Stable Bandgap-tunable Hybrid Perovskites with Alloyed Pb-Ba Cations for High-performance Photovoltaic Applications

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ABSTRACT

The intrinsic poor stability of MAPbI₃ hybrid perovskites in the ambient environment remains as the major challenge for photovoltaic applications. In this work, complimentary first-principles calculations and experimental characterizations reveal that metal cation alloyed perovskite (MABa_xPb_{1-x}I₃) can be synthesized and exhibit substantially enhanced stability via forming stronger Ba-I bonds. The Ba-Pb alloyed perovskites remain phase pure in ambient air for more than 15 days. Furthermore, bandgap of MABa_xPb_{1-x}I₃ is tailored in a wide window of 1.56 ~ 4.08 eV. Finally, MABa_xPb_{1-x}I₃ is used as capping layer on MAPbI₃ in solar cells, resulting in significantly improved power conversion efficiency (18.9%) and long-term stability (>30 days). Overall, our results provide a simple but reliable strategy toward stable less-Pb perovskites with tailored physical properties.

TOC GRAPHICS

Organo-lead halide perovskites ABX_3 ($X = I, Br, Cl$) have recently revolutionized photovoltaic research,¹⁻³ benefiting from their optimum solar absorption,⁴⁻⁵ excellent ambipolar charge mobilities and unusual defect-tolerant properties.⁵⁻⁶ To date, photovoltaic efficiencies over 23% have been recorded,⁷ thus offering promising prospects for applications.⁸⁻⁹ However, the poor stability of halide perovskites under ambient conditions remains the major challenge for outdoor solar cell deployment.³ To date, numerous efforts have been made to address this issue.¹⁰ Among the various strategies, composition tailoring via substitution of either MA, Pb or X components in the $MAPbX_3$ structure is an easy and effective approach. For example, the substitution of the I ions with Cl¹¹ and Br¹² has been established as a reliable method to improve device stability.¹³ A-site engineering, i.e., replacing MA with formamidinium (FA),¹⁴ ethylammonium¹⁵ or metal cations¹⁶ has also been reported.¹⁴

$MAPbI_3$ is known to decompose into PbI_2 , a water-soluble carcinogen, when it is exposed to polar solvents such as water.¹⁷ Thus, seeking suitable metal cations to serve as alternatives to replace toxic Pb is an imperative but challenging task. The B-site alloying approach has been demonstrated with Zn,¹⁸ Sr,¹⁹ Sn,²⁰ Ba²¹ and Ge.²² Tin analogues have shown some promise,²³ but the Sn-Pb alloyed perovskites quickly degrade and suffer from oxidation.¹⁶ Ge-based perovskites also have poor chemical stability.²⁴ According to the Goldschmidt's rule,²⁵ divalent metal cations of Ba^{2+} and Sr^{2+} , with sizes similar to Pb^{2+} (the ionic radii of Ba^{2+} and Sr^{2+} are 1.34 Å and 1.18 Å, respectively, close to that of Pb^{2+} (1.20 Å)),²¹ are suitable candidates for substituting Pb.²⁶ Pazoki *et al.* theoretically investigated the electronic structure of $MASrI_3$ and predicted an improved stability by examining its formation energy.²¹ However, compared with other composition tuning approaches, there have been few reports on metal-cation-alloyed perovskites with substituted divalent metal cations.

In the present work, we report a B-site engineering strategy based on alloyed $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ perovskites for achieving chemical stability. Our density functional theory (DFT) calculations revealed that Ba-incorporated metal-iodide perovskites are stabilized via enhanced Pb-I, Ba-I and MA-I chemical bonding. Furthermore, the band structures of the alloyed Ba-Pb perovskites are Ba-concentration dependent, and the different electronegativity and work function of Ba lead to monotonous increase of bandgap in Pb-Ba alloyed perovskites. Finally, we applied stable $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ as a capping layer on perovskite solar cells and achieved significantly improved power conversion efficiency (PCE) of 18.9% with long-term stability.

We first examined the ground-state geometry of MAPbI_3 (see details in Supporting Information (SI), **Figure S1**). The optimized lattice parameters ($a = b = 8.9125 \text{ \AA}$, $c = 13.1173 \text{ \AA}$ and $\alpha = \beta = \gamma = 90.0^\circ$, **Table S1**) are consistent with the reported results.²⁷ The alloyed $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ supercells with four chemical units were obtained by substituting Pb with Ba, where the four Pb sites were independently examined. To locate the global minimum of total energy, cubic, tetragonal (pseudocubic) and orthorhombic structures were investigated with varying x . The ground-state structures with Ba concentrations $x = 0, 0.25, 0.5, 0.75$ and 1 were calculated to be distorted tetragonal (β -phase) (**Table S1**); these structures are schematically illustrated as the insets in **Figure 1**. The structural modifications with varied Ba content originate from the difference in the Pb^{2+} and Ba^{2+} ionic radii, which are 1.20 and $1.34 \text{ \AA}$, respectively. For $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ perovskites with $x \leq 0.5$, the lattice constants and volume decrease with rising x (**Table S1**). Moreover, with increasing Ba substitution, the Pb-I interaction is strengthened, with a shorter bond length (**Table S2**).²⁸ In addition, the framework is primarily determined by the Pb-I bonds with smaller tilting angles of $\angle \text{I-Pb-I}^{\text{equatorial}}$ and $\angle \text{I-Pb-I}^{\text{apical}}$ (**Table S2** and **Figure**

S2). In the case of $x \geq 0.5$, the Ba-I bonds with larger tilting angles of $\angle \text{I-Ba-I}$ strongly affect the tetragonal geometry, thus resulting in the enlarged perovskite lattices.

We calculated the formation enthalpy as

$$\Delta H(x) \approx H(\text{MABa}_x\text{Pb}_{1-x}\text{I}_3) - (1-x)H(\text{MAPbI}_3) - xH(\text{MABaI}_3) \quad (1)$$

where $H(\text{MABa}_x\text{Pb}_{1-x}\text{I}_3)$, $H(\text{MAPbI}_3)$ and $H(\text{MABaI}_3)$ refer to the formation energies of $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$, MAPbI_3 and MABaI_3 phases, respectively. The calculated results for the alloyed $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ perovskites are shown in **Figure 1**, which can fit quite well to the function $\Delta H = \Omega x(1-x)$, where $\Omega = 64$ meV is the interaction parameter. The positive value indicates that the strain energy, as a result of the ionic radius mismatch between Pb and Ba, plays the dominant role in determining the formation enthalpy. This behavior is similar to other conventional semiconductor alloys,²⁹ in which the formation energy is largely determined by the strain energy. The corresponding miscibility-gap temperature, T_{MG} , can be estimated from the regular solution model $T_{\text{MG}} = \Omega/2k_B$,²⁹ where k_B is the Boltzmann constant. This simple estimation yielded $T_{\text{MG}} \approx 372.2$ K, indicating that the low-temperature processing of alloyed $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ perovskites is feasible.

Figure 1. DFT-calculated formation enthalpy and the corresponding polynomial fitted curve. Insets: the corresponding 3D topographic images of $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ at different Ba concentration levels ($x = 0, 0.25, 0.5, 0.75$ and 1).

The low formation entropy and miscibility-gap temperature can be partially attributed to the strong ionic character of perovskites, where the Coulomb interactions lower the formation energy.³⁰ The electronegativity difference between Pb and Ba can induce an oxidation states difference (δ) between Pb and Ba,³¹ which can lower the formation energy in proportional to $\delta^2/(r_{\text{Pb}-r} + r_{\text{Ba}-r})^2$. The Coulomb energy gain of alloyed perovskites can be enhanced after the metal-iodine bonds of $r_{\text{Ba}-r}$ and $r_{\text{Pb}-r}$ are reduced. The modification of Coulomb energy is consistent with the structural variation of the alloyed perovskites (**Table S2**). The relative binding energy and bond dissociation energy calculation further suggest $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ perovskite alloys have higher cohesive energy than MaPbI_3 , and its degradation reaction is endothermic (**Table S3**).

We carried out comprehensive synthesis and X-ray diffraction (XRD) experiments on $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ films (detail is shown in **Figure S3**). The XRD patterns of as-grown samples and those after exposure to air for 3 and 15 days were collected and displayed in **Figure 2(a-d)**. Also shown are powder-type XRD patterns simulated based on the DFT-optimized geometries of $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$. Importantly, XRD peaks experimentally detected in the $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ films are consistent with the theoretically simulated result, indicating the high crystallinity and pure phase of the Pb-Ba alloyed perovskite films. Slight shifts of peak positions can be attributed to either lattice distortions of the as-synthesized $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ samples or the well-known overestimation of lattice constants by the standard DFT calculation method.^{11, 21} Furthermore, only a small number of the simulated XRD peaks appear in the experimental patterns, and particularly, the (110) and (111) peaks of the alloyed Ba-Pb perovskite films exhibit high intensities, suggesting the films are strongly textured. The height variation of the XRD peaks in **Figure 2** suggests that

the preferred orientations of the $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ films generally depend on the chemical composition.³²

Figure 2. XRD patterns collected for the as-grown samples and after exposure to air with a humidity level of 40% for 3 and 15 days. Theoretically simulated XRD patterns are also displayed for comparison. Note that the films are highly textured and only a small number of XRD peaks were observed.

The hydrolytic stability of perovskites is now considered as the major challenge in advancing their practical device applications.^{3, 33} Indeed, we observed that the MAPbI_3 sample underwent severe degradation and that the PbI_2 phase appeared shortly after the synthesis, thus suggesting its poor stability against ambient humidity (**Figure S4**). By contrast, the XRD patterns of the as-synthesized $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ films with $x = 0.5, 0.75$ and 1 and those of the films after 15 days of exposure to air with a humidity level of 40% exhibit nearly no change, thus indicating a significantly enhanced stability. Notably, the sample $\text{MABa}_{0.25}\text{Pb}_{0.75}\text{I}_3$, which had the highest Pb content among the $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ films, was less stable, as indicated by substantial changes in its XRD patterns collected during air exposure (**Figure 2(a)**). Furthermore, SEM and optical images

of the cation-alloyed perovskites thin films indicate negligible change of surface microstructures in air (**Figure S5**).

Figure 3(a-d) shows the $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ band structures with $x = 0.25, 0.50, 0.75$ and 1.0 . Notably, regardless of the Ba composition, the band structures possess direct bandgaps. Furthermore, the band edges of the highest occupied molecular orbital (HOMO) and lowest unoccupied MO (LUMO) became flatter with increasing Ba concentration, thus giving rise to significantly modified carrier effective masses (**Table S4**). Concurrently, the conduction band minimum (CBM) and valence band maximum (VBM) move from Γ to R , and finally back to Γ as a result of symmetry breaking (band folding). Compared with the band structure of MAPbI_3 (**Figure S6**), the bandgaps of the alloyed $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ exhibited a monotonic increase with Ba concentration because of the pronounced upshift of the CBM. The approximate bandgaps were 1.98, 3.08, 3.32 and 4.08 eV for $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ with $x = 0.25, 0.50, 0.75$ and 1 , respectively. This result agrees well with previous DFT predictions²¹ and hybridized functional calculations.³⁴ However, by taking into account the on-site Coulomb interaction for the p -electrons of alkaline-earth metal, Navas *et al.* reported an opposite trend of bandgap dependence.³⁵ Such theoretical treatment is still controversial for the p -orbital, and the choice of Hubbard U parameter is also rather problematic. In our case, the experimental results are in line with the calculation prediction. Particularly, the slight downshift of the VBM was consistent with the X-ray photoelectron spectroscopy (XPS) (**Figure S7**). This large bandgap tunability of the $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ perovskites, from 1.55 to 4.08 eV, makes them highly promising for optoelectronic applications in different wavelength regimes. The bandgap tunability of the alloyed Ba-Pb perovskites is much larger than that of the widely studied mixed-halide perovskites (**Figure S8**).³⁶

Figure 3. Band structures of the alloyed perovskite $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$. (a) $x = 0.25$, (b) $x = 0.50$, (c) $x = 0.75$, and (d) $x = 1$.

Figure 4. PDOS of the alloyed perovskite $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$: (a) $x = 0.25$, (b) $x = 0.5$, (c) $x = 0.75$, and (d) $x = 1$. The PDOS with negative binding energy corresponds to the valence band (VB), whereas the DOS located within the positive binding-energy region is the conduction band (CB). Partial charge distribution patterns of the alloyed perovskites are shown as insets.

To elucidate the band-structure modification, we calculated the atomic-orbital-projected density of states (PDOS) of the alloyed $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ perovskites. **Figure 4(a-d)** shows the

dominant PDOS near the band edges of $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ with $x = 0.25, 0.50, 0.75$ and 1.00 . The 2D charge density distribution contours of the VBM and CBM at high-symmetry Γ (or R)-points are also presented. 3D charge density distributions in real space are given in **Figures S9-S13**. The distinctive difference in the electronegativity between Ba and I made the valence band (VB) orbitals more ionic in nature, thus favoring the formation of ionic rather than covalent bonds.

These data indicate that the VBM of $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ originates mainly from the $5p$ orbital of I, with some hybridization with the $6s$ orbital of Pb. In the shallow conduction band (CB) region, the contribution of the Pb $6p$ orbital decreases with increasing Ba concentration, which is accompanied by reduced Pb-I bond length (**Table S2**) and stronger Pb-I chemical interaction in $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$. Then the reduced s - p coupling pushes the CBM to a higher level and leads to a larger bandgap.³⁷ With increasing Ba concentration, the contribution of the MA orbital to the valence band DOS becomes more significant, thereby leading to reinforced MA-I interaction and enlarged bandgap.³⁸

The enhanced chemical interactions between Pb-I, MA-I and Ba-I ion pairs in $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ are responsible for the improved stability of the alloyed perovskites. The system has mixed covalent and ionic characters. Ba has a significantly lower electronegativity than Pb and the Ba-I bond are known to be much stronger than those of the Pb-I bond due to its high ionicity, thus Coulomb interactions.³⁹ After the introduction of Ba in $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$, the higher electron concentration on the I sites also increases the Coulomb interaction of the Pb-I bonds. And then the enhanced chemical bonds, especially the stronger MA-I bond, are critical to keep the $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ perovskites away from the hydrolyzation under ambient humid conditions, since the reaction barrier for the decomposition of $\text{MABa}_x\text{Pb}_{1-x}\text{I}_3$ increases with rising Ba doping concentration (**Table 1**).⁴⁰

The Calculated DOS curves for the occupied and virtual orbitals become steeper with increasing Ba concentration (**Figure 5(a)**). Furthermore, the substitution of Pb by Ba causes a significant upshift of the CB edges with an increased DOS in the shallow CB regions. In particular, the DOS of pure MABaI₃ perovskite has the steepest VB and CB edges, and its DOS exhibit the largest upshift with respect to that of MAPbI₃. The Ba-concentration dependence of the band-edge energy dispersion of the alloyed MABa_xPb_{1-x}I₃ perovskites gives rise to a high tunability of the effective mass of carriers (**Table S4**). Consistent with a previous report,⁴¹ in pristine MAPbI₃, the hole effective mass (m_h^*) is greater than the electron mass (m_e^*). Interestingly, an opposite trend is predicted in the alloyed perovskites when x is greater than 0.50. In particular, a very small electron effective mass was derived for MABaI₃, indicating that it may be a potentially excellent n -type Pb-free semiconductor.²¹

As shown in **Figure 5(b)**, the optical transition is systematically tuned by varying the Ba concentration. Compared with the calculated absorption spectrum of pure MAPbI₃, the absorption spectrum of MABa_{0.25}Pb_{0.75}I₃ shows peaks at ~2.54 eV and ~3.05 eV in addition to the band-edge transition at ~1.92 eV. With increasing Ba concentration in the alloyed perovskites, the approximate absorption edges show a significant and monotonic blue shift. The absorption edge of pure MABaI₃ was calculated to be as high as ~4.08 eV. The plots of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) in **Figure 5(c)** obtained from the experimental results are consistent with the calculation. The measured UV-Vis absorption shows the predicted monotonic blue shift of the absorption edge with increasing Ba concentration. Such a behavior differs from the reported defect-dependent slight red shift of UV-Vis absorption spectra for MAPb_{1-x}Ba_xI₃ with x less than 0.1.^{19, 26} Absorption spectra of film samples after 15 days air-exposure shows negligible decay (**Figure S14**).

Figure 5. Electronic and optical properties of the alloyed perovskite MABa_xPb_{1-x}I₃. (a) Calculated DOS of MABa_xPb_{1-x}I₃. (b) and (c) represent the calculated photo absorption spectra and the experimentally measured UV-vis absorption spectra, respectively.

MABa_xPb_{1-x}I₃ films exhibit great advantages in terms of stability, but they show enlarged bandgap (~1.92 eV for MABa_{0.25}Pb_{0.75}I₃ and ~4.08 eV for MABaI₃), which compromises their role as light absorber in solar cells. In fact, 2-dimensional (2D) perovskites face the same dilemma: they show a great tolerance to moist environment, but they also possess large bandgaps and suffer from charge transport problems.^{33, 42} As a solution to the dilemma, 2D perovskites were deposited on MAPbI₃ as capping layers to improve device stability.⁴² Inspired by this report, we used MABa_xPb_{1-x}I₃ as a thin capping layer on the MAPbI₃ light absorbing layer. **Figure 6(a)** shows the cross-section image of the MAPbI₃ layer on c-TiO₂/FTO with a MABa_xPb_{1-x}I₃ capping layer. The nominal Ba-concentration in the MABa_xPb_{1-x}I₃ layer roughly 50% (details can be found in experimental section). The energy dispersive X-ray spectroscopy (EDX) mapping result confirms that a Ba-containing layer of MABa_xPb_{1-x}I₃ was casted on

MAPbI₃. As indicated in the XRD data (**Figure 6(b)**), the perovskite bilayer exhibits new diffraction peaks at 16.2° and 19.7°, which can be assigned to the (102) and (200) planes of Ba-Pb alloyed perovskite, respectively.

Figure 6. Cross-section image of the MAPbI₃ layer on c-TiO₂/FTO with MABa_xPb_{1-x}I₃ as the capping layer. The right side is EDX element mapping of Pb (red) and Ba (green). (b) XRD pattern of the MABa_xPb_{1-x}I₃-capped MAPbI₃ active layer, and the MABa_xPb_{1-x}I₃-related peaks are marked. (c) I-V curves of the devices using MAPbI₃ with and without MABa_xPb_{1-x}I₃ capping, where the key parameters of solar cells are also presented. (d) Stability test for 30 days of the devices under ambient atmosphere without sealing, ambient humidity is about 30%. (e) Statistics of the device performance. (f) Schematic of the energy diagram and charge transport in MABa_xPb_{1-x}I₃ capped MAPbI₃ solar cell.

The J-V curves of the solar cells were presented in **Figure 6(c)**. Solar cells with MAPbI₃ light absorber being capped with MABa_xPb_{1-x}I₃ exhibited obvious improvement of V_{OC} owing to the wider band gap of capping layer. The fill factor (FF) increases from 0.684 to 0.757, which can be attributed to improved charge transport and reduced interface recombination. Moreover, the device with MABa_xPb_{1-x}I₃ capping layer showed enhanced short-circuit current density J_{SC}. The

improvements of these key photovoltaic parameters result in a PCE of 18.9%, much higher than that (15.9%) of the pristine MAPbI₃ solar cell. This performance is also better than the device using MABa_{0.02}Pb_{0.98}I₃ as the light-absorbing layer.⁴³ Such perovskite multilayers with good lattice match and minimized strain enable high-performance optoelectronic devices.⁴⁴ Furthermore, thin interfacial layers of MABa_xPb_{1-x}I₃ reduce the recombination of photo carriers.⁴⁵ The 30-day stability test (**Figure 6(d)**) clearly indicates that the MABa_xPb_{1-x}I₃ capping layer effectively improves the durability of the device, and 86% of its initial efficiency was retained. The efficiency distribution of the solar cells (**Figure 6(e)**) suggests that the solar cells with Ba-Pb alloyed perovskite thin film as capping layer is highly reproducible. Furthermore, the electrochemical impedance spectroscopy (EIS) of perovskite solar cells under dark was measured for investigating recombination resistance. In **Figure S15**, the solar cell device with MABa_xPb_{1-x}I₃/MAPbI₃ double layer exhibits a larger resistance than the pristine MAPbI₃ device, indicating reduced interface recombination in MABa_xPb_{1-x}I₃-capped device.⁴⁶ **Figure 6(g)** illustrates the energy band alignment in the n-i-p solar cell. Here the band structure of MABa_xPb_{1-x}I₃ is illustrated in the capping layer. Because the CB of MABa_xPb_{1-x}I₃ is much higher than that of MAPbI₃, it can effectively block the back transport of electrons and reduce the charge recombination. Furthermore, the VB alignment of the ultra-thin layer does not degrade the hole transport between the active MAPbI₃ layer and the spiro-OMeTAD hole-transporting layer, which might be responsible for the improvement of incident photon to collected electron efficiency (**Figure S16**).

In summary, we showed that alloying Ba into MAPbI₃ perovskites is beneficial to the stability because of strengthened Pb-I, Ba-I and MA-I chemical bonds. The bandgap can be monotonically tailored in a wide window from 1.56 eV to 4.08 eV, owing to the smaller

electronegativity of Ba with respect to Pb. Perovskite solar cells with a MAPbI₃ active layer and a MABa_xPb_{1-x}I₃ capping layer exhibit a significantly improved PCE of 18.9% and long-term stability. Overall, our results provide a simple but reliable strategy for stabilizing the less-Pb perovskites with tailored physical properties.

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Supporting Information. Theoretical section: details of DFT calculations, complementary geometric information of optimized crystal structures, band structures, partial charge density distribution. Experimental section: XRD data, XPS patterns, sample synthesis and characterization.

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