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RESEARCH ARTICLE

Luminescence properties of Tm^{3+} ions single-doped YF_3 materials in an unconventional excitation region

Yuan Chen[1] | Qing Liu[1] | Han Lin[1] | Xiaohong Yan[1,2,3,4]

[1] College of Science, Nanjing University of Aeronautics and Astronautics, Nanjing, P. R. China

[2] Key Laboratory of Radio Frequency and Micro-Nano Electronics of Jiangsu Province, Nanjing, P. R. China

[3] College of Electronic Science and Engineering, Nanjing University of Posts and Telecommunications, Nanjing, P. R. China

[4] School of Material Science and Engineering, Jiangsu University, Zhenjiang, P. R. China

Correspondence
Xiaohong Yan, College of Science, Nanjing University of Aeronautics and Astronautics, Nanjing, 211106, P. R. China.
Email: xhyan@nuaa.edu.cn

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Abstract

According to the spectral distribution of solar radiation at the earth's surface, under the excitation region of 1150 to 1350 nm, the up-conversion luminescence of Tm^{3+} ions was investigated. The emission bands were matched well with the spectral response region of silicon solar cells, achieved by Tm^{3+} ions single-doped yttrium fluoride (YF_3) phosphor, which was different from the conventional Tm^{3+}/Yb^{3+} ion couple co-doped materials. Additionally, the similar emission bands of Tm^{3+} ions were achieved under excitation in the ultraviolet region. It is expected that via up-conversion and down-conversion routes, Tm^{3+}-sensitized materials could convert photons to the desired wavelengths in order to reduce the energy loss of silicon solar cells, thereby enhancing the photovoltaic efficiency.

KEYWORDS

down-conversion, photoluminescence, solar energy, Tm^{3+}-ions single-doped, up-conversion

1 | INTRODUCTION

Owing to worldwide increasing energy demand and environmental pollution, research and development of renewable energy resources have attracted much attention, with solar cells being a topic of great interest. In recent years, great efforts have been devoted to improving the photovoltaic efficiency of semiconductor solar cells. One of the effective methods is modifying the incident solar spectrum via photon frequency conversion, such as up-conversion and down-conversion, which can reduce the sub-bandgap transmission loss of long wavelength and decrease the charge carrier thermalization loss of high-energy photons, respectively.[1–5] Benefiting from the unique and abundant energy-level structures, lanthanide ions have always been considered as good candidates to modulate the solar spectrum, such as Er^{3+} ions, Ho^{3+} ions, Tb^{3+}/Yb^{3+} ion couples and Tm^{3+}/Yb^{3+} ion couples.[6–10] In the case of Tm^{3+}/Yb^{3+} ion couples, among the most reported articles about up-conversion luminescence of Tm^{3+}-doped materials, Yb^{3+} ions are usually doped as the indispensable sensitizer,[11–13] and the energy transfer mechanisms between Tm^{3+} ions and Yb^{3+} ions are similar, described as phonon-assisted multiphoton stepwise summation process.[14] The process is initiated by one 980 nm photon absorption of a Yb^{3+} ion in the $^2F_{7/2}$ ground state ($^2F_{7/2} \rightarrow {}^2F_{5/2}$). Subsequently, the excited Yb^{3+} ion transfers its energy to a Tm^{3+} ion to excite it to the $^3H_5$ excited state: $^2F_{5/2}$ (Yb^{3+}) + $^3H_6$ (Tm^{3+}) → $^2F_{7/2}$ (Yb^{3+}) + $^3H_5$ (Tm^{3+}), then Tm^{3+} ion populates the $^3F_4$ state by non-radiative relaxation. Following that, with the help of other excited Yb^{3+} ions, Tm^{3+} ions are promoted from $^3F_4$ state to $^3F_2$ state, populating $^3H_4$ state by non-radiative relaxation, and finally promoted from $^3H_4$ state to $^1G_4$ state.

However, by careful investigation of the Tm^{3+} ions energy-level diagram,[15] the energy-level gap between $^3H_5$ excited state and $^3H_6$ ground state is about 8000 cm^{-1} (up to 1250 nm), which means that the pump energy supported by 980 nm laser (up to 10,200 cm^{-1}) will be wasted partly. Furthermore, according to the air mass 1.5 global

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Abbreviations used: NH_4F, ammonium fluoride; $TmCl_3$, thulium chloride; Tm_2O_3, thulium oxide; XRD, X-ray diffraction; YCl_3, yttrium chloride; YF_3, yttrium fluoride; Y_2O_3, yttrium oxide

(AM 1.5G) solar spectrum at sea level, as shown in Figure 1, in the infrared region, the solar radiation energy mainly distributes in three regions: 1000 nm (950–1100 nm), 1250 nm (1150–1350 nm) and 1600 nm (1500–1750 nm), while the 1250 nm region is matched with the corresponding energy-level gap of Tm^{3+} ions very well. For a long time, most attention has been attracted in the 1000 nm region (such as 980 nm) [16,17] and 1600 nm region (such as 1540 nm) [18–20], yet less attention has been attracted in the 1250 nm region. In order to make the best use of solar energy, the research of Tm^{3+} ions up-conversion luminescence under the excitation around 1250 nm will be meaningful. Lots of published articles have depicted the absorption spectra around 1250 nm of Tm^{3+} ions in various Tm^{3+}-doped materials, such as $LiYF_4$ crystals [21], chalcohalide glass [22] and tellurite glass [23,24], suggesting that Tm^{3+}-sensitized materials might have potential up-conversion luminescence performance in the 1250 nm region of the solar spectrum. Additionally, Tm^{3+} ions also have the ability of down-conversion in the ultraviolet region, providing an opportunity to combine down-conversion and up-conversion luminescence.

Fluorides have always been considered as excellent lanthanide-doped hosts, owing to the property of low phonon energy. In this work, yttrium fluoride (YF_3) phosphor was selected as the host materials, since its simple synthesis conditions which can be easily extended to industrialization manufacture. By the method of co-precipitation, Tm^{3+} ions single-doped YF_3 phosphor was synthesized. Without the conventional and indispensable Yb^{3+} ions, the up-conversion and down-conversion luminescence were achieved by single Tm^{3+} ions. Thus, excitation energy loss through energy transfer from Yb^{3+} ions to Tm^{3+} ions can be avoided.

2 | EXPERIMENTAL

The starting materials were yttrium oxide (Y_2O_3), thulium oxide (Tm_2O_3), ammonium fluoride (NH_4F) and hydrochloric acid. All reagents were analytical grade, used without further purification, and deionized water was used throughout. The synthesis of $Y_{0.95}Tm_{0.05}F_3$ phosphor was a method of co-precipitation.

The procedure is described as follows. The stoichiometric amounts of Y_2O_3 and Tm_2O_3 were dissolved in diluted hydrochloric acid by heating to prepare the stock rare earth solutions of 0.2 mol/L yttrium chloride (YCl_3) and thulium chloride ($TmCl_3$) solutions, respectively. Accurately weighed 0.0888 g of NH_4F was dissolved into deionized water as precipitator. In the synthesis of $Y_{0.95}Tm_{0.05}F_3$, 3.80 ml of YCl_3 aqueous solution and 0.20 ml of $TmCl_3$ aqueous solution were mixed under thorough stirring. Then the mixed aqueous solution of YCl_3 and $TmCl_3$ was added to the aqueous solution of NH_4F drop-by-drop, under magnetic stirring. After stirring for about an hour, the colloidal solution was transferred to a capped beaker for precipitating. Then the resulting product was separated by centrifugation and cleaned by deionized water three times. After that, the obtained product was collected and heated at 700°C for 6 h in the environment of hydrogen fluoride gas atmosphere.

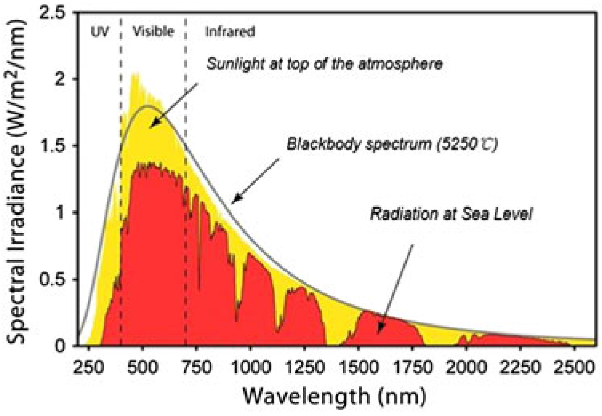

FIGURE 1 The spectral distribution of solar radiation at the earth's surface

The structure of the phosphor was investigated by X-ray diffraction (XRD) using an Ultima-III (Rigaku Corporation, Japan) equipment provided with Cu tube with K_α radiation at 1.5406 Å, scanning in the 2θ range from 20° to 60° with 0.02° increments. The photoluminescence excitation and emission spectra were measured by the FLS920 spectrophotometer (Edinburgh Instruments Ltd. England) equipped with one adjustable OPO (optical parametric oscillator) laser and xenon lamp as the excitation sources. All spectra measurements were performed at room temperature.

3 | RESULTS AND DISCUSSION

The composition and phase purity of the phosphor were examined by XRD, shown in Figure 2. Compared with YF_3 standard data (JCPDS No. 74-0911) in Figure 2(a), all the diffraction peaks of the phosphor (Figure 2b) can be indexed to the orthorhombic phase of YF_3. The dopant has little influence on the structure of the materials and does

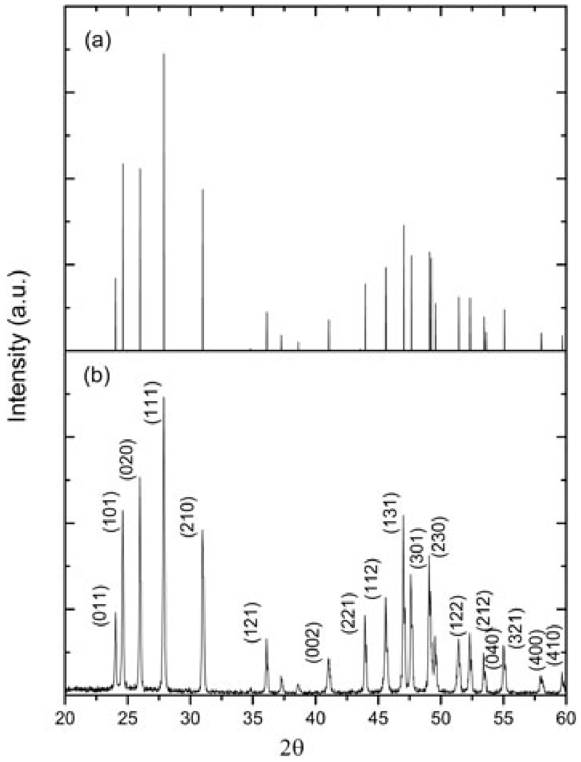

FIGURE 2 The standard data (JCPDS no. 74-0911) of orthorhombic YF_3 (a) and the XRD pattern of $Y_{0.95}Tm_{0.05}F_3$ phosphor (b)

not introduce any detectable impurity phase, suggesting that the Tm^{3+} ions have replaced the site of the Y^{3+} ions in YF_3 phosphor. Besides, according to the XRD data, it could be calculated that the crystallinity of the phosphor compound is 98.34%, while the average particle size is about 90 nm.

The photoluminescence excitation spectrum of the $Y_{0.95}Tm_{0.05}F_3$ phosphor was obtained by monitoring the 800 nm emission line, ascribed to the ${}^3H_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ions. As shown in Figure 3, there are two intense excitation bands around 1164 and 1218 nm, which were chosen as the excitation source wavelength to pump the Tm^{3+} ions.

Figure 4 depicts the photoluminescence spectrum of $Y_{0.95}Tm_{0.05}F_3$ under the excitation of 1218 nm. The 800 nm infrared and 700 nm red emission bands of Tm^{3+} ions are observed, originated from the transitions of ${}^3H_4 \rightarrow {}^3H_6$ and ${}^3F_2 \rightarrow {}^3H_6$ of Tm^{3+} ions, respectively. It should be noted that c-Si solar cells exhibit intense spectral responses around 800 nm, suggesting that the Tm^{3+}-doped material in this work, owing to its wide 800 nm infrared emission band, might be an ideal candidate to convert long wavelength photons to the desired ones which can be directly absorbed by c-Si solar cells, thus improving the photovoltaic efficiency.

Figure 5 depicts the photoluminescence spectrum of $Y_{0.95}Tm_{0.05}F_3$ under the excitation of 1164 nm. Similar to Figure 4, the emission bands centered at 800 nm and 700 nm were also observed. Furthermore, a slight blue emission signal at 475 nm was observed, assigned to the ${}^1G_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ions. The difference in the photoluminescence spectra between Figure 4 and Figure 5 suggests that the pump photon energy of 1218 nm cannot afford the population of ${}^1G_4$ state of Tm^{3+} ions to generate 475 nm blue emission signal, yet the photon energy of 1164 nm barely does.

As shown in Figure 6, by monitoring emission line at 475 nm, assigned to the ${}^1G_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ions, the photoluminescence excitation spectrum of $Y_{0.95}Tm_{0.05}F_3$ phosphor was observed. Among those excitation bands mentioned earlier, the peak at 315 nm was chosen as the pump source wavelength, obtaining the photoluminescence spectrum shown in Figure 7. In contrast to

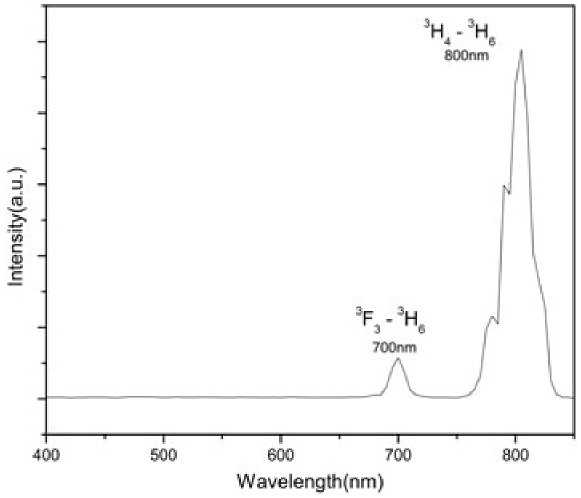

FIGURE 4 The photoluminescence spectrum of $Y_{0.95}Tm_{0.05}F_3$ phosphor, under the excitation of 1218 nm

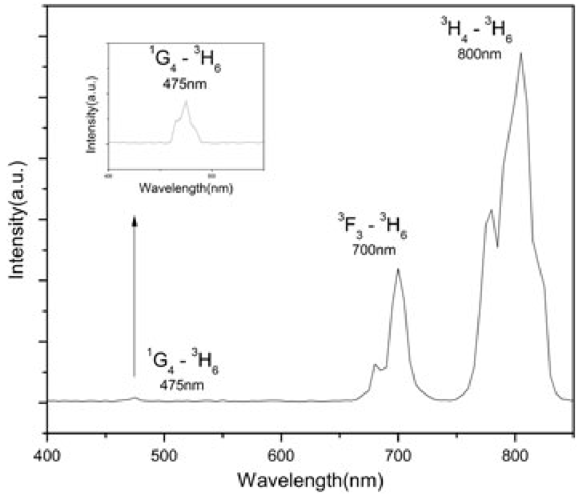

FIGURE 5 The photoluminescence spectrum of $Y_{0.95}Tm_{0.05}F_3$ phosphor, under the excitation of 1164 nm

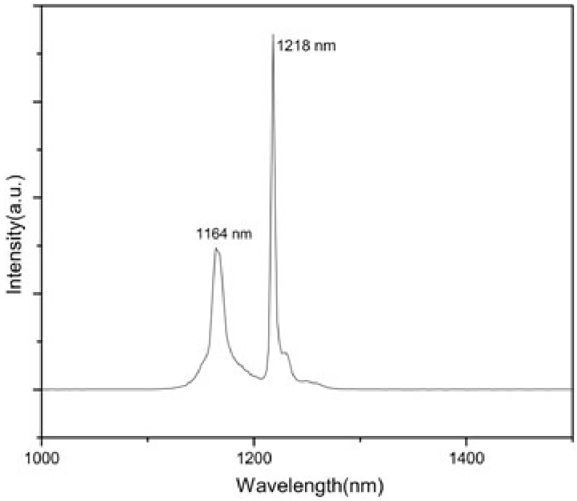

FIGURE 3 The photoluminescence excitation spectrum of $Y_{0.95}Tm_{0.05}F_3$ phosphor, by monitoring the 800 nm emission line

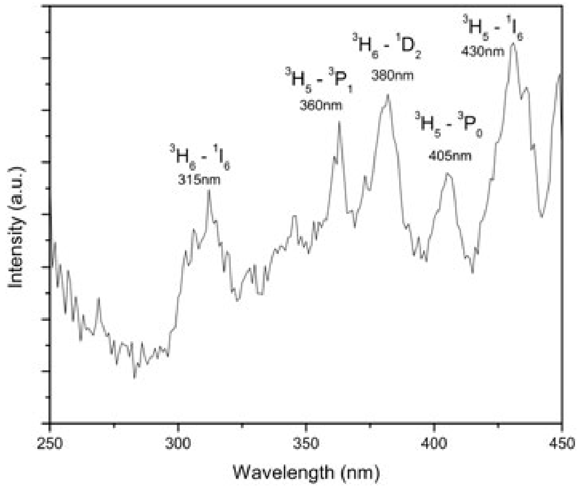

FIGURE 6 The photoluminescence excitation spectrum of $Y_{0.95}Tm_{0.05}F_3$ phosphor, by monitoring the 475 nm emission line

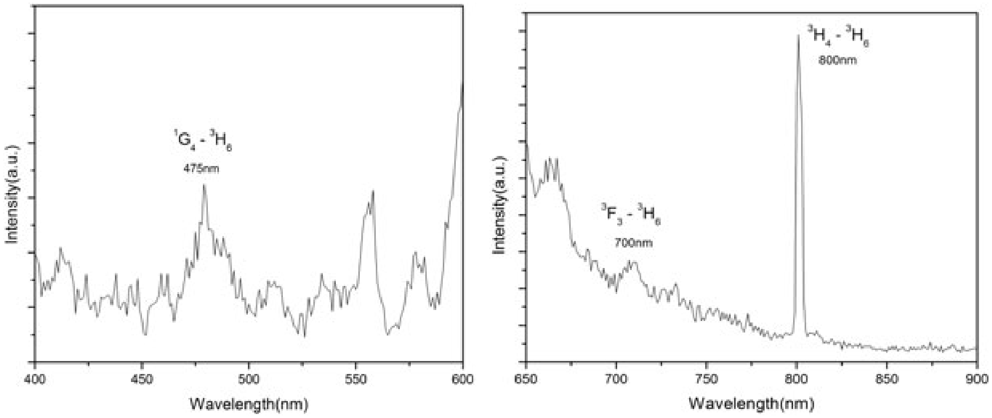

FIGURE 7 The photoluminescence spectrum of $Y_{0.95}Tm_{0.05}F_3$ phosphor, under the excitation of 315 nm

Figures 4 and 5, the same emission bands at 475 nm, 700 nm and 800 nm could also be detected. As we know, the spectral response of c-Si solar cells is mainly located in the range of 400 to 1000 nm. Thus, the Tm^{3+} -doped material in this work could absorb photons in the wavelength range of both ultraviolet (315 nm) and infrared (1164 and 1218 nm) regions, where c-Si solar cells exhibit poor performance, to generate 475, 700 and 800 nm emission to match the corresponding spectral response of c-Si solar cells.

Since Dieke and Crosswhite provided the energy-level schemes of rare earth ions in 1963,[25] a large number of followers have carried out further studies and gradually developed the relevant theories in excited-state dynamics, emission profiles, energy transfer mechanisms and so on. For example, in the analysis of Tm^{3+} ions up-conversion luminescence mechanisms, the phonon-assisted multiphoton stepwise process is predominant.[14] For the reason that Tm^{3+} ions exhibit low absorption cross-section, in the conventional experimental operation, Yb^{3+} ions are usually co-doped as sensitizer, thus facilitating efficient Tm^{3+} ions up-conversion luminescence. Taking one of the previous published articles as an example.[13] Pumped by the 980 nm laser, the excitation of Tm^{3+} ions was achieved by energy transfer from Yb^{3+} ions to Tm^{3+} ions. Absorbing 980 nm photons (up to 10200 cm^{-1}), Yb^{3+} ions in the $^2F_{7/2}$ ground state were excited to $^2F_{5/2}$ state, transferring energy to Tm^{3+} ions continuously. Since the energy of excited Yb^{3+} ions did not resonantly match with the $^3H_5$ excited state of Tm^{3+} ions (~8100 cm^{-1}), pump energy of about 2000 cm^{-1} had to be wasted through energy release as lattice phonons.[26] The Tm^{3+} ions were promoted from the $^3H_6$ ground state to the $^3H_5$ excited state, populating the $^3F_4$ state by non-radiative

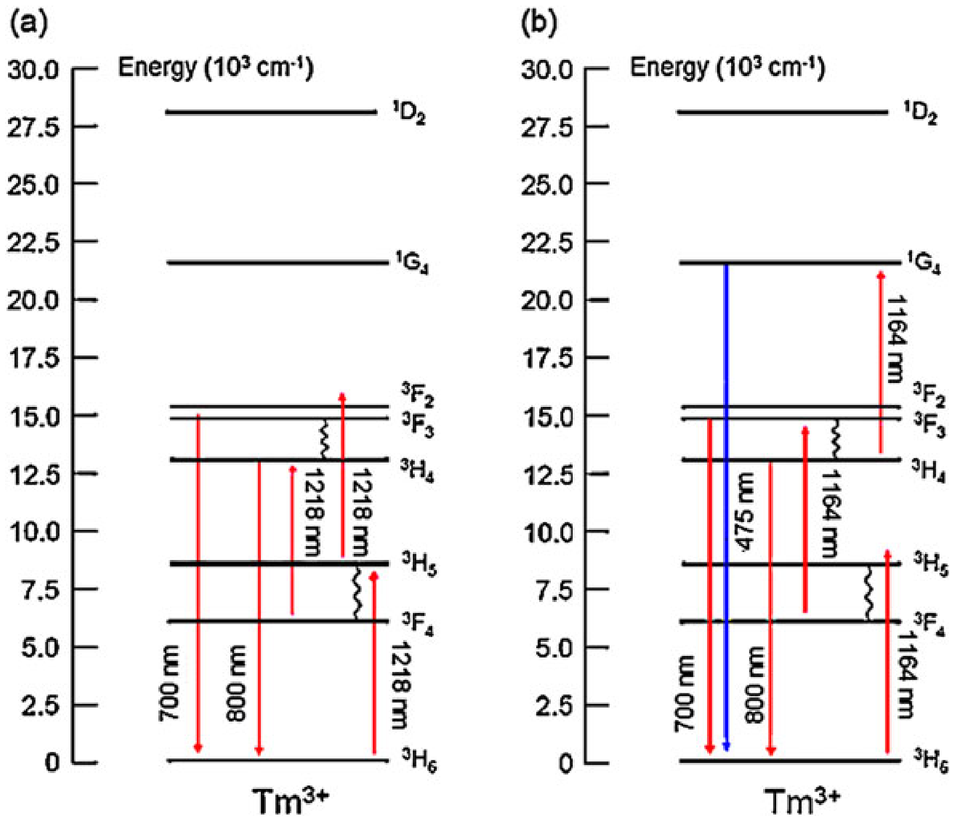

FIGURE 8 The possible up-conversion luminescence mechanisms in the system of $Y_{0.95}Tm_{0.05}F_3$

relaxation (energy loss by phonons), then promoted from $^3F_4$ state to $^3F_2$ state, populating $^3H_4$ state by non-radiative relaxation, and finally promoted from $^3H_4$ state to $^1G_4$ state.

In this work, pumped at 1164 and 1218 nm, as a result of the absence of Yb^{3+} ions, the realization of up-conversion luminescence could be achieved by Tm^{3+} ions themselves.[27] According to the energy-level diagram of Tm^{3+} ions, pump photon energy of excitation sources and energy matching conditions,[28] the possible up-conversion luminescence mechanisms in the system of $Y_{0.95}Tm_{0.05}F_3$ can be illustrated as shown in Figure 8. As depicted in Figure 8(a), under the excitation of 1218 nm (up to 8200 cm^{-1}), Tm^{3+} ions were promoted from the $^3H_6$ ground state to $^3H_5$ excited state (energy-level gap around 8100 cm^{-1}). In contrast to the energy loss of about 2000 cm^{-1} under excitation of 980 nm, the energy of 1218 nm pump source was resonantly transferred to Tm^{3+} ions, increasing energy utilization efficiency. Subsequently, part of Tm^{3+} ions in the $^3H_5$ state were excited to $^3F_{2,3}$ state (~7200 cm^{-1}), while other Tm^{3+} ions relaxed non-radiatively to the $^3F_4$ state by phonon-assisted relaxation. Then the Tm^{3+} ions in $^3F_{2,3}$ state could either return to $^3H_6$ ground state to generate the 700 nm emission ($^3F_{2,3} \rightarrow {}^3H_6$), or non-radiatively decay to $^3H_4$ state, thus generating the 800 nm emission ($^3H_4 \rightarrow {}^3H_6$). Meanwhile, the Tm^{3+} ions in $^3F_4$ state could absorb another 1218 nm photon and reach the $^3H_4$ state (~7000 cm^{-1}), thus returning to $^3H_6$ ground state to generate the 800 nm emission ($^3H_4 \rightarrow {}^3H_6$).[29,30] Thus, under the excitation of 1164 nm (~8600 cm^{-1}), Tm^{3+} ions could be promoted to the $^3F_{2,3}$ and $^3H_4$ states, subsequently generating 700 nm red signal and 800 nm infrared signal, respectively. Besides, a trace of Tm^{3+} ions in $^3H_4$ state could be promoted to the $^1G_4$ state (~8500 cm^{-1}), thus returning to $^3H_6$ ground state to generate the 475 nm blue signal ($^1G_4 \rightarrow {}^3H_6$).[31] Since the photon energy of 1218 nm was up to 8200 cm^{-1}, lower than the energy-level gap between $^3H_4$ and $^1G_4$ state, pumping at 1218 nm cannot achieve the $^1G_4$ state population and the 475 nm blue emission, which is corresponding to the emission performance shown in Figure 4. In brief, during the multiphoton stepwise process of Tm^{3+} ions up-conversion luminescence, part of the pump energy was wasted by non-resonant energy transfer and phonon-assisted relaxation. Consequently, compared with the conventional Tm^{3+}/Yb^{3+} ions co-doped system (excited at 980 nm), the Tm^{3+} ions single-doped system (excited at 1164/1218 nm) could reduce energy loss in the up-conversion luminescence process.

4 | CONCLUSIONS

The Tm^{3+} ions single-doped YF_3 phosphor was synthesized. In contrast to the conventional Tm^{3+}/Yb^{3+} ion couple co-doped materials, in this work, Tm^{3+} ions have been unleashed by Yb^{3+} ions, achieving up-conversion luminescence under the excitation region of 1150 to 1350 nm. In addition, the Tm^{3+}-sensitized down-conversion luminescence under excitation in the ultraviolet region was also studied. Via up-conversion and down-conversion routes, Tm^{3+}-sensitized materials could convert both high-energy and low-energy photons to the desired ones which have intense response for silicon solar cells. It is expected that this work will provide a new strategy in extending the application of Tm^{3+} ions and enhancing the photovoltaic efficiency of solar cells in the future.

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ORCID

Yuan Chen http://orcid.org/0000-0001-6817-0856

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