

Thin Film Deposition of $Tb_3Al_5O_{12}:Ce$ by Pulsed Laser Ablation and Effects of Low-temperature Post-annealing

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$Tb_3Al_5O_{12}:Ce$ (TAG:Ce) thin films were successfully deposited by a pulsed laser ablation method on a quartz substrate, and low-temperature post-annealing effects on luminescent properties were investigated in detail. TAG:Ce thin films were analyzed by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, and photoluminescence spectroscopy. The as-deposited films were amorphous, and post-annealing above 700 °C was required for crystallization. The post-annealed TAG:Ce thin films showed strong and broad emission bands around 542 nm and excitations at 451 nm, which all corresponded to transitions between the $4f$ ground level to the $5d^1$ excited levels of Ce ion.

Keywords : $Tb_3Al_5O_{12}:Ce$, (TAG:Ce), Pulsed Laser Ablation (PLA), Photoluminescence

OCIS codes : (310.6860) Thin films, optical properties; (160.2540) Fluorescent and luminescent materials

I. INTRODUCTION

With the prospect of a highly efficient light source, the light emitting diodes (LEDs) market will have enormous growth, and white LEDs will be a likely candidate for the replacement of the light bulb. A commercially available white LED based on phosphors has been produced by Nichia Co., which used a blue light-emitting gallium indium nitride (GaInN) chip coated with yellow $Y_3Al_5O_{12}:Ce$ (YAG:Ce) phosphor [1-3]. However, the color temperature of YAG:Ce phosphor used for phosphor-converting LEDs is too high to use in warm white LEDs application due to lack of red component [4].

As an alternative for YAG:Ce, $Tb_3Al_5O_{12}:Ce$ (TAG:Ce) has emerged as an excellent phosphor material for white LEDs, because the TAG:Ce is capable of absorbing radiation in the range from near UV to blue, and emitting a broad spectrum of visible light in the range from approximately 490 nm to approximately 770 nm [5]. It is well known that when compared with YAG:Ce, the spectrum of the TAG:Ce is slightly shifted to red range, which is advantageous

to resolve the problem of the high temperature of YAG:Ce LEDs [6].

In general, the phosphor-converting white LEDs are embedded in organic resins. However, there are several problems in these types of white LEDs, including the large difference of refractive index between phosphors and organic resins which will lead to a high amount of light scattering, and the poor heat-resistance which will lead to the degradation of luminous intensity with the change of color index [7]. In order to solve these problems, new types of white LEDs, for example, using glass ceramic or sintered ceramic phosphors have been developed [8, 9].

In this study, TAG:Ce luminescent thin films were deposited using a pulsed laser ablation (PLA) technique as a new type of white LED. The PLA offers many advantages over other thin film deposition techniques such as chemical vapor deposition (CVD) or physical vapor deposition (PVD) [10]. Unlike the CVD process in which complicated precursors are used as starting materials, PLA uses a pre-sintered solid target from which the thin film is deposited. And, film growing rate can be easily controlled by varying the

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laser parameters, background gas pressure and distance from substrate to target [11]. The main feature of the PLA method is the excellent stoichiometric transfer from the multi-compositional solid target to the thin film with homogeneity and uniformity over the designated depositing areas [12].

Phosphors in powder form usually yield higher luminescence than that of thin film types, mainly due to lower loss of light from total internal reflections. However, by modifying surface shape and morphology of the films, several significant improvements in increasing light output have been reported [13]. Comparing to powder typed phosphor, thin film typed phosphor can be more conveniently integrated with LEDs, therefore, it can be a better processing method for fabricating white light-emitting systems [14]. In this report, the crystallographic evolution, surface morphology, compositional qualities, and photoluminescence (PL) characteristics of the TAG:Ce thin films deposited by the PLA technique are discussed. Moreover, low-temperature post-annealing effects on PL properties are investigated in detail.

II. EXPERIMENT

The starting TAG:Ce powder was synthesized by a citrate complex method with a optimum Ce doping concentration of 0.8 mol% [5]. A bulk target was prepared by compressing the prepared TAG:Ce powder under a uni-axial pressure of 300 MPa and then sintering at 1500°C for 3 hrs. XRD measurement showed that the target had a single phase consistent with reported value (JCPDS 76-0111) as shown in inset of Fig. 1. An Nd-YAG laser (wavelength = 355 nm) was used for the ablation. The repetition rate and pulse width of the laser were 10 Hz and 7 ns, respectively. The laser energy was 200 mJ/pulse and focused on a target rotating at 30 rpm. The quartz glass substrates were

placed at an off-axial position with respect to the target in order to avoid large-sized particulate deposition [10, 12]. The working pressure of background Ar gas during laser ablation was 100 Pa. All deposition processes were carried out at room temperature without substrate heating. Subsequently, the as-deposited samples were post-annealed at various temperatures from 600 to 800°C in ambient atmosphere.

Phase identification was conducted with an X-ray diffractometer (XRD, Rigaku, RAD-C). The surface morphology of the deposited films was observed using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800, Japan). The surface composition and chemical bonding analysis were performed by X-ray photoelectron spectroscopy (XPS, PHI 5600 ci, USA) with a monochromated Al $K\alpha$ source (1486.5 eV, 100W). The binding energy values were calibrated with the C 1s line of adventitious carbon at 284.5 eV. Luminescent properties of the TAG:Ce thin films were measured by a spectrofluorometer (Fluorolog Tau-3, Horiba, USA) in a room temperature using a xenon lamp as an excitation source. The excitation wavelength used for measuring PL emission was 450 nm, and the excitation spectra were measured at emission maxima.

III. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of (a) JCPDS data for TAG crystal, (b) as-deposited TAG:Ce thin film and TAG:Ce thin film post-annealed at (c) 700 and (d) 800°C for 2 hrs, respectively. The as-deposited films were amorphous in nature, and did not represent any crystalline peaks. Post-annealing less than 700°C did not effectively crystallize the thin film. The thin films started to crystallize when annealed at 700°C for 2 hrs as shown in (c). However, an intermediate $TaAlO_3$ (terbium aluminum perovskite, TAP) phase coexisted with the TAG phase. Completely crystallized pure TAG phase was obtained after post-annealing at 800°C for 2 hrs as shown in (d). This post-annealing temperature is somewhat similar to that of citrate-complex derived TAG:Ce powders [5], and significantly lower than that of the conventional solid-state reaction process [15].

Figure 2 shows the surface morphologies of the TAG:Ce films (a) as-deposited and (b) post-annealed at 800°C for 2 hrs. The surface microstructure of the TAG:Ce thin films deposited by PLA was affected by a post-annealing process. Indeed, the surface of the as-deposited TAG:Ce thin film exhibits a smooth morphology without particular features. However, after post-annealing treatment at 800°C for 2 hrs, the surface became rougher resulting from grain growth and formation of particulates as shown in (b). The inset of (b) shows a cross-sectional view of the sample of thickness about 250 nm after annealing at 800°C for 2 hrs.

The surface composition of the TAG:Ce thin film post-annealed at 800°C for 2 hrs was analyzed using XPS. Figure 3(a-d) presents the high resolution XPS spectra of the (a) Tb 4d, (b) Al 2p, (c) O 1s, and (d) Ce 3d. The

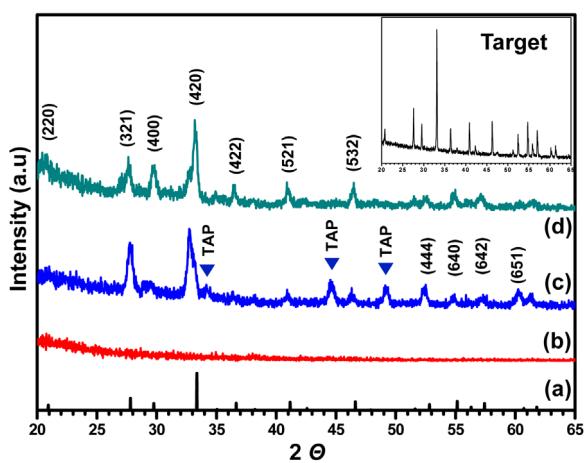


FIG. 1. XRD patterns of (a) JCPDS data for TAG crystal, (b) as-deposited TAG:Ce thin film and TAG:Ce thin film post-annealed at (c) 700 and (d) 800°C for 2 hrs, respectively.

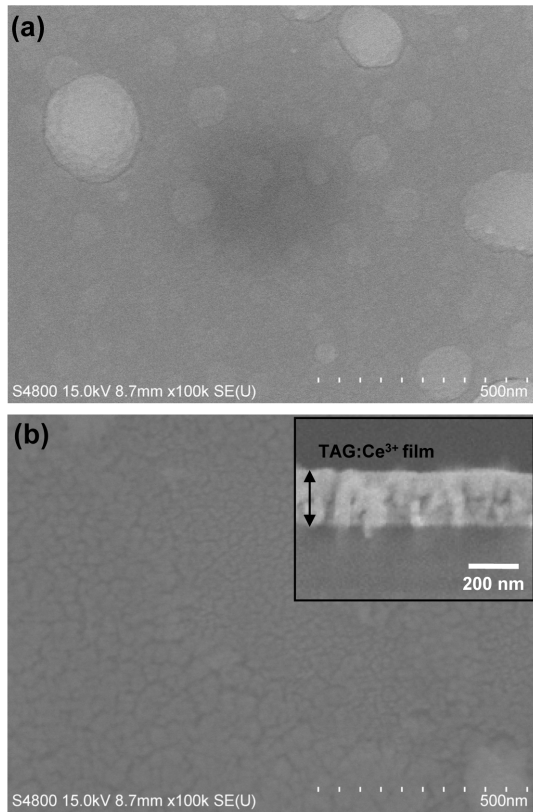


FIG. 2. SEM images of TAG:Ce thin films (a) as-deposited and (b) post-annealed at 800°C for 2 hrs. The inset of (b) show cross-sectional view of thin film post-annealed at 800°C for 2 hrs.

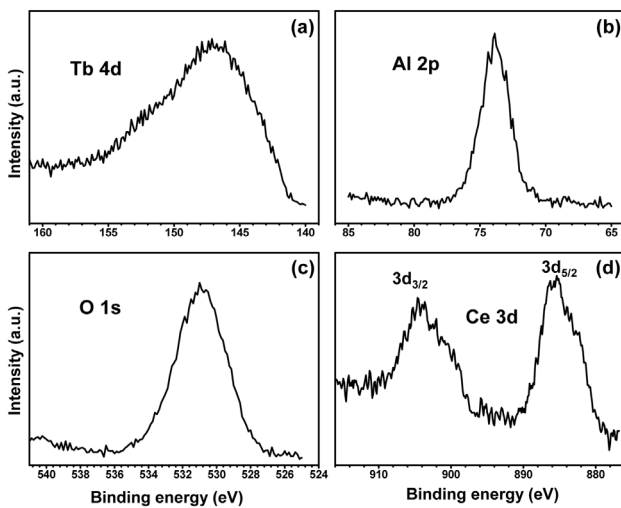


FIG. 3. XPS spectra of the (a) Tb 4d, (b) Al 2p, (c) O 1s, and (d) Ce 3d region in TAG:Ce thin film post-annealed at 800°C for 2 hrs.

binding energies of the Tb, Al, O, and Ce were well in agreement with reported values [16]. The Ce 3d feature in (d) shows a complex structure consisting of Ce 3d_{5/2} and Ce 3d_{3/2} spin-orbit doublet around 885 and 904 eV, respectively,

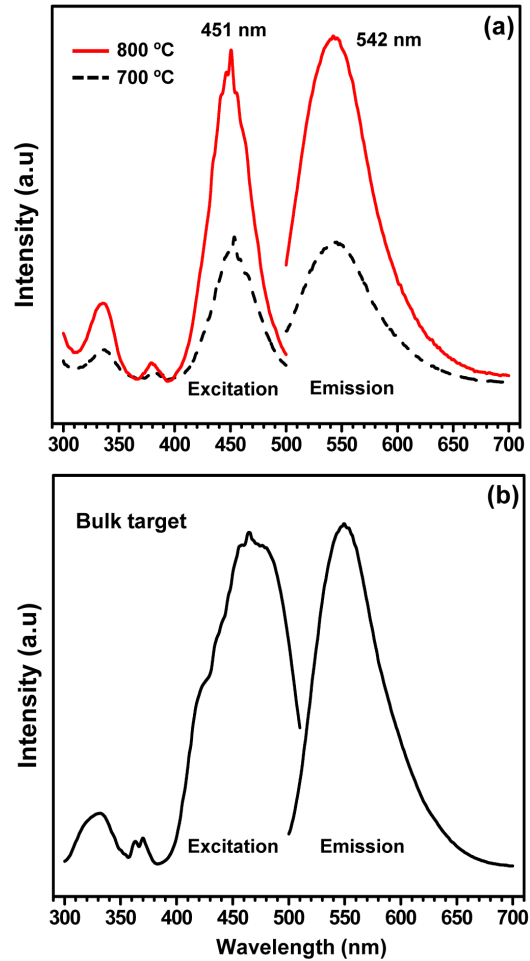


FIG. 4. Excitation and emission spectra of the (a) TAG:Ce thin films post-annealed at 700 and 800°C for 2 hrs. PL spectra of bulk TAG:Ce are shown in (b) for comparison.

vely, which is a characteristic property of the Ce³⁺ ion [17]. This spectral feature confirms that the chemical valence of Ce ions doped in the TAG:Ce thin film is trivalent. Moreover, a calculated chemical composition of Ce³⁺ in the TAG:Ce film post-annealed at 800°C for 2 hrs was 0.075, which corresponded well to the doping concentration of the bulk target (8 mol%).

Figure 4(a) depicts the excitation and emission spectra of the TAG:Ce thin film post-annealed after PLA process. The PL spectra of the bulk target used for PLA are presented in (b) for comparison with those of the TAG:Ce thin films. As shown in Fig. 4, both excitation and emission spectral shapes of the TAG:Ce thin films are almost identical to those of the target used for the PLA. The PL intensity of the as-deposited film (not shown) was almost two orders lower than those of the post-annealed thin films. The emission intensity of the TAG:Ce thin film post-annealed at 700°C for 2 hrs was about 10% of the bulk target. This low PL intensity may originate from incomplete crystallization and an intermediate TAP phase. However, enhancement of the emission spectrum up to 30% of the

bulk target was observed in the sample post-annealed at 800°C for 2 hrs. This result indicates that low-temperature post-annealing process can remarkably enhance the emission intensity of the TAG:Ce thin film deposited by PLA in room temperature. The PL excitation spectrum of the post-annealed TAG:Ce thin films showed two bands peaking at 335 (weak) and 450 nm (strong) due to the transitions from $4f^1$ ground state to higher level of $5d^1$ configuration. The broad emission spectra centered at 542 nm correspond to the well-known transition from the lowest $5d_1$ ($2D$) configuration to the unresolved ground states $4f_1$ ($^2F_{5/2,7/2}$) of the Ce ion in TAG crystal [18].

IV. CONCLUSION

In summary, Tb₃Al₅O₁₂:Ce (TAG:Ce) luminescent thin films were successfully deposited by pulsed laser ablation (PLA) with a low-temperature post-annealing process. XPS analysis showed that the PLA process preserved the chemical bonding property of the target that was effectively transferred to the deposited films after post-annealing at 800°C for 2 hrs in ambient conditions. Furthermore, the luminescent property was recovered by the low-temperature post-annealing process. The strong emission band around 542 nm was obtained by exciting the $5d_1$ energy levels of the Ce ion at 450 nm. It is considered that the TAG:Ce thin films deposited by PLA can be a promising component for new-typed white LEDs.

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REFERENCES

1. S. Nakamura, "Present performance of InGaN based blue/green/yellow LEDs," *Proc. SPIE* **3002**, 26-35 (1997).
2. H.-Y. Ryu and D.-H. Kim, "High-brightness phosphor-conversion white light source using InGaN blue laser diode," *J. Opt. Soc. Korea* **14**, 415-419 (2010).
3. C. G. Son, J. H. Yi, J. S. Gwag, J. H. Kwon, and G. Park, "Improvement of color and luminance uniformity of the edge-lit backlight using the RGB LEDs," *J. Opt. Soc. Korea* **15**, 272-277 (2011).
4. S. Ye, F. Xiao, Y. X. Pan, Y. Y. Ma, and Q. Y. Zhang, "Phosphors in phosphor-converted white light-emitting diodes: recent advances in materials, techniques and properties," *Mat. Sci. Eng. R* **71**, 1-34 (2010).
5. K. M. Kim, J. H. Ryu, S. W. Mhin, G. S. Park, and K. B. Shim, "Luminescence of nanocrystalline Tb₃Al₅O₁₂:Ce³⁺ phosphors synthesized by nitrate-citrate gel combustion method," *J. Electrochem. Soc.* **155**, J293-J296 (2008).
6. C. C. Chiang, M. S. Tsai, and M. H. Hon, "Synthesis and photoluminescent properties of Ce³⁺ doped terbium aluminum garnet phosphors," *J. Alloy Compd.* **431**, 298-302 (2007).
7. Z. Cui, R. Ye, Y. Hua, D. Deng, S. Zhao, C. Li, and S. Xu, "Spectral analysis of a novel Eu²⁺ activated SiO₂-BaO glass ceramics phosphor under UV-LED excitation," *J. Non-Cryst. Solids* **357**, 2298-2301 (2011).
8. S. Nishiura, S. Tanabe, K. Fujioka, and Y. Fujimoto, "Properties of transparent Ce:YAG ceramic phosphor for white LED," *Opt. Mater.* **33**, 258-271 (2002).
9. H. Bechtel, P. Schmidt, W. Busselt, and B. S. Schreinemacher, "Lumiramic: a new phosphor technology for high performance solid state light source," *Proc. SPIE* **7058**, 70580E1-10 (2008).
10. J. H. Ryu, J.-W. Yoon, K. B. Shim, T. Sasaki, and N. Koshizaki, "Room-temperature deposition of nanocrystalline CaWO₄ films by pulsed laser and their optical properties," *J. Appl. Phys.* **99**, 086103 (2006).
11. J. Y. Choe, "Luminescence and compositional analysis of Y₃Al₅O₁₂:Ce films fabricated by pulsed-laser deposition," *Mat. Res. Innovat.* **6**, 238-241 (2002).
12. J. H. Ryu, J.-W. Yoon, K. B. Shim, and N. Koshizaki, "Room-temperature deposition of nanocrystalline PbWO₄ thin films by pulsed laser ablation," *Appl. Phys. A* **84**, 181-185 (2006).
13. Y.-T. Nien, K.-M. Chen, and I.-G. Chen, "Improved photoluminescence of Y₃Al₅O₁₂:Ce nanoparticles by silica coating," *J. Am. Ceram. Soc.* **93**, 1688-1691 (2010).
14. N. Narendran, Y. Gu, J. P. Freyssinier-Nova, and Y. Zhu, "Extracting phosphor-scattered photons to improve white LED efficiency," *Phys. Status Solidi A* **202**, R60-R62 (2005).
15. M.-S. Tsai, G.-M. Liu, and S.-L. Chung, "Fabrication of cerium active terbium aluminum garnet (TAG:Ce) phosphor powder via the solid-state reaction method," *Mater. Res. Bull.* **43**, 1218-1222 (2008).
16. M. Kruczek, E. Talik, H. Sakowska, M. Gała, and M. Świrkowicz, "X-ray photoelectron spectroscopy investigations of Y₃Al₅O₁₂:Yb single crystal," *Cryst. Res. Technol.* **40**, 439-443 (2005).
17. B. M. Reddy, P. Saikia, P. Bharali, Y. Yamada, T. Kobayashi, M. Muhler, and W. Grünert, "Structural characterization and catalytic activity of nanosized ceria-terbia solid solution," *J. Phys. Chem. C* **112**, 16393-16399 (2008).
18. S. W. Mhin, J. H. Ryu, K. M. Kim, G. S. Park, H. W. Ryu, K. B. Shim, T. Sasaki, and N. Koshizaki, "Pulsed-laser-induced simple synthetic route for Tb₃Al₅O₁₂:Ce³⁺ colloidal nanocrystals and their luminescent properties," *Nanoscale Res. Lett.* **4**, 888-895 (2009).