

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

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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 $Fd\bar{3}m$ 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

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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.

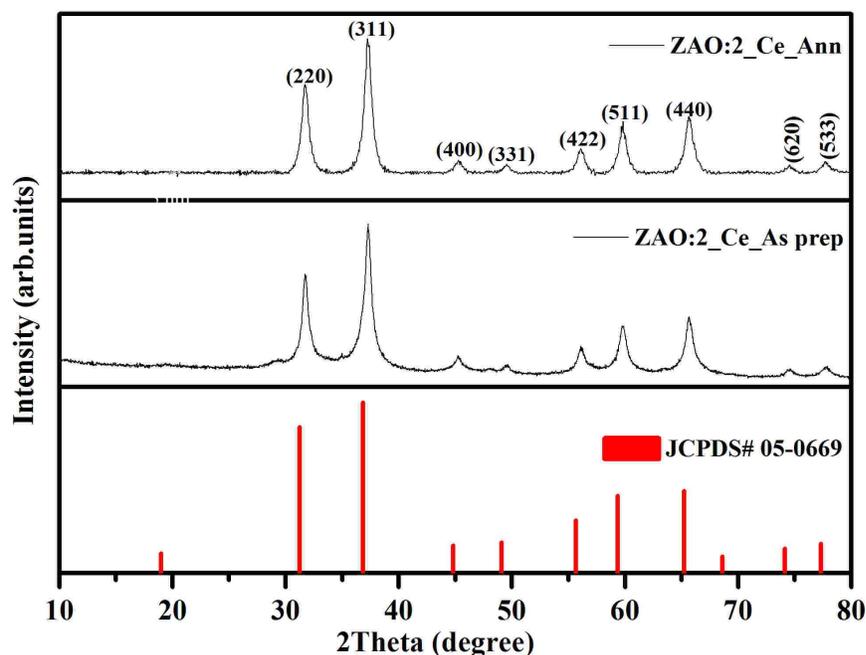


Figure 1. Room Temperature XRD pattern of $\text{ZnAl}_2\text{O}_4:2 \text{ mol}\% \text{Ce}^{3+}$ (as-prepared) and $\text{ZnAl}_2\text{O}_4:2 \text{ mol}\% \text{Ce}^{3+}$ (reduced in 4% H_2) at 700°C for 4h.

3.2. Fourier transform infrared spectroscopy

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

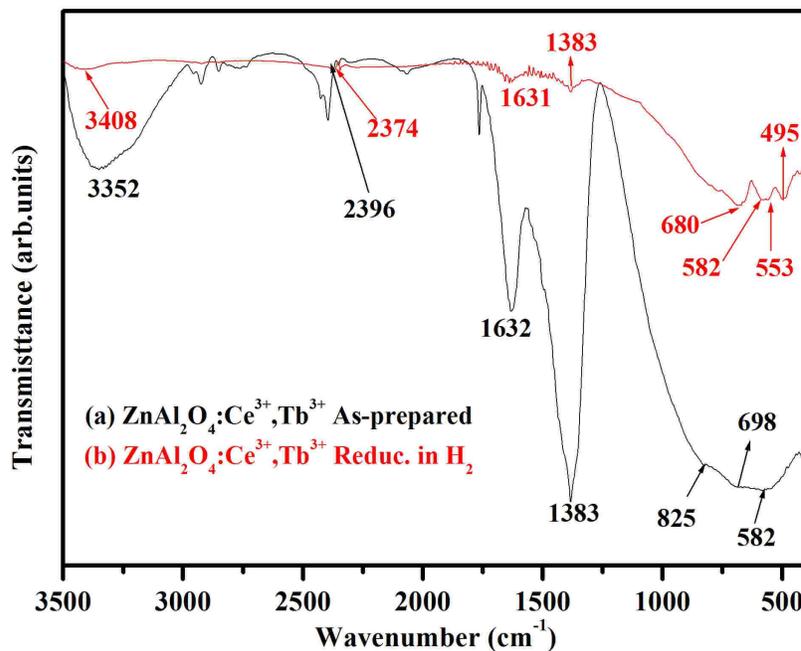


Figure 2. The FTIR spectra of the (a) as-prepared $\text{ZnAl}_2\text{O}_4: 0.75 \text{ mol}\% \text{Ce}^{3+}, 1 \text{ mol}\% \text{Tb}^{3+}$ and $\text{ZnAl}_2\text{O}_4: 0.75 \text{ mol}\% \text{Ce}^{3+}, 1 \text{ mol}\% \text{Tb}^{3+}$ reduced in H_2 atmosphere at 700°C for 4 h.

3.3. High resolution scanning electron microscopy (SEM)

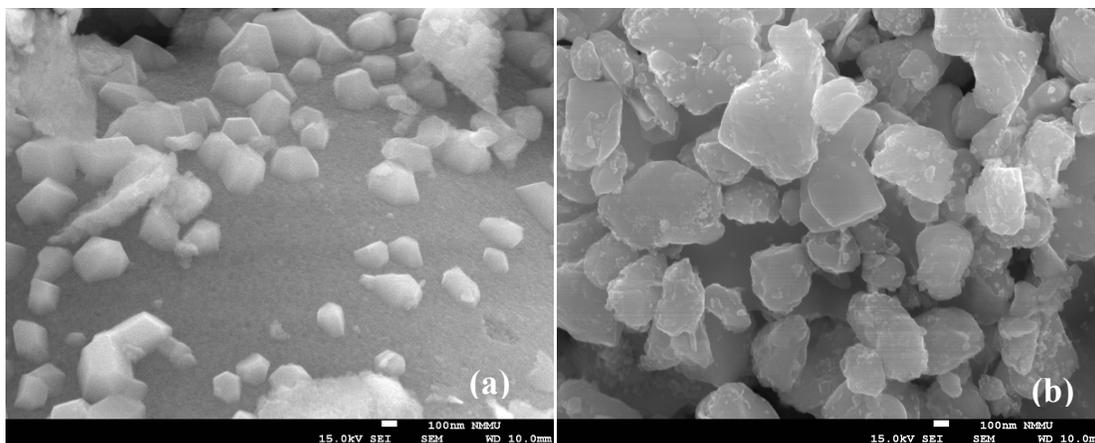


Figure 3. SEM images of the (a) ZnAl_2O_4 host and (b) $\text{ZnAl}_2\text{O}_4: 1 \text{ mol}\% \text{Ce}^{3+}$ samples.

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

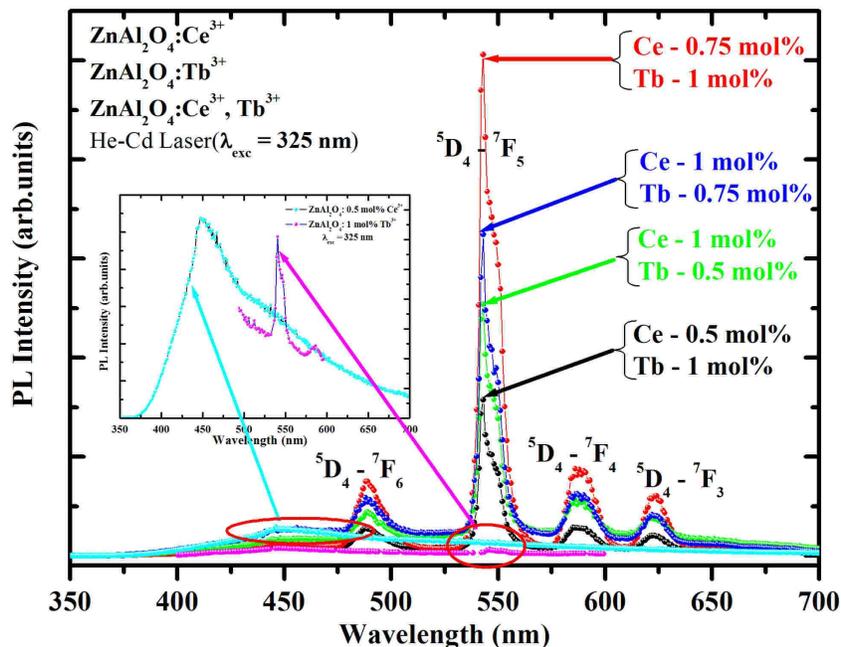


Figure 4. Emission spectra from $\text{ZnAl}_2\text{O}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ with different concentrations and annealed in hydrogen atmosphere (He-Cd laser $\lambda_{\text{exc}} = 325 \text{ nm}$). The inset is the emission spectra of $\text{ZnAl}_2\text{O}_4: 0.5 \text{ mol}\% \text{Ce}^{3+}$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

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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