Letter

Cooperative downconversion and near infrared luminescence of Tm$^{3+}$/Yb$^{3+}$ codoped Calcium Scandate phosphor

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A B S T R A C T
An efficient near infrared (NIR) quantum cutting in CaSc$_2$O$_4$:Tm$^{3+}$/Yb$^{3+}$ phosphor has been demonstrated by the visible and NIR spectra properties as well as the decay curves of Tm$^{3+}$:G$_{4}$ level. Upon excitation of Tm$^{3+}$:G$_{4}$ level with a blue photon at 466 nm, Yb$^{3+}$:F$_{2}$/G$_{2}$ level can emit two NIR photons around 1000 nm through cooperative energy transfer (ET) from Tm$^{3+}$ to Yb$^{3+}$ with the maximum energy transfer efficiency is 71%, and highest theoretical quantum efficiency reaches 171%, close to the limit of 200%. Because the energy of Yb$^{3+}$ transition is matched well with band gap of crystalline silicon, the excellent downconversion luminescence property indicates that CaSc$_2$O$_4$:Tm$^{3+}$/Yb$^{3+}$ is a promising oxide material for increasing the conversion efficiency of crystalline silicon solar cells.

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1. Introduction

Sustainable energy converted system based on the direct conversion of the sun energy into useable forms is expected to gain importance because it is the most promising source for its sufficiency and renewability to meet the long-run energy demand [1,2]. Due to converting sunlight into electricity directly, the photovoltaic solar panels have been quickly developed in recent years [2,3]. But the commercial photoelectric conversion efficiency of crystalline silicon solar cell is limited to only around 15% at present, because of the spectrum mismatch between solar spectrum and energy gap of silicon [2,4]. Silicon solar cells have the strongest absorption for the photons around 800–1100 nm. They cannot make use of the photons with $\lambda < 500$ nm due to higher reflection, while for photons with $\lambda > 1100$ nm the excess energy is lost as heat to cause the conduction band excessive heating [5,6]. To enhance the efficiency of silicon solar cells, the modification of solar spectrum through rare earth (RE) doped materials is a promising way [5,7]. The quantum cutting (QC) process can divide a high energy photon into two or more photons with lower energy, so that the converted photons can be better absorbed by the solar cells [5,7]. QC researches are mostly focused on the sensitized luminescence of Yb$^{3+}$. That is because Yb$^{3+}$ ion has an only excited state approximately 10,000 cm$^{-1}$ just above the band edge of crystalline silicon. Efficient QC using Yb$^{3+}$ as an acceptor requires the sensitizer with energy level at about 20,000 cm$^{-1}$. It has been realized with Tm$^{3+}$/Yb$^{3+}$, Pr$^{3+}$/Yb$^{3+}$, Tb$^{3+}$/Yb$^{3+}$, Mn$^{2+}$/Yb$^{3+}$, Eu$^{2+}$/Yb$^{3+}$, and Ce$^{3+}$/Yb$^{3+}$ couples [8–15]. Here, we focus on Tm$^{3+}$/Yb$^{3+}$ combination which is capable of downconverting the blue photon around 460 nm into two near infrared (NIR) photons around 1000 nm through a cooperative energy transfer (ET) form of Tm$^{3+}$:G$_{4}$ to Yb$^{3+}$:F$_{2}$/G$_{2}$ [8–11].

CaSc$_2$O$_4$ host lattice owns the low phonon energy (540 cm$^{-1}$) [16]. It is a promising host for achieving efficient downconversion luminescence, as reported the intense green emitting CaSc$_2$O$_4$:Ce$^{3+}$, CaSc$_2$O$_4$:Tb$^{3+}$ and red emitting CaSc$_2$O$_4$:Eu$^{2+}$ [17–19]. Recently, we have found that CaSc$_2$O$_4$:Tm$^{3+}$/Yb$^{3+}$ is an excellent oxide material for achieving highly efficient upconversion luminescence [16,20]. In Tm$^{3+}$/Yb$^{3+}$ codoped CaSc$_2$O$_4$ samples, there also exist the considerable Tm$^{3+}$ → Yb$^{3+}$ ET besides efficient Yb$^{3+}$ → Tm$^{3+}$ ET process [20]. As the efficient Yb$^{3+}$ → Tm$^{3+}$ ET is responsible for upconversion luminescence, the efficient downconversion can occur as well. However, until now, the cooperative ET from Tm$^{3+}$ to Yb$^{3+}$ and NIR QC in CaSc$_2$O$_4$ host have not been demonstrated yet.

In this letter, we report the efficient NIR QC in CaSc$_2$O$_4$:Tm$^{3+}$/Yb$^{3+}$ phosphor. The dependences of Yb$^{3+}$ concentration on the visible and NIR emission spectra, decay lifetime, and energy transfer efficiency have been investigated in detail. The possible mechanism of QC process has been discussed. Results show CaSc$_2$O$_4$:Tm$^{3+}$/Yb$^{3+}$ phosphor is an excellent material for the application in solar cells.
2. Experimental

The CaSc$_2$O$_4$.02%O$_4$ powder samples were synthesized by a solid state reaction [19]. The CaCO$_3$ (99.9%), Sc$_2$O$_3$ (99.99%), Yb$_2$O$_3$ (99.99%), and Tm$_2$O$_3$ (99.99%) were employed as the raw materials, which were mixed homogeneously by an agate mortar for 1 h, placed in an alumina crucible with a lid, then sintered in a box furnace at 1500 °C for 4 h in air.

Powder X-ray diffraction (XRD) datum was collected using Cu Kα radiation (λ = 1.54056 Å) on a Bruker D8 advance diffractometer. The chemical analysis of sample was inspected on a field emission scanning electron microscope (SEM, Hitachi S-4800) equipped with an energy dispersive X-ray spectrometer (EDS, JED, JXA-840). The excitation and emission spectra were measured using a FLS920 spectrometer (Edinburgh Instruments, U.K.). In fluorescence lifetime measurements, an optical parametric oscillator (OPO) was used as an excitation source, and the signals were detected by a Tektronix digital oscilloscope (TDS 3052).

3. Results and discussion

Fig. 1(a) shows the structure of CaSc$_2$O$_4$.Tm$^{3+}$/Yb$^{3+}$ characterized by the typical powder X-ray diffraction pattern. The host lattice exhibits an orthorhombic CaFe$_2$O$_4$ structure with the space group Pnam (62). The pure phase CaSc$_2$O$_4$ was synthesized in agreement with JCPDS card 20-0234, as shown by the good quality of Rietveld refinement. Tm$^{3+}$ and Yb$^{3+}$ substitutions for Sc$^{3+}$ sites had no effect on the phase structure of CaSc$_2$O$_4$ host [20]. Further the EDS in Fig. 1(b) confirms that the major constituents are Ca, Sc, O, and Yb. Due to the lower concentration of Tm$^{3+}$ and Yb$^{3+}$, it is difficult to detect doped ions accurately and obtain quantitative analysis results. Inset shows the atomic ratio of host element Ca:Sc approximates 1:2.

To investigate the QC mechanism in Tm$^{3+}$/Yb$^{3+}$ codoped CaSc$_2$O$_4$ phosphor, a series of CaSc$_2$O$_4$.02Tm$^{3+}$/x%Yb$^{3+}$ (x = 0–10) samples have been prepared. The excitation (left) and emission (right) spectra of samples as the direct evidence of Tm$^{3+}$ → Yb$^{3+}$ ET are shown in Fig. 2. In the excitation spectra, intense excitation band (solid line) centered at 466 nm for monitoring Tm$^{3+}$:G$_4$ → $^3$F$_4$ emission at 650 nm can be assigned to Tm$^{3+}$:H$_6$ → $^3$G$_4$ transition. The Tm$^{3+}$:H$_6$ → $^3$G$_4$ absorption is also observed by monitoring Yb$^{3+}$:2$^3$F$_{5/2}$ → 2$^3$F$_{7/2}$ infrared emissions at 980 nm (dashed line) and 1010 nm (dotted line), which indicates the presence of Tm$^{3+}$ → Yb$^{3+}$ ET.

The emission spectra of samples are presented under 466 nm excitation corresponding to Tm$^{3+}$:H$_6$ → $^4$G$_4$ transition. In the visible region (600–850 nm), the emission bands observed around 650 nm and 780 nm are ascribed to the Tm$^{3+}$:G$_4$ → $^3$F$_4$ and $^1$G$_4$ → $^3$H$_4$, respectively. In the NIR region (900–1300 nm), a strong emission band around 1000 nm assigned to the Yb$^{3+}$:2$^3$F$_{5/2}$ → 2$^3$F$_{7/2}$ is observed. The excitation band, associated with the charge transfer from the 2p$^6$ orbital of O$^2$ to the 4f$^1$ orbital of Yb$^{3+}$, centers around 250 nm in the CaSc$_2$O$_4$ according to our ultraviolet excitation spectrum. The direct excitation at 466 nm is far from the resonant excitation for Yb$^{3+}$ [9,21]. It is also a proof of Tm$^{3+}$ → Yb$^{3+}$ ET process.

It is noticed that the intensities of Tm$^{3+}$:G$_4$ → $^3$F$_4$ and $^1$G$_4$ → $^3$H$_4$ emissions have a decline as Yb$^{3+}$ is codoped. Simultaneously, the NIR emission of Yb$^{3+}$ increases rapidly with Yb$^{3+}$ concentration increasing. This is another evidence for the existence of ET from Tm$^{3+}$ to Yb$^{3+}$. For the higher Yb$^{3+}$ concentration over 5%, Yb$^{3+}$ emission is reduced due to concentration quenching [7]. In the present material, x = 5 represents optimal Yb$^{3+}$ doped concentration. Additionally, Yb$^{3+}$ emission contains two main peaks centered at 980 nm and 1010 nm, which are attributed to the transitions from the lowest Stark level of $^3$F$_{5/2}$ multiplet to different Stark levels of $^3$F$_{7/2}$ multiplet, respectively [22]. Due to the reabsorption of Yb$^{3+}$ ions, the relative intensity of 980 nm to 1010 nm peak decreases regularly with increasing Yb$^{3+}$ concentration [22]. Considering the nearest distance of Yb–Yb is short merely 3.19 Å [16], reabsorption of Yb$^{3+}$ ions is observed obviously in CaSc$_2$O$_4$ host. Unfortunately, the short Yb–Yb distance can speed up energy migration among Yb$^{3+}$ ions, which promotes the quenching process of Yb$^{3+}$ and back-energy transfer from Yb$^{3+}$ to Tm$^{3+}$ [3,16]. The weak emission around 1200 nm of Tm$^{3+}$:G$_4$ → $^3$H$_4$ is found, which can populate Tm$^{3+}$:H$_6$ level. The emission around 780 nm contains little influence of $^3$H$_4$ → $^3$H$_6$ emission [23]. Recently, Yu et al. have reported that three NIR photons can be obtained in NaYF$_4$ material upon excitation of Tm$^{3+}$:G$_4$ level with a blue photon by the efficient visible quantum splitting [24,25]. However, in our study, we do not find the intense NIR emissions of $^3$H$_4$ → $^3$F$_4$ around 1400 nm and $^3$F$_4$ → $^3$H$_6$ around 1800 nm in the Tm$^{3+}$ singly doped CaSc$_2$O$_4$.02%–Tm$^{3+}$ sample. It may be due to the higher phonon frequency of CaSc$_2$O$_4$ as an oxide host about 540 cm$^{-1}$, compared with that of the reported fluoride material NaYF$_4$ only 400 cm$^{-1}$. It promotes the multiphonon relaxation and inhibits radiative decay of $^3$H$_4$ level [24]. As Yb$^{3+}$ is codoped, the efficient Tm$^{3+}$ → Yb$^{3+}$ ET further suppresses quantum splitting of Tm$^{3+}$:G$_4$. In order to illustrate the QC process in CaSc$_2$O$_4$ phosphor definitively, the schematic energy level diagram with involved cooperative ET process is depicted in Fig. 3. The energy of Tm$^{3+}$:G$_4$ is located at approximately twice that of Yb$^{3+}$:2$^3$F$_{5/2}$ → 2$^3$F$_{7/2}$ transition, which can transfer to two different Yb$^{3+}$ ions through a cooperative ET mechanism: Tm$^{3+}$:G$_4$ → Yb$^{3+}$:2$^3$F$_{5/2}$ + Yb$^{3+}$:2$^3$F$_{7/2}$. The absence of energy level to the blue region allows Yb$^{3+}$ to exclusively accept energy from the red region of Tm$^{3+}$:G$_4$.
energy by cooperative ET. The process has also been demonstrated for the Tm\(^{3+}\)/Yb\(^{3+}\) codoped a range of host materials, such as borate [8], phosphate [11], fluoride [10], and oxide glass ceramic [9]. In addition, Yb\(^{3+}\):\(^{2}F_{5/2}\) level can also be populated by the phonon-assisted ET process, i.e., Tm\(^{3+}\):\(^{3}F_{4}\) + Yb\(^{3+}\):\(^{3}F_{4}\) \(\rightarrow\) Tm\(^{3+}\):\(^{2}F_{5/2}\) + Yb\(^{3+}\):\(^{5}L_{6}\) [23]. Actually, this process may be less efficient in CaSc\(_{2}\)O\(_{4}\) host. Firstly, the large energy mismatch between Tm\(^{3+}\):\(^{3}F_{4}\) \(\rightarrow\) \(^{3}H_{4}\) and Yb\(^{3+}\):\(^{3}F_{4}\) \(\rightarrow\) \(^{2}F_{7/2}\) transitions (approximately 2500 cm\(^{-1}\)) [23] together with the low phonon energy of CaSc\(_{2}\)O\(_{4}\) (only 540 cm\(^{-1}\)) makes the phonon-assisted ET process negligible [7]. Furthermore, the intensity ratio of Tm\(^{3+}\):\(^{3}F_{4}\) \(\rightarrow\) \(^{3}H_{4}\) (650 nm) to \(^{3}G_{4}\) \(\rightarrow\) \(^{3}H_{4}\) (780 nm) emission exhibits no significant change with the Yb\(^{3+}\) concentration increasing.

Fig. 3 shows the decay curves of Tm\(^{3+}\):\(^{3}G_{4}\) \(\rightarrow\) \(^{3}F_{4}\) in CaSc\(_{2}\)O\(_{4}\). Two infrared photons (around 1000 nm) are emitted by Yb\(^{3+}\) ions per absorbed one blue photon (around 466 nm) by Tm\(^{3+}\) ions. The \(\eta_{\text{QE}}\) defined as the ratio of the number of photons emitted to the number of photons that are absorbed, can be taken as:

\[
\eta_{\text{QE},X/YB} = \frac{\int I_{\text{X/YB}} dt}{\int I_{\text{abs}} dt} = 1 - \frac{\int I_{\text{X/YB}} dt}{\int I_{\text{abs}} dt}
\]

(2)

where \(I_{\text{X/YB}}\) represents for the intensity of 650 nm emission with various Yb\(^{3+}\) concentration. Considering the cooperative ET process, two infrared photons (around 1000 nm) are emitted by Yb\(^{3+}\) ions per absorbed one blue photon (around 466 nm) by Tm\(^{3+}\) ions. The \(\eta_{\text{ETE}}\) defined as a function of Yb\(^{3+}\) concentration:

\[
\eta_{\text{ETE},X/YB} = \frac{\int I_{\text{ETE,X/YB}} dt}{\int I_{\text{abs}} dt} = 1 - \frac{\int I_{\text{ETE,X/YB}} dt}{\int I_{\text{abs}} dt}
\]

(3)

where \(I_{\text{ETE}}\) and \(I_{\text{X/YB}}\) represent the quantum efficiencies of Tm\(^{3+}\) and Yb\(^{3+}\) ions, respectively. They are set to 1 [7], assuming that all excited ions decay radiatively. This assumption leads to an upper limit of the quantum efficiency. The \(\tau_{\text{eff}}\) as a function of Yb\(^{3+}\) concentration are shown in Fig. 5. The \(\tau_{\text{eff}}\) of Tm\(^{3+}\):\(^{3}G_{4}\) level decreases rapidly from 247.5 to 71.2 \(\mu\)s when Yb\(^{3+}\) concentration increases to 30%, which suggests the rather effective ET from Tm\(^{3+}\) to Yb\(^{3+}\) in CaSc\(_{2}\)O\(_{4}\) samples. With increasing Yb\(^{3+}\) concentration from 5% to 30%, the \(\eta_{\text{ETE}}\) increases from 111% to 171%, close to the limit of 200%. However, taking into account the concentration quenching of Yb\(^{3+}\), back-energy transfer from Yb\(^{3+}\) to Tm\(^{3+}\), and other non-radiative decay processes, the actual quantum efficiency in this material should be decreased [12]. The maximum energy transfer efficiency \(\eta_{\text{ETE}}\) is 71% and highest theoretical quantum efficiency \(\eta_{\text{QE}}\) reaches up to 171%, which demonstrate the Tm\(^{3+}\)/Yb\(^{3+}\) codoped CaSc\(_{2}\)O\(_{4}\) oxide material is an efficient downconversion candidate to enhance conversion efficiency of silicon solar cells.
powder materials, but CaSc$_2$O$_4$ phosphor glassy mate-
transition due to its level can emit two $^{3+}$
phosphor shows intense and broad absorption (350–
$^{43x154}$500 nm) and emission (450–700 nm)[17]. It implies that Ce
efficiency. Shimomura et al. have reported that Ce
should be combined for further improving the conversion
material by a conventional melting and quenching method are under-
is easily achieved. Studies on preparation of CaSc$_2$O$_4$ glassy
by a conventional melting and quenching method are under-
parent nature of CaSc$_2$O$_4$:0.2%Tm$^{3+}$/x%Yb$^{3+}$ (x = 0–30).

![Fig. 4. Decay curves of Tm$^{3+}$:1G$_4$ emission under 466 nm excitation in
CaSc$_2$O$_4$:0.2%Tm$^{3+}$/x%Yb$^{3+}$ (x = 0–30).](Image 48x342 to 288x520)

The application in solar cells may be hampered by non-trans-
transition of CaSc$_2$O$_4$:0.2%Tm$^{3+}$/x%Yb$^{3+}$ samples with different Yb$^{3+}$ concentration.
The narrow absorption band of Tm
forbidden 4f–4f transition, the broadband sensitizer for Tm
is the perfect sensitizer for cooperative QC of Tm
NIR photons around 1000 nm through cooperative ET from Tm$^{3+}$ to Yb$^{3+}$. The estimated maximum energy transfer efficiency ($\eta_{\text{ET}}$)
reaches up to 171%. The strong Yb$^{3+}$ emission intensity and high energy transfer efficiency indicate CaSc$_2$O$_4$:Tm$^{3+}$/Yb$^{3+}$ phosphor is a promising QC material for its application in solar cells.

4. Conclusions

In summary, an efficient NIR QC has been demonstrated for the
Tm$^{3+}$/Yb$^{3+}$ codoped CaSc$_2$O$_4$ phosphor. Upon excitation of Tm$^{3+}$:1G$_4$
level with a blue photon at 466 nm, Yb$^{3+}$:2F$_{5/2}$ level can emit two NIR photons around 1000 nm through cooperative ET from Tm$^{3+}$ to Yb$^{3+}$. The estimated maximum energy transfer efficiency ($\eta_{\text{ET}}$)
from Tm$^{3+}$ to Yb$^{3+}$ is 71%. The theoretical quantum efficiency ($\eta_{\text{TQE}}$)
reaches up to 171%. The strong Yb$^{3+}$ emission intensity and high energy transfer efficiency indicate CaSc$_2$O$_4$:Tm$^{3+}$/Yb$^{3+}$ phosphor is a promising QC material for its application in solar cells.

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