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Tunable and white emission from ZnO:Tb^{3+} nanophosphors for solid state lighting applications

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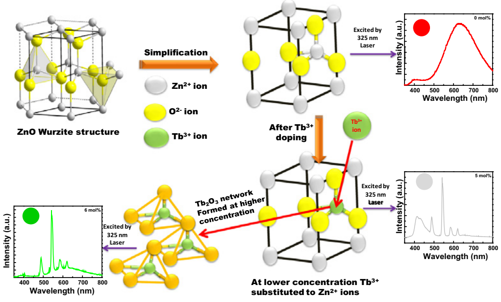
HIGHLIGHTS

- ZnO:Tb^{3+} nano-phosphors were synthesised by a solution combustion method.
- Emission bands of blue, green, and red obtained due to defect and Tb^{3+} transitions.
- The formation of different kind of defect is confirmed by XPS analysis.
- The emitting colour could easily be tuned from yellow to blue by varying the Tb^{3+}.
- Near white emission was achieved for the 5 mol% of the Tb^{3+} doping in ZnO:Tb^{3+}.

GRAPHICAL ABSTRACT



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ABSTRACT

Terbium doped Zinc oxide (ZnO:Tb^{3+}) nano-phosphors (NPr) with a hexagonal wurtzite structure were synthesised by a solution combustion method. X-ray photoelectron spectroscopy confirmed the formation of different kind of defects for the undoped and lower Tb doping concentrations and the formation of Tb_2O_3 at higher doping concentrations. A broadband orange-red emission ranging from 500 to 850 nm was obtained from the undoped ZnO while white light emission was observed from ZnO doped with 5 mol% of Tb. The colour of the emission of the ZnO:Tb3^{+} NPr was tuned by varying the concentrations of Tb^{3+} in the ZnO host. The ZnO:Tb^{3+} NPr have potential applications in solid state lighting.

1. Introduction

White light-emitting diodes (LEDs) are in high demand in solid-state lighting technology to replace conventional incandescent and fluorescent lamps [1]. There are two basic approaches to generate white light from LEDs. One is by mixing light of different colours emitted by several chips called multichip LEDs and the other is to convert the light emitted from a blue or ultraviolet (UV) LED to a longer wavelength light using phosphors, which are called phosphor-converted (pc)–LEDs [2]. Zinc oxide (ZnO) is an environmental friendly low cost phosphor with good thermal and chemical stability. Most importantly, ZnO has an exciton binding energy of 60 meV, which is much larger than the room-temperature (RT) thermal energy (25 meV) [3–4]. With these unique properties, ZnO has been extensively exploited in both the thin film and nanostructure forms for potential optical and photonic applications [5–9]. ZnO has attracted interest for pc–LEDs because of their strong and broad absorption band in the near ultraviolet region.

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It also has a broad emission spectrum due to the different kind of inherent defects [10–11]. Usually ZnO has six kinds of defects, namely oxygen vacancies (V_o), oxygen interstitials (O_i), oxygen antisites (Zn_O), zinc vacancies (V_{Zn}), zinc interstitials (Zn_i) and zinc antisites (O_{Zn}). The intensities of the blue, green and orange emission can be influenced by the concentration of different kind of defects [10–12], thereby making it possible for the emission colour to be tuned [10,11]. ZnO have been used in different kind of devices operating in green, blue and near-UV regions [12–15], but ZnO based white light emission is still not widely reported [16,17]. Till date, a lot of work has been carried out on ZnO nanostructures with various morphologies such as nanoparticles, nano/microrods, nanoballs, nanoflowers for a wide variety of applications such as photocatalytic degradation of organic dyes, sensors, etc. [18–23].

Semiconductors doped with rare earth (RE) elements such as Eu, Er, Tm, and Tb has been intensively pursued because of their important applications in optoelectronics as emitters at visible wavelengths [24]. There are two main factors leading to the stable and sharp luminescence in RE elements: one is that the 4f orbital of RE ions is shielded by the outer 6s, 5p and 5d orbitals, which weakens its coupling with the surrounding ligands; the other is that the f–f transitions are parity forbidden, thus resulting in small absorption cross sections [25], but the initial efforts of incorporating RE ions into Si and other narrow band gap semiconductors suffered severe limitations due to the solubility constraints and the thermal quenching [26,27]. ZnO doped rare earth metal ions have been investigated most frequently [28–30] because of the unique luminescent properties resulting from its stability and high emission quantum yields [31]. Rare earth material produces efficient visible emissions in a 4f shell, which is, to a large extent, insensitive to the influence of its surroundings thanks to the shielding effect of the outer 5s and 5p orbitals [31,32]. ZnO doped with transition metals has found applications in sensors, spin light emitting diodes and non-volatile memory devices, optoelectronics, and photocatalysis [18,33].

In this paper, the effect of the Tb^{3+} ions concentration on the structural, morphological, chemical and photoluminescence (PL) properties of $ZnO:Tb^{3+}$ nanophosphors (NPr) is reported. The details chemical analysis of $ZnO:Tb^{3+}$ was performed by XPS. In addition, the optical properties of ZnO nanophosphors in terms of luminescence and band gap energy were studied in details. The ZnO doped with 0%, 1% and 6% mol concentration of Tb were investigated for their compositional identification, presence of dopants and homogeneity of doping in the crystal lattice using TOF-SIMS. Additionally, a doping mechanism of Tb^{3+} ions in ZnO has been proposed and explained with the help of a schematic diagram. The novelty of the present work is the capability to achieve nano phosphors of different colours by changing the Tb^{3+} concentration.

2. Experimental section

2.1. Preparation of samples

$ZnO:Tb^{3+}$ NPr were synthesised using the solution combustion method. Zinc nitrate tetrahydrate and urea were mixed and dissolved in distilled water. Terbium nitrate pentahydrate was used as the Tb source in the solution. The concentration of Tb was varied from 0 to 6 mol%. A homogeneous solution was obtained after stirring for 20 min. The solution was transferred to a pre-heated muffle furnace maintained at a temperature of 450 ± 10 °C. All the liquid evaporated and a large amount of heat was released which resulted into a flame that decomposed the reagents further and released more gases. The flame lasted for ~60 s and the combustion process was completed within 5 min. The resulting $ZnO:Tb^{3+}$ NPr powders were cooled down to room temperature and ground gently using a pestle and mortar.

2.2. Characterisation

The structural properties were analysed with an X-ray diffractometer (XRD) (PAN analytical X'pert PRO). A Shimadzu SSX-550 Superscan scanning electron microscope (SEM) was used to analyse the particle morphology. The XPS analysis was carried out with a PHI 5000 Versaprobe-Scanning XPS Microprobe. The PL data were recorded using a He–Cd laser with a 325 nm excitation wavelength. For TOF-SIMS analysis, a pulsed 30 keV Bi^+ primary ion beam, operated at a DC current of 1pA, and pulse repetition rate of 10 KHz (100 µs) was used to acquire chemical images of the phosphor in the positive secondary ion polarities. Moreover, the O^+ with 1 kV and DC current of 250 nA was used as a sputter gun. The analytical field-of-view was $100 \times 100\ \mu m^2$ with a 512×512 pixel^2 digital raster.

3. Results and discussion

3.1. Structure and morphology analysis of $ZnO:Tb^{3+}$

XRD patterns of $ZnO:Tb^{3+}$ NPr with different concentrations of Tb are shown in Fig. 1. The $ZnO:Tb^{3+}$ NPr were highly crystalline in nature. The strong diffraction peaks at 31.7°, 34.3° and 36.2° correspond to the (100), (002) and (101) planes of the hexagonal wurtzite structure of ZnO (ICSD card no. 29272), while a small peak observed at 29.3° (marked with an asterisk "*") is assigned to Tb_2O_3 (ICSD card no. 53635). The peak intensity is much more pronounced at the higher Tb concentrations. The most prominent diffraction peak comes from the preferred (101) orientation [34]. So it is believed that the Tb^{3+}occupied the Zn^{2+} sites or interstitial sites in the ZnO up to a certain concentration limited where after Tb_2O_3 was also observed. The crystallite sizes of the $ZnO:Tb^{3+}$ NPr calculated by Scherer's formula were in the range of 13 ± 2 to 30 ± 2 nm and were found to change with increasing doping concentration [35].

The effect of Tb concentration on the morphology of the $ZnO:Tb^{3+}$ NPr is shown in Fig. 2. The morphology was strongly dependent on the doping concentration of Tb. The SEM images show a cauliflower like clusters for the undoped ZnO, and the size of the cauliflower has increased with an increase in the doping concentration of Tb. The shape of the $ZnO:Tb^{3+}$ NPr grains transformed from cauliflower structures to nanoflakes (NFs) when the Tb concentration was increased from 0 to 4 mol%. A more dense NFs structure was observed for the higher doping concentration of Tb. The change in surface morphology with an increase doping concentration of Tb is attributed to the differences of the ionic radius of the Tb ion and Zn ion as well as the differences in the

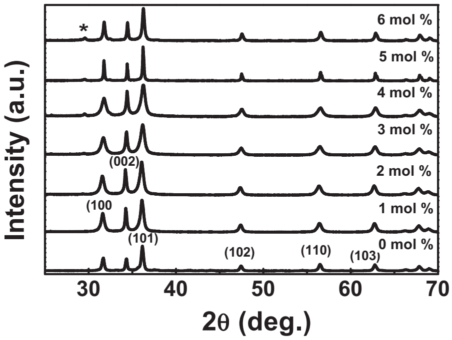

Fig. 1. XRD patterns of $ZnO:Tb^{3+}$ with different doping concentration of Tb"*" indicate presence of Tb_2O_3.