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Spectral Modification and Quantum Cutting in RE\textsuperscript{3+}-Yb\textsuperscript{3+} (R=Pr, Tm, and Tb) Codoped Transparent Glass-ceramics Containing CaF\textsubscript{2} Nanocrystals

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Abstract. We report on the cooperative energy transfer process in RE\textsuperscript{3+}-Yb\textsuperscript{3+} (RE=Pr, Tm and Tb) codoped transparent glass-ceramics containing CaF\textsubscript{2} nanocrystals, which are capable of splitting a visible photon absorbed by RE\textsuperscript{3+} into two near infrared photons emitted by Yb\textsuperscript{3+}. The formation of CaF\textsubscript{2} nanocrystals in the glass-ceramics was confirmed by X-ray diffraction measurement. Yb\textsuperscript{3+} emission in the wavelength range of 950-1100 nm (\textit{2F}_{5/2} \rightarrow \textit{2F}_{7/2}) was observed upon the excitation of \textit{3P}_0 energy level of Pr\textsuperscript{3+} at 482 nm, \textit{1G}_4 energy level of Tm\textsuperscript{3+} at 468 nm, and \textit{5D}_4 energy level of Tb\textsuperscript{3+} at 484 nm, respectively, in the RE\textsuperscript{3+}-Yb\textsuperscript{3+} co-doped glass-ceramics. The energy transfer process was proved by the excitation and emission spectra. The Yb\textsuperscript{3+} concentration dependent quantum efficiency was also evaluated individually in the codoped systems, which indicated that Pr\textsuperscript{3+}-Yb\textsuperscript{3+} is the most efficient cooperative energy transfer couple. It was supposed that besides the cooperative energy transfer process, the \textit{1G}_4 state, which may be populated by \textit{3P}_0 \rightarrow \textit{1G}_4 transition as a result of energy transfer to one Yb\textsuperscript{3+} ion from Pr\textsuperscript{3+}\textit{3P}_0 energy level, can also act as a donor state in the energy transfer to another Yb\textsuperscript{3+} ion. These rare-earth ions codoped transparent glassy materials may have potential applications for the enhancement of photovoltaic conversion efficiency of silicon solar cells via spectra modification.

1. Introduction

In face of the energy crisis, it is necessary to develop and take advantage of new and renewable energy to suppress the negative effects caused by the vast consumption and depletion of the traditional mineral fuel. As a convenient, green and renewable resource, the solar energy will surely play an important role in the future energy-structure. Now, solar photovoltaic industry is attracting more attention worldwide for it can offer a clean and high-efficient energy system to take better usage of the solar energy. At present, the most popular solar cell is crystalline silicon based. For decades, people have been trying to improve the photovoltaic conversion efficiency of solar cells by optimizing the treatment process of the materials. However, the experts in solar cell have pointed out that the further
enhancement of photovoltaic conversion efficiency should be mainly based on the modification of input solar spectra [1]-[2].

There are three technique routes for spectral modification: Up conversion luminescence process, down conversion luminescence process, and photoluminescence process [3]-[6]. Up to now, some research focused on down conversion luminescence process have been done in rare-earth ions doped systems, which can take full usage of the near-ultraviolet and visible parts of the solar spectra [7]-[11]. Among them, the transparent glass-ceramics containing fluoride nanocrystals is an promising candidate for practical application by putting it in front of solar cells due to the combination advantages of excellent chemical durability and mechanical strength, high transparency to visible light, as well as low photon energy in the precipitated fluoride nanocrystals where the doped rare-earth ions will selectively incorporated into during the crystallization process [9], [12]. In this paper, we demonstrated the infrared quantum cutting through cooperative energy transfer in RE$^{3+}$-Yb$^{3+}$ (RE= Pr, Tm, and Tb) codoped glass-ceramics containing CaF$_2$ nanocrystals. The excitation and emission spectra and the schematic energy level of the related rare-earth ions were present to prove the existence of cooperative energy transfer from one RE$^{3+}$ ion to two Yb$^{3+}$ ions, which consequently results in the infrared emission around 1000 nm, at which wavelength the silicon solar cells exhibit their greatest spectral response. The quantum efficiency was also evaluated as a function of Yb$^{3+}$ concentration, which showed different concentration dependent for Pr$^{3+}$-Yb$^{3+}$, Tm$^{3+}$-Yb$^{3+}$, and Tb$^{3+}$-Yb$^{3+}$ couples.

2. Experimental

Oxyfluoride glasses with compositions of 60SiO$_2$-20Al$_2$O$_3$-20CaF$_2$-0.4mol%Tb$^{3+}$-xRE$^{3+}$ (RE=Pr, Tm and Tb, respectively; x=0, 1, 2, 4, 8, 12, 16, 20, 24 or 28mol%, respectively) were prepared by using high purity (99.99%) SiO$_2$, Al$_2$O$_3$, CaF$_2$, PrF$_3$, TmF$_3$, TbF$_3$ and YbF$_3$ as raw materials, which were mixed homogeneously and melted at 1400 °C for 30 min in a covered corundum crucible in air. The melts were poured onto a cold brass plate and then pressed by another plate. Differential thermal analysis (DTA) measurements were carried out in a SDT Q600 differential thermal analyzer, from which we determined a heat treatment temperature of 660 °C. The thermal treatment duration was 2 h for all the as-made glasses. X-ray diffraction measurements were carried out using a Rigaku D/MAX-RA diffractometer with Cu K$_{α}$ as the incident radiation source. The excitation and emission spectra and the fluorescence decay curves in both the visible and infrared regions were recorded with a FLS920 fluorescence spectrophotometer.

3. Results and discussion

Figure 1 shows the XRD patterns of 0.4 mol% RE$^{3+}$- 4mol% Yb$^{3+}$ (RE=Pr, Tm and Yb, respectively) codoped as-made glasses and glass-ceramics obtained by heat treatment at 660 °C for 2 h.
It is observed that the as-made glass is completely amorphous with no diffraction peaks, and after crystallization by heat treatment, the XRD pattern shows intense diffraction peaks, which could be assigned to the cubic CaF$_2$ phase. The calculated average crystallite size of CaF$_2$ is 18 nm by using Scherrer’s equation. The average transmittance for both the as-made glass and glass-ceramics in the visible region is higher than 90%.

The excitation and emission spectra for 0.4 mol% RE$_3^{+}$ single doped and 0.4 mol% RE$_3^{+}$-4 mol% Yb$_3^{+}$ codoped glass-ceramics, together with the corresponding energy levels, are presented in Figs. 2, 3 and 4, respectively, to provide the direct evidence of energy transfer.

From the Pr$_3^{+}$-doped excitation and emission spectra in Fig. 2 (A) we can observe that the excitation bands situated at 482, 468, and 441 nm, assigned to the transitions of Pr$_3^{+}$ $^3$H$_4$$^3$P$_j$ transitions (j=0, 1, and 2) were detected by monitoring both the $^3$P$_0$$^3$H$_6$ transition of Pr$_3^{+}$ at 605 nm and the $^2$F$_{5/2}$$^2$F$_{7/2}$ transition of Yb$_3^{+}$ at 980 nm, which indicates the existence of energy transfer from Pr$_3^{+}$ to Yb$_3^{+}$. Moreover, in the Pr$_3^{+}$-Yb$_3^{+}$ codoped glass-ceramics, the observance of Yb$_3^{+}$ infrared emission and the decrease of Pr$_3^{+}$ $^3$P$_0$$^3$H$_6$ and $^3$P$_0$$^3$F$_2$ transition emission intensities under 482 nm excitation also shows the occurrence of energy transfer. By the way, the weak infrared emission at 1030 nm in Pr$_3^{+}$ single doped glass-ceramics is originated from Pr$_3^{+}$ $^1$G$_4$$^3$H$_4$ transition [13]. Since it was proved experimentally that the second-order process is responsible for the upconversion luminescence in Yb$_3^{+}$-Pr$_3^{+}$ codoped systems [14], the cooperative downconversion may occur as well: two infrared photons emitted by Yb$_3^{+}$ could be obtained through one visible photon absorbed by Pr$_3^{+}$.

![Figure 2. (A)](image1.png)  
![Figure 2. (B)](image2.png)  

Figure 2. (A): Left side: Excitation spectra of Pr$_3^{+}$ 605 nm emission monitored in 0.4mol% Pr$_3^{+}$ single doped glass-ceramics (black line) and Yb$_3^{+}$ 980 nm emission monitored in 0.4mol% Pr$_3^{+}$-1mol% Yb$_3^{+}$ codoped glass-ceramics (red line). Right side: Emission spectra of 0.4mol% Pr$_3^{+}$ and 0.4mol% Pr$_3^{+}$-1mol% Yb$_3^{+}$, under 482 nm excitation (green line and blue line, respectively). (B): Schematic energy level diagram of Pr$_3^{+}$ and Yb$_3^{+}$ with transitions that may be responsible for the cooperative energy transfer.

Figure 3 (A) depicts the excitation and emission spectra of Tm$_{3}^{3+}$ single-doped and Tm$_{3}^{3+}$-Yb$_{3}^{3+}$ codoped glass-ceramics. The excitation band corresponding to Tm$_{3}^{3+}$ 651 nm emission is situated at 468 nm, which is assigned to $^3$H$_6$$^3$G$_4$ absorption. In the Tm$_{3}^{3+}$-Yb$_{3}^{3+}$ codoped glass-ceramics, the excitation spectra of Yb$_{3}^{3+}$ infrared emission at 980 nm is in good agreement with Tm$_{3}^{3+}$ $^3$H$_6$$^3$G$_4$ absorption, which indicates the performance of energy transfer. Meanwhile, the emission spectra of Tm$_{3}^{3+}$ single-doped and Tm$_{3}^{3+}$-Yb$_{3}^{3+}$ codoped glass-ceramics were recorded under the excitation of Tm$_{3}^{3+}$ $^3$H$_6$$^3$G$_4$ absorption at 468 nm. By comparing these spectra we can observe that the emission
intensities of Tm$^{3+}$ at 651 nm and 786 nm decrease with the introduction of Yb$^{3+}$, and for the codoped sample, Yb$^{3+}$ emission in the infrared region is observed under the excitation of Tm$^{3+}$ $3H_6 \rightarrow G_4$ absorption. This is another evidence of the energy transfer from Tm$^{3+}$ to Yb$^{3+}$.

Figure 3. (A)
Figure 3. (B)

Figure 3. (A): Left side: Excitation spectra of Tm$^{3+}$ 651 nm emission monitored in 0.4mol% Tm$^{3+}$ single doped glass-ceramics (black line) and Yb$^{3+}$ 980 nm emission monitored in 0.4mol% Tm$^{3+}$-4mol% Yb$^{3+}$ codoped glass-ceramics (red line). Right side: Emission spectra of 0.4mol% Tm$^{3+}$ and 0.4mol% Tm$^{3+}$-4mol% Yb$^{3+}$, under 468 nm excitation (green line and blue line, respectively). (B): Schematic energy level diagram of Tm$^{3+}$ and Yb$^{3+}$ with transitions that may be responsible for the cooperative energy transfer.

Figure 4. (A)
Figure 4. (B)

Figure 4. (A): Left side: Excitation spectra of Tb$^{3+}$ 542 nm emission monitored in 0.4mol% Tb$^{3+}$ single doped glass-ceramics (black line) and Yb$^{3+}$ 980 nm emission monitored in 0.4mol% Tb$^{3+}$-4mol% Yb$^{3+}$ codoped glass-ceramics (red line). Right side: Emission spectra of 0.4mol% Tb$^{3+}$ and 0.4mol% Tb$^{3+}$-4mol% Yb$^{3+}$, under 484 nm excitation (green line and blue line, respectively). (B): Schematic energy level diagram of Tb$^{3+}$ and Yb$^{3+}$ with transitions that may be responsible for the cooperative energy transfer.
The excitation and emission spectra of Tb\(^{3+}\) single-doped and Tb\(^{3+}\)-Yb\(^{3+}\) codoped glass-ceramics are shown in Fig. 4 (A), which shows that the excitation band corresponding to Tb\(^{3+}\) 542 nm emission is located at 484 nm, and in the Tb\(^{3+}\)-Yb\(^{3+}\) codoped glass-ceramic, the excitation spectra of Yb\(^{3+}\) infrared emission at 980 nm overlaps with Tb\(^{3+}\) \(^7\)F\(_6\)\(-\)\(^5\)D\(_4\) absorption band well, indicating the performance of energy transfer. Meanwhile, Yb\(^{3+}\) emission is observed in the infrared region of 950-1100 nm with the excitation of Tb\(^{3+}\) \(^7\)F\(_6\)\(-\)\(^5\)D\(_4\) absorption at 484 nm in the codoped glass-ceramic, as a result of energy transfer from Tb\(^{3+}\) to Yb\(^{3+}\) [15].

Figures 2 (B), 3 (B) and 4 (B) depict the schematic energy levels which may be involved in the cooperative energy transfer process from one RE\(^{3+}\) ion to two Yb\(^{3+}\) ions. The \(^3\)P\(_0\) energy level of Pr\(^{3+}\), the \(^3\)G\(_4\) energy level of Tm\(^{3+}\) and the \(^3\)D\(_4\) energy level of Tb\(^{3+}\) are situated just above twice the \(^2\)F\(_{5/2}\) energy level of Yb\(^{3+}\), and the energy gap between \(^3\)P\(_0\) and \(^1\)D\(_2\) of Pr\(^{3+}\), \(^1\)G\(_4\) and \(^1\)F\(_2\) of Tm\(^{3+}\), and \(^3\)D\(_4\) and \(^1\)F\(_0\) of Tb\(^{3+}\) is large so that the multi-phonon assisted rapid non-radiative decay rate is small in the low photon energy atmosphere of oxyfluoride glass-ceramics, indicating the cooperative energy transfer process may occurs dominantly between RE\(^{3+}\) and Yb\(^{3+}\).

In order to further investigate the cooperative energy transfer process, the luminescence decays of Pr\(^{3+}\) at 606 nm (\(^3\)P\(_0\)\(-\)\(^3\)H\(_6\) transition), Tm\(^{3+}\) at 651 nm (\(^1\)G\(_4\)\(-\)\(^3\)F\(_4\) transition), and Tb\(^{3+}\) at 542 nm (\(^3\)D\(_4\)\(-\)\(^3\)F\(_3\) transition) are recorded, respectively, with 482 (\(^3\)H\(_4\)\(-\)\(^3\)P\(_0\) absorption), 468 (\(^3\)H\(_4\)\(-\)\(^3\)G\(_4\) absorption), and 484 nm (\(^3\)F\(_6\)\(-\)\(^3\)D\(_4\) absorption) excitation, as shown in Fig. 5 (A, B and C). The doping concentration of Pr\(^{3+}\), Tm\(^{3+}\) and Tb\(^{3+}\) is fixed at 0.4 mol%, while Yb\(^{3+}\) concentration is increased from 0 to 20 mol% for Pr\(^{3+}\) doped glass-ceramics and to 28 mol% for Tm\(^{3+}\) or Tb\(^{3+}\) doped glass-ceramics, respectively. The faster luminescence decay of Pr\(^{3+}\) at 606 nm, Tm\(^{3+}\) at 651 nm, and Yb\(^{3+}\) at 542 nm with the introduction and increasing doping concentration of Yb\(^{3+}\) can be attributed to the faster depopulation of \(^3\)P\(_0\) (Pr\(^{3+}\)), \(^3\)G\(_4\) (Tm\(^{3+}\)), and \(^3\)D\(_4\) (Tb\(^{3+}\)) energy level, respectively, due to the presence of Yb\(^{3+}\) acceptors as an extra decay pathway, indicating the occurrence of cooperative energy transfer from RE\(^{3+}\) to Yb\(^{3+}\).

Figure 5. Luminescence decay curves of Pr\(^{3+}\) emission at 605 nm (\(\lambda_{ex}=482\) nm), Tm\(^{3+}\) emission at 651 nm (\(\lambda_{ex}=468\) nm), and Tb\(^{3+}\) emission at 542 nm (\(\lambda_{ex}=484\) nm). The doping concentration is 0.4mol% RE\(^{3+}\)-xYb\(^{3+}\), x=0, 1, 2, 4, 8, 12, 16, and 20 mol%, respectively, for Pr\(^{3+}\) doped glass-ceramic and 0, 1, 4, 8, 12, 16, 20, 24, and 28 mol%, respectively, for Tm\(^{3+}\) and Tb\(^{3+}\) doped glass-ceramics.
The luminescence decay rate can be expressed as \( W = W_r + W_{nr} + W_{ET} \), where \( W_r \), \( W_{nr} \) and \( W_{ET} \) represents for the radiative, nonradiative and energy transfer rate, respectively, based on which, the energy transfer rate \( W_{ET} \) can be written as \( W_{ET} = W - (W_r + W_{nr}) = \tau^{-1} - \tau_0^{-1} \), where \( \tau \) and \( \tau_0 \) denotes the lifetime of the donor in the presence and absence of acceptors. The energy transfer efficiency is defined as \( \eta_{ET} = W_{ET} / W \). Based the formula above, we obtain \( \eta_{ET} = 1 - \tau / \tau_0 \) [16]-[17]. Since the luminescence decays non-exponentially, the value of lifetime is treated as mean-lifetime by \( \tau_m = \int_{t_0}^{\infty} \frac{I(t)}{I_0} dt \), where \( I(t) \) is the luminescence intensity as a function of time \( t \), and \( I_0 \) is the maximum of \( I(t) \) which occurs at the initial time \( t_0 \). The total quantum efficiency, \( \eta_{QE} \), can be defined as the ratio of the photons emitted to the photons that are absorbed, assuming that all excited \( \text{Yb}^{3+} \) ions decay radiatively. This assumption leads to an upper limit of the quantum efficiency. The relationship between the transfer efficiency and the quantum efficiency is linear and is defined as \( \eta_{QE} = \eta_{RE-r} (1 - \eta_{ET}) + 2\eta_{ET} \), in which the quantum efficiency for \( \text{RE}^{3+} \) ions, \( \eta_{RE-r} \), is set to 1 [7], [18].

According the measured lifetime data in Fig. 5, the quantum efficiency is evaluated as a function of \( \text{Yb}^{3+} \) concentration in the RE\(^{3+}\)-\( \text{Yb}^{3+} \) codoped glass-ceramics. The evaluated quantum efficiencies are presented in Fig. 6, which shows that the quantum efficiency for \( \text{RE}^{3+}\)-\( \text{Yb}^{3+} \) all increases with increasing \( \text{Yb}^{3+} \) concentration, and with the highest value of 184% for \( \text{Pr}^{3+}\)-\( \text{Yb}^{3+} \), 183% for \( \text{Tm}^{3+}\)-\( \text{Yb}^{3+} \), and 152% for \( \text{Tb}^{3+}\)-\( \text{Yb}^{3+} \), respectively. However, the quantum efficiency shows different concentration dependence. For the \( \text{Pr}^{3+}\)-\( \text{Yb}^{3+} \) codoped glass-ceramics, the quantum efficiency increases very fast with increasing \( \text{Yb}^{3+} \) concentration compared to \( \text{Tm}^{3+}\)-\( \text{Yb}^{3+} \) and \( \text{Tb}^{3+}\)-\( \text{Yb}^{3+} \) couple, and reaches its max value at comparatively low \( \text{Yb}^{3+} \) doping of 8 mol% and keeps these saturate value with higher \( \text{Yb}^{3+} \) concentration.

![Figure 6. Yb\(^{3+}\) concentration dependent quantum efficiency for RE\(^{3+}\)-Yb\(^{3+}\) codoped glass-ceramics (RE= Pr, Tm, and Tb).](image)

This can be explained as follow: From the energy level of \( \text{Pr}^{3+}\)-\( \text{Yb}^{3+} \) in Fig. 2(B) we can observe that the \( ^1G_4 \) energy level of \( \text{Pr}^{3+} \) situated almost the same as the energy level of \( \text{Yb}^{3+}\ 2F_{5/2} \), and the transition from the \( ^1G_4 \) energy level to the ground state of \( ^3H_5 \) results in an infrared emission at 1030 nm, as shown in Fig. 2 (A). We then suppose that the excited \( ^3P_0 \) energy level may transfer part of its energy to one \( \text{Yb}^{3+} \) ion by putting it into the excited state and relaxing to the \( ^1G_4 \) energy level simultaneously, and then the \( ^1G_4 \) energy level acts as another donor level and transfer the residual energy to another \( \text{Yb}^{3+} \) ion, with photon assistant. That is to say, that besides the cooperative energy...
transfer process, the $^1G_4$ energy level also plays as a donor level which may transfer energy to another Yb$^{3+}$ ion after one Yb$^{3+}$ ion is excited by Pr$^{3+}$ $^3P_0 \rightarrow ^1G_4$ transition, which leads to more efficient energy transfer from Pr$^{3+}$ to Yb$^{3+}$. However, which transfer process is mainly responsible for the infrared emission originated from Yb$^{3+}$ $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition is still under investigation.

4. Conclusion
In summary, RE$^{3+}$-Yb$^{3+}$ codoped transparent oxyfluoride glass-ceramics containing CaF$_2$ nanocrystals were investigated as downconversion layer candidates to enhance the photovoltaic conversion efficiency of silicon solar cells via spectra modification. Excitation, emission and decay measurements were performed to prove the occurrence of cooperative energy transfer between RE$^{3+}$ and Yb$^{3+}$ ions, which lead to 950-1100 nm infrared emission subsequently. The quantum efficiency as a function of Yb$^{3+}$ concentration is evaluated in Pr$^{3+}$-Yb$^{3+}$, Tm$^{3+}$-Yb$^{3+}$, and Tb$^{3+}$-Yb$^{3+}$ couples, which indicates that the Pr$^{3+}$-Yb$^{3+}$ codoped one is more efficient in energy transfer compare to the other two. It is supposed that besides the cooperative energy transfer process, the $^1G_4$ level, which may be populated by $^3P_0 \rightarrow ^1G_4$ transition as a result of energy transfer to one Yb$^{3+}$ ion from $^3P_0$ energy level of Pr$^{3+}$, can also act as a donor state which may excite another Yb$^{3+}$ ion.

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