Synthesis, characterization and photoluminescence properties of Dy\textsuperscript{3+}-doped nano-crystalline SnO\textsubscript{2}

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1. Introduction

Rare earth (RE)-doped nanoparticles have been attracting recently special attention due to their interesting physical properties, different than bulk materials, with applications in high brightness displays, laser emitters, fluorescent markers, thin-film electroluminescent (TFEL) devices, etc. [1]. In TFEL devices, luminescent properties are related to the intra-4\textsuperscript{f}–4\textsuperscript{f} rare-earth transition [2,3], because their transitions take place in a wide energy range, with emissions from the visible to the infrared, allowing their application in several kinds of optical communication devices. In case of rare-earth ions, the electronic f–f transitions involve electrons which are localized in atomic orbital of the ions. Therefore, no size-dependent quantization effect from confinement of delocalized electrons is found of these transitions. However, confinement effects of semiconductor nanoparticles create photogenerated carriers may have an interaction with f-electrons which has important manifestations in influencing the optical properties. Thus, a nanostructure controls either by judiciously choosing the nanoenvironment of the species to be excited or by utilizing a nanofunctional structure that can be utilized to manipulate the excitation dynamics. Nanoscopic interactions play key roles in controlling the excitation dynamics. The efficiency of a nanomaterial is often limited by the band-to-band recombination and non-radiative surface recombination rates [4]. Transparent oxide semiconductors are being investigated as a matrix for the incorporation of these rare-earth ions, due to a high transparency in the visible, which when allied to rare-earth emission may contribute to the development of new technologies. Since the publication of Bhargava et al. [5] where they show strong orange luminescence from Mn\textsuperscript{2+} ions-doped ZnS nanoparticles, there are many reports on the optical properties of the ions-doped nanoparticles because a quantum confinement effect of carriers can be created.

Tin oxide (SnO\textsubscript{2}), an n-type semiconductor with a wide band gap (\(E_g = 3.6\) eV at 300 K), is extensively used as a functional material for optoelectronic devices [6], conductive electrodes and transparent coatings due to its good conductivity and transparency in the visible spectrum [7,8], solar cells [9,10], and catalyst support [11]. The variation of grain size, the concentration of oxygen vacancies and electrical properties of tin oxide as bulk as well as forms of thin films are also widely studied. A large number of research works have been focused on the electrical properties of SnO\textsubscript{2}, especially for sensor and catalyst. Whereas, only a small amount of work is devoted to the luminescence properties of SnO\textsubscript{2}, namely SnO\textsubscript{2}-based phosphors. Compared with other traditional dielectric host materials, its good electrical conductivity together with high transparency at the visible and near-infrared wavelengths can be useful for developing new material combinations capable of emitting photons via electroluminescence as well as photoluminescence.

Dy\textsuperscript{3+} ion has two dominant bands in the emission spectrum. The yellow band (575 nm) corresponds to the hypersensitive transition \(4\text{F}_{9/2}^{6}\text{H}_{15/2}^{2}\) (\(\Delta L = 2, \Delta J = 2\)), and the blue band (480 nm) corresponds to the \(4\text{F}_{9/2}^{6}\text{H}_{13/2}^{2}\) transition. These hypersensitive transition relative intensities can be regulated by acting on

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factors like the excitation wavelength, the host composition and the doping concentration [12–15]. Hence it is important to understand local structural environments and spatial distribution of dopants when developing a nano-sized luminescent material activated by RE elements because absorption and emission properties of intra-4f-configurational transitions of RE ions are sensitive to their chemical and structural status in a host matrix [13].

Based on the above considerations, in this study, we have aimed at fabrication of Dy3+-doped nanocrystalline tin oxide by a chemical co-precipitation route. This method has been employed quite frequently to synthesize nanoparticles because of its low cost and good stoichiometric control. The structural and luminescence properties of the pure and doped systems are investigated.

2. Experimental

The precipitate of pure SnO2 was obtained by adding NH4OH solution and SnCl4·5H2O solution with stirring until the pH of mother liquid was 10. The precipitate was coagulated for 15 min and allowed to stand overnight. The precipitate was filtered, washed until the solution was free from Cl− ions. The precipitate obtained was oven dried at 383 K for 12 h, powdered and calcined at 773 K for 6 h.

A typical chemical co-precipitation technique was used to prepare the rare earth (0.2, 0.5, 1 and 2 wt%) designated as Dy-1, Dy-2, Dy-3 and Dy-4 respectively) doped samples. SnCl4·5H2O·5H2O (5 g) and required amount of Dy(NO3)3·6H2O were dissolved in 250 ml distilled water. Under stirring with a magnetic stirrer, NH4OH was added drop wise until the pH reached 10. The precipitate obtained was submitted to dialysis against distilled water along with centrifugation several times to eliminate Cl−, NO3− and NH4+ ions (until the supernatant solution showed no precipitation for 10 min, a drop of which was deposited on a holey carbon film coated Cu-grid.

Simultaneous determination of BET (Brunauer, Emmett, and Teller) surface area and total pore volume of the samples were achieved in a Micromeritics TRISTAR 3000 surface area analyzer by the low temperature N2 adsorption method. Prior to analysis, the samples were degassed at 120 °C overnight (12 h) under a continuous flow of N2 gas to remove adsorbed contaminants from the surface and pores of the CNTs. The crystalline phases of the samples were determined by X-ray diffraction (PAnalytical XPERT-PRO diffractometer), measurement, using Fe filtered Co Kα radiation (λ = 1.789 Å), with variable slit at 35 kV, 50 mA. FT-IR spectra of the samples were recorded using a Perkin Elmer Spectrum 100 spectrometer attached with an FT-IR Microscope accessory, equipped with a germanium crystal. Background was run before the analysis and all the spectra were baseline corrected. Raman spectra of pure and doped samples were recorded by Lab Raman system (Jobin-Yvon Horiba T64000 Spectroscopy) equipped with an Olympus BX-40 microscope. The excitation wavelength was of 514.5 nm with an energy setting of 1.2 mW from a Coherent Innova Model 308 argon ion laser. The surface morphology of the powder samples was studied by FE-SEM (JEOL 7500F SEM). Both fluorescence excitation and emission spectra were recorded at room temperature on Perkin Elmer LS-55 fluorescence spectrometer. The excitation source was 75 W Xenon lamp and the spectral resolution was 1 nm. The TEM analysis was done on a JEOL 2100 F TEM operated at an accelerating voltage of 100 kV. Powder sample was sonicated in methanol for 10 min, a drop of which was deposited on a holey carbon film coated Cu-grid.

3. Results and discussion

The BET specific surface areas of the Dy-doped samples calcined at 823 K were in the range of 39–49 m2 g−1 (see Table 1). The addition of small amount of dopant caused the doped system to show smaller particle size and higher surface area compared to the pure system and the reduction in grain size was gradual with Dy3+ content. This increase may be due to the formation of Dy–Sn composite oxide, which effectively hinder the boundary mobility and hence the grain growth [14,15].

The powder X-ray diffractograms of the pure, Dy-doped sample (2 wt%) calcined at 773 K are given in Fig. 1. The sharp peaks in the XRD pattern of pure tin oxide show that it is highly crystalline and the position of the peaks reveals that SnO2 is in tetragonal rutile phase. Broadening of diffraction peaks can be observed, in the doped sample implying the reduction in crystallite size. The absence of the known crystalline phases of Dy2O3 in the sample suggests that the dopant is well dispersed in the host SnO2 material.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m2 g−1)</th>
<th>Pore volume (cm3 g−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SnO2</td>
<td>29.87</td>
<td>0.0768</td>
</tr>
<tr>
<td>Dy-1</td>
<td>39.56</td>
<td>0.0972</td>
</tr>
<tr>
<td>Dy-2</td>
<td>42.58</td>
<td>0.0932</td>
</tr>
<tr>
<td>Dy-3</td>
<td>45.77</td>
<td>0.0891</td>
</tr>
<tr>
<td>Dy-4</td>
<td>49.53</td>
<td>0.0933</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of pure and Dy3+-doped (2 wt%) SnO2 samples calcined at 773 K.

Fig. 2. FTIR spectra of pure and Dy3+-doped SnO2 samples.

Fig. 3. Raman spectra of pure and Dy3+-doped SnO2 samples.
The FT-IR transmittance spectra of different samples are given in Fig. 2. The broad absorption band between 3100 and 3400, the peaks at 1620 and 1230 cm$^{-1}$ are attributed to vibration of hydroxyl groups associated with structural water [16]. The bands at 2980 and 2900 cm$^{-1}$ are assigned to C–H vibrations which could be attributed to the organic trace impurities, which were incorporated during calcination process. The bands observed in the range of 1060 and 970 cm$^{-1}$ are due to the vibration of Sn=O and Sn–O surface cation-oxygen bonds [17]. The typical M–O–M (in this case Sn–O–Sn) vibrations appear in the range of 530–700 cm$^{-1}$ [18]. No additional absorption peaks were observed with Dy$^{3+}$ addition, indicating its homogeneous dispersion in the support material.

Fig. 3 shows the Raman spectra of pure and Dy-doped samples calcined at 823 K. Pure SnO$_2$ shows three prominent Raman peaks at 476, 633 and 774 cm$^{-1}$ which are assigned to $E_g$, $A_{1g}$ and $B_{2g}$ modes respectively [19]. All these Raman features confirm the tetragonal rutile structure for the SnO$_2$ sample. The broad peak around 350 cm$^{-1}$ which was reported in extra-fine (3–5 nm) nanoparticles [20,21] is observed in all the doped samples. This
attributes to relaxation of Raman selection rule by reduction in the particle size or by the high concentration of surface defects such as oxygen vacancies and lattice disorder [22]. Another feature to be noted is the decrease in A1g mode intensity in the doped samples. The decrease in the intensity suggests that the dopant interacts strongly with the support and is probably covering the SnO2 grains with monolayer. The interaction between the Dy3+ atoms and the support oxide hinders the crystallization, which is reflected in the reduction of peak intensity. The absence of the known crystalline phases of Dy2O3 in the doped samples suggests that it is finely dispersed in SnO2 matrix. This observation supports BET, XRD and FTIR results.

The typical morphology of the pure and Dy3+-doped SnO2 samples after calcination at 773 K is shown in Fig. 4a–e. All the images showed the presence of porous aggregates composed of smaller individual particles. The particle size ranges obtained from the SEM data were 24–121 nm (Pure), 19–99 nm (Dy-1), 16–68 nm (Dy-2), 10–38 nm (Dy-3) and 4–21 nm (Dy-4) respectively. It is thus clear that on incorporation of Dy3+, the particle size of SnO2 reduces suggesting that the dopant influences the grain growth of SnO2 material. The reduction in particle size is quite gradual with dopant concentration which is in agreement with BET surface area results. The higher grain growth inhibition could be attributed to the increased nucleation sites resulting from higher stacking fault energy due to Dy3+ addition to the pure material [23].

The excitation spectrum in Fig. 5a is the scanning of excited wavelength from 300 to 440 nm when the emission wavelength was set at 488 nm, for the sample with 2 wt% of Dy3+ content. The excitation maxima for the 488 nm emission is located at 360 nm corresponding to the transition from the ground level 6H15/2 to the hypersensitive level 6P7/2, from where it relaxes non-radiatively to the 4F9/2 metastable level. The general observed peaks distribution agrees well with the reported structure distribution spectra for Dy3+ doped nanocrystalline ZrO2 [24,25]. The PL spectrum acquired for pure SnO2 (see Fig. 5b) consisted of broad red-green band peaked at about 650 nm.

The experimental results in Fig. 5c show the fluorescence emission from 400 to 650 nm of the pure and Dy3+-doped SnO2 (Dy-1) samples calcined at 773 K, under excitation at 360 nm. The strongest emission band was observed in the blue region centred at 488 nm (4F9/2→6H15/2) with a weak band in the yellow region centred at 580 nm (4F9/2→6H13/2) attributed to f–f transitions of Dy3+ in a solid solution and are very sensitive to the environment of the rare earth ion [26].

Gu et al. [27] reported the emission spectrum yields for sol–gel prepared Dy3+-doped SnO2 calcined at 673 K, which contained exclusively the characteristic emission lines of Dy3+, peaking at 575 nm (4F9/2→6H15/2), and 658 nm (4F9/2→6H11/2). The hypersensitive transition (4F9/2→6H13/2 of Dy3+) is dominant in the emission spectra resulting from the distorted crystal lattice at which Dy3+...
ions located. The emission spectrum of pure SnO₂ presented two bands centred at 400 and 430 nm, respectively. As the \( \Delta \ell = 2 \) emission of Dy³⁺ belongs to hypersensitive transition, which is strongly influenced by outside surroundings. When Dy³⁺ ion is located at a low symmetry local site (without an inversion centre), this emission transition is often prominent in its emission spectrum [28].

In the present case the dominance of the magnetically allowed \( \Delta \ell = 2 \) transition for all the doped samples can be explained as follows. Since the radius of Sn³⁺ (0.76 Å) is larger than that of Dy³⁺ (0.91 Å), the host lattice will not easily accommodate Dy³⁺ and hence only a minor fraction of the total amount of Dy³⁺ introduced into the SnO₂ goes to the Sn-substitutional positions, most of the Dy³⁺ ions may well be precipitated into SnO₂-Dy³⁺ clusters. The excess Dy³⁺ phases will likely reside on the surface or on the grain boundaries of the nanoparticles to yield optimum strain relief which is evident from the TEM image (refer Fig. 6). Thus, in this case, the \( \Delta \ell = 2 \) transition emission will not show prominent in the emission spectrum [27,29]. The difference in the emission characteristics in the samples may be due to the changes in the preparation conditions and calcination temperature.

Fig. 5d depicts the influence of Dy³⁺ concentration on the emission intensity of various Dy³⁺ doped SnO₂ samples. One can also observe that the highest emission corresponds to the 0.2 wt% Dy₂O₃ doped sample and concentration quenching of the Dy³⁺ luminescence is observed as Dy³⁺ concentration increases over 0.2 wt% Dy₂O₃. The quenching of the luminescence is best observed for the 2.0 wt% Dy₂O₃ doped sample. The most plausible explanation for such behaviour is cross-relaxation among Dy³⁺ pairs to the intermediate levels Dy³⁺ \( \ell = 2 \) and Dy³⁺ \( \ell = 4 \), from where the ions decay non-radiatively or by IR emission [30,31]. These quenching transitions are mainly Dy³⁺ \( \ell = 2 \) + Dy³⁺ \( \ell = 4 \) → Dy³⁺ \( \ell = 6 \) with increase in dopant concentration, most of the Dy³⁺ ions may be absorbed at the SnO₂ grain surface, which offers much more opportunity for the cross-relaxation processes [29]. So for the Dy doped SnO₂ systems 0.2 wt% is found to be the optimum concentration for maximum Dy³⁺ luminescence.

4. Conclusions

Pure and Dy³⁺-doped nanocrystalline SnO₂ were prepared by chemical co-precipitation method. Structural characterization of the samples using XRD, FTIR and Raman revealed tetragonal rutile phase for the host material. Dy³⁺ addition to pure SnO₂ increased the surface area and decreased the crystallite size. The emission spectra of the Dy³⁺-doped samples showed characteristic \( \Delta \ell = 2 \) emission and concentration quenching when the doping level was above the optimum concentration of 0.2 wt%.

Acknowledgement

Authors thank the Council for Scientific and Industrial Research executive and Department of Science and Technology, South Africa for the financial support.

References


