Upconversion of 1.54 μm radiation in Er^{3+} doped fluoride-based materials for c-Si solar cell with improved efficiency

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Abstract Upconverted emission from erbium ions in fluoride materials (glass and disordered crystal of the system $\text{CaF}_2\text{-YF}_3$) are observed in a wide spectral range (from the visible to the near infrared) under infrared excitation at 1.54 μm . In both cases, the upconverted emission in the near infrared ($\sim 1 \mu\text{m}$) dominates the spectrum. Absolute UC efficiency defined as the ratio between the UC luminescence power and the absorbed pump power has been experimentally measured. The NIR ($\sim 1 \mu\text{m}$) luminescence energy yield for the glass and the disordered crystal varies from 2.4 to 11.5% for the glass and from 7.7 to 16% for the crystal for an infrared excitation power density ranging from 2 W/cm^2 to 100 W/cm^2 . This is of a particular interest for their use as upconverter to improve the c-Si cells quantum efficiency since the energy of the excitation lies below the c-Si absorption edge (1.12 eV at 300 K) and is well located compared to the AM1.5G solar spectrum, outside of the absorption lines due to different atmospheric gases. Furthermore, the most efficient upconverted emission recorded in the investigated materials occurs at an energy just above the gap. A current generated in a bifacial c-Si solar cell is observed when the Er^{3+} doped material (1.55 mA and 2.15 mA for the glass and the crystal respectively), placed at the rear face of the cell, is excited at 1.54 μm . The current dependence as a function of the sub-bandgap excitation power has been measured and modelled. Finally the EQE of the complete device is deduced from the measured short-circuit current and the incident photon flux on the cell. An increase of the cell quantum efficiency of 2.4% and 1.7% is obtained at 1.54 μm with adding the glass and the crystal respectively at the rear face of the c-Si cell. The results are compared to those already obtained with Er: NaYF_4 known as the most efficient upconverter.

1 Introduction

Researches on sustainable energy sources underwent a strong impulse these last years. Among different opportunities, solar energy offers the most abundant sustainable source but, up to now, its use still remains low compared to other sustainable energy sources such as hydraulic, biomass, wind. The main hindrance to a wide development of solar energy has several causes such as the cost of the kWh produced (20–40 cts/kWh), that is in part limited by the efficiency of commercially available solar cells (5–20%)[1]. Important technological breakthroughs only will allow overcoming these difficulties and investigations in this field are directed toward researches on third generation solar cells. Hot carriers, solar concentrators, nanostructured silicon, tandem cells represent the most popular orientations to achieve third generation solar cells.

In these cases, predicted efficiency is drastically improved and may lead to devices with a much higher cost. In this frame, a possibility based on down- (photon cutting) and up- conversion (photon addition) has been proposed. The efficiency increase is provided by adding materials able to convert photons of high energy or sub-bandgap photons into useful ones for the semiconductor [2,3]. Theoretically, the Shockley-Queisser efficiency limit [4] can be pushed from close to 30% up to 40.2% for a silicon solar cell with an upconverter illuminated by non concentrated light [5].

Upconversion processes represent a convenient way to convert sub-bandgap photons into visible ones, they are easily observed with rare earth (RE) doped materials as well as with organic materials [6]. Moreover, the particular energy level scheme of the rare earth ions offers many opportunities for different semiconductors (c-Si, a-Si, AsGa ...); several RE combinations and their up-conversion ability can be adapted to improve the enhanced photon current generation by the semiconductor

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depending on its energy gap. This approach exhibits several advantages. First of all, the introduction of an upconverter in the device does not require drastic modification of the fabrication process since the optical material and its reflector will be placed at the rear face of the cell. Moreover, each part of the complete device (semiconductor and upconverter) can be separately optimized, thus a low cost modification should be possible to improve the solar irradiance – current efficiency of solar cells with upconversion. Crystalline silicon is the most common material for solar cells today and in this case, about $\sim 20\%$ of solar energy contained in the air mass global AM1.5G terrestrial solar spectrum is lost due to the transmission, conversion of sub-band gap infrared into near infrared and/or visible emissions should provide improvement. In this aim, the optical conversion of infrared excitation (IR) at about $1.5 \mu\text{m}$ to near infrared (NIR) photons near $1 \mu\text{m}$ in Er^{3+} doped materials is of particular interest since the energy of excitation photons lies below the c-Si absorption edge (1.12 eV at 300 K) and the converted photons can be efficiently absorbed by the semiconductor leading to an efficient light – current conversion. Furthermore, the Er^{3+} absorption in this spectral range, corresponding to the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ transition, exhibits a quite important cross-section; it is usually broad due to the large number of populated Stark components of the ground state. Another interest to work with Er^{3+} ions is linked to the location of the fundamental absorption compared to the terrestrial AM 1.5G solar spectrum as shown on Figure 1. Up to now, the validity of the concept has been demonstrated using NaYF_4 as upconverter by studying the effect of upconverted emissions obtained by a sub-bandgap excitation of a composite material composed of Er^{3+} -doped NaYF_4 nanoparticles dispersed into a mixture of white oil and rubberizer on a photocurrent generation [7–9] or Er^{3+} : NaYF_4 compacted powder [10]. In [7–9], the unoptimized device has been demonstrated to respond effectively to wavelengths in the range of $1480\text{--}1580 \text{ nm}$ with an external quantum efficiency (EQE) of 3.4% occurring at 1523 nm at an illumination intensity of 2.4 W/cm^2 . A selection of some materials has been already reported although their absolute conversion efficiency is unknown [11].

In this paper, we are especially interested in upconversion, from Er^{3+} ions, observed under IR excitation at $1.54 \mu\text{m}$ and its conversion efficiency at about $1 \mu\text{m}$. Disordered fluoride based materials, a ZBLAN glass and a disordered crystal of the $\text{YF}_3\text{--CaF}_2$ system, were selected as hosts for three reasons. The first one is obvious, it is now well known that upconversion processes are more efficient in materials with a low phonon cut-off frequency in which non-radiative de-excitation by multiphonon relaxation rates are minimized. Among them, halides satisfy this criterion, however only fluorides represent interest, others are instable with regard to moisture. The second one is related to the ability of Er^{3+} to absorb the widest possible spectral range, so we have chosen to investigate glasses and disordered crystals in which the spectral features exhibit inhomogeneous broadening of the spectral features induced by the local disorder.

Fig. 1. Er^{3+} Absorption from the ground state to the first excited state ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$) and upconverted emission in the near infrared ($^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$) in comparison with the AM1.5G solar spectrum.

Since their discovery [12, 13], upconversion processes observed in RE doped materials are extensively studied. However, if a huge amount of papers on upconversion have been published in literature, very few of them report absolute conversion efficiency values and all of them concern the upconversion process between $\text{Yb}^{3+}\text{--RE}^{3+}$ ($\text{RE} = \text{Er}^{3+}, \text{Tm}^{3+}$ mainly) upon 980 nm excitation [14–17]. For the targeted application, the knowledge of the upconverted luminescence yield is the most important factor to evaluate the potentiality of a material as upconverter. Recently, we have reported the procedure to measure absolute upconversion conversion efficiencies [18]. In this paper, we are especially interested in upconversion from Er^{3+} ions under IR excitation at $1.54 \mu\text{m}$ and the conversion efficiency at about $1 \mu\text{m}$. Only the results obtained with the optimized Er^{3+} doped fluoride based glass and disordered crystal giving the highest upconversion efficiency will be presented. The absolute conversion efficiency measured for the $\text{IR} \rightarrow \text{NIR}$ ($\sim 1 \mu\text{m}$) upconverted luminescence depends as usually on the excitation power, from 2.4 to 11.5% for the glass and from 7.7 to 16% for the crystal with an infrared excitation power density ranging from 2 W/cm^2 to 100 W/cm^2 . The measurements have been done between the available laser diode power ranging from 20 mW to 100 mW so in our experimental conditions, the lower excitation power density was limited to 2 W/cm^2 . From extrapolation of the experimental data, an absolute conversion efficiency of 1% and 4% is expected at 1 W/cm^2 for the glass and the crystal respectively.

In a second part, we will concentrate on the current generated in a c-Si cell following the absorption of the upconverted emission obtained with an infrared excitation @ $1.54 \mu\text{m}$ of the investigated samples placed at rear face of the cell. The current dependence as a function of the sub-bandgap excitation power is observed and modelled. Finally the EQE of the complete device is deduced from the measured short-circuit current and the incident photon flux on the cell. An increase of the cell efficiency of 2.4% and 1.7% is obtained at $1.54 \mu\text{m}$ with adding the glass and the crystal respectively at the rear face of the c-Si cell.

2 Experiments

The composition of the investigated glass is the following $54.0 \text{ ZrF}_4 - 26.6 \text{ BaF}_2 - 2.8 \text{ LaF}_3 - 4.8 \text{ AlF}_3 - 6.6 \text{ NaF} - 0.5 \text{ InF}_3 - 4.7 \text{ ErF}_3$ (mol%). This glass, noted Z18 in the following, was synthesized according to the particular procedure described in the reference [19]. The $\text{Ca}_{0.89}\text{Y}_{0.11}\text{F}_{2.11}$ disordered crystal (noted as CYF), synthesized using the Storbarger-Bridgman technique, crystallizes with the fluorite structure. The synthesis procedure and optical properties of Er^{3+} : CYF are described in [20, 21]. The crystal doped with 5% of Er^{3+} ions was investigated in this study.

Infrared excitation at 1.54 μm was provided by a CW pig-tailed Er fiber laser (ELT-100 IRE Polus Group) delivering power up to 100 mW via a single mode fiber with 8 μm core diameter. A splitter and a photodiode integrated into the device permitted to control the excitation power.

The experimental device and procedure to measure the absolute $\text{IR} \rightarrow \text{NIR}$ conversion efficiency have been already reported [18], the details are only briefly recalled here. Plates with polished parallel faces of samples under study were brought as close as possible to the pumping laser fiber termination. The ensemble was introduced inside an integrating sphere covered with SpectralonTM, the luminescence was sent to a spectrometer (AVASpec-1024TEC) by an optical fiber (Fig. 2a). The whole setup (integrating sphere + spectrometer) is calibrated with the use of a halogen tungsten lamp (10 W tungsten halogen fan-cooled Avalight-HAL). The IR-visible luminescence spectra (1100–380 nm) are recorded in absolute energy units. The infrared luminescence of the samples in the range of 900–1700 nm was dispersed by a monochromator (SpectraPro 750, resolution 1.2 nm/nm), detected by a liquid nitrogen cooled PbS detector and corrected from the spectral response of the system. To scale the IR part (900–1700 nm) of the emission spectrum recorded in the same experimental conditions (excitation power, geometry of the experiment...), the luminescence intensity has been multiplied by a constant factor in order to obtain the same luminescence power of the band at $\sim 0.98 \mu\text{m}$ as that in spectra recorded using the calibrated setup. Both setups allow to record spectra in energy per wavelength units.

The bifacial Si cell used in this set of experiments was prepared at the University of New South Wales – UNSW (Australia). The cell is an untextured monocrystalline cell with buried contacts and front and rear sides antireflection coatings. Measured Quantum Efficiency of this cell (using a double beam, calibrated setup) at 0.980 nm was found equal to 0.27 and the measured efficiency under 1000 W/m^2 AM1.5 spectrum was found to be 12%.

Photocurrent generated in the bifacial c-Si cell by up-converted photons has been collected through connectors welded to the opposite sides of the cell. The intensity of the current is measured by a 485/4853 Keithley picoammeter, the scheme of the experimental setup is represented on Figure 2b. The samples were attached to a reflector using a glue to ensure a contact between the samples

Fig. 2. Experimental setup (a) for the 1.5 $\mu\text{m} \rightarrow \text{Visible}$, NIR absolute conversion efficiency of studied samples; (b) for the photocurrent measurement in the bifacial c-Si solar cell generated by sub bandgap excitation of an upconverter material.

Table 1. Relevant parameters used for short – circuit current calculations (the effective absorption cross-section is calculated by integrating σ_λ (abs) ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$) over in the spectral range corresponding to the FWHM of the excitation laser line).

	Z18	CYF
N (ions/ cm^3)	8.07×10^{20}	6.488×10^{20}
d (cm)	0.289	0.093
n	1.51	1.426
$\int \sigma_{\text{abs}}(\lambda) d\lambda$ (cm)	1.41×10^{-18}	2.05×10^{-18}
σ_{eff} (cm^2)	1.6×10^{-20}	2.6×10^{-20}
$R_{\text{reflector}}$	0.90	0.96

and the reflector as good as possible; the glue was deposited only at the corners of the samples, out of the excitation/collection zones. The reflection coefficient of the reflector, tabulated in Table 1, has been checked by measuring, after removing the samples, the laser power before and after reflection at angle as small as possible to reproduce the experimental conditions.

The photocurrent measurement as a function of excitation power was done either changing the diode current (high power regime) or modifying the excitation density

Fig. 3. Er³⁺ fundamental absorption (⁴I_{15/2} → ⁴I_{13/2}) for both studied materials and the laser excitation.

by varying the distance between the cell and the end fiber, keeping the diode current for the maximum output power (low power regime).

3 Experimental results

3.1 Absolute conversion efficiency

Absorption spectrum of Er³⁺ from the ground state to the first excited state (⁴I_{13/2}) in Z18 is represented on Figure 1. As shown in Figure 1, the Er³⁺ transition from the ground state to the first excited state is beneficially located compared to the AM1.5G solar spectrum, out of the absorption due to O₂, H₂O and CO₂ in the atmosphere and below the c-Si gap absorption edge. For all investigated samples, this absorption band is quite large ($\Delta\lambda \approx 70$ nm) and exhibits a high oscillator strength that is required for the concerned application (Fig. 3). Furthermore, the excited states from which upconverted emissions are observed are well located well above the c-Si gap, especially the transition ⁴I_{11/2} → ⁴I_{15/2} (Er³⁺) as shown on Figure 1.

In order to measure the absolute conversion 1.5 μ m → NIR-VIS efficiency of the samples under study, the IR excited luminescence was registered in power per wavelength units. The spectra, represented on Figure 4a–b, were recorded with an excitation power of 75 mW and 65 mW for Z18 and CYF respectively. The contribution of each observed transition to the total emitted power is calculated following:

$$\eta_i^{\text{exp}} = \frac{\int_{\lambda_0}^{\lambda_1} P_{\text{meas}}(\lambda) d\lambda}{P_{\text{lum}}^{\text{int}}} \quad (1)$$

where, $P_{\text{meas}}(\lambda)$ represents the luminescence power displayed in energy per nanometer units for the transition i extending from λ_0 to λ_1 , and $P_{\text{lum}}^{\text{int}} = \int_{380 \text{ nm}}^{1700 \text{ nm}} P_{\text{meas}}(\lambda) d\lambda$ is the total emitted power. The fractions η_i^{exp} calculated from the luminescence spectrum (displayed in Figure 4a–b) are summarized in Table 2.

Fig. 4. Er³⁺ calibrated emission spectrum excited at 1.54 μ m for CYF ($P_{\text{exc}} = 65$ mW) (a) and Z18 ($P_{\text{exc}} = 75$ mW) (b); Absolute conversion efficiency as a function of the 1.5 μ m excitation power density (c).

For applications such as display or upconverter for PV, the most important criteria to select a material is the ratio of the luminescence power emitted in the whole spectral range $P_{\text{lum}}^{\text{int}}$, or in a particular range of interest, to the absorbed pump power. Thus, the absolute conversion efficiency is defined following:

$$\eta_{\text{tot}}^{\text{exp}} = \frac{P_{\text{lum}}^{\text{int}}}{P_{\text{abs}}^{\text{pump}}} \quad (2)$$

Table 2. Er^{3+} Electronic transitions observed in emission, η_i^{exp} is the fraction of power emitted in a specific spectral domain of the transition “ i ”, η_i , the absolute efficiency of the emission “ i ”.

i	Electronic transition	Z18		CYF	
		η_i^{exp}	η_i	η_i^{exp}	η_i
1	$^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$	61.5%	20.3%	49.9%	16.8%
2	$^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$	34.8%	11.5%	47.6%	16.0%
3	$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$	0.7%	0.2%	0.2%	0%
4	$^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$	1.2%	0.4%	1.6%	0.5%
5	$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	1.7%	0.6%	0.7%	0.2%
6	$^2\text{G}_{9/2} \rightarrow ^4\text{I}_{15/2}$	0.1%	0%	0%	0%

The total absolute energy yield of the 1.5 $\mu\text{m} \rightarrow \text{NIR} - \text{VIS}$ upconversion is calculated by considering all upconverted emissions (from the NIR to the visible) $\sum_{i=2}^6 \eta_i^{\text{exp}} \cdot \eta_{\text{tot}}^{\text{exp}}$ and for a particular emission “ i ” the absolute energy yield is obtained from the product $\eta_i^{\text{exp}} \cdot \eta_{\text{tot}}^{\text{exp}}$. Then, for the 1.5 $\mu\text{m} \rightarrow \text{NIR}$ conversion which is of a particular interest in our purpose, the absolute energy yield was found equal to 11.5% and 16.7% for Z18 and CYF respectively for an excitation power density of 100 W/cm^2 . The excitation power dependence of the $\text{IR} \rightarrow \text{NIR}$ absolute conversion efficiency is represented in Figure 4c for both studied samples. Such a power dependence of the conversion efficiency is commonly observed and results from a competition between several processes which occur at high excitation power. A complete analysis of the power dependence of the upconverted luminescence is developed in [22]. From the values gathered in Table 2, it is clear that most part of upconversion emission energy is contained in the NIR part of the spectrum (at $\sim 1 \mu\text{m}$), which demonstrates that the studied samples are promising for application as active layer for solar cells with enhanced efficiency, since the NIR light has an absorption depth of only 100 μm and is thus strongly absorbed in a wafer-based silicon solar cell. For crystalline-silicon-based solar cells, approximately a half of the energy contained in the VIS part of the UC spectrum will be released as heat during thermalization of carriers created after absorption of VIS photons.

3.2 Generated current with a sub band gap excitation of a c-Si solar cell

The light-generated current in a c-Si cell was measured following two approaches. In both cases, the sample was pasted on a mirror in order to avoid excitation and emission losses and the sample was closely brought on the rear face of the cell. In a first step, the photocurrent was measured as a function of the excitation power, the power was varied between 75 mW and 20 mW (the lower limit of the fiber laser operation), the distance between the fiber and the front face was kept constant (equal to 1.3 mm). In a second experiment, the excitation power was set at 75 mW and the light-generated current measured as a function of the distance between the fiber and the entrance face of the cell allowing a larger range of the excitation density

Fig. 5. Photocurrent generated in the bifacial c-Si solar cell measured by excitation at 1.54 μm as a function of the excitation power (a) and as a function of the distance between the sample and the end fiber, the laser power was constant and set equal to 75 mW (b).

than the previous experiment due to the divergence of the laser. Without the upconverting material, infrared excitation at 1.54 μm does not produce measurable current in the cell. The results of both experiments are represented on Figure 5.

4 Modelling the experimental results

A first model has been proposed by Byung-Chul Hong and Katsuyayasu Kawano, concerning the short circuit current generated by $\text{KMgF}_3:\text{Sm}$ layer placed at a top of a CdS/CdTe solar cell [23]. Here the configuration is quite different since the light converter is placed on the rear face of the solar cell, the used formalism, very close to that proposed in [23], is developed in Appendix A. The calculation of the short circuit current generated by upconverted emission was performed in a first step using equations (A.1–A.9) and, in a second step, using equations (A.10–A.13) which include internal reflections in the upconverter. These results were checked using a transfer

Fig. 6. Photocurrent as a function of the $1.54 \mu\text{m}$ excitation power of the upconverter: experimental results and calculated values using the simple model.

matrix formalism [24]. The emission flux is calculated by taking into account either only the NIR emission or all observed upconverted emissions.

Even if the laser peak is fixed at $1.54 \mu\text{m}$, the laser excitation has a finite line width and an effective absorption cross section should be taken into account. Effective absorption cross-sections were determined by integrating the curves represented on Figure 3 over the FWHM of the laser line, all values considered in the following are gathered in Table 1 with the refractive index.

4.1 Dependence on the excitation power

Applying equation (A.2) with the emission flux given by equation (A.9) and using the set of data summarized in Table 1, the calculated photogenerated current is represented on Figure 6 in comparison with the experimental data obtained with both samples. Taking account for the geometry of the different samples (polished and parallel faces) internal reflections are expected to occur, the short circuit current has been calculated using equation (A.13) for the emission flux from the upconverter. As shown on Figure 7, addition of internal reflections does not introduce great modifications of the results obtained by equation (A.9). This is explained by the quite high absorption coefficient and the poor reflectivity of the mirror in the case of Z18. The correction due to the term $(1 - R_1 R_2 \exp(-2\alpha d))^{-1}$ is close to 1 (1.0006 for Z18 and 1.007 for CYF). Calculating step by step the contribution of the different possible reflections, the second reflection contributes for only 1% to the first step.

As it can be observed on Figure 7, the calculated I_{sc} values are slightly underestimated compared to experimental data for high excitation power. In the case of CYF, other upconverted emissions can contribute to the photovoltaic effect. Equation (A.9) has been applied by taking into account for the conversion efficiencies of the green and red emissions to the total short-circuit current. From the result of the calculation (Fig. 7b), these contributions become non negligible from 40 mW of incident power and

Fig. 7. Photocurrent as a function of the $1.54 \mu\text{m}$ excitation power of the upconverter: experimental results and calculated values considering multiple reflections in the upconverter (a) only the upconverted in the NIR is considered in the calculations; (b) all upconverted emissions are considered in the calculations.

the agreement between experimental and calculated values is better.

4.2 Dependence on excitation power density

The short circuit current registered as a function of the distance between the cell and the end fiber results, due to the divergence of the laser beam, in a decrease of the power density. According to the divergence and the distances involved in the experiment, the irradiated surface can be approximated to: $S = 0.01\pi D^2$, here D is the distance between the upconverter surface and the fiber (in cm) and gives the same result as the exact formulae for $D > 0.05 \text{ cm}$. This experiment was performed keeping the laser power constant and equal to 75 mW, the excitation density varies from 141 to 0.65 W/cm^2 . In this range, the

Fig. 8. (a) Comparison between the photocurrent and the intensity of the NIR upconverted emission as a function of the distance sample-end fiber laser; (b) comparison between the calculated values of the photocurrent (I_{sc}) using equation (A.9) and the experimental data including both experiences (I_{sc} measured as a function of the excitation power, I_{sc} measured as a function of the sample-end fiber distance).

conversion efficiency is not constant as shown on Figure 4c and the following calculations were done using the η^{UC} determined as a function of the excitation density.

First, the experimentally measured short circuit current measured as a function of the distance exhibits a variation which is perfectly parallel to the intensity of the NIR upconverted emission recorded in the same conditions but without the cell between the end fiber and the sample as shown on Figure 8(a) for the CYF sample. For a better comparison, the two set of data were normalized to the maximum value (i.e. for the shortest distance) and the excitation density corrected from the reduced transmission of the c-Si cell for curve (2) on Figure 8(a). This result confirms the role of the NIR upconverted emission to the short circuit current. The model has also been applied to calculate the I_{sc} value under these experimental conditions. First, the incident power was calculated from a reduction factor taking into account the ratio between the excitation surface at the minimum distance and the

Fig. 9. Excitation power dependence of EQE and the IR $\rightarrow$ NIR absolute conversion efficiency.

varying distance. Then, applying equation (A.9), the I_{sc} calculated is in perfect agreement with experimental data recorded in the first experiment (Fig. 8b).

The simple model, we propose, reproduces quite well the experimental data and can help to predict roughly the expected short circuit current if all spectroscopic parameters are carefully determined as well as the absolute energy conversion efficiency and its excitation power density dependence. Visible upconverted emissions with noticeable conversion efficiency can contribute also for a small part to the photocurrent even if the most part is due, in the case of c-Si cell, to the NIR upconverted emission.

5 External quantum efficiency (EQE)

The performance of a photovoltaic cell is quantified by the external quantum efficiency (EQE) which is defined as the ratio between the flux of collected electrons and the flux of incident photons. Since the final aim of this work is to improve the c-Si cell efficiency, the EQE of the complete device (c-Si cell and upconverter) noted UC-PV similarly to [8] was calculated @ 1.54 μm . The results obtained for the investigated materials as a function of the excitation power are represented on Figure 9. On contrary to classical PV devices, a slight dependence of EQE on the incident power is observed. As already discussed in [8], a particular behaviour of EQE with the incident power is obtained when using an upconverter. The photons responsible for the creation of electron-hole pairs in the semiconductor result from a non linear process as briefly described in the introduction. The number of electron-hole pairs is proportional to the number of NIR photons ($\phi_{e-h} \propto (\phi_p)^n$) as it is observed in Figure 5a in most of the power range. In particular for the IR (1.54 μm) $\rightarrow$ NIR (0.98 μm) conversion with Er^{3+} , two IR photons are required for one NIR photon. Then EQE in a UC-PV device is expressed as [8]:

$$EQE = \frac{(\phi_p)^n}{\phi_p} \propto (\phi_p)^{n-1} \text{ with } n = 2 \text{ in our case.} \quad (3)$$

Thus, a linear dependence of EQE is expected with such a UC-PV device. This explains the EQE behaviour with the incident power represented on Figure 9. Moreover, the deviation from a linear dependence is observed at high incident power especially for Z18. Considering the absolute IR $\rightarrow$ NIR conversion efficiency versus the excitation power, represented on Figure 9 (upper curves), η^{UC} is quite constant for CYF over the incident power range and EQE increases linearly from 20 to 75 mW while η^{UC} increases from 20 to 30 mW, then stays stable up to 60 mW and then decreases for higher excitation power. This results are in agreement with the dependence of the conversion efficiency with the excitation power due to competing mechanisms occurring at high pump power in the upconversion processes as described in [22]. The EQE power dependence obtained for Z18 reflects quite well the η^{UC} dependence with the excitation power as observed in Figure 9.

An absolute increase of the quantum efficiency is found at 1.54 μm (2.4%, 1.7% for CYF, Z18 respectively, at maximum flux) by adding an upconverter at the rear face of the c-Si cell. These results are lower than that reported in [8] but still in the same range of order.

Although the UC systems reported are among the most efficient ones (a photon to photon quantum efficiency of 10.8% corresponding to a photon to photon power efficiency of 16.7%, see Table 2), the global system quantum efficiency is plagued by 3 issues that could be rather easily improved on:

- The transmission of the Si Cell in the IR (at 1.54 μm) is only about 60%. These losses come from the degraded AR coating (a good AR coating should yield less than 10% losses from reflection), a non optimal grid with shadowing from both grids and a doping level in the n/p parts that yields free carrier absorption.
- The rather low EQE of the cell at 980 nm, slightly less than 40%, due to the degraded AR coating. With texturing and improved AR coating, the EQE of the cell could well approach 80% in this region for such a thick cell.
- The non-optimized optical coupling between the cell and the UC crystals (with a very small air gap) as well as between UC and the mirror. From our evaluation, using a transfer matrix formalism to take into account all internal reflections, this induces losses that can be up to 50% of the UC photons absorbed in the Si cell.

With a UC quantum efficiency equal to 16.7% (Table 2), this yields the system EQE close to 2.4%. In terms of power efficiency, assuming a cell output voltage of 700–900 mV (this depends on solar concentration); this EQE translates into a 1.3 to 1.8% efficiency of power conversion of the 1.5 μm wavelength. With a somewhat optimized system, especially with optical coupling and NIR response of the Si cell, a factor of 3 to 5 of improvement could be obtained: 5 to 10% power conversion efficiency of the IR photons in the 1.5 μm band that can be absorbed by Er ions seems therefore an achievable target.

6 Conclusion

In this work, we could compare internal photon to photon conversion in UC compounds (something that is rarely measured) to the total photovoltaic system efficiency. We could show that quite efficient (up to 16.7% efficiency powerwise) compounds do exist for the 1.5 μm to 0.98 μm conversion that is well suited for use in combination with Si solar cells. In such a non optimal system, the power conversion efficiency was found around 1–2%, but a careful analysis of the losses showed that 5% is a realistic goal.

Of course, these systems have the drawback that they work only under very high concentration ($\times 2000$ to $\times 20\,000$) at the present state of the art. This is something that can hardly be improved unless the absorption coefficient of the UC material can be improved, but still, with present day technology, this represents a few W/m^2 more that could be harvested.

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Appendix A

Model for the calculation of the photogenerated current by upconverter materials

1. Simple model neglecting internal reflections in the upconverter (Fig. A.1)

The used formalism is very close to that proposed in [23] but some modifications are needed due to the configuration of the experiments performed with an upconverter. The short circuit current generated by upconverted emission extending between λ_0 to λ_1 from the samples excited at 1.54 μm is given by the following expression:

$$I_{sc}(\lambda_{em}) = q \int_{\lambda_0}^{\lambda_1} \eta^{cell}(\lambda) F(\lambda_{em}) d\lambda, \quad (\text{A.1})$$

where q is the electron charge (Coulombs), $\eta^{cell}(\lambda)$ the quantum efficiency of the cell at the emission wavelength, $F(\lambda_{em})$ the emission photon flux from the upconverter material.

First, the emission flux is calculated by taking into account for the NIR emission since UV-visible upconverted

Fig. A.1. Schematic diagram of the incoming and outgoing incident excitation and converted emission in the complete system (solar cell + upconverter + reflector) (For details see text).

emissions observed between 400 nm and 800 nm contribute only for a minor part. Considering that the internal quantum efficiency of the cell $\eta^{cell}(\lambda)$ is only slightly dependent on the wavelength in the NIR emission range, Equation (A.1) can be simplified as:

$$\begin{aligned} I_{sc}(\lambda_{av}) &= q\eta^{cell}(\lambda_{av}) \int_{\lambda_0}^{\lambda_1} f(\lambda) d\lambda \\ &= q\eta^{cell}(\lambda_{av}) F(\lambda_{av}). \end{aligned} \quad (\text{A.2})$$

The integrated emission photon flux from the upconverter material $F(\lambda_{av})$ depends on the incident flux on the upconverter and on the $\text{IR} \rightarrow \text{NIR}$ conversion efficiency. First of all, the incident flux on the material is reduced from the incident flux on the cell due to reflections at the different interfaces (entrance and rear faces of the cell, cell-upconverter). In addition, if the semiconductor is transparent at 1.54 μm , the presence of contacts on both faces of the cell induces losses in the 1.54 μm transmission.

The incident flux $\phi_{cell}^{inc}(\lambda_{exc})$ on the cell is calculated from the excitation power at the excitation wavelength (i.e. 1.54 μm) following:

$$\phi_{cell}^{inc}(\lambda_{exc}) = \frac{P_{cell}^{inc}(\lambda_{exc}) \lambda_{exc}}{hc}. \quad (\text{A.3})$$

In a first approximation, the incident flux on the upconverter material $\phi_{Mat}^{inc}(\lambda_{exc})$ is obtained from $\phi_{cell}^{inc}(\lambda_{exc})$ and reflections at the different interfaces following:

$$\phi_{Mat}^{inc}(\lambda_{exc}) = (1 - R_c)(1 - R_1)\phi_{cell}^{inc}(\lambda_{exc}) \quad (\text{A.4})$$

with R_c , R_1 the reflection coefficients at the air-cell interface, at the cell-upconverter interface respectively, given by Fresnel's equations:

$$R_c = \frac{(n_a - n_c)^2}{(n_a + n_c)^2} \quad (\text{A.5a})$$

$$R_1 = \frac{(n_{UC} - n_c)^2}{(n_{UC} + n_c)^2} \quad (\text{A.5b})$$

n_a , n_c , n_{UC} are the refractive index of the air (equal to 1), the cell and the upconverter respectively.

To achieve the calculation of the short-circuit current, n_c has to be evaluated. To this aim, we consider the cell as a whole system to calculate an effective index since we do not know exactly the thickness of the coating layers. The transmission of the system has been measured at 1.54 μm , out of the absorption range of the device. The loss of the excitation power is due to reflections from the entrance face, and internal reflections at interfaces coating-semiconductor. From the measured transmission behind the cell it is possible to calculate the effective refractive index of the system by taking into account reflections at the different interfaces.

$$I_{Trans} = (1 - R_C)^2 I_{inc} \quad (\text{A.6})$$

with R_C is given by equation (A.5a). The squared transmission coefficient is due to two interfaces air-cell in this configuration.

The transmitted power was found to be half of the incident one. Solving equations (A.5a) and (A.6) give rise to an effective index equal to 3.35. This value seems quite reasonable considering the refractive indices of the coating and the semiconductor equal to 2.1 and 3.48 respectively at 1.5 μm .

Absorption in the upconverter is due first from the direct absorption along the optical path d and in the second part due to the non absorbed photons which are reflected by the mirror and absorbed travelling in the opposite direction (see Fig. A.1), thus the rate of absorption of the excitation photons in the upconverter $\phi_{Mat}^{abs}(\lambda_{exc})$ is expressed as:

$$\begin{aligned} \phi_{Mat}^{abs}(\lambda_{exc}) &= \phi_{Mat}^{inc}(\lambda_{exc}) [(1 - \exp(-\alpha d)) \\ &\quad \times (1 + R_2 \exp(-\alpha d))] \end{aligned} \quad (\text{A.7})$$

where α is the absorption coefficient of the upconverter at the excitation wavelength, d is the upconverter thickness, and R_2 is the reflection coefficient of the mirror.

The complete expression of the absorbed flux by the upconverter is given by:

$$\begin{aligned} \phi_{Mat}^{abs}(\lambda_{exc}) &= (1 - R_c)(1 - R_1)\phi_{cell}^{inc}(\lambda_{exc}) \\ &\quad [(1 - \exp(-\alpha d))(1 + R_2 \exp(-\alpha d))] \end{aligned} \quad (\text{A.8})$$

Neglecting internal reflections in the upconverter slab, that is neglecting R_I , the emission photon flux $F(\lambda_{av})$ is then expressed as:

$$F(\lambda_{av}) = \phi_{Mat}^{abs}(\lambda_{exc}) \eta^{UC} \quad (\text{A.9})$$

with η^{UC} the absolute efficiency of the 1.54 $\mu\text{m} \rightarrow 0.98 \mu\text{m}$ conversion.

2. Model including internal reflections in the upconverter material

If the incident light is reflected on the interface upconverter/cell, the non absorbed part of the incident flux

will be reflected and then absorbed travelling through the upconverter to the mirror and so on (Fig. A.1). This can be expressed by the following relationships between the reflection coefficients (R_1 and R_2) of the different interfaces, the absorption coefficient α and d the thickness of the upconverter

$$\begin{aligned}\phi_1^{abs} &= \phi_{Mat}^{inc} (1 - \exp(-\alpha d)) \\ \phi_2^{abs} &= \phi_{Mat}^{inc} (1 - \exp(-\alpha d)) R_2 \exp(-\alpha d) \\ \phi_3^{abs} &= \phi_{Mat}^{inc} (1 - \exp(-\alpha d)) R_1 R_2 \exp(-2\alpha d) \\ \phi_4^{abs} &= \phi_{Mat}^{inc} (1 - \exp(-\alpha d)) R_1 R_2^2 \exp(-3\alpha d) \dots\end{aligned}\quad (\text{A.10})$$

with ϕ_{Mat}^{inc} defined by equation (A.4).

For a large number of internal reflections, we get

$$\begin{aligned}\phi_n^{abs} &= \phi_{Mat}^{inc} (1 - \exp(-\alpha d)) \left[\sum_{i=0}^{i=\infty} R_1^i R_2^i \exp(-2i\alpha d) \right. \\ &\quad \left. + \sum_{i=0}^{i=\infty} R_1^i R_2^{i+1} \exp(-(2i+1)\alpha d) \right]\end{aligned}\quad (\text{A.11})$$

where the first and second terms of the above expression can be considered as geometrical series which sum is:

$$A = \frac{1}{1 - R_1 R_2 \exp(-2\alpha d)} \text{ for the first term, and for the second term } B = \frac{R_2 \exp(-\alpha d)}{1 - R_1 R_2 \exp(-2\alpha d)}.$$

Finally, the absorbed flux within the upconverter is given by:

$$\phi_{Mat}^{abs} = \phi_{Mat}^{inc} (1 - \exp(-\alpha d)) \frac{1 + R_2 \exp(-\alpha d)}{1 - R_1 R_2 \exp(-2\alpha d)} \quad (\text{A.12})$$

that gives for the emission flux:

$$\begin{aligned}F(\lambda_{av}) &= \phi_{cell}^{inc}(\lambda_{exc}) (1 - R_C) (1 - R_1) \\ &\quad \times (1 - \exp(-\alpha d)) \frac{1 + R_2 \exp(-\alpha d)}{1 - R_1 R_2 \exp(-2\alpha d)} \eta^{UC}.\end{aligned}\quad (\text{A.13})$$

The final expression for the photogenerated current is obtained using equation (A.2) with the emission flux given by equation (A.13).

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