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Modifying the solar spectrum to enhance silicon solar cell efficiency— An overview of available materials

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Abstract

There are three ways in which the cell efficiency of silicon solar cells may be improved by better exploitation of the solar spectrum: down-conversion (cutting one high energy photon into two low energy photons), photoluminescence (shifting photons into wavelength regions better accepted by the solar cell) and up-conversion (combining low energy photons to one high energy photon). In this paper, we present the state of the art of these three methods and discuss the suitability of materials available today for application to silicon solar cells.

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1. Introduction

Spectrum modification is a well researched topic in physics and in chemistry and has been applied, for example to infrared quantum counter (IRQC) [1] or efficient lamp phosphors [2]. It is also one of the Third Generation concepts suggested to overcome the classical efficiency limit of silicon solar cells [3]. These concepts show extreme promise. While the classical efficiency limit is currently estimated to be 29% [4], detailed-balance calculations show that this could improve to approximately 37% [5,6] using spectrum modification at one sun. In this paper we concentrate on down-conversion [7], photoluminescence [8] and up-conversion [9] and assess the potential of different systems for application to silicon solar cells.

There are three losses in a silicon solar cell that spectrum modification can reduce. The first of these is thermalization, which occur when an electron–hole pair with energy greater than the band gap of silicon ($E = 1.12$ eV,

$\lambda = 1100$ nm) is created and the excess energy is lost as heat because the electron (and hole) relax to the conduction (and valence) band edges. Thermalization losses can be reduced by using down-conversion whereby, for example, a photon with twice the energy of the band gap is converted into two photons with exactly the energy of the band gap. The second loss mechanism is imperfect collection due to recombination close to or at the surface. Since high energy photons are absorbed in this region they are more likely to be affected and the result is a reduced spectral response at shorter wavelengths. This loss can be reduced by using photoluminescence, whereby photons are shifted into an energy range where the cell has a higher spectral response. For a typical, industrial solar cell, photoluminescence would be beneficial if wavelengths shorter than approximately 500 nm could be shifted into the range 500–1000 nm. The third loss mechanism is transmission, which occurs because photons with energy less than the band gap of silicon are not absorbed. Transmission losses can be reduced by using up-conversion whereby two or more low energy photons combine to create one higher

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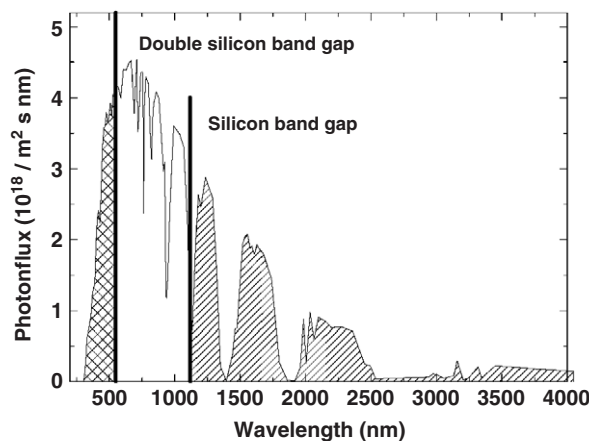


Fig. 1. AM1.5G Solar Spectrum [117]. The vertical lines show the band gap and twice the band gap of silicon. All photons with wavelengths longer than the silicon band gap are transmitted (hatched). The excess energy of the photons in the checkered part of the spectrum is adequate to create an additional electron-hole pair per photon, but is wasted due to thermalization losses.

energy photon. Use of these concepts is illustrated in Fig. 1, which shows photon flux as a function of wavelength.

Modifying the incoming spectrum can be realized by incorporating layers above (for down-conversion and photoluminescence) or below (for up-conversion) existing solar cells made with established high-efficiency processes. No modification of the active layer is needed, as is the case with the impurity photovoltaic effect (IPV) [10] and the intermediate band solar cell [11]. Neither a complicated structure such as that used for tandem solar cells [12] or quantum well solar cells [13] is necessary.

The first application of up-conversion on solar cells was reported by Gibart et al. [14] in 1995. On a GaAs cell they applied a vitroc ceramic co-doped with trivalent erbium (Er^{3+}) and trivalent ytterbium (Yb^{3+}), and saw a response of the cell at an energy of 1.391 eV (the band gap of GaAs is 1.43 eV) under excitation of $1 \text{ W}/0.039 \text{ cm}^2$. The first application of an up-converter to a silicon solar cell was reported by Shalav et al. [15] in 2003. The up-converter consisted of NaYF_4 doped with Er^{3+} and was located on the rear side of a bifacial cell. This led to a response of the cell under excitation at 1500 nm.

Photoluminescent materials have also been applied to solar cells. This was done by van Sark using CdSe quantum dots in a transparent matrix [16]. At this stage no improvement in the solar cell response was evident. Application of photoluminescent silicon nano-crystals in a SiO_2 matrix was done by Švrček et al. [17], which led to enhanced spectral response at shorter wavelengths.

2. Conversion to lower energies

There are two possibilities to use the high energy part of the solar spectrum ($\sim 3.5\text{--}2.3 \text{ eV}$ or $350\text{--}550 \text{ nm}$) more efficiently: photoluminescence and down-conversion. The two techniques are distinguished by their quantum

efficiencies. For photoluminescence, the quantum efficiency is always less than or equal to one, whereas for down-conversion the quantum efficiency exceeds one (more than one photon is emitted for each incoming photon) provided non-radiative losses can be prevented.

Much of the early work in these topics was aimed at finding lamp phosphors that efficiently convert the vacuum ultraviolet (VUV) light emitted by Mercury discharge lamp (254 nm) into visible light [2]. Today the main aim is to displace the environmentally harmful Mercury by noble gases, which means that photoluminescence and down-conversion under excitation at higher energies is necessary (for example xenon with emission at 172 nm). Photoluminescence is also applied in cathode ray tubes, where three phosphors (blue ZnS:Ag , green ZnS:Cu,Au and red $(\text{Zn,Cd})\text{S:Ag}$) compose the colored picture [2]. Since the past focus of these research areas has not been for photovoltaic applications, many of the wavelength ranges investigated (mostly $\leq 200 \text{ nm}$) are not relevant for application to terrestrial solar cells. It is possible, however, that better suited materials will be found in the future.

Most of the systems that show photoluminescence or down-conversion consist of host-materials doped with one or more active ions. Absorption takes place either via the host-material (band-to-band-absorption, broad band in the absorption spectrum) or within the active ions (sharp lines in the absorption spectrum). Excitation of a host-material normally occurs at higher energies than excitation of active ions. Photoluminescence and down-conversion differ in the emission process. While photoluminescence takes place via phonon emission, which corresponds to a loss of the excess energy, down-conversion takes place via a two-step emission process, which allows more than one photon to be generated for each incoming photon. This is shown schematically in Fig. 2.

In order for a silicon solar cell to benefit from photoluminescence or down-conversion, the following conditions should hold:

- excitation at wavelengths longer than 350 nm (high energy border of the terrestrial solar spectrum);
- excitation at wavelengths shorter than 550 nm for down-conversion (550 nm corresponds to twice the band gap of silicon) or approximately 500 nm for photoluminescence (depending on the cell design);
- emission between 350 and 1100 nm;
- low excitation intensity (in the range of W/cm^2);
- high quantum efficiency and
- low absorption in the regions of the spectrum that will not be shifted or down-converted, since these wavelengths must be transmitted to the underlying solar cell (see Fig. 2c).

By using photoluminescence to shift the high energy photons to lower energies, the probability of losing the created electron-hole pair due to surface recombination, Auger and Shockley-Read-Hall recombination in the sub-

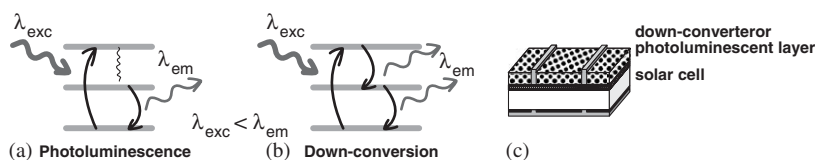


Fig. 2. (a) Photoluminescence: after excitation non-radiative relaxation takes place followed by radiative relaxation, which leads to an emission of photons with lower energy. (b) Down-conversion: after excitation, step-wise relaxation takes place, which leads to the emission of two (or more) low energy photons. (c) A photoluminescent layer or a down-converter has to be placed in front of the cell, since the high energy photons are absorbed by the solar cell [5].

surface region is reduced. This results in an increased spectral response of the solar cell at higher energies. Application of a down-converter leads to a higher number of photons in the solar cell, provided the quantum efficiency is larger than one. For both systems, therefore, a higher short circuit current, J_{sc} , a slight increase in open circuit voltage, V_{oc} , and therefore a higher efficiency of the solar cell is expected. The benefit of down-conversion was calculated by Trupke et al. [5]. Under the assumptions of an ideal down-converter on the front side of a silicon solar cell under non-concentrated sunlight, they showed using detailed-balance calculations that the efficiency limit was increased to 36.6% (without converter 30%).

2.1. Down-conversion

The theoretical possibility of down-conversion was first proposed in 1957 by Dexter [7]. Today this process is also called quantum cutting, quantum splitting, multi-photon emission (MPE) or photon cascade emission (PCE). Experimentally, down-conversion was seen independently by Piper et al. [18] and Somerdijk et al. [19] in 1974 using the trivalent rare earth praseodymium (Pr^{3+}) in a YF_3 host-material. Down-conversion has since been seen in various Pr^{3+} -doped materials [20,21], using other rare earth ions [22–24] and in transition-metal-doped materials [25,26]. Down-converters can be divided into ionic-like and band-like down-converters. In ionic-like down-converters both absorption and emission take place via the energy levels of the active ion. In band-like down-converters, absorption takes place via a band-to-band-excitation in the host-material and emission occurs via the energetic levels of the doping ions.

2.1.1. Ionic-like down-converters

The first down-converting doping ion found was trivalent praseodymium (Pr^{3+}). The properties of this ion are investigated in a wide range of host-materials. For all materials the excitation of the down-conversion process is between 125 and 215 nm. The emission takes place in the visible range of the spectrum. Trivalent gadolinium (Gd^{3+}) is found in many down-converting systems. Single doped [27], co-doped (with trivalent europium Eu^{3+} [23,28,29]) and triple doped (with trivalent erbium Er^{3+} and trivalent terbium Tb^{3+} [23]) systems have been investigated. In each of these cases, the excitation takes place via the Gd^{3+} ion and the emission can take place in all doping ions. In most

of these systems, the Gd^{3+} -ion is an element of the host lattice and the energy transfers often occur via this ion. Due to the presence of Gd^{3+} all systems show strong absorption at around 200 and 275 nm, but only the absorption at about 200 nm leads to down-conversion processes [24]. Theoretical calculations propose a quantum efficiency of 190% in $\text{LiYF}_4 : \text{Eu}^{3+}$ and 194% in $\text{BaF}_2 : \text{Gd}^{3+}, \text{Eu}^{3+}$ if losses (migration and transfer to non-radiative quenching centers) can be prevented [30]. Despite the high potential in quantum efficiency, ionic-like down-converters do not seem to be suitable for application to solar cells under terrestrial conditions because the absorption is limited to only the low wavelength range. In Table 1 a selection of ionic-like down-converters is listed.

2.1.2. Band-like down-converters

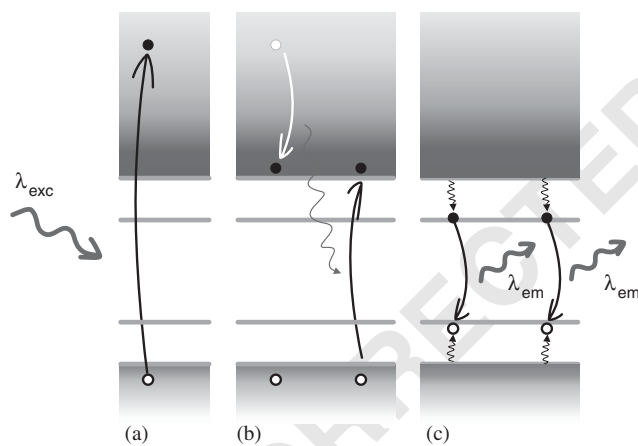
In band-like down-converters, absorption takes place via excitation of the host-material. If the incoming energy exceeds twice the energy of the band gap, Auger processes are possible. This can lead to the creation of a second electron hole pair using the excess energy of the first excited electron. Both electron hole pairs relax via the energy levels of the doping ion and it is the doping ion that therefore determines the emission properties [25]. The process, also called interband Auger process, is illustrated in Fig. 3.

This effect has been seen in a broad range of materials and an overview is given in Table 2. Neglecting non-radiative relaxations, the quantum efficiency of the interband Auger process is the integer part of the ratio of excitation energy to band gap energy. In reality, due to parasitic relaxations, only a few materials show a quantum efficiency greater than one [25]. There exists an excitation energy, E_{one} , above which the quantum efficiency exceeds one. This is theoretically twice the band gap energy, E_g , but non-radiative relaxations means that in reality it lies at higher energies. Experimentally determined values of E_{one} are listed in Table 2 for several different materials. Many other materials have been investigated, but only those for which quantum efficiencies larger than one were found are mentioned. Also listed are the quantum efficiencies measured at 21 eV for [31] or 25 eV for [25,26]. Since the thresholds are at very high energies or short wavelengths, most of the systems are not suitable for an application to terrestrial solar cells.

1 Table 1
 Selection of ionic-like down-converters

3	Material	Excitation (nm)	Emission (nm)	Quantum efficiency (%)	Reference
5	SrAlF ₅ : Pr ³⁺	190	(405) (480)	5	[93,94]
7	YF ₃ : Pr ³⁺	180–213.9	(400 or 405 or 407) (470 or 483 or 484) (605)	140 Theo. 157	[19,95] [18,96]
9	NaYF ₄ : Pr ³⁺	213.5	407		[19,95]
11	CaAlF ₅ : Pr ³⁺	175–210	(410) (470)	5	[94]
13	NaMgF ₃ : Pr ³⁺	125–190	(410) (470)	10	[94]
15	KMgF ₃ : Pr ³⁺	180	(400) (470)	Theo. 124	[96]
17	LaZrF ₇ : Pr ³⁺	150–200	(408)(480)		[20]
19	SrAl ₁₂ O ₁₉ : Pr ³⁺	195	(404) (484.5)		[21]
21	LiYF ₄ : Gd ³⁺	194.7	(593 or 614 or 636) (311)		[27]
23	LiGdF ₄ : Eu ³⁺	183;195	(Many lines between 525 and 700) (590)	Theo. 190	[22,28,30]
25	GdF ₃ : Eu ³⁺	202	(Many lines between 570 and 640) (590) (740–810)		[23,24] [28]
27	BaF ₂ : Gd ³⁺ , Eu ³⁺	202	(527 or 556 or 594 or 620 or 656 or 702)	Theo. 194	[29]
29	LiGdF ₄ : Er ³⁺ , Tb ³⁺	145	(522 or 545 or 550) (380–500) (544–620)	Theo. 130	[23]

25 The down-converters in this table are divided in two groups: Pr³⁺-based (upper part) and Gd³⁺-based (lower part). In the down-conversion process a pair
 27 of photons is emitted, each with a wavelength of the group shown in the brackets. If only one wavelength is noted, the other one is experimentally not
 measured in the reference. A third pair of brackets corresponds to an additional possible radiative de-excitation.



31 Fig. 3. The interband Auger process, after Berkowitz and Olsen [25]. (a) A
 33 high energy photon creates an electron–hole pair and excites the electron
 35 deep into the conduction band. (b) This is followed by a non-radiative
 37 relaxation to the band edge of the conduction band, the excess energy is
 39 used to create a second electron–hole pair. (c) The radiative recombination
 41 of both electron–hole pairs via energy levels of the active ion leads to the
 43 emission of two low energy photons.

51 2.2. Photoluminescence

53 A wide range of materials show photoluminescence or
 55 Stokes-shift. Reviews have been given for example by Kitai
 57 [32] or Blasse and Grabmaier [8]. For a deeper understanding of the processes leading to photoluminescence and the properties of luminescent materials the reader is

Table 2
 Selection of band-like down-converters

Host-material	Doping ion	E_g (eV)	E_{one} (eV)	Max. QE (%)	Reference
Zn ₂ SiO ₄	Mn	5.5	12–14.5	175–200	[25,26]
Zn ₃ (PO ₄) ₂	Mn	6.5–6.9	14–17	160–190	[25,26]
Cd ₃ (PO ₄) ₂	Mn	5.5	11	220	[26]
Y ₂ O ₃	Eu	5.6–6.25	14.5–15	200–240	[25,26,31]
YVO ₄	Eu	3–4	15	160	[25]
ZnS	Ag	3.8	23.5	120	[25]
ZnS	Cu, Ag	3.8	20	145	[25]
ZnS	Cu, Al	3.8	22	125	[25]
ZnS	Zn	3.4	21	113	[25]

E_g is the band gap of the host-material and E_{one} the experimentally determined threshold above which the quantum efficiency (QE) exceeds one. The quantum efficiencies were measured at excitation energies of 21 eV for [31], and 25 eV for [25,26].

referred to the appropriate literature (see for example Ref. [33]). In contrast with quantum cutting, a solar cell with a photoluminescent photon converter (quantum efficiency lower than 1) does not have a larger limiting efficiency than a single junction solar cell. The concept can, however, be useful for industrial type solar cells which have a poor blue response, by shifting the spectrum towards wavelengths with a higher IQE. In the following, photoluminescent systems that have been applied to solar cells will be presented: quantum dots or nano-crystals in a transparent matrix.

The experimental application of CdSe quantum dots in a polymeric matrix to multi-crystalline silicon solar cells has been done by van Sark [16], but no improvement was evident due to the converter. Theoretical calculations assuming quantum dots emitting at 603 nm in a transparent matrix on top of a multi-crystalline solar cell predict an increase in short circuit current by nearly 10% relative [34].

Recently there have been reports on the morphological and optical properties of non-stoichiometric silica (SiO_x) [17,35,36] and silicon nitride (SiN_x) [36,37] layers containing silicon nano-structures in view of their application for solar cells efficiency improvement through photoluminescence. Such materials are very promising for application to silicon solar cells because:

- the silicon nano-structures photoluminesces at 600–800 nm under excitation at about 400 nm [17,35];
- the host-material is transparent over a wide range of wavelengths [38] and
- the host-material can be used as surface passivation [39] and anti-reflection coating.

The photoluminescence emission for such converters exhibits a rather high efficiency in both kind of layers with an intensity only a factor ~ 100 lower than that of porous silicon. On the other hand, the photocurrent spectroscopy showed a significant increase of absorption at high photon energy excitation most probably related to photon absorption within quantized states in the silicon nano-structures. This signal has been related to absorption within silicon nano-structures and could be used to improve the blue-UV response in conventional solar cells. The agreement between the absorption characteristics obtained from photocurrent spectra and the photoluminescence emission states unambiguously demonstrates the same origin, related to Q-confined excitons within the silicon nano-structures. Fig. 4 compares the internal

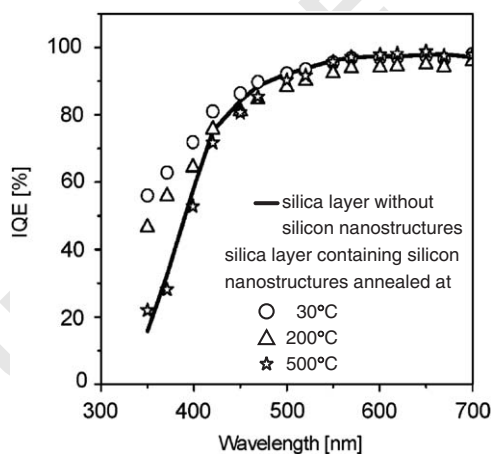


Fig. 4. Internal quantum efficiency as function of wavelength for solar cells with a silica layer containing silicon nano-crystals (symbols) and without (solid line). As the annealing temperature increases (open circles 30 °C, open triangles 200 °C, stars 500 °C) the photoluminescence and IQE decreases where silicon nanocrystals are present [17].

quantum efficiency (IQE) of crystalline silicon solar cells coated with a silica layer that contains silicon nano-crystals (symbols) or not (solid line). Because of their size and shape, these silicon nano-structures are emitting at 650–700 nm when excited at 350–400 nm [17]. An increase in IQE in the region 350–600 nm is clearly observed in the case where the cell is coated with spin-on-glass containing silicon nano-structures. The photoluminescence signal serves as photon converter by transforming the high-energy photons into lower-energy ones permitting an easier absorption by the silicon substrate underneath and the excess photocurrent observed at high energy improved the cell's performance in this region. These results were corroborated by illuminated $I-V$ measurements which showed a slight increase in short circuit current, J_{sc} , but no change in open circuit voltage, V_{oc} , resulting in an increase in efficiency by nearly 0.4% absolute [17]. A better use of this phenomena requires a higher photoluminescence efficiency that can be obtained through the increase of the density of silicon nano-structures in the host-matrix and the decrease of defects.

3. Conversion to higher energies

For a solar cell, photons with energy less than the band gap are not absorbed. This low energy part of the spectrum can be accessed by using up-conversion processes. The basic principle of up-conversion is shown in Fig. 5a. Two or more incoming photons react with the up-converter, which emits at least one photon with higher energy than the incoming photons.

Up-conversion is investigated for application as infrared indicator cards, bio-labels [40] or for three-dimensional displays [41]. Since the purpose of an up-converter is to use photons transmitted by the cell, it can be placed at the rear side where it can be electrically isolated from the silicon solar cell (Fig. 5b). A good optical coupling is necessary to ensure high transmission of the low energy light to the up-converter and of the up-converted light back into the cell. For application to silicon solar cells the properties that will ultimately determine the benefit of the process include:

- absorption range higher than 1100 nm ($E < 1.12$ eV);
- emission lower than 1100 nm;
- low excitation intensity (range of W/cm^2);
- high up-conversion efficiency and
- high transmittance of the up-converted light.

Since the absorption of silicon is relatively low in the range 950–1100 nm, absorption by the up-converter at wavelengths as low as 950 nm is also of interest, especially for thinner solar cells.

Up-conversion in the near-infrared region (approximately 1000 nm) has received much more attention than up-conversion at longer wavelengths [42]. The fact that investigations are made only at about 1000 nm does not exclude the possibility of excitation up-conversion pro-

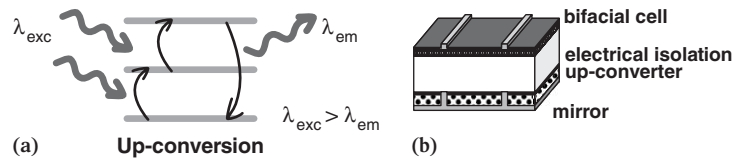


Fig. 5. (a) Basic principle of an up-converter: two incoming, low energy photons excite an electron to the highest energy level. A single, high energy photon is emitted when the electron relaxes to the ground state. (b) Application of an up-converter: since the low energy photons are transmitted by a silicon solar cell, the up-converter can be placed on the rear side of a bifacial cell. Electrical isolation between the cell and the up-converter is necessary to prevent additional recombination at the rear side.

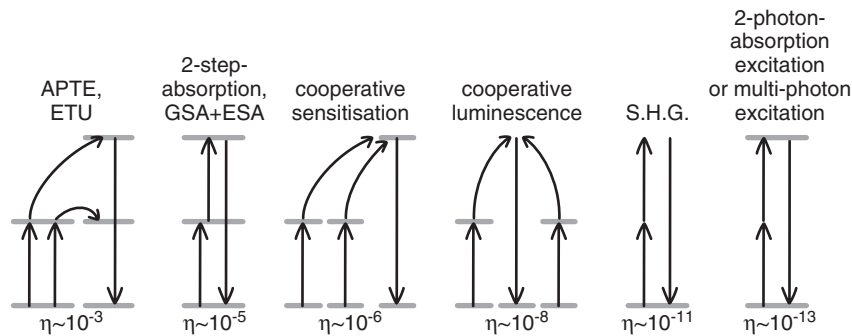


Fig. 6. Overview of various up-conversion mechanisms (after Auzel [45]). Excitation (or de-excitation) of energy levels are indicated by the vertical arrows. The arrows connecting different ions assign energy transfer. Vertical lines are real existing energy levels. The efficiency of the processes decreases from left to right as indicated by the efficiency approximation.

cesses at longer wavelengths. In this paper we consider therefore systems with excitation at wavelengths longer than 900 nm.

The expected improvement due to the application of an up-converter is a higher number of available photons and therefore additional electron-hole pairs in the cell bulk. This would result in an increase in short circuit current, J_{sc} , and therefore in the efficiency of the cell. Theoretical studies based on detailed-balance calculations predict a maximum conversion limit of 37.4% [6] for an ideal up-converter on the rear side of a cell (without converter 30%) under non-concentrated sunlight. The efficiency enhancement due to an up-converter can also be increased by using concentrated light—up to about 55% at 100 suns.

A successful application of an up-converter consisting of NaYF_4 doped with trivalent erbium (Er^{3+}) on the rear side of a bifacial silicon solar cell was shown by Shalav et al. [15] in 2003. Further investigations revealed an external quantum efficiency of 2.5% under 5.1 mW laser excitation at 1523 nm [43]. There are two main groups of up-conversion processes, which differ in the number of required photons. The anti-Stokes-shift requires only one photon since the additional energy is provided by phonons. The amount of additional energy is very small (in the range of meV or nm). Anti-Stokes-shifting occurs permanently in silicon. This effect together with exciton formation determines the shape of the absorption edge [44].

The other group of up-conversion processes is based on the absorption of two photons. An overview of two photon up-conversion processes is shown in Fig. 6.

A detailed description and theoretical calculations of the different processes is given by Auzel [45]. The most efficient

process is the so-called APTE (addition de photon par transferts d'énergie) or ETU (energy transfer up-conversion) process. The next most efficient process is a two-step-absorption, which is also often described as ground state absorption (GSA) followed by an excited state absorption (ESA). In this appellation APTE is a GSA followed by an energy transfer, often written GSA/ETU. The APTE process, two-step-absorption and cooperative sensitization take place via real, existing energetic levels. This is the reason for the higher efficiencies compared to the processes that occur via virtual levels: second harmonic generation (SHG), cooperative luminescence and two-photon absorption (TPA) or multi-photon-excitation (MPE). For the latter group, high excitation energies are necessary. For example SHG occurs only at excitation intensities in the range of 10^{13} Wm^{-2} [46], which corresponds to about 10^{10} times the integrated intensity of the terrestrial solar spectrum. In reality, in an up-converter many of the processes shown in Fig. 6 take place simultaneously.

Most up-converters have a similar structure. They consist of the active ion, which provides the energy levels for the absorption and de-excitation, and the host-material, where the ion is embedded. In the following, the two main groups of active ions (rare earth and transition metal) are discussed with their different host-materials. In addition, organic up-converters and nano-structured up-converters are presented.

3.1. Rare earth based up-converters

Up-conversion has been seen in many rare earth ions, for example in trivalent praseodymium (Pr^{3+}) and trivalent

erbium (Er^{3+}). These ions are intensively investigated for laser applications [47,48]. Due to the filled outer shell in these ions the transitions between the 5d orbital and 4f orbital are widely shielded from the influence of the host-material. Despite this shielding, the host-material influences the excitation and emission in two ways:

- (1) Stark splitting of the energetic levels: The electric field created by the surrounding host-material results in a splitting of the energetic levels of the active ion, called Stark splitting. This determines the shape of the absorption and emission spectrum. The splitting decreases with increasing ionic radius, which results in a smaller absorption range [49]. As can be seen in Fig. 7, this results in a broader absorption range for fluorides compared to chlorides.
- (2) Phonon energy: Since non-radiative relaxations are due to creation of phonons, these processes depend strongly on the energy of the phonons in the host-material. This is responsible for the occurrence (or not) of optical transitions and determines the quantum efficiency [50]. In Fig. 7, transitions of Er^{3+} in two different classes of host-materials after excitation at 1500 nm are shown. Due to a lower phonon energy chlorides (Cl), bromides (Br) and iodides (I) show less non-radiative relaxation compared to fluorides (F) and oxides (O) and therefore different emission processes take place.

3.1.1. Erbium-doped up-converters

Erbium is a very promising up-converting ion due to the absorption at about 1500 nm and emission within the absorption range of silicon. The transitions that result in up-conversion processes under excitation at 1500 nm are listed in Table 3. The denotation of the energy levels are depicted in Fig. 7(a).

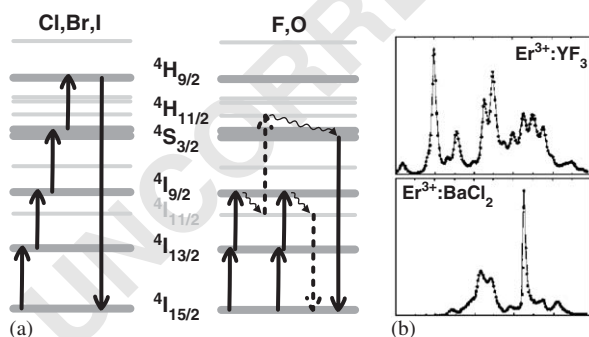


Fig. 7. Influence of the host-material on the up-conversion properties. (a) Different processes in chlorides, bromides and iodides (Cl, Br, I) compared to fluorides and oxides (F, O) due to higher phonon energies of the latter. In the first group a GSA/ESA process takes place, while under phononic relaxations in the latter GSA/ETU process occur (after [50]). (b) Influence of different host-materials on the excitation spectrum (measured at emission of 550 nm). Due to a stronger Stark splitting in fluorides, the excitation range is much broader than in chlorides [49].

Table 3

Possible emissions in Er^{3+} -doped materials under excitation at about 1500 nm

Emission (nm)	Transitions	Minimum number of photons required
980	$4\text{I}_{11/2} \rightarrow 4\text{I}_{15/2}$	2
810	$4\text{I}_{9/2} \rightarrow 4\text{I}_{15/2}$	2
660	$4\text{F}_{9/2} \rightarrow 4\text{I}_{15/2}$	3
550	$4\text{S}_{3/2} \rightarrow 4\text{I}_{15/2}$	4
410	$4\text{H}_{9/2} \rightarrow 4\text{I}_{15/2}$	5

Since absolute intensity measurements of light emitted from an up-converter are very challenging, comparative measurements of different host-materials are used. One such comparative measurement of Er^{3+} -doped materials was done by Ohwaki and Wang [49]. As expected from electronic and phononic properties, they found that $\text{BaCl}_2 : \text{Er}^{3+}$ showed the highest up-conversion efficiency. This was followed by YBr_3 , YI_3 as host-materials and the lowest up-conversion efficiency was found in the host-material YF_3 . These results agree with the investigations of van der Ziel et al. [51]. The direct compounds ErCl_3 , ErBr_3 , ErI_3 and ErF_3 they found to show less efficiency than the doped materials, but the same hierarchy. The lower efficiency is due to concentration quenching because cross-relaxations between different active ions occur at higher concentrations [49]. Since lower concentrations of active ions lead to lower efficiencies due to a lack of energy exchange necessary for ETU processes an optimum ion concentration exists. This has been found to be approximately 28 mol% for $\text{BaCl}_2 : \text{Er}^{3+}$ [52] and approximately 10 mol% for $\text{CaF}_2 : \text{Er}^{3+}$ [53]. The excitation intensities used by Ohwaki and Wang [49] were very low (1 W/cm^2) and the response was visible with the naked eye. Er^{3+} has also been used to dope LiYF_4 (YLF) and is used as lasing medium. The up-conversion properties have been investigated by several groups [47,54].

Detailed investigations of the up-conversion processes were done by Pollnau, Lüthi and Gamelin in Er^{3+} -doped $\text{Cs}_3\text{Lu}_2\text{Cl}_9$, $\text{Cs}_3\text{Lu}_2\text{Br}_9$ and $\text{Cs}_3\text{Y}_2\text{I}_9$ and in $\text{Cs}_3\text{Er}_2\text{Cl}_9$ [42,50]. There have also been attempts to enhance the exchange possibilities by using host lattices, where erbium-ions occur in pairs, so-called dimers. This has been investigated by Hehlen et al. [55]. The presence of dimers leads to a more complex system of processes since not only the energy transfer for radiative processes is enhanced (higher up-conversion efficiency), but also that for non-radiative processes (cross-relaxation, enhanced concentration quenching). No improvement due to dimer-pairs has been seen.

Examples of Er^{3+} in an oxide host-material include YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$ or yttrium–aluminum–garnet) [54,56,57], $\text{SiO}_2 - \text{TiO}_2$ -sol-gel powder [58] and tellurite glass [59].

A selection of host-materials and the absorption and emission properties are listed in the upper part of Table 4.

1 Table 4
 Selection of Er³⁺ single-doped host-materials (upper part) and other examples of rare earth ions showing up-conversion under excitation with wavelengths
 3 longer than 900 nm

Host-material	Absorption peak (nm)	Emission (nm)	Reference
YF ₃	1490	410, 530, 550, 660, 810, 980	[49,51,97]
SrF ₂	1510	410, 550, 660, 980	[54]
CaF ₂	1510	410, 550, 660, 980	[54,98]
LiYF ₄ (YLF)	~1500	410, 544, 650, 702, 850	[47,99,100]
BaYF ₅		410, 550, 660, 990	[101,102]
Fluorindate glass	1530	407, 530, 550, 670, 808, 827, 854, 980	[103,104]
BaCl ₂	1535	410, 550, 660, 810	[49,52]
YCl ₃ –ErCl ₃ –PbCl ₂ –KCl		410, 550, 660, 980	[97]
Cs ₃ Er ₂ Cl ₉		413, 457, 495, 555, 667, 826, 862	[42]
Cs ₃ Lu ₂ Cl		413, 535, 555, 826, 862	[42]
IBr ₃	1540	410, 550, 660, 810	[49]
Cs ₃ ErBr ₉	~1540	413, 457, 495, 555, 667, 826, 862	[42]
Cs ₃ Lu ₂ Br ₉	~1540	413, 535, 555, 826, 862	[42]
YI ₃	1543	410, 550, 660, 810	[49]
Cs ₃ Er ₂ I ₉	~1540	413, 457, 555, 667, 826, 862	[42]
Cs ₃ Y ₂ I ₉	~1540	457, 495, 535, 555, 667, 826, 862	[42]
SiO ₂ –TiO ₂		550	[58]
Tellurite glass		530, 550, 660	[105]
NaYF ₄ : Yb ³⁺ , Er ³⁺	980	555, 670	[106]
Y ₂ O ₃ : Yb ³⁺ , Er ³⁺	980	670	[106]
Y ₂ O ₃ S : Yb ³⁺ , Er ³⁺	980	560, 680	[106]
Ga ₂ S ₃ –La ₂ O ₃ : Er ³⁺ , Yb ³⁺	1064	555	[107]
YF ₃ : Yb ³⁺ , Tm ³⁺	970	810, 475	[108]
NaYF ₄ : Yb ³⁺ , Tm ³⁺	980	480, 650	[106]
Y ₂ O ₃ S : Yb ³⁺ , Tm ³⁺	980	490, 660, 705	[106]
Fluorohafnate glass : Yb ³⁺ , Tm ³⁺	974	544, 650, 750, 802	[109]
YVO : Yb ³⁺ , Ho ³⁺	975	550, 650	[110]
NaYF ₄ : Yb ³⁺ , Tb ³⁺	976	350, 370, 417, 455, 476, 526, 540, 645, 667	[111]
Tellurite glass: Yb ³⁺ , Tb ³⁺	1064	485, 550, 590, 625, 655	[59]
BaCl ₂ : Er ³⁺ , Dy ³⁺	1300	460, 550, 670, 810	[66]
ThBr ₄ : U ⁴⁺	940, 950, 1170	689, 690	[62]
LaCl ₃ : U ³⁺	975.2	555, 681	[63]
Phosphate glass: Yb ³⁺	980	500	[60]
SrCl ₂ : Tm ³⁺	1064, 1130	704, 715	[64]
CsCdBr ₃ : Ho ³⁺	909	491	[65]
YAG : Pr ³⁺	900	471, 473, 475, 476, 480, 481, 482	[112]
LiYF ₄ : Pr ³⁺	900	466, 467, 471, 474	[113]
ZrF ₄ –BaF ₂ –LaF ₃	930	488, 522, 539, 605, 634	[61]

3.1.2. Other rare earth ions as up-converters and co-doping

Host-materials single-doped with Yb³⁺ show up-conversion under excitation at 980 nm followed by emission at about 500 nm [60]. Also in trivalent praseodymium up-conversion has been seen under excitation at about 835–950 nm. This is due to two TPA and therefore requires very high excitation energies, which makes it unsuitable for solar cells [61]. Suitable absorption and emission properties for application to silicon solar cells were found in uranium- [62,63], thulium- [64] and holmium-doped [65] materials. A

selection of single rare earth-doped up-converters is listed in lower part of Table 4.

Several rare earth ions show emission at the wavelengths suitable for silicon solar cells, but suffer from low absorption. To enhance the absorption, sensitizers are used, whereby an ion with good absorption properties (sensitizer) absorbs and transfers the energy to a second ion (activator), in which emission occurs. Most famous examples are ytterbium–erbium couples. A higher up-conversion efficiency occurs due to absorption of 980 nm-

photons in the trivalent ytterbium (Yb^{3+}), and after de-excitation of this state, the energy is transferred to the erbium-ion. To date $\text{NaYF}_4 : \text{Yb}^{3+}, \text{Er}^{3+}$ is one of the most efficient up-converters.

Due to absorption at 1300 nm and emission similar to Er^{3+} single-doped materials [66] co-doping with trivalent dysprosium Dy^{3+} and Er^{3+} is very promising for application to silicon solar cells. It is very interesting that neither the Er -single-doped nor Dy -single-doped materials show up-conversion under excitation at 1300 nm. The content of Dy^{3+} ions has to be very small ($<0.1 \text{ mol}\%$), because dysprosium also acts also as a quenching center [45].

van der Ziel et al. [51] investigated YF_3 co-doped with trivalent thulium (Tm^{3+}) and Er^{3+} . Compared to single doping with Er^{3+} this was found to show an enhanced emission at 660 nm, while the emission at 550 and 410 nm was reduced. This originates from the Tm^{3+} -induced relaxation of the energy states in Er^{3+} , which normally emit the 550 and 410 nm wavelengths. Tm^{3+} itself does not emit. The optimum content of Tm^{3+} is very low ($y = 0.001$ in $\text{Y}_{1-x-y}\text{Er}_x\text{Tm}_y\text{F}_3$).

3.2. Transition metal based up-converters

Several transition metals show up-conversion [45,67]. The main structure (activator-sensitizer-host) is the same as for rare earth-doped up-converters. Contrary to rare earth ions, where the energetic levels involved in up-conversion processes are also observed in the free rare earth ions, the energetic levels in transition metals result from the influence of the crystal field. Therefore, the absorption- and emission-properties in the visible and near-IR depend strongly on the host (much more than for rare earth). This allows the possibility of tuning the optical properties by changing the chemical surrounding of the active ion. Up-conversion was found in materials doped with fourvalent rhenium (Re^{4+}) [67–69], fourvalent osmium (Os^{4+}) [67,70,71] or divalent titanium (Ti^{2+}) [67,72,73]. All of these ions have demonstrated up-conversion under excitation at about 1000 nm followed by an emission in the visible range of the spectrum.

Several investigations of host-materials co-doped with two transition metals [74,75] or with a rare earth and a transition metal have been done. A promising combination

Table 5
Transition metal based up-converters, which show up-conversion under excitation of about 1000 nm

Material	Excitation (nm)	Emission (nm)	Reference
$\text{MgCl}_2 : \text{Ti}^{2+}$	1060–1075	750, 764	[67,72,73]
$\text{NaCl} : \text{Ti}^{2+}$	1064	828	[73]
$\text{Cs}_2\text{ZrBr}_6 : \text{Os}^{4+}$	959		[67]
$\text{Cs}_2\text{ZrCl}_6 : \text{Re}^{4+}$	1047–1064	720, 728	[67–69,114]
$\text{YAlO}_3 : \text{Cr}^{3+}, \text{Yb}^{3+}$	962, 968	695, 714	[76,77]
$\text{Y}_3\text{Ga}_5\text{O}_{12} : \text{Cr}^{3+}, \text{Yb}^{3+}$	969, 969.6	695, 700	[77,78]

consists of trivalent ytterbium (Yb^{3+}) and trivalent chromium (Cr^{3+}) [76–78]. After excitation of the Yb^{3+} ion at about 950 nm emission at about 700 nm takes place via the Cr^{3+} ion. Transition-metal-doped materials that have shown up-conversion under excitation at about 1000 nm are listed in Table 5.

3.3. Nano-structures as host-materials

Nano-structured materials doped with active ions show changed properties because:

- there is a change in electron-phonon interaction (which changes the radiative lifetime);
- the photon density of states (PDOS) is discrete and the low frequency phonons are cut off (which may reduce energy transfers [79]);
- the enlarged surface has an influence because there are more active ions on the surface and also additional surface states due to impurities;
- the matrix material differs from the material of the quantum dot (which is the host-material of the active ion) and
- due to restrictions in spatial distances, restrictions in energy transfer between the dots occur (lower quenching rates at higher concentrations).

Up-conversion is found in nano-crystalline powders [79–82] and in quantum dots in solution [76,83]. Investigations of quantum dots in solution are typically done with the aim of getting luminescent materials in a transparent colloidal solution for application in image formation and bio-labeling [40,76]. Nano-structured material does not always result in an increased up-conversion efficiency. Capobianco et al. [82] found for $\text{Y}_2\text{O}_3 : \text{Ho}^{3+}$ a reduced up-conversion efficiency compared to bulk material. Also in fluorescence investigations reduced emissions were found ($\text{Y}_2\text{O}_2\text{S} : \text{Er}^{3+}$ [79], $\text{Y}_2\text{O}_3 : \text{Eu}^{3+}$ [84]). On the other hand, enhancements in fluorescence (not up-conversion) with a nano-structured material were found in ZnS:Mn [85] and in Er^{3+} doped II–VI-semiconductor quantum dots [86]. A lowered up-conversion efficiency observed by

Table 6
Nano-structured materials, which show up-conversion under excitation at longer wavelengths than 900 nm

Material	Excitation (nm)	Emission (nm)	Reference
$\text{Y}_2\text{O}_3 : \text{Er}^{3+}$	980	550	[79]
$\text{ZrO}_2 : \text{Er}^{3+}$	980	550, 660, 675	[80,81]
$\text{NaYF}_4 : \text{Er}^{3+}, \text{Yb}^{3+}$	974	417, 588, 667	[83]
$\text{NaYF}_4 : \text{Tm}^{3+}, \text{Yb}^{3+}$	974	364, 455, 476, 667	[83]
$\text{LuPO}_4 : \text{Yb}^{3+}, \text{Tm}^{3+}$	978	360, 455, 476, 660, 800	[76]
$\text{YbPO}_4 : \text{Er}^{3+}$	978	550, 660	[76]

1 Table 7

Organic materials that have shown up-conversion under excitation of about 1000 nm

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Material	Excitation (nm)	Emission (nm)	Input-power	Reference
5 Rhodamine B	1054	617–620	> GW/cm ²	[90]
Rhodamine 6G	1054, 1064	570 or 600–610	> GW/cm ²	[90,91]
7 PYC	1054	599	> GW/cm ²	[90]
<i>trans</i> -4-... ^a	940–1030	595	Laser exc.	[115,116]
9 APSS	1064 962, 968	550, 600	Laser exc.	[88,92]

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11 ^a[*trans*-4-*p*-(*N*-*n*-butyl)-*N*-*n*-butylamino)-styryl]-*N*-methyl-pyridinium *tris*(thiocyanato)cadmates(II).

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13 Capobianco was explained by carbonate and water-ions present on the surface. A selection of nano-structured materials showing up-conversion under excitation at wavelengths longer than 900 nm is listed in Table 6.

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17 Porous silicon can be described as an array of nano-wires and therefore as nano-structured material. The experimental proof of multi-photon-excitation (MPE) in porous silicon was shown by Diener and Shen [87]. With an excitation energy between 0.115 (10 800) and 0.135 eV (9200 nm) photons with energies up to 2.4 eV were detected (this means one pulse required 17 photons). This process requires extremely high excitation energies and is therefore not suitable for silicon solar cells.

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27 3.4. Up-conversion in organic materials

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29 Up-conversion has been seen in various organic materials [88]. Potential applications include optical storage memory [89] and biophotonics (multi-photon confocal laser scanning microscopy or multi-photon photodynamic therapy for cancer [88]). The most mature systems rely on TPA, but the efficiency of the process is relatively low and requires high pumping intensity. Examples of organic materials that have exhibited up-conversion are rhodamine B [90], rhodamine R6G [90,91] or PYC [90].

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39 Three-photon up-conversion has been reported in 4-[*N*-(2-hydroxyethyl)-*N*-(methyl)amino phenyl]-4'-(6-hydroxy hexyl sulphonyl) stilbene (APSS) dissolved in dimethyl sulphoxide (DMSO). This occurs at longer excitation wavelengths (~1300 nm) and results in an emission at 550 nm [92]. For this experiment, a very high pump power was necessary (response at 50 GW/cm² = 5 × 10¹¹ W/m²).

45 In Table 7 examples of systems that have shown up-conversion with excitation at wavelengths of approximately 1000 nm are listed.

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41 4. Conclusions

51 In this paper we presented different materials that are able to modify the wavelength of incoming light and assess their potential for application to silicon solar cells. Wavelength modification can be achieved using down-conversion, photoluminescence and up-conversion and is seen in a broad range of materials.

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Down-converting systems that have been studied to date seem unlikely to be suitable for application to terrestrial silicon solar cells because the excitation energies required are too high (wavelength lower than the lower band of the solar spectrum).

Many of the materials that demonstrate photoluminescence are well suited for application to silicon solar cells. Particularly promising are quantum dots in transparent matrices.

Several systems that show up-conversion are also well suited for application to silicon solar cells. Because of their absorption range, materials doped with trivalent erbium or co-doped with trivalent erbium and trivalent dysprosium are particularly promising. Up-conversion with excitation at lower wavelengths (around 1000 nm) is of interest for thinner solar cells and in this wavelength range, many suitable materials exist. The most efficient are materials doped with trivalent ytterbium (excitation at 980 nm). In this lower wavelength range, transition metals (for example) have also demonstrated up-conversion. Up-conversion processes have also been demonstrated in organic materials, but in these materials, excitation is via virtual levels and the energies required are therefore too high to be of interest for application to silicon solar cells.

Although there has been much work on down-conversion, photoluminescence and up-conversion, the application to solar cells has formed a comparatively small branch of this research to date. It is therefore possible that future systems will be found with properties that match more closely than those that are available today the requirements of a silicon solar cell.

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