

Determination of Efficiency Parameters in tin Halide Perovskite Solar Cells

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Abstract

Perovskite solar cells have gained significant attention in photovoltaic research. Just within a few years, the efficiencies of perovskite-based solar cells have been improved significantly to over 20% which makes them comparably efficient to silicon-based solar cells. The reason for such high recorded efficiencies are due to perovskites ease of processing, a high carrier diffusion length, low exciton binding energy and high absorption coefficient. Theoretical calculations were carried out based on the detailed balanced model on some Tin Halide Perovskite absorbers. For $\text{CH}_3\text{NH}_3\text{SnI}_3$, results obtained for V_{oc} , J_{sc} , FF and η are 1.14V, 34.4 mA/cm², 0.725 and 5.56% respectively. For $\text{CH}_3\text{NH}_3\text{SnI}_2\text{Br}$ values obtained for V_{oc} , J_{sc} , FF are 1.37V, 24.03mA/cm², 0.784 and 5.22% respectively. For $\text{CH}_3\text{NH}_3\text{SnI}_2\text{Br}$ values obtained for V_{oc} , J_{sc} , FF are 1.38V, 20.04 mA/cm², 0.810 and 4.69% Also for $\text{CH}_3\text{NH}_3\text{SnBr}_3$, results obtained for V_{oc} , J_{sc} , FF are 1.44V, 14.52mA/cm², 0.881 and 3.21% respectively.



Introduction

Perovskite solar cells are presently considered leading hybrid solar cells materials due to their ease of fabrication, high solar absorption coefficient and low non-radiative carrier recombination rates (Amu, 2014), and the relative increase in the power conversion efficiency of perovskite solar cells ($\text{CH}_3\text{NH}_3\text{PbI}_3$) which has risen from as low as 3.6% to as high as 20% in just five years with yet a projected value of over 20% in the next few years by experimentalist (Snaith *et al.*, 2014).

However, the presence of lead in the high efficiency perovskite halides such as ($\text{CH}_3\text{NH}_3\text{PbI}_3$) is an impediment in the use of perovskite solar cells for most technological applications and as such a possible substitute for lead in the perovskite structure is sought. Amongst other element to be considered as substitute for lead in the perovskite structure, tin stands out as a suitable substitute, because tin has a similar s^2 valence electronic configuration to lead, and similar ionic radius (Pb:119pm, Sn: 110pm), which makes it possible to form a perovskite with a basic formular (ABX_3) in analogy to lead compounds (Chen *et al.*, 2015).

Different authors have worked on perovskite solar cells as recorded in the literature. The authors in (Xiangang *et al.*, 2017), through integrating the detailed balance theory with the drift diffusion model, considering only radiative recombination as the only recombination mechanism within the perovskite solar cell ($\text{CH}_3\text{NH}_3\text{PbI}_3$) and the influence of both selective and non-selective contact obtained an efficiency of 23.83% for selective contacts and an efficiency of 29.86% for non-selective contacts.

While (Granás *et al.*, 2016) established the limit of efficiency of some metal-halide perovskites from first principles modelling and arrived at an efficiency range of 25-27% with a bandgap range of 1.1-1.6eV for most of the hybrid organic-inorganic compounds. In establishing the theoretical efficiency, they assume ideal interfaces and defect free crystals. Their result was able to show a direct relation between higher efficiencies and the device engineering of both the perovskite absorber layer and carrier transporting materials of the solar cell.

Similarly, the authors (Noel *et al.*, 2014), considering ($\text{CH}_3\text{NH}_3\text{SnI}_3$) and ($\text{CH}_3\text{NH}_3\text{SnBr}_3$) with bandgap values of 1.3eV and 1.56eV respectively, employing the density functional theory (DFT) estimated their respective efficiency values at 6.4% and 4.32% respectively.

With angular restriction, the authors (Sha *et al.*, 2014) exploring the detailed balance model,

calculated the efficiency limit of ($\text{CH}_3\text{NH}_3\text{PbI}_3$) perovskite solar cell on both flat and textured surface architecture with consideration of photon recycling effect light-trapping designs still play an important role in improving the efficiency of thin-film perovskite cells, even if perovskite material has a strong optical absorption their shows power conversion efficiency (PCE) as a function of cell thickness. The PCE limit of the perovskite cell is about 31%, which approaches to the Shockley-Queisser limit (33%) achievable by gallium arsenide (GaAs) solar cells (Wehrenfennig *et al.*, 2014).

Considering radiative losses as the only recombination mechanism within the cell, and applying the detailed balance model (Ugwuoke, 2014), in his work, arrived at a limiting efficiency of 27.5% for ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$), 29.2% for ($\text{CH}_3\text{NH}_3\text{PbI}_3$). His result shows that for thicker absorbers the short-circuit current density will be higher and conversely for thinner absorber. The reason for this is that charge collection at short-circuit is always assisted by the electric field in the absorber. Also, that thinner absorbers give the highest open-circuit voltage and for Fill Factor, he observed a quick drop in Fill Factor as the absorber thickness increases. The result shows that thicker absorbers give high efficiency.

Using a simulator device known as the solar cell capacitance simulator (SCAPS) (Amu, 2014) developed a configuration with reduced acceptor doping concentration of the absorber layer, and this configuration was used to solve the Poisson and hole and electron continuity equations in order to obtain relevant properties of tin-based perovskites solar cells, arrived at a theoretical efficiency of approximately 6.4%. From his result, he observed that there is a decrease in device performance as doping concentration in the perovskite material increases. He was able to establish that doping concentration increases recombination and reduces the lifetime of charge carriers.

While much work has been done on lead halide perovskite solar cells, there are relatively few reports on tin halide perovskite solar cells. Additionally, there is need to develop models to complement experimental work which are relatively difficult to understand. To this end, this work aims to explore a theoretical model that can be used to efficiently reduce the identified energy losses and improve the overall cell conversion efficiency which will serve as benchmark for possible design and fabrication of technologically efficient Tin-Halide based perovskite solar cells.

Theoretical background

The main parameters that are used to characterize the performance of solar cells are the peak power (P_{max}), the short-circuit current density

(J_{sc}), the open-circuit voltage (V_{oc}), the Fill Factor (FF), and photoelectric efficiency (η) These parameters are determined from the J-V characteristic curve as illustrated in Figure 1:

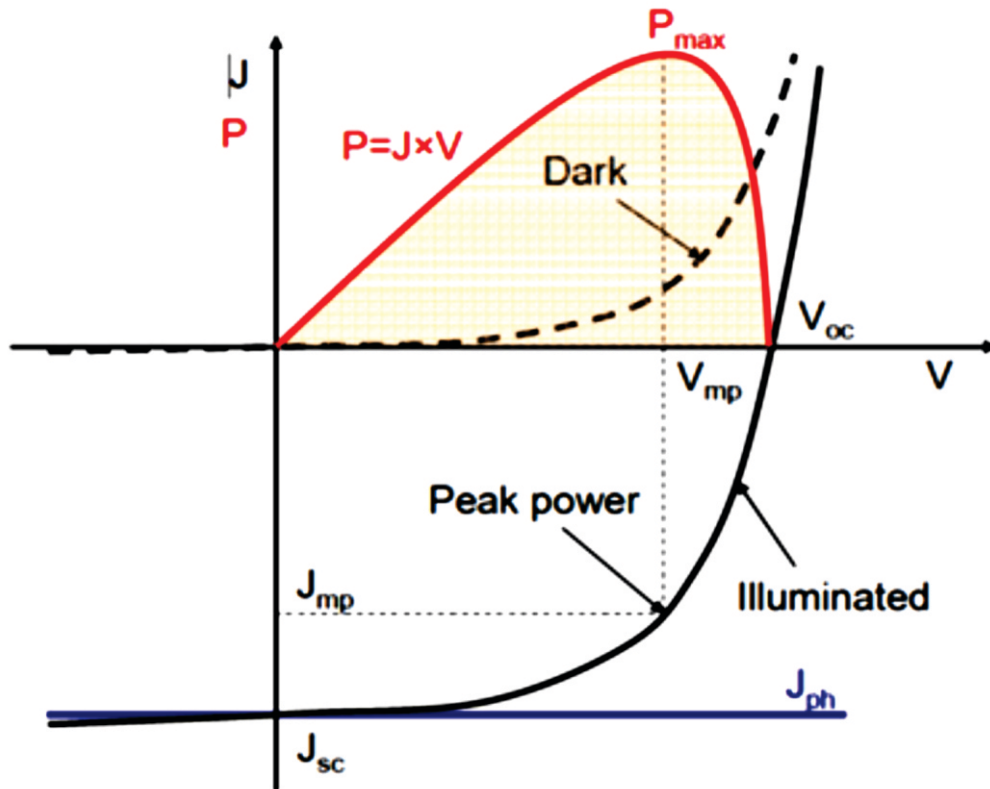


Figure 1: J-V characteristic parameters of a p-n junction in the dark and under illumination (Nelson, 2003)

Short-Circuit Current Density (J_{sc})

The short-circuit current density measured in mA/cm² is the maximum photo-generated current delivered by a solar cell when the solar cell is not matched to an external load or when matched to a load with a zero resistance ($V=0$).

The short-circuit current density of a solar cell depends on the photon flux density incident on the solar cell, the area of solar cell under illumination, the number of photo-generated charge carriers and their separation and collection rates in the external circuit (Heo *et al.*, 2013).

$$J_{sc} = q\phi(E) \tag{1}$$

Open-Circuit Voltage (V_{oc})

The Open-circuit voltage (V_{oc}) measured in volts (V) is the voltage at which no current flows through the external circuit when the terminals of the solar cell are not connected to each other or when it is matched to a load with infinite resistance ($J=0$). It is the maximum voltage that a solar cell can deliver. The open-circuit voltage depends on the photo-generated current density (J_{sc}) and the saturation current density (J_0). For the simple p-n junction, we have (Amu, 2014):

$$V_{oc} = V_c \ln\left(\frac{J_{sc}}{J_0} + 1\right) \tag{2}$$

Where $V_c = \frac{KT}{q}$ K is the Boltzmann constant and

T is temperature and q is the electronic charge.

Fill Factor

The fill factor is defined as the ratio of the maximum theoretical power from the solar cell ($P_{max} = J_{mp} \times V_{mp}$) generated by a solar cell and the product of the open circuit voltage (V_{oc}) and the short circuit current (J_{sc}) (Ugwuoke, 2014):

$$FF = \frac{V_{mp}J_{mp}}{V_{oc}J_{sc}} = \frac{P_{max}}{V_{oc}J_{sc}} \tag{3}$$

V_{mp} and J_{mp} are the maximum point voltage and current density generated by a solar cell. The fill factor is essentially a measure of quality of a solar cell. The values of the fill factor range from 0.80-0.95 but never approaches 1.0 except for a lossless solar cell (Heo *et al.*, 2013). The fill factor quantifies the efficiency of the transport and extraction of the charges in a solar cell, hence is not influenced only by the active material, but also by the device design and architecture.

Photoelectric Efficiency of Solar Cells

The photoelectric efficiency (η), which describes the ability of the solar cell to convert

light energy to electrical energy, is the ratio of maximum power generated to the incident solar irradiance. It is the percentage of power that can be converted from photo-generated current to useable electricity when a solar cell is connected to an external circuit (Heo *et al.*, 2013):

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}} \times 100\% \quad 4$$

Estimation method

The detailed balance model

The principle of detailed balance states that “A sample is said to be in thermodynamic equilibrium when the temperature of the sample is the same as the temperature of its environment, when there is no change of temperature in time, and when there is no external forces acting on the sample for instance an applied voltage or excess illumination from a light source. If a sample is in thermal equilibrium, then all microscopic processes in the sample are exactly compensated by their respective inverse process” (Darrow, 1924).

The calculations in this model involves calculating the absorption flux and emitted flux from a solar cell. The difference between these two multiplied by the electronic charge (q) is the current from the solar cell (Shockley and Quiesser, 1961).

The detailed balanced model (a thermodynamical balanced model) is based on the statistical balance between generated exciton and the possible recombination within the solar cell. In order to determine the efficiency, we shall consider the following assumptions;

- i. The solar cell has an infinite thickness and hence an infinite volume.
- ii. Infinite charge mobility, allowing collection of carriers no matter where they are generated.
- iii. Radiative band-to-band (bimolecular) recombination mechanism is the only existing loss mechanism. Non radiative recombination, such as Auger recombination and Trap assisted recombination is ignorable. The term for radiative recombination from the semiconductor follows from the Van Roosbroeck Shockley (VRS) relation (Van Roosbroeck *et al.*, 1954).
- iv. Quantum efficiency reaches 100%. When a photon is absorbed, it produces one electron-hole pair, and when one electron-hole pair recombines, it produces one photon. A single electron-hole pair is created per absorbed photon and it is extracted at a voltage

$$V_g = E_g/q$$

The absorption and emission of photons follows a step function:

$$a(E)/e(E) = \begin{cases} 1 & \text{for } E \geq E_g \\ 0 & \text{for } E < E_g \end{cases}$$

For a steady state condition, the total rate of photon emission must be the same as the rate at which photons are absorbed corrected by the fraction that is drawn off as current. Hence we can write (Green *et al.*, 2014):

$$J(V) = q(R_{gen} - R_{rec}^{rad} - R_{rec}^{non-rad}) \quad 5$$

Where R_{gen} is the rate of generation of electron-hole pair due to absorption of incident photons from the sun which is equal to the photon flux $R_{gen} = \phi(E)$

R_{rec}^{rad} is the rate of radiative recombination of the photo-generated carriers.

$R_{rec}^{non-rad}$ is the total rate of non-radiative recombination which is equal to zero $R_{rec}^{non-rad} = 0$

V is the applied voltage of the solar cell.

J is the current extracted from the cell per unit area (Van-Roosbroeck *et al.*, 1954):

$$J = q \left[\frac{2\Omega_s}{h^3 c_0^2} \int_0^\infty a(E) \frac{E^2 dE}{\exp\left(\frac{E}{kT_s}\right) - 1} - \frac{2\pi n^2}{h^3 c_0^2} \int_0^\infty e(E) \frac{E^2 dE}{\exp\left(\frac{E}{kT_c}\right) - 1} \right] \quad 6$$

This allows us to define the photo-generated current density as:

$$J_{ph} = q\phi(E) \quad 7$$

Also we can define the radiative current as (Ugwuoke, 2014):

$$J_{rad} = qR_{rec}^{rad} = J_0 \left(\exp\left(\frac{qV}{kT_c}\right) - 1 \right) \quad 8$$

Where

V_c is the solar cell voltage

$$V_c = \frac{kT_c}{q}$$

J_0 is the dark saturation current

T_c is the solar cell temperature

q is electronic charge

This follows that

$$J_{rad} = J_0 \left(\exp\left(\frac{V}{V_c}\right) - 1 \right) \quad 9$$

$$J(V) = J_{sc} - J_0 \left(\exp\left(\frac{V}{V_c}\right) - 1 \right) \quad 10$$

$$J(V) = (J_{sc} - J_0) + J_0 \left(1 - \exp\left(\frac{V}{V_c}\right) \right) \quad 11$$

Under illumination, $J_{sc} - J_0 \approx J_{sc}$

$$J V = J_{sc} + J_0(1 - \exp(\frac{V}{V_c})) \quad (12)$$

Where J_{sc} is the current generated from the solar cell at $V=0$, defined as the photogenerated current ($J_{sc} = J_{ph}$)

Hence, the current extracted from the solar cell at maximum power (J_{mp}) is given as

$$J_{mp} = J_{sc} + J_0(1 - \exp(\frac{V_{mp}}{V_c})) \quad (13)$$

Also, the voltage at maximum power (V_{mp}) can be determined by combining (13) and (12) which yields (14):

$$V_{mp} = V_{oc} + V_c \ln(1 - \exp(\frac{V_{oc}}{V_c})) \quad (14)$$

Theoretical method for predicting efficiency parameters

The theoretical methods for predicting J_{sc} , V_{oc} , FF, and η have been established in equations (1), (2), (3), and (4) respectively. The results obtained for the bandgap energy range be used in this work are given in the next chapter with details of their validation also established.

Results

Estimated parameter values of the present theoretical method (PTM) and those from reference method for tin halide perovskite solar cells with E_g (eV) at 1.30, 1.56, 1.65 and 2.15 are presented in Figures 2-5 for validation.

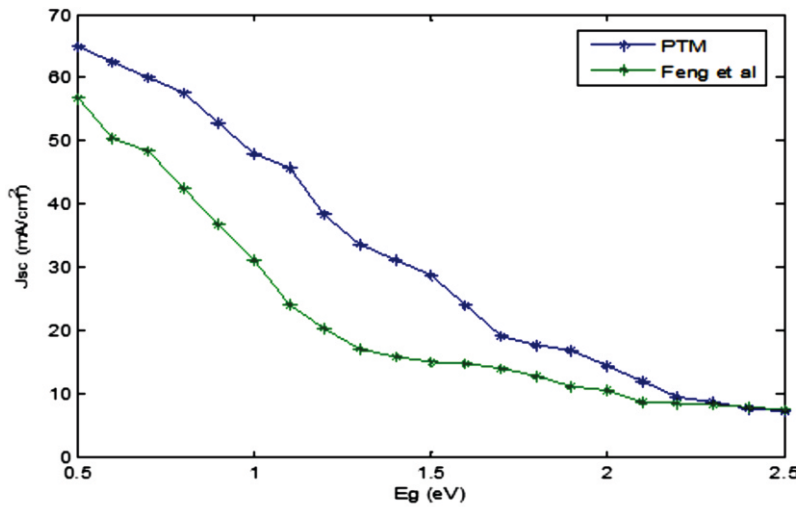


Figure 2: Present theoretical method in comparison with referenced method for J_{sc}

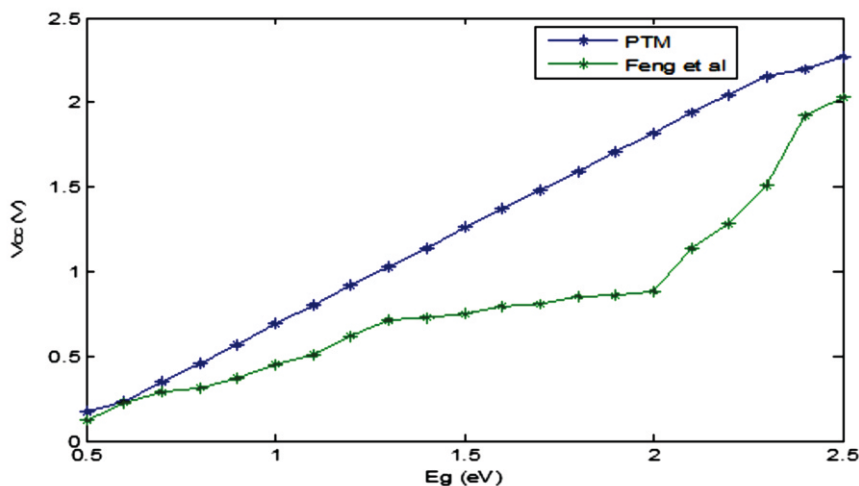


Figure 3: Present theoretical method in comparison with referenced method for V_{oc}

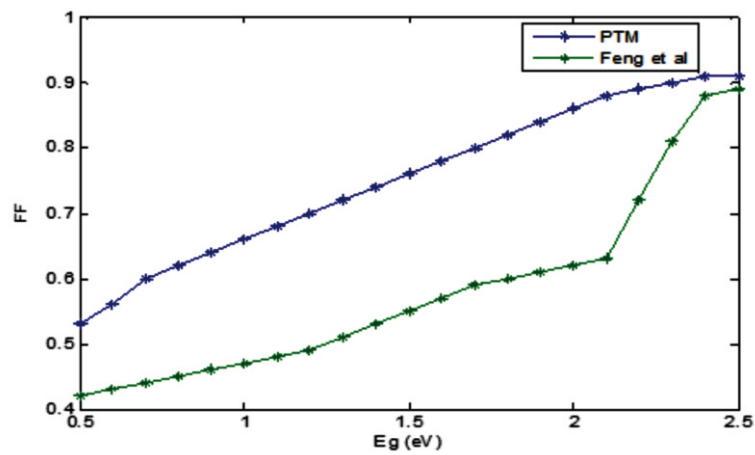


Figure 4: Present theoretical method in comparison with reference work for FF

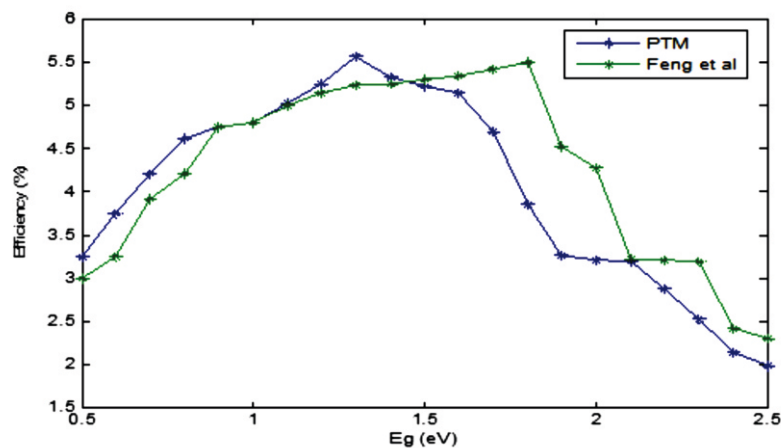


Figure 5: Present theoretical method in comparison with referenced work for η

Discussion

Figure 2 shows the representation for the short circuit current density (J_{sc}) versus band gap (E_g). From the Figure, we see a decrease in J_{sc} with increasing E_g . This happens because at short-circuit condition, the solar cell is expected to encounter no recombination, and that charge collection is always assisted by the inbuilt absorber electric field. Therefore, efficient light absorption requires smaller band gap (E_g) materials. Hence we observed high J_{sc} in $\text{CH}_3\text{NH}_3\text{SnI}_3$ with $E_g = 1.30$ as compared to $\text{CH}_3\text{NH}_3\text{SnI}_2\text{Br}$ with $E_g = 1.75$, $\text{CH}_3\text{NH}_3\text{SnI}_2\text{Br}$ with $E_g = 1.56$ and $\text{CH}_3\text{NH}_3\text{SnBr}_3$ with $E_g = 2.15$.

This agreed with Ugwuoke (2014) for lead halide perovskite. Additionally, J_{sc} values obtained in this work shows similar progression with those obtained in Feng *et al* (2014) Figure 3 gives the results for V_{oc} and as can be inferred, a linear curve is obtained with V_{oc} increasing with increasing E_g . The V_{oc} values obtained for the different E_g shows close proximity with those obtained in Feng *et al* (2014). The linear increase is attributed to the fact that the dark saturation current density (J_0) is a measure of recombination process within the solar cell which reduces significantly with increasing band gap. Hence

generating higher V_{oc} is achieved with $\text{CH}_3\text{NH}_3\text{SnBr}_3$ where the absorbed flux equals the emitted flux under open circuit condition.

Figure 4 shows the result for FF, and from the graph there is a noticeable quick rise in FF as the E_g increases until a saturation point is reached for higher E_g . The reason for this is that the induced electric field in the absorber material as a result of illumination decreases with increasing forward bias, and the collection of photo-generated carriers which was initially assisted by the electric fields becomes weaker. We obtained the highest FF values for $\text{CH}_3\text{NH}_3\text{SnBr}_3$, however results obtained in this work shows variation as compared with those from Feng *et al.*, (2014), and can be attributed to the assumption of radiative recombination as the only loss mechanism in this study leading to higher values of J_{sc} and V_{oc} which are determining factors for FF.

The result for η across different E_g values are shown in Figure 5. In this, we obtain highest η value for E_g at E_g at 1.30eV as contained in Feng *et al.*, (2014). Increasing value of E_g however, shows a decrease in η especially for E_g at 1.56eV, 1.65eV and 2.15eV. . Increasing bandgap leads to decreasing efficiency due to the instability of the Sn^{2+} oxidation state of tin which can easily be oxidized to more stable Sn^{4+} leading to self-doping

where the Sn^{4+} acts as a p-dopant leading to the reduction in the solar cell efficiency (Lee *et al.*, 2016).

Conclusion

A semi-empirical and theoretical method to determine the efficiency of tin halide perovskite solar cell is presented. The present method show appreciable agreement with the reference method with a difference of about 5.56% for the efficiency value at optimal band gap energy value. This variation notwithstanding, the objectives of the present method to determine the efficiency parameters of tin halide perovskite solar cells as a means of improving fabrication of tin-based solar cells is achieved.

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