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Tb$^{3+}$–Er$^{3+}$ couples as spectral converters in NaYF$_4$ for GaAs solar cells

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Abstract

In order to reduce the thermal loss due to spectral mismatch of solar cell absorption, the quantum cutting with Tb$^{3+}$–Er$^{3+}$ couples as spectral converters is experimentally observed. One high-energy ultraviolet photon (Tb$^{3+}$ $^7F_6 \rightarrow ^5L_1$) is quantumly cut into two lower energy photons: one in the near-infrared region (Er$^{3+}$ $^4I_{9/2} \rightarrow ^4I_{15/2}$) and the other in the blue region (Tb$^{3+}$ $^5D_4 \rightarrow ^7F_6$), both of which can be efficiently absorbed by solar cells. A quantum efficiency, $\eta_{QE}$, of up to 188% is calculated, which is close to the theoretical limit of 200%. The energy mismatch in the energy transfer from Tb$^{3+}$ ($^5L_1 \rightarrow ^5D_4$) to Er$^{3+}$ ($^4I_{9/2} \rightarrow ^4I_{15/2}$) is 237 cm$^{-1}$, less than the phonon energy of 400 cm$^{-1}$ in NaYF$_4$, making the energy transfer nearly resonant. The energy migration among Tb$^{3+}$ donors is treated approximately by the diffusion model and the initial process of energy transfer among the Tb$^{3+}$–Er$^{3+}$ couples is found to be dipole–dipole interactions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Despite the abundance of solar energy, a very small part of it has been used directly in human activities. The enormous gap between the potential of solar energy and our applications is attributed to the high cost and low conversion efficiency [1]. The main causes of energy loss (over 70%) are related to the spectral mismatch of incident solar photon energies and the energy band gap $E_g$ of the hosts in solar cells [2, 3]. Photons with energies lower than the band gap are not absorbed, and for photons with energies exceeding the band gap, the ‘hot’ electrons and holes can be excited by the energy difference in the conduction and valence bands, respectively [4]. The population distribution of hot electrons follows the Maxwell–Boltzmann model,

$$N = N_0 \exp(-E/kT_{eff}),$$

where $T_{eff}$ is the effective temperature of the hot electrons in the conduction band. During the fast thermalization of the hot charge carriers, $T_{eff} \rightarrow T_L$ (lattice temperature), the excess energy is lost as heat.

There are two approaches to resolving the spectral mismatch: upconversion and downconversion (DC) or quantum cutting. DC is defined as the ‘cutting’ of one high-energy photon into two lower energy photons, both of which can be absorbed by the solar cells. This process can reduce the energy loss related to the thermalization of hot charge carriers after the absorption of a high-energy photon. The possibility of obtaining luminescent quantum yield greater than unity was proposed by Dexter more than 50 years ago [5]. The DC for increasing the efficiency of solar cells was realized by Trupke et al in 2002 [6]. The first experimental demonstration of DC for solar cells involving Tb$^{3+}$–Yb$^{3+}$ couples, where quantum cutting was achieved through cooperative energy transfer from a Tb$^{3+}$ to two Yb$^{3+}$ ions, was carried out by Vergeer et al in 2005, which also gave an approach to estimating energy transfer efficiency, $\eta_{ET}$, and quantum efficiency, $\eta_{QE}$ [7]. The band-gap energy of c-Si solar cells is 1.12 eV (1110 nm), which is close to the Yb$^{3+}$ $^2F_{7/2} \rightarrow ^2F_{5/2}$ emission at 1000 nm. Therefore, Yb$^{3+}$ is ideally suited for use in the DC for c-Si solar cells. Further results were also reported on Tb$^{3+}$–Yb$^{3+}$ [8, 9], Tm$^{3+}$–Yb$^{3+}$ [10–12], Pr$^{3+}$–Yb$^{3+}$ [10, 13–15], Er$^{3+}$–Yb$^{3+}$ [16] and Nd$^{3+}$–Yb$^{3+}$ [17] ion couples or reviewed [3, 18].

The air mass coefficient characterizes the solar spectrum after travelling through the atmosphere. The coefficient is defined as the ratio of the solar radiation path length $\ell$ to the atmosphere thickness $\ell_0$, namely $\ell/\ell_0$. It is commonly used to characterize the performance of solar cells under
standardized conditions referred to as ‘AM’ followed by a number. DC is therefore expected to provide the greatest benefits for solar radiation of smaller air mass coefficients, especially for the extraterrestrial solar radiation (air mass coefficient AM0), and for diffuse terrestrial solar radiation (air mass coefficient AM1.5G) [2]. A solar cell based on GaAs ($E_p = 1.43$ eV, ~867 nm) has a higher conversion efficiency up to 32% and tolerance to cosmic ray, providing the potential for applications in space, e.g. for satellites and space vehicles. In the extraterrestrial space the solar radiation has stronger ultraviolet (UV) radiation compared with that on the earth surface. By cutting a high-energy UV photon ($\lambda_{ex} = 294$ nm) into two lower energy photons, one in the near-infrared region at $\lambda_1 = 800$ nm and the other in the blue region at $\lambda_2 = 470$ nm, the energy loss due to thermalization in GaAs solar cells can be significantly reduced.

Hexagonal sodium yttrium fluoride, NaYF$_4$ or NYF, is the most efficient host material to date for green (Yb$^{3+}$/Er$^{3+}$-doped) and blue (Yb$^{3+}$/Tm$^{3+}$-doped) upconversion phosphors. Recently, NYF has also been demonstrated to be a good host material for DC. The phonon energy of fluoride crystals is smaller than that of oxide crystals. The maximum phonon energy is only ~400 cm$^{-1}$ in NYF [16].

This work reports the dipole–dipole interaction governed interaction between Tb$^{3+}$–Er$^{3+}$ couples. The energy migration dynamics of the donor Tb$^{3+}$ can be well described by the diffusion limited model. The energy transfer efficiency $\eta_{ET}$ for the Tb$^{3+}$–Er$^{3+}$ couples in NYF is as high as 88%. Efficient quantum cutting is observed for Tb$^{3+}$–Er$^{3+}$ couples, i.e. DC from Tb$^{3+}$ 5L$_1$ level occurs through energy transfer to Er$^{3+}$ ions with a quantum efficiency $\eta_{QE} = 188\%$, which is close to the theoretical limit of 200%.

2. Experimental

A sunlight (optical parametric oscillator, OPO) laser was used as the exciting source. Emission spectra were detected using a JY TRIAX 550 monochromator with a R955 photomultiplier tube. A TDS 3052 digital phosphor oscilloscope was used to record the luminescence decay curves. The lifetime measurements were performed monitoring donor Tb$^{3+}$ emission at 470 nm ($^5$D$_4 \rightarrow ^7$F$_{g}$) under excitation of Tb$^{3+}$ $^7$F$_6 \rightarrow ^5$L$_1$ (294 nm). The luminescent and decay signals were processed by a Boxcar Averager (Model 162).

To study the conversion efficiency and mechanism of DC by the Tb$^{3+}$–Er$^{3+}$ couples, a series of crystalline powder samples NYF : Tb$^{3+}$ 1 mol%, Er$^{3+}$ x mol% ($x = 0, 1, 2, 3, 5$) was prepared by the solid-state method similar to the description in [15]. The powders of fluorides NaF, TbF$_3$, ErF$_3$ and Y$_2$O$_3$ were mixed and pestled carefully. Firing was done in a nitrogen atmosphere at temperatures between 650 and 950 °C in the presence of excess NH$_4$F.

3. Results and discussion

Energy levels and quantum cutting mechanism for the Tb$^{3+}$–Er$^{3+}$ couples are shown in figure 1. Under UV excitation of Tb$^{3+}$ $^7$F$_6 \rightarrow ^5$L$_1$ (294 nm), depopulation of $^5$L$_1$ state can occur through resonant energy transfer Tb$^{3+}$ ($^5$L$_1 \rightarrow ^5$D$_4$, 12 737 cm$^{-1}$) $\rightarrow$ Er$^{3+}$ ($^4$I$_{15/2} \rightarrow ^4$I$_{9/2}$, 12 500 cm$^{-1}$) with $^5$D$_4$ acting as an intermediate level. The results in the creation of two photons, 800 and 470 nm. In figure 2 the emission spectra are shown for five samples prepared under identical conditions. The spectra are corrected for instrumental response. The strong emissions of Er$^{3+}$ $^4$I$_{15/2} \rightarrow ^4$I$_{9/2}$ under excitation of Tb$^{3+}$ $^7$F$_6 \rightarrow ^3$I$_1$ are observed in the emission spectra of co-doped NYF : Tb$^{3+}$ 1 mol%, Er$^{3+}$ x mol% ($x = 1, 2$), indicating the efficient energy transfer Tb$^{3+}$ $\rightarrow$ Er$^{3+}$. The intensity of Er$^{3+}$ $^4$I$_{15/2} \rightarrow ^4$I$_{9/2}$ gradually decreases with an increase in Er$^{3+}$ concentration ($x = 3, 5$). In figure 3, the luminescent decay curves of Tb$^{3+}$ at 470 nm of the donor Tb$^{3+}$ emission
can be characterized, in particular, for disordered decay upon the multipole–multipole interaction in our case; therefore, Eq. (1) can be ignored compared with that from the dipole–dipole and dipole–quadrupole couplings, respectively. The contributions from quadrupole couplings, especially for small values of time $t \ll 0.006$, where $t_0 = 46.19 \mu s$ is the lifetime of singly doped donor Tb$^{3+}$.

The experimentally measured functions $\ln[I(t)/I(0)] + t/t_0$ is plotted versus $t/t_0$ for small times ($t/t_0 < 0.006$, where $t_0 = 46.19 \mu s$ is the decay time of donor Tb$^{3+}$ in the acceptor-free sample (see figure 4). By fitting the linear parts of the decay curves in figure 4 by equation (2), the constants $\gamma_{dd}$ are estimated, then parameters $C_{DA}$ are computed using equation (2).

2. The migration-limited decay (corresponding to the migration of the excitation energy through donors towards an acceptor), where

$$I(t) = I(0)\exp[-\Delta - W^*t - t/t_0].$$

Here the constants $\Delta$ and $W^*$ are shape parameters. The expression for $W^*$ essentially depends on the ratio $Z = C_{DA}/C_{DD}$. The energy migration is diffusion-limited [19] or hopping-limited [20] if $Z \gg 1$ or $Z \ll 1$. The initial non-exponential part in the presence of an exponential tail indicates that the energy migration is diffusion-limited [22], i.e.

$$W^* = \frac{1}{2}(4\pi)^2(1/2)^{3/4}N_A N_D(C_{DA})^{1/4}(C_{DD})^{3/4}.$$  

Moreover, the shape parameters for the hopping mechanism is

$$W^{sh} = \frac{8\pi^3}{9 \times 2^{1/2}} N_A N_D(C_{DA}C_{DD})^{1/2}.$$  

Using $C_{DA}$ and $W^*$, and assuming diffusion-limited energy migration, one can compute the parameter $C_{DD}$ by solving equation (6). The values of $\gamma_{dd}$ and $W^*$, together with the computed values of $C_{DA}$ and $C_{DD}$, are listed in table 1. Note that the ratio of $Z = C_{DA}/C_{DD}$ is of the order of $10^5$. This supports the hypothesis that energy migration in the Tb$^{3+}$-doped samples is diffusion-limited. At the same time, assuming hopping-limited migration, one comes to a contradiction: solving equation (7), we obtained $Z$ of the order of $10^5$ to $10^7$, which is inconsistent with inequality $Z \ll 1$. It is just indicated in figure 5 that the experimental values $W_{exp}$ of energy migration in the Tb$^{3+}$-doped samples approach that of the diffusion-limited one.
Figure 5. The shape parameters describing the energy migration dynamics of donor Tb\(^{3+}\). \(W^{\text{exp}}\) (squares, for hopping-limited, equation (6)), \(W^{\text{h}}\) (circles, for hopping-limited, equation (7)) and experimental value \(W^{\ast}_{\exp}\) (triangles) for various acceptor concentrations are plotted, respectively.

The energy transfer efficiency \(\eta_{\text{ET}}\) is defined as the ratio of the number of donors that are depopulated by energy transfer to the acceptors to the total number of donors being excited. By dividing the mean lifetime of the defect emission of Er\(^{3+}\)-doped NYF by that of the Er\(^{3+}\)-free NYF, the transfer efficiency is obtained as a function of Er\(^{3+}\) concentration [7]:

\[
\eta_{\text{ET},x\%\text{Er}} = 1 - \frac{\int I_{x\%\text{Er}} \, dt}{\int I_{0\%\text{Er}} \, dt}, \quad (8)
\]

where \(x\) represents the Er\(^{3+}\) concentration. It is observed that the transfer efficiency reaches a maximum of 88% when 2 mol% Er\(^{3+}\) is doped.

From these luminescent decay curves, the quantum efficiency \(\eta_{\text{QE}}\) can be estimated by the following equation:

\[
\eta_{\text{QE}} = \eta_{\text{TB}} (1 - m_{\%\text{Er}}) + 2 m_{\%\text{Er}}, \quad (9)
\]

where \(\eta_{\text{TB}}\) stands for the luminescent quantum efficiency of Tb\(^{3+}\) and is set to 1. For lower concentrations \((x \leq 5)\), this method of estimating \(\eta_{\text{QE}}\) is available. Accordingly, it has been determined that the \(\eta_{\text{QE}}\) from the \(5D_{4}\) level are 176%, 188%, 124% and 163% for samples with 1 mol%, 2 mol%, 3 mol% and 5 mol% Er\(^{3+}\), respectively. A maximum \(\eta_{\text{QE}}\) of 188% close to the limit of 200% is obtained for two possible reasons: (1) the mismatch of 237 cm\(^{-1}\) in the energy transfer from Tb\(^{3+}\) \(5L_{1} \rightarrow 5D_{4}\) (12 737 cm\(^{-1}\)) to Er\(^{3+}\) \(4I_{15/2} \rightarrow 4I_{13/2}\) (12 500 cm\(^{-1}\)) is less than the phonon energy 400 cm\(^{-1}\), making the transfer nearly resonant; (2) the energy loss of non-radiative transitions to the defects and impurities is negligible or the process is dominated by resonant energy transfer (1).

4. Conclusions

In summary, a series of crystalline powder samples NYF: Tb\(^{3+}\) 1 mol%, Er\(^{3+}\) \(x\) mol% \((x = 0, 1, 2, 3, 5)\) was prepared and effective quantum cutting of Tb\(^{3+}\)-Er\(^{3+}\) couples in NYF was observed. The results may improve the energy absorption in GaAs solar cells and increase their efficiency. The initial process of the energy transfer between Tb\(^{3+}\) and Er\(^{3+}\) is nearly resonant and it is governed by the dipole–dipole interaction. The energy transfer efficiency, \(\eta_{\text{ET}}\), from Tb\(^{3+}\) to Er\(^{3+}\) in NYF and quantum cutting efficiency, \(\eta_{\text{QE}}\), are observed to be 88% and 188%, respectively. The latter is close to the theoretical limit of 200%.

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References


[18] Zhang Q Y and Huang X Y 2010 *Prog. Mater. Sci.* **55** 353


