

# Harvesting sub-bandgap photons via up-conversion for perovskite solar cells

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## ABSTRACT

Lanthanide-based up-conversion (UC) allows harvesting sub-bandgap near-infrared photons in photovoltaics. In this work, we investigate UC in perovskite solar cells by implementing an UC single crystal  $\text{BaF}_2:\text{Yb}^{3+}, \text{Er}^{3+}$  at the rear of the solar cell. Upon illumination with high-intensity sub-bandgap photons at 980 nm, the  $\text{BaF}_2:\text{Yb}^{3+}, \text{Er}^{3+}$  crystal emits upconverted photons in the spectral range between 520 to 700 nm. When tested under terrestrial sunlight representing one sun above the perovskite's bandgap and sub-bandgap illumination at 980 nm, upconverted photons contribute to  $0.38 \text{ mA/cm}^2$  enhancement in the short-circuit current density at lower intensity. The current enhancement scales non-linearly with the incident intensity of sub-bandgap illumination and at higher concentration;  $2.09 \text{ mA/cm}^2$  enhancement in current was observed. Hence, our study shows that using fluoride single crystal like  $\text{BaF}_2:\text{Yb}^{3+}, \text{Er}^{3+}$  for UC is a suitable method to extend the response of perovskite solar cells to near-infrared illumination at 980 nm with a subsequent enhancement in current for very high concentrations.

## INTRODUCTION

Record power conversion efficiency (PCE) of perovskite solar cells (PSC) recently surpassed 25% after just over one decade of research and development.<sup>1</sup> Enhancing the PCE further is a key measure to decrease the cost of electricity generated from perovskite photovoltaics (PV) and one strategy to achieve this is to utilize the solar spectrum more efficiently.<sup>2,3</sup> Of all the third-generation PV concepts, the field of perovskite PV tandem devices – comprised of a wide-bandgap PSC combined with a low bandgap absorber, such as silicon – currently exhibit the record PCE.<sup>4,5</sup> Considering, the PCE has surpassed that of record silicon single junction devices, these advances raise significant interest in research and industry.<sup>6</sup> The technology however, still faces severe challenges in the device architecture related to the required current matching in the monolithic two-terminal PSC<sup>7</sup> or parasitic absorption losses in multi-terminal silicon-perovskite tandem cells, that require several transparent conductive oxides.<sup>8</sup> An alternative third-generation PV concept is spectral conversion, which targets tailoring the incident solar spectrum such that it is more suitable for light harvesting by a solar cell with a single absorber.<sup>2,3,9,10</sup> There are two ways to realize this. On the one hand, a down-conversion (DC) layer is used on top of the solar cell that reduces thermalization losses by generating two or more low-energy photons from a single high-energy photon.<sup>9,11,12</sup> On the other hand, an up-conversion (UC) layer can be implemented at the rear of a bifacial solar cell to minimize sub-bandgap (SB) transmission losses by generating a single higher-energy photon from the annihilation of two low-energy photons.<sup>10,13,14</sup> This way, the implementation of UC allows effectively extending the response of perovskite solar cells to the NIR range below the perovskite's bandgap.

UC itself was first explored by using lanthanide doped materials in infrared quantum counters in 1959<sup>15</sup> with their history being summarized in the review by Auzel<sup>16</sup>. In the mid-90s, Yb<sup>3+</sup>/Er<sup>3+</sup>

co-doped UC phosphors were employed in GaAs PV devices,<sup>17</sup> while in 2005 singly-doped Er<sup>3+</sup> UC layers were applied on the rear of bifacial silicon solar cells.<sup>18</sup> Fischer *et al.* reported the record enhancement in  $J_{SC}$  of 9.4 mA/cm<sup>2</sup> under concentrated sunlight (94 suns) by using  $\beta$ -NaYF<sub>4</sub>:25% Er<sup>3+</sup> micro-powder embedded in a polymer on the rear side of bifacial silicon solar cell.<sup>19</sup> First studies on UC in PSCs can be broadly divided into three categories. Firstly, UC nanocrystals were doped into different layers of the PSCs, namely, hole transport layer (HTL),<sup>20</sup> the perovskite absorber layer itself,<sup>21</sup> and at the interfaces.<sup>22</sup> While doping improved the performance up to an optimal concentration, doping beyond the optimum proved to be disadvantageous as the nanocrystals now acted as recombination centers.<sup>20,22</sup> Secondly, triplet-triplet annihilation up-conversion (TTA-UC) was applied to PSCs.<sup>23,24</sup> Organic dyes, which are a part of TTA up-converter, were embedded in polymeric sheets and placed behind a PSC as an UC layer.<sup>25</sup> Despite the promising enhancement in  $J_{SC}$ , the high excitation intensity (10 W/cm<sup>2</sup> or higher)<sup>25</sup> still required to up-convert near-infrared (NIR) illumination into the visible range remains to be the main limitation on the use of TTA-UC for PSCs. The third category uses UC inorganic materials in the form of single crystals or microcrystalline powders together with a PSC device stacked on top. These materials exhibit a much higher UC quantum yield compared to nanocrystals, since the latter have an increased number of surface defects that can cause additional luminescence quenching.<sup>26</sup> In addition, integration of nanoparticles into the various PSC layers limit the UC layer thickness to a few hundred nanometers.<sup>19-21</sup> Given the low absorption coefficient of lanthanide-doped materials (typically  $\sim 13$  cm<sup>-1</sup> for 15 mol.% of Yb<sup>3+</sup> at 980 nm),<sup>27</sup> a 200 nm thick layer of densely packed UC nanoparticles should absorb very small fraction < 0.03% of incident radiation at 980 nm. In contrast, a single crystal (or layer with dispersed UC microcrystals) can guarantee >90% absorption at 980 nm with a thickness of 1-2 mm. To date, there is only one study

by Chen *et al.* that reported the use of  $\text{LiYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  single crystal placed on the front side of a PSC and demonstrated 7.9% increase in PCE when excited with concentrated air-mass 1.5 global (AM1.5G) sunlight at an intensity of  $0.73 \text{ W/cm}^2$  (7-8 solar constants).<sup>28</sup> Hence, there is a lot of scope for exploring the excellent UC potential of these inorganic crystals for utilization of SB photons.

In this article, a  $\text{BaF}_2:\text{Yb}^{3+}, \text{Er}^{3+}$  single crystal doped with 15% of  $\text{Yb}^{3+}$  and 2% of  $\text{Er}^{3+}$  is used for harvesting of the SB photons in a bifacial PSC. A brief description of the optical properties of the  $\text{BaF}_2:\text{Yb}^{3+}, \text{Er}^{3+}$  single crystal along with an explanation of the UC process under NIR illumination is presented. Excitation of the combined PSC-UC device is performed with SB illumination to confirm that the enhancement in  $J_{\text{SC}}$  is indeed originating from UC of the SB photons. The possible effects of light soaking and temperature on the enhancement in  $J_{\text{SC}}$  are investigated and the interrelation of UC and illumination intensity with SB photons is explored. Finally, a conversion factor is calculated to determine the broad-band (BB) illumination intensity (AM1.5G) that is equivalent to the intensity of 980 nm laser used.

## EXPERIMENTAL DETAILS

### **Solar cells fabrication**

The bifacial solar cells with a layer stack of glass/ITO/ $\text{SnO}_2$ /SAM- $\text{C}_{60}/\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_3$ /Spiro-OMeTAD/ $\text{MoO}_x$ /ITO/Au grid were prepared on  $16 \times 16 \text{ mm}^2$  patterned indium doped tin oxide (ITO) substrates with sheet resistance  $15 \Omega/\square$  (Luminescence Technology). The substrates were cleaned in an ultra-sonic bath with acetone and isopropyl alcohol followed by oxygen plasma treatment for 3 minutes.  $\text{SnO}_2$  layer was deposited by spin coating using tin (IV) oxide 15% in  $\text{H}_2\text{O}$  colloidal dispersion (Alfa Aesar). The colloidal  $\text{SnO}_2$  was diluted with de-ionized water in

the ratio 1:6.5 and spin-coated at 4000 rpm followed by annealing at 250 °C for 30 minutes. Post annealing, oxygen plasma treatment was done on the substrates for 1 minute before further processing. C<sub>60</sub>-self-assembled monolayer (SAM) (Luminescence Technology) was used as a passivation for the electron transport layer (ETL). 7.5 mg of C<sub>60</sub>-SAM was mixed in 1 mL of 1, 2-dichlorobenzene (Sigma Aldrich) and was left on a magnetic stirrer at 65 °C over-night for dissolving. The solution was filtered with a 0.2 µm Polytetrafluoroethylene (PTFE) filter before it was spin coated on top of the SnO<sub>2</sub> at 4000 rpm and annealed at 120 °C for 5 minutes. Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>3</sub> perovskite solution was prepared by dissolving 1.3 mmol lead iodide in 1 mL solvent mixture of N,N-dimethylformamide (Sigma Aldrich, CAS: 68-12-2): dimethylsulfoxide (Sigma Aldrich, CAS: 67-68-5) in 4:1 ratio at 130 °C. In a separate glass vial, 1 mmol of formamidinium iodide (Dyesol, CAS: 879643-71-7) and 0.17 mmol of CsCl (Alfa Aesar, CAS: 7647-17-8) were weighed. The lead iodide solution was added to this vial after it was cooled down. The perovskite solution was spin coated using a two-step program of 1000-5000 rpm for 10 sec-30 sec. 120 µL of chlorobenzene (Sigma Aldrich, CAS: 108-90-7) was dropped on the center of the substrates at 15 sec of the second step. The samples were annealed at 150 °C for 30 minutes in an inert atmosphere. 80 mg of spiro-OMeTAD (Luminescence Technology) dissolved in 1 mL of chlorobenzene (Sigma Aldrich) doped with 17.5 µL lithium bis(trifluoromethanesulfonyl) imide (Sigma Aldrich) and 28.5 µL 4-tert-butylpyridine (Sigma Aldrich) was spin-coated on top of the perovskite solution. The Li solution was made beforehand by dissolving 520 mg/mL of lithium bis(trifluoromethanesulfonyl) imide in acetonitrile (Sigma Aldrich). The films were kept for aging for approximately 12 h in a dry box. 5 nm of MoO<sub>x</sub> (Sigma Aldrich) was thermally evaporated (Lesker) on top of the aged spiro-OMeTAD before 160 nm ITO was sputtered (Lesker) as top contact. Finally, gold bands were evaporated on the edges for ease of probing.

## Characterization of solar cells

The current density-voltage ( $J$ - $V$ ) characteristics and stabilized PCE of the bifacial devices were measured using class AAA light-emitting diode (LED)-based solar simulator (Wavelabs, Sinus 70). The solar simulator provided a close match to the AM1.5G spectrum, as plotted in **Figure S1**. The calibration was achieved using a certified silicon reference solar cell (Fraunhofer) with KG5 filter (Schott). A source-meter (Keithley, 2450) was used to conduct  $J$ - $V$  measurements and maximum power point (MPP) tracking. Probes with gold pins (fabricated in-house) were used to contact the cells for electrical measurements. The active area of the cell was 0.105 cm<sup>2</sup> and entire active area was completely illuminated during measurement. Initial characterization of the fabricated PSCs showed high reproducibility. The statistics of the batch with 24 PSCs used for the experiment demonstrated similar device performance as depicted in **Figure S2**. The  $J$ - $V$  characteristics of the champion cell exhibited a PCE of 18% with a stabilized power output (SPO) of 17% under MPP tracking for 300 s – see **Figure S3**.

External quantum efficiency (EQE) and ultraviolet-visible-near infrared (UV-Vis-NIR) spectra for PSC were measured in a Photovoltaic Device Characterization System (Bentham, PVE300). A monochromator was used to modulate the Xenon lamp. The chopper frequency of 905 Hz was used. The average  $J_{SC}$  of the PSC under 100 mW/cm<sup>2</sup> of AM1.5G is ~21 mA/cm<sup>2</sup>, which is within 4% as calculated from the EQE measurement shown in **Figure S4**. Transmittance and reflectance of the device stacks were also measured using an integrating sphere in the same setup. Absorptance was calculated using the formula  $A = 1 - T - R$ , where,  $T$  is the transmittance and  $R$  is reflectance. The EQE for PSC-UC device was calculated from  $J_{SC}$ , which was measured using source-meter (Keithley, 2450) excited via a titanium:sapphire (Ti:Sa) continuous-wave (CW) laser (M-Squared Lasers Ltd., SolsTis)

### **Optical characterization of UC single crystal**

The detailed description of the optical setup can be found elsewhere.<sup>27,29</sup> Briefly, to measure UC quantum yield – the ratio of the number of photons emitted via UC to the number absorbed at the excitation wavelength – the sample was placed in the middle of an integrating sphere (Labsphere, Ø15cm, 3P-LPM-060-SL). It was excited with a 976 nm laser diode (Thorlabs, L980P200) mounted on a temperature-controlled mount (Thorlabs, TCLDM9) and driven using a laser diode controller (Thorlabs, ITC4001). The excitation intensity was changed with a computer-controlled filter wheel (Thorlabs, NDC-100C-2) and the excitation power was measured with a power meter (Thorlabs, PM320E) using a fraction of laser intensity (4%) reflected off a glass wedge placed into the beam path. The whole optical system was calibrated using a calibration lamp (Ocean Optics, HL-3plus-INT-CAL-EXT). The UC emission spectra were recorded using the setup for measurements of UC quantum yield.

### **Characterization of PSC-UC device**

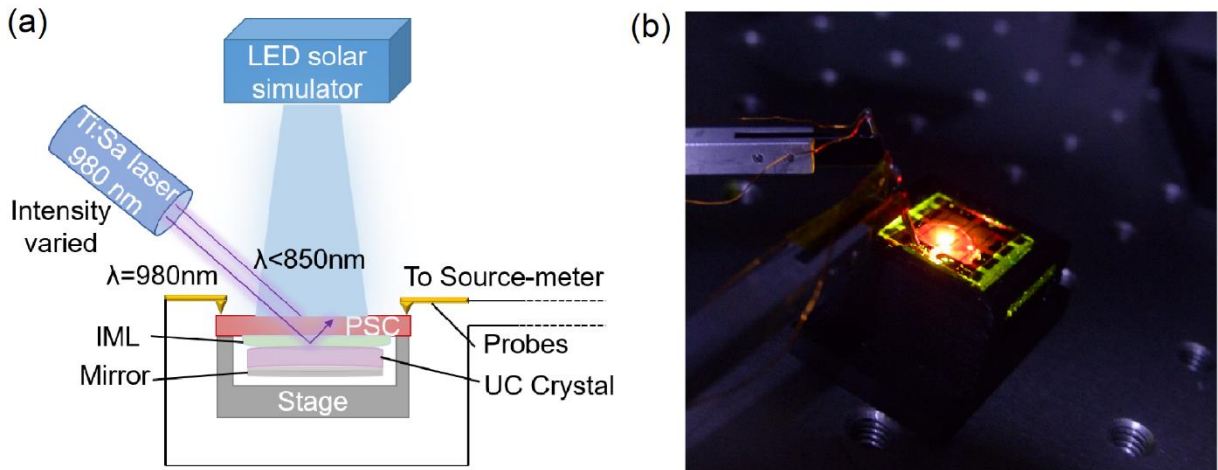
The details of the BaF<sub>2</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> single crystal synthesis have been reported earlier.<sup>30</sup> A tunable Ti:Sa CW laser (M-Squared Lasers Ltd., SolsTis) pumped by 532 nm laser (Coherent, Verdi-V18) was used as a source of 980 nm emission. A fraction of the beam reflected off a quartz wedge placed in the beam path was directed at a photodiode power sensor (Thorlabs, S122C) connected to a power meter (Thorlabs, PM100D) and used to control the laser intensity. This power measured was calibrated to the actual power reaching the sample. The size of the laser beam was measured with a camera-based beam profiler (Thorlabs, BC106N, VIS/M). The device was placed in the same position as crystal and image was taken. It was assumed that the beam has elliptical shape and two axis of the ellipsoid were calculated from fitted Gauss functions as  $1/e^2$  width = 1.699



FWHM. 100cm focal length lens (Thorlabs) was additionally used to enhance the geometric concentration of the Ti:Sa laser.

The experimental setup used for the measurement of enhancement in  $J_{SC}$  and the overall influence of UC on PSC is illustrated in [Figure 1\(a\)](#). A holder was used to accommodate the bifacial PSC with the UC crystal at the rear. This combination of PSC with UC crystal is referred to as PSC-UC device. To ensure light coupling between the two and avoid unwanted reflections from surfaces, silicone immersion oil was used between the glass side of the PSC and the UC crystal as an index matching liquid (IML). The refractive index of the IML ( $n = 1.49$ )<sup>31</sup> is close to that of the UC crystal ( $n = 1.48$ )<sup>32</sup> at 980 nm. A LED-based solar simulator was used to excite the samples. The solar simulator was programmed such that output wavelengths were chosen to match the AM1.5G spectrum in range 350 – 850 nm. This was achieved by turning the channels at higher wavelengths ( $> 850$  nm) off. This precautionary measure was taken to ensure that the excitation in the SB range of  $> 850$  nm, comes only from the NIR bias light source (Ti:Sa laser) – even though the intensity of NIR part of the spectrum provided by solar simulator is low in comparison. The intensity of the solar simulator was  $\sim 70$  mW/cm<sup>2</sup> throughout the experiment, and is referred to as BB illumination. The wavelength of the illumination of Ti:Sa laser was tuned to 980 nm, as BaF<sub>2</sub>:15% Yb<sup>3+</sup>,2% Er<sup>3+</sup> crystal exhibits its highest absorption coefficient at 974 – 980 nm (attributed to the transition Yb<sup>3+</sup>:<sup>2</sup>F<sub>7/2</sub> to <sup>2</sup>F<sub>5/2</sub>) – shown in [Figure S1](#). In the experiments conducted within this work, the intensity of the NIR light source was varied and is referred to as the SB illumination. Continuous BB illumination and additionally cycled SB illumination at 980 nm ( $\sim 4.2$  W/cm<sup>2</sup>) having a period of 200 s and 50% duty cycle was used as an excitation source for spectral dependence and MPP tracking experiments. The stabilized power output (SPO) from MPP tracking was normalized to maximum power value. In our setup, since the BB+SB illumination

was excited from the top, cooling of the PSC could only be implemented from the bottom of the PSC. However, due to the presence of the UC crystal (which acts as a thermal insulator) beneath the PSC, cooling mechanism could not be applied. Convection cooling might also not be effective for such highly concentrated source of illumination as laser.<sup>33</sup> Therefore, temperature of the PSC was not maintained to standard test condition (STC) of 25°C. The green and red emissions from the PSC upon illumination by NIR illumination is shown in [Figure 1\(b\)](#).

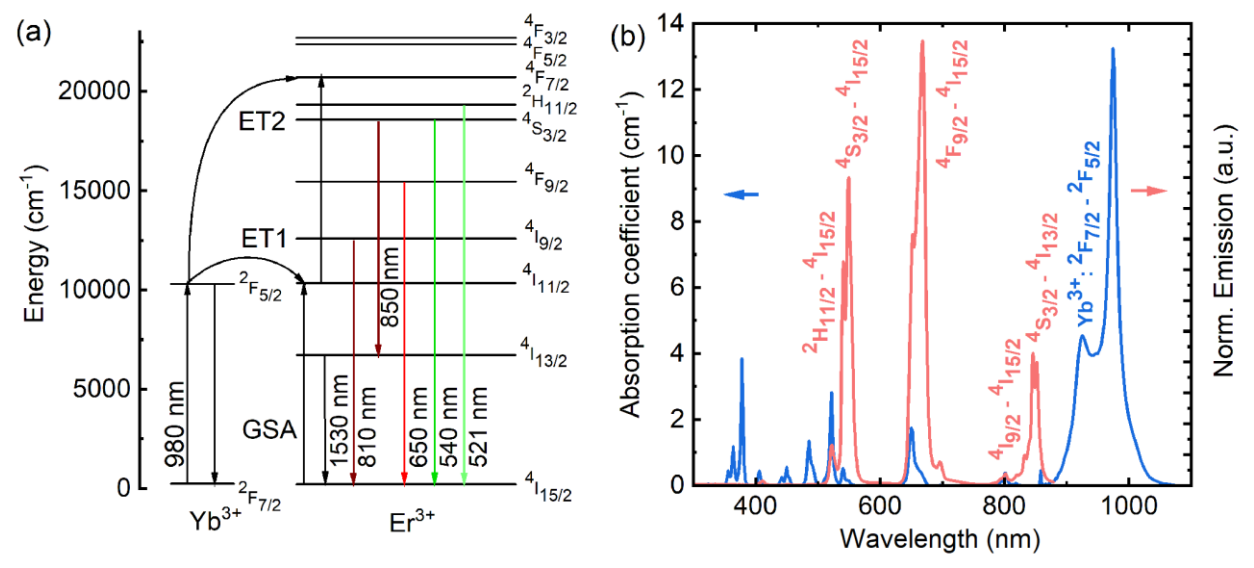


**Figure 1.** (a) Schematic representation of the experimental setup used for the measurement of enhancement in  $J_{sc}$  and the overall influence of UC on PSC-UC device (b) Image of bifacial cell and UC crystal under only 980 nm SB illumination at the intensity of  $4.5\text{ W/cm}^2$ .

## RESULTS

Here, a  $\text{BaF}_2:\text{Yb}^{3+}, \text{Er}^{3+}$  is used as UC material as it can be grown as a single crystal and possesses a low phonon energy ( $\sim 240\text{ cm}^{-1}$ ).<sup>30</sup> The latter contributes to reduced non-radiative losses and thus results in a high UC quantum yield.<sup>30</sup> The  $\text{Yb}^{3+}$  ion functions as a sensitizer and harvests light in the SB range (860 – 1080 nm). It then transfers the energy to  $\text{Er}^{3+}$  ion that performs as an activator and emits the upconverted photons.<sup>34</sup> The co-doping using  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  ions is

favorable for the UC process. This is due to the fact that  $\text{Yb}^{3+}$  exhibits a higher absorption cross-section of the excited state ( $^2\text{F}_{5/2}$ ) compared to that of  $\text{Er}^{3+}$  state with similar energy ( $^4\text{I}_{11/2}$ ).<sup>35</sup> Besides this, the near-resonant nature of these two levels allows an efficient energy transfer (ET) process from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  as shown in [Figure 2\(a\)](#). The UC emission spectrum – displayed in [Figure 2\(b\)](#) – illustrates the multiple emission bands of  $\text{Er}^{3+}$ , all resulting from transitions from a range of excited states back to the ground state  $^4\text{I}_{15/2}$ . While the emissions  $\geq 810$  nm as shown in [Figure 2\(a\)](#) will either be transmitted or reflected by the perovskite layer, the energy of the red and green emission exceeds the bandgap of the perovskite absorber. Hence, these photons can be absorbed by the perovskite layer and thereby contribute to the photocurrent generation.



**Figure 2.** (a) Energy level diagrams of the  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  ions along with the energy transfer (ET) UC mechanism (b) Absorption coefficient and normalized emission spectra of the UC crystal (emission measured under 980 nm excitation).

The PSCs in focus of this study were prepared in a bifacial architecture, details of which was described earlier. The double-cation  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_3$  perovskite layer exhibits a bandgap of 1.57

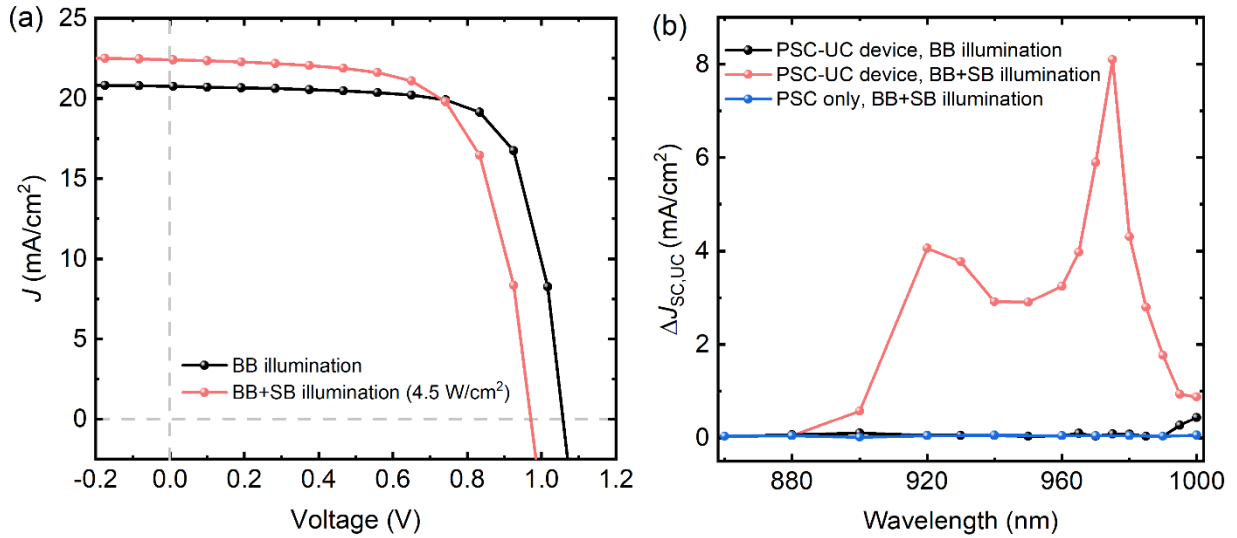
eV.<sup>36,37</sup> Thus, any photon with energy <1.57 eV (> 810 nm) cannot generate electron-hole pair in the perovskite absorber. To realize the contribution of the photocurrent from photons with energy above the bandgap of the perovskite absorber and from the upconverted photons, a custom measurement setup was used in this study as illustrated in [Figure 1\(a\)](#) and described in detail in experimental section. At 980nm, around 60% of the SB photons are transmitted through the bifacial perovskite solar cell – see transmission in [Figure S5](#)– and subsequently absorbed by the UC crystal. When re-emitted as higher energy photons by the UC crystal as depicted in the picture in [Figure 1\(b\)](#) and absorbed by the perovskite layer, they contribute to photocurrent generation in the PSC.

To obtain an insight about the contributions of the upconverted photoemission to the photocurrent generation in the PSCs,  $J$ - $V$  scans were performed under BB+SB illumination. The intensity of SB illumination was set to  $\sim 4.5 \text{ W/cm}^2$ . A noticeable enhancement (red) in  $J_{SC}$ , as compared to only BB illumination (black), was observed in the PSC-UC device as shown in [Figure 3\(a\)](#). A maximum value of  $22.4 \text{ mA/cm}^2$  was measured for the PSC-UC device at 980nm ( $4.5 \text{ W/cm}^2$ ). To further comprehend the contribution of the spectral response in the increased  $J_{SC}$ , the excitation wavelength of the Ti:Sa laser was varied from 860 nm to 1000 nm and the photocurrent was measured. Absolute enhancement in  $J_{SC}$  due to UC ( $\Delta J_{SC,UC}$ ) was calculated – presented in [Figure 3\(b\)](#) – based on the following [Equation 1](#):

$$\Delta J_{SC,UC} = \frac{I_{SC(BB+SB \text{ illumination})} - I_{SC(BB \text{ illumination})}}{A_{spot}} \quad (1)$$

where,  $I_{SC(BB+SB \text{ illumination})}$  is the short-circuit current measured under BB+SB illumination,  $I_{SC(BB \text{ illumination})}$  is the short-circuit current only under BB illumination and  $A_{spot}$  is the size of the laser beam spot. The results indicated the PSC-UC device excited with both BB+SB illumination yields an increase in current density a  $\Delta J_{SC,UC}$  if the SB illumination appears in the wavelength

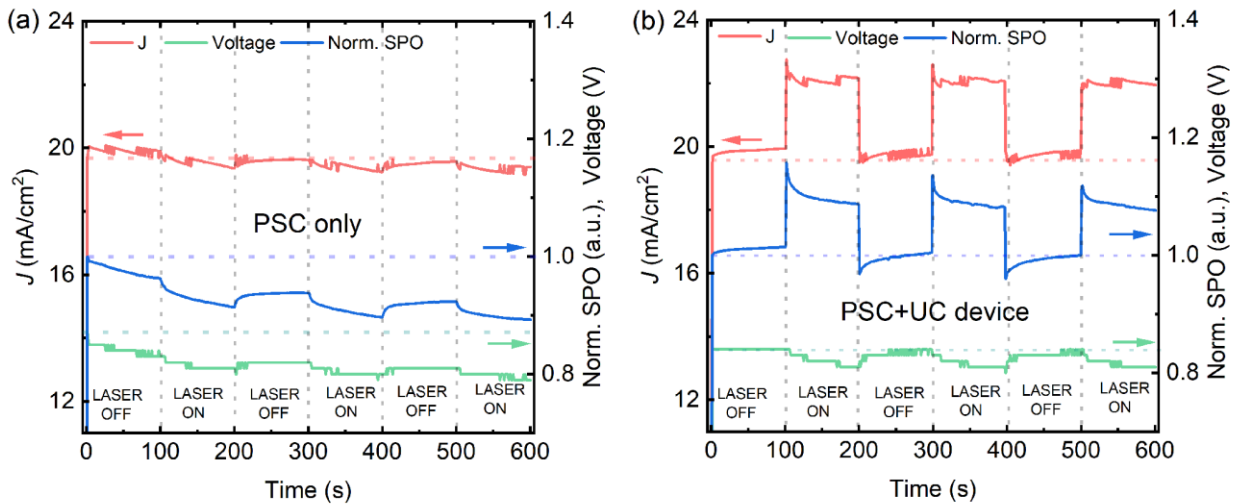
range 974 – 980 nm. This observation is well in line with the absorption spectra of the UC crystal as shown in [Figure 2\(b\)](#) and implies that the resultant increase in the  $J_{SC}$  originates from the UC crystal. External quantum efficiency measured from the  $J_{SC}$  showed that the maximum EQE ( $2.75 \times 10^{-2} \%$  at 975nm,  $4.2 \text{W/cm}^2$ ) contribution was below 1% for these PSC-UC devices. The rather low enhancement in EQE is attributed mostly to the low UC quantum yield of  $\text{BaF}_2: \text{Yb}^{3+}, \text{Er}^{3+}$  UC crystals of max.  $\sim 1\%$  at these intensities (refer to [Figure S6](#)). Furthermore, it must be taken into account that there are additional reflection and parasitic absorption losses of these upconverted photons before they can be converted into charge carriers by the perovskite absorber. Nevertheless, the results indicate that if the UC quantum yield of the UC crystal can be increased, more SB photons can be harvested. The results presented in [Figure 3\(a\)](#) also show that along with the desired increase in  $J_{SC}$  with increasing excitation intensity of SB illumination, both the open-circuit voltage ( $V_{OC}$ ) and the fill factor (FF) of the PSC decreased. This decrease could be due to the increased temperature of the PSC due to a prolonged exposure to the intense SB illumination.<sup>38,39</sup> An increase in temperature will reduce the built-in voltage,<sup>40,41</sup> which subsequently increases the minority charge carrier recombination<sup>42,43</sup> and decreases the  $V_{OC}$ .<sup>44,45</sup> Furthermore, due to heat, the activation energy of the ions are reduced, which can lead to ion migration. During ion migration, ions accumulating at the perovskite/charge transport layer interface act as a barrier to the extraction of charge carriers and decrease the FF.<sup>46</sup>



**Figure 3.** (a) Current density-voltage ( $J$ - $V$ ) characteristic of the PSC-UC device excited with only BB illumination (black) and BB+SB illumination (red). Intensity of at SB illumination was at 4.5  $W/cm^2$  (b) Spectral dependence of  $\Delta J_{sc,uc}$  measured from 860 nm – 1000 nm,  $\sim 4.2 W/cm^2$  at different conditions (i) PSC-UC device and with only BB illumination (black) (ii) PSC-UC device with BB+SB illumination (red) (iii) PSC only with BB+SB illumination (blue).

Light soaking is a phenomenon where the PCE of the PV device is known to change as a function of time under constant illumination. As the samples were excited with BB and/or SB illumination continuously in the previous experiment, understanding the contribution of light soaking in the observed enhancement of  $\Delta J_{sc,uc}$  is necessary. To investigate the same, the transient response ( $J$ , SPO and voltage) of the PSC-UC device to the SB illumination were investigated. The PSC-UC device was excited with BB illumination along with an additional cycled SB illumination as shown in [Figure 4\(a\)](#). The result showed that for PSC only, the  $J$  remained constant both during the on and off cycle of the SB illumination. This indicated that the SB illumination does not affect the value of  $J$ . Although  $J$  was unchanged, the voltage was reduced during the on cycle, presumably due to additional heat that was generated in the cell. As a result, decrease in the SPO was observed.

As soon as the off cycle started, the SPO increased and stabilized close to its initial value. For PSC-UC device, a sudden increase was observed in the value of  $J$  as the SB illumination was switched on as shown in [Figure 4](#)(b). Even though the voltage was reduced in a more gradual trend (as PSC only), during the on cycle, the increase in the  $J$  compensated for the losses. Hence, an overall increase in the SPO was observed. It should also be noted that during the on cycle with PSC-UC device, the  $J$  remained steady, while a decay response for both the voltage and the SPO is observed. This transient response of the PSC could be associated with ion migration in the perovskite layer with accumulation of the charge carriers at the perovskite/charge transport layer interface, as discussed above.



**Figure 4.**  $J$  (red), normalized stabilized power output (blue), voltage (green) tracked for (a) PSC only and (b) PSC-UC device near the maximum power point (MPP) over 600 s with continuous air-mass 1.5 global (AM1.5G) illumination and additional cycled sub-bandgap excitation at (980 nm, 4.2 W/cm<sup>2</sup>) having a period of 200 s and 50% duty cycle

UC is a non-linear process, which means that the quantum yield depends highly on the intensity of the incident photons.<sup>10</sup> To vary the intensity of SB illumination, the laser power was increased

between 0.6-4.5 W/cm<sup>2</sup> while keeping the wavelength at 980 nm. The UC crystal showed the highest absorption at this wavelength. To achieve even higher intensity of the excitation, a lens was placed in the beam path such that it focused the laser beam on the crystal with a relatively smaller beam spot (see **Figure S7**). For the given UC crystal, the UC quantum yield is depicted in **Figure S6**. At low illumination intensity of about 0.6 W/cm<sup>2</sup>, an UC quantum yield of  $\phi_{UC} = 0.2\%$  is achieved. However, with increasing excitation intensity, the UC quantum yield increases steadily with values  $>1\%$  at intensity exceeding 10 W/cm<sup>2</sup>.

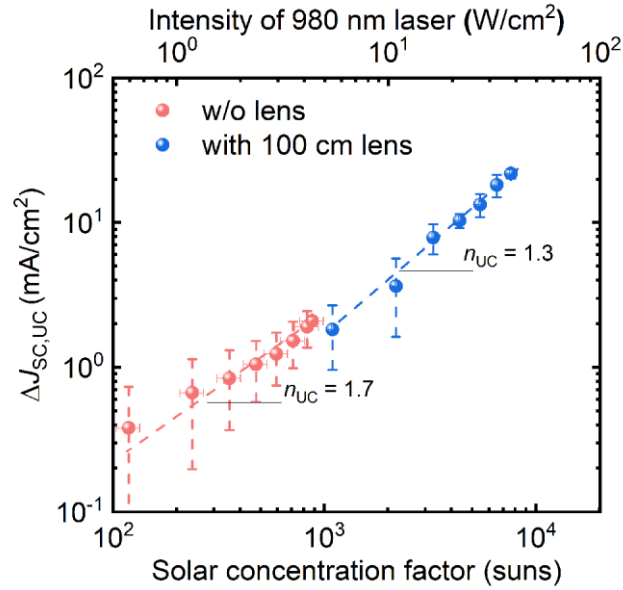
The source of sub-bandgap illumination is spectrally concentrated with narrow linewidth. In order to estimate how concentrated a broadband spectrum such as AM1.5G was needed to get the same photon intensity in the NIR range and achieve the same  $\Delta J_{SC,UC}$ , a concentration factor ( $C$ ) was calculated. **Equation S1** in [Supporting Information](#) gives further details on  $C$ , which is followed from a previous work by Fisher *et al.*<sup>16,47</sup> It was approximated that a concentration of 197 times AM1.5G sunlight (from 860 nm to 1080 nm at 70 mW/cm<sup>2</sup>) would be necessary to achieve the same effect as 1 W/cm<sup>2</sup> of laser illumination at 980 nm. The lowest intensity of the CW laser that provided a measurable value of  $\Delta J_{SC,UC}$  (0.38 mA/cm<sup>2</sup>) was equivalent to 120 suns (0.6 W/cm<sup>2</sup>). A maximum of  $\Delta J_{SC,UC} = 2.09$  mA/cm<sup>2</sup> was measured at 880 suns (4.5 W/cm<sup>2</sup>) without using any focusing lens. By integrating optics into the system, the geometric concentration and the incident excitation can be increased. There are two options for placing this optics: (i) between the PSCs and the single crystal and (ii) between the light source and the solar cell. As shown in the experiments with silicon solar cells, although the optical element introduced between the solar cell and the UC layer can increase the quantum yield of the UC process, it also disrupted the collection of the UC emission by the solar cell.<sup>47</sup> In another example, the wavefronts of both the excitation and emission fields were modulated with incorporation of dielectric microbeads.



Due to extremely short Rayleigh range and small absorption cross-section of lanthanide materials, the fraction of light, efficiently upconverted, was very small and had a rather weak impact on the generated UC photon flux. In order to avoid unwanted absorption and maximize the external UC generation efficiency, the Rayleigh range of the focused radiation should correlate to the size of the UC material.<sup>48</sup> In our experiment, this range was about 3 mm. Hence, a lens of 100 cm focal length was introduced in between the SB illumination source and the solar cell. Such high concentrations of illumination might be of little significance in the field of PV, but this experiment helps to understand the non-linear behavior of the  $\Delta J_{SC,UC}$ . The results of the absolute enhancement as a function of the laser intensity is reported in [Table 1](#). [Figure 5](#) shows the relationship between  $\Delta J_{SC,UC}$  and intensity.

**Table 1.** Enhancement in  $J_{SC}$  due to UC with constant BB illumination of 70 mW/cm<sup>2</sup> and intensity variation of SB illumination

SB illumination intensity (W/cm <sup>2</sup> )	Solar concentration factor (suns)	$\Delta J_{SC,UC}$ (mA/cm <sup>2</sup> )
0.60±0.08 (no lens)	120±15	0.38±0.35
4.50±0.56 (no lens)	880±110	2.09±0.13
10.00±0.19 (100 cm lens)	2230±37	4.01±2.01
38.80±0.65 (100 cm lens)	7650±128	21.81±1.59



**Figure 5.** Enhancement in upconverted current density ( $\Delta J_{SC,UC}$ ) obtained for various solar concentrations. Red represents data without focusing and blue represents use of lens of focal length 100cm.

The measurement of  $\Delta J_{SC,UC}$  at lower intensity has higher deviation. This could arise from the inaccuracy with which the  $\Delta J_{SC,UC}$  or the area of beam spot ( $A_{spot}$ ) was measured. Since error in measurement of  $A_{spot}$  is more likely, a further discussion of how  $A_{spot}$  was measured is also presented in [Supporting Information](#). For measurements without the lens  $A_{spot} = 0.105 \pm 0.01 \text{ cm}^2$ . The obtained beam sizes and their deviation are presented in [Table S1](#), alongside [Figure S7](#), depicting  $A_{spot}$  for laser source measured without and with lens. The enhancement in  $\Delta J_{SC,UC}$ , compared to the reference, at 120 suns is only about  $\sim 0.38 \text{ mA/cm}^2$ . However, significant enhancement up to  $\sim 2.09 \text{ mA/cm}^2$  is demonstrated at 880 suns. It should be noted that introduction of the lens decreased the area of the beam spot ( $A_{spot} = 0.0165 \pm 1.77 \times 10^{-4} \text{ cm}^2$ ). A maximum enhancement of  $\sim 21.81 \text{ mA/cm}^2$  was achieved at 7650 suns.

## DISCUSSION

Further comparison with state-of-the-art literature shows potential of device based on PSC and BaF<sub>2</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> UC crystal for third generation PV. Recently, Kinoshita *et al.* reported the use of a TTA-UC film at the rear of a PSC. Upon excitation with a diode laser (938 nm, 10 W/cm<sup>2</sup>), a  $\Delta J_{SC,UC}$  of 0.5 mA/cm<sup>2</sup> was observed.<sup>25</sup> While the approach is similar to that presented in this study, the novel BaF<sub>2</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> UC single crystal shows nearly 8 times stronger enhancement (4 mA/cm<sup>2</sup>) at the same intensity. This enhanced performance can be attributed to the higher absorption of single crystal at 980 nm as compared to the TTA-UC film used in the report by Kinoshita *et al.*<sup>19</sup> Another important reference with this context is the work by Chen *et al.* with a remarkable enhancement of 7-8%.<sup>28</sup> However, it is unclear to the authors how such a high enhancement was achieved by placing the LiYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> UC single crystal in front of the PSC, taking into account that placing UC crystal in the path of the incident light may induce additional parasitic absorption losses. Parasitic absorption can arise as the UC crystal may absorb certain part of the incident solar excitation in the range of 350-850 nm, reducing the amount of photons reaching the solar cell in the first place. It is also surprising how with an absorption coefficient of approximately 3 cm<sup>-1</sup> compared to 13 cm<sup>-1</sup> at 980 nm in the present work, a high UCQY of 1.75% was obtained at very low excitation intensity. It is also not clear from their manuscript how a light concentration of 7-8 solar constant was realized using only solar simulator. Details of the type of laser used, filter implemented to achieve the stimulated sunlight (>800 nm) and how beam area was measured is also lacking. In essence, it was not possible to make direct comparison of LiYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> and BaF<sub>2</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> single crystals applied for PSC.

Considering lower  $J_{SC}$  enhancement observed in our work compared to LiYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> single crystal, possible optical losses were examined in more detail. It is well known that UC is a non-

linear process.<sup>10</sup> As a result, the UC quantum yield increases with rise of the excitation intensity. The trend for the freestanding BaF<sub>2</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> crystal is depicted in **Figure S6** of [Supporting Information](#). Intensity dependence of UC luminescence demonstrates power coefficient  $n_{UC} = 1.7$  at intensity  $> 10$  W/cm<sup>2</sup>. As demonstrated in [Figure 5](#), demonstrates that  $\Delta J_{SC,UC}$  increases with power coefficient  $n_{UC} = 1.3$  at similar intensity. The observed difference in the power coefficient suggested that there are additional loss mechanisms in the device compared to the freestanding crystal. A reflection loss of 4% can be expected for normal incidence from air on a surface with  $n > 1$  in PSC only.<sup>49</sup> In case of PSC-UC device, additional reflection loss can be expected between UC crystal-air and air-PSC interface, if the PSC and UC crystal are not optically coupled. However, the use of IML in this work eliminated this additional loss. A significant portion of the incident excitation  $\sim 26\%$  is lost through the escape cones.<sup>49</sup> Even implementing a back reflector, as done in this work, does not help curb this problem as the reflected light is lost from the front face.<sup>49</sup> Additionally, PSC has  $\sim 30\%$  absorptance at 980 nm, which is dissipated only as heat. It has been previously discussed that heating of the device modifies its PV characteristics. Thus, the temperature negatively affected the performance of PSC-UC device. In-depth understanding of the effects of increased temperature and precautionary measures to be taken to avoid its detrimental effects is a topic of further research. Two questions remain as yet unanswered. First, what is the most effective manner to properly utilize UC in PV. Second, considering the size of single crystals is limited with the established synthesis techniques, what methods can be applied to effectively upscale such crystals for incorporation into large-scale devices while maintaining their effectiveness. Fluoride materials in the form of large discs are possible to implement by means of optical ceramics production, as described in the review.<sup>50</sup> A recent review by Richards *et al.* indicates that several orders of magnitude increase in the generation rate is required before UC can

begin to be an efficient process,<sup>51</sup> thus taking advantage of nanophotonic structures,<sup>52</sup> plasmonics<sup>53</sup> and concentrated light<sup>54</sup> all become interesting approaches.

## CONCLUSION

This work reports that the utilization of SB photons for photovoltaics is indeed possible via the use of an UC single crystal like BaF<sub>2</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup>. The following conclusions can be drawn. Firstly, upon irradiating the PSC-UC device with BB+SB illumination, noticeable enhancement in  $J_{SC}$  as compared to BB illumination was observed. This confirms that the UC of SB photons with an UC material such as BaF<sub>2</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> is a viable way to increase the response of PSC to NIR illumination. An enhancement of 0.38 mA/cm<sup>2</sup> as compared to the reference (without UC) was achieved at 0.6 W/cm<sup>2</sup> (equivalent to 120 suns). Secondly, transient effect of light soaking was investigated by performing MPP tracking with cycling SB illumination at 4.2 W/cm<sup>2</sup> along with constant BB illumination. PSC-UC device showed drastic increment in  $J$ , during SB illumination on cycle. However, in PSC only, detrimental effect of increased temperature was observed. This proved that  $\Delta J_{SC,UC}$  is not a time-dependent, light-soaking phenomenon. Thirdly,  $\Delta J_{SC,UC}$  at lower intensity was not significant, however, upon increment in intensity of SB illumination, a prominent enhancement of 2.09 mA/cm<sup>2</sup> was observed at 4.5 W/cm<sup>2</sup> (equivalent to 880 suns). Different losses and increase in temperature can limit the  $\Delta J_{SC,UC}$ . However, by implementing methods to minimize the losses or by preventing the increment in temperature, one could also prevent these adverse effects. It would also help prevent increased dark saturation current and ion accumulation in the solar cell. Synthesis of more efficient UC material, development of advanced synthesis techniques and fabrication of devices more suited for such applications can make the future prospects of UC crystals more promising in the context of SB energy harvesting.

## ASSOCIATED CONTENT

**Supporting Information.** The Supporting Information is available free of charge at ACS Publications website <http://pubs.acs.org> at DOI:

Details of device fabrication along with supporting data. ([PDF](#))

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### Author Contributions

U.W.P and A.T. conceived the idea; A.F. and D.B. performed initial investigation; R.S. fabricated and characterized the solar cells; S.G. developed the double cation perovskite and I.H. developed the semi-transparent ITO top contact; V.A.K., A.N.N. and S.V.K. synthesized  $\text{BaF}_2:\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$  UC single crystal. E.M. characterized the  $\text{BaF}_2:\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$  UC single crystal. R.S. and E.M. performed experimentation involving  $\text{BaF}_2:\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$  UC single crystal and solar cell. R.S. wrote the manuscript. B.S.R. provided extensive guidance on the measurement approach of combining UC materials with the solar cells as well as developing a clear story for the manuscript. U.W.P and A.T. supervised the project.

All authors have given approval to the final version of the manuscript.

‡ R.S. and E.M. have contributed equally to this work.

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## **Notes**

The authors declare no competing financial interest.

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# TOC Graphic

