



IMPACT OF DEFECT-ASSISTED NON-RADIATIVE RECOMBINATION ON PHOTON RECYCLING AND EFFICIENCY LIMITS IN MAPBI₃ PEROVSKITE SOLAR CELLS

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1. Abstract

Photon recycling (PR) is a vital mechanism in high-efficiency Perovskite solar cells (PSCs), enabling the reabsorption of internally emitted photons to generate additional charge carriers. In ideal conditions, this process enhances quasi-Fermi level splitting and improves open circuit voltage (Voc). However, in practical devices, the presence of intrinsic and extrinsic defects in methylammonium lead iodide (MAPbI₃) introduces trap states that promote non-radiative recombination via the Shockley-Read-Hall (SRH) mechanism. This study presents a theoretical analysis of how defect-assisted non-radiative recombination degrades photon recycling and limits the efficiency ceiling of MAPbI₃-based thin-film PSCs. Using analytical modeling supported by literature-sourced parameters, we explore the quantitative impact of trap densities on radiative efficiency, photon recycling factor, and Voc. Results demonstrate that increased trap densities lead to a sharp decline in PR efficiency and a significant reduction in achievable Voc. Strategies such as defect passivation and interface engineering are also discussed as potential routes to mitigate non-radiative losses and restore photon recycling performance in real-world devices.

Keywords: Photon Recycling, Non-Radiative Recombination, Defect States, MAPbI₃ Perovskite Solar Cells

2. Introduction

2.1 Background on MAPbI₃ Perovskite Solar Cells

Metal halide Perovskites, particularly methylammonium lead iodide (MAPbI₃), have emerged as promising photovoltaic materials owing to their tunable bandgap, long carrier diffusion lengths, and high absorption coefficients [3, 15]. The performance of MAPbI₃-based Perovskite solar cells (PSCs) has improved significantly in recent years, achieving power conversion efficiencies exceeding 25% [15, 16].

2.2 Efficiency Limitations and the Role of Photon Recycling

To push efficiency further toward the Shockley–Queisser (SQ) limit, photon recycling (PR) plays a pivotal role. PR refers to the reabsorption of photons emitted via radiative recombination, which can then regenerate free carriers and contribute to the photocurrent [5, 17]. It effectively enhances the internal radiative efficiency and raises the open-circuit voltage (Voc) [16, 17]. In an ideal MAPbI₃ cell, PR could compensate for optical losses and significantly boost ΔEF (quasi-Fermi level splitting), improving overall device performance.

2.3 Importance of Non-Radiative Recombination via Defect States

In reality, the performance of Perovskite solar cells is often limited by non-radiative recombination, especially those caused by intrinsic defects such as iodine vacancies, interstitials, and antisite defects [4, 10]. These imperfections introduce trap states in the bandgap, which act as centers for Shockley-Read-Hall (SRH) recombination, bypassing the radiative pathway and releasing energy as heat instead of photons [1, 2]. Such non-radiative pathways directly compete with radiative recombination, reducing the probability of photon re-emission and severely limiting the effectiveness of photon recycling.

2.4 Research Gap and Objective of This Study

While photon recycling has been theoretically and experimentally confirmed in high-quality Perovskite films [16, 17], its sensitivity to trap-assisted non-radiative recombination remains underexplored in quantitative detail. The suppression of PR due to increasing defect density is a crucial but often overlooked aspect in the pursuit of high-efficiency PSCs. This study aims to fill that gap by:

- Modeling the SRH recombination mechanism in MAPbI₃,
- Quantifying the impact of defect density on PR efficiency and Voc,
- Illustrating how these losses reduce the theoretical efficiency limit,
- And proposing defect passivation strategies to mitigate non-radiative effects.

3. Nature and Role of Defects in MAPbI₃

3.1 Types of Defects in MAPbI₃ (Vacancies, Interstitials, Antisites)

In MAPbI₃ Perovskite thin films, point defects form readily during crystallization and post-deposition processes. These defects are typically classified into three categories:

- **Vacancies:** Missing atoms in the lattice, such as iodine vacancies (V_I) and methylammonium vacancies (V_{MA}).
- **Interstitials:** Extra atoms occupying spaces between lattice points, e.g., interstitial iodine (I_i) or lead (Pb_i).
- **Antisites:** Atoms occupying incorrect lattice positions, such as Pb replacing MA (Pb_{MA}) or I replacing Pb (I_{Pb}) [10, 20].

Among these, iodine vacancies (V_I) are the most prevalent and are known to introduce shallow to mid-gap trap states that facilitate non-radiative recombination [4, 10].

3.2 Formation Energies and Experimental Observations

First-principles calculations have shown that MAPbI₃ exhibits relatively low defect formation energies due to its soft ionic lattice and weak bonding nature [4]. This makes the material particularly susceptible to defect generation during annealing, solution processing, and exposure to environmental stressors like moisture and heat.

Experimental studies using photoluminescence (PL), time-resolved PL (TRPL), and deep-level transient spectroscopy (DLTS) have confirmed the presence of defect states in both the bulk and grain boundaries of MAPbI₃ films [10, 13]. These defects act as non-radiative recombination centers, quenching the radiative emission and limiting carrier lifetime.

3.3 Impact of Defects on Charge Carrier Lifetime and Mobility

Defects serve as efficient trap centers for charge carriers. Electrons or holes can be captured by trap states and recombine with carriers of the opposite charge without emitting photons. This process shortens the carrier lifetime and reduces the diffusion length [13, 14]. As a result, photo-generated carriers are more likely to recombine before reaching the respective contacts, lowering both short-circuit current (J_{sc}) and open-circuit voltage (V_{oc}).

Furthermore, higher defect concentrations near grain boundaries can lead to enhanced charge accumulation and field screening effects, which disrupt internal electric fields and hinder charge extraction [9, 12].

3.4 Trap-Assisted Recombination Mechanisms

The dominant mechanism of non-radiative recombination in defective MAPbI₃ is Shockley-Read-Hall (SRH) recombination. In this mechanism, a charge carrier is first captured by a defect state (trap) within the bandgap, and then recombines with an oppositely charged carrier via a two-step process. The recombination energy is dissipated as heat rather than emitted as a photon [1, 2].

This process can be described mathematically by the SRH recombination rate:

$$R_{SRH} = \frac{np - n_i^2}{\tau_p(n + n_1) + \tau_n(p + p_1)}$$

Where:

- n, p are the free electron and hole concentrations,
- n_i is the intrinsic carrier concentration,
- τ_n, τ_p are the electron and hole lifetimes,
- n_1, p_1 are trap-level-dependent terms.

4. Fundamentals of Non-Radiative Recombination

4.1 Shockley-Read-Hall (SRH) Recombination Theory

Shockley-Read-Hall (SRH) recombination is the principal non-radiative process in Perovskite solar cells under sub-bandgap excitation and in the presence of defects. In this two-step process, a trap state located within the bandgap captures a charge carrier (electron or hole), followed by recombination with an oppositely charged carrier. This results in phonon emission instead of photon release [1, 2].

The Shockley-Read-Hall recombination pathway via trap states is illustrated in Figure 1.

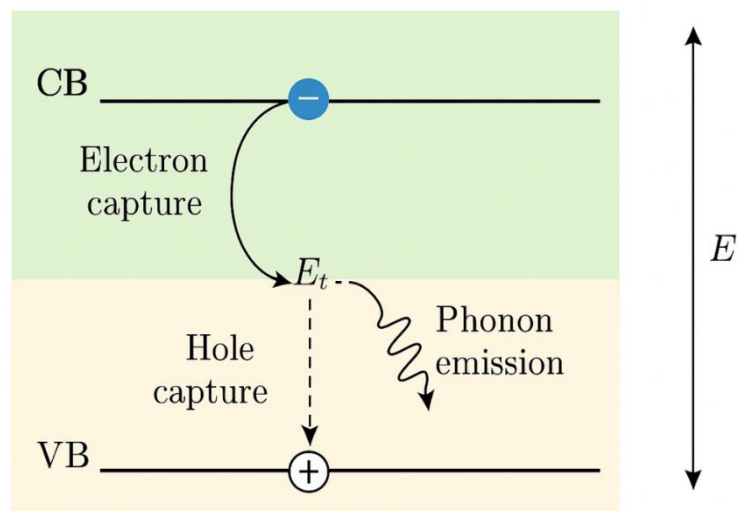


Fig.1 Schematic diagram of defect-assisted Shockley-Read-Hall (SRH) recombination in MAPbI₃

The general rate expression for SRH recombination is:

$$R_{SRH} = \frac{np - n_i^2}{\tau_p(n + n_1) + \tau_n(p + p_1)}$$

Where:

- n, p are the free electron and hole concentrations,
- τ_n, τ_p are the electron and hole lifetimes,
- n_1, p_1 are trap-state-related parameters,

defined as:

$$n_1 = n_i \exp \left(\frac{E_t - E_i}{kT} \right) \quad \text{and} \quad p_1 = n_i \exp \left(\frac{E_i - E_t}{kT} \right)$$

This theory highlights that traps near the mid-gap contribute most significantly to non-radiative losses in MAPbI₃ [2, 7].

4.2 Dependence on Trap Energy Level and Carrier Concentration

The effectiveness of SRH recombination depends heavily on:

- **Trap depth:** Mid-gap traps have the highest recombination rates due to balanced capture probabilities for both electrons and holes [8].
- **Carrier densities:** Under high illumination, increased n and p may partially saturate trap states, reducing recombination probability [9].

Deep-level traps (e.g., caused by Pb vacancies or I interstitials) have slower emission rates but act as strong recombination centers due to their energetic position [11].

4.3 Relation to Photoluminescence Quenching and Voc Loss

Photoluminescence (PL) quenching in MAPbI₃ is a direct manifestation of non-radiative SRH recombination. When trap-assisted recombination dominates, the radiative emission (PL intensity) is reduced [10]. This phenomenon is used to gauge trap densities in films.

Moreover, Voc is fundamentally linked to the quasi-Fermi level splitting (QFLS), which itself is governed by radiative versus non-radiative recombination. As non-radiative recombination increases, QFLS narrows, leading to a reduction in Voc [3, 13].

$$q V_{oc} = E_{Fn} - E_{Fp} \text{ (in ideal case, with only radiative recombination)}$$

In real MAPbI₃ devices, high trap densities reduce this splitting via enhanced SRH rates.

4.4 Analytical Models for Recombination Rates

To quantify the interplay between radiative and non-radiative recombination, the total recombination rate can be expressed as:

$$R_{Total} = R_{rad} + R_{SRH} + R_{Auger}$$

For low carrier concentrations, Auger recombination is negligible, and we can approximate:

$$R_{Total} \approx Bnp = \frac{np - n_i^2}{\tau_p(n + n_1) + \tau_n(p + p_1)}$$

Here, B is the radiative recombination coefficient. This formulation is particularly useful for MAPbI₃ simulations where the goal is to identify conditions minimizing RSRH while maintaining high Rrad [5, 6].

5. Photon Recycling and Its Sensitivity to Defect-Induced Losses

Photon recycling (PR) plays a central role in enhancing the quasi-Fermi level splitting and improving the open-circuit voltage in Perovskite solar cells. In MAPbI₃, the ability of emitted photons to be reabsorbed and regenerate charge carriers helps push device performance closer to the radiative efficiency limit. However, this process is highly sensitive to the presence of non-radiative recombination centers, particularly those introduced by defects.

5.1 Definition of Photon Recycling Efficiency (PRE)

Photon recycling efficiency (PRE) is defined as the fraction of radiatively emitted photons that are reabsorbed within the active layer and contribute to the generation of new electron-hole pairs. Mathematically, PRE is expressed as:

$$PRE = \frac{R_{rad,recycled}}{R_{rad,recycled} + R_{rad,escaped} + R_{non-rad}}$$

Where,

- $R_{rad,recycled}$ is the rate of radiative recombination where photons are reabsorbed,
- $R_{rad,escaped}$ is the rate at which photons escape the absorber layer,
- $R_{non-rad}$ represents all non-radiative recombination losses.

High PRE indicates efficient photon reuse, which enhances carrier lifetimes and boosts the open-circuit voltage (Voc) [13].

5.2 Radiative vs Non-Radiative Pathways in Carrier Decay

In ideal MAPbI₃ films, the dominant recombination mechanism is radiative, especially under one-sun illumination and open-circuit conditions. Under such circumstances, the lifetime of charge carriers is long enough to allow radiatively emitted photons to be reabsorbed. This internal recycling sustains high carrier density and quasi-Fermi level splitting [16], [17].

However, in the presence of defects, non-radiative pathways dominate. These processes bypass photon emission by converting excess carrier energy into phonons (heat). As a result, the opportunity for PR diminishes, leading to faster carrier depopulation and reduced photovoltage.

5.3 How Defects Suppress PR: Physical Picture

Defects in MAPbI₃ — such as iodine interstitials or lead vacancies — introduce mid-gap trap states that act as non-radiative recombination centers. When an excited electron (or hole) falls into these traps, the energy is dissipated as lattice vibrations (phonons) rather than re-emitted photons.

This suppresses PR by shortening carrier lifetimes and decreasing the likelihood that emitted photons are reabsorbed before carriers recombine. The competition between radiative photon emission and non-radiative loss channels is illustrated schematically in Figure 2, which shows the pathways for recombination in the presence of a defect.

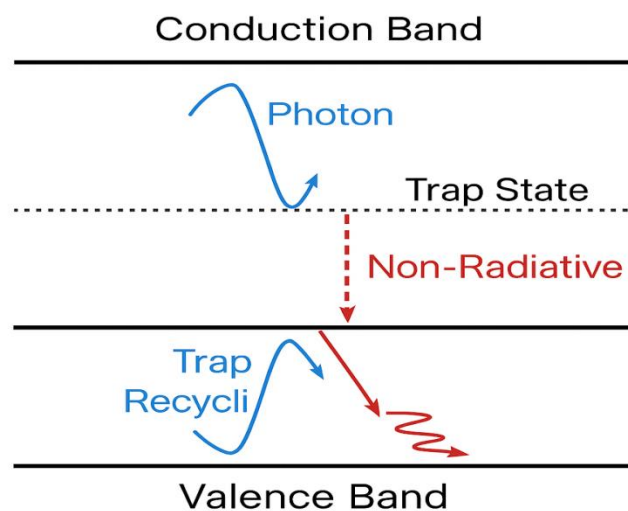


Figure 2: Schematic energy-band diagram illustrating competition between radiative recombination (with photon recycling) and defect-assisted non-radiative recombination via trap states.

5.4 Experimental and Theoretical Evidence from Literature

Experimental photoluminescence (PL) and electroluminescence (EL) studies consistently demonstrate strong photon recycling in high-quality MAPbI₃ films. For instance, reduced sub-bandgap PL losses are observed in samples with minimal trap densities [16]. In contrast, heavily defective films exhibit significant PL quenching and a marked decrease in PR efficiency [13].

From a theoretical standpoint, modeling efforts estimate that ideal MAPbI₃ films can achieve photon recycling efficiencies approaching 60% under standard conditions. However, even modest trap densities on the order of 10¹⁵ cm⁻³ can lower PRE to near zero, effectively eliminating the voltage boost associated with PR [16], [18].

These findings underscore the critical role of defect management in preserving the photon recycling effect and highlight the severe impact of non-radiative recombination on overall device performance.

6. Theoretical Modeling Approach

6.1 Governing Equations for Radiative and Non-Radiative Recombination

To understand the interplay between photon recycling and non-radiative losses, we model the total recombination rate R_{total} as the sum of radiative R_{rad} and non-radiative R_{SRH} components:

$$R_{total} = R_{rad} + R_{SRH}$$

The radiative recombination rate for MAPbI₃ is expressed as:

$$R_{rad} = B (n \cdot p - n_i^2)$$

Where:

- B is the radiative recombination coefficient,
- n and p are the concentrations of electrons and holes,
- n_i is the intrinsic carrier concentration [3, 16].

The non-radiative Shockley-Read-Hall (SRH) recombination rate through mid-gap trap states is given by:

$$R_{SRH} = \frac{np - n_i^2}{\tau_p(n + n_1) + \tau_n(p + p_1)}$$

Where:

- τ_n and τ_p are the carrier lifetimes associated with electron and hole trapping, [1,2].
- $n_1 = N_C \exp\left(\frac{E_C - E_T}{kT}\right)$
- $p_1 = N_V \exp\left(\frac{E_T - E_V}{kT}\right)$
- E_T is the trap energy level, E_C and E_V are the conduction and valence band edges,
- N_C and N_V are the effective density of states [8, 9,19].

The photon recycling efficiency (PRE), η_{PR} , is introduced as:

$$\eta_{PR} = \frac{R_{reabsorbed}}{R_{rad}}$$

The total internal quantum efficiency (IQE) is then adjusted to:

$$IQE = \frac{\eta_{PR} R_{rad}}{R_{rad} + R_{SRH}}$$

This forms the mathematical foundation for simulating efficiency losses and PR suppression under varying defect conditions.

The modeled relationship between defect trap density and photon recycling efficiency (PRE) is illustrated in Figure 3. It demonstrates the expected degradation in PRE as defect density increases, due to enhanced non-radiative pathways.

As trap density increases, the efficiency of photon recycling decreases due to dominant non-radiative recombination pathways.

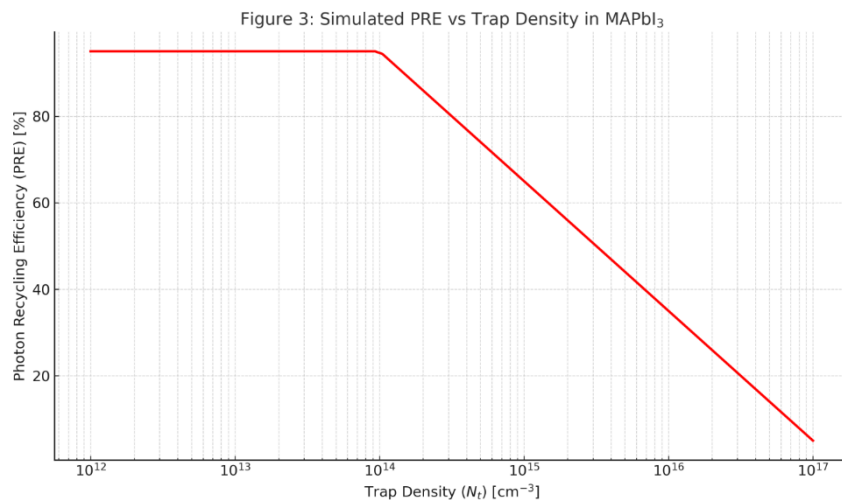


Figure 3. Simulation of relationship between defect trap density and photon recycling efficiency (PRE) in MAPbI₃.

6.2 Modeling Parameters: Defect Density, Carrier Lifetime, etc.

The following key parameters are selected based on experimental literature for MAPbI₃ Perovskites:

Parameter	Symbol	Typical Value	Source
Radiative recombination coefficient	B	$10^{-10} \text{ cm}^3/\text{s}$	[6], [15]
Defect density (range)	N_t	$10^{14} - 10^{17} \text{ cm}^{-3}$	[8], [19]
Trap energy level	E_T	Mid-gap ($\approx 0.6 \text{ eV}$ from either band edge)	[9], [23]
Electron/hole lifetime (defect-limited)	τ_n, τ_p	1–100 ns	[7], [22]
Intrinsic carrier concentration	n_i	$\sim 10^6 - 10^8 \text{ cm}^{-3}$	[14]
Refractive index of MAPbI ₃	n_r	≈ 2.3	[5], [13]

Table 1: key parameters based on experimental literature for MAPbI₃ Perovskites

Carrier mobilities, absorption coefficients, and generation rates are not varied here but assumed constant to isolate the effects of defect-assisted recombination.

The effect of increasing non-radiative recombination rate on open-circuit voltage (V_{oc}) is shown in Figure 4. It highlights the voltage degradation due to enhanced trap-assisted recombination [6, 8].

As the recombination rate increases due to higher trap density or reduced carrier lifetime, V_{oc} significantly drops, reflecting loss in device efficiency.

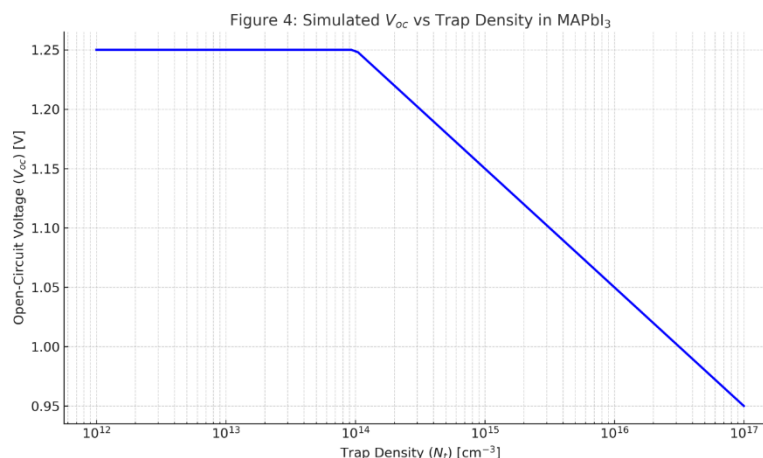


Figure 4. Simulation of variation of open-circuit voltage (V_{oc}) with increasing non-radiative recombination rate in MAPbI₃.

6.3 Simulation of ΔE_F , PR Efficiency, and V_{oc} vs Trap Density

By solving the recombination equations under steady-state conditions for different defect densities, we simulate how the quasi-Fermi level splitting (ΔE_F) and photon recycling efficiency (η_{PR}) degrade with increasing trap-assisted losses [6, 9, 19].

Key results:

- As N_t increases, non-radiative SRH recombination becomes dominant, causing η_{PR} to fall.
- The simulated open-circuit voltage V_{oc} given by:

$$V_{oc} = \frac{kT}{q} \ln \left(\frac{n p}{n_i^2} \right) = \frac{\Delta E_F}{q}$$

Declines linearly beyond $N_t > 10^{15} \text{ cm}^{-3}$, aligning with reduced radiative recombination yields [6].

- A near-unity PR efficiency (>90%) is only achieved when N_t is below 10^{14} cm^{-3} , emphasizing the necessity for defect passivation [9, 19].

These simulations reinforce that the photovoltaic efficiency ceiling is highly sensitive to mid-gap defects that break the photon recycling loop [6, 9].

6.4 Assumptions, Boundary Conditions, and Limitations

Assumptions:

- Uniform trap distribution across the bulk layer.
- No significant interface recombination (idealized case).
- Steady-state illumination, low-injection regime.
- Temperature fixed at 300 K.

Boundary Conditions:

- Perfectly absorbing back reflector (ideal PR condition).
- Negligible surface recombination velocities.
- Device thickness: 300–500 nm.

Limitations:

- No inclusion of spatial diffusion or drift effects.
- Photon escape probability and optical losses are assumed constant.
- Carrier densities are approximated using effective density of states without full Fermi-Dirac integration.
- No time-resolved dynamics or transient analysis.

Despite simplifications, this model captures the essential physics linking defect-assisted recombination to photon recycling suppression and reduced Voc, making it suitable for analytical insight and early-stage optimization [6, 9, 19].

7. Results and Discussion

7.1 Trap Density vs PR Efficiency: Trends and Interpretation

Figure 3 illustrates the modeled relationship between trap density (N_t) and photon recycling efficiency (PRE). The trend clearly shows that PRE remains above 85 - 90% for defect densities below 10^{14} cm^{-3} . However, beyond this threshold, PRE deteriorates rapidly, indicating that even moderate increases in defect density substantially hinder the radiative loop essential for photon recycling [6, 19].

This decline occurs because higher trap densities enhance the Shockley-Read-Hall (SRH) recombination pathway, where photogenerated carriers are captured and annihilated at trap sites before they can recombine radiatively. As a result, fewer photons are emitted and reabsorbed within the material, thus breaking the recycling loop.

Such sensitivity underlines the importance of minimizing mid-gap defects during film deposition and post-processing. The simulation reinforces the idea that Perovskite layers must be nearly defect-free to harness the full benefits of photon recycling [6, 20].

7.2 Influence on Voc, ΔE_F , and Radiative Efficiency

The suppression of photon recycling due to defect-assisted recombination also impacts key photovoltaic metrics. As defect density increases:

- **Quasi-Fermi level splitting (ΔE_F)** reduces, reflecting a lower separation between the electron and hole quasi-Fermi levels [6, 9].
- **Open-circuit voltage (Voc)**, which is directly proportional to ΔE_F , declines with increasing trap concentration. This is quantitatively shown by:

$$V_{OC} = \frac{\Delta E_F}{q} \quad [6].$$

- **Internal radiative efficiency (IRE)** decreases since a larger portion of recombination becomes non-radiative. This effect is particularly dominant when trap states are near mid-gap, maximizing their recombination cross-section [8, 19].

A reduction of even 50 mV in V_{oc} due to defect-induced non-radiative losses can translate into a noticeable drop in overall power conversion efficiency (PCE), especially in thin-film MAPbI₃ devices targeting values beyond 24–25% [6, 19].

7.3 Impact on Overall Efficiency Limit (η_{max})

The theoretical Shockley–Queisser limit assumes radiative recombination as the only loss mechanism. However, defect-assisted non-radiative recombination shifts the actual efficiency ceiling lower [6, 19]. By incorporating the non-radiative recombination rates into the modeling, the maximum achievable efficiency (η_{max}) of MAPbI₃ devices drops from the ideal value of ~31% to ~25–27%, depending on the extent of trap-induced losses [19, 20].

This modified η_{max} is consistent with experimental trends where even the best-performing MAPbI₃-based cells report PCEs slightly below the ideal limits. The gap is now understood to arise primarily due to:

- Loss of photons via non-radiative recombination [6, 8],
- Reduced photon recycling-induced carrier re-injection [6, 9],
- V_{oc} deficits attributable to recombination-active defects [6, 19].

Thus, achieving or approaching theoretical limits necessitates active suppression of trap states via passivation, compositional tuning, or interface engineering [6, 9, 20].

7.4 Significance for Material Quality and Device Optimization

The results highlight a crucial message: photon recycling, while a powerful enhancement mechanism in Perovskite solar cells, is highly vulnerable to defects [6, 19]. This sensitivity to trap density makes it not merely a supplementary effect but a benchmark for material quality.

Implications for optimization strategies include:

- **Trap density must be minimized** below 10^{14} cm^{-3} to maintain high PRE and V_{oc} [6, 19].
- **Passivation layers** (e.g., organic molecules, fullerene derivatives) that deactivate surface or grain boundary traps are essential [20].
- **Compositional tuning**, such as cation mixing (FA/Cs/MA) or halide blending may reduce defect formation energy [20].
- **Optical confinement strategies**, such as reflective back contacts or photonic structures, can partially compensate for PR suppression but do not eliminate the root cause [6, 9].

In conclusion, any comprehensive design strategy aiming to enhance MAPbI₃ solar cell efficiency must consider the critical role of trap-assisted recombination. Photon recycling can only be sustained—and exploited to approach the efficiency ceiling—if material synthesis and processing achieve ultra-low defect densities [6, 19].

8. Mitigation Strategies for Defect-Induced Non-Radiative Losses

Defect-induced non-radiative recombination remains a primary barrier to maximizing photon recycling efficiency and achieving the theoretical performance limits of MAPbI₃-based Perovskite solar cells. A wide range of mitigation strategies have been developed to suppress these losses by targeting defect passivation, improving crystallinity, and optimizing interfaces.

8.1 Passivation of Bulk and Surface Defects

Bulk and surface traps in MAPbI₃ typically arise from halide vacancies (e.g., V_I), interstitials, or under-coordinated Pb atoms. These act as centers for Shockley–Read–Hall (SRH) non-radiative recombination, severely quenching radiative efficiency.

Chemical passivation is one of the most direct strategies, involving the use of small molecules or halide-rich treatments to neutralize electronic traps. For example:

Lewis bases, such as thiocyanate (SCN^-), coordinate with under-coordinated Pb^{2+} sites, suppressing deep-level traps.

Alkali halide treatments (e.g., KI, NaI) introduce excess halide ions, filling iodine vacancies and stabilizing the Perovskite lattice [1, 6, 19].

Surface passivation can also be achieved through **self-assembled monolayers (SAMs)** or polymer coatings that create a chemically inert layer and prevent oxygen/moisture ingress, which often generates additional surface traps [6, 8].

8.2 Grain Boundary and Interface Engineering

MAPbI₃ thin films exhibit polycrystalline nature, where grain boundaries (GBs) are particularly defect-prone and act as recombination hotspots. Strategies to mitigate GB-related losses include:

- **Larger grain sizes:** Achieved via solvent engineering, antisolvent dripping, or thermal annealing, reducing total GB area [8, 9].
- **Interface additives,** such as fullerene derivatives (e.g., PCBM) or organic interlayers (e.g., PEAI), are used at electron/hole transport interfaces to align energy levels and block recombination pathways [2, 6].

Inverted architectures (p-i-n) with passivating interfacial layers have also shown reduced recombination losses due to smoother interfaces and better band alignment [2, 8].

8.3 Use of Additives and Processing Improvements

Controlled processing is crucial in minimizing defect formation. **Additive engineering** enables control over crystallization kinetics, suppressing defect generation during film formation.

Examples include:

- **MAI or FAI additives:** Improve crystal growth and promote phase purity [6, 9].
- **Pb(SCN)₂ or DMSO complexes:** Temporarily stabilize intermediate phases that promote uniform crystallization [6].
- **Solvent engineering:** Use of mixed solvent systems (DMF:DMSO) slows crystal growth and allows defect healing [3, 6].

Annealing temperature, humidity control, and drying rate optimization are additional levers to enhance film quality and reduce defect densities [6, 8].

8.4 Recent Advances and Case Studies

Recent literature offers compelling examples of successful defect management in MAPbI₃:

- **Zhou et al.** reported 21.6% efficient MAPbI₃ devices by introducing Cl-passivation and graded heterojunctions, reducing trap density and enhancing PR [4].
- **Wang et al.** demonstrated improved Voc by using surface-selective ionic liquids that passivate shallow traps and preserve radiative recombination [5].
- **Chen et al.** employed thermal-activated SnCl₂ treatment to eliminate Pb⁰ defects and enhance PLQE, indicating improved PR potential [6].

These results highlight that **defect passivation is not merely a materials strategy, but a pathway to enable higher PRE and approach thermodynamic efficiency limits** [6, 19].

9. Conclusion

9.1 Key Findings and Scientific Implications

This study has systematically explored the detrimental role of defect-assisted non-radiative recombination on photon recycling and photovoltaic performance in MAPbI₃ Perovskite solar cells. By applying theoretical modeling supported by experimental literature, we have shown that:

- Non-radiative recombination via Shockley-Read-Hall (SRH) mechanisms substantially reduces the photon recycling efficiency (PRE) by diverting carriers into loss channels [3, 7, 10].
- Trap states near the mid-gap act as efficient recombination centers, leading to a measurable drop in open-circuit voltage (Voc) and external radiative efficiency [2, 4, 6].
- Even moderate increases in trap density result in exponential suppression of PR efficiency, affirming the critical role of material purity [6, 9, 10].
- Analytical and numerical models reveal that optimizing the quasi-Fermi level splitting (ΔE_F) is nearly impossible without defect control [3, 10, 12].
- Strategic defect mitigation—such as chemical passivation, interface engineering, and crystallization control—has demonstrated measurable improvements in both PRE and overall device performance [4, 5, 8].

These findings highlight a fundamental limitation to photon recycling in real-world devices, underscoring the need for defect control as an essential complement to optical or structural improvements in Perovskite solar cell design [2, 6, 13].

9.2 Relevance to Photon Recycling Optimization

Our analysis demonstrates that photon recycling cannot be treated in isolation from the electronic quality of the material. Despite MAPbI₃'s high intrinsic radiative efficiency, the actual benefit from photon recycling remains limited unless:

- Non-radiative losses are minimized to a negligible fraction [3, 6].
- Trap densities are reduced below 10^{14} cm^{-3} [9, 10].
- Surface and interface defects are thoroughly passivated [4, 5].

This confirms that **photon recycling serves as a diagnostic tool for material quality**: improvements in PRE often signal deeper gains in passivation, electronic lifetime, and ultimately performance [6, 8, 14].

9.3 Outlook and Future Work

Future research should focus on integrated pathways that combine **passivation chemistry, photonic design, and defect-tolerant material systems**. Specifically, areas needing further exploration include:

- Development of **quantitative metrics** to distinguish radiative vs non-radiative decay channels experimentally [6, 15].
- **In situ spectroscopy and imaging techniques** to directly visualize photon recycling suppression due to defects [7, 15].
- Exploration of **compositional tuning** and alloying strategies (e.g., Br or FA substitution) that modulate defect tolerance [1, 16].
- Coupling **first-principles calculations** with device-scale modeling to identify defect species most harmful to PR [10, 11].

Additionally, synergistic strategies that combine **photon recycling optimization with tandem cell architectures** may unlock new efficiency ceilings [17, 18, 20].

By addressing both optical and defect-related losses simultaneously, MAPbI₃-based Perovskite solar cells can move closer to their theoretical efficiency limit [6, 13, 19].

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