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THE APPLICATION OF UP-CONVERTING PHOSPHORS FOR INCREASED SOLAR CELL CONVERSION EFFICIENCIES

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ABSTRACT

Up-conversion (UC) is the generation of one higher energy visible/near infrared (NIR) photon for two or more lower energy (NIR) photons. Most commercial applications for UC materials require the emission of visible light. However, a silicon solar cell is able to absorb NIR radiation and is not constrained to just visible light. Erbium-doped fluoride-based UC phosphors with known visible and NIR emission were attached to the rear of a bi-facial silicon solar cell. The external quantum efficiency (EQE) of solar cell system is reported and compared with the absorption properties of the phosphors.

1. INTRODUCTION

1.1 Motivation

Photons with a lower energy than the bandgap of a silicon solar cell usually travel straight through the device and therefore will not contribute to the electrical output of the cell, resulting in sub bandgap losses. Up-conversion occurs when a material is photoexcited at a longer wavelength resulting in photoemission at a shorter wavelength. An UC material could be placed behind a bi-facial solar cell to 'up-convert' sub-bandgap photons (Fig. 1) and then reflect these higher energy photons back through the cell where they may contribute to an increase in overall efficiency.

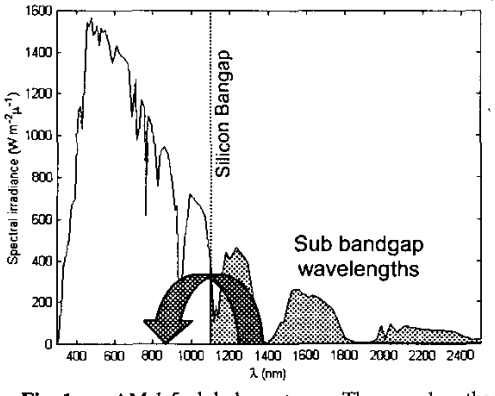

Fig. 1 AM 1.5 global spectrum. The wavelengths shaded could be 'up-converted' and therefore contribute to the power output of a silicon solar cell.

1.2 UC Materials

Common UC materials usually consist of a rare earth doped into an inorganic host. These materials are usually in the form of phosphors, crystals or fibres. Phosphors would be the most practical morphology for solar cell applications since they are more versitile.

Trivalent rare-earth-doped materials are commonly used for potential UC devices. Due to the high shielding of the rare earth 4*f* electrons, these ions are very insensitive to their host environment. There are very few instances in the literature of research being performed on UC phosphors in conjunction with solar cells. Saxena describes the use of terbium-doped lanthanum fluoride and thulium-doped calcium tungstate materials for application with photovoltaic (PV) devices [1], however actual measurements with solar cells were never reported. While the measured quantum efficiency (QE) was not very high, the predicted optical efficiency (IR light transmitted into the solar cell compared to light incident on the phosphor sheet) was not discouragingly low either [1]. Trupke *et. al.* have predicted that the upper limit of the conversion efficiency to be 63.2% for concentrated sunlight and 47.6% for non-concentrated sunlight can be achieved [2]. However, these efficiencies require a semiconducting material with a bandgap of about 2 eV [2].

1.3 UC Mechanisms

The concept of UC was first proposed in 1959 and called "quantum counter action" [3]. If an electron is lifted to a higher energy state due to photon absorption, it is said to be excited. Excited state absorption (ESA) occurs when an excited electron is raised to an even higher energy state due to absorption of another photon. The electron may then drop to a lower state releasing a photon with an energy greater than either of the two photons previously absorbed. A more efficient UC mechanism is energy transfer UC (ETU). This occurs if a nearby ion (which is also excited) absorbs the photon emitted by a neighbouring ion. The electron in the second ion is lifted to an even higher energy level and may therefore drop to the ground state releasing an even higher energy photon. ESA and ETU mechanisms require the presence of metastable energy levels and could be used to up-convert wavelengths ~1500nm within Erbium ions (refer to Fig. 2). At low power densities, typical for non-concentrated sunlight, the UC QE increases with the square of the incident power density. This situation changes at higher power densities to become a linear relationship [4].

Other UC mechanisms consist of second-harmonic generation (SHG) [5] and simultaneous two-photon absorption (STPA) [6]. While both SHG and STPA can achieve NIR to visible conversion efficiencies of up to 25% [7], both methods benefit from an intense coherent light source, typically a pulsed or continuous-wave laser.

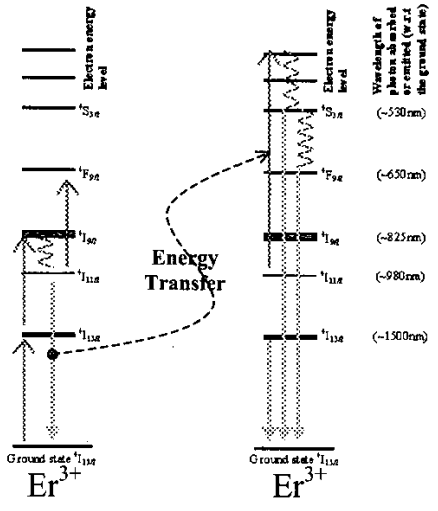

Fig. 2 Diagram showing ESA and ETU UC mechanisms between two Erbium ions under 1500nm excitation. Adapted from Shionoya *et. al.*[8]

2. EXPERIMENTAL

2.1 Phosphor Selection

In this work polycrystalline samples of erbium-doped sodium yttrium fluoride ($NaYF_4$: 20% Er^{3+}) were used. Similar samples, co-doped with ytterbium ($NaYF_4$:18% Yb^{3+}, 2% Er^{3+}) have exhibited NIR to visible UC external quantum efficiencies (EQE) of 5% with 980 nm laser light (200 W/cm^2) [9]. Yb has a broad metastable energy level and is often used as a sensitiser. Yb absorbs between 930 and 980 nm and emits between 980 and 1030 nm. Since silicon also absorbs at these wavelengths, Yb was not added to the phosphor samples. A commercial IR UC laser detection card (that also utilises UC phosphors) was also used in place of the $NaYF_4$: 20% Er^{3+} phosphors. This was done to allow a comparison between the $NaYF_4$: 20% Er^{3+} and commercially available phosphors. The composition of the commercial phosphors in unknown.

2.2 Experimental set-up

The polycrystalline UC samples were adhered to the rear of a bifacial buried contact silicon solar cell using an optically transparent acrylic adhesive medium (Fig. 3) with a refractive index $n=1.33$. The solar cell had an efficiency of 15% and 12% when illuminated from the front and rear respectively. Reflective white paint was used on the rear of the system and reflected over 80% of NIR photons.

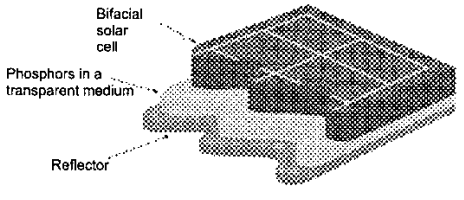

Fig. 3 PV device used to measure

2.3 Phosphor properties

2.3.1 Absorption measurements

Fig. 4 shows the absorption A for a 2 mm thick sample of $NaYF_4$:20% Er^{3+} phosphors mixed with an adhesive gel (with a weight ratio of 40:60). This curve was calculated using $A=100-R-T$ where R and T represent the measured reflection and transmission.

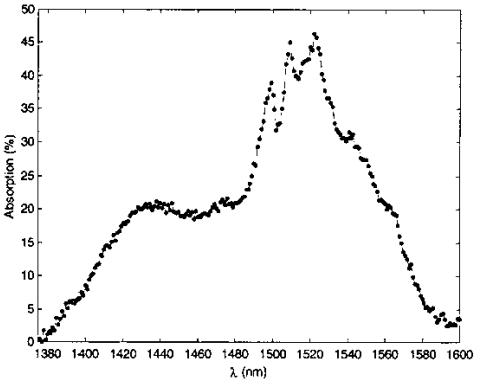

Fig. 4 Absorption of $NaYF_4$:20% Er^{3+} phosphors mixed with an adhesive gel.

2.3.2 Photoluminescence measurements

The PL spectrum for $NaYF_4$:20% Er^{3+} and gel mixture can be seen in Fig. 5. The photoluminescence (PL) of the sample on white paper was measured (980nm laser excitation). All absorption and PL measurements were taken at room temperature resulting in similar spectra (the peaks differ in wavelength by less than 2nm).

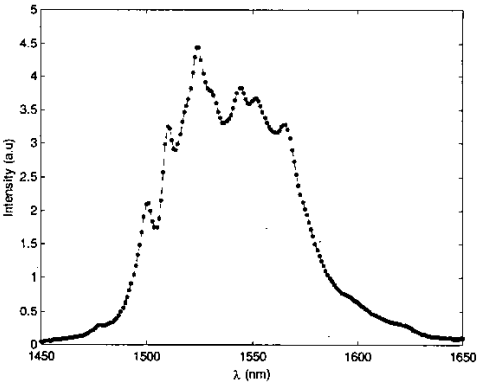

Fig. 5 PL Emission spectrum for $NaYF_4$:20% Er^{3+} and gel mixture (980nm

Similarly, Fig. 6 shows the emission spectrum for a commercial IR UC laser detector card, again by measuring the photoluminescence (980nm laser excitation).

Both the $NaYF_4$:20% Er^{3+} and the commercial IR UC laser detection card phosphors exhibit UC when excited by 1535nm laser excitation (Fig. 7). The peak at ~980nm corresponds to the Er $^4I_{11/2}$ transition energy level (refer to Fig. 2).

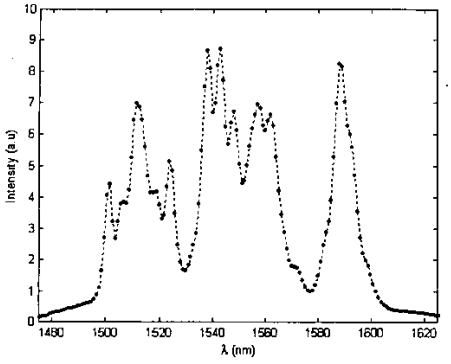

Fig. 6 PL Emission spectrum for a commercial IR UC laser detection card (980nm excitation).

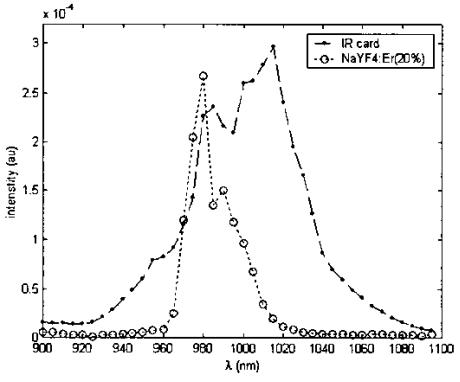

Fig. 7 Comparison of PL UC spectra for various phosphors (1535nm excitation) showing UC at 980nm.

3. SOLAR CELL RESPONSE

Fig. 8 shows the EQE (%) of a bi-facial solar cell with $NaYF_4$:20% Er^{3+} phosphors adhered to the rear, compared to the EQE measured without the phosphors attached. It can be seen that the solar cell by itself still has a response up to about 1350nm.

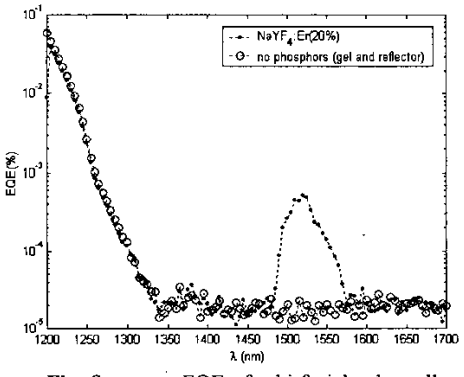

Fig. 8 EQE of a bi-facial solar cell with and without $NaYF_4$:20% Er^{3+} phosphors attached.

EQE measurements (1nm interval) of a bi-facial solar cell with $NaYF_4$:20% Er^{3+} compared with a commercial IR UC detector card adhered to the rear can be seen in Fig. 9. The peaks in the EQE curves correspond to the peaks in the absorption curves of the up-converting phosphors.

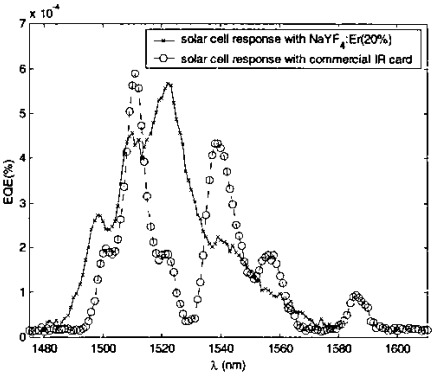

Fig. 9 EQE of a bi-facial solar cell with UC phosphors adhered to the rear.

4. CONCLUSION

Both $NaYF_4$:20% Er^{3+} and commercially available phosphors have been used to up-convert sub-bandgap photons and improve the spectral response of a solar cell at longer (NIR) wavelengths. Furthermore, $NaYF_4$:20% Er^{3+} phosphors yield UC results similar in magnitude to commercially available phosphors.

UC phosphors have a very low UC efficiency, but any non up-converted light would have otherwise been 'lost'. UC is a non-linear process implying that significantly larger efficiencies are predicted at higher light intensities. UC phosphors adhered to an optimised bi-facial solar cell operating under many suns may increase the overall efficiency of the solar cell.

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