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Investigations on Structural and luminescence of Anatase/Rutile Titania Stimulated RE^{3+} ions

G.Subalakshmi[a*], R. Thilagaraj Benisha[a], K.Theerthi[a], S.Santhiya[a]

[a]Department of Physics, Theivanai Ammal College for Women, Villupuram-605401

Abstract

The present paper reports infrared emission from upconversion luminescence spectra of RE3+ doped TiO2 phosphor. Sample was prepared by precipitation method at variable doping concentration of ytterbium using $TiCl_4$ as a raw material. Their structure, band gap energy and luminescence properties are investigated using X-ray diffraction, diffuse reflectance spectroscopy, and photoluminescence spectroscopy. The photoluminescence spectra recorded under the 330 nm excitation with the variable concentration of ytterbium. The PL emission spectra shows intense emission peaks near infrared regions.

Keywords : Precipitation method, RE^{3+}, PL, X-ray diffraction

Introduction

Solar energy deems much attention to overcome the global energy crisis being a renewable, pollution free and abundant source of energy in the universe [1]. Solar cells are used to convert the solar energy to electricity, Si-based solar cells in particular predominate the solar cell market due to the 15% conversion efficiency [2]. The spectral discrepancy in the c-Si solar cell is the principal reason for major energy loss [3].

Downshifting- converting high energy photons into lower energy photons is much recommended technique to modify spectrum, enhancing the efficiency of Si-based solar cells thereby minimize the energy loss [4]. Luminescent industries widely use rare earth ions in 4f states, completely filled $5S^2$ and $5S^6$ orbital for emitting wide range luminescence from ultraviolet to NIR region [5]. Yb^{3+}, known for possessing only two energy levels, $^2F_{5/2}$ and $^2F_{7/2}$ is much consistent for string NIR emission around 1000 nm betwixt the transition level, therefore Yb^{3+} in the NIR region is the maximum spectral response of the c-Si solar cell [6].

The host material chosen determines the down-conversion luminescence property. Of late doping semiconducting compounds with RE ions either to control or tune the optical property utilizing unique band gap structure has proven successful [7]. Due to its good thermal, chemical and mechanical properties TiO_2 is taken for study to assess the NIR emission intensity [8,9]. The method synthesis, purity and presence of dopants defines the optical property of TiO_2 which may alter the impact if found wanting [10,11]. Of varies methods developed for the synthesis of TiO_2 nanoparticles, flame synthesis[12], ultrasonic irradiation [13], chemical vapour deposition [14], sol-gel process [15], hydrothermal 16], solvothermal [17], and precipitation [18], the last method simple, effective.

In this study, study the performance of mixed Anatase and Rutile titania properties. The structure formation, luminescence properties and energy transfer mechanism are discussed in detail.

Material and methods

The TiO_2:xYb^{3+} ions at different compositions (x = 0.03, 0.06, 0.09, 0.12) is prepared by precipitation method. $TiCl_4$, Yb_2O_3, H_2SO_4 and ammonia solution are used in the experiments without any further purification. Fresh distilled water is used for making aqueous solution. In precipitation process, 10 ml of $TiCl_4$ is dissolved in 100 ml of ice-cold deionized H_2O followed by constant and steady stirring overnight to obtain the solution. Yb_2O_3 solution (Yb_2O_3 dissolved in the sulfuric acid) is added to the host solution and stirred well. Then mixed solution is added drop by drop to ammonia solution which is used as the precipitation agent. Once the precipitate settles

at the bottom of the flask, it is filtered and washed with several times with distilled water. The washed precipitate is dried by muffle furnace for 24 hours. Finally, the obtained material is calcined for 4 hours at 600˚C in Muffle furnace and allowed to cool naturally.

The X- ray diffraction pattern (XRD) is obtained on a D8 advance X-ray diffractometer (Bruker) equipment using Cu-Kα (λ = 1.54065 Å) radiation to identify the structure and phase purity. The XRD patterns of the sample are collected at2θ, between 20˚ and 60˚. The Varian Model 5000 UV-Vis spectrophotometer is used to measure the absorbance spectrum of the samples different doping concentration. The Photoluminescence emission spectra are recorded using Spectroflurometer (JY Fluorolog-FL3-11). The excitation and emission measurement are effected by 450W Xenon lamp. All measurements are recorded at room temperature.

Results and discussion

The diffraction pattern gives an idea about the crystallinity and phase structure of the synthesis sample. Fig.1 shows the diffraction patterns of ytterbium doped titania compound. From this analysis, it is clear that the sample annealed at 600˚C shows diffraction peaks implies the presence of anatase and rutile phase which well match with the JCPDS data of Card No. 076173 & 89-4920. Present composition suppresses the intensity of the rutile phase (110) peak aggravates the intensity of anatase phase revealing the mixed phase of TiO_2 [19]. The relative propositions of anatase and rutile can be evaluated using spurr equation [20]

$$F_R = \frac{1}{1+8\left[I_{A(101)}+I_{R(110)}\right]} \times 100 \qquad (1)$$

Where, F_R is the mass fraction of rutile, and I_A (101) and I_R (110) are the intensities of anatase and rutile peaks, respectively. From the calculation, it is noted the percentage of the rutile phase is 30.89, 36.93 and 21.80.

UV-Visible reflectance spectrum is focused in order to characterize the optical absorbance of the TiO_2 doped ytterbium ions (Fig.2).The absorption spectrum of the doping samples is show a shift towards blue region as compared to the pure TiO_2. Although the spin transition originates from Yb^{3+}:$^2F_{5/2}$ to $^2F_{7/2}$ the absorption peaks around ~1000 nm. The reflectance data were converted into absorption ones using the Kubelka-Munk transformation according to Equation

F(R) = (1-R) /2R

The band gap energy for each sample was estimated by the Tauc's law described

$$F(R)=\alpha h\vartheta = A\,(h\vartheta - Eg)^n \qquad (2)$$

Where α is absorption coefficient, h represents the Planck's constant, ϑ denotes the frequency of light, A is the characteristic parameter for transition, Eg is the band gap value and n is a constant depending on the nature of the electron transition (n= 2 for direct transition or ½ for indirect transition). The indirect band gap is plotted for $(\alpha h\vartheta)^{1/2}$ versus photon energy ($h\vartheta$) (Fig. 3). The indirect band gap energy of present compound is 2.89eV, 3 eV, 3.01eV,3.02 and 3.04eV.

The photoluminescence spectrum of the synthesis materials at different doping concentrations (x = 0.03, 0.06,0.09 and 0.12) is shown in Fig.4. The excitation at 330 nm and near NIR emission intensity at 982, 997, 1026, 1055nm wavelength and intense emission is observed at 1026 nm. The doping concentrationof Yb^{3+} varying at 0.03 to 0.12. Peak position of PL spectrum shows significant steep at 1026 nm due to the varying concentration of ytterbium ions. Despite several weak peaks due to transition at different stark level ^2F_J (J=5/2, 7/2), the intensity of emission from theTiO_2:xYb^{3+} at 1026 nm is relatively higher than the band edge of c-silicon solar cell.

The energy transfer mechanism of the host material to Yb^{3+}ions is explain in the schematic energy levels diagram in Fig.5. First, the material is excited under ultraviolet (UV) region at 330 nm and the electron transition

takes place from the valence band to the conduction band in TiO2 compound. This causes intense emission around NIR region due to the ET process of Yb^{3+} ions for, Yb^{3+}ions have two electronic states namely $^2F_{7/2}$and $^2F_{5/2}$ and the energy transfer occurs between$^2F_{7/2}$and $^2F_{5/2}$. The two energy states splits into seven stark levels, 1 to 4 levels forthe ground 2F5/2 and 5-7 levels for 2F7/2 excited state.The intense peak at 1026 nm attributed to the transition from starkthe peaks at lower wavelength 982, 997 and 1055 nm and are due to transition 5 →1, 2,3 and 4 transition states respectively. The concentration of the ytterbium ions is place a pivotal role on the increasing the emission intensity.

Micro electronics industry development relies much on c-Si based solar cell due to its abundance, high energy conversion efficiency and economy [23]. Yet the c-Si solar cells suffer major drawback of spectral loss due to low efficiency output caused by thermalization of hot carrier. To recap this loss, the down-conversion material is used to increase photocurrent generation. The sample down-conversion material ($TiO2:Yb^{3+}$) equates the c-Si bases solar cell in the spectral region around 1000 nm. Thus the down-conversion material taken for the study conform efficiency enhancement of c-Si solar cell.

Conclusion

The sum up,$TiO_2:Yb^{3+}$ is synthesized by precipitation method and its phase structure, luminescence properties and energy transfer mechanism are discussed in detail. Posing against different doping concentration of ytterbium ions recorded to be the concentration registering efficient emission in NIR region. Excited at 330 nm formation of several weak peaks may distract concentration level that the intensity formed at 1026 nm ensures the characteristic emission of $^2F_{5/2} \rightarrow {}^2F_{7/2}$electronic state transition of Yb^{3+} ions. The $TiO_2:Yb^{3+}$NIR material is authenticated for a solar spectral converter development and is adept for c-Si solar cell devices.

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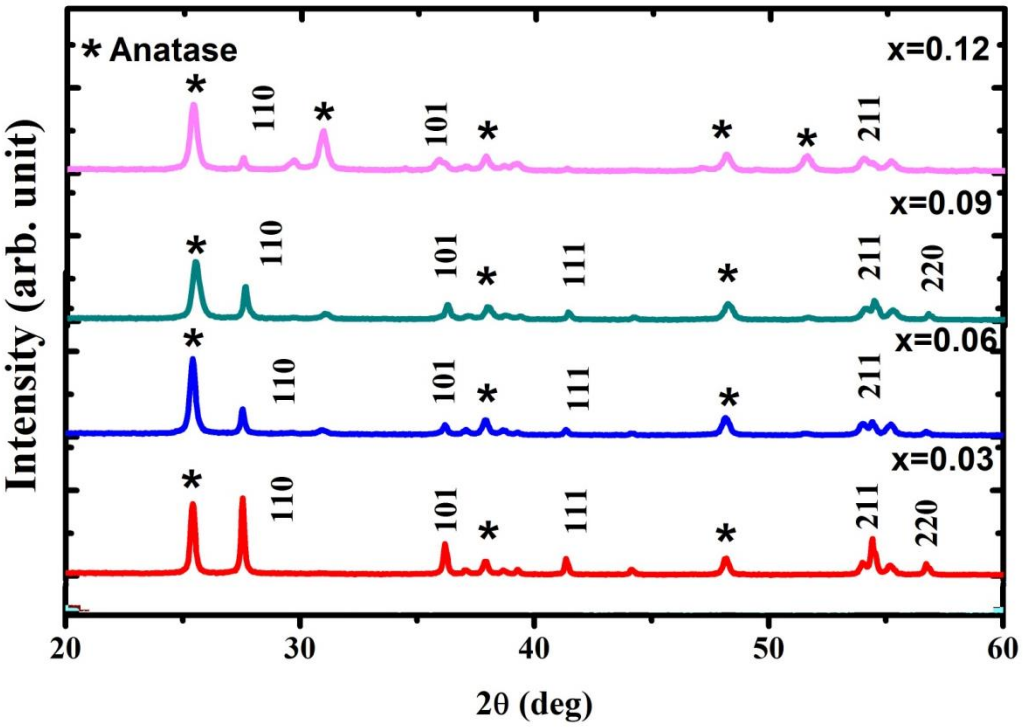
* Anatase
x=0.12
x=0.09
x=0.06
x=0.03
110
101
111
211
220
Intensity (arb. unit)
2θ (deg)
20
30
40
50
60

Fig. 1

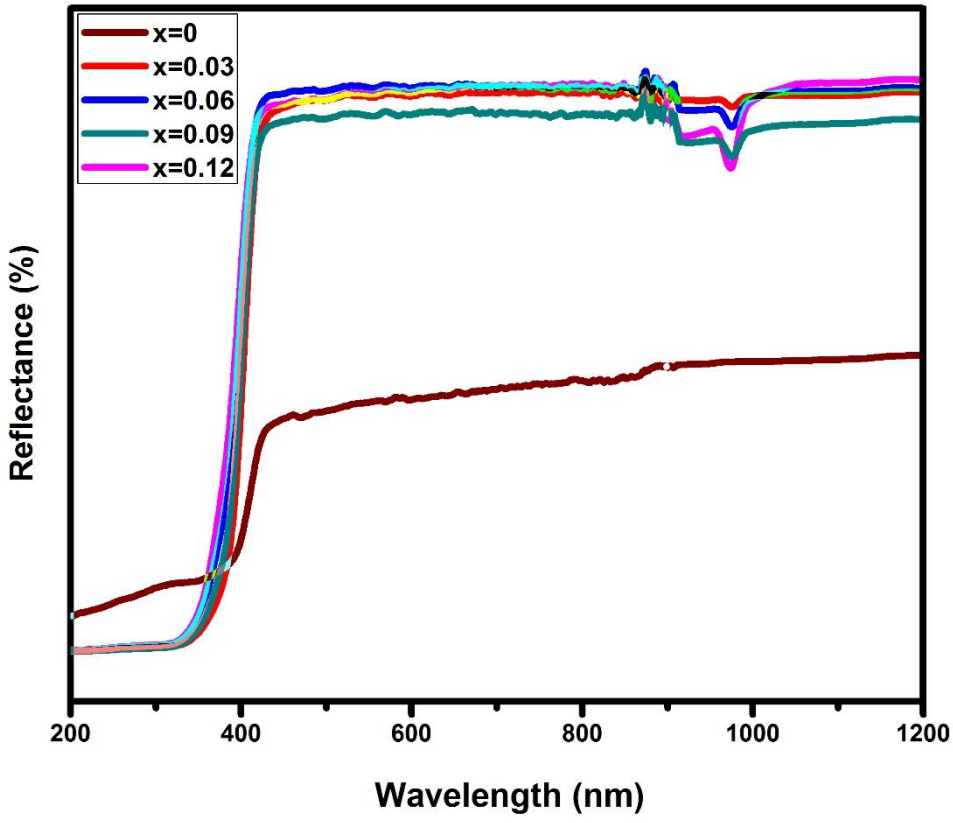
x=0
x=0.03
x=0.06
x=0.09
x=0.12
Reflectance (%)
Wavelength (nm)
200
400
600
800
1000
1200

Fig. 2

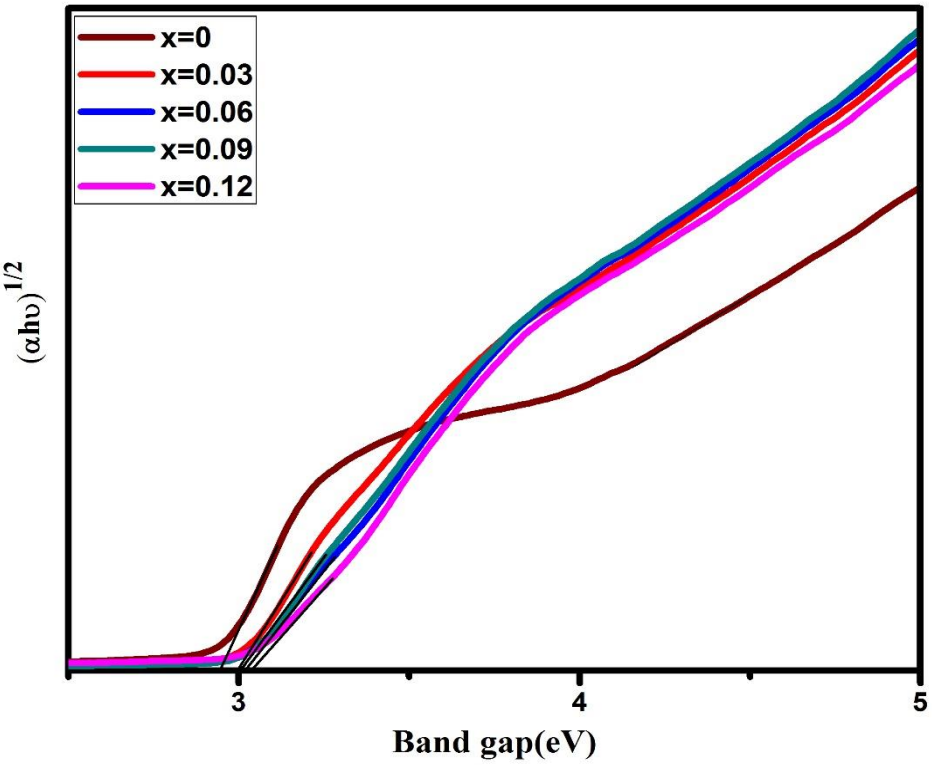
x=0
x=0.03
x=0.06
x=0.09
x=0.12
$(\alpha h\upsilon)^{1/2}$
3
4
5
Band gap(eV)

Fig. 3

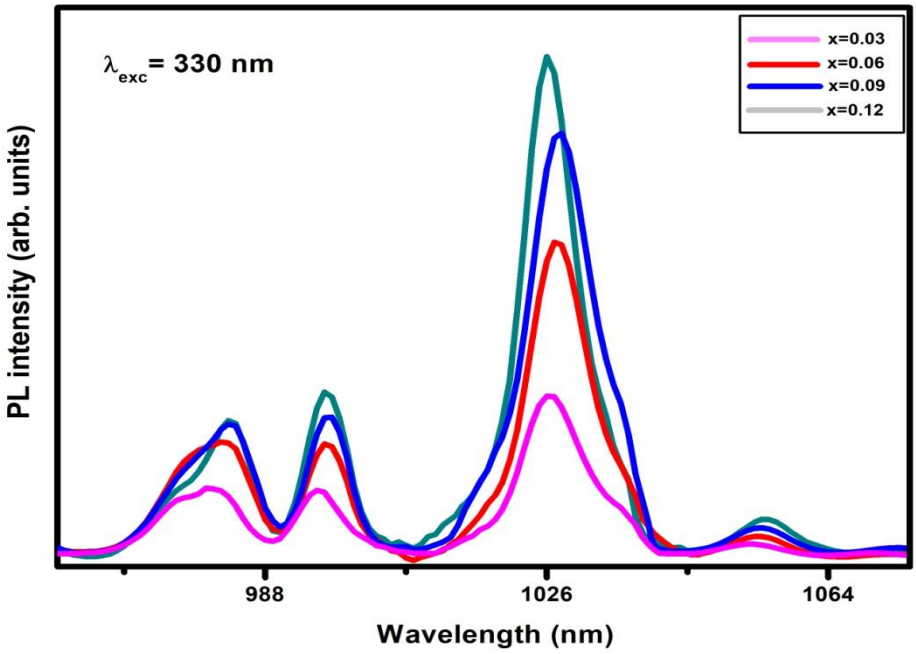
λ_{exc}= 330 nm
x=0.03
x=0.06
x=0.09
x=0.12
PL intensity (arb. units)
988
1026
1064
Wavelength (nm)

Fig. 4

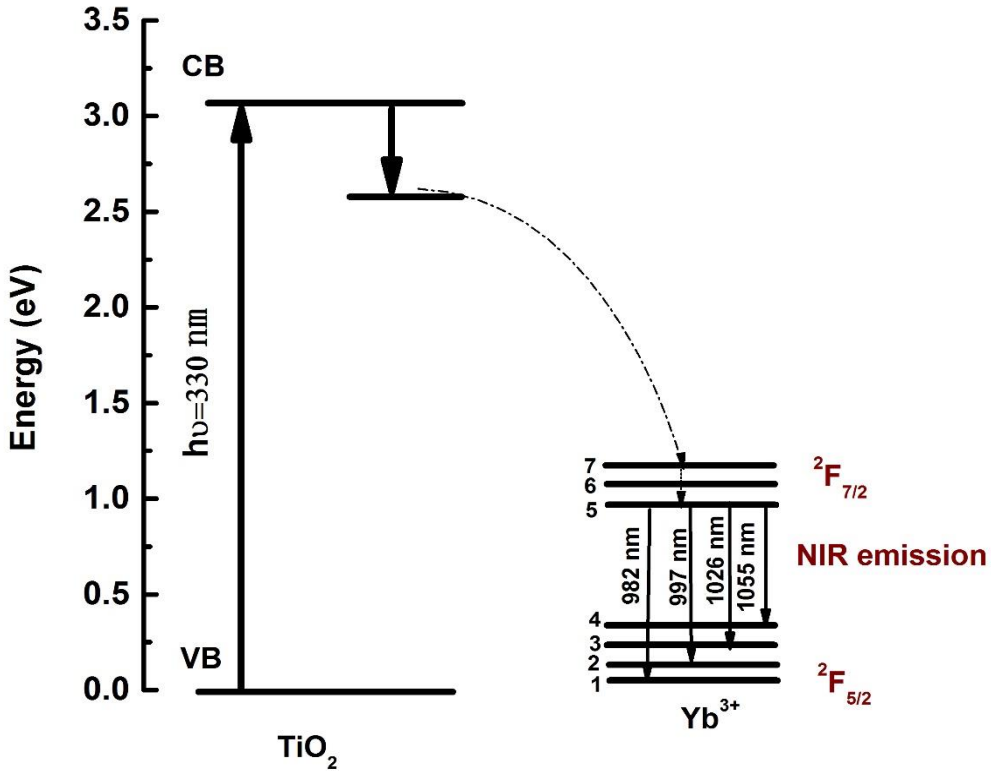

Fig. 5

Figure caption

Fig. 1 X ray diffraction of rutile phase $TiO_2$and Yb^{3+} doped TiO2phosphor(x=0.03 to 0.12)

Fig. 2 Diffuse reflectance spectrum of rutile phase $TiO_2$and Yb^{3+} doped TiO2phosphor(x=0.03 to 0.12)

Fig. 3 Indirect band gap energy rutile phase $TiO_2$and Yb^{3+} doped TiO2 phosphor (x=0.03 to 0.12)

Fig. 4 photoluminescence emission spectrum of Yb^{3+} doped TiO_2phosphor(x= 0.03,0.06, 0.09 and 0.12)

Fig. 5 Energy level diagram of ytterbium dopedTiO_2