

Reconsidering the Shockley–Queisser limit of a ferroelectric insulator device

To the Editor — Spanier and co-authors recently presented BaTiO₃ ferroelectric insulator devices that were reported to exceed the Shockley–Queisser detailed balance limit of solar-photovoltaic-cell power conversion efficiency under AM1.5G illumination (*Nat. Photon.* **10**, 611–616; 2016). We would like to discuss a few important details that we feel warrant more attention.

The illuminated current–voltage (*I*–*V*) characteristics of the BaTiO₃ devices with 3.2 eV bandgap were measured under simulated 1-sun AM1.5G irradiance (input power, $P_{\text{in}} = 0.1 \text{ W cm}^{-2}$). The BaTiO₃ devices were reported (Methods section in Spanier *et al.*) to have area dimensions of 5 mm × 5 mm. For the BaTiO₃ device measured with a single probe, the short-circuit current density (J_{sc}) was reported to be 19.1 mA cm⁻², and the open-circuit voltage (V_{oc}), fill factor (FF) and efficiency (η) were reported to be 1.2 V, 21% and 4.8%, respectively. For the BaTiO₃ device probed with a 1 μm × 1 μm array of 24 nanoscale indium tin oxide (ITO) electrodes, the effective J_{sc} was reported as 17.0 mA cm⁻² after presuming a 30× corrected increase in the measured photocurrent, and the measured V_{oc} was reported as ~0.35 V, assumed to be corrected to a new value of 1.1 V. The FF remained the same at 21% resulting in a reported efficiency of 3.9%. For context, under a 1-sun AM1.5G spectrum, a material with a 3.2 eV bandgap would only be able to generate a maximum J_{sc} of 1.06 mA cm⁻² and a maximum V_{oc} of 2.81 V, FF of 95% and η of 2.8% at 25 °C, calculated from the fundamental detailed balance limit for the typical case of one absorbed above-bandgap photon generating one electron and one hole.

To accurately determine J_{sc} and η of a solar cell it is critical to use an accurate value for the cell area. The physical length and width of a 1-sun non-concentrator solar cell defines its area. Even when gridlines, busbars and bond pads are present, they still count as part of the cell area. In the case of the BaTiO₃ devices reported by Spanier and co-authors, this would correspond to an area of 5 mm × 5 mm, or 0.25 cm². To calculate

J_{sc} and η , the authors used an effective carrier collection area instead of the actual 0.25 cm² total device area. Nonetheless, it is the total device area that governs J_{sc} and, in part, η of a 1-sun non-concentrator solar cell. Spanier and co-authors state that the photogenerated electron effective carrier collection area is equivalent to a hemispherical surface (under the top contact probe) of radius l_0 , where l_0 is a term referred to as the thermalization length. This hemispherical area is $2\pi l_0^2$. Spanier and co-authors report the term l_0 to be 100 nm. If $l_0 = 100 \text{ nm}$, then the area used for determining J_{sc} is $6.28 \times 10^{-10} \text{ cm}^2$, resulting in the reported J_{sc} of 19.1 mA cm⁻² (12 pA / $6.28 \times 10^{-10} \text{ cm}^2$; from Table 1 in Spanier *et al.*) and AM1.5G efficiency of 4.8%, where efficiency is given by $\eta = (J_{\text{sc}} \times V_{\text{oc}} \times \text{FF}) / P_{\text{in}}$.

Spanier and co-authors reported the efficiency from 5 mm × 5 mm (0.25 cm²) BaTiO₃ devices, either measured with a single contact probe or with a 1 μm × 1 μm array of 24 nanoscale ITO electrodes. The AM1.5G solar simulator was set up with a 25 mm × 25 mm aperture mask, which means that the much smaller 5 mm × 5 mm (0.25 cm²) BaTiO₃ devices were fully illuminated. It is important to point out that if a 0.25 cm² device is illuminated, then 0.25 cm² is the area that is used to determine J_{sc} , not an effective carrier collection area with a 100 nm thermalization length as its defining radius. Otherwise, according to this methodology, any 0.25 cm² solar cell could be claimed to have an artificially large J_{sc} by collecting electrons photogenerated from an area of 0.25 cm² but then using a much smaller area to compute the J_{sc} . To make this point more clear, the globally accepted definition of J_{sc} of a solar cell is not predicated on a circular or hemispherical area defined by a nanoscale thermalization length, but instead is a function of the actual area of the cell.

In our view, it seems plausible that the carrier collection area may be much larger than the contact area between the sample and the probe tip, and may be as large as the entire 5 mm × 5 mm sample area itself. The authors report that the measured short-circuit current I_{sc} under

monochromatic 405 nm illumination was not significantly different when measured with 25 nm versus 5 μm radii probe tips. This outcome is not unexpected. This suggests that the 100 nm thermalization length does not govern the carrier collection area and certainly not J_{sc} of the BaTiO₃ device. It also suggests that the carrier collection area is larger than the contact area between the probe tip and the device. If the full BaTiO₃ device area of 0.25 cm² is considered, the true J_{sc} will be $4.8 \times 10^{-8} \text{ mA cm}^{-2}$ (12 pA / 0.25 cm²). The small J_{sc} value of $4.8 \times 10^{-8} \text{ mA cm}^{-2}$ coupled with the small V_{oc} of 1.2 V and FF of 21% yields device power conversion efficiency of $1.2 \times 10^{-8}\%$, far less than the Shockley–Queisser 1-sun AM1.5G efficiency limit of 2.8% for a 3.2-eV-bandgap material at 25 °C. Additionally, the atomic force microscopy probes and 5 μm tungsten-coated probes used by Spanier *et al.* produce a shadow region over the probe/sample contact interface with dimensions much greater than the 100 nm thermalization length, and therefore the photogenerated electrons are collected from an area with a radius larger than 100 nm. Also, the small V_{oc} of 1.2 V, compared with the detailed balance limit of 2.81 V, does not lend support for collection of hot, non-equilibrium electrons from the 3.2-eV-bandgap BaTiO₃. In contrast, the authors claim that their BaTiO₃ devices collect hot, non-equilibrium electrons.

We believe, from the view of basic scientific protocol, that it is of utmost importance that the authors corroborate their claim that the fundamental Shockley–Queisser detailed balance limit of solar-photovoltaic-cell power conversion efficiency has been broken by providing independently verifiable photovoltaic cell test data — for example from the National Renewable Energy Laboratory (USA). Independent and certified *I*–*V* data is an absolute minimum requirement to validate whether or not the Shockley–Queisser limit has been exceeded. □

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