

Enhanced green emission from UV down-converting Ce³⁺ and Tb³⁺ co-activated ZnAl₂O₄ phosphor

K.G. Tshabalala¹, S-H. Cho², J-K. Park², I.M. Nagpure¹, J.H. Neethling³, J.R. Botha³, H.C. Swart¹ and O.M. Ntwaeaborwa^{1,4}

¹Department of Physics, University of the Free State, Bloemfontein, ZA 9300, South Africa

²Nano-Materials Research Center, Korea Institute of Science and Technology, 39-1 Hawolkok, Seoul 136-791, South Korea

³Department of Physics, Nelson Mandela Metropolitan University, Port Elizabeth, ZA 6031, South Africa

E-mail: ntwaeab@ufs.ac.za

Abstract. The Ce³⁺ and Tb³⁺ co-activated ZnAl₂O₄ nanocrystal phosphors were successfully prepared by a solution combustion method, using urea as a fuel. X-ray diffraction results confirmed the formation of a cubic spinel structure of ZnAl₂O₄. Distorted hexagonal and irregular platelet-like particles were observed from the SEM images of undoped ZnAl₂O₄ and Ce³⁺-doped ZnAl₂O₄ respectively. The microstructural environment of aluminium ions (Al³⁺) were shown to change with heat treatment, as observed from the Fourier transform infrared spectra. The photoluminescent data demonstrated enhanced green emission from Tb³⁺ due to energy transfer from Ce³⁺ to Tb³⁺ in the ZnAl₂O₄ host by a down-conversion process.

1. Introduction

Zinc aluminate (ZnAl₂O₄) is a wide band gap semiconductor ($E_g = \sim 3.8$ eV) and it belongs to the class of inorganic materials called spinels. It has a closed-packed face-centered-cubic structure with *Fd3m* space group symmetry [1,2]. In a polycrystalline form, ZnAl₂O₄ is found to be highly reflective in the UV regime (300 nm) of the electromagnetic spectrum. It has attracted considerable interest among researchers for a variety of applications including catalysis, ceramics and optoelectronics. As a catalyst, ZnAl₂O₄ spinel is widely used in reactions such as cracking, dehydration, hydrogenation and dehydrogenation [3]. In this study, ZnAl₂O₄ was used as a host matrix of Ce³⁺ and Tb³⁺ ions to prepare an efficient green emitting phosphor that can be used as a UV down-converting layer to improve the absorption efficiency of the conventional silicon (Si) photovoltaic (PV) cells. Down-converted green emission, as a result of energy transfer from Ce³⁺ to Tb³⁺, was observed when ZnAl₂O₄:Ce³⁺, Tb³⁺ powders were excited by a 325 nm HeCd laser.

2. Experimental procedure

Nanocrystals of ZnAl₂O₄ co-doped with nominal concentrations of 0.5 mol% Ce³⁺– 1 mol% Tb³⁺, 0.75 mol% Ce³⁺– 1 mol% Tb³⁺, 1 mol% Ce³⁺– 0.5 mol% Tb³⁺ and 1 mol% Ce³⁺– 0.75 mol% Tb³⁺ were prepared by a solution combustion method as described in refs [4,5]. The equivalence (oxidizer:fuel) ratio was calculated based on oxidizing (*O*) and fuel (*F*) valences of the reactants, keeping *O/F* = 1, as reported previously [6]. Zinc nitrate and aluminum nitrate were used as oxidizers, urea (CH₄N₂O) was used as fuel and both cerium and terbium nitrates were used as dopant precursors. All the samples prepared were annealed in a reducing H₂ atmosphere at 700°C for 4 h. The structure and morphology were analyzed using X-ray diffraction (XRD), Scanning electron microscopy (SEM) respectively. The

⁴ Corresponding author: email: ntwaeab@ufs.ac.za (OM Ntwaeaborwa)

stretching mode frequencies were determined using Bruker Tensor 27 FTIR spectrometer. A photoluminescence system consisting of a 325 nm HeCd laser, SPEX 1870 0.5 m monochromator and a photomultiplier tube detector was used to record photoluminescence (PL) spectra.

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns of the $\text{ZnAl}_2\text{O}_4: \text{Ce}^{3+}$ powders shown in figure 1 indexed well to a pure and highly crystalline face-centered cubic spinel ZnAl_2O_4 consistent with the JCPDS file No. 05-0669. The spectra were recorded from as prepared and post-preparation annealed samples. The fact that the patterns were almost identical suggests that highly crystalline ZnAl_2O_4 can be obtained using the combustion method even without post-preparation annealing.

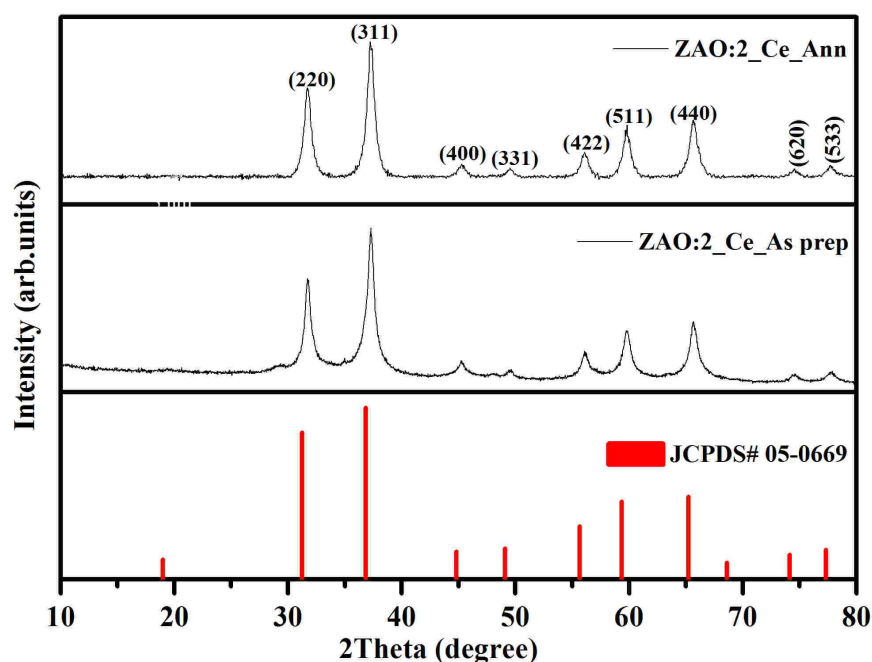


Figure 1. Room Temperature XRD pattern of $\text{ZnAl}_2\text{O}_4:2 \text{ mol\% Ce}^{3+}$ (as-prepared) and $\text{ZnAl}_2\text{O}_4:2 \text{ mol\% Ce}^{3+}$ (reduced in 4% H_2) at 700°C for 4h.

3.2. Fourier transform infrared spectroscopy

The FT-IR spectra of the (a) as-prepared $\text{ZnAl}_2\text{O}_4: 0.75 \text{ mol\% Ce}^{3+}, 1 \text{ mol\% Tb}^{3+}$ and (b) $\text{ZnAl}_2\text{O}_4: 0.75 \text{ mol\% Ce}^{3+}, 1 \text{ mol\% Tb}^{3+}$ reduced in H_2 atmosphere at 700°C for 4 h are shown in figure 2. The bands at low energy (400–1000 cm^{-1}) are related to Al—O stretching mode with peaks at 825, 698 and 582 cm^{-1} in (a) and 680, 582, 495 and 553 cm^{-1} in (b). These bands are the characteristic of zinc aluminate spinel structure [7]. Generally, the bands from the as prepared sample at low energy values (500 - 1000 cm^{-1}) were less intense than similar bands from the annealed sample. The bands at 495, 553, 582, 680 and 698 cm^{-1} from both samples are assigned to the stretching modes of AlO_6 (octahedral site) [8],[9]. A shoulder related to Al^{3+} in a tetrahedral coordination is observed around 825 cm^{-1} [10] in the as-prepared sample, suggesting partial inversion of the spinel structure. The as-prepared $\text{ZnAl}_2\text{O}_4:\text{Ce}, \text{Tb}$ sample in spectrum in figure 2 (a) exhibits strong vibration modes at 1360 – 1570 cm^{-1} that can be assigned to the groups originating from the organic compounds [11], and these bands were less intense in figure 2 (b) probably due to heat treatment. Furthermore, the bands at 3408,

3352, 1631 and 1632 cm^{-1} can be assigned to the vibration mode of carbon containing groups and to the deformation vibration of water molecules [12]

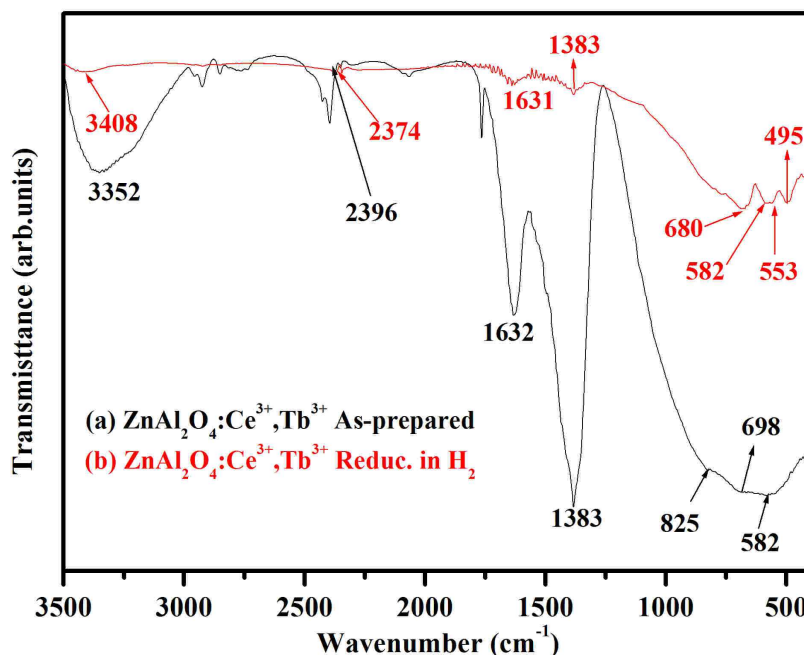


Figure 2. The FTIR spectra of the (a) as-prepared $\text{ZnAl}_2\text{O}_4: 0.75 \text{ mol}\% \text{Ce}^{3+}, 1 \text{ mol}\% \text{Tb}^{3+}$ and $\text{ZnAl}_2\text{O}_4: 0.75 \text{ mol}\% \text{Ce}^{3+}, 1 \text{ mol}\% \text{Tb}^{3+}$ reduced in H_2 atmosphere at 700°C for 4 h.

3.3. High resolution scanning electron microscopy (SEM)

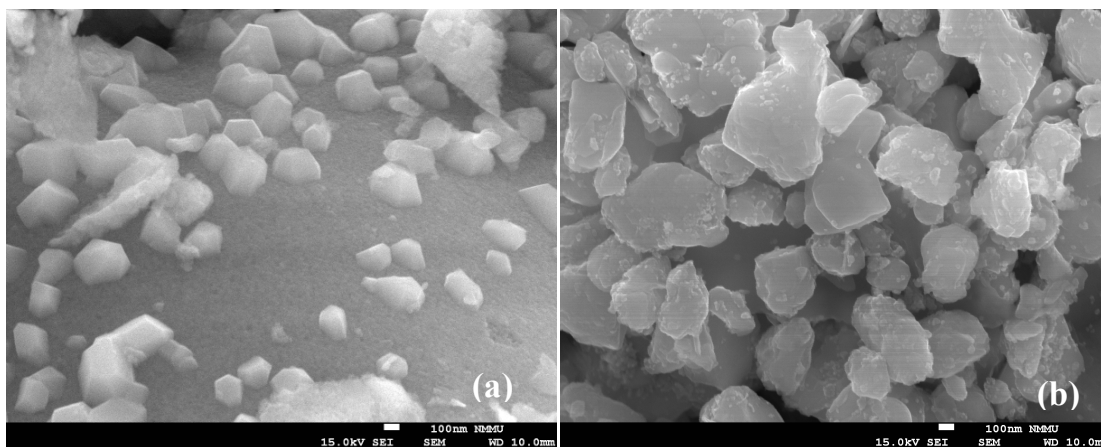


Figure 3. SEM images of the (a) ZnAl_2O_4 host and (b) $\text{ZnAl}_2\text{O}_4:1\text{mol}\% \text{Ce}^{3+}$ samples.

The SEM images in figure 3, provides the general morphology of the (a) ZnAl_2O_4 host and (b) $\text{ZnAl}_2\text{O}_4:1\text{mol}\% \text{Ce}^{3+}$ respectively. As shown in figure 3 (a), the ZnAl_2O_4 host was made up of particles with distorted hexagonal edges and corner angles and the well known characteristic platelet-like particles (figure 3(b)) of the combustion method where obtained after incorporating Ce^{3+} ions.

3.4. Photoluminescence studies

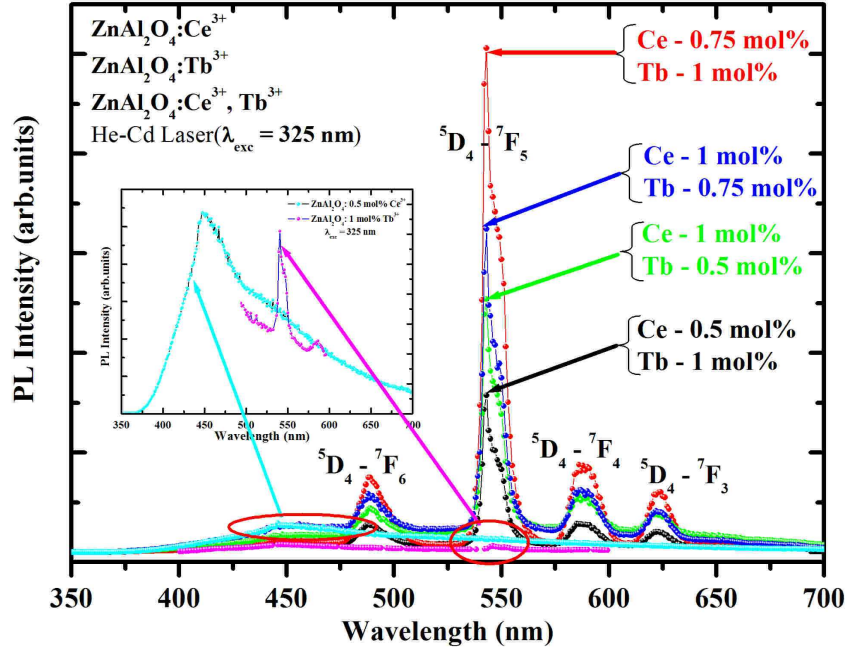


Figure 4. Emission spectra from $\text{ZnAl}_2\text{O}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ with different concentrations and annealed in hydrogen atmosphere (He-Cd laser $\lambda_{\text{exc}} = 325 \text{ nm}$). The inset is the emission spectra of $\text{ZnAl}_2\text{O}_4: 0.5 \text{ mol\% Ce}^{3+}$ (cyan) and $\text{ZnAl}_2\text{O}_4: 1 \text{ mol\% Tb}^{3+}$ (magenta) respectively.

The emission spectra of $\text{ZnAl}_2\text{O}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ nanocrystal powders with different concentrations of Ce^{3+} and Tb^{3+} are presented in figure 4. The spectra were recorded when the powders were excited with a 325 nm HeCd laser in air at room temperature. The inset of figure 4 shows the emission spectra of $\text{ZnAl}_2\text{O}_4: 0.5 \text{ mol\% Ce}^{3+}$ (cyan) and $\text{ZnAl}_2\text{O}_4: 1 \text{ mol\% Tb}^{3+}$ (magenta). The Ce^{3+} singly doped ZnAl_2O_4 gave blue broad band emission at 447 nm while the Tb^{3+} singly doped ZnAl_2O_4 gave green line emission at 543 nm as shown in the inset of figure 4. These emissions are associated with the $5d \rightarrow 4f$ and $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transitions of Ce^{3+} and Tb^{3+} respectively. The green line emission of Tb^{3+} at 543 nm was enhanced considerably and the blue Ce^{3+} emission was suppressed when different concentrations of Ce^{3+} and Tb^{3+} were incorporated simultaneously in the ZnAl_2O_4 host. The enhancement of the green line emission was maximized when 1 mol% of Tb^{3+} was co-activated with 0.75 mol% of Ce^{3+} . These results suggest that Ce^{3+} absorbed the UV excitation energy and transferred it non-radiatively to Tb^{3+} enhancing its green emission at 543 nm. Energy transfer from Ce^{3+} to Tb^{3+} was most probably by phonon-mediated process as previously reported [13]. The act of absorbing high energy (UV) photons and a subsequent emission of low energy (visible) photons is referred to as down-conversion. As previously reported, UV down-converting phosphors can be used as coatings to improve absorption efficiency of Si PV solar cells [14]. Similarly, as a potential UV down-converting phosphor, $\text{ZnAl}_2\text{O}_4:\text{Ce}, \text{Tb}$ was also evaluated for possible application as coating to improve the absorption efficiency of Si PV cells.

4. Conclusions

The green emitting $\text{ZnAl}_2\text{O}_4:\text{Ce}^{3+},\text{Tb}^{3+}$ phosphor was successfully prepared by the solution combustion method. The phosphor crystallinity indexed well to a pure face-centered cubic ZnAl_2O_4 with a spinel structure. No reflections attributable to other impurity phases such as ZnO , Al_3O_2 or CeO_2 are observed in XRD patterns of both the as prepared and reduced samples. The SEM data showed that the samples were made up of either distorted hexagons or platelet-like particles. The green emission was enhanced by energy transferred from Ce^{3+} to Tb^{3+} and this is mainly on the excitation cross-section of Ce^{3+} that is proportional to the f-d radiative transition of Ce^{3+} and the concentrations of both Ce^{3+} and Tb^{3+} .

Acknowledgements

This work is supported by the South African National Research Foundation (NRF), National Research Foundation of Korea, Korea Institute of Science and Technology (KIST) and Nanomaterials Cluster fund of the University of the Free State. The Centre for High Resolution Transmission Electron Microscopy at the Nelson Mandela Metropolitan University is gratefully acknowledged for the SEM results. The research supported by the South African Chairs Initiative of the Department of the Science and Technology and National Research Foundation for the maintenance of the He–Cd laser at the Nelson Mandela Metropolitan University is gratefully acknowledged for the PL results.

References

- [1] Hill R J, Craig J R and Gibbs G V 1979 *Phys. Chem. Minerals.* **4** 317
- [2] Sampath S K and Cordaro J F 1998 *J. Am. Ceram. Soc.* **81** 649
- [3] Nabarawy T El, Attia A A and Alaya 1995 *Mater. Lett.* **24** 319-25
- [4] Patil K C, M S Hegde, Rattan T and Aruna S T 2008 *Chemistry on Nanocrystalline Oxide Materials, Combustion Synthesis, Properties and Application.* (Singapore:World Scientific Publishing) p. 42
- [5] Pitale S S, Kumar V, Nagpure I M, Ntwaeaborwa O M and Swart H C 2011 *Appl. Surf. Sci.* **257** 3298-3306
- [6] Jain S R, Adiga K C and Pai Vernekar V R 1981 *Combustion Flame.* **40** 71
- [7] Zhu Z, Li X, Zhao Q, Liu S, Hu X and Chen 2011 *Mater Lett.* **65** 197
- [8] Maaza D, Vallino M and Busca G 1992 *J. Am. Ceram. Soc.* **75** 1929
- [9] McMillan P and Piriou B 1982 *J Non-Cryst Solids.* **53** 279
- [10] Da Silva A., Goncalves A and Davolos M 2009 *J. Sol-Gel Technol.* **49** 103
- [11] Staszak W, Zawadzki M and Okal J 2010 *J. Alloys Comp* **492** 500 – 7
- [12] Gammard A, Babaot O, Jousseaucne B, Rascle M, Toupance T and Campet G 2000 *Chem Mater* **12** 3419 - 26
- [13] Ntwaeaborwa O M, Swart H C, Kroon R E, Holloway P H and Botha R J 2007 *J. Phys. Chem. Sol.* **67** 1753 -94
- [14] Chung P, Chung H-H and Holloway P H 2007 *J. Vac. Sci. Technol A* **25**(1) 61- 66