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Perspective

The influence of strain on phase stability in mixed-halide perovskites

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SUMMARY

Lead halide perovskites are at the forefront of semiconductor research because of the tremendous efficiency increase of the corresponding devices together with low-cost fabrication. In sharp contrast with conventional semiconductors (e.g., silicon), they exhibit a soft and disordered lattice that directly affects their optoelectronic properties, making them particularly susceptible to strain. This perspective highlights the most common strategies to manipulate strain in lead halide perovskites at different length scales, focusing on how compressive and tensile strain affect ion migration and thereby undesired phase segregation in mixed-halide perovskites. We emphasize the role of the reduced unit cell volume and the polarizability of the lattice in the suppression of phase segregation. Finally, we highlight some of the most puzzling questions about the phase segregation mechanism, we propose targeted experiments for filling the gap in understanding, and we discuss the potential of using the apparent weaknesses of this class of materials (softness and phase segregation) as a strength.

INTRODUCTION

Nowadays, humanity's growing demand for energy mostly relies on fossil fuels such as oil, coal, and gas. Fossil fuels are responsible for almost three-quarters of the greenhouse gas emissions[1] from human activities that drive climate change, with dramatic consequences for the Earth's ecosystem. Solar energy is the most abundant renewable energy source, potentially able to supply most of the world's energy demand. To achieve the net zero by 2050, the annual capacity additions should be 630 GW of solar photovoltaics, 4 times the capacity additions achieved in 2020.[2] Therefore, the installation rate of solar energy capacity should significantly increase. This increase in installation rate can be achieved by increasing the solar cell efficiency.

Metal halide perovskites are arguably the most promising materials for increased solar cell efficiency. They offer outstanding properties and straightforward compositional tunability that make them a rare gem in the collection of semiconductors. For example, the material quality (e.g., measured by photoluminescence yield) can be as good as the best semiconductors we know, i.e., III–V materials; yet, in contrast to these III–V materials, perovskites can be made by cheap and easily scalable processing methods. A striking difference between lead halide perovskites and conventional semiconductors (e.g., silicon, III–V's) is the dual ionic-covalent bond nature[3] within the inorganic framework, whereas electrostatic interactions dominate between the inorganic framework and the monovalent cation.[4] This weaker bond nature, compared with the purely covalent bond of conventional semiconductors, results in the mechanically soft and dynamically disordered perovskite lattice whose alteration affects the optoelectronic properties and the stability of these solids.

CONTEXT & SCALE

The demand for energy is growing globally, and there is an urgent need to exploit the full potential of climate-neutral energy sources such as solar power to reduce greenhouse gas emissions and fight climate change. In this regard, lead halide perovskites emerge as an excellent candidate for highly efficient solar cells. However, these perovskites are unstable under continuous illumination where a process called ion migration occurs. Ion migration can cause phase instabilities, hampering the long-term performance of the corresponding devices and preventing commercialization. Thus, understanding the origin of and manipulating the ion migration in these materials are crucial for exploiting their full potential. Ion migration arises in part because of the soft nature of these semiconductors. At the same time, the softness leads to large strain under various conditions, which could provide a solution for stabilizing these perovskites. Yet, a complete picture of the role of strain on ion migration remains elusive. Unveiling the connection between the dynamically disordered perovskite lattice and the optoelectronic properties can provide concrete guidelines for compositional engineering toward a rational design of mixed-halide devices, where targeted

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Thus, metal halide perovskites are particularly sensitive to variations in composition, fabrication, and external stimuli that can induce strain in the material, extending their applications to straintronics where strain-induced physical effects can be used for developing next-generation memory devices, sensors, and energy-storage technologies.

strain engineering strategies can be used as fabrication routes to obtain phase-stable and band-gap-tunable materials.

In this perspective, we will first introduce the effect of strain on phase stability on the different length scales with a few examples, then we will focus on the phase segregation of mixed-halide perovskites from the atomic scale to nanoscale to macroscale. We highlight some of the missing information for a comprehensive picture of this phenomenon, and we propose targeted experiments that could potentially fill the gap in understanding. Finally, we make suggestions on how phase segregation can be used to develop technologies with new functionalities.

MULTILENGTH STRAIN AND ITS IMPACT ON THE STABILITY OF METAL HALIDE PEROVSKITES

Strain can be defined as the amount of deformation experienced by a body and can be categorized as normal (i.e., tensile and compressive strain) and shear strain.[5] Strain can change the perovskite at various length scales: atomic scale, nanoscale, and macroscale. For a more extensive classification of strain, we refer to the review by Liu et al.[6]

Strain at the atomic scale can originate from the misfit of the ion size into the perovskite structure, e.g., when the ion size fails to meet the requirements for satisfying the tolerance factor and the octahedral factor.[7] To accommodate the larger or smaller ion, the bond length and bond angle between the lead and halides within the inorganic framework $[PbX_6]^-$ have to reduce or increase, resulting in the formation of strain. Similarly, structural defects (e.g., vacancies, interstitial, and antisite occupations) can contribute to the formation of local strain and strain fields in the volume of crystal. Strain at the nanoscale is induced by light/bias stimulation, the presence of grain boundaries, and lattice mismatch at the interface between the perovskite and the substrate. Inhomogeneities in the perovskite elemental distribution[8] can result in perovskite domains with different lattice parameters building up additional strain within the film. Strain at the macroscale develops in the presence of external stress (e.g., pressure, temperature gradients) and mechanical deformation (i.e., bending stress due to a large load at a particular point), and it can arise during the fabrication process, e.g., during the cooling from the annealing process due to a mismatch of the coefficient of thermal expansion (CTE) between the perovskite and the substrate.[9] The implications of strain buildup on the stability of lead halide perovskites are numerous. For example, the instability of the pseudocubic α-$FAPbI_3$ phase has been attributed to its anisotropically strained lattice, where the high strain localized in the (111) plane acts as a driving force for the phase transition to the undesirable yellow non-perovskite δ-$FAPbI_3$ phase.[10] Alloying $FAPbI_3$ with MABr to reduce the lattice size and relax the strain,[10] growing $FAPbI_3$ on substrates with a tailored lattice parameter that can induce compressive strain,[11] and incorporating chloride-based additives have resulted in the stabilization of $FAPbI_3$ pseudocubic phase and suppressed defect formation.[12] Similarly, the high-temperature $CsPbI_3$ pseudocubic phase is metastable relative to its non-perovskite δ-$CsPbI_3$ at room temperature, hindering the application of this composition in photovoltaics. Growing the perovskite on a substrate with different CTE (also called substrate clamping) introduces anisotropic strain field at the interface between the perovskite and the substrate that energetically favors the pseudocubic phase, rendering this

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phase stable at room temperature.[13] Further discussions on the phase stability of such compositions can be found in more extensive reviews.[14]

Strain has a dramatic impact also on the performances of devices based on lead halide perovskites. Strain-free solar cells have demonstrated superior performance and stability with respect to strained devices.[8,15] Temperature-dependent photoluminescence combined with hyperspectral photoluminescence imaging of quasi-cross sections revealed the presence of a strain-induced gradient in the valence band of perovskite thin films, which is released over a layer thickness of about 300 nm.[15] On one hand, this band-gap gradient efficiently promotes carrier extraction but results, on the other hand, in an increased defect density. We refer to more extensive reviews[6,14,16] for the effects of strain on the performance and stability of photovoltaics devices.

The presence of defects in the perovskite lattice,[17–19] combined with the weak ionic bond nature, unlocks the possibility for ions to migrate within the lattice or to drift toward the electrode of reverse polarity in a device stack (e.g., solar cells or light-emitting diodes [LEDs]). This process, known as *ion migration*,[20] is observed in the presence of external stimuli such as exposure to light[21] and electrical bias,[22] and its strain-induced effects will be discussed in this perspective. Therefore, a profound understanding of strain in these materials is quintessential to support the efforts of strain engineering, which demonstrated to be a powerful tool to manipulate both the optical properties and the stability of the perovskite thin films.

MODEL TO DESCRIBE PHASE SEGREGATION IN MIXED-HALIDE PEROVSKITES

Ion migration has been identified as one of the main drivers for degradation[23–25] affecting the long-term stability of perovskite-based devices. Ion migration is observed both in single-halide and in mixed-halide compositions. Theoretical calculations and experimental observations reveal that the activation energy (E_a) for the ions to move is lower for the halide species, followed by the organic cation and the lead ions ($E_a(Pb^{2+}) \gg E_a(A^+) > E_a(X^-)$).[25,26] Thus, halide ions are the most mobile ions in the lattice.

Mixed-halide perovskites, e.g., $MAPb(Br_xI_{1-x})_3$ (with MA = methylammonium), are particularly interesting systems for applications that require band-gap tunability such as photocatalysts, LEDs, lasers, and tandem solar cells. For instance, mixing iodide and bromide in $MAPb(Br_xI_{1-x})_3$ results in any intermediate band gaps between the full iodide $MAPbI_3$ ($x = 0$, 1.6 eV) and full bromide $MAPbBr_3$ perovskites ($x = 1$, 2.3 eV).[27,28] As for the single-halide systems, the process of ion migration occurs also in the mixed-halide systems. However, when the bromide fraction in the composition is higher than 20% ($x > 0.20$), the halide migration within the perovskite lattice results in an additional instability that leads to the demixing of the halides into separate phases. This process, known as *phase segregation* and first reported by Hoke et al.,[21] consists of halide migration that then forms halide-enriched domains, disrupting the band-gap homogeneity of the initial mixed composition. As a result, domains exhibiting lower and higher band gaps are formed. Phase segregation has a dramatic impact on devices that rely on band-gap tunability, because the photogenerated charges transfer into the low-band-gap iodide-rich domains where they recombine (Figure 1A). Surprisingly, phase segregation is a reversible process, where the original band gap is recovered in the dark even after many illumination cycles (Figure 1B).

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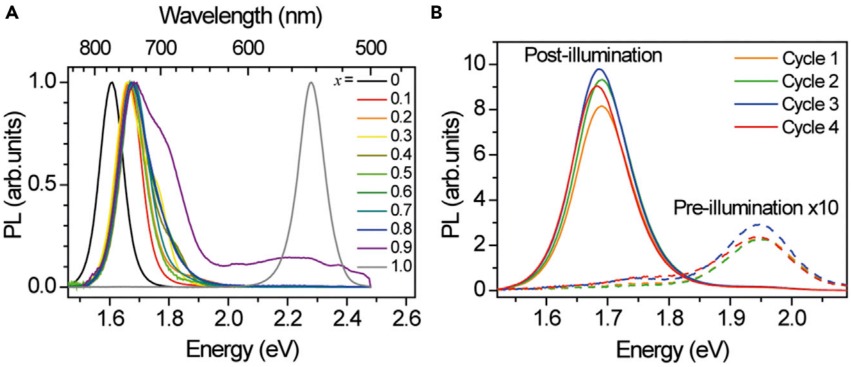

Figure 1. Phase segregation in mixed-halide perovskites

(A) Normalized PL spectra of $MAPb(Br_xI_{1-x})_3$ thin films after illuminating for 5–10 min with 10–100 mW/cm^2 with 457 nm light.

(B) PL spectra of thin film with $x = 0.6$ after sequential cycles of illumination (solid lines) for 2 min (457 nm, 15 mW/cm^2) followed by 5 min in the dark (dashed lines). Reproduced from Hoke et al.[21] with permission from the Royal Society of Chemistry.

Reducing the ion migration would be beneficial for both single-halide and mixed-halide perovskites. The driving force of the light-induced phase segregation is still heavily under debate, and the proposed models to describe the process are discussed extensively in the review by Brennan et al.[29] These models can be categorized into three groups. The first group of models suggest that the phase segregation originates from trapped charges attracting the ion by Coulombic force. Thus, a reduction of this phenomenon could be achieved by increasing the activation energy of halide migration or reducing the concentration of the mobile ions. Both would lead to slower ion migration, also called *kinetic stabilization*.[30–32]

The second group of models have a purely thermodynamics foundation, pointing to composition or band-gap differences as the origin of the demixing.[33] Thus, one could also engineer the material such that the thermodynamically most stable state is the mixed-halide crystal (rather than the phase-segregated one). This so-called *thermodynamic stabilization*[34] of the mixing ratio would relax the requirements for the kinetic stabilization. The accessible solubility range for a solid solution such as $MAPb(Br_xI_{1-x})_3$ perovskite is determined by the free energy of mixing ΔG_{mix}:

$$\Delta G_{mix}(x) = \Delta H_{mix}(x) - T\Delta S_{mix}(x)$$

where ΔH_{mix} is the enthalpy of mixing, T is the temperature in kelvin, and ΔS_{mix} is the entropy of mixing. The lower the ΔG_{mix} for a mixing ratio x, the higher is the stability of the mixed phase with respect to the segregated iodide and bromide phases. Upon increasing the temperature, a suppression of phase segregation[35] but also a faster recovery rate of the original mixed phase[36] were both observed. The effect of temperature is associated to the increase in the entropic term ($T\Delta S_{mix}$), leading to a higher thermodynamic stability of the mixed phase composition.[30] An additional lever to manipulate the Gibbs free energy of mixing is the enthalpic term, ΔH_{mix}, which is associated with strain in the perovskite. First-principles calculations of mixed $MAPb(Br_xI_{1-x})_3$ perovskite report a positive enthalpic term $\Delta H_{mix}(x = 0.5) \sim 2$ kJ/mol due to chemical strain associated to the difference in the lattice parameters of the bromide and iodide domains.[37]

In the third group of models, phase segregation is *intrinsic*, and strain-induced polaron formation (i.e., lattice distortion induced after photoexcitation) is invoked as the driving force for phase segregation.[38,39] These polarons directly relate to

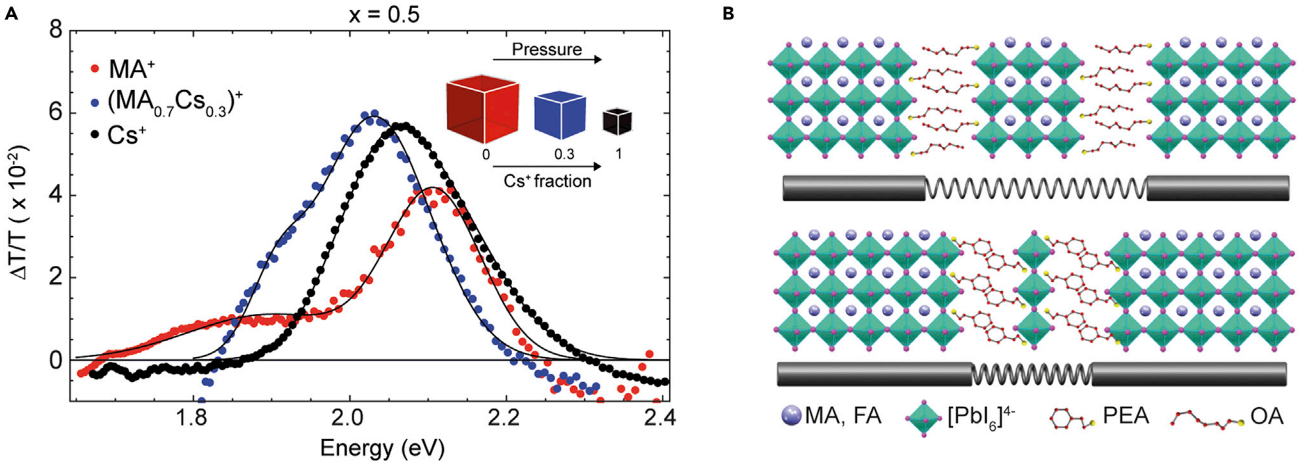

Figure 2. Compositional engineering and low-dimensional/3D interfaces to prevent phase segregation

(A) $\Delta T/T$ traces after 20 min of light soaking of composition $(MA_yCs_{1-y})Pb(I_xBr_{1-x})_3$ with $x = 0.5$ where the cation MA^+ (red trace) is partially (blue trace) or fully replaced by Cs^+ (black trace), adapted from Hutter et al.[34] Inset: a schematic depicting the similitude between the reduction in the unit cell volume obtained by applying external pressure and by replacing the large MA^+ cation with the small Cs^+.

(B) Schematic of the residual stress relaxation of 3D lead halide perovskites with soft and stiff structural subunits of layered 2D perovskites grown at the surface. Reprinted from Wang et al.[43]

the local strain in the lattice, and engineering stiffer lattice or strategies to screen the charge would reduce the phase segregation.

To reduce the effect of phase segregation, we should urgently invest in understanding its reversibility and unveil how strain plays a role in its mechanism at each length scale. If ion migration can be prevented or mitigated, these perovskite-based devices will become more stable and are hence likely to outperform traditional semiconductor devices in many applications. Additionally, a thorough understanding of how to manipulate at our will the magnitude, the timescale, and the conditions at which the phase segregation and recovery occur would be a powerful tool to design smart materials with new functionalities.

Understanding phase segregation at the atomic scale

At the atomic scale, strain and the crystal structure are inherently coupled, and so is the composition. Hence, compositional engineering strategies that involve the mixing of different cations have been adopted to suppress the phase segregation in mixed-halide perovskites, yet aiming to retain the original band gap of the MA-based composition and prevent phase segregation.[32,34,38] For instance, replacing MA^+ or formamidinium (FA^+)[40] with Cs^+ reduces the unit cell volume and decreases the local strain gradient induced by the incorporation of the larger organic cation in the perovskite structure, thus suppressing the phase segregation (Figure 2A). The reduction of the lattice parameter, induced by the incorporation of Cs^+, and physical compression of the lattice have a similar effect on the phase segregation process, as described later in this perspective.[39] However, Cs-based mixed-halide compositions still exhibit phase segregation,[9] and triple-cation $(FA^+/MA^+/Cs^+)$ compositions require much higher photon doses and longer time for halide redistribution than those needed in single- or double-cation mixed-halide perovskites.[41,42] Systematic studies on the extent of phase segregation as a function of the contracted unit cell volume upon incorporation of both MA^+ and Cs^+ in FA^+-based compositions are still lacking. Quantitative assessment of strain at the atomic scale for mixed-cation compositions is of importance to determine the ideal volume for a stable unit cell and how changes in bond length and angles affect the

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activation energy for halides to migrate. For this purpose, we propose that combining *in situ* single-crystal X-ray diffraction and absorption measurements during illumination could be a powerful approach to quantify halide migration as a function of the varying structural parameters.

Changing the mixing ratio of cations leads to differences in crystallization,[42] which in turn affects the formation of defects, a source of strain within the film. Thus, a direct comparison based only on the unit cell volume cannot be made. Recently, it was proposed that two different mechanisms of phase segregation occur in single- and multi-cation compositions, likely due to a difference in crystallinity.[44] In the MA^+-based composition, the presence of fast ionic pathways initially results in the halide segregation into small local volumes of material, which later grow at the expense of the well-mixed bulk phase whose composition remains unchanged under illumination. On the other hand, FA–Cs mixed-cation compositions lack these fast ionic pathways because the phase segregation mechanism consists of an initial segregation of the A-site cations, which enriches the bulk perovskite in either FA^+ or Cs^+, thus reducing the stability of the perovskite.

Strategies for manipulating the strain at the atomic scale are not limited to alloying A-site cations. When chloride is present in the $[PbX_6]^-$ framework in Br/I mixed compositions, the phase segregation is suppressed,[45] and the activation energy and intensity threshold for phase segregation significantly increases,[46] even at small Cl^- concentrations.[47] The suppressed phase segregation has been attributed to the enhanced lattice rigidity and higher formation energy of the inorganic framework bonds. Passivation of structural defects that reduces the local strain and decreases the phase segregation kinetics has been achieved by using chemical additives such as trioctylphosphine oxide, chloride-, bromide-, and iodide salts.[48] However, the incorporation of such additives during the fabrication process alters the perovskite crystallization and the nature of the grain boundaries, thus resulting in an effective but complex method to reduce phase segregation, where it is not possible to control one parameter at the time.

We suggest ball milling as an alternative fabrication method to achieve better control over the synthesis. This solid-state technique is still largely underexplored in the perovskite community. Ball milling consists of a vigorously shaken vessel, containing stainless steel balls, that allows for solvent-free synthesis at room temperature. The collisions of the raw materials with the walls of the vessel and stainless steel balls allow for the transfer of energy to the raw materials, intensifying the diffusion of atoms and reducing the operational temperature usually required during the annealing process. The resulting powder can be pressed to be used as a target for dry techniques such as physical vapor deposition (PVD) and pulsed laser deposition (PLD), which allows for a near-stoichiometric transfer of multi-cations and a finer control of the film growth. In addition, varying the ball milling parameters (e.g., time and frequency of the collisions) could be used to modulate the relative portion of antisite defects and vacancies in perovskite, as previously shown in $Bi_2(Se,Te)_3$,[49] without the need for chemical additives. Thus, the ball milling approach could be potentially used to investigate the phase segregation as a function of antisite defects and vacancies.

A separate class of additives, long organic molecules most often with one or two ammonium groups, can be employed to form layered 2D perovskites. The layered 2D perovskites can be incorporated into a 3D film to manage the strain on the atomic scale. Wang et al.[43] demonstrated that post-processing deposition of phenetylammonium iodide or octylammonium iodide on $FA_{0.85}MA_{0.15}Pb(Br_{0.85}I_{0.15})_3$ results in the formation of low-dimensional layered 2D perovskite accompanied by a decrease in the residual strain,

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an extended stability, and enhanced photovoltaic performance of the devices. The more flexible octylammonium molecule has a larger impact in the strain relaxation compared with the stiffer benzene ring of the phenetylammonium. We believe that the same approach to release additional strain in the thin film could be applied to mixed-halide perovskites with $x > 0.20$ to achieve stability against phase segregation. The structural flexibility offered by the organic spacer in layered 2D perovskites for tuning their mechanical properties and rigidity seems to play a key role in preventing lattice distortion by creating structural subunits at the mixed-halide perovskites surface where the strain can be accommodated by the flexible organic spacer[43,50] (Figure 2B). However, little is known about the impact of their crystallization at the 2D/3D interface and how the spacer packing affects such strain release. In addition, the impact of the simultaneous formation of several 2D phases (n = 1, 2, 3, …) on the mechanical properties of the resulting thin films is yet to be addressed. Heterojunctions built by 1D perovskitoids[51] and 3D perovskites have also been used to suppress the ion migration. The introduction of 1D perovskitoid structures provides a stiffer lattice with enhanced ionic bonds and releases residual tensile strain in thin films, resulting in extended phase stability of perovskite-based devices under operational conditions.[52–54]

UNDERSTANDING PHASE SEGREGATION AT THE NANOSCALE

Continuous light illumination has been widely recognized as one of the main initiators of phase segregation. According to the polaron-based theory, light-induced lattice polarization (polarons) is responsible for generating strain within the lattice. Polarons form due to displacements of the atoms in the perovskite lattice in the presence of photogenerated charge carriers (Figure 3A). A combination of femtosecond diffuse X-ray scattering measurements and modeling suggests the formation of nanoscale structural distortions upon charge carrier injection, consistent with expansive-type (i.e., tensile) strain.[55] Polarons reach their maximum size in a few tens of picoseconds, decaying on the timescale of hundreds of picoseconds after a short excitation pulse. Under continuous illumination, a steady-state density of photogenerated charges forms. The strong electron-phonon interaction in the perovskite lattice can result in the formation of a polaron population, which locally changes the free energy of mixing of the mixed-halide composition by inducing the local gradient of strain that in turn favors the halide demixing. Bischak et al.[38,39] propose that spontaneous stochastic fluctuations of iodide-rich clusters (Figure 3B) cause trapping of the polarons formed due to the polarizability of the perovskite lattice. Thus, the trapped polarons stabilize some of the iodide clusters promoting the accumulation of more iodide ions. Despite the large fraction of bromide in the composition, bromide clustering and their polaron-induced stabilization are not observed.[38] Shedding light on the role of the bromide is a missing part of the phase segregation puzzle. Why are polarons causing only iodide clustering? Is this effect related to the polarizability of the lattice, which is higher for larger iodide fraction? Would strain be distributed over a large volume of the lattice for large iodide concentrations? Are the polarons also trapped at bromide clusters and therefore not observable via the common photoluminescence-based technique? Is the activation energy for the remixing associated with the destabilization of the polarons?

Reducing the polarizability of the lattice would be reflected in a weaker electron-phonon coupling, which has a direct consequence for the extent of polaron formation, and thus for phase segregation. The correlation between the electron-phonon coupling and the extent of phase segregation as a function of temperature reveals that decreasing the electron-phonon coupling effectively reduces the phase segregation, even at room temperature. Reducing the unit cell volume is a proposed strategy to relax bulk strain. In this case, the polarons would distribute across a larger

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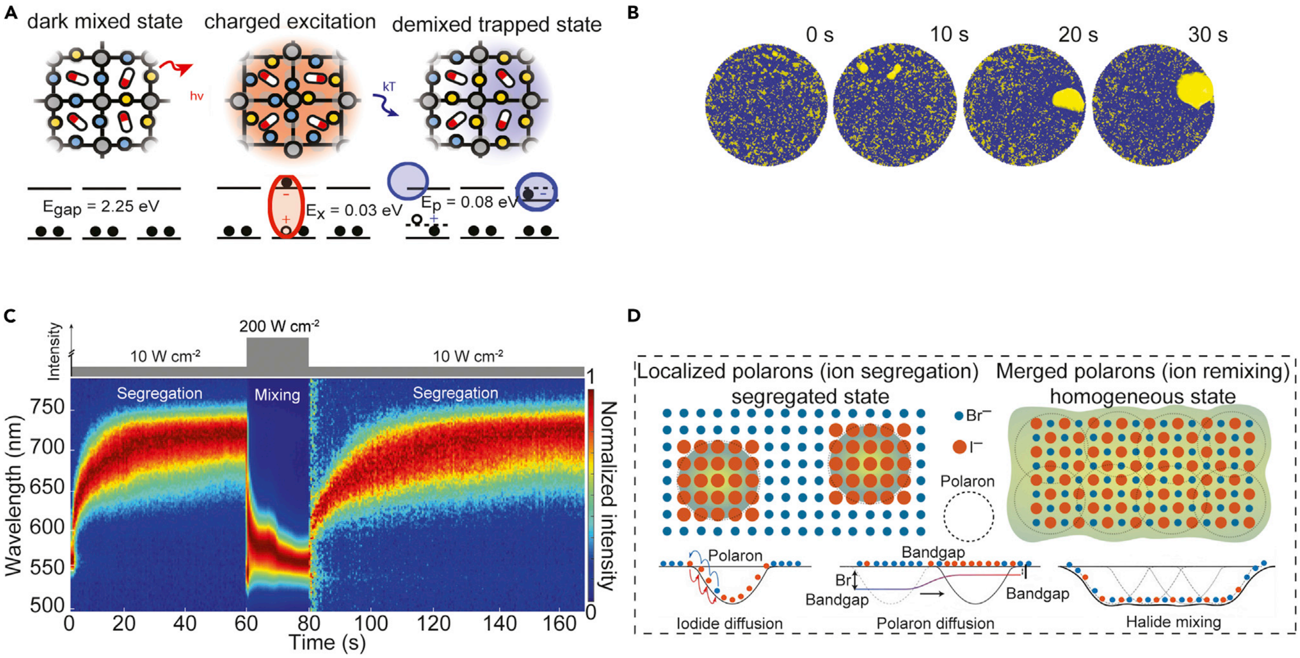

Figure 3. Manipulations of polaron-induced local strain as lever to control and revert phase segregation

(A) Schematic representation of the photoinduced polaron trapping associated with the phase segregation. The gray circles represent the lead ions; the blue and yellow circles represent the bromide and iodide, respectively; and the red and white obround represents methylammonium.

(B) A series of snapshots from a cluster formation simulation of a 100 nm region with iodide-rich regions in yellow and bromide-rich regions in blue. (A and B) Reprinted from Bischak et al.[39] 2017 American Chemical Society.

(C) Normalized photoluminescence spectra of single-crystal microplatelet $MAPb(Br_{0.8}I_{0.2})_3$ illuminated at low excitation intensity (10 W cm^{-2}) resulting in the formation of iodide-rich domains, followed by high intensity (200 W cm^{-2}) excitation that promotes halide remixing, and excited at low intensity (10 W cm^{-2}) to induce again phase segregation.

(D) Schematic representation of the three driving forces of phase segregation as proposed by Mao et al.,[56] which include the diffusion of iodide along polaron strain gradients, polaron diffusion along iodide concentration gradients, and halide mixing in the absence of strong strain gradients. (C and D) Reprinted from Mao et al.[56]

number of unit cells, reducing the gradient of strain. This hypothesis is corroborated by Mao et al.[56] who suggest a strategy to promote homogeneous distribution of the local strain within the lattice by increasing the input carrier density. At low and intermediate carrier density, the presence of the local strain due to polarons promotes the phase segregation. However, at high carrier density, where the polarons overlap, the lattice is uniformly deformed and the strain gradient driving the phase segregation disappears, hence promoting the halide remixing (Figure 3C). Their model consists of three driving forces (Figure 3D): first, a force that locally attracts the iodide toward the polarons formed due to the local strain generated upon photoexcitation; second, the generated iodide clusters attract the carriers/polarons to populate and stabilize those clusters due to the smaller band gap; and third, a force that drives the homogeneous remixing of halides when the gradient in local strain is absent.

The original band gap exhibited by the mixed phase is recovered in the dark, suggesting that the phase segregation process is not favored in the absence of light. This is consistent with the absence of a steady-state population of trapped polarons in the dark, thus preventing the stabilization of the iodide clustering. To probe the model, we suggest employing spatially resolved impulsive vibrational spectroscopy, a time-domain Raman technique, combined with nano X-ray fluorescence (nano-XRF). This approach can simultaneously reveal vibrational modes of mixed-halide perovskites and probe the structural rearrangement of the inorganic cage upon photoexcitation while probing

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the composition associated to the strained regions where the polarons form. In addition, the effect of light intensity along the thin film thickness direction should be investigated as well. An inhomogeneous distribution of halides throughout the depth of the film might locally affect the formation of the polarons. To address this additional complexity resulting from the solution-processed film formation, the activation energy for halide migration could be investigated in thin films obtained via PLD, where the elemental distribution through the depth of the film can be more carefully controlled.

With the current understanding, it is puzzling that the phase segregation occurs only for mixing ratios from $x > 0.20$ (systems enriched in bromide). They are, according to their bulk moduli, stiffer in comparison with their iodide counterpart. Here, the polaron theory that attributes the stabilization of polarons in iodide domains to local strain seems counterintuitive. Introducing more bromide into the composition would make the lattice stiffer, which should reduce the polarizability. We speculate that the presence of more bromide induces the formation of a larger strain gradient because of the formation of more localized polarons on the iodide sites. Macroscale strain (see below) may further explain the increase of phase segregation with higher bromide ratios.

Both the reduction of electron-phonon coupling and reduction of unit cell volume can be achieved by altering the chemical composition of the perovskite (i.e., replacing MA^+ ions with Cs^+ ions). When MA^+ ions are replaced by Cs^+, the polarizability of the lattice is reduced. Thus, the interaction between the injected charge carriers and the ionic lattice is lower. Even though fluctuations of higher iodide concentration are still present within the perovskite film, the local strain gradient produced by polaron formation may be insufficiently strong to locally favor the phase segregation. We note again that a change in the composition does not only affect the strain at the atomic scale but also at the nano- and even macroscale.

UNDERSTANDING PHASE SEGREGATION AT THE MACROSCALE

At the macroscale, mechanical deformations can arise through different mechanisms, e.g., from bending and twisting of thin films on flexible substrates, from crystallization of the perovskite on a substrate of different CTE, or by external pressure. Mechanical deformations (i.e., bending stress) of thin films in a concave shape reduce the residual strain in the films, which increases the activation energy in the dark and in the light for ion migration in single-halide compositions.[57] Thus, it is expected that mechanical deformation in a concave or convex shape would play a role in mixed-halide compositions as well.

Pressure-dependent transient absorption spectroscopy (Figure 4A) studies reveal that the isotropic compression of the unit cell volume of $MAPb(Br_{0.5}I_{0.5})_3$ and other bromide-iodide mixing ratios affect both the thermodynamics[34] and the kinetics[32] of the phase segregation. Increasing pressure from ambient to 0.3 GPa, the composition of the halide-rich phases in $MAPb(Br_xI_{1-x})_3$, after illumination is closer to the original mixing ratio, suggesting a suppression mechanism of the phase segregation (Figure 4B). In addition, the formation rates of halide-rich phases reduce by two orders of magnitude, from 10^{-1} to 10^{-3} s^{-1}.[32] The origin of the suppression of the phase segregation under pressure can be found in the alteration of the $P\Delta V$ term embedded in the enthalpic ΔH_{mix} term of the Gibbs free energy. The positive enthalpic term that originates from the ionic size mismatch of iodide (2.22 Å) and bromide (1.96 Å) is reduced due the different bulk modulus exhibited by the iodide (9 GPa for $MAPbI_3$) and bromide (18 GPa for $MAPbBr_3$) compositions. The iodide-rich regions undergo larger volume change and pay a larger enthalpic penalty, which

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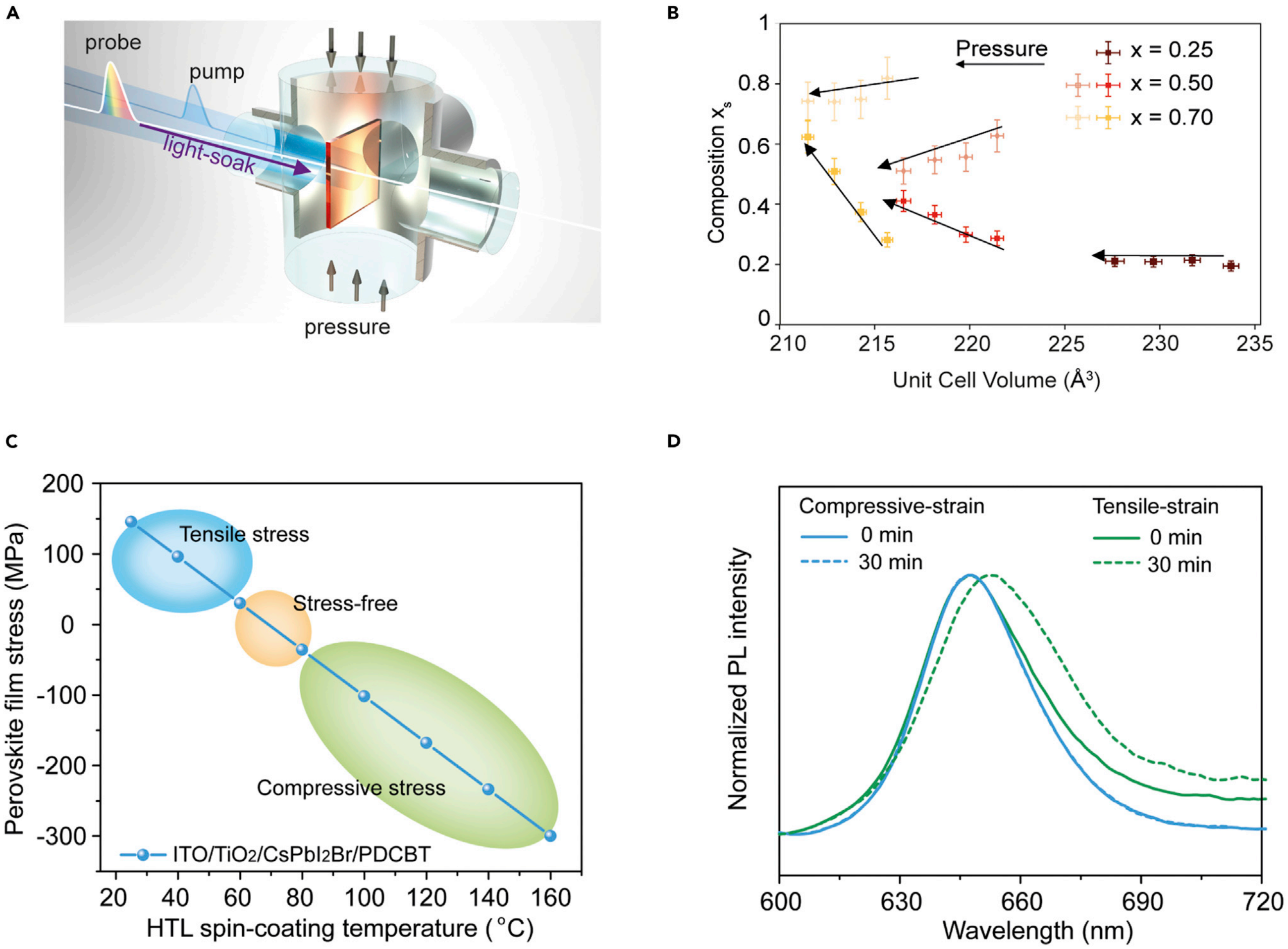

Figure 4. Strain management at the perovskite interface and physical compression suppresses phase segregation

(A) Schematic representation of the pressure-dependent transient absorption spectroscopy setup used to evaluate phase segregation upon increasing isotropic compressive strain, reprinted from Hutter et al.[34]

(B) Bromide fraction (x_s) and corresponding error bars in the low-band-gap (I-rich) and high-band-gap (Br-rich) phases of $MAPb(Br_xI_{1-x})_3$ after segregation, plotted against initial (average) unit cell volume, adapted from Hutter et al.[34] The compression of the unit cell volume is obtained by applying external physical pressure.

(C and D) (C) The calculated net average stress in an $ITO/TiO_2/CsPbI_2Br/PDCBT$ structure as a function of the HTL (PDCBT) processing temperature, reprinted from Xue et al.[9] and the corresponding (D) photoluminescence spectra under illumination for 0 and 30 min in the presence of tensile strain and after compensating with compressive strain, reprinted from Xue et al.[9]

will lower the microscopic strain of the mixed system. Thus, the $T\Delta S_{mix}$ term can dominate at high pressure, extending the range of thermodynamically stable mixed-halide compositions. Therefore, external pressure has demonstrated to be an effective tool to understand the fundamentals of strain manipulation in perovskite thin films to control phase segregation. Whereas the effect of strain at the macroscale clearly affects the phase segregation rate and the stability of the mixed-halide compositions, studies on the effect of such strain on the recovery of phase segregation are still underrepresented. Further investigations on the recovery would make it possible to infer whether pressure impacts mainly the activation barrier for halides to migrate or the energy levels of the initial mixed state and final segregated phase.

Obviously, applying large external pressure is impractical in real devices. A similar strain compensation to manipulate the phase segregation can be achieved via ad hoc

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fabrication strategies. Stress σ can be "baked-in" during fabrication[58] using the thermal expansion of the perovskite and the substrate according to the following formula

$$\sigma_{\Delta T} = \frac{B_p}{1 - \nu_p} (\alpha_s - \alpha_p)\Delta T$$

where B_p is the bulk modulus of the perovskite; ν_p is Poisson's ratio in the perovskite; α_s and α_p are the CTE of the substrate and the perovskite, respectively; and ΔT is the temperature difference during cooling from the annealing temperature of the film to room temperature. B_p is used when the compression of the perovskite is isotropic, whereas the Young's modulus E_p can be used if the stress response of the perovskite is anisotropic, e.g., in layered 2D perovskites where the out-of-plane direction is more sensitive to stress. The CTE of perovskite is an order of magnitude larger than that of common substrates such as indium tin oxide (ITO) and quartz. If $\alpha_s < \alpha_p$, the expansion of the perovskite film at a certain annealing temperature is larger compared with the substrate. Thus, upon cooling to room temperature, the perovskite would contract more than the substrate. Therefore, the perovskite will endure tensile strain along the in-plane direction and a compressive strain along the out-of-plane direction. In addition to the CTE, the presence of a temperature gradient within the thickness of the film may induce a different volume shrinkage during the cooling and a strain gradient within the film.

To compensate the tensile strain gradient in the film, several approaches have been proposed. Zhu et al.[8] suggest providing an inverse temperature gradient by flipping the sample during the annealing process, which successfully led to a reduced tensile strain within the film thickness. Xue et al.[9] propose a strain-management approach to compensate the tensile stress induced during the fabrication with the aid of a layer with higher CTE, compared with the perovskite film, able to induce external compressive strain. When annealing the perovskite film deposited on TiO_2 (used as electron-transport layer [ETL]) at several different temperatures, the difference in CTE between the perovskite and the ETL will result in a different extent of residual tensile strain in the film upon cooling. This tensile strain can be compensated by coating a layer with larger CTE than the perovskite on top, e.g., poly[5,5-bis(2-butyloctyl)-(2,2- bithiophene)-4,4′-dicarboxylate-alt-5,5′-2,2′-bithiophene (PDCBT, used as hole-transport layer [HTL]). The annealing of this layer will result in a compressive strain that can offset the residual tensile strain induced by the TiO_2. Three regimes have been found and are shown in Figure 4C. At a low HTL processing temperature (20°C–60°C), the tensile stress induced by the CTE mismatch between the ETL and the perovskite film is dominating. At a high HTL processing temperature (80°C–160°C), the compressive strain induced by the HTL layer dominates. If the HTL is processed at an intermediate temperature (60°C–80°C), the HTL can fully compensate the tensile strain induced by the ETL, leading to a strain-free regime. We note here that the strain compensation depends on the properties of the perovskite, HTL and ETL, and the processing temperature.

The compensation of tensile strain with external compressive strain exerted by the HTL layer has a similar effect as physically compressing the perovskite film. $CsPb(I_{0.5}Br_{0.5})_3$ films with excess tensile strain show a redshift of the emission peak after 30 min of continuous illumination, indicative of the formation of iodide-rich domains and thus phase segregation. Phase segregation is suppressed when the tensile strain is compensated by compressive strain. Thus, strain management, achieved by the presence of the HTL layer, suppresses phase segregation, and the compressively strained film showed no change of PL peak position (Figure 4D). DFT calculations for the vacancy-assisted

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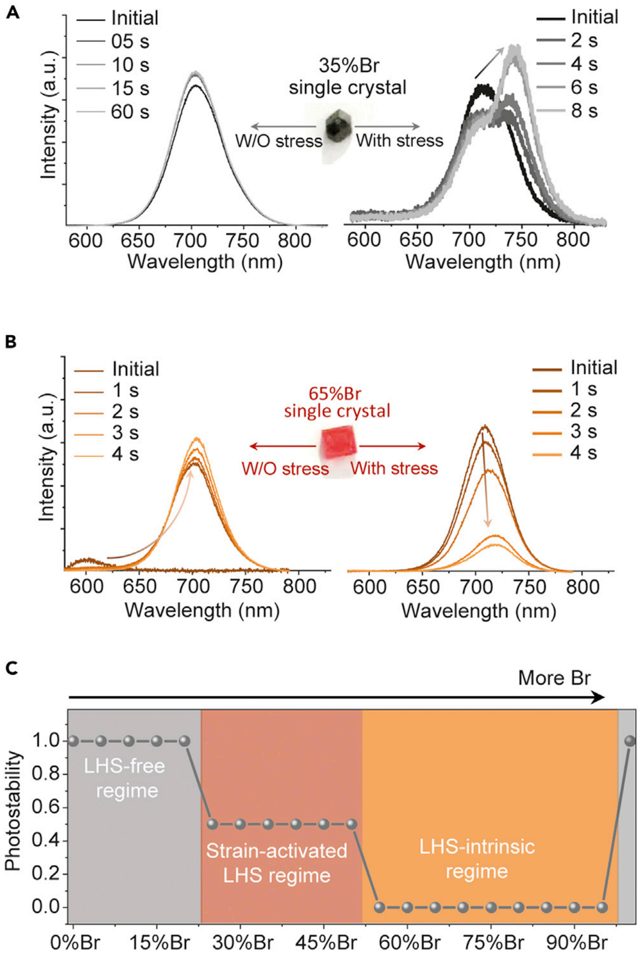

Figure 5. Three regimes of phase segregation: free, strain-activated, and intrinsic

(A and B) (A) *In situ* photoluminescence of single crystals with 35% and (B) 65% bromide concentration with no stress applied and with tensile uniaxial stress applied, adapted from Zhao et al.[59]

(C) Schematic representation of the three regimes suggested for light-induced phase segregation as a function of the bromide fraction, adapted from Zhao et al.[59]

migration of halide ions corroborate the expected increase in the activation energy for the migration of the halide species in compressed films, compared with the activation energy found under biaxial strain.[9]

Zhao et al.[59] report similar findings on strain-activated phase segregation in single crystals containing 35% bromide. While single crystals under continuous illumination do not show phase segregation, the application of tensile stress (i.e., mechanical deformation) in the in-plane direction, and thus compression in the out-of-plane direction, leads to the formation of iodide-rich domains (Figure 5A). By contrast, single crystals containing 65% bromide suffer already from intrinsic light-induced phase segregation (Figure 5B), even with no stress applied. Applied tensile strain further redshifts the photoluminescence, implying that strain also influences the final segregation product. The authors propose the presence of three regimes for light-induced phase segregation (Figure 5C) for $MAPb(Br_xI_{1-x})_3$, depending on the bromide concentration: below 20% bromide concentration ($x < 0.2$), the composition does not suffer from light-induced phase segregation; between 20% and 50% bromide concentration ($0.2 < x < 0.5$), phase segregation is a

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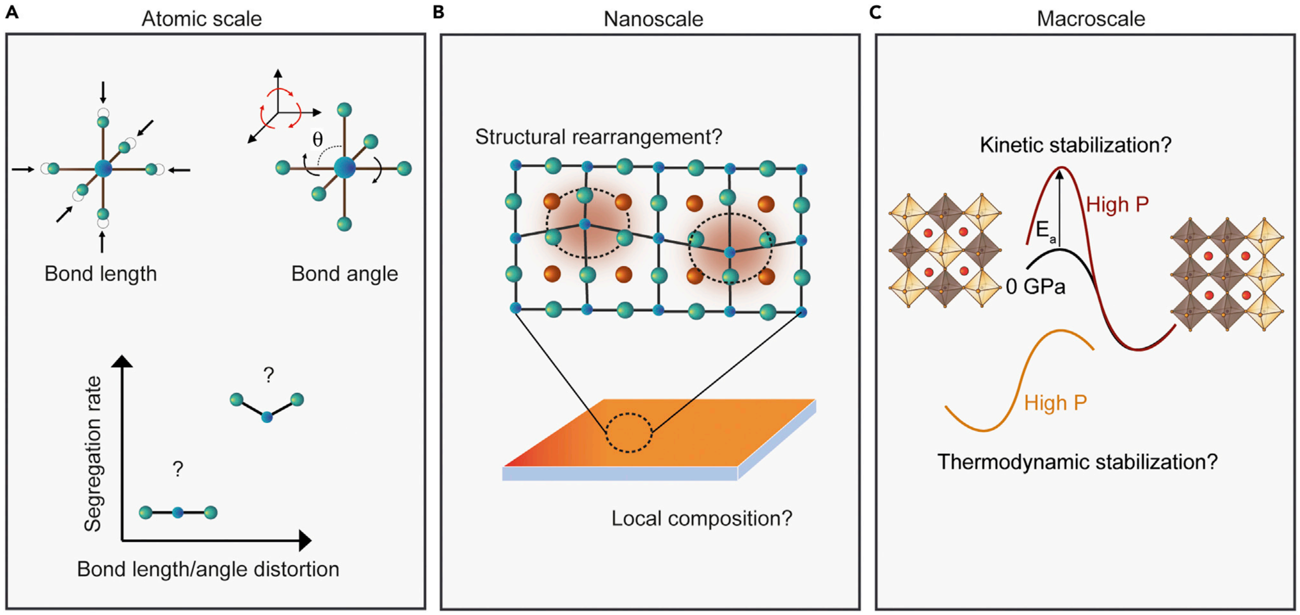

Figure 6. Tracing the path toward a deeper understanding of strain-induced phase segregation

(A) At the atomic scale, bond length and angle distortions due to smaller/larger ions at the A-site result in strain. Combining single-crystal X-ray diffraction and absorption measurements during illumination can be used to quantify halide migration as a function of the varying structural parameters, e.g., Pb–X and X–Pb–X bond length and angles (lead in blue and halides in green).

(B) At the nanoscale, light-induced polaron formation is one of the sources of strain. Spatially resolved impulsive vibrational spectroscopy combined with nano X-ray fluorescence (nano-XRF) could probe the structural rearrangement of the inorganic cage upon photoexcitation while probing the composition associated to the strained regions where the polarons form. The lead is in blue, halides in green, and the A-site cation in red.

(C) Strain at the macroscale can arise from processing and from bending and twisting the substrate. External pressure can also be used to induce strain at the macroscale. Pressure-dependent studies on the recovery will make it possible to infer whether the pressure impacts the activation barrier for halides to migrate or the energy levels of the initial mixed state and final segregated phase. Yellow and brown octahedra are perovskite unit cells enriched in bromide and iodide, respectively.

strain-activated process; and above 50% bromide concentration ($x > 0.5$), phase segregation is an intrinsic process and strain only enhances it. Investigations on polycrystalline thin films with similar compositions reveal that phase segregation is more pronounced at the grain boundaries for the strain-activated phase segregation compositions, whereas for the compositions exhibiting intrinsic phase segregation, the phase instability is shown both in the center of the grain and at the boundaries. Thus, passivation strategies of polycrystalline thin films can only reduce the phase segregation in compositions exhibiting strain-activated phase segregation. Most of the studied compositions fall in the intrinsic phase segregation range identified by Zhao et al.,[59] with bromide content well above 50% of the total composition. It would be of great interest to explore single crystals of compositions that fall in the strain-activated regime and their phase instability.

FINDING THE MISSING PIECES OF THE PHASE SEGREGATION PUZZLE

So far, the observations reported on the effect of strain on the phase segregation point toward a synergic effect of the stress induced at a variety of length scales, from the atomic to the macro level.

In this perspective, we highlighted the source of strain that might trigger the phase instability typical of mixed-halide perovskites. Several models and approaches have been proposed to unify the theory of phase segregation and how to manipulate the process. However, a complete picture of how each strain contribution affects the mechanism inducing the phase segregation is still missing.

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In this context, multimodal techniques, which are able to correlate local structural deformation and local optical properties of iodide- and bromide-rich domains, would provide significant insights for deciphering the complicated strain-induced effects on phase segregation in mixed-halide perovskites. In Figure 6, we suggest a guideline for strain-related investigations needed for advancing in the understanding of the effect of strain on the phase segregation at the atomic scale, nanoscale, and macroscale.

Although the light-induced phase instability is a detrimental process for many devices that rely on the band-gap tunability of mixed-halide perovskites, the possibility to perform write-erase operations, as demonstrated by Mao et al.,[56] opens the application areas to optical switching and memory applications.[60–63] In addition, light management of the emissive iodide- and bromide-rich domains could be useful also in photocatalysis applications where targeted chemical reactions could be performed in spatially confined region of the same perovskite film used as a photocatalyst. Careful control (in time and magnitude) of the formation and the recovery of such halide-rich domains would open opportunity for cascade photocatalysis reactions, a process in which chemical bonds of a molecule (i.e., the reactant) are sequentially formed and cleaved, and the product of the reaction is subsequently adsorbed on another halide-rich domain for further chemical reactions.

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AUTHOR CONTRIBUTIONS

L.A.M. and B.E. wrote the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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