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Luminescence properties of Ce^{3+} and Tb^{3+} co-activated $ZnAl_2O_4$ phosphor

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ABSTRACT

In this study, a solution combustion method was used to prepare green emitting Ce^{3+}–Tb^{3+} co-activated $ZnAl_2O_4$ phosphor. The samples were annealed at 700 °C in air or hydrogen atmosphere to improve their crystallinity and optical properties. X-ray diffraction study confirmed that both as-prepared and post-preparation annealed samples crystallized in the well known cubic spinel structure of $ZnAl_2O_4$. An agglomeration of irregular platelet-like particles whose surfaces were encrusted with smaller spheroidal particles was confirmed by scanning electron microscopy (SEM). The fluorescence data collected from the annealed samples with different concentrations of Ce^{3+} and Tb^{3+} show the enhanced green emission at 543 nm associated with $^5D_4 \rightarrow {}^7F_5$ transitions of Tb^{3+}. The enhancement was attributed to energy transfer from Ce^{3+} to Tb^{3+}. Possible mechanism of energy transfer via a down conversion process is discussed. Furthermore, cathodoluminescence (CL) intensity degradation of this phosphor was also investigated and the degradation data suggest that the material was chemically stable and the CL intensity was also stable after 10 h of irradiation by a beam of high energy electrons.

1. Introduction

Zinc alluminate ($ZnAl_2O_4$) is one of the metal oxides which are currently being investigated as possible hosts for rare-earth ions to prepare light emitting materials (phosphors), which can be used in different types of light emitting devices. Traditionally, $ZnAl_2O_4$ is widely used as a catalyst or ceramic [1]. Because of its excellent optical properties, and high chemical and thermal stability it is also used in optoelectronic devices [2,3]. In addition, it has been demonstrated that pure (undoped) and impurities-activated (-doped) $ZnAl_2O_4$ produces efficient emissions that can be used in lighting. Emission from pure $ZnAl_2O_4$ is characterized by two broad bands with maxima at ~450 and ~770 nm, which are, respectively, ascribed to $Al^{3+} \rightarrow O^{2-}$ charge transfer and anionic oxygen vacancies (V_O) [4] while the impurities-activated $ZnAl_2O_4$ emission is due to the intrinsic nature of the incorporated impurity. Today, orange, green and red emissions have, respectively, been observed from Mn^{2+}, Tb^{3+} and Eu^{3+} ions incorporated in $ZnAl_2O_4$ host [5–7].

In this study, Ce^{3+} and Tb^{3+} ions were simultaneously incorporated with different concentrations in $ZnAl_2O_4$ resulting in a green emitting phosphor that was evaluated for possible applications in, among other things, photovoltaic cells and display technologies. We demonstrated that upon excitation by UV radiation the UV photons were absorbed and transferred from Ce^{3+} to Tb^{3+} by a down conversion process. The down conversion process involves absorption of UV photons in the short wavelength range (typically ~200–350 nm) and emission of visible photons in the wavelength range of ~400–700 nm. Today, rare-earths doped phosphors are extensively investigated for possible application as down-converting layers to improve the absorption efficiency of the silicon (Si) photovoltaic (PV) cells [8]. That is, by shifting the sunlight wavelengths from the UV region where the spectral response of the Si PV cells is low to the visible region where the spectral response is high. In this study, the down-conversion press between Ce^{3+} and Tb^{3+} in $ZnAl_2O_4$ was investigated. The possible down-conversion mechanism through energy transfer from Ce^{3+} to Tb^{3+} is discussed. In addition cathodoluminescence intensity of the $ZnAl_2O_4$:Ce^{3+},Tb^{3+} phosphors was also investigated for its possible application as a green emitting phosphor in low voltage field emitting displays (FEDs). These were prepared by the solution combustion method.

2. Experimental

A detailed procedure about the combustion reaction synthesis of impurities-activated $ZnAl_2O_4$ can be found in Refs. [5,7,9]. In a typical synthesis, stoichiometric amounts of zinc nitrate, aluminum nitrate, cerium nitrate, terbium nitrate and urea were dissolved in

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de-ionized water. A homogeneous transparent solution was obtained after stirring vigorously for 20 min. The solution was transferred to a muffle furnace maintained at $400 \pm 10\,^{\circ}C$. After all the liquid had evaporated, the mixture decomposed and released large amounts of gases. Due to the exothermic nature of the combustion process, the reaction continued for a while and the mixture swelled to a larger volume. Large exothermicity resulted in a high-temperature flame that further decomposed the mixture into gaseous phases and aluminates. The combustion process was completed in less than 5 min. The resulting powders were gently ground and annealed in hydrogen atmosphere. $ZnAl_2O_4:Ce^{3+},Tb^{3+}$ powder phosphors with different concentrations of Ce^{3+} and Tb^{3+} were prepared. These were analyzed with x-ray diffraction (XRD), scanning electron microscopy, photoluminescence spectroscopy, and Auger electron spectroscopy (AES) coupled with cathodoluminescence (CL) spectroscopy.

3. Results and discussions

Fig. 1 shows the XRD patterns of undoped $ZnAl_2O_4$ (annealed in air at 700 °C) and $ZnAl_2O_4:Ce^{3+},Tb^{3+}$ powders (annealed at 700 °C in H_2 atmosphere). Annealing in H_2 was meant to, among other things, reduce Ce from non-luminescing Ce^{4+} oxidation state to the luminescing Ce^{3+} state. The XRD patterns confirm that both undoped and Ce^{3+}–Tb^{3+} co-doped samples crystallized in a well known spinel structure of $ZnAl_2O_4$ as indexed by JCPDS file No. 082-1043. Note that the diffraction peaks of the Ce^{3+}–Tb^{3+} co-doped sample were more broadened than those of the undoped sample. This is probably due to lattice strains [10] as a result of incorporation of Ce^{3+} and Tb^{3+} ions. The HR-SEM images of the $ZnAl_2O_4$ powders in Figs. 2(a) and (b) show the platelet-like particles encrusted with smaller particles on the surface. Fig. 2(b) shows an agglomeration of spheroidal particles on the surface of a platelet-like particle. It is therefore clear that the powders composed of platelet-like particles encrusted with spherical nanoparticles (with some degree of faceting) with an average diameter of ~20 nm.

The emission spectrum of Ce^{3+} singly doped $ZnAl_2O_4$ phosphor excited at 256 nm in Fig. 3 consists of a broad band with two maxima at 350 and 410 nm. These emissions correspond to the allowed transitions from the lowest sublevel of the 5d state to the $^2F_{7/2}$ and $^2F_{5/2}$ multiplets of the 4f configuration in Ce^{3+} [4]. Dual emission was observed from the $ZnAl_2O_4$ powders co-activated with different concentrations of Ce^{3+} and Tb^{3+} when excited at 256 nm. This was a combination of line emissions from Tb^{3+} ions and broad emission from Ce^{3+}. The green line emission associated with $^5D_4 \rightarrow {}^7F_5$ transitions of Tb^{3+} at 543 nm was more intense than the purplish-blue broad emission of Ce^{3+} at 350–410 nm. The green emission was maximized when 1 mol% of Tb^{3+} was co-doped with 0.75 mol% of Ce^{3+}. The enhancement of the green emission and the subsequent decrease in the blue emission suggests that energy was transferred, most probably by phonon mediated processes, from Ce^{3+} to Tb^{3+}. The proposed mechanism for this transfer is presented in Fig. 4. According to this mechanism, the excitation energy absorbed by Ce^{3+} is transferred by the low lying $^5D_{3/2}$ of the Ce^{3+} to the $^5D_4$ state

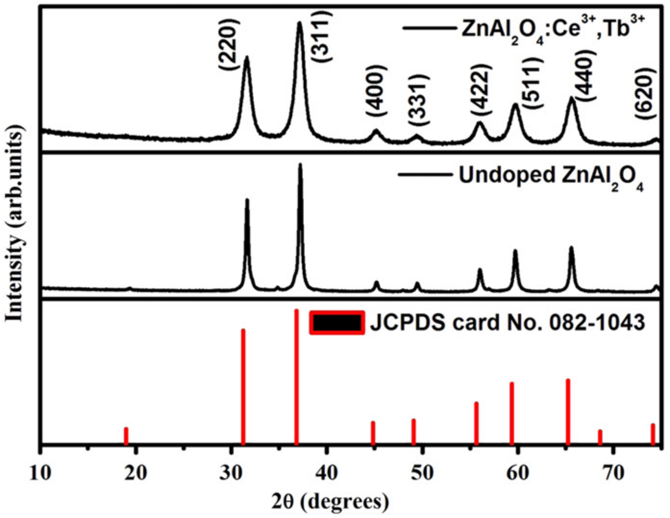

Fig. 1. The XRD patterns of $ZnAl_2O_4$ and $ZnAl_2O_4:Ce^{3+},Tb^{3+}$ powders annealed at 700 °C.

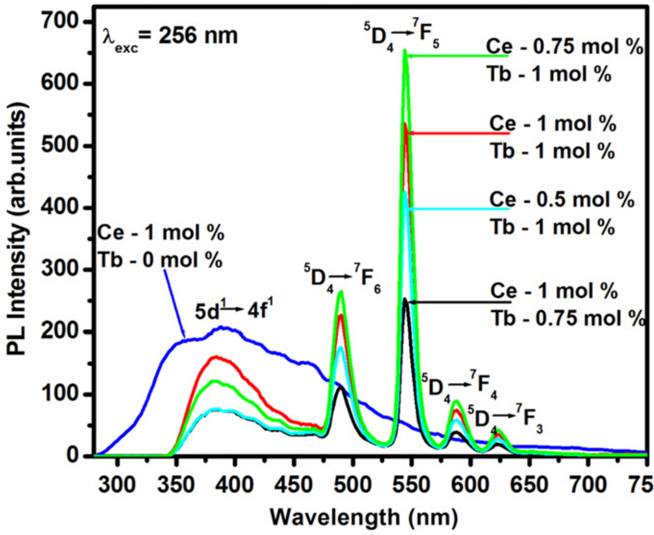

Fig. 3. PL emission and excitation of $ZnAl_2O_4:Ce^{3+},Tb^{3+}$ with different concentrations of Ce^{3+} and Tb^{3+}.

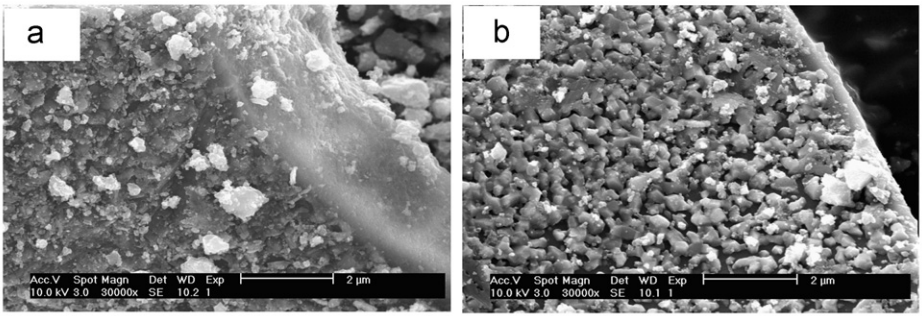

Fig. 2. High resolution SEM images of the $ZnAl_2O_4:Ce^{3+},Tb^{3+}$ powder annealed at 700 °C.