterns of the commercial and prepared $Y_3(Al_x,Ga_y)O_{12}$:Tb powder, showing the change in the peak position with different Ga concentrations.

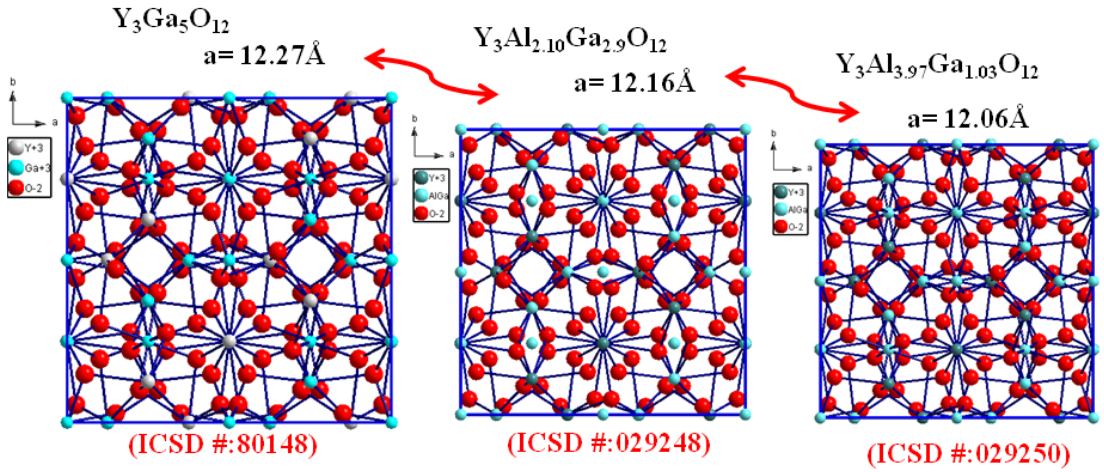

Figure 2 Change in lattice parameter of the garnet crystal structure with different Ga concentrations.

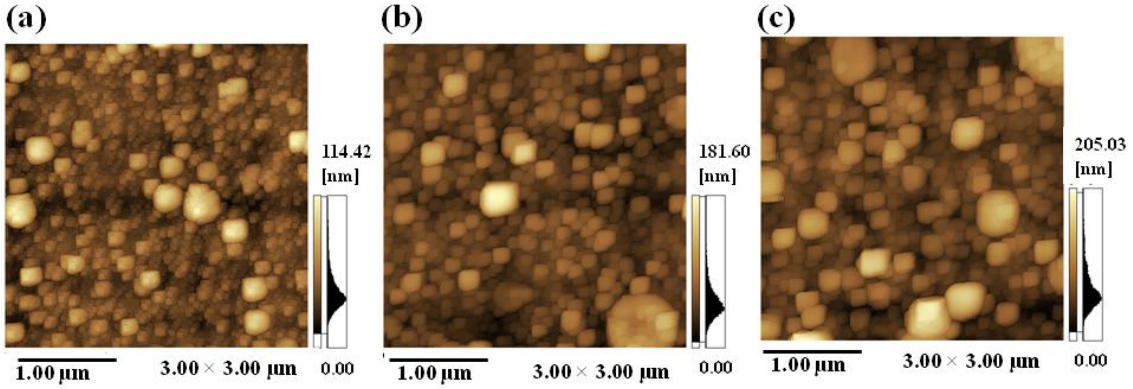

Figure 3 AFM images of the surface of the $Y_3(Al, Ga)_5O_{12}$:Tb films (a) as prepared and annealed at 800 °C for (b) 1 h and (c) 2 h.

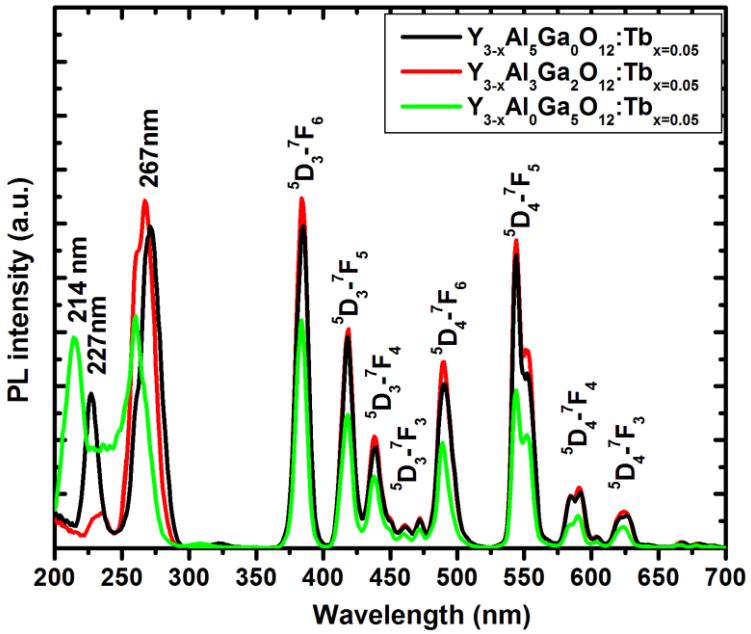

Figure 4 PL excitation and emission of the prepared $Y_{3-x}(Al_x, Ga_y)_5O_{12}:Tb_{x=0.05}$ powder with different Ga concentration.

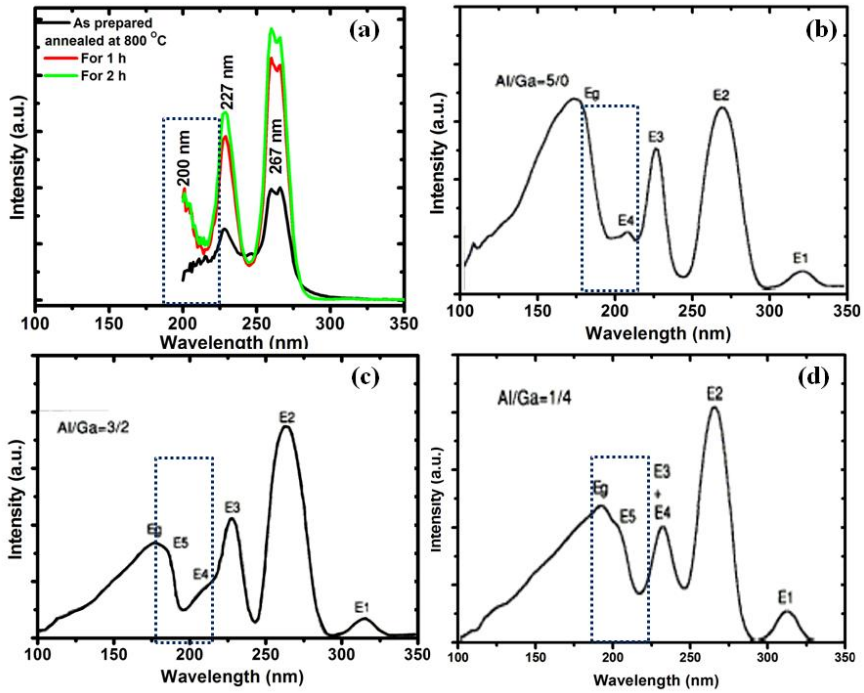

Figure 4 (a) PL excitationof the $Y_3(Al, Ga)_5O_{12}$:Tb films as prepared and annealed at 800 °C for 1 h and 2 h. **(b)- (d)** PL excitation of the $Y_3(Al, Ga)_5O_{12}$:Tb powder with different Ga concentration.

4. Conclusion

The influence of different annealing time on the optical and structural properties was observed as a new excitation band located at 200 nm and a shift in the diffraction peak position to lower diffraction angles, respectively. Both of them were attributed to an increase in the Ga concentration of the annealed films. An increase in the grain size with an increase in annealing time was also observed form the film morphology.

Acknowledgment

This work is financial support by African Laser Center (ALC) and it is based on the research supported by the South African Research Chairs Initiative of the Department of Science and Technology and National Research Foundation of South Africa, the University of the Free State Cluster program - financial support. We would like to thank the National Laser Center for allowing us to use their PLD system.

References

[1] O. Katsutoshi, A. Tomohiko, K. Tsuneo, 1990 *J. Appl. Phys.* **29** 103.
[2] A. Yousif, H.C. Swart, O.M. Ntwaeaborwa, 2012 *Appl. Surf. Sci.* **258** 6495.
[3] A. Yousif, H.C. Swart, O.M. Ntwaeaborwa, E. Coetsee,2013 *Appl. Surf. Sci.* **270** 331.
[4] H. Matsukiyo, H. Toyama, Y. Ueharab, H. Yamamotoc, 1997 *J. Lumin.* **229** 72.
[5] Q. Li, F. Qiu, J. Zhang, X. Pu, X. Liu, W. Zhang, 2009 *J. Alloys and Comp.* **474** 441.
[6] L.P. Peng, L. Fang, X.F. Yang, Y.J. Li, Q.L. Huang, F. Wu, C.Y. Kong, 2009 *J. Alloys and Comp.* **484** 575.
[7] A. Yousif, H.C. Swart, O.M. Ntwaeaborwa, 2013 *J. Lumin* **143** 201
[8] A. Yousif, H.C. Swart, O.M. Ntwaeaborwa, *Physica B*, in press.
[9] P. Y. Jia, J. Lin, X. M. Han, M. Yu, 2005 *Thin Solid Films* **483** 122.
[10] Rachael Hansel, Steve Allison, Greg Walker, 2008 *J. Materials Research Society* **K 06-06** 107.
[11] A Nakatsuka, S. Yoshiasa, S. Takeno, 1995 *Acta Crystallogr. Sec. B: Structural Science*, **51** 737.
[12] M. Marezio, J. P. Remeika, P. D. Deernier, 1968 *Acta Crystallogr., Sec. B* **24** 1670.
[13] Marezio, M., Remeika,J.P., 1968 *Acta Crystallogr., Sec.B* **24** 1670.
[14] F. X. Gil, D. Rodriguez and J. A. Planell, 1995 *J. Scripta Metallurgica et Materialia* **33** 1361.
[15] A. Mayolet, W. Zhang, E. Simoni, J.C. Krupa, P. Martin, 1995 *J. Optical Materials* **4** 757.