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Facile wet chemical synthesis of Er^{3+}/Yb^{3+} co-doped $BaSnO_3$ nano-crystallites for dye-sensitized solar cell application

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ABSTRACT

We report synthesis of pure and rare earth ion Er^{3+}/Yb^{3+} co-doped barium stannate ($BaSnO_3$) nano-crystallites by facile wet chemical route. The nano-crystallites at the Ba^{2+} lattice site substitution of 0.1 and Er/Yb ratio of 0.00, 0.11, 0.18 and 0.25 exhibited band gap of 3.64, 3.66, 3.67 and 3.68 eV, respectively. The electrical conductivity of the nano-crystallites was found to increase with increase in Er/ Yb content ratio. All samples revealed a broad emission peak between 380 and 400 nm at the excitation wavelength of 350 nm. The up-conversion emission intensity has been found to increase with Er^{3+}/Yb^{3+} content for the excitation wavelength of 980 nm. Further, the influence of the up-conversion behavior on the photovoltaic performance of dye-sensitized solar cell has been investigated. The highest photon conversion efficiency of 4.2% was observed for the composition of Ba(Er/Yb: 0.25)SnO_3 with J_{SC} = 9.69 mA/cm^2, V_{oc} = 0.63 V, FF = 0.690, which was about 40% increase in efficiency in comparison to pristine $BaSnO_3$ (3.0%).

1. Introduction

The term 'transparent conducting oxides (TCOs)' is generally used for materials with high electrical conductivity ($\geq \sim 10^3$ S cm^{-1}) and high optical transmittance ($\geq$ 80%). The similar term 'transparent oxide semiconductors (TOSs)' is used to represent materials with intermediate conductivity ($\sim 10^{-8}$–10^3 S cm^{-1}) and high optical transmittance ($\geq$ 80%). The high electric conductivity and high optical transmittance make TCOs and TOSs promising materials for the passive or active components of various optoelectronic and electronic devices [1–6].

Barium stannate ($BaSnO_3$) is one of the ABO_3 type cubic n-type perovskite semiconductors with space group symmetry $Pm\bar{3}m$, where values of ionic radii for Ba^{2+}, Sn^{4+} and O^{2-} are 1.61 Å, 0.69 Å, and 1.35 Å in coordination 12, 6 and 2, respectively. It shows Schmidt tolerance factor, $\frac{1}{\sqrt{2}}(r_A + r_O)/(r_B + r_O)$, of 1.026, where r_A, r_B and r_O ionic radii of Ba^{2+}, Sn^{4+} and O^{2-}, respectively. The cubic perovskite structure of $BaSnO_3$ is very flexible for lattice ion substitution and oxygen non-stoichiometry, which, in turn, form a vast set of technologically promising materials [7–9]. The $BaSnO_3$ has band-gap energy similar to alternative transparent oxide semiconductors such as TiO_2 and ZnO, exhibits high electron mobility at room temperature, and remains stable up to 1000 °C [7,10,11]. In comparison to binary oxide semiconductors, ternary oxides such as barium stannate, strontium stannate, etc., have shown better control of chemical and electrical properties [11–13]. The band structure and electrical properties of barium stannate can further be engineered by ionic substitution at barium or tin site [14].

The nano-structured barium stannate has been used in various applications such as electro-chemical activity, ferromagnetism and electricity, multiferroics, electron transport material in various opto-electronic devices and sensors due to their interesting structural, electrical, optical and magnetic properties [10,11,15–25]. Barium stannate nano-crystallites have been synthesized by various techniques such as solid state reaction [26] co-precipitation [27], hydrothermal [28] and polymerized complex [29]. However, sol-gel is a promising technique which provides high yield at low reaction temperatures [30].

Nano-materials usually show novel physical and chemical properties due to their small size and reasonably large surface area [31–34]. Consequently, various doped nano-crystalline materials have been investigated for their emission behavior [35–38]. Lanthanide ions such as Er^{3+}, Ho^{3+}, Tm^{3+}, Pr^{3+} have been widely used as up-converter, and Yb^{3+} ion as sensitizer to increase NIR absorption intensity [39–42]. Till today, the most common pair for up-conversion has been Er^{3+}/Yb^{3+}

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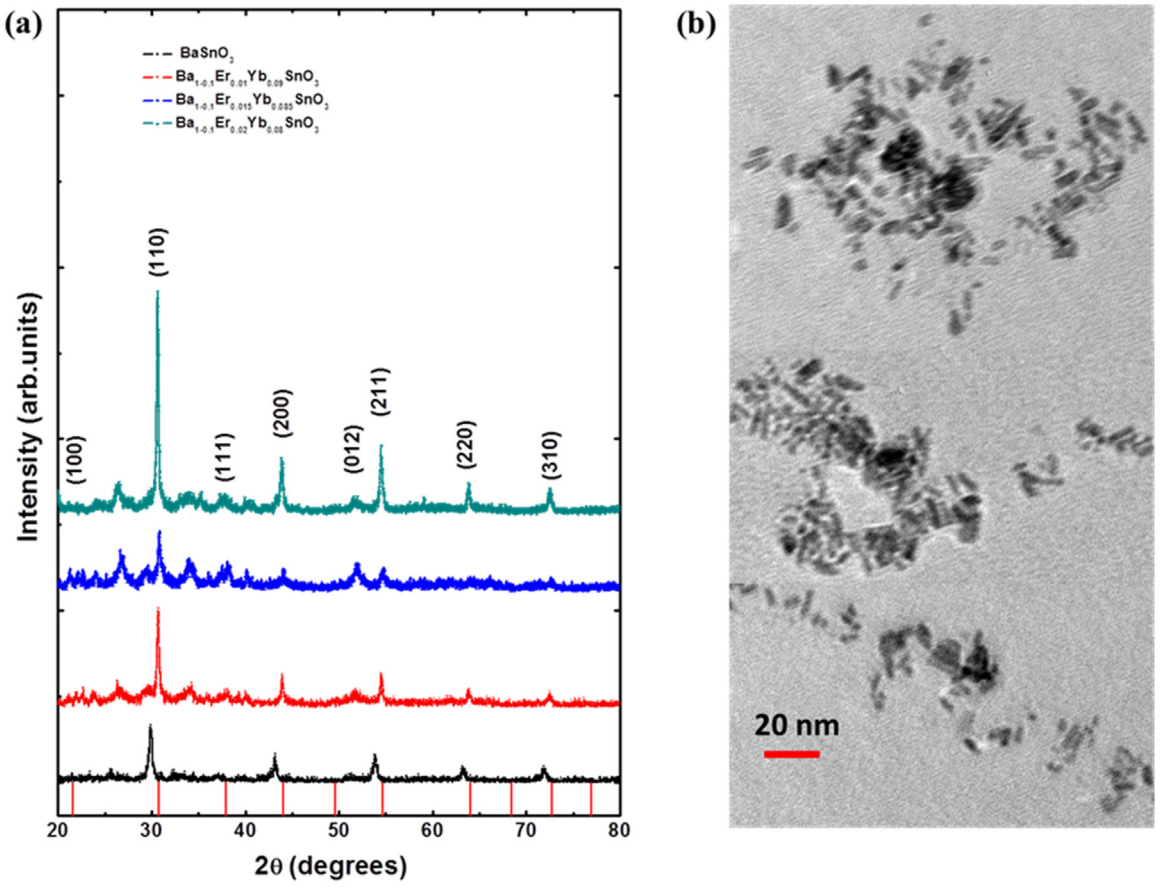

Fig. 1. (a) X-ray diffraction patterns of pristine and Er^{3+}/Yb^{3+} co-doped $BaSnO_3$ nano- crystallites and **(b)** Transmission electron micrograph of pristine $BaSnO_3$.

[40,43]. In recent years, up-conversion oxides such as TiO_2:Er^{3+}, Yb^{3+}, Lu_2O_3:Tm^{3+}, Yb^{3+} , ZnO:Er^{3+}, Yb^{3+}, Y_2O_3:Yb^{3+}, Tm^{3+}, etc., have been widely explored in photovoltaic devices [40,44]. The highest efficiency for yttrium oxyfluoride: (Yb^{3+}, Er^{3+}) and TiO_2: (Er^{3+}, Yb^{3+}) have been 6.57% and 8.98%, respectively [45,46].

In this study, we have used facile wet chemistry sol-gel route for the synthesis of pristine and co-doped (Er^{3+}/Yb^{3+}) barium stannate nano-crystallites. There are reports available on the photovoltaic behavior of barium stannate [47,48]. Zhang and coworker suggested that N719-sensitized barium stannate nano-crystallites offered the potential for its use as photo-anode in dye sensitized solar cell (DSSC) [47,49]. However, report on the photovoltaic behavior of co-doped (Er^{3+}/Yb^{3+}) barium stannate nano-crystallites are not available in literature. Therefore, an attempt has been made to synthesize pristine and co-doped (Er^{3+}/Yb^{3+}) barium stannate nano-crystallites, and investigate their structural, morphological, optical, semiconducting and photovoltaic behavior. We report about 40% increase in efficiency for (Er^{3+}/Yb^{3+}) co-doped barium stannate photo-anode based DSSC in comparison to pristine $BaSnO_3$ photo-anode based DSSC.

2. Experimental

Facile wet chemical sol-gel process has been used to synthesize pristine and Er^{3+}/Yb^{3+} containing nano-crystalline $BaSnO_3$. Barium nitrate ($Ba(NO_3)_2$), stannic chloride penta-hydrate ($SnCl_4{\cdot}5H_2O$), erbium nitrate penta-hydrate ($Er(NO_3)_3{\cdot}5H_2O$) and ytterbium nitrate penta-hydrate ($Yb(NO_3)_3{\cdot}5H_2O$) were used as precursors, oxalic acid ($C_2H_2O_4{\cdot}2H_2O$) as chelating agent and de-ionized water as solvent. The amount of oxalic acid was taken equal to gram equivalent weight of metals in the reaction. All the precursors were dissolved separately in de-ionized water, mixed subsequently via slow stirring to form a homogenous solution. The oxalic acid was dissolved separately in de-ionized water and mixed slowly to the former precursor solution to obtain a gel product. The gel was dried afterward at 100 °C to obtain flakes of presumably oxalate, which were subsequently, ground to get fine powder. These powders were decomposed at 650 °C to obtain pristine and Er/Yb co-doped barium stannate nano-crystallites.

The crystal structure of the samples was examined by the X-ray diffractometer (Rigaku Mini Flex). Optical absorption spectra were recorded by UV–Vis–NIR spectrophotometer, Varian model Carry 5000 in the diffuse reflectance mode. Photoluminescence spectra were collected in the wavelength range of 330–750 nm by using Simadzu RF-530 spectroflurometer with the excitation wavelength of 350 nm. Morphological visualization of as-synthesized samples was performed by transmission electron microscopy (TEM) (Hitachi H-7500). Samples for impedance analysis were pelletized at 5 kN in 10 mm diameter and 1.2 mm thickness pellets, sintered afterward at 800 °C for 4 h and subsequently, silver pasted in 3 mm diameter area. The impedance analysis was performed with interfaced potentiostat (Biologic SP-240).

Fluorine-doped tin oxide (FTO) coated glass substrates were used for the fabrication of photo-anode and counter electrode. For the fabrication of pristine and (Er^{3+}/Yb^{3+}) co-doped $BaSnO_3$ photo anode, initially, the respective nano- crystallites are mixed in de-ionized water, 0.2 ml of HNO_3 and two drops of Triton-X 100 to make the paste. The paste is subsequently used to tape cast uniform film on FTO coated glass substrate which is already coated with 10 μm thick TiO_2 blocking layer. The coated films were annealed for 2 h, and afterward kept in dye solution for 12 h to soak dye molecules. These films then rinsed thoroughly with ethanol to remove un-adsorbed dye molecules and dried afterward. Platinum counter electrode was prepared by spin coating of chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$) solution in 2-propanol, followed by the reduction in the presence of $NaBH_4$ and sintering at