Journal of Luminescence 187 (2017) 141–153

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Structural, photoluminescence and XPS properties of Tm^{3+} ions in ZnO nanostructures

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ARTICLE INFO

Article history:
Received 1 March 2016
Received in revised form
7 February 2017
Accepted 8 February 2017
Available online 10 February 2017

Keywords:
ZnO nanostructures
Thulium
Bandgap
XPS
O 1s
Tm 4d

ABSTRACT

In the present study, a succession of thulium (Tm)-doped zinc oxide (ZnO) nanostructures samples were prepared by sol-gel method using zinc acetate dihydrate, thulium nitrate pentahydrate and sodium hydroxide species with absolute ethanol as solvent. The X-Ray diffraction (XRD) revealed phase purity (hexagonal Würtzite structure) and high crystalline nature of both Tm^{3+} doped and undoped ZnO samples. Furthermore, defects mediated levels in the samples were investigated by means of photoluminescence (PL) spectroscopy. Finally, Tm 4d core level was detected in ZnO: 0.5 mol% Tm^{3+} sample from high resolution X-Ray Photoelectron Spectroscopy (XPS) scan.

1. Introduction

The undoped and doped ZnO semiconductor nanostructures are gaining more interest within the scientific community. In fact, these nanostructures are suitable tunable bandgap semiconductors for a wide range of applications such as light-emitting device and drug delivery applications [1–3]. The wide direct bandgap (~3. eV) of ZnO becomes more attractive when defects such as lanthanides are intentionally incorporated in its lattice, it then exhibit unique optical properties.[4] Various physical and chemical synthesis approaches are reported for doping purpose of ZnO nanostructures [5,6]. However, sol-gel is of particular interest due to its low cost, flexibility when it comes to tuning the reaction parameters and easy to handle. In the present study, we report on the defect state within the bandgap of ZnO nanostructures with the incorporation of thulium ions. In spite of abundant investigations found in the literature on Tm^{3+} doped ZnO or co-doped with ZnO in other host matrix, only few studies reported the presence of Tm^{3+} ions in ZnO semiconductor nanostructures [7–13].

There is a worldwide agreement on the critical role played by defects within the bandgap of semiconductor materials and especially in wide bandgap based devices. Being applied in various devices such as optoelectronics, dilute magnetic semiconductors, UV emitting phosphors, gas sensors and solar cells, just to cite a few, these defects dependent semiconductors are found to exhibit tailored optical, electronic, photocatalytic, surface and magnetic properties [14–20]. Furthermore, the surge in investigating and understanding the controversial issue of defects mediated in ZnO nanostructures and its wide bandgap counterpart materials have driven scientists within the materials physics community to diversify their research approaches through intensive theoretical computational and experimental studies [21–27].

Being a potential white light emitting phosphor and one of the most efficient rare-earth [28], Tm^{3+} ions incorporated into ZnO nanostructures could be synthesized using various synthetic methods to elucidate on the brightness of its emissions detected in the visible range of the electromagnetic spectrum. The reason being the rise of interest on white light emitting phosphors in the promising photonic device industry, which industry may also be attracted by enhanced UV emission reported in the current study. Besides, much research has been focused on ZnO doped with rare earth ions such as Tm, Nd, Eu, Tb, and Er lately. Among these rare earth elements, Tm is not only the most efficient rare earth ions for solid state lighting applications but also the most widely used

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http://dx.doi.org/10.1016/j.jlumin.2017.02.024
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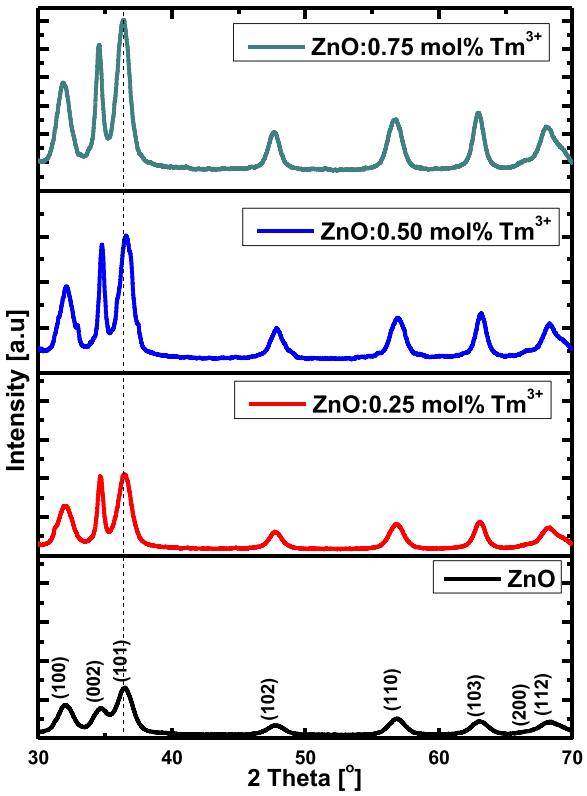

Fig. 1. XRD patterns of undoped and ZnO:Tm^{3+} (0.25, 0.5, 0.75 mol%) nanostructures dried at 200 °C.

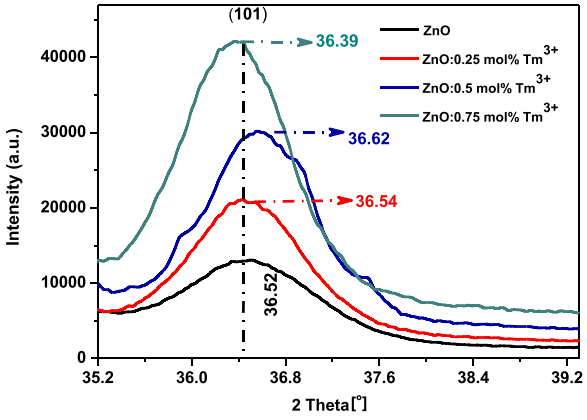

Fig. 2. Magnified (101) diffraction peak of undoped and ZnO:Tm^{3+} (0.25, 0.5, 0.75 mol%) samples.

element for high power laser applications. It has also been demonstrated to reduce the band-gap energy thus enhancing the possibility of the photo-degradation using visible light when used as dopant. It is however worth mentioning that to the best of our knowledge, no report on the detection of Tm 4d core level in ZnO nanostructures was found in the literature. In the current study, detailed analysis was devoted to the Tm^{3+} ions observed through their *4f-4f* electronic transitions in the PL emission spectra and their effect on native defects. Furthermore, same attention was dedicated to the observation and discussion of the XPS Tm 4d core level in ZnO nanostructures.

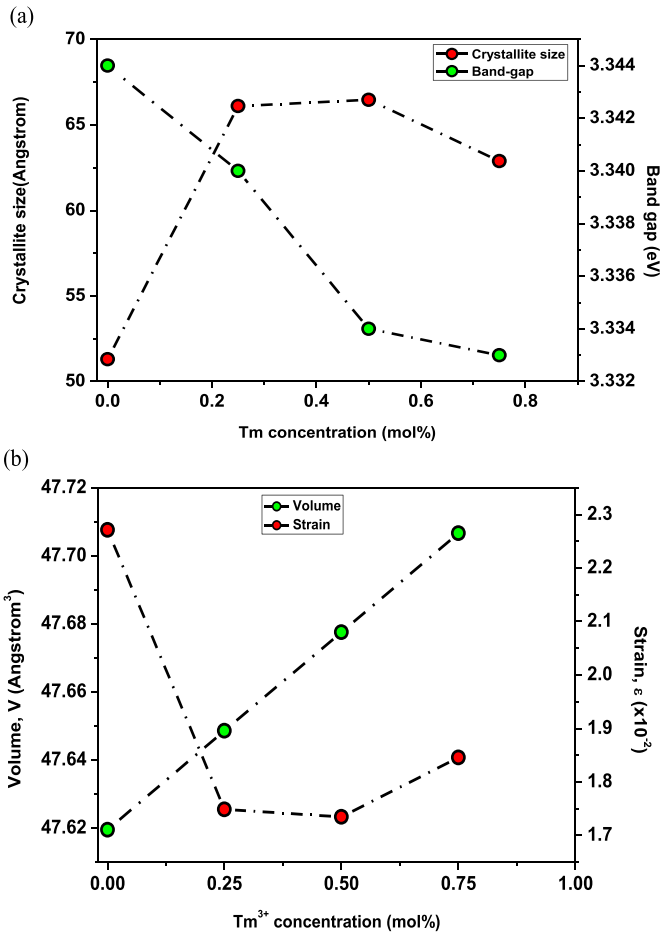

Fig. 3. (a) Variation of crystallite size and bandgap and (b) micro-strain and lattice volume of undoped and Tm^{3+} doped ZnO nanostructures as a function of Tm^{3+} concentration.

2. Experimental section

2.1. Preparation of undoped and Tm^{3+} doped ZnO nanostructures

ZnO:Tm^{3+} nanostructures were prepared using a sol-gel method following the same procedure as reported in our previous studies with slight changes [5]. The solution of sodium hydroxide dissolved in ethanol was also prepared separately, then cooled in

Table 1
(101) plane lattice constants (*a,c,c/a*), inter-planar distance (d_{hkl}), crystallite size, volume of the unit cell (*V*), bond length (*L*), micro-strain (ε) and bandgap of the undoped and Tm^{3+} doped ZnO nanostructures.

Sample	2Θ (°)	$d_{(101)}$ [Å]	Crystallite size, D [Å]	Lattice parameters			V [Å^3]	L [Å]	$\varepsilon \times 10^{-2}$	Bandgap [eV]
				a [Å]	c [Å]	c/a				
Undoped ZnO	36.52	2.4758	51.30	3.2498	5.2066	1.60	47.62	1.956	2.27	3.344
0.25 mol% Tm^{3+}	36.54	2.4763	66.10	3.2505	5.2074	1.60	47.65	1.957	1.75	3.340
0.50 mol% Tm^{3+}	36.62	2.4768	66.47	3.2512	5.2083	1.60	47.68	1.957	1.74	3.334
0.75 mol% Tm^{3+}	36.39	2.4773	62.88	3.2519	5.2092	1.60	47.71	1.958	1.85	3.333