



Synthesis and optical characterization of sub-5 nm Terbium oxalate nanocrystals: A novel intense green emitting phosphor



Dinu Alexander, Kukku Thomas, S. Sisira, P.R. Biju, N.V. Unnikrishnan, M.A. Ittyachen, Cyriac Joseph*

School of Pure and Applied Physics, Mahatma Gandhi University, Kerala 686560, India

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ABSTRACT

Green emitting novel Terbium oxalate decahydrate nanophosphor ($\text{Tb}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$) with particle size in the range 2–4 nm, was synthesized by microwave assisted co-precipitation method. The structure and particle size of the sample were elucidated by X-ray powder diffraction and TEM analysis. The photoluminescence excitation spectra of the terbium oxalate nanophosphor exhibited several peaks in the 200–500 nm range of DUV to visible region with the strongest one at 369 nm in n-UV region and these excitation peaks matches well with the emission peaks of commercially available LED sources. The emission spectra recorded at the representative excitations exhibit intense and sharp green emission ($^5\text{D}_4 \rightarrow ^7\text{F}_5$, at 543 nm) owing to the heavy population of $^5\text{D}_4$ level at the expense of $^5\text{D}_3$ level of Terbium ion. The decay curve is fitted to single exponential function with a decay time of 0.82 ms. The chromaticity co-ordinate is found to be (0.25, 0.54) and is located in green region with a colour purity of 68%. The experimental observations revealed that the synthesized ultrafine terbium oxalate nanocrystal is a suitable candidate as green emitting phosphor.

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1. Introduction

Nowadays, Rare earth doped inorganic luminescent nanoparticles have been the research interest of scientists because of their intriguing applications in luminescent devices such as fluorescent lamps, WLED, solid-state laser, scintillators, plasma display panels etc. More importantly, Rare earth based nanofluorescent materials with smaller particles (quantum dots) is the most suitable alternative of semiconductor quantum dots in bio imaging and medical diagnostics [1–4]. Among the various solid-state lighting applications, WLED's with tricolour phosphors (RGB) coated on UV-LED chips that can emit intense red, green and blue under n-UV excitation have attracted significant attention owing to its better colour purity and CRI [5–8]. Especially, the green component of tricolour centre plays a significant role, as the maximum of human eye sensibility falls in this region and the green colour constitutes more to the pixel ratio 3:6:1 (red: green: blue) for precise display applications [9]. Thus it is highly desirable to develop new green emitting phosphors with excitation wavelengths coinciding with

the emission of commercially available UV LED's.

Terbium is used as an activator in various host lattices for green luminescence owing to its sharp emission originating from the intraconfigurational f-f transitions [9]. Most of the reports on green emitting luminescent materials are based on the doping of Tb^{3+} ion in different host lattices. Generally low doping of Tb^{3+} yields only weak luminescence while heavy doping results in quenching of luminescence. The most essential prerequisite for a favourable phosphor material is its intense and sharp luminescence “without concentration quenching” - but quenching free materials are less attempted despite of its assured intense luminescence. The high active ion concentration of the order of 10^{21} ions cm^{-3} in rare earth oxalate crystals facilitates high optical gain and hence it can find potential optical applications. Moreover, as an important bridging ligand, oxalate anion makes intriguing structures among the rare earth compounds and they exhibit superior optical properties [10]. Single crystals of Cerium oxalate, Neodymium praseodymium oxalate, Dysprosium praseodymium oxalate and Samarium oxalate were studied in recent years but the detailed spectroscopic investigations were not attempted [11–14].

In our previous work on the synthesis and photo luminescent properties of Terbium oxalate decahydrate single crystals, we reported intense green luminescence in the oxalate matrix without

* Corresponding author.

E-mail address: cyriacmgu@gmail.com (C. Joseph).

concentration quenching [15]. It is of scientific interest to investigate the spectroscopic properties of nanostructured terbium oxalate as the nano counterpart exhibits promising properties compared to the bulk. Hence in the present work attention has been paid on the synthesis of Tb³⁺ activated fully concentrated Terbium oxalate decahydrate nanocrystals and to explore the photoluminescence properties. To the best of our knowledge, no work has been reported so far on terbium oxalate nanocrystals. As the particle size of nanophosphors becomes very low better resolution in flat panel displays can be achieved and also it exhibits reduced loading effects in fluorescent lamps [16,17]. In this context, the synthesis and luminescence studies on terbium oxalate decahydrate nanocrystals with size as much low deserves special attention. In the present work, Terbium oxalate nanocrystals with extremely low particle size in the sub 5 nm range without concentration quenching was synthesized by a simple microwave assisted co-precipitation method and a detailed structural and spectroscopic characterization have been undertaken.

2. Material and method

Terbium oxalate decahydrate nanocrystals were synthesized via microwave assisted co-precipitation method. The initial reactants used for the synthesis are Terbium Chloride hexahydrate (TbCl₃·6H₂O, 99.9%, Alfa Aesar), Oxalic acid dihydrate (C₂H₂O₄·2H₂O, 98%, Alfa Aesar) and Ethylene glycol (99% Merck). All the reactants employed for the synthesis were of analytical grade and used as obtained from the commercial sources. In a typical optimized procedure for the synthesis of ultrafine nanocrystals, 12.5 ml of 0.1 M Terbium chloride aqueous solution was mixed with 12.5 ml of Ethylene glycol and the solution was kept for stirring for 30 min and then mixed with 0.15 M aqueous solution of oxalic acid prepared in the same manner. The resulting white colloidal solution was then placed in a domestic microwave oven (2.45 GHz, 700 W) and was subjected to total 2 min microwave irradiation with a time interval of 10s. The Terbium oxalate nanocrystals thus formed was centrifuged, washed with de-ionized water in several times and finally with acetone, then dried at 60 °C for 24 h. Finally, the sample was grinded using agate mortar for further studies.

X-ray powder diffractogram of the terbium oxalate nanocrystals was recorded on PANalytical X'pert Pro diffractometer with CuK α radiation ($\lambda = 1.546 \text{ \AA}$) in the 2θ range 10–40° with a step size of 0.02. Thermogravimetric analysis was carried out on Shimadzu thermal analyzer DT-40. The morphology and crystalline size were ascertained by Transmission electron microscopy (TEM) JEOL JEM 2100. UV-VIS absorption spectrum of the sample was obtained on a Varian Cary UV-Visible-NIR spectrophotometer in the wavelength region 200–800 nm. The photoluminescence excitation and emission spectra of the nanocrystals were recorded using HORIBA Jobin-Yvon Fluoromax-4 spectro fluorometer. The decay time of the sample was determined on Edinburgh UV-VIS-NIR (FLS-980) spectrometer.

3. Results and discussions

3.1. X-ray powder diffraction and EDS analysis

The X-ray diffraction pattern of the terbium oxalate nanocrystals synthesized by the as described microwave assisted co-precipitation method is shown in Fig. 1(a) and the diffractogram closely matches with the standard data file (JCPDS CARD No. 22-0487) of Terbium oxalate decahydrate. All the diffraction peaks of Terbium oxalate crystals can be perfectly indexed to the monoclinic phase with space group $P2_1/c$. The absence of impurity peaks in the

diffractogram demonstrates that the as prepared crystals were of pure phase. The lattice parameters calculated from Unit Cell Win software are found to be $a = 10.96 \text{ \AA}$, $b = 9.60 \text{ \AA}$, $c = 10.05 \text{ \AA}$ and $\beta = 114.40^\circ$, consistent with that provided in the JCPDS data ($a = 10.99 \text{ \AA}$, $b = 9.61 \text{ \AA}$, $c = 10.02 \text{ \AA}$ and $\beta = 114.11^\circ$) and hence confirmed the formation of terbium oxalate with chemical formula Tb₂(C₂O₄)₃·10H₂O. The broadening of the peaks in the X-ray diffraction pattern indicates that the as formed Terbium oxalate decahydrate crystals are in the nano regime. The crystallite size calculated using Debye–Scherrer equation from the half width of (020) line of X-ray diffraction pattern was found to be 8 nm. Energy dispersive spectrum (EDS) of Terbium oxalate nanocrystals shown in Fig. 1(b) is a clear indicative of the presence of constituent elements Terbium, Carbon and Oxygen.

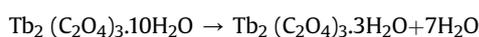
3.2. Thermogravimetric analysis

Thermal analysis of terbium oxalate decahydrate nanocrystals were carried out in air atmosphere from room temperature to 800 °C with a heating rate of 10 °C/min and the thermogram is shown in Fig. 2.

It is well evident from the TG-DTG curve that there exist three weight loss regions for the sample. The first two stages correspond to the step wise dehydration of the terbium oxalate decahydrate nanocrystals and the third stage is the decomposition of the anhydrous terbium oxalate to its sesquioxide. The observed and calculated weight loss for each stage is given in Table 1. The close agreement with the observed and calculated weight losses in each decomposition step confirms the composition of the terbium oxalate nanocrystal as Tb₂(C₂O₄)₃·10H₂O.

From the thermogravimetric analysis it is clear that seven water molecules were escaped in the temperature range 60–125 °C and the remaining three water molecules were escaped in the temperature range 125–400 °C leading to the formation of anhydrous terbium oxalate. A close examination of the TG curve reveals that even though this dehydration stage extends from 125 to 400 °C, major part of mass loss is in the range 350–400 °C, and hence the corresponding DTG peak is centred around 378 °C. It is then decomposed to terbium oxide in the temperature range 400–700 °C with the liberation of three CO and three CO₂ molecules. The three distinct steps observed in TG analysis are accompanied by the corresponding peaks in DTG curve showing a one to one correspondence between thermogravimetric and differential thermogravimetric analysis.

The step wise dehydration of Terbium oxalate decahydrate crystals in steps of seven and three water molecules are in fair agreement with the single crystal structure data of Lanthanum oxalate decahydrate which is isostructural to terbium oxalate decahydrate reported by Sheng Hua et al. [18]. According to them each Lanthanum atom being surrounded by three chelating oxalate groups and three aqua ligands. The intervening space is filled by lattice water molecules disordered over seven major sites. The three co-ordinated water molecules will take longer time to come out from the crystal compared to the seven water molecules distributed randomly in crystal lattice. Thus undoubtedly the seven lattice water molecules which are distributed randomly in the terbium oxalate crystal will escape in the early temperature region and the three co-ordinated water molecules will leave the crystal only at a higher temperature. Based on TG/DTG analysis we can summarize the whole decomposition mechanism for terbium oxalate decahydrate crystal as follows



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