



Temperature induced upconversion behaviour of Ho³⁺-Yb³⁺ codoped yttrium oxide films prepared by pulsed laser deposition



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ARTICLE INFO

Article history:

Received 4 November 2015

Received in revised form

11 February 2016

Accepted 15 February 2016

Available online 18 February 2016

Keywords:

Frequency upconversion

Thin films

PLD technique

Substrate temperature

Power dependence

Auger electron spectroscopy

ABSTRACT

Pulsed laser deposited Ho³⁺-Yb³⁺ codoped yttrium oxide films were grown on silicon substrates in vacuum at different substrate temperatures (373, 573, 773 and 973 K). The deposited films have shown a phase transition on increasing the substrate temperature, as confirmed by the X-ray diffraction analysis. The grain distribution and surface roughness of the deposited thin films have been estimated by atomic force microscopy measurements. In the optical properties study upconversion luminescence at 547, 656 and 758 nm was revealed upon 980 nm excitation. 773 K was found to be the best substrate temperature owing to the thickest deposited layer, as indicated by Auger depth profile analysis of the prepared films. A non-tunable bright green upconversion emission due to the involvement of a two photon process was established and a possible excitation-emission mechanism is explained by using an energy level diagram of the dopant ions.

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1. Introduction

Demand for advanced luminescent materials has motivated modern researchers to improve the quality of existing materials and technology [1]. Optical emissions observed from these materials are mainly by upconversion (UC) and down conversion (DC) processes. UC is the nonlinear optical process in which more than one lower energy photons are converted into a single high energy photon by means of an energy transfer process [2]. UC emissions from rare earth (RE) ion doped materials have received much consideration for designing luminescent devices, lasers, sensors, and bio-probes over the past decades [3–5]. Thin films of UC materials make them more promising for technological applications e.g. optical storage disks, optical displays, photovoltaic cells, etc. [6–8]. Several attempts have been made to achieve UC luminescence from Er³⁺ activated ZnO [8], Y₂O₃ [9], TiO₂ [10], BaTiO₃ [11], Bi₂Ti₂O₇ [12], GaN [13], NaYF₄ [14,15], LaF₃ [16], YF₃ [17] and BaGdF₄ [18] films but very rarely from Ho³⁺ activated films [6]. Ding et al.

[6] have reported green UC emission from a bismuth titanate ferroelectric film codoped with Ho³⁺-Yb³⁺, prepared by the chemical solution deposition method.

In fact, trivalent holmium (Ho³⁺) is the most promising active centre along with erbium (Er³⁺) in the lanthanide series for UC luminescence owing to its abundant energy level structure favorable for efficient near infrared (NIR) excitation [19,20]. Codoping with Yb³⁺ ions improved the green and red UC luminescence from Ho³⁺ doped materials due to its large absorption cross section around NIR (980 nm) excitation and its high energy transfer efficiency to the activator ions [6,19–21]. Y₂O₃ has been widely used as a host matrix, for its excellent ability to serve as the luminescent media and several other features such as good photochemical stability, wide transparency range, large refractive index, high melting point and low cut-off phonon frequency suitable for optical investigations [20,22–24]. Y₂O₃ occurs as a RE sesquioxide, with the Y³⁺ ions having an ionic radius and electronegativity very close to the lanthanide elements, and exhibits the cubic structure at ambient temperature and pressure [25,26]. Previously, we have reported very intense green upconversion emission from Ho³⁺-Yb³⁺ codoped Y₂O₃ phosphor upon 980 nm diode laser excitation for security applications [22]. We achieved that the maximum fraction of the total UC emission was centered in the green band resulting from the ⁵F₄/⁵S₂ → ⁵I₈ transition of Ho³⁺ ions. In this

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context, we seek to investigate the UC emission behaviour of thin films prepared from $Y_2O_3:Ho^{3+}-Yb^{3+}$ phosphor. An important feature in the deposition of phosphor thin films is the stoichiometric allocation of target material at the substrate, which should display mostly the same characteristics of the target powder. Pulsed laser deposition (PLD) is a well-known and versatile technique for this purpose [27–29]. Y_2O_3 thin films grown on silicon substrates display good optical characteristics and have low lattice mismatch with Si [30,31]. Although a number of investigations have been performed upon Y_2O_3 thin films doped with RE ions [9,23,24,32–34], no report was found for Ho^{3+} activated Y_2O_3 films. At the early stage of the growth of the thin films by PLD, the species impinge from the plume to a surface and transfer their kinetic energies to the substrate surface atoms via their collisions. As a result, the collisions can produce atomic scale heating, displacement, and creation of mobile vacancy or interstitial defects, ion mixing, etc. The film growth mode, the crystalline quality and number of defects in the films are found to be sensitive to the ion energy. The other parameters such as substrate temperature can fundamentally influence the surface morphology evolution of the thin films [35]. Substrate temperature is considered as one of the important factors in the thin film growth process. Raising the substrate temperature will significantly improved the motion of adatoms due to temperature-dependent thermal vibrations.

In the present research we prepared $Ho^{3+}-Yb^{3+}$ codoped Y_2O_3 films by the PLD technique at different substrate temperatures. Structural, morphological and depth profile characterizations were performed by X-ray diffraction (XRD), atomic force microscopy (AFM) and Nano scanning Auger microscopy (SAM). The UC emission study has been done upon exciting the films by a 980 nm diode laser and the involved mechanisms were explained on the basis of a power dependence study and energy level diagram.

2. Experimental details

2.1. Preparation of powder sample

Phosphor samples were prepared by the solution combustion method using reagent grade Y_2O_3 , Ho_2O_3 and Yb_2O_3 as raw materials, nitric acid and double deionized water as solvents, while urea was used as the organic fuel. The detailed explanation of synthesis and optimizations of the concentrations of dopants is reported in our previous work [22]. The optimized (0.2 mol%) Ho^{3+} and (3.0 mol%) Yb^{3+} codoped Y_2O_3 phosphor powder was annealed at 1073 K before being used to prepare the target for PLD.

2.2. Deposition of thin films

In order to prepare the target, the optimized phosphor powder was pressed in a home-made sample holder without any binder and annealed further to remove the water containing species. For substrate, Si (100) wafers were cut into small pieces of size $2 \times 2 \text{ cm}^2$ and cleaned using acetone and ethanol in an ultrasonic bath for 20 min. The washed substrates were dried properly by using nitrogen gas and stuck on the substrate holder by silver/nickel pastes. A pulsed Nd:YAG laser of operating wavelength 266 nm, frequency about 10 Hz and energy about 40 mJ was used to ablate the target in vacuum with a fixed target to substrate distance and deposition time of about 4.0 cm and 2 h, respectively. The films were prepared at 373, 573, 773 and 973 K substrate temperatures with a background pressure of about 5×10^{-5} mbar. Without post thermal treatment, the films were not crystalline and it didn't show any visible emission. The prepared films were annealed in air atmosphere at 873 K to improve the crystallinity and luminescence properties. To prevent any interdiffusion at higher temperatures we

decided to anneal the films at the lower 873 K temperature.

2.3. Characterization performed

The annealed films were used for the structural and optical characterization. The XRD patterns were measured by a Bruker-D8 Advance X-ray diffractometer with a $Cu-K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) in 15° – 40° range to identify the phase formation and crystalline nature of the films. AFM images of the prepared films were taken in contact mode using a Shimadzu SPM-9600 atomic force microscope to understand the surface characteristics. A PHI 700 Scanning Auger Nanoprobe of 25 kV–10nA electron beam and 2 kV–1.5 μ A Ar ion gun was used for the depth profile measurements with a sputtering rate of 15 nm/min. Photoluminescence (PL) behaviour has been investigated by recording the UC emission spectra pumped with a fibre coupled 980 nm diode laser using a Horiba iHR320 monochromator. The roughness and colour coordinates were calculated by analyzing the topographic scan of the film and using GoCIE software, respectively.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the diffraction patterns of $Y_2O_3:Ho^{3+}-Yb^{3+}$ films as a function of growth temperature along with its powder pattern. The powder sample corresponds to the cubic Y_2O_3 phase (JCPDS No.: 25-1200) and the main peak corresponds to the (222) plane [22] whereas the films had different phases depending on the growth temperature. Y_2O_3 can exist in three polymorphic forms, namely, hexagonal (space group $P3m1$), monoclinic (space group $C2/m$), and cubic (space group $Ia3$)²⁶. In Fig. 1 it is observed that Y_2O_3 did not keep the same symmetry if different substrate temperatures from 373 to 973 K were used, which is very obvious in the sesquioxide series as a function of temperature [36]. The Y_2O_3 film has a nearly cubic phase at the lowest substrate temperature, but the monoclinic phase [37,38] occurs for samples grown with the substrate temperature of 573 K. Further increase of the substrate temperature to 973 K produces the cubic phase similar to the powder characteristics. This might be due to the large variation in unit cell volume (monoclinic to cubic) of the host matrix on varying

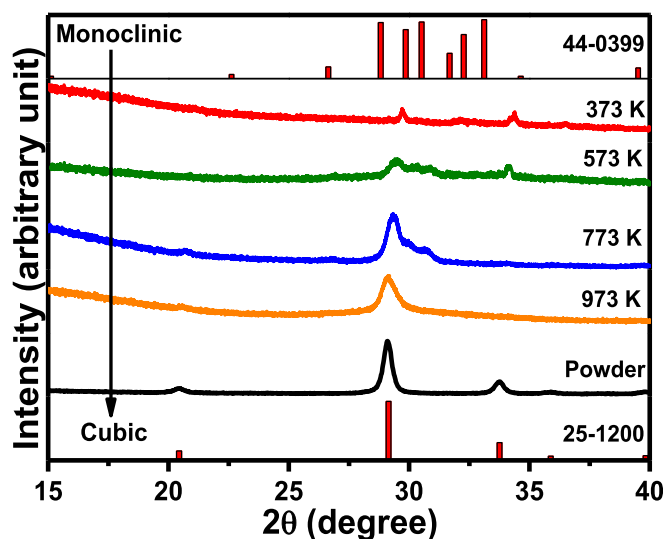


Fig. 1. Room temperature X-ray diffraction patterns of the $Ho^{3+}-Yb^{3+}$ codoped Y_2O_3 films produced using different substrate temperatures.

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