Enhanced green emission from UV down-converting Ce\(^{3+}\) and Tb\(^{3+}\) co-activated ZnAl\(_2\)O\(_4\) phosphor

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Abstract. The Ce\(^{3+}\) and Tb\(^{3+}\) co-activated ZnAl\(_2\)O\(_4\) 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 ZnAl\(_2\)O\(_4\). Distorted hexagonal and irregular platelet-like particles were observed from the SEM images of undoped ZnAl\(_2\)O\(_4\) and Ce\(^{3+}\)-doped ZnAl\(_2\)O\(_4\) respectively. The microstructural environment of aluminium ions (Al\(^{3+}\)) were shown to change with heat treatment, as observed from the Fourier transform infrared spectra. The photoluminescent data demonstrated enhanced green emission from Tb\(^{3+}\) due to energy transfer from Ce\(^{3+}\) to Tb\(^{3+}\) in the ZnAl\(_2\)O\(_4\) host by a down-conversion process.

1. Introduction

Zinc aluminate (ZnAl\(_2\)O\(_4\)) is a wide band gap semiconductor (\(E_g \approx 3.8\) 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, ZnAl\(_2\)O\(_4\) 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, ZnAl\(_2\)O\(_4\) spinel is widely used in reactions such as cracking, dehydration, hydrogenation and dehydrogenation [3]. In this study, ZnAl\(_2\)O\(_4\) was used as a host matrix of Ce\(^{3+}\) and Tb\(^{3+}\) 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 Ce\(^{3+}\) to Tb\(^{3+}\), was observed when ZnAl\(_2\)O\(_4\):Ce\(^{3+}\),Tb\(^{3+}\) powders were excited by a 325 nm HeCd laser.

2. Experimental procedure

Nanocrystals of ZnAl\(_2\)O\(_4\) co-doped with nominal concentrations of 0.5 mol% Ce\(^{3+}\)– 1 mol% Tb\(^{3+}\), 0.75 mol% Ce\(^{3+}\)– 1 mol% Tb\(^{3+}\), 1 mol% Ce\(^{3+}\)– 0.5 mol% Tb\(^{3+}\) and 1 mol% Ce\(^{3+}\)– 0.75 mol% Tb\(^{3+}\) 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 \((\text{CH}_2\text{N}_2\text{O})\) was used as fuel and both cerium and terbium nitrates were used as dopant precursors. All the samples prepared were annealed in a reducing H\(_2\) atmosphere at 700°C for 4 h. The structure and morphology were analyzed using X-ray diffraction (XRD), Scanning electron microscopy (SEM) respectively.

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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 ZnAl$_2$O$_4$: Ce$^{3+}$ powders shown in figure 1 indexed well to a pure and highly crystalline face-centered cubic spinel ZnAl$_2$O$_4$ 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$_2$O$_4$ can be obtained using the combustion method even without post-preparation annealing.

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

3.2. Fourier transform infrared spectroscopy

The FT-IR spectra of the (a) as-prepared ZnAl$_2$O$_4$: 0.75 mol% Ce$^{3+}$, 1 mol% Tb$^{3+}$ and (b) ZnAl$_2$O$_4$: 0.75 mol% Ce$^{3+}$, 1 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 ZnAl$_2$O$_4$:Ce, 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](image1.png)

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

3.3. High resolution scanning electron microscopy (SEM)

![Figure 3](image2.png)

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

The SEM images in figure 3, provides the general morphology of the (a) ZnAl$_2$O$_4$ host and (b) ZnAl$_2$O$_4$:1mol% Ce$^{3+}$ respectively. As shown in figure 3 (a), the ZnAl$_2$O$_4$ 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](image)

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

The emission spectra of ZnAl$_2$O$_4$:Ce$^{3+}$, 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 ZnAl$_2$O$_4$: 0.5 mol%Ce$^{3+}$ (cyan) and ZnAl$_2$O$_4$: 1 mol% Tb$^{3+}$ (magenta). The Ce$^{3+}$ singly doped ZnAl$_2$O$_4$ gave blue broad band emission at 447 nm while the Tb$^{3+}$ singly doped ZnAl$_2$O$_4$ 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 $5D_4 \rightarrow 7F_5$ 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$_2$O$_4$ 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, ZnAl$_2$O$_4$:Ce,Tb was also evaluated for possible application as coating to improve the absorption efficiency of Si PV cells.
4. Conclusions
The green emitting ZnAl$_2$O$_4$:Ce$^{3+}$,Tb$^{3+}$ phosphor was successfully prepared by the solution combustion method. The phosphor crystallinity indexed well to a pure face-centered cubic ZnAl$_2$O$_4$ with a spinel structure. No reflections attributable to other impurity phases such as ZnO, Al$_2$O$_3$ 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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