Nonreciprocal photonic management for photovoltaic conversion: design and fundamental efficiency limits

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Abstract. Significant progress in the development of nonreciprocal optical components with broken Kirchhoff symmetry paves the way for increasing the photovoltaic (PV) conversion efficiency beyond the Shockley–Queisser limit due to reuse of emitted photons. Recent papers have analyzed the PV converter with several or an infinite number of multijunction cells, in which the cells are coupled via nonreciprocal filters (optical diodes) in such a way that the light emitted by one cell is absorbed by another cell. We proposed and investigated a single cell converter with nonreciprocal external photon recycling, which provided reabsorption and reuse of the emitting light by the same cell. We considered properties of photons in the sunbeam in terms of ergodicity, disorder, energy availability, information entropy, and coherence, and established fundamental limitations imposed by endoreversible thermodynamics on conversion efficiency at maximal power output. Our results show that the nonreciprocal converter with an ideal multijunction cell can approach the Carnot efficiency, whereas operating exactly at the Carnot limit requires an infinite number of photon recycling processes. This requirement resolves the famous thermodynamic paradox of the optical diode because any small dissipation in the cell or optical system enhanced by infinite recycling will stabilize the converter operation below the Carnot limit. We generalized endoreversible thermodynamics to photonic distributions with nonzero chemical potential and derived the limiting efficiency of the nonreciprocal single-junction PV converter. The performance of this converter with available GaAs solar cells was evaluated. © The Authors. Published by SPIE under a Creative Commons Attribution 4.0 International License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: 10.1117/1.JPE.12.032207]

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1 Introduction

Recent progress in nonreciprocal optics1 raises a set of principal questions about limiting efficiencies of photovoltaic (PV) converters with nonreciprocal photonic management. Fundamental limit imposed by thermodynamic laws on PV conversion efficiency is a critical issue for basic science and numerous applications, such as PV conversion of solar light, thermal radiation, and laser light. In this work, we consider perspectives for integration of PVs with nonreciprocal photonics. We propose and investigate an architecture of a PV converter and calculate limiting efficiencies on the base of endoreversible thermodynamics, which will be generalized to photonic systems with nonzero chemical potential.

Maximal efficiencies of traditional PV devices are given by the Shockley–Queisser (SQ) limit.2 The SQ limit is established by the balance between the absorbed photon flux, \( \dot{N}_{ab} \), and the emitted photon flux, \( \dot{N}_{em} \), which is proportional to the flux emitted in thermodynamic equilibrium, \( \dot{N}_{eq}^{em}(T) \). In the absence of nonradiative recombination, the balance of incoming and outgoing fluxes is described by two parameters. Spectral characteristics of the incoming flux and the cell absorption are taken into account by the average photon energy per a photon

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absorbed via creation of an electron–hole pair, $\epsilon^\ast = \hat{E}_{in}/\hat{N}_{ab}$. The balance between absorption and emission is described by the parameter, $A = \hat{N}_{ab}/\hat{N}_{em}^\ast(T)$. The open circuit voltage, $V_{OC}$, the voltage at maximal power, $V_m$, and the conversion efficiency, $\eta_{SQ}$, are given as

$$V_{OC} = \frac{kT}{q} \cdot \ln A,$$

$$V_m = \frac{kT}{q} \cdot [\text{LW}(A \cdot e) - 1] \approx \frac{kT}{q} \cdot \text{LW}(A),$$

$$\eta_{SQ} = \frac{kT}{e^\ast} \cdot \left[ \text{LW}(A \cdot e) - 2 + \frac{1}{\text{LW}(A \cdot e)} \right] \approx \frac{kT}{e^\ast} \cdot [\text{LW}(A) - 1],$$

where LW(x) is used for the Lambert W function and $e = 2.71828$ is Euler’s number. Let us note that the model and its solution can be generalized to include nonradiative recombination. In the general case, parameter $A$ should be multiplied by the external luminescence quantum yield (the external radiative efficiency), $A = (\hat{N}_{ab}/\hat{N}_{em}^\ast) \cdot k_i$. The approximated formulas for $V_m$ and $\eta_{SQ}$ correspond to an asymptotic solution at $A \gg 1$, which is well satisfied for solar energy conversion as well as for thermophotovoltaic (TPV) applications. The SQ efficiency is the conversion efficiency at maximal power, i.e., it is essentially endoreversible efficiency.

A significant part of the PV research traditionally focused on the improvement of light absorption to increase $\hat{N}_{ab}$ and reduce $\epsilon^\ast$. For $6000^\circ$ K black-body unconcentrated solar radiation and 100% absorption, the maximal SQ conversion efficiency [Eq. (3)] of a single-junction cell is 32.8%. For concentrated radiation, the limiting efficiency increases to 40.7%. The absolute maximum of the SQ efficiency is reached in the solar cell with an infinite number of junctions, each converting the quasimonochromatic radiation with the photon energy (color) that corresponds to the junction bandgap. This multicolor SQ limit of PV conversion efficiency is 86.8%.

Let us highlight that the SQ efficiency [Eq. (3)] gives the efficiency at maximal output power, whereas thermodynamics operates with infinite time processes that deliver null power. The thermodynamic PV efficiency is reached at the open circuit regime,

$$\eta_{th} = \frac{q \cdot V_{OC}}{e^\ast} = \frac{kT}{e^\ast} \cdot \ln A,$$

and corresponds to infinite photocarrier collection time (zero photocurrent). Comparing Eqs. (3) and (4), let us take into account that at $A \gg 1$ the Lambert function may be approximated as LW(A) $\approx \ln(A) - \ln \ln(A)$; therefore, in the first order in $\ln(A)$, Eq. (3) for SQ efficiency reproduces the thermodynamic efficiency, $\eta_{th}$ [Eq. (4)]. The second-order term in the SQ efficiency, $-\ln \ln(A)$-term, is negative, and the SQ efficiency [Eq. (3)], i.e., efficiency at maximal output power, is always below the thermodynamic efficiency [Eq. (4)], which gives the efficiency at zero output power.

In accordance with thermodynamics, the maximal conversion efficiency of solar energy by any converter at zero output power is the Carnot efficiency, which is the maximal thermodynamic efficiency for any engine. According to Eq. (4), the thermodynamic conversion efficiency for the monochromatic radiation is also given by the Carnot formula. As it is required by thermodynamics, the Carnot efficiency is reached in the open circuit regime in a state of equilibrium between semiconductor and the Sun, when the light absorption angle matches the emission angle. Moreover, in the case of monochromatic radiation, the detailed balance that assumes 100% reuse of the emitted radiation also leads to the Carnot efficiency (Eq. 4.27 in Ref. 4 and Eq. 4.5 in Ref. 6). As explained in Ref. 4, the reuse of the emitted radiation means that “the energy returns to the Sun perhaps for later use (slowing down, for example, the Sun’s energy loss process!” TPV system is designed to avoid losses of photons reflected and emitted by the cell, so the efficiency limit for the monochromatic TPV converter operating at maximal power is given by the Carnot formula.

At the same time, in many books and papers, the maximal conversion efficiency of solar energy at zero and nonzero power is associated with the Landsberg limit, which is derived for
the equilibrium (isotropic) black body radiation and employs the corresponding black body entropy, which includes entropy related to the random direction of photon wavevectors at any space point. For the 600 K radiation, the Landsberg limit is 93.3%, while the Carnot limit in this case is 95%. The difference between thermodynamic Carnot and Landsberg limits in PV conversion is still not well understood.

The SQ limiting efficiencies are based on the detailed balance (Kirchhoff’s law), not on thermodynamic functions. As SQ limiting efficiencies are associated with 100% absorption, the efficiencies beyond the SQ limit require a reduction of photon emission below the value established by the detailed balance under SQ model assumptions. In recent years, there has been an increasing interest in PV devices with the angle restricted emission, which was proposed and theoretically investigated in Ref. 7. In Refs. 8 and 9, various optical tools were used to restrict the light emission angles. In Ref. 8, the emission angle was limited by the photonic crystal placed at the front surface of the GaAs cell. In Ref. 9, the light emitted from the cell was reflected back by a high-quality mirror doom with a narrow hole for incoming solar light. The ultimate arrangement of angle restricted emission provides the optimal reciprocal photonic coupling between the Sun and the solar cell. In this case, the ultimate efficiency is equal to the Shockley–Queisser limit for maximal light concentration, i.e., 40.7% for a single junction cell and 86.8% for the cell with an infinite number of junctions. Thus, the reciprocal optical management of the absorption–emission balance does not allow one to overcome the SQ limitations.

Let us highlight that the reciprocity of absorption–emission processes is not a thermodynamic law but a consequence of Kirchhoff’s law, according to which, the absorptivity, \( \alpha(\omega, \mathbf{n}) \), and emissivity \( e(\omega, \mathbf{n}) \) should be equal for any photon energy, \( \hbar \omega \), and for any propagation direction, \( \mathbf{n} \). In fact, the reciprocity (nonreciprocity) in Kirchhoff’s law is the consequence of the Onsager–Casimir reciprocity (nonreciprocity) relations, which are totally general and employ time-reversal symmetry (asymmetry) of basic electromagnetic, mechanical, and quantum-mechanical processes. Time-reversal asymmetry in the system may be generated by a magnetic field, magnetization, electric current, directed particle flux, time-modulation of optical properties, and various relaxation processes. In general, all of these phenomena may be used for engineering nonreciprocal light propagation and transmission.

Advanced photonic nanostructures with broken time-reversal symmetries demonstrate a strong potential to revolutionize numerous applications ranging from optical quantum-information technologies to solar energy conversion. Nonreciprocal optical structures can provide high absorptivity, \( \alpha(\omega, \mathbf{n}) \approx 1 \), together with near-zero emissivity, \( e(\omega, \mathbf{n}) \approx 0 \), in some narrow absorption cone \( \Delta \Omega \) with the axis direction \( \mathbf{n} \) and high emissivity, \( e(\omega, \mathbf{n'}) \approx 1 \), together with near-zero absorptivity, \( \alpha(\omega, \mathbf{n'}) \approx 0 \), in the strongly different direction \( \mathbf{n'} \). Due to the separation of emission and absorption, nonreciprocal optical structures can drastically reduce emission from a PV converter without a reduction in the light absorption. When employing these structures, one may exceed the SQ efficiency limit.

Nonreciprocal properties are experimentally established in variety of optoelectronic materials and structures. The most common nonreciprocal structures are based on magneto-optically active materials with a strong Faraday effect. Kirchhoff’s law can be also violated in nonlinear and nonequilibrium processes with energy redistribution between some electromagnetic modes. The corresponding nonlinear phenomena include Raman amplification and stimulated Brillouin scattering. The broken reciprocity is also demonstrated in devices with a time-dependent refractive index. Nonequilibrium nonreciprocal photonic management includes the well-known greenhouse effect. Due to reduced emission, a solar cell covered by the greenhouse filter can achieve efficiency beyond the SQ limit.

In spite of significant theoretical research in time-asymmetric PVs, key questions about the limiting PV efficiency at maximal power and realization of corresponding photonic management are still under discussion. Practically, all papers in this area conclude that the upper limit of solar energy conversion efficiency for nonreciprocal PV converters is the Landsberg limit. Although the authors of Ref. 25 have not challenged the Landsberg limit for solar energy conversion, for the TPV conversion, they proposed a converter design that provides the Carnot efficiency at maximal output power. According to Ref. 25, such a converter includes an infinite set of absorbers with temperatures \( T_{in} \), which change gradually from the emitter temperature, \( T_{em} \), to the environment temperature \( T_0 \). This set of absorbers is integrated with two infinite sets of...
nonreciprocally coupled engines. The first set of engines operates between the emitter and absorbers, and the second set operates between absorbers and the environment. Although operation with the Carnot efficiency at maximal output power is disputed, the authors of Ref. 25 highlight that the proposed converter with infinite numbers of absorbers and engines is of infinite size and strictly speaking thermodynamic consideration is not applicable to infinite systems. The well-known example of such problems is the heat death of the universe introduced by William Thomson in 1851. As pointed out by Max Planck, “entropy of the universe” has no meaning because it cannot be defined for an infinite system.26

Current active debates about maximal efficiencies of various engines are not limited by PV conversion. The general question of whether the Carnot efficiency can be achieved at finite output power is intensively investigated within the well-established linear response formalism introduced by Onsager. Reference 27 claims that the broken time-reversal symmetry in thermoelectric phenomena makes possible the thermoelectric converter with Carnot efficiency at nonzero output power. However, this conclusion is strongly criticized in several papers.28,29 In particular, in Ref. 29, it was found that the two-terminal thermoelectric Carnot engine is impossible due to an intrinsic instability that keeps the engine from reaching a steady operating regime at finite power. Although the Onsager approach describes well the thermoelectric conversion, it is not applicable to the PV conversion, which is a substantially nonlinear process [see Eq. (3)]. Analysis of some engines operating in nonlinear regimes, such as quantum Otto engines, shows that the Carnot efficiency can be achieved at nonzero output power.30 Thus, the limiting efficiencies of solar light conversion are still under debate.

In summarizing the introduction, we would like to highlight that the fundamental limits of the PV conversion efficiency at maximal power are conceptually described by (i) the Landsberg approach, (ii) endoreversible thermodynamics, and (iii) the Shockley–Queisser detailed-balance approach. In the Landsberg model, the efficiency is limited by the thermodynamic entropy of the heat carriers (photons) inside the emitter cavity. In general, in endoreversible thermodynamics, the efficiency is limited by the entropy production in the operating engine as well as by the entropy production in the heat transfer from the emitter to the engine. The Shockley–Queisser detailed-balance approach focuses on the engine (converter) operation and takes into account solely entropy production in the engine. As the solar light propagates without photon scattering and dissipation, the SQ approach follows from the general endoreversible thermodynamics. In the next section, we discuss the Landsberg limit associated with the entropy of the black body radiation in a cavity and show that the black body entropy is not applicable to the solar light. The Shockley–Queisser detailed balance approach [Eqs. (1)–(4)] is not applicable to the nonreciprocal photonic management because, in this case, the emitted radiation does not leave the PV converter. For the nonreciprocal photonic management, we consider fundamental limits established by endoreversible thermodynamics and generalize the endoreversible thermodynamics to photonic distributions with nonzero chemical potential.

2 Entropy of Solar Light: Disorder, Relativity, Information, and Unavailability of Energy

Entropy is a universal measure of disorder, information, and unavailability of energy. For example, in the black body, the motion of photons is random and ergodic. Black body radiation does not provide any information about matter and its distribution inside the blackbody. For black body radiation, the energy density is $U(T) = (4/c)\sigma T^4$, and the corresponding entropy is $S(T) = (4/3c)\sigma T^3 = (1/3)U(T)/T$, where $c$ is the light velocity and $\sigma$ is the Stefan–Boltzmann constant. In accordance with thermodynamics, the maximum useful work possible during a process that brings the black body radiation with initial temperature $T_0$ into equilibrium with a heat reservoir with temperature $T_s$ is31

$$W = U(T_s) - U(T_0) - T_0 \cdot (S(T_s) - S(T_0)) = U(T_s) \cdot \left[1 - \frac{4}{3} \frac{T_0}{T_s} + \frac{1}{3} \left(\frac{T_0}{T_s}\right)^4\right]. \quad (5)$$

Therefore, the maximal conversion efficiency of the black body radiation with the temperature $T_s$ by any converter with the heat sink at temperature $T_0$ is given by the expression in square
brackets of Eq. (1). Landsberg proposed that the photon motion in the solar light is random similar to the motion in the black body cavity, i.e., it may be characterized by the same entropy per photon, and therefore, the maximal conversion efficiency of the solar light is the same as for the radiation in the black body cavity.32

In fact, photons in solar light propagate along straight lines without scattering, and their motion is highly correlated. Therefore, statistical and thermodynamic properties of photons in directed solar fluxes are substantially different from these characteristics in the black body radiation. Inapplicability of the entropy of the black body radiation to the photon fluxes was discussed by Lorentz,33 von Laue,34,35 Landau,31 Schrödinger,36 and Brillouin37 in terms of statistical physics, coherent optics, information theory, and dynamics of hierarchical systems. The discussion was initiated by Lorentz, who showed that, if the entropy of the directed light is associated with the entropy of the black body radiation, the sum of entropies of the reflected and refracted photon fluxes is larger than the entropy of the incident light. Lorentz highlighted that this entropy production would lead to the irreversibility of the light refraction. The paradox was resolved by Laue, who showed that the directed light is highly correlated and, when calculating the sum of entropies, one should take into account coherent correlations between the reflected and refracted lights. Entropy reduction due to coherent correlations is a keystone of modern resource theory, which is successfully applied to various systems of fermions and bosons.38

Light propagation and its thermodynamic characteristics were also intensively instigated in cosmology.39 Let us consider the one-dimensional (1D) photonic flux emitted by the black body cavity. In the medium without dispersion, all electrons in this flux propagate along straight lines in the same direction and with the same velocity. According to Einstein (see Ref. 39), the photonic temperature in the frame moving with photons is

\[ T = \sqrt{1 - u^2/c^2} T. \]  

Thus, in vacuum in the frame moving with photons, the photonic temperature is zero. Landsberg40 argued the Einstein formula [Eq. (6)] because “a bath which is thermal in an inertial frame S is nonthermal in an inertial frame S', which moves with some velocity with respect to S.” In other words, the equilibrium radiation will be nonequilibrium in the moving frame because the angle distribution in the moving frame “cannot be associated with a legitimate thermal bath (which is necessarily isotropic)”.40 Anyway, the conclusion regarding zero temperature of 1D photons propagating in the same direction has a simple physical meaning: as all photons move with the same velocity, the whole energy of this system is the mechanical kinetic energy that is available for conversion without any thermodynamic limitations. This interpretation is obvious for the 1D photons propagating in the medium with large refractive index \( n \gg 1 \), in which relativistic effects may be ignored.

The huge difference between the black body radiation in a cavity and the radiation emitted from the cavity is also well understood in statistical physics. In 63 Black Body Radiation of the Statistical Physics textbook,31 Landau highlighted this difference in the following way: “Let us imagine a black body emitting into surrounding vacuum. The radiation is propagated freely along straight lines and will not be in thermal equilibrium outside the body; it is by no means isotropic, as equilibrium radiation must be. . . . For equilibrium radiation the density exists for all directions, here it exists only for certain interval of directions.” Landau proposed describing the propagating radiation by the nonequilibrium temperature, which depends on the angle distribution in the flux and approaches zero for highly directed fluxes (see Eq. 63.26 in Ref. 31).

Strictly speaking, the solar light cannot be described even by the nonequilibrium entropy, i.e., by the entropy of a boson gas, \( S_b = (1 + N_e) \ln(1 + N_e) - N \ln N_e \), calculated with nonequilibrium photon distribution function, \( N_e \). This is a direct consequence of the nonergodic motion of photons in a solar flux. To proof this statement, let us consider the solar radiation in a thin spherical layer with the Sun in the center of this sphere (Fig. 1). Let the layer be divided into \( n \) small subsystems, so each of these subsystem has a volume \( \Delta V = V/n \), where \( V \) is the volume of the layer and consists of photons that propagate in a narrow solid angle \( \Delta \Omega = 4\pi \Delta V/V = 4\pi/n \), as shown in Fig. 1. Each photon subsystem moves along the radius directed from the Sun to this subsystem, and therefore, each subsystem moves with respect to other subsystems. However, thermodynamic equilibrium only allows for a motion of the whole system with a
constant velocity and a rotation of the whole system with a constant angular velocity (§10 in Ref. 31). Internal macroscopic motion of the subsystems shows that our system of Sun photons is not in equilibrium, and therefore, the mechanical kinetic energy related to the motion of these parts should be taken into account.

Next, if we try to distinguish mechanical and thermal components in the total energy of our photon system, we find that our system is nonergodic. To prove it, let us calculate the entropy of Sun photons in the thin spherical layer (Fig. 1) in accordance with thermodynamics. Thermodynamic entropy of the system per a unit volume is given as

$$S_V = -\frac{\partial}{\partial T} kT \sum \ln \left( 1 - \exp \frac{\hbar \omega(k)}{kT} \right),$$

where the sum is taken over all photon states described by the wavevector $\vec{k}$.

The thermodynamic entropy per a unit volume in the small subsystem is given as

$$\Delta S_{\Delta V} = -\frac{\partial}{\partial T} kT \sum_{\Delta \vec{k}} \ln \left( 1 - \exp \frac{\hbar \omega(k)}{kT} \right),$$

where the sum is taken just over photon wavevectors $\Delta \vec{k}$ directed in the narrow solid angle $\Delta \Omega = 4\pi \Delta V/V = 4\pi/\Delta$ (see Fig. 1). The specific entropy of the photon subsystem turns out to be smaller than the specific entropy of the whole system [Eq. (2)] because there is no mixing of photon states in the space of wavevectors and the phase volume available for a subsystem decreases as $n^2$. If we split our system into smaller subsystems, we will further reduce the specific entropy related to these subsystems. This consideration shows that the system and its subsystems are nonergodic. Entropy can be only introduced for ergodic systems, which assumes a strong mixing of particle states in a system.31,41

Let us note that, for the same reasons, the thermodynamic description of the thermal radiation in terms of view factors is also inapplicable to the TPV systems with reflecting mirrors and refracting lenses. For the directed photonic flux emitted by a hot emitter, “the Liouville’s description remains fully valid if reflecting mirrors and refracting lenses are present”... and therefore, “by means of lenses or mirrors the radiation can be focused.”31 In particular, in our recent works,42 we developed a diagrammatic technique for calculations of view factors in TPV systems with reflecting mirrors.

Let us note that the solar light propagation is collisionless and dissipationless. Similar to coherent quantum transport, the light propagation does not produce entropy.41,43,44 Thus, the solar energy is delivered to the PV converter or any other engine without losses. When a unit volume of photonic gas travels far away from the Sun, the solar light becomes more directed [the solid angle of photon wavevectors $\Delta \vec{k}$ in Eq. (8) decreases], and the motion of photons approaches to the uniform translational motion, i.e., macroscopic motion, which does not
contribute to the internal energy and entropy (§10 in Ref. 31). Although the photon number and energy fluxes in the narrow solid angle may be calculated via the black body emission formulas, a significant part of the photon energy is the macroscopic kinetic energy, which may be used without thermodynamic limitations.

From the optical point of view, the light propagating far away from the Sun becomes more coherent, i.e., entropy free. For this reason, the limiting conversion efficiency of a solar rectenna does not have any thermodynamic limitations and equals 100% for quasimonochromatic light. A multi-rectenna cell with an infinite number of rectennas can potentially convert the entire energy of a solar light into electricity.

Brillouin connected entropic characteristics of light with the information theory. He explained that “it is impossible to see anything in the interior of a black body.” So if we were surrounded by the black body radiation and have the same or a smaller temperature than the radiation temperature, we could not see the Sun. To see something inside the black body and obtain corresponding information, one should be equipped with the high temperature source of directed light, such as an electric torch, which “pours negative entropy into the system.” Brillouin shows that, in terms of the information theory, the directed light, e.g., the light from electric torch or from the Sun, should be described by the negative entropy (negentropy), which is given by $\Delta E/kT$, where $\Delta E$ is the photonic energy of the source.

In his famous essay “What is life?”, Schrödinger explains that the life is possible due to solar light, which provides negative entropy to the food chain of living things: “A living organism feeds upon negative entropy, attracting a stream of negative entropy upon itself, to compensate the entropy increase it produces by living and thus to maintain itself on a stationary and fairly low entropy level... Plants have their most powerful supply of negative entropy in the sunlight.” Thus, plants—living solar cells—collect the negative entropy from the sunlight and provide the negentropy hub for life on Earth.

Emerging PV technologies mimic energy conversion systems found in nature. The negative entropy of solar light is collected via the light-induced coherent electronic excitations that create chromophores. Recent two-dimensional electronic spectroscopy experiments have demonstrated the existence of coherence among vibronic levels in the initial response of light-harvesting proteins. Coherent kinetic and transport processes in plants have strong implications on light harvesting and conversion. Negentropic analysis of ecology and economic processes shows that it is possible to replace part of the natural entropy production with societal entropy production by making use of solar energy and, in this way, to suppress climate change effects.

### 3 Nonreciprocal Multicolor Limit

In this section, we employ classical endoreversible thermodynamics to investigate the limiting performance of the PV converter with nonreciprocal photonic management. We consider a rather simple one-terminal nonreciprocal system with a PV cell as a dissipative load. This design of a nonreciprocal PV converter is different from the previously considered PV architecture, which combines several two-terminal PV converters in such a way that the directional absorption of the next converter matches the directional emission of the previous converter, as shown in Fig. 2(a).

![Fig. 2](https://example.com/fig2.png)

**Fig. 2** (a) Multimodule PV converter with nonreciprocal photonic management. (b) Single module nonreciprocal PV converter (this work).
Any optical isolator with the PV cell load may be considered to be a one-terminal non-reciprocal dissipative system. Various designs of optical isolators have been discussed in recent papers. Here, we consider the PV converter with broken Kirchhoff symmetry, which absorbs 100% of light directed in the absorption cone without any emission into this cone and 100% emission in the different direction without any absorption in this direction (see Fig. 2). In Refs. 11, 12, 21, and 25, the authors considered PV systems with several PV cells that were arranged in such a way that light emitted by one cell was directed to another cell and contributed to its power output [Fig. 2(a)]. In our design, we split the absorption cone into two parts. The first part is used for absorption of solar light. The second part of the cone is employed for re-absorption of the SQ emission by the same PV cell, as presented in Fig. 2(b). Alternatively, we can employ the design of Ref. 9 with a high-quality mirror doom, which reflects the emitted light back to the cell. In this design, the nonreciprocal high absorption–low emission electrodynamics should be realized just in the narrow angle directed to the narrow hole for incoming solar light.

To calculate the multicolor limit for nonreversible PVs, we employ the endoreversible (finite time) thermodynamics. Endoreversible thermodynamics splits the conversion process into two stages. The first stage is the delivery of thermal power from the emitter to the hot side of the engine. In general, this process is described by nonequilibrium thermodynamics of transport phenomena. The second stage is the power conversion by the engine, which is described by classical thermodynamics and gives the Carnot efficiency for an ideal engine. The total endoreversible power conversion efficiency will be smaller than the thermodynamic engine efficiency only if we have energy losses at the first stage, when the thermal energy is delivered from the emitter to the hot side of the engine. In general, such losses may be related to dissipation in the heat delivery (thermodynamic dissipation losses) and to the emission of some part of the heat back to the emitter (emission losses, i.e., nonthermodynamic Kirchhoff losses).

Figure 3(a) shows an endoreversible scheme consisting of the heat source with the temperature $T_s$, the absorber with temperature $T_a$, and the heat reservoir with the temperature $T_0$. Sun photons propagate from the Sun to the converter without any dissipation and dissipation losses. However, in traditional reciprocal PV converters, a part of solar energy is always emitted back to the emitter in accordance with Kirchhoff’s law. In particular, for the Stefan–Boltzmann heat transfer, the heat flux obtained by the converter is $Q(T_a) = \sigma(T_s^4 - T_a^4)$, where $\sigma$ is the Stefan–Boltzmann constant. A Carnot engine operating between the absorber temperature and the reservoir temperature has the efficiency $1 - T_0/T_a$ and, therefore, provides the useful output power $W(T_a) = \dot{Q}(T_a) \cdot (1 - T_0/T_a)$. For the multijunction PV cell with an infinite number of junctions—solar energy converter with the Stefan–Boltzmann power supply—the maximum output power of the cell is realized at $T_a = 2544$ K, and the corresponding efficiency at maximal power is $\eta = W/\sigma T_a^4 = 85.4\%$. The obtained efficiency of the endoreversible converter is below the thermodynamic efficiency of the Carnot engine operating between $T_s$ and $T_0$ due to emission part of the heat, $\sigma(T_a^4)$, back to Sun.

As the description of nonreciprocal optical systems in terms of thermodynamics was debated for many years, it makes sense to discuss briefly the well-known thermodynamic paradox and

**Fig. 3** (a) General finite-time (endoreversible) thermodynamic schema of solar energy converter. (b) Finite-time thermodynamics of the PV converter with nonreciprocal photonic management presented in Fig. 2(b).
its less-known resolution. The paradox formulated by Rayleigh in 1855 states that the optical isolator could increase a temperature of the absorber above the Sun temperature, $T_s$, violating the second law of thermodynamics. For the popular Faraday’s isolator based on two polarizes and a ferrite placed between the polarizers, the paradox was resolved by Rayleigh himself 16 years later. Rayleigh pointed out that, although the Faraday’s isolator breaks the time-reversibility of the light propagation, the isolator does not provide the nonreciprocal propagation.53 Accurate consideration of this system shows that the light entering from the left as well as the light entering from the right can go through the Faraday’s isolator. In the first case, it requires just one trip across the device. In the second case, the light exits the system after three trips through the ferrite. For some nonreciprocal system, such as unidirectional microwave ferrite waveguide structures, the paradox was resolved by Ishimaru in 1962,54,55 who demonstrated by detailed calculations that any small dissipation in the ferrite puts limitations on the thermal energy transfer through the waveguide to the load. When the load temperature approaches the temperature of the oscillator, the ferrite is overheated and emits back to the oscillator in accordance with the second law. As usually in thermodynamics, the nonphysical solution only exists in the absence of fluctuations and related dissipation processes.56 Thus, in accordance with the second law of thermodynamics, a maximal value of the absorber temperature $T_a$ is limited by $T_s$. We return to the thermodynamic paradox after consideration of nonreciprocal PV systems and show its resolution for PV converters.

Now we apply the endoreversible thermodynamics to the solar energy converter with broken Kirchhoff symmetry. In the ideal nonreciprocal system, the thermal conductor will provide the entire power to the cell without any re-emission to the Sun. In this case, the maximum output power of the engine is realized at $T_a = T_s$, and the corresponding efficiency at maximal power is the Carnot efficiency $\eta_C = 1 - T_0/T_s$. In general, the nonreciprocal thermal power supply reduces the endoreversible thermodynamics to classical thermodynamics because the nonreciprocal one-way transfer of solar power suppresses the emission losses.

Next, we find the multicolor limit for the nonreciprocal PV converter, i.e., PV cell with an infinite number of junctions, each converting the quasimonochromatic radiation with the photon energy, $\hbar\omega$, that corresponds to the junction bandgap. In the ideal cell with nonresiprocal photon management, the light-induced electron distribution function, $f_e$, is described by the Fermi function with the same temperature, $T_s$, as the source of radiation (according to the second law, the electron temperature cannot exceed the Sun temperature). Then, useful energy of an electron at the edge of conducting band with the bandgap $\sigma_g$ is given as $^{31}$

![Fig. 4 Limiting efficiency of the nonreciprocal single-junction converter (blue line) and the Shockley–Queisser PV efficiency (red line).](image-url)
Taking into account that this junction converts photons with energy $h\omega = \sigma_g$ and every photon generates an electron at the edge of the conducting band, the conversion efficiency, $w_c/h\omega = 1 - T_0/T_s$, is independent on the photon energy. In Appendix A, we directly calculate the maximal efficiency of the PV converter presented in Fig. 2(a) and show that this efficiency in the multicolor limit is given by the Carnot formula in accordance with Eq. (9) obtained from thermodynamic consideration. Thus, the multicolor limit for the nonreciprocal PV converter is the Carnot efficiency, $1 - T_0/T_s$, which significantly exceeds the multicolor limit for the reciprocal converter of 86.8%.

As discussed in Sec. 1, in the case of 100% reuse of emission power, the monochromatic conversion efficiency is given by the Carnot formula (Eq. 4.27 in Ref. 4 and Eq. 4.5 in Ref. 6). The monochromatic conversion may be extrapolated to the multicolor limit in the following way. For the quasimonochromatic radiation with a finite bandwidth of $\Delta \nu$, which is smaller than the thermal energy $kT$, the Carnot formula remains valid with the accuracy of $\Delta \nu/\nu$. In the frequency domain, the power spectral density has the form of $\nu^2$ as the frequency approaches zero and the form $\nu^3 \cdot \exp(-\nu)$ as the frequency approaches infinity. Therefore, within any small accuracy of $\delta/2$, we can find the spectral range between $\nu_{\text{min}}$ and $\nu_{\text{max}}$, which consists of practically all radiation power. In this frequency range, we can choose the cell bandwidth $\Delta \nu$ for which the Carnot formula is valid within an accuracy of $\delta/2$. Thus, for any small $\delta$, we can find the finite number of quasimonochromatic junctions, $(\nu_{\text{max}} - \nu_{\text{min}})/\Delta \nu$, which provide conversion of the incoming radiation with the Carnot efficiency within the $\delta$-accuracy. In particular, we employed this procedure to check our modeling tools for TPV conversion with reuse of the emitted radiation.42

Let us highlight that the energy balance and corresponding efficiency of the nonreciprocal solar light converter is the same as that for traditional TPV converter with 100% photon reuse. The photon reuse in TPV systems is realized due to the back surface mirror, which reflects the emitted photons to the emitter. In a solar energy converter with nonreciprocal photonic management, the photon reuse is realized via photon reabsorption in the PV cell. Despite different mechanisms of the photon reuse, the energy balance for the TPV system and solar energy converter with nonreciprocal management is the same. Therefore, both systems have the same multicolor limiting efficiency given by the Carnot formula.

### 4 Nonreciprocal Single Junction Limit

As in the S-Q model, we accept that photocarrier relaxation processes are substantially faster than the recombination processes and, as a result, the electron distribution function is described by the light-induced chemical potential $\mu$. The photons emitted in radiative recombination processes have the same chemical potential as electrons. To determine the conversion limits in this model, we generalize the endoreversible thermodynamics to distributions with nonzero chemical potential. This generalization is possible because the photocarriers and emitted photons are concentrated in a narrow energy interval on the order of $kT_0$ near semiconductor bandgap and all conversion processes occur in this narrow energy interval.

In accordance with the second law of thermodynamics, we accept that the nonequilibrium distribution function of emitted photons near the semiconductor bandgap cannot exceed the distribution function of photons related to the radiation source. In the limiting case, a value of the distribution of emitted photons reaches the value of an equilibrium distribution with temperature $T_s$:

$$f_{\text{ph}}(T_s, \mu = 0, \epsilon = \sigma_g) = f_{\text{ph}}(T_0, \mu, \epsilon = \sigma_g), \quad (10)$$

where $f_{\text{ph}}$ is the Bose–Einstein function. From Eq. (10), we get the limiting value of the light-induced chemical potential, $\mu = \sigma_g(1 - T_0/T_s)$. The corresponding output electric power is $\mu J/q$, where electric current, $J$, corresponds to the incoming flux of sun photons absorbed
by the cell, \( J/q = \dot{N}_{ab} \). Presenting the energy of the photon flux as \( \epsilon/C_3 \cdot \dot{N}_{ab} \), where \( \epsilon/C_3 \) is the average photon energy in the flux per a photon absorbed [see Eqs. (3) and (4)], we get the efficiency of the nonreciprocal single junction cell

\[
\eta_{\text{nrc}} = \frac{\sigma_g}{e^\epsilon} \left( 1 - \frac{T_0}{T} \right). \tag{11}
\]

Taking into account that, for a traditional solar cell, the limiting value of the open circuit voltage is \( V_{OC} = \sigma_g (1 - T_0/T) \),\(^{52}\) we see that the obtained limiting efficiency for a nonreciprocal PV single-junction system at maximal power [Eq. (11)] corresponds to the limiting efficiency of a traditional cell at zero power [Eq. (4)]. The limiting efficiency of the nonreciprocal single-junction cell as a function of the semiconductor bandgap [Eq. (11)] is shown in Fig. 4.

Finally, we consider the practical limitations of the conversion efficiency in real asymmetric PV converters and clarify the resolution of the thermodynamic paradox in terms of nonreciprocal PVs. Let us take into account the nonradiative recombination in the PV cell. Suppose our nonreciprocal optical systems may reduce the equilibrium emission from the PV converter by a factor of \( A \). In particular, in the ergodic limit, the recycling factor is given by the well-known Yablonovitch formula, \( \phi = \pi n^2 d \alpha \),\(^{58}\) where \( n \) is the refractive index of the cell material, \( \alpha \) is the absorption coefficient, and \( d \) is the cell thickness. For example, in the GaAs thin films, the Asbeck recycling factor is 6 to 10,\(^{59}\) and the external radiative efficiency of GaAs cells is 0.3. In the nonreciprocal PV converters, the huge recycling factor drastically reduces the external radiative efficiency. As discussed, the PV conversion with nonradiative recombination is described by Eqs. (1)–(3), where parameter \( A \) is \( k_l \cdot (\dot{N}_{abs}/\dot{N}_{em}(T)) \). Taking into account suppression of the photon emission and corresponding reduction of the external radiative efficiency, for the nonreciprocal PV system with \( \phi_{\text{nrc}} \gg 1 \), we get

\[
A_{\text{nrc}} = k_l^{\text{nrc}} N_{\text{abs}}(T) \frac{N_{\text{em}}(T)}{N_{\text{em}}^{\text{nc}}(T)} = \dot{N}_{\text{abs}} \frac{\tau_{\text{nr}}}{\tau_r} = \frac{\dot{N}_{\text{abs}}}{R_{\text{nr}}(T)}. \tag{13}
\]

As expected, in this case the detailed balance is determined by the photon absorption rate, \( \dot{N}_{\text{abs}} \), and the nonradiative recombination rate in the cell, \( R_{\text{nr}} \). Equation (13) shows that the nonreciprocal photon management increases parameter \( A \) by the factor of

\[
\frac{\tau_{\text{nr}}}{\tau_r} = \frac{k_l^{\text{n}}}{1 - k_l^{\text{n}}}, \tag{14}
\]

where \( k_l^{\text{n}} \) is the internal photoluminescence quantum yield or internal radiative efficiency. Management of radiative emission is only important when the radiative recombination dominates over nonradiative processes. Among popular PV materials, GaAs has the high radiative efficiency. In particular, Ref. 60 reported 99.7% internal radiative efficiency. In this case, the open circuit voltage may be increased by \( (kT/q) \ln(\tau_r/\tau_{\text{nr}}) \approx 150 \text{ meV} \).

Our analysis of the PV converter with nonreciprocal light management also provides a rather simple resolution of the thermodynamics paradox, according to which the breakdown of the detailed balance leads to a violation of the second law.\(^{1,53-55,61}\) In the ideal PV system with ideal nonreciprocal optics, the suppression of emission from the PV converter would increase the
chemical potential of photocarriers above the thermodynamic limit given by Eq. (10). However, this solution exists only in the absence of dissipation in the optical system and in the absence of nonradiative recombination in the cell. As shown above, when the PV conversion regime approaches the thermodynamic limit, any small value of the nonradiative recombination rate ($\tau_{nr}/\tau \ll 1$) stabilizes the light-induced chemical potential [Eq. (13)] due to the strong enhancement of photon recycling and corresponding decrease of the external radiative efficiency. Contradictions with the second law arise only in models that ignore dissipation (fluctuation) processes.56

5 Conclusion

In this work, we proposed the practical design of the nonreciprocal single cell converter, generalized the finite time thermodynamics to electron distributions with the photon-induced chemical potential, calculated the limiting efficiency of the nonreciprocal converter with a single junction cell, and evaluated efficiency of the converter with available GaAs cells. The proposed single cell design [Fig. 2(b)] provided 100% reuse of the emitted photons as the design with an infinite number of cells [25,25] [Fig. 2(a)] due to broken Kirchhoff symmetry that violates the absorption–emission balance. Using cells with a large number of junctions, we also suppressed the losses related to the relaxation of photocarriers. In the multicell design, the Carnot efficiency can be approached in the PV converter with an infinite number of multijunction PV cells coupled via nonreciprocal components in such a way that the light emitted by one cell is absorbed by another cell [Fig. 2(a)].25 Operation of the proposed PV converter [Fig. 2(b)] with a multijunction cell at the Carnot limit required an infinite number of external recycling processes. So, any small dissipation in the nonreciprocal optics or in the solar cell limited the conversion efficiency in accordance with the second thermodynamic law. This result also provided a straightforward resolution of the thermodynamics paradox related to optical diodes.1,53–55,61

The Shockley–Queisser detailed balance approach and our approach based on endoreversible thermodynamics do not associate highly directed solar light with the entropy of the black body radiation. In addition to the energy unavailability, the entropy is a universal measure of disorder, information, decoherence, and complexity. In Sec. 2, we mathematically proved that any photon system in a sunbeam is nonergodic, and therefore, it cannot be described by thermodynamics in terms of temperature, entropy, and any other thermodynamic functions, at least in traditional thermodynamic meaning. As noted in textbooks on thermodynamics, we should clearly distinguish the equilibrium black body radiation and the radiation emitted by the black body (e.g., solar light). Is the solar light disordered as the black body radiation? Surely not, for the photon emission balance. Using cells with a large number of junctions, we also suppressed the losses related to the relaxation of photocarriers. In the multicell design, the Carnot efficiency can be approached in the PV converter with an infinite number of multijunction PV cells coupled via nonreciprocal components in such a way that the light emitted by one cell is absorbed by another cell [Fig. 2(a)].25 Operation of the proposed PV converter [Fig. 2(b)] with a multijunction cell at the Carnot limit required an infinite number of external recycling processes. So, any small dissipation in the nonreciprocal optics or in the solar cell limited the conversion efficiency in accordance with the second thermodynamic law. This result also provided a straightforward resolution of the thermodynamics paradox related to optical diodes.1,53–55,61

The limiting conversion efficiencies at maximal power are described by the endoreversible thermodynamics. The efficiency is limited by two factors: the entropy production in the heat transfer from the emitter to the hot side of engine and the entropy production in the operating engine (see Fig. 3). For a thermodynamic system with the entropy of thermal carriers $S_h$, the heat delivery is realized by the entropic thermal force, $F_{th} = -S_h \nabla T$ (see Refs. 31, 43, 44, and 64), which transfers the system from the hot area (emitter) to the cold area (in our case, the hot side of the engine) via mixing of particle states, which is usually realized due to interparticle scattering or interaction of...
particles with boundaries and other particles or waves. The light beam is the nonergodic system and the sunbeam moves from Sun to a cell without dissipation and entropy production. In this way, the whole energy that the beam had near the Sun is delivered to the cell. In the case of zero power losses in the heat delivery and zero emission from the cell, the ideal cell (engine) converts the whole sunbeam power into electricity with the Carnot efficiency. In the outstanding work by Scully (Ref. 65), the Carnot conversion efficiency is reached due to the suppression of the radiative recombination by quantum effects. In the TPV system with a multijunction cell, the Carnot efficiency is reached due to 100% reuse of the emitted radiation in the TPV emitter. In the nonreciprocal PV converter, the Carnot efficiency is reached due to 100% reuse of the emitted radiation by the same multijunction cell. Thus, in all of these PV converters, the Carnot efficiency is reached due to the suppression of radiative losses.

To derive the limiting efficiency of a single-junction nonreciprocal PV converter [Eq. (11)], we have generalized the finite time thermodynamics to nonequilibrium electron distribution functions specific for PV conversion. Nonreciprocal photonic management of PV cells with high radiative efficiency may substantially increase the PV performance. In particular, for a high-quality GaAs cell, the nonreciprocal management may add ~5% to the conversion efficiency, which is currently 29.1%. The nonreciprocal photonic management can be applied to advanced solar cells, such as quantum dot cells with the intermediate band and cells with charged quantum dots that create nanoscale potential and optimize kinetics of photocarriers. Let us note that, for the nonreciprocal solar light conversion, the high absorption–low emission should be realized just in a very narrow angle range (9.3 × 10⁻³ rad) and the narrow photon energy range of 5 to 7 kₜₚ T above the bandgap. The development of such PV converters may be expected in the very near future.

It is well understood and experimentally demonstrated that Kirchhoff’s law is not universal and is limited by the opaque bodies and thermodynamic equilibrium. Violation of the detailed balance and strong suppression of emission may also be achieved in specific nonequilibrium states of heterocarriers, which can be created without the use of nonreciprocal optical components. In particular, such an effect may be realized in the III–V semiconductor cell with a back-surface reflector and specific front-surface greenhouse filter that reflects low energy photons and creates a photonic bandgap above the semiconductor bandgap. In the p-doped III–V semiconductors, energy relaxation of hot photoelectrons occurs due to fast energy transfer from electrons to holes. This process drastically reduces a population of hot photoelectrons that can emit photons with energy above the photonic bandgap. The efficiency limit of the greenhouse cell is given by Eq. (11) and corresponds to the operating regime with negligible emission from the cell. The nonequilibrium greenhouse converter can convert directed and diffusive light with the PV efficiency larger than the SQ limit.

Finally, one of reviewers attracted our attention to the recent paper Ref. 72, which was published during the reviewing process. In this work, the authors calculated the Landsberg efficiency for a specific multijunction PV converter, in which the junctions are separated by nonreciprocal filters. In this design, every junction converts the monochromatic radiation from the Sun and the whole spectrum radiation emitted by the previous junction with a slightly larger bandgap. As the emitted radiation is converted with notable thermalization losses, the Landsberg efficiency obtained for this converter may be further increased. In Appendix B, we show that suppression of thermalization losses in conversion of the emitted radiation will lead to the Carnot efficiency in accordance with results of Sec. 3.

6 Appendix A

In the PhD thesis “Ultimate Efficiency Limit of Multiple Energy Threshold Photovoltaic Devices” (2003), Brown analyzed the multicolor limit of conversion efficiency for the PV converter with nonreciprocal photonic design shown in Fig. 2(a). The multicolor efficiency of this converter is given by Eq. 7.15 of the thesis:

\[ \eta = \frac{15r^4}{k^2} \int_0^\infty \frac{1}{\sin \theta} \left[ \sum_{i=1}^{N} x_i \left( \frac{1}{\exp(u - x_{i+1}) - 1} - \frac{1}{\exp(u - x_i) - 1} \right) \right]. \] (15)
where $x_i = \mu_i / k_B T$ is the normalized chemical potential of the $i$-cell, $u = h\omega / k_B T$ is the normalized photon energy, and $t = T / T_s$ (we employ the same notations as in the thesis). The $i$-cell absorbs light from the $(i+1)$-cell [the first term in square brackets in Eq. (15)] and emits light to the $(i-1)$-cell. The $N$'th cell absorbed light directly from the Sun, and therefore, the chemical potential $x_{n+1}$ is $(1-t)u$. Equation (15) describes the conversion efficiency of the multicell converter as a function of operating regimes of all cells. Brown proposed the following solution. The chemical potential $x_i$, i.e., the voltage of the first cell, is freely chosen, and the operating regimes (voltages) of the other cell are chosen to match photon fluxes between cells. In this way, Brown found a numerical solution for converters with 1 to 6, 8, 10, 20, and 40 cells. Extrapolating these results to an infinite number of cells, he obtained the Landsberg limit (see Fig. 7.5 in the thesis). Let us highlight that Eq. (15) is the Shockley–Queisser balance equation, which does not employ photon entropy. Therefore, the Lansberg limit is not expected from Eq. (15).

For the converter with an infinite number of cells, Eq. (15) has a simple and rather obvious solution that leads to the Carnot efficiency, which is obviously the maximal possible efficiency. If all cells have the same chemical potential

$$
\mu = h\omega \left( 1 - \frac{T}{T_s} - \delta \right),
$$

where $\delta$ is the infinitesimal quantity, Eq. (15) immediately leads to the Carnot formula. In this case, the Carnot factor of $(1 - T / T_s) - \delta$ may be moved outside the integral and sum. The summation of photon fluxes over all cells keeps only the flux from the Sun. This brings the corresponding photon distribution function. Finally, the integration over photonic modes (frequencies) with the Sun temperature distribution gives the total solar energy, which cancels with the normalization factor. This simple solution has a rather simple physical interpretation. In this case, all cells operate in the regime close to the regime of the open circuit ($\delta$ shows that we approach the open circuit regime from the side of the infinitesimal electric currents in the cells). For a single cell, it provides maximal light-induced chemical potential $\mu = qV_{OC} = h\omega(1 - T / T_s)$ at a negligible output power because of the negligible electric current. In the converter with an infinite number of cells, we can simultaneously realize the maximal chemical potential and the finite electric current that corresponds to the incoming photon flux. The electric current will be collected from the very large number of cells operating at very small currents. Thus, the efficiency of the system in Fig. 2(a) is given by the Carnot formula.

7 Appendix B

In Ref. 72 the authors proposed and investigated the multijunction PV converter, in which the junctions are separated by nonreciprocal filters. As in the traditional multicolor PV converter, the front-surface junction has the highest bandgap, $E_n$, and converts only photons with very high energies, while most of photons pass through this junction to the inner junctions. The back-surface junction has the narrowest bandgap, $E_1$. In the converter with an infinite number of junctions and without nonreciprocal filters, all junctions operate in the SQ monochromatic regime, i.e., without thermalization losses, and the converter efficiency of 86.8% is limited (see Refs. 4, 5, 51). In the proposed design, nonreciprocal filters redirect the whole radiation emitted by the $(n+1)$th junction to the next $n'$th junction in the stack (see Fig. 3 in Ref. 72). The operation of every junction is described by the SQ model. The detailed balance SQ equation for the photocurrent generated in the $n$’th junction with the bandgap $E_n$ is (Eq. 3 in Ref. 72)

$$
I_n = q \left[ f_s(E_n, E_{n+1}, 0, T_s) + f_c(E_{n+1}, \infty, V_{n+1}, T_C) - f_c(E_n, \infty, V_n, T_c) \right],
$$

where the first term in brackets is the quasimonochromatic photon flux with the bandwidth $E_{n+1} - E_n$ from the Sun with temperature $T_s$ and zero chemical potential, the second term is the wideband photon flux that was emitted by the previous $(n+1)$’th junction, and the third term is the flux emitted by this junction and redirected to the $(n-1)$’th junction. As mentioned, by ignoring the second term, we obtain 86.8% conversion efficiency. The second term is not a
quasimonochromatic radiation because its effective bandwidth is of several $kT_c$, where $T_c$ is the cell operating temperature. Therefore, the radiation emitted by the previous $(n+1)'th$ junction creates photocarriers with energies of several $kT_c$ above the bandgap $E_{n+1}$ in the junction with the bandgap $E_n$. With respect to the $E_n$ bandgap, these photocarriers are nonequilibrium hot carriers. To fill the energy interval between the $E_{n+1}$ and $E_n$ bandgaps, these photocarriers relax to the $E_n$ bandgap edges and lose their energy via interaction with phonons. As a result, a notable part of the solar energy is converted into heat. As shown in Ref. 72, in the optimal regime, the output voltage from the junction with the bandgap $E_n$ is given as (see Eq. 10 in Ref. 72)

$$V_n = \frac{E_n}{q} \left(1 - \frac{T_c}{T_s}\right),$$ (18)

and the corresponding conversion efficiency for this junction is given as

$$\eta_n = \frac{E_n}{c_n^*} \left(1 - \frac{T_c}{T_s}\right),$$ (19)

where $c_n^*$ is the average energy of photons, which are absorbed and converted by the $n$'th junction with the bandgap $E_n$. As a junction absorbs photons in the wide bandwidth, the average photon energy $c_n^*$ exceeds the bandgap $E_n$, and the conversion efficiency is below the Carnot limit. According to the calculations of Ref. 72, the efficiency of this converter is the Landsberg efficiency.

Thus, the Landsberg conversion efficiency may be realized even in the nonreciprocal converter with notable thermalization losses proposed in Ref. 72. Obviously, this efficiency is not a nonreciprocal multicolor conversion limit, at which any thermalization losses should be completely absent. The conversion efficiency can be further increased due to reduction of the thermalization losses. Equation (19) shows that redistribution of the emitted photons between junctions in accordance with their energies will provide $c_n^* = E_n$, which leads to the Carnot efficiency for every junction [Eq. (19)] as well as for the whole converter.

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References


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