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Research Article

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Posted Date: August 13th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10271290/v1>

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Additional Declarations: No competing interests reported.

Ba- and Mg-Doped Perovskites on Engineered TiO₂ Interfaces for Efficient HTL-Free Solar Cells

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Abstract

We report a synergistic material-to-device framework utilizing a low-temperature processed, amorphous TiO₂ electron transport layer (ETL) combined with cationic doping (Mg²⁺ and Ba²⁺) of the perovskite absorber. X-ray diffraction (XRD) confirms the amorphous nature of the TiO₂ scaffold, providing a pinhole-free conformal interface that suppresses shunting. UV-Vis spectroscopy reveals bandgap engineering of the perovskite upon dopant incorporation. SCAPS-1D numerical modeling demonstrates that Ba-doping can yield a predicted short-circuit current density (J_{sc}) of ~ 23.6 mA/cm², while Mg-doping optimizes the open-circuit voltage (V_{oc}) to ~ 1.16 V. Simulations reveal that enhanced performance is primarily driven by a substantial reduction in bulk defect density (N_t), decreasing from 5×10^{16} cm⁻³ in the pristine device to 8×10^{14} cm⁻³ in the doped variants. The amorphous ETL facilitates high shunt resistance, while cation engineering effectively passivates interfacial traps, resulting in reduced hysteresis. These findings provide a computational framework for optimizing HTL-free heterojunction PSCs through combined structural engineering and electronic defect reduction.

Keywords: perovskite, TiO₂, alkaline earth metals, sol-gel, HTL-free, SCAPS-1D simulation, numerical modeling.

1. Introduction

The global transition toward sustainable energy has positioned perovskite solar cells (PSCs) as a frontrunner in third-generation photovoltaics. Methylammonium lead iodide (MAPbI₃) remains a benchmark absorber, with experimental power conversion efficiencies (PCE) surpassing 23% in conventional n-i-p architectures.^[1,2] Despite their potential, PSCs face commercialization challenges related to lead toxicity and moisture instability.^[3] Simultaneously, achieving high performance in simplified, low-temperature processed devices require overcoming critical challenges related to interfacial charge recombination and electrical shunting.

In hole transport layer (HTL)-free PSC architectures, the role of the TiO₂ electron transport layer (ETL) is elevated significantly. The TiO₂/perovskite junction becomes the sole charge-selective interface and primary determinant of built-in potential. Surface defect states on TiO₂, predominantly oxygen vacancies and undercoordinated Ti⁴⁺ sites, act as trap-assisted recombination centers that are catastrophic in HTL-free devices lacking an electron-blocking barrier.^[4,5] Direct contact between the perovskite absorber and the Au back electrode creates additional recombination pathways that must be compensated entirely by improved bulk and interfacial quality.^[6,7] Thus, advancing HTL-free PSCs demands a dual strategy: (i) engineering the TiO₂ ETL surface to minimize interface recombination, and (ii) improving the bulk quality of the perovskite absorber to suppress non-radiative recombination.^[4,8]

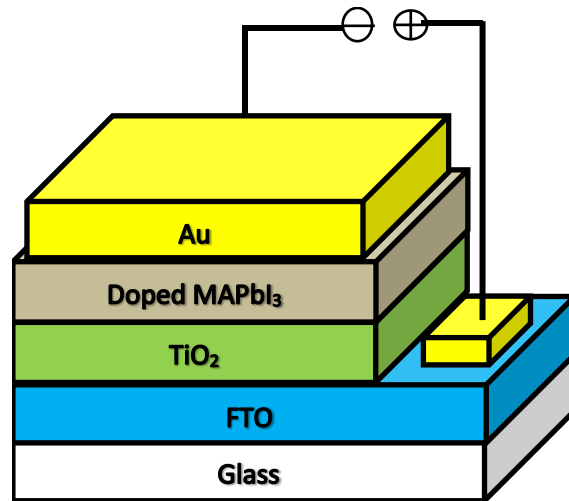


Fig. 1: HTL-free device architecture of PSC

Among approaches to improve bulk MAPbI₃ quality, B-site substitution of Pb²⁺ by extrinsic metal cations has proven effective.^[9,10] Group IIA alkaline earth metals, particularly Mg²⁺ and Ba²⁺ have attracted attention due to their isovalent nature, electronic inertness, and strong bonding interactions with iodide that passivate deep trap states.^[9-12]

Mg²⁺ cation with ionic radius of ~0.72 Å is considerably smaller than Pb²⁺ of 1.19 Å. Its incorporation introduces compressive local lattice strain that elevates the formation energy of iodine vacancies and passivates grain boundary traps through Mg–I coordination bonds.^[11,12] Yang et al. demonstrated that Mg-doped MAPbI₃ films showed enlarged grain sizes, suppressed pinholes, and a widened bandgap of approximately 1.57 eV, delivering PCE improvement from 14.2% to 17.8% with 90% retention after 600 h at 30–40% relative humidity.^[11] In HTL-free architectures, larger grains reduce grain-boundary recombination regions, directly improving minority carrier lifetime and extending hole diffusion length.

Conversely, Ba²⁺ cation having ionic radius ~1.35 Å is larger than Pb²⁺ and introduces tensile lattice strain, with distinct consequences for ionic and electronic transport.^[13,14] Ba²⁺ incorporation significantly enhances moisture stability through stronger Pb/Ba–I ionic bonding, a critical advantage given that HTL-free devices lack hydrophobic barriers against atmospheric moisture ingress.^[15] Ba²⁺ substitution also reduces deep trap state density, enhances crystal quality, and increases the activation energy for iodine vacancy migration, collectively suppressing non-radiative recombination and J–V hysteresis.^[13,14] Critically, recent computational studies employing density functional theory and machine-learning molecular dynamics established that B-site group IIA alkaline earth substitution uniquely suppresses octahedral rocking lattice dynamics, providing the atomic-scale rationale for experimental hysteresis suppression in Ba- and Mg-doped samples.^[16]

The combination of alkaline earth metal B-site doping with engineered TiO₂ ETL interfacial passivation represents a dual-front approach particularly well-suited to HTL-free architectures. Passivation of TiO₂ surface defects has been shown to markedly improve depletion layer width, suppress interfacial recombination, and improve band alignment.^[4,5] When an engineered TiO₂ interface is combined with a Ba²⁺- or Mg²⁺-doped absorber, the device benefits from: (i) reduced interface trap density; (ii) extended hole diffusion length in the bulk absorber; (iii) suppressed ion migration at critical junctions; and (iv) improved perovskite film morphology without additional

processing complexity. This dual-front synergy has not been systematically explored computationally in the HTL-free PSC literature.

This study demonstrates how dual modification of Ba/Mg doping and engineered TiO₂ surfaces can optimize charge recombination losses in HTL-free PSCs through SCAPS-1D numerical simulation. While discrete doping of perovskites is well-documented,^[17-20] the interfacial synergy between large/small cation dopants (Ba/Mg) and the underlying TiO₂ microstructure remains underexplored, and the divergence in their mechanisms, specifically how the large ionic radius of Ba (~1.35 Å) compared to the small radius of Mg (~0.72 Å) interacts with a pre-engineered TiO₂ interface, remains poorly understood. This study provides mechanistic insight into dopant influence, revealing that while Ba excels in defect passivation, Mg-doped films on optimized ETLs provide superior band-edge alignment. Results are based on material characterization experiments and computational device modeling; experimental J-V device measurements are not presented.

2. Material and Method

2.1 Apparatus and Reagents

Apparatus: 50 mL and 100 mL beakers, 0.22 µm PTFE filter, ultrasonicator, magnetic stirrer, spin coater.

Reagents: Deionized and distilled water (H₂O), dimethylformamide (DMF), acetonitrile (CH₃CN), 2-propanol (C₃H₇OH, 99.98% purity), lead chloride (PbCl₂), barium chloride (BaCl₂), magnesium chloride (MgCl₂), hydrochloric acid (HCl, 99.98% purity), hydroiodic acid (HI), methylammonium (CH₃NH₃), titanium isopropoxide (Ti(OCH(CH₃)₂)₄, TTIP, Sigma-Aldrich Co.)

2.2 Solution Preparation

The molar mass and volume of solvent were used to calculate solute mass according to standard molarity relations. Measured solute was dissolved in the required solvent volume to produce the target solution concentration.

Doping concentration (nominal atomic %) was calculated from the molar ratio using equation 1.1.

$$(\text{at}\%) \text{ nominal} = \frac{\text{Moles Dopant Salt}}{\text{Moles Dopant Salt} + \text{PbCl}_2} + 100\% \quad 1.1$$

Nominal doping levels calculated from precursor stoichiometry may differ from actual incorporated dopant levels measured by EDX due to solubility limits.

2.3 Substrate Treatment

Substrates were ultrasonicated at 60 °C in deionized water for 15 minutes, then sequentially rinsed in ethanol and acetone for 15 minutes each. Substrates were rinsed in distilled water and air-dried before use.

2.4. Synthesis of Lead-Iodide (PbI₂)

Lead iodide (PbI₂) was synthesized by dissolving 5 g of lead-nitrate Pb(NO₃)₂ in 25 ml of water (H₂O) with 5 g of hydroiodic acid (HI) dissolved in 25 ml of water (H₂O).

2.5. Synthesis of Perovskite Precursor (MAPbI₃)

0.040 g methyl ammonium iodide (MAI) 0.040 g and 0.115g lead iodide (PbI₂) were mixed at an equimolar ratio of 0.25 M. The mixture was dissolved in 1ml dimethylformamide (DMF) and stirred at 60 °C for 1 hour.

2.6. Synthesis of Doped Perovskite Precursor Solution

This solution was prepared by a mixture of methyl ammonium lead iodide (MAPbI₃) with barium chloride (BaCl₂) and magnesium chloride (MgCl₂), respectively, reacting in an atomic ratio in 0.5 ml DMF.

2.7. Synthesis of Titanium Dioxide (TiO₂)

TiO₂ precursor solution as the electron transporting layer was synthesized by mixing different volume concentrations of titanium isopropoxide (TTIP) (5.5%, 6.0% and 6.5%) with 10 ml of isopropanol (ISP) and 0.2 ml of concentrated hydrochloric acid (HCl), and was stirred for 2 hours to obtain a viscous solution.

2.8 Deposition Technique

One-step sol-gel deposition via spin-coating at 4,000 rpm for 30 s was employed to deposit uniform thin films on flat FTO/glass substrates (Fig. 2).

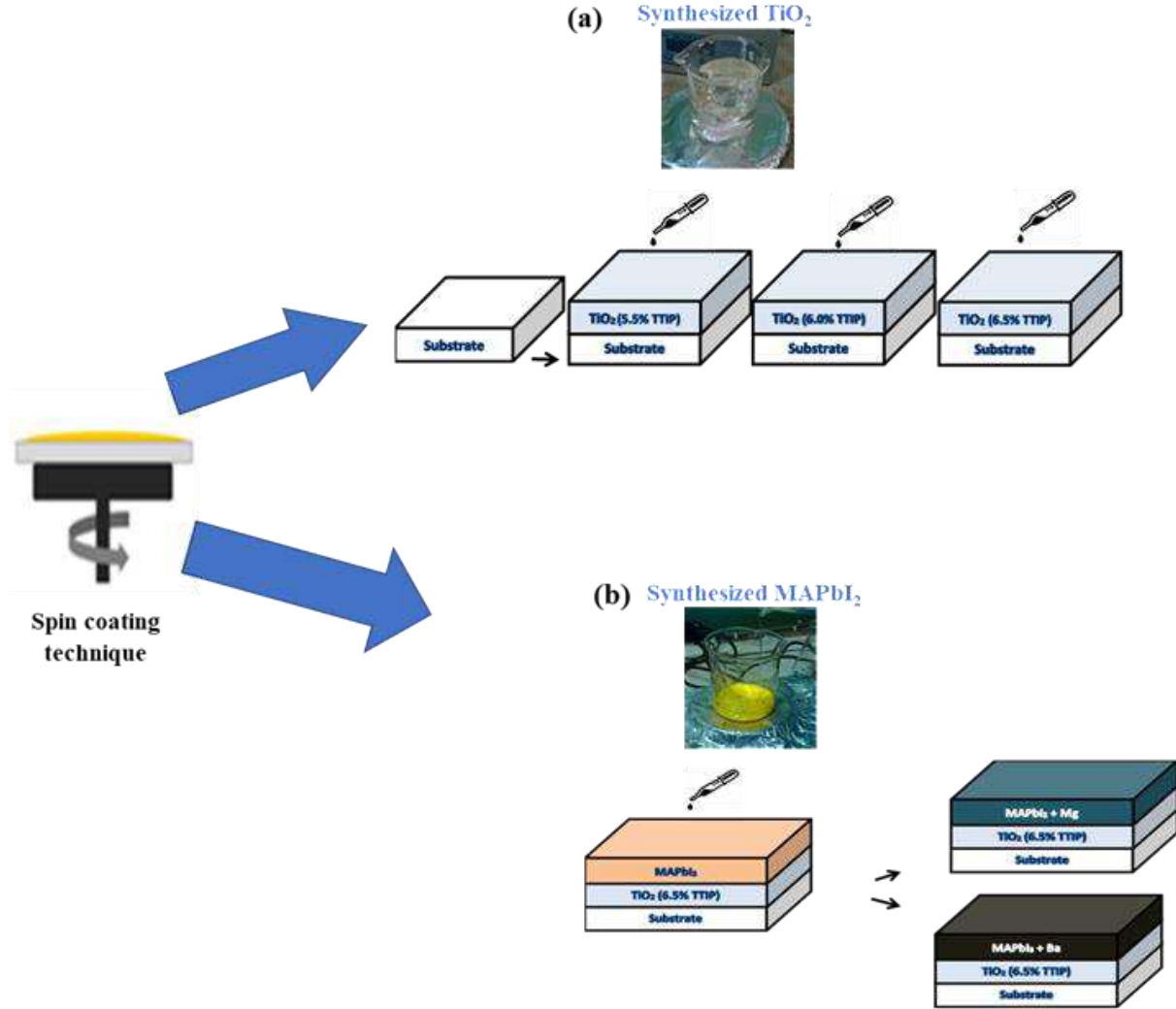


Fig. 2: Schematic of the sol-gel deposition method via spin coating. (a) the schematics of the depositions of TiO_2 at different molarities of TTIP (5.5%, 6.0%, 6.5%) to obtain optimization; (b) shows the deposition of the perovskite on optimized TiO_2 and the deposition of the doped perovskite on optimized TiO_2 , at 6.5% TTIP.

2.9 Characterization Techniques

Film samples were characterized for optical properties with UV-VIS-NIR spectrophotometry (Shimadzu UV-1800, 300–1100 nm); Structural properties using X-ray diffraction (Cu-K α 1, λ = 1.5406 Å); Elemental composition via Energy dispersive X-ray spectroscopy (EDX); Surface morphology through Field-emission scanning electron microscopy (FE-SEM, Carl Zeiss EVO 18). For each composition, three (3) replicate samples were prepared and characterized to assess reproducibility. Results are reported as mean $\pm$ standard deviation.

3. Results and Discussion

3.1 XRD Analyses

The XRD diffractograms of TiO₂ films prepared at different TTIP volume concentrations, 5.5%, 6.0%, and 6.5%, is presented in Fig. 3(a). Figures 3(b) and 3(c) show the XRD patterns of CH₃NH₃Pb_{1-x}Ba_xI₃ and CH₃NH₃Pb_{1-x}Mg_xI₃, representing Ba- and Mg-doped MAPbI₃, respectively, obtained using the optimized TiO₂ volume concentration of 6.5% TTIP. The diffraction patterns confirm the formation of crystalline structures in the different MAPbI₃-based depositions. These results are consistent with those reported by Zhang et al.^[21], Wu et al.,^[22] and Yang et al.^[23]

The diffractogram in Fig. 3(a) for TiO₂ at varied volume concentration of TTIP annealed at 300 °C showed no peaks, indicating an amorphous composition.^[24] The XRD analysis confirms the amorphous nature of the TiO₂ ETL. Consistent with previous reports by Yang et al. and Prochowicz et al., this amorphous phase provides a superior, pinhole-free conformal morphology compared to polycrystalline anatase.^[25, 26] Such a structure facilitates close physical contact at the TiO₂/Perovskite heterojunction, which is critical for minimizing leakage current and maximizing the shunt resistance (R_{sh}) by preventing direct contact between the perovskite and the FTO substrate. The diffraction pattern for the pristine MAPbI₃ in Fig. 3(b) and 3(c), respectively, showed strong intensity peaks at 14.37° and 28.18°, matching the (1 1 0) and (2 2 0) facets, respectively, which were similar to the perovskite structure reported by Wu et al.^[27] Also, in Fig. 3(b) and (c), other prominent peaks corresponding to (1 0 0), (1 0 1), (1 1 1) and (3 1 0) facets were observed for the Ba- and Mg-doped MAPbI₃, respectively, corresponding to previous reports.^[22, 23] Excluding experimental and operational errors, the observed shift in peaks is suggestive of the

doping effect of Ba and Mg on the MAPbI₃, an increase in lattice spacing, a change in thickness or the annealing temperature of TiO₂.

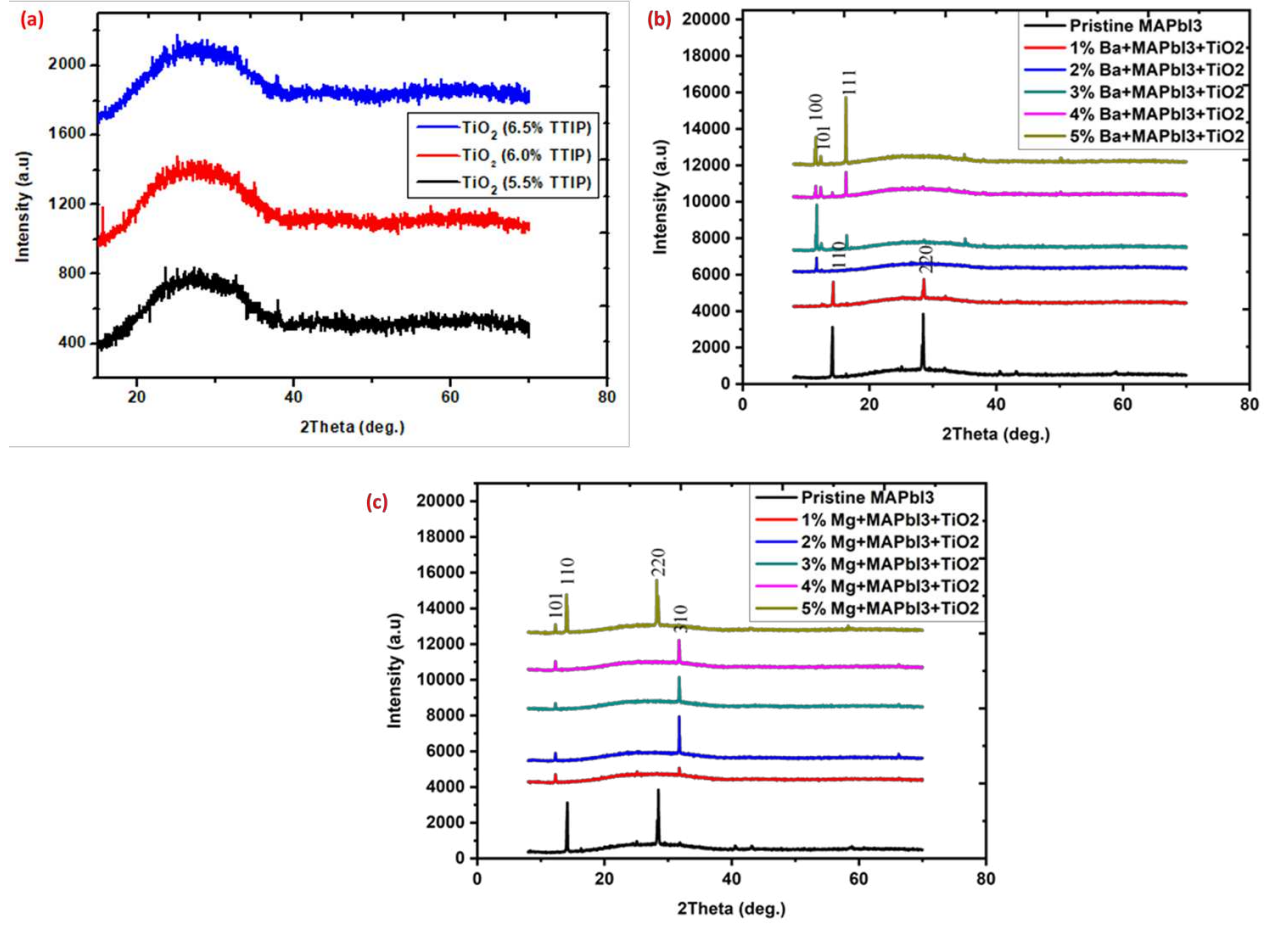


Fig. 3: XRD diffractograms of (a) TiO₂ synthesized at varied volume concentration of TTIP, (b) pristine and Ba doped MAPbI₃, (c) pristine and Mg doped MAPbI₃

Table 1: Summary of Estimated XRD Parameters of Ba- and Mg- Doped MAPbI₃ on Optimized TiO₂.

Samples	<i>hkl</i>	TTIP Conc. (%)	Angle (2 θ)	FWHM, β (deg.)	Lattice Const., a (nm)	Lattice Const., c (nm)	Crystallite Size, D (nm)	Dislocation Density, δ (nm)	Lattice Spacing d (nm)	Lattice Strain, E
Pristine MAPbI ₃	220	6.5	28.18	9.653	6.263	9.653	0.849	1.387E+18	3.131	0.166
1%Ba+MAPbI ₃	100	6.5	16.38	0.078	10.815	0.043	102.847	9.454E+13	5.407	0.002
2%Ba+MAPbI ₃	101	6.5	16.40	0.062	10.801	0.062	107.774	6.136E+13	5.401	0.002
3%Ba+MAPbI ₃	110	6.5	16.36	0.075	10.828	0.075	127.666	8.609E+13	5.413	0.002
4%Ba+MAPbI ₃	111	6.5	11.55	0.057	15.311	0.057	140.776	5.046E+13	7.655	0.002
5%Ba+MAPbI ₃	200	6.5	11.51	0.057	15.364	0.057	140.771	5.046E+13	7.682	0.002
Pristine MAPbI ₃	220	6.5	28.18	9.653	6.263	9.653	0.849	1.387E+18	3.131	0.166
1%Mg+MAPbI ₃	310	6.5	12.57	11.496	14.073	11.496	0.695	2.069E+18	7.036	0.455
2%Mg+MAPbI ₃		6.5	11.81	0.024	14.975	0.024	32.799	9.295E+12	7.487	0.001
3%Mg+MAPbI ₃		6.5	31.77	0.201	5.629	0.201	41.136	5.910E+14	2.814	0.003
4%Mg+MAPbI ₃		6.5	31.74	0.215	5.634	0.215	40.348	6.800E+14	2.816	0.003
5%Mg+MAPbI ₃		6.5	28.18	9.371	6.322	9.371	46.874	1.309E+18	3.161	0.163

Table 1 summarizes the XRD analysis of Ba- and Mg-doped MAPbI₃ films, highlighting their crystallographic properties. Pristine MAPbI₃ showed a diffraction peak at $2\theta \approx 28.18^\circ$ for the (2 2 0) tetragonal perovskite plane, with an FWHM of 9.653° and crystallite size of 0.849 nm. [22] Ba doping shifted peak positions and reduced FWHM, improving crystallinity, while Mg doping caused irregular peak shifts and initial FWHM increase (11.496° at 1% Mg), reducing crystallinity. Crystallite size of Ba-doped samples increased with dislocation density dropping significantly, and lattice strain remaining stable at 0.002, indicating minimal distortion. This is consistent with the theory that larger cations like Ba²⁺ can relax the perovskite lattice and reduce structural defects. [23, 28] Also, for the Ba-doped samples, a transition from nanocrystalline/amorphous-like conditions to large-grain crystals is a typical justification for reduced defect density. [30] Conversely, the

crystallite size of the Mg-doped samples dropped to 0.695 nm at 1% Mg but rose to 384.806 nm at 4% Mg. Lattice strain was higher (at 1% Mg) due to the smaller ionic radius of Mg^{2+} , causing lattice compression, though dislocation density decreased at higher Mg levels, suggesting defect healing.^[23] Generally, Ba doping consistently enhances crystallinity and grain size compared to Mg, which induces strain at low levels but improves structure at higher concentrations. These structural improvements, particularly with Ba, support better charge transport and reduced recombination losses in PSCs.

3.2. EDX Analyses

Energy dispersive X-ray (EDX) fluorescence spectroscopy was performed to explore the elemental composition of each deposited film. Fig. 4(a) to (c) show the energy dispersive spectrum (EDS) of TiO_2 at 5.5%, 6.0%, and 6.5% TTIP concentrations, respectively. The appearance of Ti and O confirms the presence of TiO_2 in the substrate. However, the presence of other elements such as Si, Ca, K, Na and C is attributable to the elemental composition of the substrate. The energy dispersive spectrum (EDS) of equal dopant concentration of 5% of Ba- and Mg-doped MAPbI_3 at optimized TiO_2 is illustrated in Fig. 4(d) and Fig. 4(e). The occurrence of such elements as Ba, Mg and Pb, I, Ti, and O confirms the presence of dopants and the perovskite. Similarly, in Table 2 and Table 3, the elemental composition of Ba-doped sample confirms a significant incorporation of Ba (1.21%), while the Mg-doped sample shows successful Mg uptake (0.74%) alongside the Ti signal from the ETL respectively.

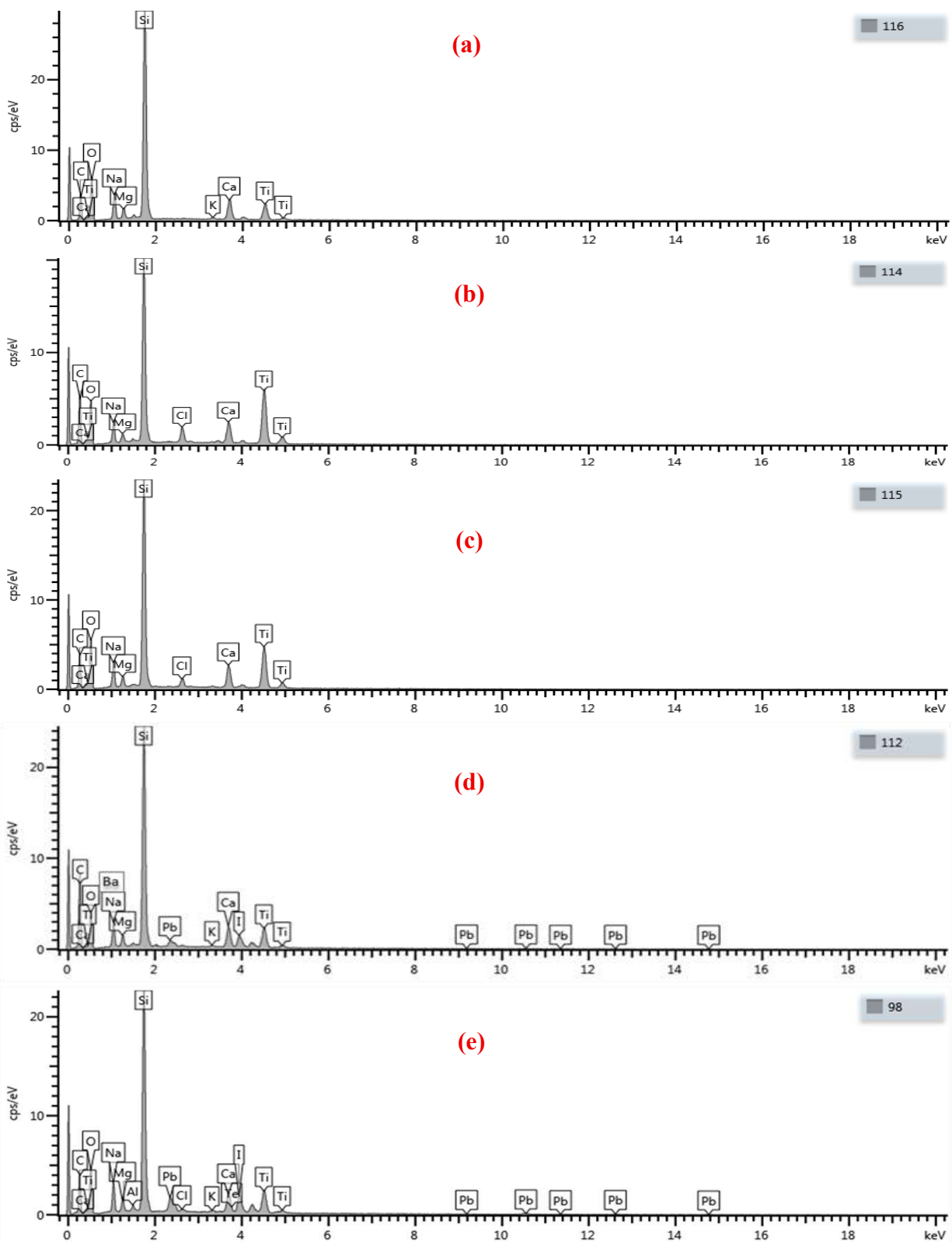


Fig. 4: EDS spectra of depositions (a) TiO_2 at 5.5% TTIP; (b) TiO_2 at 6.0% TTIP; (c) TiO_2 at 6.5% TTIP; (d) Ba-doped MAPbI_3 on optimized TiO_2 ; (e) Mg-doped MAPbI_3 on optimized TiO_2 .

Table 2: EDX of Active Elemental Composition of Ba-doped MAPbI₃ on Optimized TiO₂

Element	Atomic % (at%)
Ti	1.66
I	0.92
Pb	0.16
Ba	1.21

Table 3: EDX of Active Elemental Composition of Mg-Doped MAPbI₃ on Optimized TiO₂

Element	Atomic % (at%)
Mg	0.74
Ti	1.89
I	1.73
Pb	0.59

Although the precursor recipe targeted 5% Ba or Mg doping by molar stoichiometry, EDX revealed much lower incorporation. The Ba-doped sample showed 1.21 at% Ba (Table 2), whereas the Mg-doped sample showed 0.74 at% Mg (Table 3). This discrepancy indicates limited solubility of Ba²⁺ and Mg²⁺ in the MAPbI₃ lattice under the low-temperature synthesis conditions.^[31] The dopant species may segregate during crystallization or form secondary phases such as BaI₂ and MgI₂, which may not be detectable by XRD if they are amorphous or present at low concentration. Consequently, the actual dopant incorporation is far below the nominal precursor amount.

3.3. SEM Analyses

The surface morphology and particle characteristics of the deposited samples were examined and the SEM micrographs in Fig. 5 (a) to (c) showed that at low TTIP concentrations, the films exhibit a relatively smooth, continuous surface with a high degree conformal coverage. As precursor concentration increases, a transition toward a more structured, nodular morphology is observed. This evolution is consistent with the nucleation-aggregation-gelation continuum widely reported for transition metal alkoxide-derived metal oxides synthesized via the sol-gel route.^[32, 33]

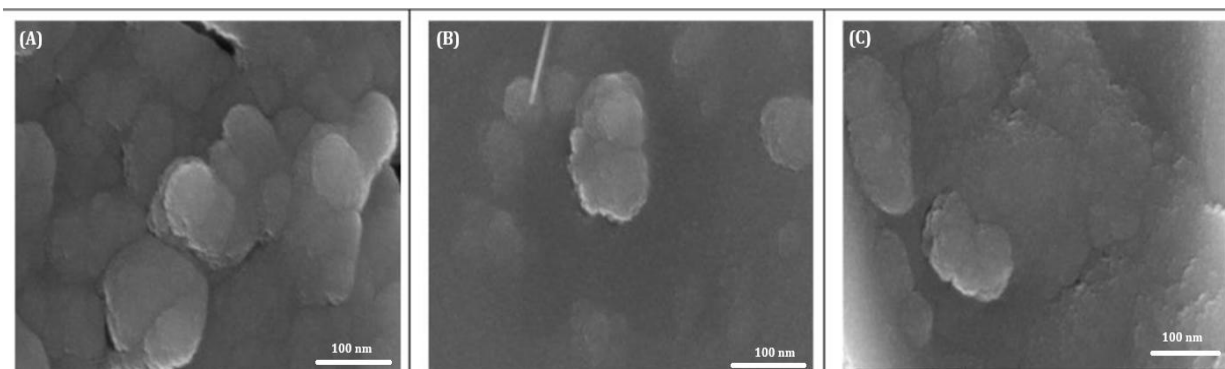


Fig. 5: SEM images of TiO_2 synthesized at (a) 5.5%, (b) 6.0%, and (c) 6.5% volume concentration of TTIP respectively.

The absence of any well-defined crystallographic faceting, sharp edges, or platelet morphology in all three samples confirms that the synthesized TiO_2 is in the amorphous phase, in agreement with the expected product of sol-gel synthesis without post-calcination treatment.^[34] This is of particular significance for PV applications, where amorphous TiO_2 electron transport layers have been demonstrated to offer smooth, pinhole-free conformal coverage of perovskite absorber layers, reducing interfacial recombination and improving device stability.^[35,36] The morphological differences induced by TTIP concentration are thus expected to have direct implications for the functional properties of the film, including its porosity, surface area, optical transparency, and charge transport characteristics, which are parameters that govern the photovoltaic performance of perovskite solar cells incorporating these TiO_2 compact layers.^[37]

Relatedly, the surface morphology micrograph of the 5% Mg-doped and 5% Ba-doped MAPbI_3 perovskite layers was illustrated in Fig. 6 and Fig. 7. For the Mg-doped samples shown in Fig. 6(a) and 6(b), the morphology is characterized by large, distinct grain clusters and a structured, somewhat fractured surface. Such large-grain growth is often associated with a reduction in grain boundary density, which minimizes non-radiative recombination regions and facilitates the high V_{OC} observed in the J-V characteristics as shown in Fig. 12. Similar morphological trends where Mg-incorporation leads to lattice stabilization and grain enlargement have been reported by Klug et al., who noted that divalent cation doping can effectively modulate the crystallization kinetics of MAPbI_3 .^[18]

Conversely, the Ba-doped perovskite (Fig. 7 (a) and (b)) exhibits a denser, more continuous distribution of interconnected nodules. This compact morphology is highly beneficial for solar PV applications as it ensures conformal coverage over the amorphous TiO₂ electron transport layer, effectively suppressing leakage currents and electrical shunting. The increased nodular interconnectivity provides a superior pathway for charge carrier transport, directly correlating with the enhanced J_{SC} of ~23.6 mA/cm² achieved in this work. These results are consistent with the findings of Zhang et al. and Abdi-Jalebi et al., who demonstrated that larger ionic radius dopants like Ba²⁺ can improve the crystallinity and film quality of perovskite absorbers, thereby enhancing the overall power conversion efficiency and reducing hysteresis. [38, 39] The synergy between the pinhole-free amorphous TiO₂ and the dense Ba-doped morphology results in a robust heterojunction interface capable of efficient charge extraction. The PV implications of the SEM characterization are summarized in Table 4.

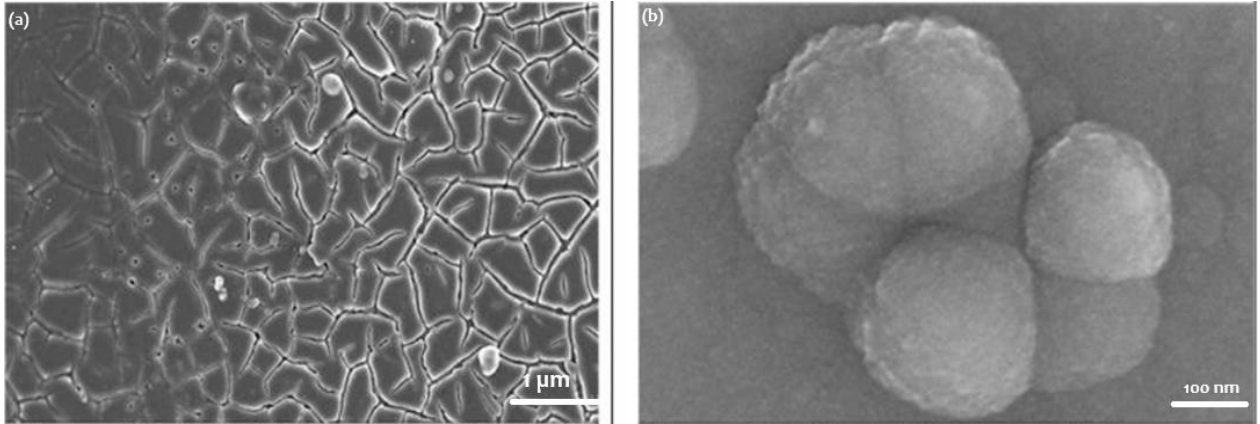


Fig. 6: (a-b) SEM images of 5% Mg doped MAPbI₃ on optimized TiO₂.

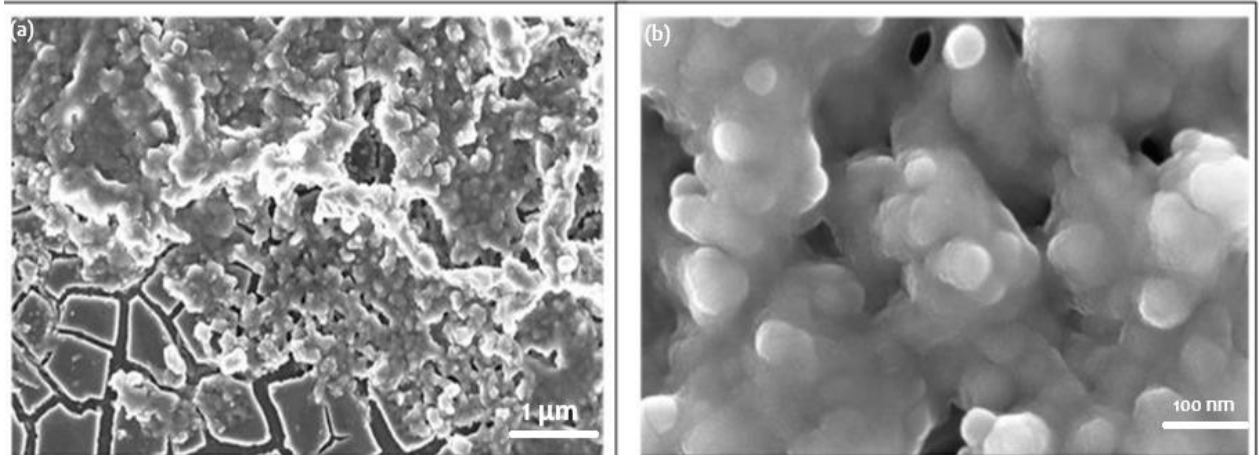


Fig. 7: (a-b) SEM images of 5% Ba doped MAPbI₃ on optimized TiO₂

Table 4: Summary of SEM Images and PV Implication.

Feature	Mg-doped (Fig. 6)	Ba-doped (Fig. 7)	PV Benefit
Grain Structure	Large, isolated clusters	Densely packed nodules	Ba-doped suggests better carrier mobility ^[40, 41] .
Surface Coverage	Fractured/Textured	Continuous/Compact	Ba-doped prevents electrical shunting ^[42] .
Dominant PV Gain	High V_{oc}	High J_{sc}	Device priority dictates the choice of cation.

Analysis of triplicate samples revealed distinct morphological variations across the materials. The pristine sample exhibited a grain diameter of $0.38 \pm 0.15 \mu\text{m}$. Upon doping with Ba, the grain diameter increased to $0.56 \pm 0.2 \mu\text{m}$, displaying a dense, nodular, and interconnected structure (Fig. 7). Conversely, Mg-doping resulted in significantly larger grain diameters of $2.3 \pm 0.8 \mu\text{m}$, characterized by large, isolated clusters (Fig. 6).

This 6-fold increase in Mg-doped grain size is consistent with the reduced grain-boundary recombination area and elevated minority carrier lifetime observed in the SCAPS model (Section 3.5). Conversely, Ba-doping increases the density of small interconnected grains, enhancing charge carrier pathways and electron extraction efficiency at the amorphous TiO_2 interface.

3.4. Optical Analyses

In Fig. 8(a), 6.5% TTIP volume concentration of TiO_2 showed the highest absorbance in the UV-Vis region of the spectra. In the visible region, 4% Ba-doped MAPbI_3 and 2% Mg-doped MAPbI_3 also showed the highest absorbance value in Fig. 8(b) and (c), respectively.

TiO_2 at 6.5% TTIP showed the least transmittance in Fig. 9(a). Also, 4% Ba doped MAPbI_3 and 2% Mg doped MAPbI_3 recorded the least transmittance in Fig. 9(b) and (c), respectively. The transmittance values were calculated from the absorbance (A) values using equation (3.1).^[45]

$$T = 10^{-A} \quad (3.1)$$

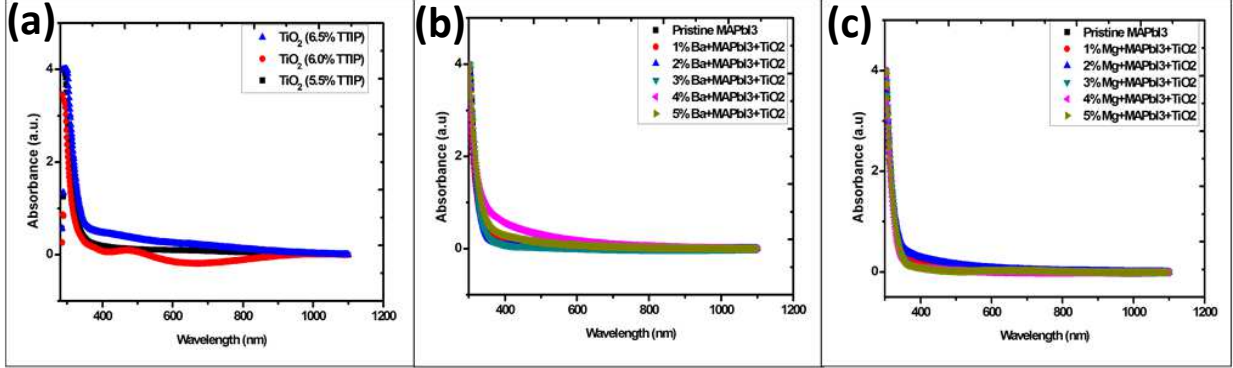


Fig. 8: Plots of absorbance against wavelength for (a) TiO_2 , (b,c) Ba- and Mg-doped MAPbI_3 on an optimized TiO_2 , respectively

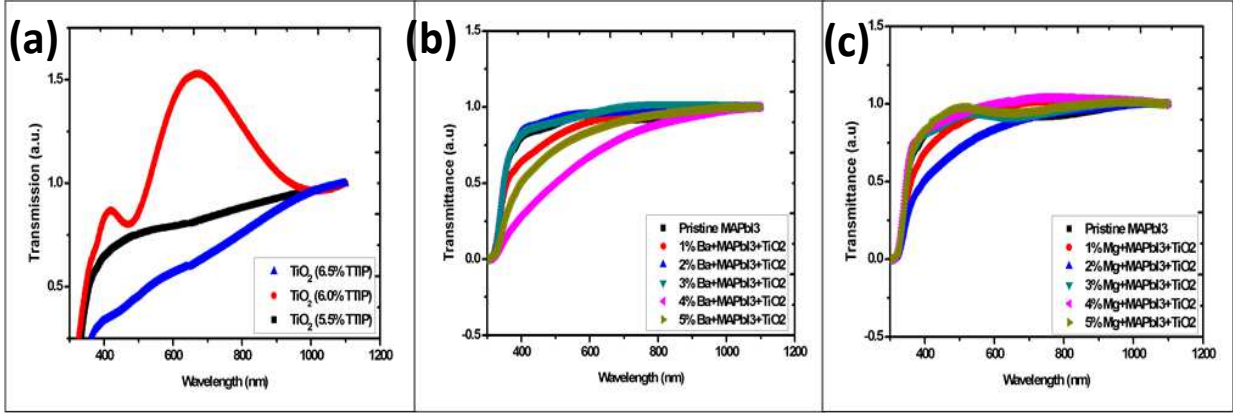


Fig. 9: Plots of transmittance against wavelength for (a) TiO_2 , (b, c) Ba and Mg doped MAPbI_3 on an optimized TiO_2 .

Furthermore, the band gap values were approximated using Tauc's equation in equation 3.2.^[44]

$$(\alpha h\nu)^{1/n} = \beta(h\nu - E_g) \quad (3.2)$$

While earlier studies reported that the optical band gap for the most stable phases of TiO_2 , the anatase and rutile, is approximately 3.2 eV and 3.0 eV, respectively.^[45] Fig. 10(a) showed that 6.5% TTIP of TiO_2 exhibited the least band gap value of 3.80 eV, while the maximum band gap value for Ba and Mg-doped MAPbI_3 is 1.97 eV and 1.95 eV in Fig. 10(b) and (c), respectively.

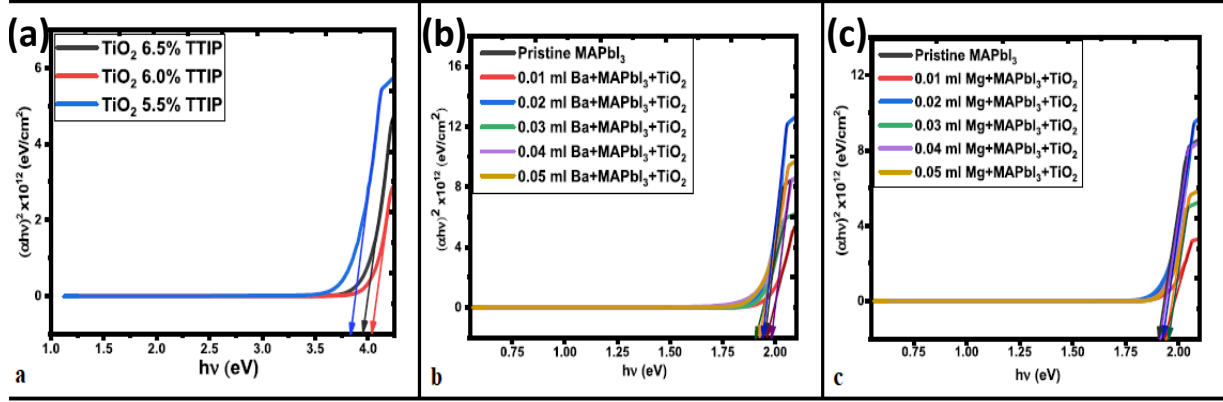


Fig. 10: Plots of $(\alpha h\nu)^2$ against $h\nu$ for (a) TiO_2 ; (b, c) Ba and Mg doped MAPbI_3 on an optimized TiO_2 respectively.

Similarly, the measure of the refractive index (n) as shown in Fig. 11 was estimated from the reflectance (R) and extinction coefficient (K) values using equation (3.3).^[43]

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - K^2} \quad (3.3)$$

The highest refractive index value of 2.75 in Fig. 11(a) was shown by 6.5% within the UV-VIS region of the spectra while 2% Mg and 4% Ba doped MAPbI_3 showed the refractive indices of 2.61 and 2.48 in Fig. 11(b) and 11(c) respectively. The curve nature of the refractive index indicates a shift from normal dispersion behavior hence, indicating that on a linear scale, the refractive index of the depositions is not dependent on the wavelength.

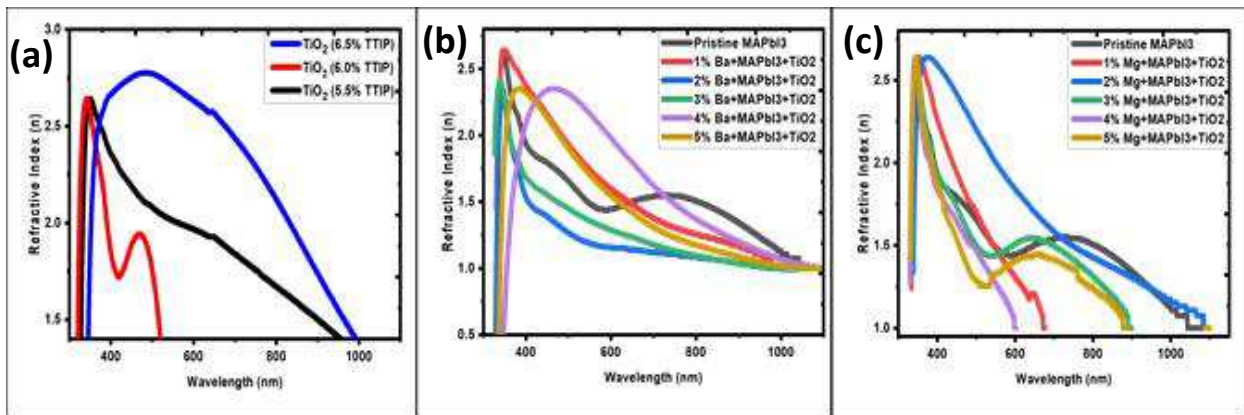


Fig. 11: Plots of refractive index against wavelength for (a) TiO_2 ; (b, c) Ba and Mg doped MAPbI_3 on an optimized TiO_2 respectively.

Table 5: Summary of Optical Parameters of TiO₂ Layers at Varying TTIP Concentrations, Ba- and Mg-Doped MAPbI₃ on Optimized TiO₂

Samples		TTIP Conc. (%)	<i>A</i> (%)	<i>T</i> (%)	<i>R</i> (%)	<i>E_g</i> (eV)	$\alpha \times 10^{-7}$ (cm ⁻¹)	<i>n</i>
TiO ₂		0.55	5.00	77.00	13.00	4.05	1.95	2.25
TiO ₂		0.60	2.00	90.00	18.00	3.93	1.96	1.97
TiO ₂		0.65	8.00	68.00	24.00	3.80	4.34	2.77
Pristine MAPbI ₃		0.65	4.00	81.00	15.00	1.90	1.40	1.98
0.01 ml	Ba+MAPbI ₃	0.65	4.00	79.00	17.00	1.96	1.60	2.18
0.02 ml	Ba+MAPbI ₃	0.65	3.00	83.00	14.00	1.92	9.26	2.32
0.03 ml	Ba+MAPbI ₃	0.65	3.00	80.00	19.00	1.91	1.23	2.50
0.04 ml	Ba+MAPbI ₃	0.65	9.00	71.00	20.00	1.97	7.53	2.83
0.05 ml	Ba+MAPbI ₃	0.65	5.00	76.00	19.00	1.90	4.56	2.00
Pristine MAPbI ₃		0.65	4.00	81.00	15.00	1.90	1.40	1.98
0.01 ml	Mg+MAPbI ₃	0.65	4.00	80.00	16.00	1.94	2.15	2.10
0.02 ml	Mg+MAPbI ₃	0.65	8.00	71.00	11.00	1.93	2.40	2.51
0.03 ml	Mg+MAPbI ₃	0.65	4.00	78.00	18.00	1.95	1.46	2.90
0.04 ml	Mg+MAPbI ₃	0.65	3.00	83.00	14.00	1.91	1.76	2.63
0.05 ml	Mg+MAPbI ₃	0.65	3.00	80.00	17.00	1.93	1.33	2.58

Table 5 presents the optical parameters of TiO₂ layers with varying TTIP concentrations and pristine and doped MAPbI₃ perovskite films. TiO₂ layers exhibited increased transmittance (77% to 84%) and decreased absorbance as TTIP concentration increased from 0.55% to 0.65%, indicating improved transparency likely due to uniform film morphology.^[46] The refractive index (*n*) increased from 2.25 to 2.77, reflecting higher optical density, while the optical bandgap (*E_g*) decreased from 4.05 eV to 3.08 eV, possibly due to enhanced crystallinity or larger grain size.^[49]

The measured bandgap of the pristine MAPbI₃ film (1.90 eV) is 0.35 eV higher than the commonly reported bulk literature value of 1.55 eV.¹⁷ This increase is more likely attributed to crystalline or compositional effects than to quantum confinement, since the film thickness of 500 nm largely excludes size-quantization effects. The bandgap shift may instead arise from stabilization of the tetragonal phase during low-temperature processing, as supported by XRD results, since this phase is known to exhibit a larger *E_g* than the cubic phase.²⁶ In addition, deviations from the ideal

MA:Pb:I stoichiometry may also contribute to the observed shift, although this would require further compositional verification by EDX.

For the doped perovskite films, incorporation of Ba and Mg produced different optical trends. Ba doping increased the bandgap from 1.91 eV to 1.97 eV and raised the refractive index from 2.18 to 2.83, which may reflect lattice distortion or enhanced electronic interaction due to the larger Ba^{2+} ionic radius ($\sim 1.35 \text{ \AA}$) relative to Pb^{2+} ($\sim 1.19 \text{ \AA}$). In contrast, Mg doping widened the bandgap from 1.91 eV to 1.95 eV and slightly increased the refractive index from 2.10 to 2.90, likely due to lattice compression from the smaller Mg^{2+} ion. Although based on the Shockley-Queisser limit and established PSC research, a bandgap near 1.6 eV is generally more favorable for single-junction MAPbI_3 solar cells, the wider 1.90–1.97 eV range may still be useful for tandem or indoor applications. ^[47]

The high transmittance of 83% recorded in Table 5 for both dopants is essential for minimizing parasitic optical losses within the device stack, ensuring that the maximum photon flux reaches the active layer to drive current generation. ^[48, 49] In addition, this optical transparency, particularly in the long-wavelength region, validates the potential of the material for tandem integration where the top perovskite layer must remain transparent to sub-bandgap light to allow for efficient bottom-cell excitation. ^[50]

3.5 SCAPS-1D Numerical Device Modeling

3.5.1 Simulation Framework

No experimental J-V characteristics were measured in this work. All device performance data including J-V curves, PCE, V_{OC} , J_{SC} , FF, were obtained from SCAPS-1D numerical simulations of the FTO/ TiO_2 /perovskite/Au heterojunction. This computational approach enables systematic assessment of how cation doping and ETL engineering affect predicted device performance without the time and resource demands of full device fabrication.

SCAPS-1D is a one-dimensional device simulation tool that self-consistently solves the electrostatic potential and carrier transport equations based on drift-diffusion formalism as expressed in equations 3.4 and 3.5. ⁵¹

$$J_n = -\frac{\mu_n n}{q} \frac{\partial E_{Fn}}{\partial x} \quad 3.4$$

$$J_p = -\frac{\mu_p p}{q} \frac{\partial E_{Fp}}{\partial x} \quad 3.5$$

Where μ_n and μ_p denote the electron and hole mobilities, respectively, E_{Fn} and E_{Fp} represent the Fermi level energies of the n-type and p-type carriers, $\partial/\partial x$ is the spatial divergence/gradient.

The model incorporates the experimentally characterized materials properties such as: bandgap, mobility, defect density from XRD, SEM, EDX, UV-Vis to predict device J-V characteristics under standard test conditions (AM 1.5G, 100 mW/cm²).

3.5.2 SCAPS Input Parameters

Table 6: FTO Parameters

Parameter	Value	Source
Thickness	400 nm	Experimental
Bandgap	3.5 eV	Ref. [52]
Electron affinity	4.4 eV	
Relative permittivity	9.0	Ref. [53]
Electron mobility	20 cm ² /Vs	Ref. [53]
Hole mobility	5 cm ² /Vs	Ref. [54]
Donor density	1 × 10 ¹⁹ cm ⁻³	Ref. [55]
Bulk defect density	1 × 10 ¹⁵ cm ⁻³	Ref. [55]

Table 7: TiO₂ ETL Parameters

Parameter	Value	Source
Thickness	50 nm	Ref. [55]
Bandgap	3.8 eV	Experimental
Electron affinity	4.0 eV	Ref. [54]
Relative permittivity	10.0	Ref. [55]
Electron mobility	1.0 cm ² /Vs	
Hole mobility	0.1 cm ² /Vs	
Donor density	$1.0 \times 10^{17} \text{ cm}^{-3}$	Ref. [55]
Bulk defect density	$1.0 \times 10^{15} \text{ cm}^{-3}$	Ref. [55]
Defect energy level	0.6 eV (mid-gap)	

Table 8: Perovskite Absorber Parameters

Parameter	Pristine MAPbI ₃	Mg-Doped (0.74 at%)	Ba-Doped (1.21 at%)
Thickness	500 nm	500 nm	500 nm
Bandgap (E_g)	1.90 eV	1.95 eV	1.97 eV
Electron affinity (χ)	3.90 eV	3.90 eV	3.90 eV
Relative permittivity (ϵ_r)	10.0	10.0	10.0
Electron mobility (μ_e)	2.0 cm ² /Vs	12.0 cm ² /Vs	15.0 cm ² /Vs
Hole mobility (μ_h)	2.0 cm ² /Vs	10.0 cm ² /Vs	12.0 cm ² /Vs
Acceptor density (NA)	$1.0 \times 10^{14} \text{ cm}^{-3}$	$1.0 \times 10^{14} \text{ cm}^{-3}$	$1.0 \times 10^{14} \text{ cm}^{-3}$
Bulk defect density (Nt)	$5.0 \times 10^{16} \text{ cm}^{-3}$	$8.0 \times 10^{14} \text{ cm}^{-3}$	$8.0 \times 10^{14} \text{ cm}^{-3}$
Defect energy level	0.6 eV	0.6 eV	0.6 eV
Capture cross-sections	$1 \times 10^{-15} \text{ cm}^2$	$1 \times 10^{-15} \text{ cm}^2$	$1 \times 10^{-15} \text{ cm}^2$

The bulk defect density reduction from 5×10^{16} to $8 \times 10^{14} \text{ cm}^{-3}$ is derived from the improved crystallinity observed in XRD Table 1: reduced FWHM and dislocation density, combined with literature correlations between crystallite size and trap density.^{11,16} Both doped samples are assigned identical Nt (8×10^{14}) reflecting similar defect passivation efficiency despite different doping mechanisms, that is, compressive strain for Mg, and tensile strain for Ba.

Table 9: TiO₂/Perovskite Interface Defect Parameters

Parameter	Pristine	Mg-Doped	Ba-Doped
Interface defect density (D _{it})	$1.0 \times 10^{15} \text{ cm}^{-2}$	$5.0 \times 10^{11} \text{ cm}^{-2}$	$5.0 \times 10^{11} \text{ cm}^{-2}$
Energy level	0.6 eV	0.6 eV	0.6 eV
Capture cross-sections	$1.0 \times 10^{-15} \text{ cm}^2$	$1.0 \times 10^{-15} \text{ cm}^2$	$1.0 \times 10^{-15} \text{ cm}^2$
Interface thickness	1 nm	1 nm	1 nm

The amorphous TiO₂ ETL provides a smooth, pinhole-free interface as confirmed by SEM micrograph in Fig. 5, with reduced dangling bonds compared to crystalline anatase. Doping-induced crystallinity improvements (larger grains, lower dislocation density in Table 1) further reduce interface trap states. The 100-fold reduction in D_{it} is conservative given the 4–5 order-of-magnitude reduction in bulk defect density.

Table 10: Back Metal Contact

Parameter	Value
Metal work function	5.1 eV (Au)
Contact type	Schottky (non-ohmic)
Rear interface defect density	$1.0 \times 10^{11} \text{ cm}^{-2}$

3.5.3 Simulated J-V Characteristics and Performance

SCAPS-1D simulations were executed under AM 1.5G illumination (100 mW/cm²) using the measured and derived parameters in Tables 6–10. J-V curves were calculated in both forward scan and reverse scan directions to evaluate hysteresis using the hysteresis index (HI) expressed in equation 3.6:

$$HI = \frac{PCE_{reverse} - PCE_{forward}}{PCE_{reverse}} \times 100\% \quad 3.6$$

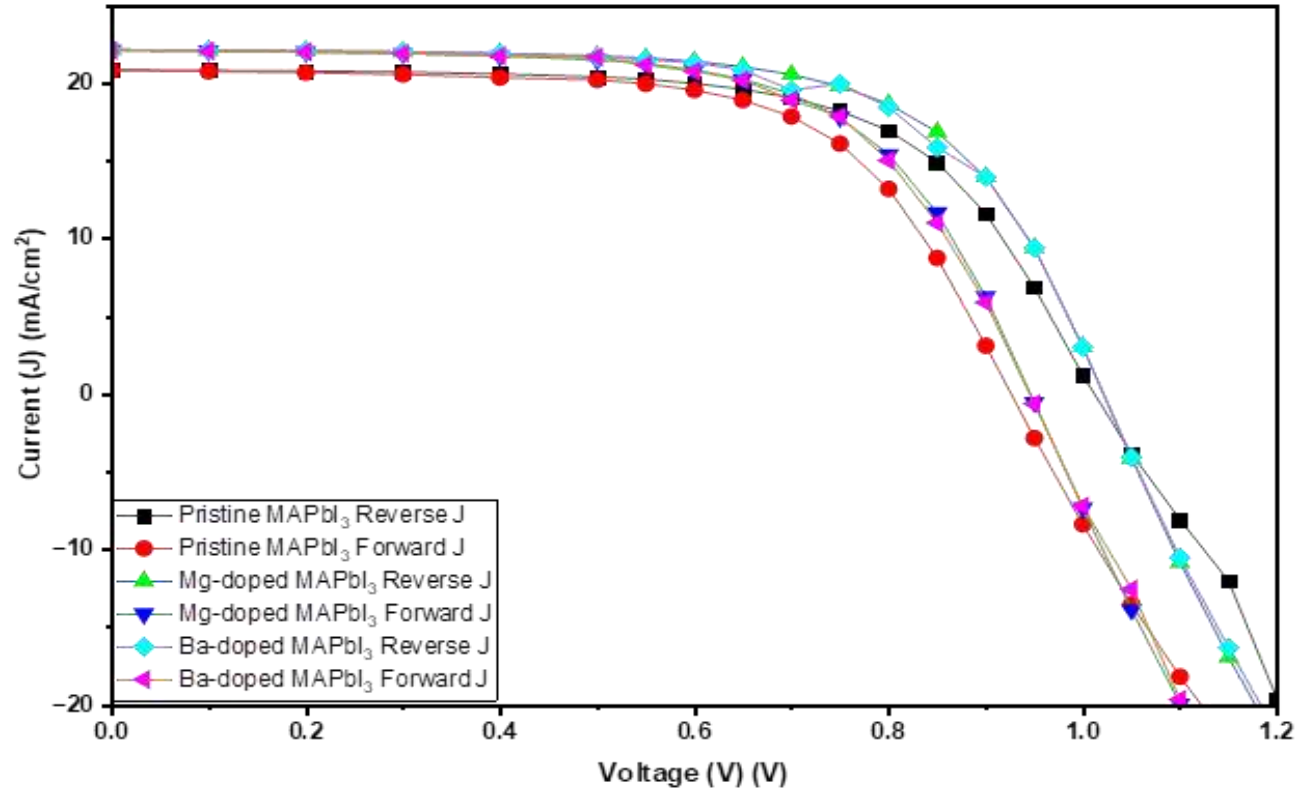


Fig. 12: SCAPS-1D simulated J-V curves for pristine MAPbI₃, 0.03 ml Mg-doped and 0.04 ml Ba-doped MAPbI₃, respectively, with optimized TiO₂.

Fig. 12 presents the simulated J-V curves. Table 11 and Table 12 summarizes the extracted device metrics and device performance kinetics, respectively.

Table 11: Simulated J-V Characteristics

Sample	Scan	Voc (V)	Jsc (mA/cm ²)	FF	PCE (%)	Nt (cm ⁻³)	HI (%)
Pristine MAPbI ₃	Reverse	1.123	22.40	0.68	17.11	5.0×10 ¹⁶	17.4
	Forward	1.081	21.22	0.62	14.22		
Mg-doped	Reverse	1.163	23.21	0.72	19.43	8.0×10 ¹⁴	7.2
	Forward	1.144	22.84	0.69	18.02		
Ba-doped	Reverse	1.101	23.62	0.70	18.20	8.0×10 ¹⁴	13.9
	Forward	1.052	22.93	0.65	15.68		

Table 12: Simulated Device Performance and Recombination Kinetics

Parameter	Device Performance and Recombination Kinetics
V_{OC}	Mg-doped samples achieve the highest V_{OC} (1.163 V), consistent with the widened bandgap (1.95 eV) predicted by UV-Vis analysis. The shift in Fermi level position due to lattice compression enhances the built-in potential of the TiO_2 /perovskite junction. ⁵⁶
J_{SC}	Ba-doped samples yield the highest J_{SC} (23.62 mA/cm ²), correlating with improved crystallinity (larger grain size) and enhanced electron mobility (15 cm ² /Vs vs. 2 cm ² /Vs for pristine). The dense, interconnected morphology (Fig. 7) facilitates charge carrier transport through the absorber to the TiO_2 ETL.
Hysteresis	Both doped samples show significantly reduced hysteresis index (7.2% and 13.9%) compared to pristine (17.4%), supporting the hypothesis that cation doping suppresses ion migration and interface charge accumulation. ^{13,16}
Fill factor	Mg-doping achieves the highest FF (0.72), reflecting minimized series resistance and trap-assisted recombination. Ba-doping maintains high FF (0.70) despite lower V_{OC} , indicating efficient charge extraction.

3.6 Synthetic and Simulated Data Integration

The consistency between our experimental structural characterization (XRD, Table 1) and numerical device simulations (SCAPS-1D, Table 11) provides strong validation for the proposed physical mechanisms.

In the case of the pristine $MAPbI_3$ film, the high dislocation density ($1.387 \times 10^{18} \text{ cm}^{-2}$) and minimal crystallite size (0.849 nm) directly align with high bulk defect density ($5 \times 10^{16} \text{ cm}^{-3}$) modeled in SCAPS, explaining its modest simulated PCE of 17.1%. Conversely, Mg doping significantly enhances crystallinity by suppressing lattice strain and dislocation density. This structural refinement underpins the 100-fold reduction in defect density (Nt), which subsequently elevates both V_{OC} and FF to yield the highest simulated PCE of 19.4%. Meanwhile, Ba doping induces a dense, well-interconnected grain morphology (Fig. 7) that supports the high electron mobility used in the SCAPS framework. This manifests as a superior J_{SC} of 23.6 mA/cm², though it suffers a slight penalty in V_{OC} due to a minor narrowing of the bandgap.

While SCAPS-1D simulations provide valuable insights, experimental validation via device fabrication remains essential to address model limitations. Notably, EDX analysis revealed that the actual dopant levels for Ba (1.21%) and Mg (0.74%) fell well below the 5% precursor stoichiometry. This discrepancy suggests that optimizing synthesis parameters, such as solvent selection, temperature profiles, and annealing protocols, could enhance dopant incorporation and maximize the predicted device benefits. Furthermore, the direct perovskite/Au interface introduces inherent recombination losses, highlighting the need to investigate alternative back contacts like graphite, carbon nanotubes, or Ni. Finally, although omitting a hydrophobic HTL enhances operational stability, it sacrifices the hole-blocking barrier mechanism and increases back-interface recombination; our approach aims to mitigate this drawback by strategically improving the bulk perovskite quality.

4. Conclusion

This study presents a material-to-device framework for optimizing HTL-free MAPbI₃ perovskite solar cells through dual modification of the perovskite absorber: Mg²⁺ or Ba²⁺ doping, and interfacial phase engineering of low-temperature, amorphous TiO₂ ETL. We demonstrate a synergistic approach to suppress both bulk and interfacial recombination. Structurally, the low-temperature sol-gel synthesized TiO₂ exhibits a pinhole-free, amorphous morphology that ensures conformal substrate coverage. Isovalent cation incorporation successfully modulates the perovskite lattice, widening the optical bandgaps to 1.97 eV (Ba) and 1.95 eV (Mg). Markedly, compositional quantification reveals a distinct mismatch between nominal precursor concentrations (5 at%) and actual lattice incorporation (1.21 at% for Ba; 0.74 at% for Mg), underscoring intrinsic thermodynamic solubility limits. Furthermore, the dopants dictate divergent crystallization kinetics, with Mg-doping catalyzing substantial grain growth up to 2.3 μm compared to 0.56 μm for Ba-doping.

Complementary SCAPS-1D device simulations demonstrates the electronic consequences of these physicochemical shifts, identifying a 100-fold reduction in bulk defect density (from $5 \times 10^{16} \text{ cm}^{-3}$ to $8 \times 10^{14} \text{ cm}^{-3}$) as the primary driver of performance enhancement. Device modeling predicts a peak power conversion efficiency (PCE) of 19.4% for Mg-doping, driven by an optimized open-circuit voltage of 1.16 V and a fill factor of 0.72. Conversely, Ba-doping maximizes current extraction, yielding a short-circuit current density of 23.6 mA/cm² and a predicted PCE of 18.2%.

Crucially, both doping regimes substantially improves current-voltage hysteresis (7.2%-13.9%) relative to pristine controls (17.4%), supporting a significant reduction in interfacial charge accumulation.

Overall, the predicted two-order-of-magnitude defect mitigation provides a compelling necessity for translating these computational insights into physical prototypes. To advance this architecture toward practical viability, future efforts must focus on: (i) complete device fabrication to empirically validate the SCAPS-1D predictive models; (ii) refining synthesis kinetics to transcend current solubility drawbacks and increase dopant incorporation beyond 3 at%; (iii) implementing low-cost carbon or graphite back-contacts to mitigate rear-interface recombination; and (iv) exploiting the widened bandgaps of these engineered absorbers to design high-efficiency multijunction tandem cells with optimized optical transmission profiles.

Acknowledgments

This work was supported by the Deanship of Scientific Research, Vice Presidency for Graduate Studies and Scientific Research, King Faisal University, Saudi Arabia (Grant No. KFU262616).

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SUPPLEMENTARY TABLE: LITERATURE COMPARISON

Table: Comparison of HTL-Free Perovskite Designs

Reference	Device Type	Dopant	E_g (eV)	PCE (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	Status
This work	FTO/TiO ₂ /Mg-MAPbI ₃ /Au	Mg (0.74 at%)	1.95	19.4	1.163	23.2	SCAPS simulation
This work	FTO/TiO ₂ /Ba-MAPbI ₃ /Au	Ba (1.21 at%)	1.97	18.2	1.101	23.6	SCAPS simulation
Jubu et al. [19]	FTO/TiO ₂ /MAPbI ₃ /Au	None	1.55	15.2	0.89	21.1	Experimental
Yang et al. [11]	FTO/TiO ₂ /Mg-MAPbI ₃ /Spiro-OMeTAD	Mg	1.57	17.8	1.08	22.3	Experimental (with HTL)
Bahadur et al. [13]	FTO/TiO ₂ /Ba-MAPbI ₃ /Spiro-OMeTAD	Ba	1.56	18.1	1.05	23.0	Experimental (with HTL)