**UV-Vis-NIR QUANTUM CUTTING SUITABLE FOR c-Si SOLAR CELL APPLICATION**

Yagoub M.Y.A, Swart H.C and Coetsee E. *

*Author for correspondence  
Department of Physics  
University of the Free State, PO Box 339  
Bloemfontein, 9300,  
South Africa,  
E-mail: coetsee@ufs.ac.za

**ABSTRACT**

The possibility of using the broad band spectra of Eu$^{2+}$ to improve the absorption of the Pr$^{3+}$-Yb$^{3+}$ quantum cutting couple was investigated. The energy transfer mechanisms between Eu$^{2+}$ and Pr$^{3+}$ in the SrF$_2$ host are briefly discussed in order to evaluate the potential of Eu$^{2+}$ as a sensitizer for the Pr$^{3+}$-Yb$^{3+}$ couple. The results showed that Eu$^{2+}$ could be a good sensitizer for the absorption of UV photons and efficiently enhancing the Pr$^{3+}$ emission, and hence improving the near infrared emission. The investigated system can therefore enable the c-Si solar cell to utilize the solar spectrum more efficiently in the broad wavelength region where c-Si shows a weak response.

**INTRODUCTION**

Phosphor materials have been successfully used to improve the efficiency of various applications [1, 2]. Recently, the use of lanthanide materials based on lanthanide ions to boost the efficiency of the Si solar cells have been suggested [3, 4, 5]. The major problem that limits the solar cells’ efficiency is their insensitivity to the whole solar spectrum which is the so-called spectral mismatch. Therefore, several mechanisms have been explored based on photoluminescence (PL) to convert the solar cell spectrum where the spectral response of the solar cell is low to regions where the spectral response of the solar cell is high. These mechanisms are: quantum cutting (or downconversion) [3], up-conversion [4, 5] and downshifting [5]. Up-conversion is where two or three IR photons combine to give one higher energy photon that can be absorbed by the solar cell. Down-conversion is where one UV/visible photon split into two near-infrared photons. Both these photons can then be absorbed by the solar cell [3]. Downshifting is a process of shifting one higher energy photon into one lower energy photon [5]. The absorption of high energy photons by a solar cell generates heat during the fast thermalization of the hot charge carriers. Downconversion can be utilized to reduce the thermalization loss since the external quantum efficiency exceeds unity and hence the current doubling can occur. A theory has predicted that by using a downconversion layer in conjunction with a Si solar cell, 38.6% energy efficiency can be achieved [3].

Experimentally, downconversion have been investigated in various rare earth couples Tb$^{3+}$-Yb$^{3+}$, Tm$^{3+}$-Yb$^{3+}$, Ce$^{3+}$-Yb$^{3+}$, and Pr$^{3+}$-Yb$^{3+}$ in various hosts [4, 5]. SrF$_2$: Pr$^{3+}$-Yb$^{3+}$ is one of the best quantum cutting phosphor materials [3, 6]. In SrF$_2$: Pr$^{3+}$-Yb$^{3+}$, absorption of a blue photon results in feeding two Yb$^{3+}$ ions, which turns out to emit two near infrared photons (centred at 977 nm) that can be used for creating two electron-hole pairs. Unfortunately, despite this promising results, the weak absorption cross-section of the 4f-4f transition of the Pr$^{3+}$ ion limit the implementation of such application. In order to overcome the weak absorption of Pr$^{3+}$ a third sensitizer have been investigated [4, 7]. Such a sensitizer is required to have cross-sections that can efficiently absorb most of the light in the UV and visible part of the solar spectrum and efficiently transfer the energy to the quantum cutting couple, e.g. $^3P_1$ levels of Pr$^{3+}$. In this respect, Eu$^{2+}$ shows a broad band that originates from a fully allowed 4f-5d transition [8, 9]. Such transition strongly depends on the crystal field of the matrix. This is because efficient energy transfer between a sensitizer and donor can occur only when the emission band of the donor overlaps the excitation band of the acceptor. In the SrF$_2$ host, Eu$^{2+}$ emits a broad emission band centred at 416 nm [9], which could make it suitable to sensitize the $^3P_1$ levels of Pr$^{3+}$. SrF$_2$ was chosen for the host because lanthanide ions form clusters as charge compensation when substituted into the SrF$_2$ crystal and because of its low phonon energy [6]. In this paper we investigated to what extend the NIR emission of the Pr$^{3+}$-Yb$^{3+}$ couple can be improved with the Eu$^{2+}$ ion as a sensitizer.

**EXPERIMENTAL**

For the co-precipitation process, analytical grade of Sr(NO$_3$)$_2$, Pr(NO$_3$)$_3$·6H$_2$O, Eu(NO$_3$)$_3$·5H$_2$O, Yb(NO$_3$)$_3$·5H$_2$O and NH$_4$F were used without further purification. Sodium hydroxide was used to adjust the pH of the system, which were 8.5 in this study. For a typical synthesis of SrF$_2$:Eu$^{2+}$-Pr$^{3+}$-Yb$^{3+}$, 30 mmol of NH$_4$F and 0.1 mol/mL of sodium hydroxide were
added drop-wise to an aqueous solution containing Sr(NO₃)₂, Pr(NO₃)₃, 6H₂O. Yb(NO₃)₃, 5H₂O and Eu(NO₃)₃, 5H₂O in period of about 30 min. After one hour of stirring, the mixture was left for 5 hours. Then, the product was collected by using a centrifugal and washed with water and ethanol. Finally, the product was dried for 48 hours in an oven at 80 °C. The samples were annealed under a reducing atmosphere (Ar 96%/H₂ 4%) in order to reduce Eu³⁺ into Eu²⁺ ions.

UV-Vis-NIR diffuse reflection spectra were measured using a Perkin Elmer Lambda 950 spectrophotometer with an integrating sphere and using spectralon as the reference material. Photoluminescence spectra (PL) were collected by using a Cary Eclipse fluorescence spectrophotometer equipped with a xenon lamp and also the He-Cd laser PL system with a 325 nm excitation wavelength. NIR PL was observed with a He-Cd laser PL system with a 325 nm excitation wavelength and 2 mm InGaAs photodiode detector. Luminescence decay curves of Eu²⁺ were recorded under pulsed excitation (HORIBA scientific) with 375 LH NanoLED diode with a 375 nm excitation wavelength. The luminescence decay curves of Pr³⁺ were measured under pulsed excitation using a diode pumped YAG laser with a 335 nm excitation wavelength, power of 1.3 milliwatt and a SR430 Multichannel scaler photomultiplier (Linköping, Sweden). All measurements were performed at room temperature.

RESULTS AND DISCUSSION

Figure 1 depicts the diffuse reflectance spectra of Eu²⁺ sensitized Pr³⁺:Yb³⁺ couple in the SrF₂ matrix. A number of absorption bands occurred in the reflectance spectrum. The sharp small bands centred at 440, 466, 482, 588 nm are ascribed to 4f→4f transition from the ground state ³H₄ to the excited states ³P₂, ³P₁, ³P₀ and ¹D₂ of the Pr³⁺ ion (labelled in figure 1), respectively. The broad absorption band below 400 nm is as a result of the strong absorption of the Eu²⁺ (4f⁷-4f⁵5d) ion. The absorption of Eu²⁺ and Pr³⁺ cover a large part of the UV and Vis region ranging from 310 to 505 nm. The additional absorption peak in the NIR part with a maximum at 976 nm is assigned to the 4f→4f transition of the Yb³⁺ ion. The weak sensitivity of our system in the NIR region resulted in the weak intensity and noise for all the samples below 5 mol% Yb concentration (see 1 mol% Yb). As expected, the intensity of this NIR absorption increased with an increasing Yb doping concentration. Thus, the diffuse reflectance results confirm that the dopant ions were incorporated well in the host material.

Figure 2 shows the emission spectrum in the visible region of Eu²⁺ and Pr³⁺ for the samples triply doped with Yb³⁺ ions in the SrF₂ host. The spectrum was obtained by using the He-Cd laser PL system with a 325 nm excitation source. It can clearly be seen that the spectrum consists of both the emissions from Eu²⁺ and Pr³⁺. The strong broad emission centred at 416 nm is assigned to the inter-configuration 4f⁷5d¹⁴f̃ allowed transition of Eu²⁺ [7, 8]. Excitation of Eu²⁺ ions with 332 nm excitation wavelength also resulted in the PL spectra of Pr³⁺ and this is suggesting that energy transfer occurs between Eu²⁺ and Pr³⁺. The narrow emission bands centred at 488, 524, 605, 638, 715 and 730 nm were originated from the 4f→4f transition due to the ³P₀→³H₄, ³P₀→³H₅, ³P₀→³H₆ and ³P₀→³F₂ transitions, respectively [10]. There was no emission from Eu³⁺ which confirmed that all the Eu³⁺ ions convert to Eu²⁺ [9]. The strong emission of Eu²⁺ suppressed the weak emission bands of the Pr³⁺ ion, i.e., ³P₀→³F₃ and ³P₀→³F₄ transitions centred at 715 and 730 nm, respectively.

To study the influence of the Yb³⁺ concentration on the Eu²⁺:Pr³⁺ couple, a series of powder samples were prepared with 1.5 mol% of Eu²⁺, 2 mol% Pr³⁺ and various Yb³⁺ concentrations. In figure 3(a) and (b), the emission spectra of Eu²⁺ (4f⁷5d→4f̃ transition) and Pr³⁺ samples with varied Yb³⁺ concentrations are shown under identical conditions. The PL spectra of Eu²⁺ related emission as a function of the Yb concentration, excited by xenon lamp under 332 nm excitation
wavelength are shown in figure 3 (a). The emission spectra of Eu$^{2+}$ in SrF$_2$ clearly consist of a broad emission band centred at 416 nm, which is similar to that measured by the laser excitation source shown in figure 2. It is well known that such a broad emission band are mainly originating from the interconfiguration $4f^55d→4f^6$ allowed transition of Eu$^{3+}$ [8, 9]. The $4f^55d→4f^6$ allowed transition of Eu$^{3+}$ is characterized by fast emission rates, which is called fluorescence. The sharp peak centred on 488 nm is assigned to the Pr$^{3+}$,P$_0→$H$_4$ transition. The 4f-4f emission which is classified as a phosphorescence emission arises from triplet excitation states in which the electron in the excited state has the same spin orientation as the ground state electron. Such transitions are forbidden and the emission rates are slow. By using our Carry Eclipse PL system equipped with a xenon lamp such transition should be measured in phosphorescence mode. Whereas Eu$^{2+}$ emission should be measured in fluorescence mode. The observed 4f-4f emission of Pr$^{3+}$ in fluorescence mode can be explained by a decrease in the emission rates of Pr$^{3+}$ emission with increasing Yb concentrations.

From figure 3(a) it can be seen that the Eu$^{2+}$ emission (4f$^55d→4f^6$ transition) decreased with the increased Yb$^{3+}$ concentration. This indicates the existence of energy transfer from Eu$^{3+}$ to Yb$^{3+}$ since the Pr$^{3+}$ concentration (2 mol%) is fixed in all the samples with different Yb concentrations. The PL spectra of Pr$^{3+}$-related emissions as a function of Yb$^{3+}$ concentration is shown in figure 3(b). The emission spectra of Pr$^{3+}$ show the characteristic $\Gamma_0$ emission line of Pr$^{3+}$ [10]. All the Pr$^{3+}$ in SrF$_2$ emission bands were significantly enhanced in the co-doped sample. The biggest enhancement was found for the 488 nm band ($\Gamma_0→$H$_4$ transition). From figure 3(b) it can be seen that all bands for the Pr$^{3+}$ emission decreases significantly with the increasing Yb$^{3+}$ concentration. A drastic decrease in intensity can be seen in the sample with 10 mol% of Yb$^{3+}$. This result shows the efficient energy transfer from Pr$^{3+}$ to the Yb$^{3+}$ ion. The energy transfer between Pr$^{3+}$ and Yb$^{3+}$ was proposed to occur by the two step first order resonant energy transfer quantum cutting process, which can occur from the $\Gamma_0$ and $\Gamma_4$ of Pr$^{3+}$ to the excited state of Yb$^{3+}$ resulting in the emission of two NIR photons [11].

![Figure 3](image3.png)

**Figure 3** Visible PL emissions of (a) Eu$^{2+}$ and (b) Pr$^{3+}$ as a function of Yb$^{3+}$ concentration, excited by 332 nm using the xenon lamp.

![Figure 4](image4.png)

**Figure 4** NIR emission spectra as a function of Yb$^{3+}$ concentration excited by He-Cd laser system with 325 nm excitation wavelength. The 10 % Yb spectrum is drawn with a different scale.

In figure 4 the PL of the NIR spectra are presented. For the sample co-doped with Eu$^{2+}$ (1.5 mol) and Pr$^{3+}$ (2 mol%) (shown in figure 4 as 0.0 % Yb), a number of NIR bands located at 993, 1080, 1307 and 1495 nm is ascribed to the transitions of $\Gamma_4→\Gamma_6$, $\Gamma_5→\Gamma_6$, $\Gamma_2→\Gamma_6$, $\Gamma_6→\Gamma_5$ and $\Gamma_2→\Gamma_7$ in Pr$^{3+}$, respectively. The observation of emission bands originating from $\Gamma_2$ implies that cross-relaxation between the Pr$^{3+}$ ion pairs occurred since the multi-phonon relaxation process from $\Gamma_0$ to $\Gamma_2$ level is negligible [10]. After doping with Yb$^{3+}$ a sharp and small PL peak appears at 977 nm, which is attributed to the 4f-4f transition of Yb$^{3+}$,F$_{52}→$F$_{02}$ [6]. The energy transfer between
Pr$^{3+}$ and Yb$^{3+}$ was attributed to the quantum cutting mechanism resulting from the two-step first order resonant energy transfer quantum cutting process, which can occur from the $^1P_0$ and $^1G_4$ state of Yb$^{3+}$ resulting in emission of two NIR photons [11]. By increasing the Yb$^{3+}$ concentration the Yb$^{3+}$ emission gradually appeared. At 10 mol% Yb$^{3+}$, the Pr$^{3+}$ emissions are completely quenched as a result of strong interaction with Yb$^{3+}$. This indicates that the energy transfer between Pr$^{3+}$ and Yb$^{3+}$ efficiently occurred at high Yb concentration. Although the energy transfer occurred at high Yb concentration the Yb$^{3+}$ emission intensity is relatively weak. This is suggesting that the spectral effect of Yb$^{3+}$ in the current system is small.

Results obtained for the luminescence decay curves for Eu$^{2+}$ and Pr$^{3+}$ emission also contributed to the energy transfer efficiency process with different Yb$^{3+}$ concentrations. Figure 5 shows the decay curves of Eu$^{2+}$:4f$^6$5d$^1$–4f$^7$ (416 nm) with Pr$^{3+}$ and Pr$^{3+}$-Yb$^{3+}$. All the decay curves exhibit multi-exponential behaviour. For the Eu$^{2+}$ singly doped this might be due to the surface effect of the crystal [14, 15]. The decay time for the singly doped Eu$^{2+}$ was 435 ns. This decay time was due to radiative decay from 4f$^6$5d$^1$($T_{2g}$) level, which is in agreement with reported values for the decay time of Eu$^{2+}$ emission [16]. Co-doping with 2 mol% of Pr$^{3+}$ induced faster decay, which can be attributed to the energy transfer from Eu$^{2+}$ to Pr$^{3+}$. An estimation of energy transfer efficiency can be obtained from $\eta_{ET} = 1 - t_1/t_0$ as outline in literature [12, 13]. Here, $t_1$ and $t_0$ are the corresponding lifetimes of Eu$^{2+}$ in the presence and absent of Pr$^{3+}$, respectively. The corresponding energy transfer efficiency is 39%. Co-doping again with 1 mol% of Yb$^{3+}$ into the Eu$^{2+}$-Pr$^{3+}$ couple dramatically decreased the decay lifetime of Eu$^{2+}$. This indicates that energy transfer from Eu$^{2+}$ to Yb$^{3+}$ also exist. The energy transfer between Eu$^{2+}$ and Yb$^{3+}$ has been reported to occur through cooperative quantum cutting energy transfer [6, 11]. The calculated value of energy transfer efficiency between Eu$^{2+}$ and Yb$^{3+}$ was founded to be 62%.

The luminescence decay curves for the Pr$^{3+}$ related transition $^3P_0 \rightarrow ^1H_4$ is shown in figure 6. The decay time for Pr$^{3+}$ rapidly decreased when the system was co-doped with 1 mol% Yb$^{3+}$. This indicates an additional decay pathway, i.e. the energy transfer between Pr$^{3+}$ and Yb$^{3+}$. The energy transfer is roughly estimated to be 60%. Yb$^{3+}$ induced faster decay times to both the Eu$^{2+}$ and Pr$^{3+}$ but the Yb$^{3+}$ emission intensity is however significantly low. This might be due to the concentration quenching and other non-radiative decay processes for Yb$^{3+}$. The overlap between the Yb$^{3+}$ emission and the strong Pr$^{3+}$ emission in the NIR regions might contribute to the weak Yb$^{3+}$ band.

Figure 5 Normalized decay curves of the Eu$^{2+}$ emission at 416 nm of SrF$_2$:Eu$^{2+}$, SrF$_2$:Eu$^{2+}$,Pr$^{3+}$ and SrF$_2$:Eu$^{2+}$,Pr$^{3+}$,Yb$^{3+}$.

Figure 6 Normalized decay curves of the Eu$^{2+}$ emission at 488 nm for SrF$_2$:Eu$^{2+}$,Pr$^{3+}$ and with 1 mol% Yb$^{3+}$.

It is well known that the transition $^3H_4 \rightarrow ^3P_0$ of the Pr$^{3+}$ ion is parity forbidden and therefore it has a low absorption cross-section. On the contrary, the 4f-5d transition of Eu$^{2+}$ is a fully allowed transition. Absorption by the Eu$^{2+}$ ions is therefore strong and most of the incident energy will then be absorbed by the Eu$^{2+}$ ions. The energy can then be transferred to the Pr$^{3+}$ ions. Thus, the light yield is much more significant in the Eu$^{2+}$ co-doped systems than in the Pr$^{3+}$-Yb$^{3+}$ system. The idea of enhancing the excitation cross-section of Pr$^{3+}$ by broadband ions has been previously reported. A. Guille et al. [7] studied CaYAlO$_4$ thin film and bulk co-doped with Pr$^{3+}$ and Ce$^{3+}$, where the Ce$^{3+}$ ions feed the $^1D_2$ level of Pr$^{3+}$. The energy transfer from $^1D_2$ level of Pr$^{3+}$ ion to the Yb$^{3+}$ is only possible via photon assistant energy transfer and hence it would not lead to a quantum cutting process. In this study it is shown that the energy transfer from Eu$^{2+}$ to Pr$^{3+}$ leads to an enhancement of the $^3H_4$ level of Pr$^{3+}$. The quantum cutting from Pr$^{3+}$ to Yb$^{3+}$ via resonance and cross-relaxation energy transfer occurred but the strong emission for Pr$^{3+}$ in the NIR region suppressed the weak intensity for Yb$^{3+}$. The weak Yb$^{3+}$ emission was clearly observed at high concentration where the intensity of Pr$^{3+}$,$^1G_4$,$^3H_4$ is quenched. Therefore, these results suggest that Eu$^{2+}$ can be used as an efficient sensitizer to feed the Pr$^{3+}$ ions.

The c-Si spectral response is high (around 1100 nm). The response becomes weak at the high energy region due to thermalization loss, especially in the 300-400 nm region. By using the Eu$^{2+}$-Pr$^{3+}$ or Eu$^{2+}$ doped Pr$^{3+}$-Yb$^{3+}$ couple in SrF$_2$, the energy transfer from 250-450 nm to the response region for c-Si can be achieved.
CONCLUSION
Energy transfer from Eu$^{2+}$ to Pr$^{3+}$ and Yb$^{3+}$ ions was studied. The Eu$^{3+}$ (4f$^7$5d→4f$^5$) emission band lead to efficient energy transfer from Eu$^{3+}$ to the Pr$^{3+}$ ions in the SrF$_2$ samples and it showed the quantum cutting process with Yb$^{3+}$. It is demonstrated that the Eu$^{2+}$ could be an efficient sensitizer to Pr$^{3+}$. It was also shown that Pr$^{3+}$ emits strongly in NIR region where it overlap with the Yb$^{3+}$ emission. Emission from Yb$^{3+}$ was only observed at high Yb$^{3+}$ concentration after the Pr$^{3+}$ emission was quenched. The results suggested that the Eu$^{2+}$ ions sensitized the Pr$^{3+}$–Yb$^{3+}$ couple in the current system and can be used as a solar spectral down-converter for the c-Si solar cells application.

ACKNOWLEDGMENT
This work is based on the research supported by the South African Research Chairs Initiative of the Department of Science and Technology (84415). The financial assistance of the National Research Foundation (NRF) and the Cluster program of the University of the Free State towards this research is hereby acknowledged.

REFERENCES