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# Downconversion in $Tb^{3+}$, $Yb^{3+}$ Co-Doped $ZrO_2$

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***Abstract***— *Despite relevant photovoltaic (PV) technologies being available for more than fifty years, the production of solar energy remains costly, largely owing to low power conversion efficiencies of solar cells. Ultraviolet (UV) -visible (VIS) to near-infrared (NIR) quantum cutting (QC) materials are promising materials to increase the conversion efficiency of solar cells. $Tb^{3+}$ and $Yb^{3+}$ co-doped luminescent material that can cut one photon of around 480 nm into two NIR photons of around 1000 nm could be used as a downconversion luminescent convertor in front of crystalline silicon solar cell(c-Si) panels to reduce thermalization loss of the solar cell. The energy transfer mechanism from $Tb^{3+}$ to $Yb^{3+}$ is studied. $Tb^{3+}$ ions in the $4f^7 5d^1$ state relax down to the $^5D_4$ level and cooperatively transfer energy to two $Yb^{3+}$ ions, which is followed by the emission of two photons ($\lambda \sim 1000$ nm).The material $ZrO_2$ provide suitable environment as host lattice for $Tb^{3+}$- $Yb^{3+}$ ion system. The material was synthesized by combustion method and annealed at high temperature. It was characterize by X-ray powder diffraction and spectroscopic properties were studied by NIR spectrometer. Unfortunately, the low $Yb^{3+}$ concentration leads to poor result. But at high (below the limiting value of concentration quenching) we can get much better result.*

***Keywords***— *Energy transfer, downconversion, quantum cutting and $ZrO_2$: $Tb^{3+}$, $Yb3^+$.*

## 1. INTRODUCTION

Sunlight is such huge source of energy, it is reported that sunlight delivered about 10,000 times more energy that human being consume now [1]. We have developed PV technology in order to convert solar energy into electrical energy which is simply inadequate. Shockley *et al.* [2] reported a theoretical efficiency limit of 30% for a single-junction crystalline silicon (c-Si) solar cell. There are transmission losses due to photons with less energy than band gap and thermalization losses due to photons with more energy than band gap, responsible for limiting value of conversion efficiency of c-Si cells. The phenomenon of QC has the potential to overcome thermalization losses. The process of QC has ability to split a single high energy photon of UV - (VIS) region into two or more than two low energy photons of NIR region 950 nm-1100 nm where the response of c-Si solar cell is maximum. In general, QC can be realized by photon cascade emission from a single lanthanide ion or by downconversion (DC) via energy transfer (ET) through different sets of lanthanide ions. The first successful demonstration of efficient visible quantum-cutting in a $LiGdF_4:Eu^{3+}$ phosphor was reported by Wegh *et al.* in 1999 with a theoretical quantum efficiency of 190% [3-4].

Ion couples such as $Nd^{3+}$–$Yb^{3+}$, $Pr^{3+}$–$Yb^{3+}$, $Er^{3+}$–$Yb^{3+}$, and $Tb^{3+}$–$Yb^{3+}$, appear promising for this purpose because the $Nd^{3+}$, $Pr^{3+}$, $Er^{3+}$, and $Tb^{3+}$ ions absorb in the UV-VIS region and then transfer the energy to $Yb^{3+}$ ions which emit in the NIR region at 950 -1000 nm [5-15]. $ZrO_2$ provide favorable conditions as host material. Because of characteristics such as hardness, optical transparency, thermal and chemical stability, high refractive index (2.15–2.18) [16-18] and wide band gaps of 5.0 eV for monoclinic-$ZrO_2$ and 5.8 eV tetragonal-$ZrO_2$, this material is found to be an excellent host [19]. ZrO2 is suitable host for $Tb^{3+}$ and $Yb^{3+}$ ions as the ionic radii of $Tb^{3+}$, $Yb^{3+}$ and $Zr^{4+}$ are 1.040 $A^0$ (C.N. 8), 0.985$A^0$ (C.N.8) and 0.84$A^0$ (C.N. 8) respectively [20]. The aim of this work is to study the spectroscopic properties and QC mechanism in $Tb^{3+}$-$Yb^{3+}$ co-doped $ZrO_2$.

## 2. EXPERIMENTAL

The precursors $ZrO(NO_3)_2$. $2H_2O$ (Loba 99.9%), $Tb_4O_7$ (Loba 99.9%), $Yb_2O_3$ (Loba 99.9%), $NH_4NO_3$ (Loba 99.9%) and $NH_2CH_2COOH$ were used for synthesis of $ZrO_2$ co-doped with $Tb^{3+}$-$Yb^{3+}$ ions. The composition of each chemical weighed in proper stoichiometric ratio. Sample of $ZrO_2$ doped and co-doped with $Tb^{3+}$ and $Yb^{3+}$ ion having molar concentration of 1.0% each was prepared by combustion method. The precursors $ZrO(NO_3)_2$. $2H_2O$ (1.2460gm, Loba 99.9%), $Tb_4O_7$ ( 0.0093gm, Loba 99.9%), $Yb_2O_3$ (0.0098gm, Loba 99.9%), $NH_4NO_3$ (2.4015gm, Loba 99.9%) and $NH_2CH_2COOH$ (1.1260gm, Loba 99.9%) were mixed together in china basin and put in resistive furnace at $500^0$C where combustion reaction took place. The mixture molted first and gases like $CO_2$, $N_2$, and $H_2O$ etc were evolved. Frothing and swelling of mixture took place and then combusted with the formation of foam. The foam was gently pressed. The powder of $ZrO_2$: $Tb^{3+}$, $Yb^{3+}$ was slowly calcinated at $900^0$C in muffle furnace for 2 h. The PL emission and PL excitation spectra were recorded with

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QM51 NIR spectrophotometer. The confirmation of sample was done by XRD method by using Rigaku miniflex II X-ray diffractometer with scan speed of 2.000°/min and Cu Kα (λ = 1.5406 Å) radiation in the range 10° to 90°.

## 3. RESULTS AND DISCUSSION

### 3.1 XRD Analysis

The formation of the $ZrO_2$ sample in the crystalline phase synthesized by combustion method was confirmed by XRD pattern as shown in Figure. 1. The XRD pattern for $ZrO_2$:$Tb^{3+}$, $Yb^{3+}$ very well agreed with the standard data from ICDD file (01-083-0944). For the $ZrO_2$: $Tb^{3+}$, $Yb^{3+}$ material, the dominant structure is the monoclinic phase, where a= 5.14 Å, b= 5.20 Å and c= 5.31 Å. The space group for $ZrO_2$ is P21/c(14).

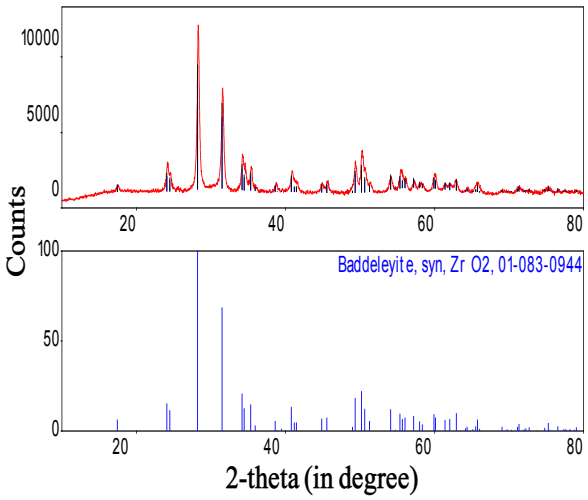


**Fig. 1: XRD pattern of $ZrO_2$ codoped with $Tb^{3+}$ and $Yb^{3+}$ at conc. of 1% each.**

### 3.2 Energy Transfer in $Tb^{3+}$–$Yb^{3+}$ System and Photoluminescence Properties

NIR quantum-cutting for $Tb^{3+}$–$Yb^{3+}$ co-doped systems was first reported by Vergeer *et al.* in 2005 on $Yb_xY_{1-x}PO_4$:$Tb^{3+}$ powder phosphors [21]. In case of $Tb^{3+}$–$Yb^{3+}$ system, the energy of $^5D4 \rightarrow {}^7F6$ transition of $Tb^{3+}$ (~20 000 $cm^{-1}$) is approximately twice the energy of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of $Yb^{3+}$ (~10 000 $cm^{-1}$). Although various $Tb^{3+}$–$Yb^{3+}$ co-doped materials have been well studied but ET mechanism from $Tb^{3+}$ to $Yb^{3+}$ ions is still debatable [22-25]. It is reported that a nonlinear second-order downconversion process should be responsible for the cooperative quantum-cutting (Fig. 2) [22-23]. The slope of $Yb^{3+}$ luminescence intensity versus the excitation power was found to be nearly 0.5, indicating the emission of two lower-energy photons upon the absorption of one photon.[24] While two different groups found the slope of luminescence intensity curves to be near 1 instead of 0.5, indicating a one-photon process for the $Yb^{3+}$ ion [15].

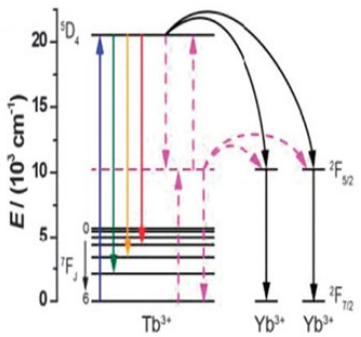


**Fig. 2**

Fig. 2 Energy-level diagram of the $Tb^{3+}$–$Yb^{3+}$ system, showing the ET mechanism of NIR quantum-cutting under the excitation of the $^7F6$ - $^5D_4$ ($Tb^{3+}$) transition. Black solid lines show the second-order nonlinear Quantum-cutting process, whereas the pink dotted lines show the linear downconversion process where a virtual energy level located at the middle position (around 10,000 $cm^{-1}$) between the ground state and the $^5D_4$ energy level of $Tb^{3+}$ participates in the quantum-cutting process.

Fig. 3 shows the excitation spectra of $ZrO_2$ doped with $Tb^{3+}$ and $Yb^{3+}$ at 1% concentration each monitored at emission wavelength of 996 nm.

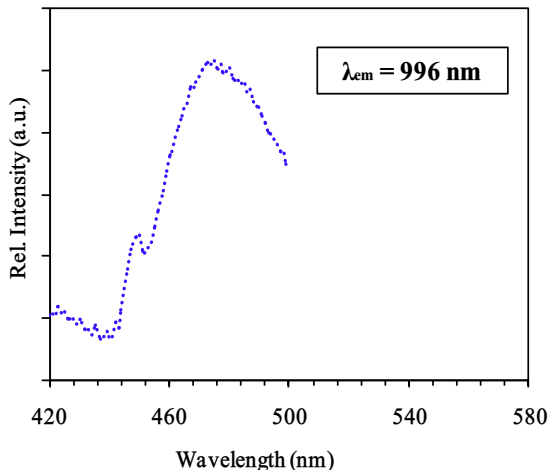


**Fig. 3: Excitation spectra of ZrO2 doped with $Tb^{3+}$ and $Yb^{3+}$ at molar concentration of 1% each.**

The NIR emission spectra of $ZrO_2$ doped with $Tb^{3+}$ and $Yb^{3+}$ at 1% concentration each is as shown in Fig. 4. The NIR emission profile of the prepared sample consist of two peaks centered at 984 nm and 996 nm of $Yb^{3+}$ ion at an excitation of 475 nm of $Tb^{3+}$ ion. This is nothing but the phenomenon of DC. But the comparison of the relative intensities showed that relative intensity of emission is found to be slightly than that of excitation. If the emission intensity was found to be approximately two times than that of excitation then it results in QC. However the NIR emission profile that we observed cannot confirm the QC process which was accepted at such low concentration of dopants.

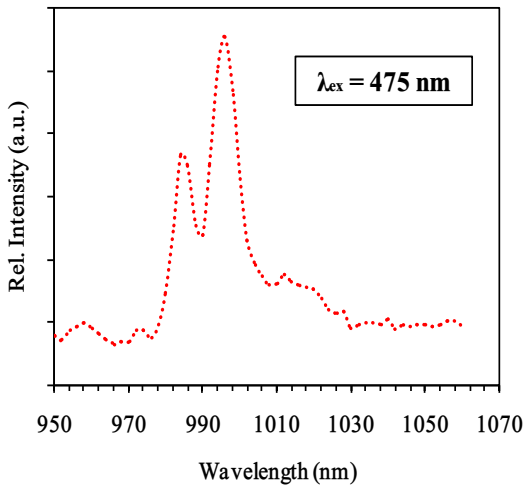


**Fig. 4: NIR Emission spectra of $ZrO_2$ doped with $Tb^{3+}$ and $Yb^{3+}$ at molar concentration of 1% each.**

## 4. CONCLUSIONS

In our result, it observed that there is effective energy transfer from $Tb^{3+}$ ions to $Yb^{3+}$ ions which is responsible for NIR emission. However we could not observed QC due to low concentration of $Yb^{3+}$ ion. The result of QC will be dominant in the same host at sufficiently high concentration of doping. In future the $Tb^{3+}$–$Yb^{3+}$ system can be utilized in another stable host so as to synthesis of highly efficient QC materials in order to enhance the spectral response of c-Si solar cells which have maximum conversion efficiency in the range of 950 nm – 1100 nm.

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