A Novel Strong Cyan Luminescence Emission of Tb_2O_3 Particles

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Research Article

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Abstract

Terbium oxide (Tb_2O_3) particles (NPs) were synthesized by precipitation method using ammonium carbonate as precipitation agent. Effects of precursor molarity (0.1, 0.15 and 0.2 M) on photoluminescence (PL) behaviour of the NPs were investigated. The presence of the Tb_2O_3 phase was confirmed by X-Ray Diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR) analyses. Morphological investigations of the produced powders were made by Field Emission Gun-Scanning Electron Microscopy (FEG-SEM). It showed that the morphology of Tb_2O_3 particles transformed from the nanograin chain to bundles morphology of rod-like as the amount of precursor molarity increased. Emission spectrum were investigated by Photoluminescence (PL) Spectroscopy. All the Tb_2O_3 particles exhibited the strongest peak at 493 nm ascribed to $^5\text{D}_4\text{-}^7\text{F}_6$ (magnetic dipole (MD), C_2) transition. The increase in the number of C_2 sites released from the MD transition with the increase of the precursor molarity caused a negative increase in the b^* (yellowness/blueness of the emission) value in the CIE diagram, indicating that the colour shifted to the blue region. The Tb_2O_3 particles produced by the precipitation method exhibited novel strong cyan colour and the PL emission intensity increased with increasing molarity.

1. Introduction

In recent years, rare earth (RE) oxides are come upon in many areas due to their optical, chemical, electrical, catalytic and magnetic properties such as high melting temperature, excellent thermal and corrosion resistance, very good dielectric constant, and luminescence behaviour, etc. originating from their 4f electronic structure [1] [2] [3] [4] [5]. Besides, their functional properties are highly dependent upon crystallite size, composition, morphology, shape, size, precursor molarity, production method [4] [6] [7][1] [8]. Among them, terbium oxide (Tb_2O_3) materials are used widely in many areas such as magneto-optical [9] [10] [11] [12], optical application [13] [1] [6] [14] [15] [16] [11] [17], magnetic application [3], electronic [7], optoelectronic devices [18], MRI contrast agents [19], electrochemical applications [6]. They can be synthesized by solvothermal [17], hydrothermal [20], precipitation [6] [7], template-assisted hydrothermal [1], self-propagating high-temperature [12] [9], thermal decomposition [3], sol-gel [21] [22], magnetron sputtering [15] and metal-organic (MO) CVD [14] methods.

In the light of the literature search, several studies have been found examining the PL emission properties of Tb_2O_3 powder [13][1] [16] [6] [17]. Wakefiel et al. found that Tb_2O_3 nanoparticles produced by a colloidal precipitation technique exhibited green emission [13]. Tang et al. compared the PL emission characteristics of Tb_2O_3 bulk and nanotubes under 325 nm [1]. Candela et al. investigated the effect of high-pressure behavior on the PL properties of cubic Tb_2O_3 phase (C-type) [17]. However, there are no reports examining the effect of molarity on PL emission of Tb_2O_3 particles. Therefore, the aim of this study is to examine the effect of molarity and powder morphology on the PL properties of the Tb_2O_3 particles.

2. Experimental Study

Tb₂O₃ particles with precursor molarity (0.10, 0.15 and 0.2 M) were produced by precipitation method. Firstly, Tb(NO₃)₃·xH₂O nitrate salt with analytical grade 99.99% purity was used as a starting source in order to produce the Tb₂O₃ particles. The amounts of the salts were determined according to their precursor molarities and dissolved in 200 ml ultrapure water. Then 8 ml of 1 M ammonium carbonate ((NH₄)₂CO₃) solution was slowly dropped into the each solution and precipitates formed. The solutions were continued to be stirred on the magnetic stirrer for 2 h at room temperature. After mixing, centrifugation was performed at 500 rpm for 5 minutes to separate the precipitates from water. Afterwards, the collected precipitates were washed with distilled water followed by ethanol. The washed precipitates were dried at 80°C for 24 h and finally the particles were calcined at 1100°C for 2 h. Table 1 shows sample codes.

Table 1
Sample codes of Tb₂O₃ particles.

Sample code	Temperature (°C) / Time (h)	Molarity (M)
0.10M	-	0.10
0.10M-Tb ₂ O ₃	1100 / 2	0.10
0.15M-Tb ₂ O ₃		0.15
0.20M-Tb ₂ O ₃		0.20

Phase analysis of the calcined particles was performed with Cu-K_α radiation at a 1° scan rate in the 2θ range of 15–75° degrees by X-ray diffraction (XRD) using Bruker D8 Discover. Crystallinity index (CI) value was computed, benefiting XRD diffraction peaks' broadenings [23]. Fourier-Transform Infrared Spectroscopy (FT-IR) analysis was recorded between 4000 and 400 cm⁻¹ using Perkin Elmer Spectrum Two. Field Emission - Scanning Electron Microscopy (FE-SEM) was used for morphology and grain size analyses using FEI Quanta 650 FEG. Photoluminescence (PL) emission spectra were taken in the range of 300–800 nm under 245 nm excitation. The PL optical spectra of all the particles were converted into CIE_{XYZ} and CIE_{LAB} colour space coordinates using CIE (2006) colour matching transformation methods. The colour space coordinates were computed using D65 reference white point (6504 K colour temperature) [2].

3. Results And Discussion

3.1 XRD Analysis

The XRD pattern (Fig. 1) of the particles exhibited body-centred Tb₂O₃ cubic (space group *Ia-3*) structure (JCPDS No. 00-043-1032) and the sample did not contain any impurity phases. The diffraction peaks at

$2\theta \cong 17.91, 21.79, 29.19, 33.69, 39.08, 43.14, 48.52, 50.37, 55.31, 57.62, 60.44, 69.62, 71.03$ were ascribed to (200), (211), (222), (400), (332), (431), (440), (433), (541), (622), (444), (651), (800) planes, respectively. CI value of the sample was found to be 78 %.

3.2 FT-IR Analyses

The FT-IR analyses of the particles were given in Fig. 2. Absorption peaks of as-received 0.1M coded sample were at 686, 753, 833, 1409, 1496 and around 3500 cm^{-1} while absorption peaks of calcined particles were at 475, 478, 484 cm^{-1} due to the vibrational mode of metal-oxygen bonds (Tb-O) for 0.10M-Tb₂O₃, 0.15M-Tb₂O₃ and 0.20M-Tb₂O₃ coded samples, respectively [4]. Characteristic peak at 478 cm^{-1} was associated with Tb-O bonds belonging to the Tb₂O₃ phase [22]. The absorption peaks at 1409 and 1496 cm^{-1} were associated to C-O stretching vibration, while the absorption peak at around 3500 cm^{-1} was O-H stretching vibration [4].

3.3 FE - SEM Analysis

It is clearly seen from the scanning electron microscopy (FE- SEM) images in Fig. 3 that the samples exhibited a homogeneous structure. Morphology of 0.10M-Tb₂O₃ coded sample in Fig. 3a had an agglomerate structure of regular nanograins. 0.15M-Tb₂O₃ coded sample had the nanograins formed a chain structure and revealed a rod-like morphology while 0.20M-Tb₂O₃ coded sample had bundles morphology of rod-like. These chains in 0.20M-Tb₂O₃ sample came together, reducing the surface energy and formed the bundles morphology. Average grain sizes were 204, 222 and 240 nm for 0.10M-Tb₂O₃, 0.15M-Tb₂O₃ and 0.20M-Tb₂O₃ samples, respectively. The average sizes of the chains were 1.87 microns and 3.76 microns for 0.15M-Tb₂O₃ and 0.20M-Tb₂O₃ coded samples, respectively. Both average grain size and chain length increased with the increase of the precursor molarity.

3.4 PL Measurements

In PL emission spectra of all the particles, only two emission peaks which were sharp peak at 493 and broad peak at around 537 nm were observed (Fig. 4). Although the peak at 493 nm increased and sharpened with increasing the precursor molarity, no change was observed in the peak at around 537 nm. The peaks at 493 and around 537 nm were associated to $^5\text{D}_4\text{-}^7\text{F}_6$ (magnetic-dipole (MD) transition, C₂) and $^5\text{D}_4\text{-}^7\text{F}_5$ (electron-dipole (ED) transition, C₂) transitions, respectively [17]. Tb₂O₃ particles were exhibited a novel cyan emission. Since it was not possible to understand actual colour released from the PL optical spectra, these data were converted to the CIEXYZ fundamental chromaticity diagram. The CIEXYZ colour system was converted to the CIELab colour space and L*, a* and b* parameters provided information about lightness, redness/greenness and yellowness/blueness of the emission, respectively. CIEXYZ diagram and colour space coordinate values of all the particles were given in Fig. 4b and Table 2, respectively. MD transitions are responsible for “blueness” while ED transitions are responsible for

“greenness”. As the precursor molarity increased, the number of C₂ sites released from MD transition increased and b* value increased negatively; this showed that the colour had shifted to blueness. There are a limited number of studies in the literature examining the PL emissions of Tb₂O₃ particles, and there are many peaks in the PL spectra obtained in these studies, with the strongest emission peak around 545 nm [13] [6] [1] [16]. However, it was found for the first time that Tb₂O₃ powder exhibited the strongest PL emission at 493 nm in this study. The PL intensity was also increased with both the increase in the precursor molarity and the change of morphology to bundles.

Table 2
Sample codes of Tb₂O₃ particles.

Sample code	CIEXYZ chromaticity coordinates			CIELab chromaticity coordinates		
	x	y	z	L*	a*	b*
0.10M-Tb ₂ O ₃	0,080	0,430	0,488	71.614	-157.953	-2.049
0.15M-Tb ₂ O ₃	0,076	0,433	0,489	71.787	-162.452	-1.905
0.20M-Tb ₂ O ₃	0,055	0,422	0,522	71.049	-181.567	-6.464

Figure 5 showed PL intensity versus grain size graph as a function of the precursor molarity for λ_{em} = 493 nm. The precursor molarity caused an increase in grain size indicating a positive correlation between grain size and PL intensity.

4. Conclusions

The effect of precursor molarity (0.10, 0.15 and 0.2 M) of particles produced by precipitation method on the PL properties was investigated in this study. It was determined by XRD analysis that the produced powder had a body-centred cubic crystal structure and the CI value of the 0.10M-Tb₂O₃ coded sample was 78%. In FE-SEM analysis, it was observed that the particles displayed a homogeneous structure and transformed into bundles morphology as the precursor molarity increased. In the PL measurements, all the particles were exhibited extremely strong cyan emission at 493 nm. It was observed that the precursor molarity, grain size and morphology were effective on the PL intensity of the particles. The increase in molarity increased the particle size and transformed the morphology into the bundles, and increased in the PL intensities were observed. There was an increase of 208% in the PL intensity of the peak at 493 nm of the particle with bundles morphology according to the PL intensity of the particle with an agglomerate structure of regular nanograins. As the precursor molarity increased, there was a negative increase in the b* value, indicating that the PL emission colour shifts to blueness.

Declarations

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Figures

Figure 1

XRD pattern of 0.10M-Tb₂O₃ coded sample.

Figure 2

FT-IR analysis of all the particles.

Figure 3

SEM images of (a) 0.10M-Tb₂O₃, (b) 0.15M-Tb₂O₃ and (c) 0.20M-Tb₂O₃ coded sample.

Figure 4

(a) PL emission spectra, (b) CIE diagram of all the Tb_2O_3 particles.

Figure 5

PL intensity and grain size as a function of the precursor molarity for $\lambda_{\text{em}} = 493 \text{ nm}$.