Materials Chemistry and Physics 130 (2011) 1187–1190

Contents lists available at SciVerse ScienceDirect

Materials Chemistry and Physics

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

Photoluminescence and preparation of $ZnNb_2O_6$ doped with Eu^{3+} and Tm^{3+} nanocrystals for solar cell

Yu-Jen Hsiao[a], Te-Hua Fang[b,*], Liang-Wen Ji[c]

[a] National Nano Device Laboratories, Tainan 741, Taiwan
[b] Department of Mechanical Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 807, Taiwan
[c] Institute of Electro-Optical and Materials Science, National Formosa University, Yunlin 632, Taiwan

ARTICLE INFO

Article history:
Received 21 January 2011
Received in revised form 16 July 2011
Accepted 27 August 2011

Keywords:
Optical materials
Sol–gel growth
Differential thermal analysis (DTA)
Photoluminescence
Spectroscopy

ABSTRACT

Synthesis and luminescence properties of Eu^{3+} and Tm^{3+}-doped $ZnNb_2O_6$ nanocrystals by the sol–gel process were investigated. The products were characterized by differential thermal analysis (DTA), scanning electron microscopy (SEM), and photoluminescence spectroscopy (PL). $ZnNb_2O_6$:Eu^{3+} shows bright red luminescence with maximum peak at 613 nm attributed to $^5D_0 \rightarrow {}^7F_2$ transition. The major blue emission peak of $ZnNb_2O_6$:Tm^{3+} was at 483 nm, corresponding to the transitions $^1G_4 \rightarrow {}^3H_6$. The optimum concentration of Eu^{3+} and Tm^{3+} showing the maximum PL intensity was 4 mol% and 1 mol%, respectively.

1. Introduction

Rare-earth (RE)-doped materials have been of great scientific interest in next-generation flat-panel displays and the wavelength conversion conception for solar cells. This feature can be used to tune the emission spectra for specific applications. Thus, it is important for the systematic research of RE ions doped in different kinds of host materials having good thermal, electrical and electro-optical properties [1,2].

Recently many Eu^{3+}-doped materials have been extensively studied because of the intra-4f-shell transitions that occurs from the excited level down to the lower levels: $^5D_0 \rightarrow {}^7F_j$ ($j = 1–4$) for Eu^{3+} ions [3,4]. The emission intensity was dominated by wavelength peaks at around 610–630 nm. Tm^{3+} ion is widely used as activator of blue emission corresponding to its $^1D_2 \rightarrow {}^3F_4$ and $^1G_4 \rightarrow {}^3H_6$ transitions with potential applications [5]. Their luminescence spectra consist of several very narrow bands, which make them effective luminescent centers. These investigations of Tm^{3+}-doped materials mainly focused on host matrix, such as fluorides [6] and vanandates [7].

The absorption wavelength of the general solar cell is about between 400 and 1000 nm. If we used it as optical wavelength conversion layer, the material of $ZnNb_2O_6$ doped Eu^{3+} or Tm^{3+} Li_3NbO_4 which absorb a portion of the incident solar radiation and re-emit part of it at lower energies, thus performing a spectral down-shift that will enhance the efficiency for solar cell [8]. The $ZnNb_2O_6$ doped Eu^{3+} or Tm^{3+} photoluminescence is very promising for application to solar cells because the excitation wavelengths shorter than 400 nm.

The major advantages of sol–gel process are: (i) high purity of precursors, (ii) ambient temperature of sol preparation and gel processing, (iii) product of homogeneity, (iv) low temperature sintering, and (v) good control of particle size and also size distribution of particles [9]. The electro-optical and the luminescent properties of $ZnNb_2O_6$ [10] compounds have been studied extensively. To our knowledge, Eu and Tm-doped $ZnNb_2O_6$ nanocrystals have not been thoroughly investigated yet, which was the motivation for this research. Therefore, the morphology and luminescent properties of the $ZnNb_2O_6$ nanocrystals will be studied and discussed.

2. Experiments

The $ZnNb_2O_6$:Eu/Tm powders were prepared by the sol–gel method using zinc nitrate [$Zn(NO_3)_2$ $6H_2O$], niobium chloride ($NbCl_5$), europium nitrate $Eu(NO_3)_3{\cdot}6H_2O$, thulium nitrate $Tm(NO_3)_3{\cdot}5H_2O$, ethylene glycol (EG) and citric acid anhydrous (CA). Their purities are over 99.9%. First, the stoichiometric amount of zinc nitrate, niobium ethoxide, and europium nitrate (or thulium nitrate) was dissolved in distilled water. Niobium ethoxide, $Nb(OC_2H_5)_5$, was synthesized from niobium chloride and ethanol, C_2H_5OH, according to the general reaction:

$$NbCl_5 + 5C_2H_5OH \rightarrow Nb(OC_2H_5)_5 + 5HCl. \quad (1)$$

Sufficient amount of citric acid was added to the former solution as a chelating agent to form a solution. Citric acid to the total metal ions in the molar ratio of 3:2 was used for this purpose. EG is also added to the above solution as a stabilizing agent. The precursor was dried in an oven at 120 °C for 10 h and then the final Eu^{3+}

---

* Corresponding author. Tel.: +886 7 381 4526x5336.
E-mail address: fang.tehua@msa.hinet.net (T.-H. Fang).

0254-0584/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2011.08.053

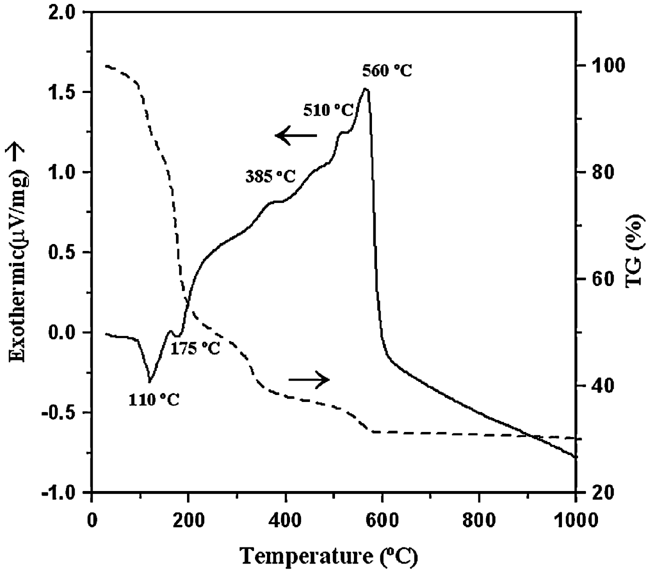

Fig. 1. DTA and TG curves for $ZnNb_2O_6$ precursor.

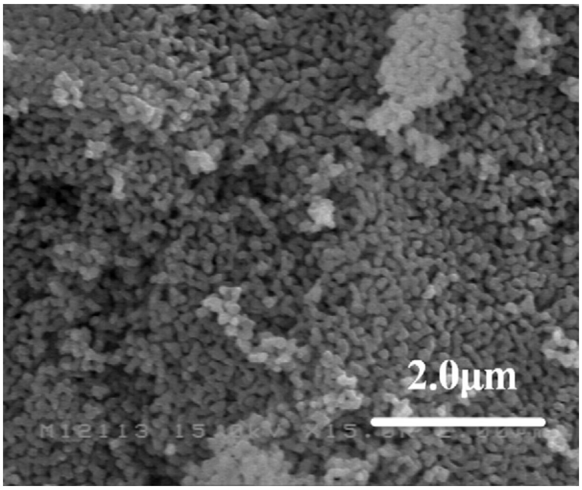

Fig. 2. Scanning electron micrographs of $ZnNb_2O_6$ powders annealed at 700 for 3 h.

and Tm^{3+} doped $ZnNb_2O_6$ powders were obtained after calcinations at 700 °C for 3 h in air. All of the optical measurements were taken at room temperature.

3. Results and discussion

The thermogravimetric (TG) and differential thermal analyzer (DTA) curves of the dry $ZnNb_2O_6$ precursor are shown in Fig. 1. The small endothermic peak at about 110 °C in DTA accounted for 11% of the initial weight loss in TG, was assigned to the loss of free water. The exothermic peak at 175 °C and 385 °C was due to the burnout of excessive citric acid and ethanol and the other exothermic peak originated from the burnout of the organic groups in citric acid. The exothermic peak above 510 °C was associated with the decomposition into the oxide from the amorphous gel to the polycrystalline ceramic. In this experiment, the possible chemical reactions for the synthesis of $ZnNb_2O_6$ powders can be expressed as following:

$$\begin{aligned}&Zn(NO_3)_2 + 2Nb(OC_2H_5)_5 \xrightarrow{CA} ZnNb_2(OC_2H_5)10 \cdot x(CA) + 2NO_3\\&{}^- + 2H^+ \rightarrow ZnNb_2O_6 + 2NO_2 \uparrow + yH_2O\\&\uparrow + zCO_2 \uparrow + (10 - z)C_2H_5OH \uparrow \qquad (2)\end{aligned}$$

Therefore, the weight loss between 175 °C and 560 °C in the TG curve was caused by the generation of polymer, organic groups and many kinds of gas from the dry precursor. Poly(citric acid)-g-poly(ethylene glycol) copolymers exhibited sol-to-gel transition with increasing temperature. The CA signified citric acid in the expression (2).

The scanning electron microscope (SEM) pictures of the materials sintered at 700 °C for 3 h are shown in Fig. 2. The particle diameters of $ZnNb_2O_6$ powders annealed was about 50 nm. The circular particles seemed to be distributed homogeneously. The $ZnNb_2O_6$ powders with a Eu^{3+} and Tm^{3+} doping concentration in the range of 0.5–6 mol% do not have any obvious differences in morphology.

When the precursor was sintered at temperatures above 500 °C, the samples exhibited a single phase and all of the peaks were identified to be the orthorhombic $ZnNb_2O_6$ phase in previous report [10]. Fig. 3 shows the XRD patterns of different concentrations of Eu^{3+}-doped $ZnNb_2O_6$. The $Eu^{3+}:ZnNb_2O_6$ powders did not change their orthorhombic phase crystal structure when increasing the doping concentrations from 0 to 6 mol%. However, as the europium (Eu) concentration was increased beyond a certain limit, the redundant Eu ions nullified the precipitation effect. It showed the existence of a small amount of second phase crystallization at Eu $^{3+}$ doped concentrations over 4 mol% that were sintered at a temperature of 700 °C. The second phase peaks were identified to be the $EuNbO_4$ phase (JCPDS file: 22-1099). The second phase will influence the emission properties because the defect density is increased in the samples.

A strong blue emission band centered at 450 nm can be observed for pure $ZnNb_2O_6$ samples [10]. The peaks of excitation was associated with charge transfer bands of $[NbO_6]^{7-}$ in the undoped $ZnNb_2O_6$ system at about 276 nm and a strong blue emission band centered at 450 nm can be observed for pure samples in Fig. 4. Here, the edge-shared NbO_6 groups are efficient luminescent centers for the blue emission [11]. The $Eu^{3+}:[NbO_6]^{7-}$ group exhibited the red emission about 613 nm excited at $\lambda_{ex} = 288$ nm in Fig. 5(a). This luminescence effect depends on the Nb–O–Nb bonding that the conduction band is composed of Nb^{5+} 4d orbitals, and the valence

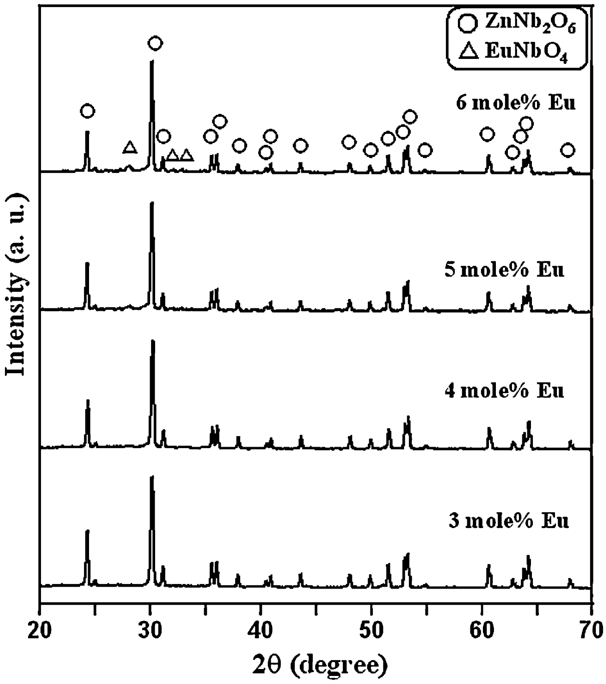

Fig. 3. XRD patterns of $ZnNb_2O_6$ at different Eu^{3+} concentrations at 700 °C.