Upconverting glasses for high-efficiency solar cells

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A suitable back layer can improve harvesting of light energy by changing two or more low-energy photons into a single energetic one.

Increasing the efficiency of solar cells is essential to make renewable energy sources compete commercially with petrochemicals. One difficulty is that photovoltaics can only harvest light which has at least a certain amount of energy, known as the bandgap. Light with less energy than this, i.e., the infrared part of the spectrum, cannot be used.

Many ways to improve efficiency have been suggested. Our approach, however, does not modify the solar cell itself but the light harvesting system as a whole by developing materials that can be applied as an additional layer to the reverse side. The performance of the solar cell and the module can thus be optimized independently of each other. Estimates¹ suggest that the efficiency of a bifacial solar cell, i.e., one that absorbs light in the front and back, could be increased to almost 50% by placing an upconverting material on the reverse side. We used this method to convert low-energy photons into high-energy ones demonstrating an increase in the efficiency of a photovoltaic system. Specifically, our system is glass doped with the trivalent rare-earth ion erbium (Er^{3+}).

Upconversion is the sequential absorption of two low-energy infrared photons by a rare-earth ion followed by a subsequent emission of a visible photon. The efficiency of this process is dependent on the lifetime of the intermediate energy level of the ion, which itself depends on the lattice vibrations (phonons) of the host material. Low-phonon energy glasses, like fluorozirconate (FZ) ones,² are desirable hosts for rare-earth ions because they enable emission from levels that would be quenched by high-phonon energy glasses.³

We prepared a set of FZ glasses doped with Er^{3+} ions to show the potential of this system for upconversion applications.⁴ The glasses are derived from a standard 'ZBLAN' formulation,⁵ made from zirconium, barium, lanthanum, aluminum, and sodium fluorides. Upon excitation with a 1540nm continuous

Figure 1. Upconverted fluorescence spectra of the 9.1mol% Er-doped FZ glass sample. Excitation is carried out with a CW laser diode operating at 1540nm with 17.2 (black), 7.8 (blue), 3.55 (red), and 1.15mW (green). The range from 900–400nm was blown up by a factor of 5. All spectra have been normalized to the 2-photon near infrared (NIR) emission at 980nm. eV: electron volts.

wave (CW) laser diode, the Er-doped FZ glasses show intense upconverted fluorescence. The corresponding spectra for a 9.1mol% Er-doped sample in the 400–1100nm spectral range can be seen in Figure 1. For around 1mW excitation power at 1540nm, an external quantum efficiency (EQE) of 1.6% was found for a 9.1mol% Er-doped FZ glass. Besides the 980nm emission in the near infrared (NIR), the most intense visible light emissions are green (530nm and 550nm) and red (660nm). In addition to the spectral behavior of the Er^{3+} emission, Figure 1 shows that the relative intensity of the upconverted fluorescence bands depends significantly on the excitation power. With increased excitation power from 1.15mW (green curve) to 17.2mW

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Figure 2. Digital photo of the experimental setup to measure the external quantum efficiency of a commercial monocrystalline silicon solar cell⁶ with an upconverting Er-doped FZ glass sample on top. Excitation is carried out from the top with a CW laser diode operating at 1540nm (not shown). The incident light is perpendicular to the cell and the glass. The cell measures 2×2cm and the sample 7×7×2mm.

(black curve), the relative intensity ratio between the emission at 980nm (where two photons are needed to excite this emission, and the emissions at 530nm, 550nm, and 660nm, where three photons are needed to excite these emissions) changes in favor of the 3-photon upconversion processes.

To demonstrate the effect and to show the potential of the glass, we measured the EQE of a commercial monocrystalline silicon solar cell with a typical bandgap of 1.1eV. Our glass sample is placed on top of the cell, as shown in Figure 2. (Please note that this is not a bifacial solar cell.) We repeated our measurement for a range of glasses, doped with Er^{3+} ions in varying amounts. We did not optically couple the samples to the cell, i.e., we did not use index matching oil between the glasses and the cell. We measured the power dependence shown in Figure 3 by recording the short-circuit current of the solar cell (with an upconverting glass on top) for different laser-diode output power. We observed a short-circuit current from 18mW (maximum laser-diode output power) down to approximately 100μW. Under direct illumination with the 1540nm laser, the short-circuit current was negligible, showing that our glasses made it possible for the cell to

Figure 3. External quantum efficiency (EQE) in 2, 5, 9.1 and 13mol% Er^{3+} -doped FZ glass samples, recorded under CW laser diode excitation at 1540nm.

harvest light energy that would not usually have been absorbed. We saw saturation of the EQE for all doping levels, which happens when the upconversion processes changes in favor of the 3-photon ones. Thus, one more photon is needed to emit a photon that can be absorbed by the solar cell. For the 2mol% doped sample, it occurs at over 10mW excitation power, but for the 13mol% Er-doped glass, it is about 0.8mW, with a trend to even lower values.

In summary, upon excitation in the IR-region, FZ glasses doped with Er^{3+} emit strong upconverted fluorescence in the NIR and in the visible spectral region. Measurements of the EQE of a commercial monocrystalline silicon solar cell with an Er-doped FZ glass on top demonstrate the potential of these upconverters for photovoltaic applications. Future experiments will aim to increase upconversion efficiency, which could be achieved by increasing the Er-doping level or by using glass ceramics such as a glass containing fluorescent nanocrystals.

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