Photoluminescence and preparation of ZnNb$_2$O$_6$ doped with Eu$^{3+}$ and Tm$^{3+}$ nanocrystals for solar cell

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Synthesis and luminescence properties of Eu$^{3+}$ and Tm$^{3+}$-doped ZnNb$_2$O$_6$ 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$_2$O$_6$: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$_2$O$_6$: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.

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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 vanadates [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$_2$O$_6$ doped Eu$^{3+}$ or Tm$^{3+}$, U$_2$NbO$_4$ 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$_2$O$_6$ 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$_2$O$_6$ [10] compounds have been studied extensively. To our knowledge, Eu and Tm-doped ZnNb$_2$O$_6$ nanocrystals have not been thoroughly investigated yet, which was the motivation for this research. Therefore, the morphology and luminescent properties of the ZnNb$_2$O$_6$ nanocrystals will be studied and discussed.

2. Experiments

The ZnNb$_2$O$_6$:Eu/Tm powders were prepared by the sol–gel method using zinc nitrate [Zn(NO$_3$)$_2$ 6H$_2$O], niobium chloride (NbCl$_5$), europium nitrate Eu(NO$_3$)$_3$, H$_2$O, thulium nitrate Tm(NO$_3$)$_3$ 5H$_2$O, 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(OCH$_2$CH$_3$)$_5$, was synthesized from niobium chloride and ethanol, C$_2$H$_5$OH according to the general reaction:

$$\text{NbCl}_3 + 5\text{C}_2\text{H}_5\text{OH} \rightarrow \text{Nb}(	ext{OC}_2\text{H}_5)_5 + 3\text{HCl}.$$  (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$^{3+}$...
stokes shift effect from Nb–O charge transfer. The energy of the excited state of the Nb–O bonds can come to the excited state of the Eu³⁺ ions through energy transfer with non-radiative process. With the multiphonon relaxation transition, the excited electrons come to the lower excited states (⁵D₀, ⁵D₁, ⁵D₂). It gives the radiative transitions of ⁵D₀ → ⁷F_j (j = 0–3). Fig. 7 shows possible schematic energy level diagram of the overall view of Eu³⁺ emission by energy transfer (ET). Excitation into 288 nm light leads to partial ET from the excited state of [NbO₆]³⁻ to the ²D₀ band of Eu³⁺ via the down-converting ET process. This process involves fast multiphonon assisted non-radiative relaxation (NR) processes in Eu³⁺. Based on their optical properties and downconversion (DC) emission performance, we conclude that polycrystalline ZnNb₂O₆:Eu³⁺ phosphors could be suggested as promising materials for achieving efficient silicon-based solar cells.

4. Conclusion

We have successfully synthesized a series of Eu³⁺ and Tm³⁺-activated ZnNb₂O₆ nanocrystals by the sol–gel method at a low temperature of 700 °C. ZnNb₂O₆:Eu³⁺ shows bright red luminescence with maximum peak at 613 nm attributed to ⁵D₀ → ⁷F₂ transition. The major blue emission peak of ZnNb₂O₆:Tm³⁺ was at 483 nm, corresponding to the transitions ¹G₄ → ³H₆. The optimum concentration of Eu³⁺ and Tm³⁺ showing the maximum intensity was 4 mol% and 1 mol%, respectively.

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