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## Photo de-mixing in mixed halide perovskites: the roles of ions and electrons

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E-mail: [d.moia@fkf.mpg.de](mailto:d.moia@fkf.mpg.de) and [office-maier@fkf.mpg.de](mailto:office-maier@fkf.mpg.de)**Keywords:** mixed halide perovskites, photo de-mixing, ion transport, defect chemistry, optoionics

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**Abstract**

Mixed halide perovskites have attracted great interest for applications in solar cells, light emitting diodes and other optoelectronic devices due to their tunability of optical properties. However, these mixtures tend to undergo de-mixing into separate phases when exposed to light (photo de-mixing), which compromises their operational reliability in devices. Several models have been proposed to elucidate the origin of the photo de-mixing process, including the contribution of strain, electronic carrier stabilization due to composition dependent electronic energies, and light induced ionic defect formation. In this perspective we discuss these hypotheses and focus on the importance of investigating defect chemical and ion transport aspects in these systems. We discuss possible optoionic effects that can contribute to the driving force of de-mixing and should therefore be considered in the overall energy balance of the process. These effects include the selective self-trapping of photo-generated holes as well as scenarios involving multiple defects. This perspective provides new insights into the origin of photo de-mixing from a defect chemistry point of view, raising open questions and opportunities related to the phase behavior of mixed halide perovskites.

**1. Introduction**

De-mixing has been extensively investigated in multicomponent systems including metallic alloys and ionic solids [1]. As the thermodynamics of mixtures is characterized by the counter-play of enthalpy and entropy of mixing, temperature is a decisive parameter (besides other thermodynamic variables such as pressure, mole number etc.). Recently, Hoke *et al* reported the striking finding that mixed halide perovskites MAPb(I<sub>x</sub>Br<sub>1-x</sub>)<sub>3</sub> de-mix into I-rich and Br-rich phases under illumination (photo de-mixing) and re-mix to their initial composition in the dark (dark re-mixing) [2]. This opened a number of questions and suggested intriguing opportunities regarding the thermodynamic behaviour of mixtures in energetically pumped systems. Besides fundamental interest, this process has also been in the spotlight of application research as it has hindered the development of suitable, phase stable mixed halide perovskite thin films for use in optoelectronic devices [3]. Several studies have attempted to explain the experimental observations by invoking polaron formation and strain effects [4], bandgap reduction due to iodide rich phase formation [5] charge carrier trapping and concentration gradients from surface to bulk [6], halide oxidation and mass transport [7]. As the underlying process enabling photo de-mixing is the transport of ions occurring in the mixed halide perovskite, a detailed knowledge of the defect chemistry in these materials is important for addressing the questions on its origin [8]. In addition, given the central role of light in triggering the halide ion redistribution, there is a need to extend such knowledge to the non-equilibrium situation [9].

In this perspective, we will discuss some of the recent work devoted to clarifying the chemical factors in the thermodynamic description of de-mixing in mixed halide perovskites. After a brief description of the thermodynamics of mixing and de-mixing, we summarize key experiments which have revealed important

signatures of the photo de-mixing process in mixed halide perovskites, and the models proposed to date to explain its origin. Finally, we discuss the potential contribution of defect formation due to the interplay between electronic and ionic defects to the overall driving force for de-mixing under light, emphasizing some important aspects and questions for future research in this field.

## 2. De-mixing: general remarks

This section starts with a brief description of the thermodynamics of mixing and de-mixing (for further reading one finds treatments in the literature, e.g. Guggenheim's book [10]). Let us consider a binary mixture  $C \equiv (A, B)$  that can be thought to be formed according to



For the discussion on mixed halide perovskites, this could be for example  $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3 \equiv (\text{MAPbBr}_3, \text{MAPbI}_3)$ .

The contributions of the enthalpy ( $\Delta_m H$ ) and entropy ( $\Delta_m S$ ) of mixing to the free enthalpy ( $\Delta_m G$ ) determine if mixing or de-mixing is favored. In ideal mixtures (figure 1(a)), the enthalpy of mixing is zero and mixing is always governed by entropy, in other words, thermodynamically favorable (if the vibrational contribution to the entropy is neglected). The same applies for a negative mixing enthalpy. If the mixing enthalpy is positive, temperature is a decisive parameter with respect to potential de-mixing. At sufficiently high temperatures, mixing is favored (figure 1(b)). At lower temperatures, where the mixing entropy does not completely dominate, the free enthalpy of mixing presents a double-minimum profile (figure 1(c)). Such curve will look rather symmetrical if A and B are similar. Figure 1(d) shows the general case where A and B are dissimilar. In either case, the double minimum profile identifies a region of compositions, referred to as miscibility gap, where the mixed situation is not thermodynamically stable.

A simplified treatment uses a random distribution of A and B atoms for determining the enthalpy of mixing irrespective of the energetics. Strictly speaking this is only correct for an ideal mixture for which  $\Delta_m H = 0$ . In the general case ( $\Delta_m H \neq 0$ ), the energetics may be described by an interaction parameter  $\Omega$ . Its meaning is obvious when the transition from A and B to C is approximated by resorting to the reaction



Here one assumes that A is constituted by a–a pairs, B by b–b pairs and that C exhibits also mixed pairs (there may be other structure elements that are common to A and B but are not varied by the mixing process). Casting the reaction enthalpy of equation (2) and hence  $\Delta_m H$  in the form

$$\Delta_m H = W(x) = x(1 - x)\Omega \quad (3)$$

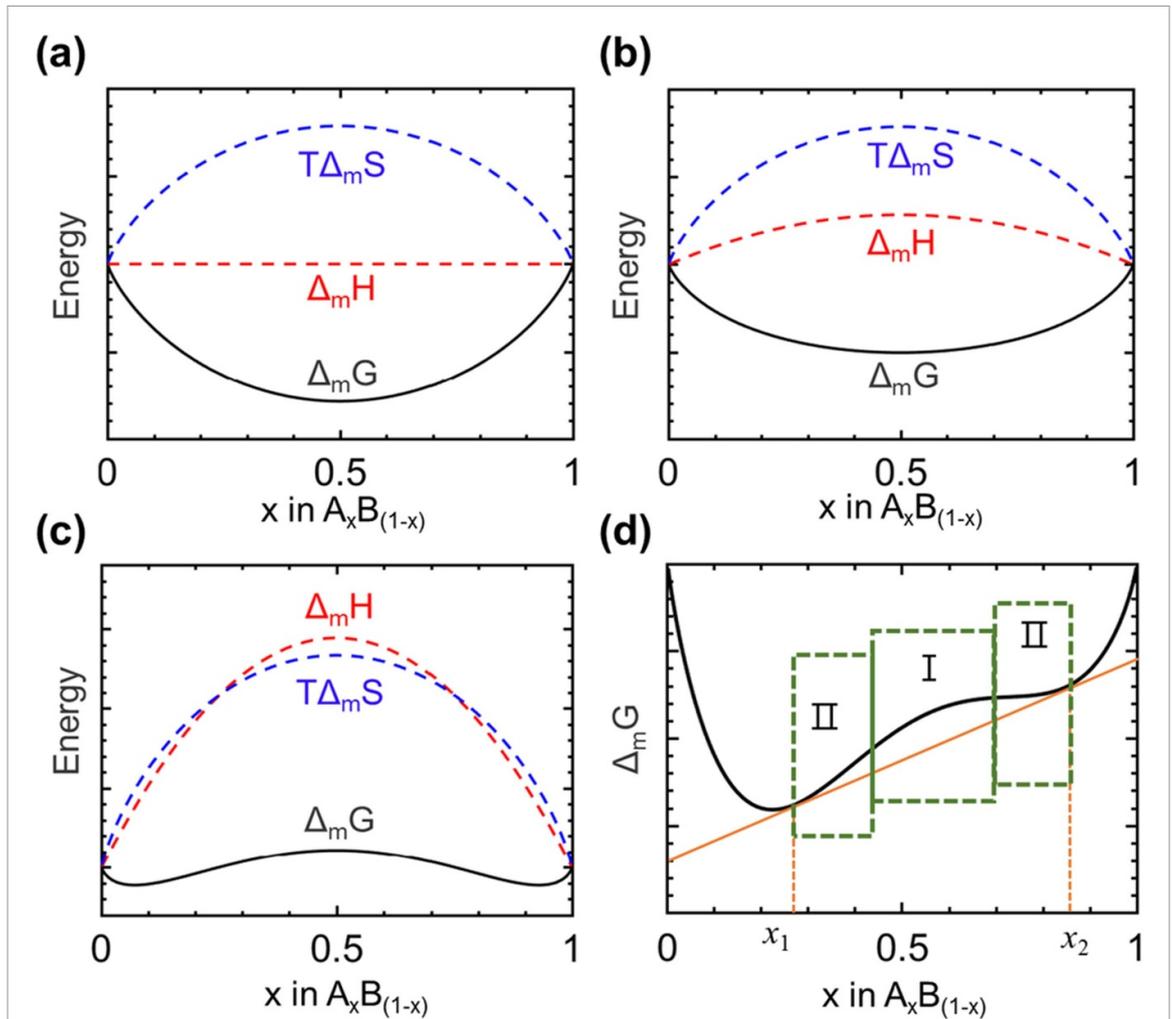
the free enthalpy curve follows as

$$\Delta_m G = RT(x \ln x + (1 - x)\ln(1 - x)) + x(1 - x)\Omega. \quad (4)$$

The last term disappears for an ideal mixture ( $\Omega = 0$ , i.e. it does not matter whether a is connected with a or b). If there are asymmetrical interactions, but a and b are similar,  $\Omega$  is non-zero but approximately constant and  $\Delta_m G$  is symmetrical about  $x = 1/2$ . It is straightforward to show that the critical temperature below which the miscibility gap closes and thus the dome-like form of the free enthalpy of mixing develops into a double minimum form is given by

$$T_c = \Omega/2R. \quad (5)$$

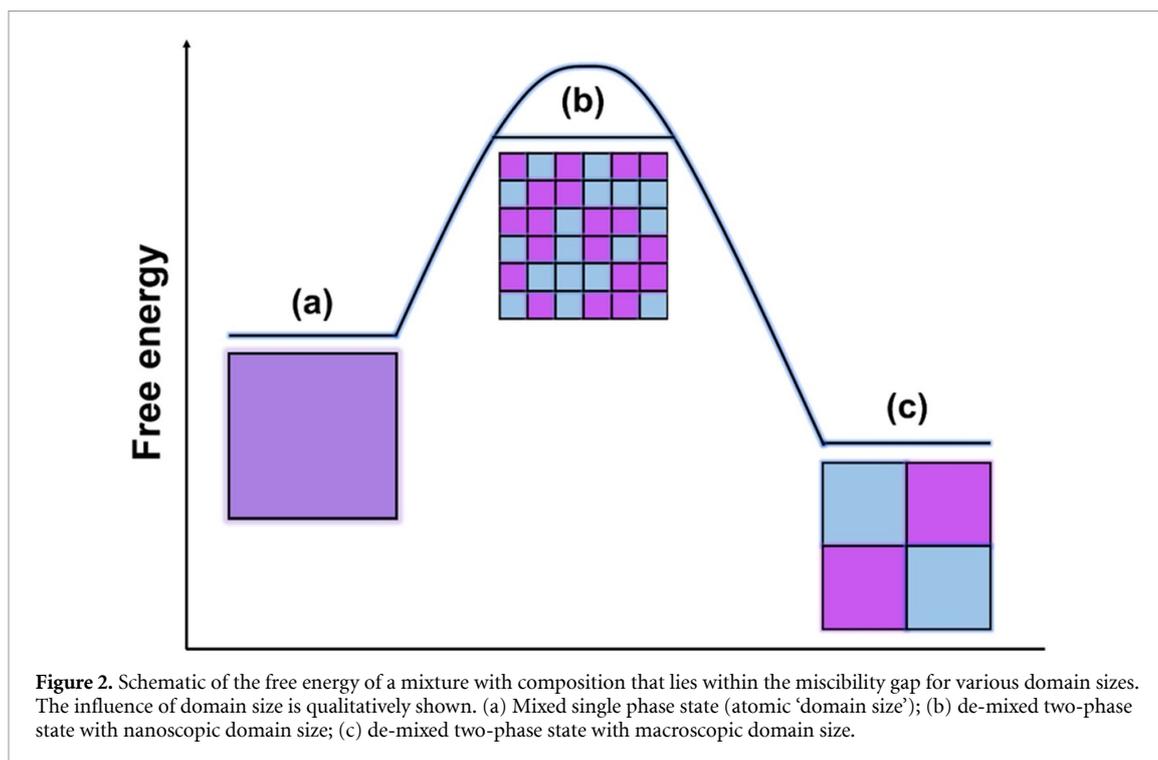
More realistic approximations assume  $\Omega$  to be a function of  $x$  typically making  $\Delta_m H(x)$  and  $\Delta_m G(x)$  asymmetrical (sub-regular mixtures) (figure 1(d)). For temperatures  $T < T_c$ , the coexistence compositions  $x_1$  and  $x_2$  can be obtained from constructing a double tangent to the  $\Delta_m G$  curve. The fact that it is not the minimum values that correspond to the stable compositions but the points of tangency is due to mass conservation which has to be fulfilled. When considering the kinetics of de-mixing, it is relevant to distinguish between regions of positive and negative curvature. In the middle of the phase diagram (figure 1(d), region I, region between the two inflection points), the curvature is negative such that an infinitesimal compositional fluctuation leads to a decrease in  $\Delta_m G$  and hence to spontaneous de-mixing (this region is called regime of spinodal decomposition). In the two neighboring regions (figure 1(d), region II, region between  $x_1$  and  $x_2$  where the curvature is positive), a sufficiently large variation in composition is needed to drive de-mixing. In other words, decomposition requires nucleation and transport of longer range



**Figure 1.** Mixing free enthalpy ( $\Delta_m G$ ), mixing enthalpy ( $\Delta_m H$ ) and mixing entropy term ( $T\Delta_m S$ ) for mixture  $A_x B_{1-x}$  for the case of (a) an ideal mixture, (b) a regular mixture at high temperature ( $T > T_c$ ) where mixing is favoured and (c) a regular mixture at low temperature ( $T < T_c$ ) where de-mixing is favoured. (d) Free enthalpy of mixing of a sub-regular mixture. The two regions in (d) indicated with green dashed squares refer to the (I) spinodal and the (II) binodal regions. By constructing a common tangent to the free enthalpy curve (orange solid line), the de-mixed compositions of  $x_1$  and  $x_2$  can be obtained.

to bring the system into the thermodynamically favored compositional range. It follows that  $T_c$  can be evaluated as the temperature at which the two inflection points coincide (meaning that at the critical composition the third derivative is zero).

The above treatment (equations (3) and (4)) assumes random distribution of atoms, which is inconsistent with assuming a non-zero interaction energy. A better approach is to only assume random distribution of pairs, and to partially account for the non-zero interaction energy in the evaluation of the enthalpy and entropy of mixing by applying a mass action law for equation (1). The latter approach is termed quasi-chemical approximation and results in a more complex, but more accurate, formulation, in which the complete randomness is not assumed. Accurate statistical treatments are very involved. A particular shortcoming of the above treatment is its referring to pair potentials which is not sufficient for columbic systems. A further shortcoming is the neglect of gradient effects. The latter point has been addressed by the Cahn-Hilliard treatment. Here the free enthalpy exhibits, beyond the homogeneous term (no gradients), a correction term being proportional to  $\int (\nabla c)^2 dV$  (where  $\nabla c$  is effectively the gradient in local composition, which is integrated in the volume of the system). In terms of pair considerations, this is essentially referring to the fact that, in a non-zero compositional gradient, the pair interactions to the 'left' are different from the pair interactions to the 'right', as already pointed out by Becker [11]. This theory is more precise in describing the correct transitions between spinodal and binodal behavior. It is also able to predict the influence of the 'domain size' in mixtures (see figure 2), whereby an additional contribution to the free enthalpy of mixing due to the surface energy associated with the formation of domain boundaries appears in the balance.



In the next sections, we summarize some of the important aspects related to photo de-mixing in mixed halide perovskites addressed in the literature and discuss them in the context of a non-ideal mixture model.

### 3. Photo de-mixing in mixed halide perovskites

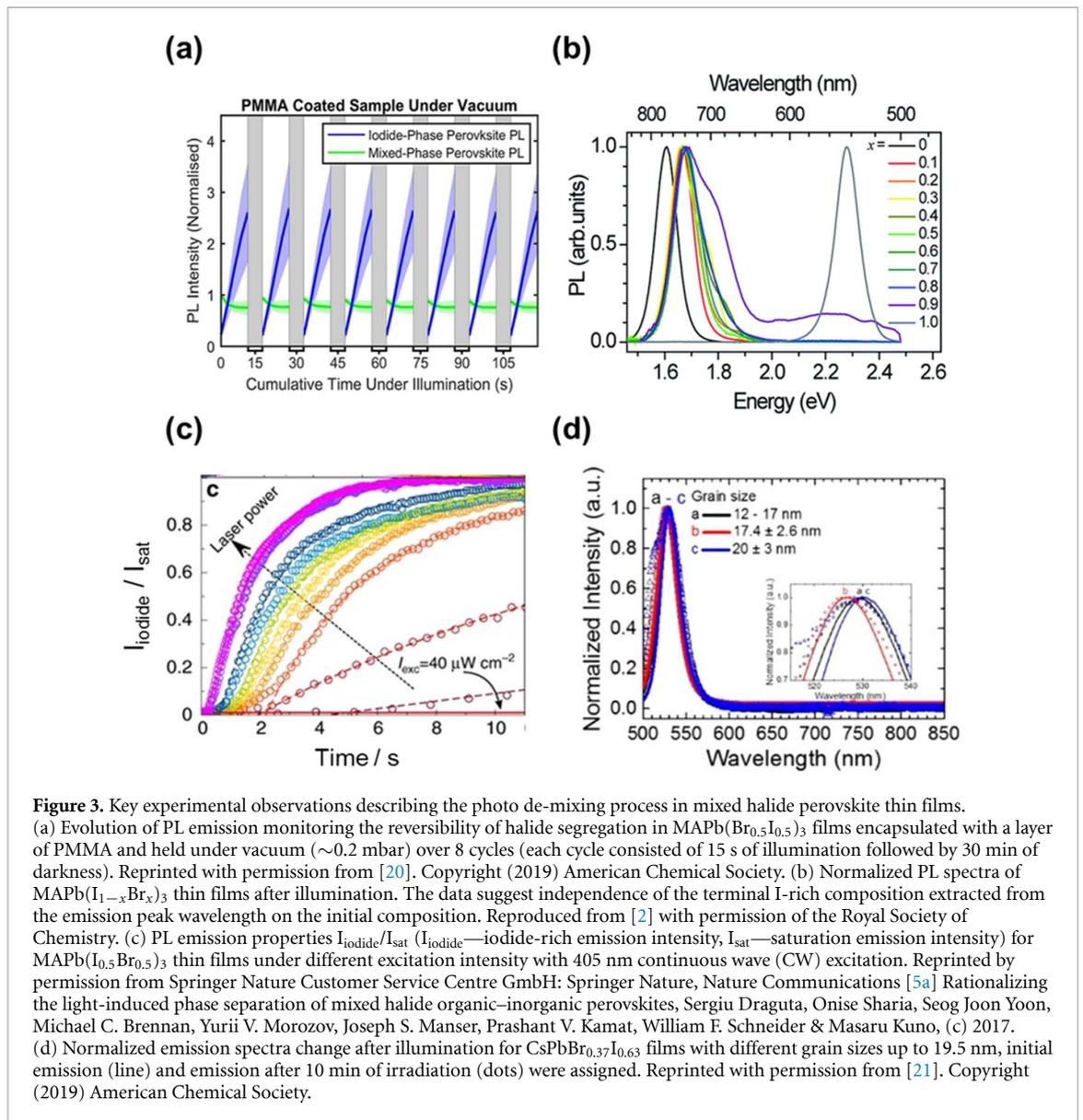
The occurrence of photo de-mixing in mixed halide perovskites has been identified by recording changes in the optical, structural, morphological and electrical properties of these materials under illumination. *In-situ* UV–Vis and PL measurements were used to quantify the changes in optical properties, and correlating them with the change in phase composition under illumination [2, 5a, 12, 13]. From a structural point of view, splitting or broadening of the diffraction peaks measured with x-ray techniques [2, 14] was observed during de-mixing. Additionally, the long stabilization time of optoelectronic devices using mixed halide compositions compared with its end members has been interpreted as an ‘electrical signature’ for photo de-mixing [3a, b, 15]. Other techniques including luminescence mapping, combined with SEM have also aided the investigation of the phase separation process in terms of spatial distribution of the de-mixed phases [4d, 16]. Various reviews on this topic can be found in the literature [7, 14, 17].

For the scope of this perspective, we focus on some key findings that can help us understand the mechanism of photo de-mixing:

1. The de-mixing process is reversible, at least partially (figure 3(a)) [2, 18]. The experimental situation is complicated by concomitant decomposition and it was shown that encapsulation which works against decomposition, increases the reversibility [19].
2. The de-mixed I-rich composition after illumination is approximately the same regardless of the initial composition (figure 3(b)) [2, 22].
3. A light intensity threshold for the occurrence of the photo de-mixing (figure 3(c)) was observed. With increase of the light intensity, the de-mixing rate increases and saturates at a sufficiently intense illumination [5a]. Photo-remixing has also been observed at very high light intensity [23].
4. Photo de-mixing phenomena disappear in nano-crystals with size  $\leq 50$  nm (figure 3(d)) [21, 24].
5. Photo de-mixing occurs also for 2D mixed halide perovskites [25]. The estimated photo-miscibility-gap indicates a critical temperature above 420 K [22].

On a very general level there are two possibilities to explain the role of light for the de-mixing:

- (i) The mixtures in the dark are metastable and illumination enables faster kinetics of de-mixing [26].
- (ii) The energetic input by illumination drives the initially stable mixture into instability. Then the two phases formed should re-mix if light is shut off.

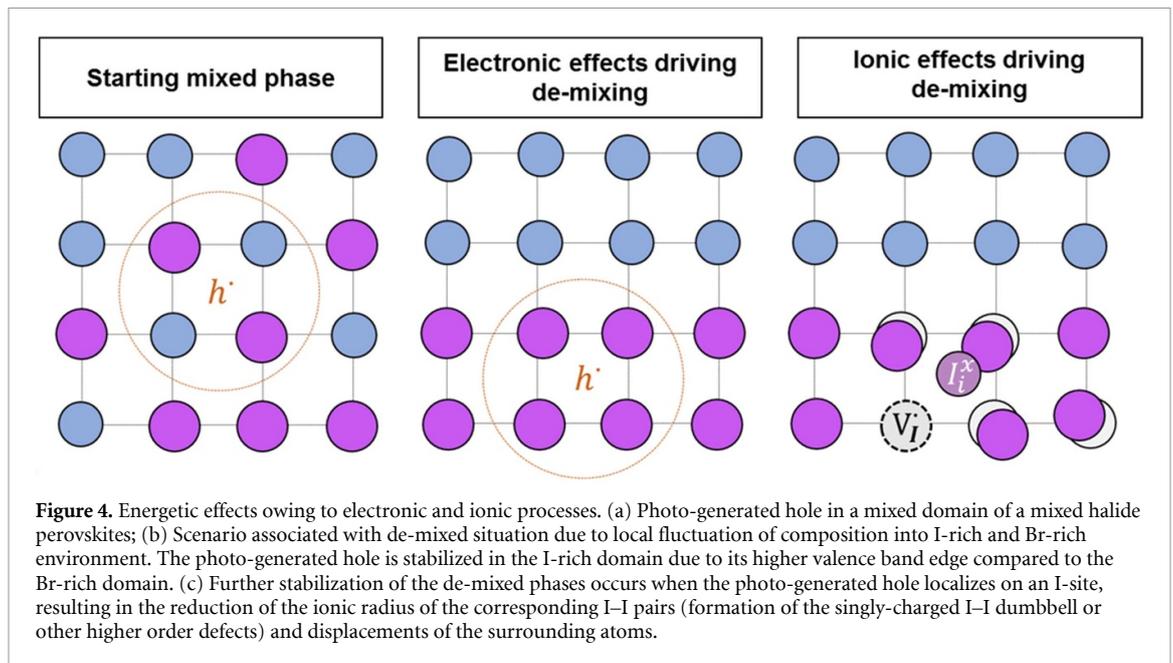


**Figure 3.** Key experimental observations describing the photo de-mixing process in mixed halide perovskite thin films. (a) Evolution of PL emission monitoring the reversibility of halide segregation in MAPb(Br<sub>0.5</sub>I<sub>0.5</sub>)<sub>3</sub> films encapsulated with a layer of PMMA and held under vacuum ( $\sim 0.2$  mbar) over 8 cycles (each cycle consisted of 15 s of illumination followed by 30 min of darkness). Reprinted with permission from [20]. Copyright (2019) American Chemical Society. (b) Normalized PL spectra of MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> thin films after illumination. The data suggest independence of the terminal I-rich composition extracted from the emission peak wavelength on the initial composition. Reproduced from [2] with permission of the Royal Society of Chemistry. (c) PL emission properties  $I_{\text{iodide}}/I_{\text{sat}}$  ( $I_{\text{iodide}}$ —iodide-rich emission intensity,  $I_{\text{sat}}$ —saturation emission intensity) for MAPb(I<sub>0.5</sub>Br<sub>0.5</sub>)<sub>3</sub> thin films under different excitation intensity with 405 nm continuous wave (CW) excitation. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature, Nature Communications [5a] Rationalizing the light-induced phase separation of mixed halide organic–inorganic perovskites, Sergiu Draguta, Onise Sharia, Seog Joon Yoon, Michael C. Brennan, Yurii V. Morozov, Joseph S. Manser, Prashant V. Kamat, William F. Schneider & Masaru Kuno, (c) 2017. (d) Normalized emission spectra change after illumination for CsPbBr<sub>0.37</sub>I<sub>0.63</sub> films with different grain sizes up to 19.5 nm, initial emission (line) and emission after 10 min of irradiation (dots) were assigned. Reprinted with permission from [21]. Copyright (2019) American Chemical Society.

Clarifying the presence or absence of a miscibility gap for mixed halide perovskites in the dark at room temperature is critical to this discussion. Early studies using x-ray diffraction on thin films and synchrotron x-ray powder diffraction showed conflicting results on whether CH<sub>3</sub>NH<sub>3</sub>Pb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> exhibits full miscibility or not [27]. While the conflicting evidence may be related to the different excitation intensity of the light source [28], the question of whether these systems exhibit full miscibility in the dark at room temperature is still open. The additional uncertainty on the structural reversibility of these systems upon photo de-mixing and dark re-mixing complicates the matter. Nevertheless, most reports seem to point towards (i) being in contradiction with the fact that the photo de-mixing process is (at least partially) reversible (see point (1) and figure 3(a) above) [2, 19]. This fact leaves us with (ii), which indeed currently represents the most accredited interpretation.

Concerning the driving force which induces phase instability in mixed halides perovskites, various aspects regarding the de-mixing mechanism have been discussed:

- The formation of small clusters, identified as I-rich domains, near grain boundaries has been related to possible polaron-induced strain effects. Molecular and mean-field phenomenological models were used to show that this localized strain can change the free energy landscape and favor de-mixing [4a, d, 29].
- The energy of photo-generated electrons and holes in these mixtures are given by the edges of conduction and valence band (CBM and VBM), both of which depend on composition. Therefore, de-mixing brings



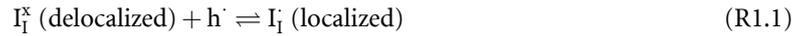
about an energy change that depends on  $x$  and on light intensity (concentration of electrons and holes). In [5a, 18] the greater portion of the photo de-mixing driving force is attributed to the valence band edge variation and to the energy gain associated with holes stabilization in I-rich domains.

- (c) An additional optoionic effect has been proposed to contribute to the photo de-mixing. The defect chemical mechanism, corroborated by calculations [9a, b, 30], involves holes self-trapping on iodide sites in the I-rich domains further leading to the formation of iodine interstitials, dumbbells or even higher aggregates via ionic rearrangement. For the Br-analogue, the same mechanism does not occur to the same extent as holes tend to be more delocalized.

In addition to these aspects, concentration gradients of halide species resulting from the photo-generated charge carriers concentration gradient have also been described as a factor underlying the photo de-mixing process [31]. Surface defect carrier trapping leading to Electric-field-induced anion drift have additionally been proposed as a possible driving force for phase separation [6]. The fact that photo de-mixing is observed in mixed halide perovskites under uniform illumination [25b] as well as in the bulk of single crystal samples [16] suggests that these aspects, while insightful for the analysis of experiments, are not critical in terms of fundamental driving force of the process. We summarize the energetic contributions stemming from electronic and ionic effects described above in figure 4. Compared with the situation in the dark, energy variations due to electronic effects are related to electronic energy variations due to electron and hole transfer between phases. A higher VB-edge and a lower CB-edge are related to electronic stabilization for holes and electrons, respectively. As the halide composition predominantly affects the position of the VB-edge [32], we concentrate on hole stabilization here (electron stabilization is also discussed at the end of the perspective). This involves the difference in the energy of the valence band maximum between the mixed halide perovskites and the I-rich phase. The interested reader may refer to the literature for more details on (a) and (b) above [4d, 5a, 7, 26], while below we discuss (c) in more detail. As mentioned in the previous section, photo-generated holes in an I-rich phase can be further stabilized by the formation of complex defects involving ionic relaxation. Let us inspect in more detail the energetics of hole localization and of ionic/electronic relaxation.

If we consider the process whereby a photo-generated delocalized hole localizes on an iodide site and participates in the formation of singly-charged I-I dumbbell, a number of contributions have to be taken into account. Firstly, we have to overcome the delocalization energy ( $\Delta E_{loc}$ ) usually taken as half the (valence) band width (corresponding to the difference of the lowest bonding orbital energy to the non-bonded state or to the difference to the highest anti-bonding orbital state to the non-bonded state). Secondly, we have to consider the energy gain due to the formation energy of the dumbbell ( $\Delta E_f$ ) and to the following polarization energy ( $\Delta E_p$ ) of the crystal due to electronic shells and ionic defect displacement.

In defect notation this sequence is written as:



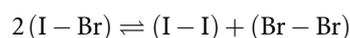
$I_1^\times$  (relaxed) is short for the final complex defect which is approximately an iodine dumbbell (involving another formerly regular iodine) with covalent contributions.

The reaction energy for (R1.1) is roughly half the valence band width ( $\sim \frac{4eV}{2}$ ) [33] (the localization energy can even be smaller than this value for accurate consideration [34]). The reaction energy of (R1.3) may be estimated from the energy of forming a dumbbell ( $I_2^-$  molecule). As the reaction energy of (R1.2) is not available we alternatively compose (R1) as follows



where (R2.1) describes the excorporation of an iodine atom ( $I_g$  corresponds to an iodine atom in the gas phase,  $V_1^\times$  is called F center), (R2.2) refers to the ionization energy of a neutral vacancy minus the bandgap, (R2.3) refers to iodine incorporation from the gas phase to an interstitial. Here we estimate the reaction energy for the defect reactions mentioned above by using data from [9b], where  $\text{CsPbI}_3$  was theoretically investigated. While it has been shown that A-site substitution can vary significantly the kinetics of ion transport and de-mixing [35], this analysis based on  $\text{CsPbI}_3$  may still be representative in terms of the energetics involved in the de-mixing process (hole trapping is mostly influenced by the halide orbitals). The reaction energy for (R2.1) is estimated as 3.0 eV (formation energy of F center), the one for (R2.2) as  $-1.6$  eV (ionization energy of a neutral iodide vacancy by hole) and the energy for (R2.3) as  $-0.4$  eV (formation of H center), so that the total energy balance is slightly positive,  $+1.0$  eV. We note that, if this value is taken for granted, the reaction energy for (R1.2) and (R1.3), describing the transfer of a neutral iodine from a regular site to a relaxed interstitial position, follows as  $-1.0$  eV. This value refers to the process where  $V_1^\times$  and  $I_1^\times$  are independent. If however an associated pair ( $V_1^\times I_1^\times$ ) is formed, which is a more likely scenario, the value is substantially lower. For  $\text{CsPbI}_3$  a relaxation energy of the order of  $\sim 1.8$  eV has been reported. [9b, 36] Considering such value in our treatment would indeed change the sign of the energy associated to (R1) = (R2) from positive to negative ( $\sim -0.8$  eV). Given the very approximate character of the assessment, the finding that the final value can be negative but will be small, is realistic. Future experimental and computational effort is needed to evaluate more accurate values for the ionic contribution to the driving force for photo de-mixing. We also note that, if the majority of self-trapped hole centers is associated with the vacancies, it is clear that such dissociation adds a high value (association energy/2  $\sim 0.9$  eV) to the ion migration process. When considering the complete picture, additional interactions of the trapped hole center with trapped electrons (see below) may lower this value. On the basis of this discussion, including the effect related to ionic defect formation is supposed to lead to a stronger de-mixing tendency (higher  $T_c$ ).

If we simplify our de-mixing problem by considering pairs, as described in the previous sections, and we neglect the illumination effects in the bromide-rich domains, we have approximately to distinguish two reactions,



which refers to the sites that are hole-free and

$$2(\text{I} - \text{Br})^* \rightleftharpoons (\text{I} - \text{I})^* + (\text{Br} - \text{Br})$$

which refers to the sites where photo-generated holes are present.

It is clear that the reaction of  $(\text{I} - \text{Br})^*$  to  $(\text{I} - \text{I})^*$  and Br-Br brings about a slight energy gain due to electronic but also the ionic relaxation.

Only the latter reaction is considered to be responsible for driving segregation. Its reaction free energy is characterized not only by an electronic, but also an ionic contribution. Nonetheless, the overall value is rather small. An evident first conclusion is that defect formation effects depend, similarly to the electronic contribution, on the total hole concentration and hence on light intensity. Secondly, in order to have appreciable energetics that drive de-mixing, a large fraction of holes should be trapped (possibly the vast majority of the holes are not free). Thirdly, the fact that both de-mixing kinetics and photostriction effects show saturation when increasing light intensity may also be correlated with a saturated concentration for self-trapped holes [4c, 5a].

At this point it is worth summarizing that, for the analysis of photo de-mixing in mixed halide perovskites based on a non-ideal solution model: (i) the  $\Omega$  parameter includes hole stabilization by the higher valence band edge of the iodide plus the self-trapping energy. (ii)  $\Omega$  is proportional to the self-trapped hole concentration. (iii)  $T_c$  in 2D mixed halide perovskites is estimated from photo-miscibility-gap to be above 420 K [22], which provides a lower bound estimate of 0.07 eV for  $\Omega$ ; (iv) the fact that the de-mixing phenomenon disappears in the nano-crystals ( $\leq 50$  nm) at room temperature [21, 24] ( $T_c \leq 300$  K) can be attributed to the additional G-cost of forming an interface [37]. This latter point should be considered in more detail.

According to (iv), the free energy of (de-)mixing (equation (4)) is, at the critical temperature, compensated by the additional interfacial energy cost of forming the interface between de-mixed domains. The latter can be expressed as  $G_{\text{ex}} = 2\frac{\gamma}{L}V_m$  ( $\gamma$  is the interfacial tension of the domains,  $L$  is the domain size and  $V_m$  is the molar volume), and it is significant for small  $L$ . In view of equation (4), one can then write for the interaction parameter  $\Omega$

$$\Omega = \frac{\left[2\frac{\gamma}{L}V_m - RT_c(x\ln x + (1-x)\ln(1-x))\right]}{x(1-x)}. \quad (6)$$

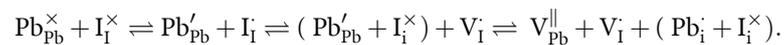
Therefore, the absence of photo de-mixing in  $\text{CsPbI}_{1-x}\text{Br}_x$  nanocrystals at room temperature allows us to estimate an upper limit for the interaction parameter ( $\Omega_{\text{max}}$ ). By evaluating equation (6) for  $T_c = 300$  K,  $x = 0.5$ ,  $L = 50$  nm, and using an estimate of the halide molar volume for mixed halide perovskites [38], one obtains  $\Omega_{\text{max}} = 4 \left[1.8\frac{\text{m}^2}{\text{J}}\gamma + 1.7\right] \text{kJ mol}^{-1}$ . If we then consider values of surface tension in the range of 0.1–1 J m<sup>-2</sup> [37d, 39],  $\Omega_{\text{max}} = 0.07$ –0.14 eV. The  $\Omega$  parameter is a property related to the interaction between the halides in this model, and therefore it is not expected, to a first order approximation, to vary with the domain size. It follows that the same value of  $\Omega_{\text{max}}$  obtained above is relevant also to the macroscopic domain case, where negligible interfacial contribution are expected, resulting in an estimate for  $T_{c,\text{max}} = 420$ –840 K.

Large concentration of the self-trapped holes and higher order defects formation in soft, ionic halide perovskite lattice [40], can be responsible for large lattice strain and lattice deformation as already mentioned above [4c, 41]. It is also worthy to note that the photo-induced strain [41d] and photo-ionic effect [30a] decrease on substituting iodide with bromide in these perovskites. The extent to which defect formation may be playing a role on the observed photo-induced strain is therefore an interesting question for future research [30a]. In this context, it is revealing to refer to Darken's model of de-mixing in alloys when oversize-substitutions are introduced [42]. Here the effect of 'squeezing' an additional volume element into a solid is considered. The oversize  $\Delta V'$  converts into a volume increase of the matrix  $\Delta V$ , given by  $\Delta V = \Delta V' \frac{3(1-\nu)}{(1+\nu)}$ . A typical Poisson ratio ( $\nu$ ) of 0.3 leads to  $\Delta V$  exceeding  $\Delta V'$  by 60%. By considering the oversize introduced by a large substitutional impurity and applying the regular solution model, Darken could explain Hume-Rothery's rule stating that the substituting atom in alloy systems should not have a size exceeding the one of the substituted atom by more than 15% in order for it to be stable [42, 43]. The reasoning is as follows: if the volume is increased by  $\Delta V' = V' - V$ , the elastic energy density can be estimated according to ( $M_s$ : shear modulus)

$$E = \frac{2}{3}M_s V \left(\frac{V' - V}{V}\right)^2. \quad (7)$$

This energy may be equated to  $\Omega$  and hence to  $2RT_c$  in order to get an estimate of  $T_c$  within the regular solution model. Interestingly, if  $(V'/V)$  is replaced by  $(r'/r)^3$  with  $r$  being the radius of the introduced oversized sphere, and representative values for alloys of  $M_sV$  are introduced, a critical radius of 15% can be assessed to be a necessary upper bound for the size mismatch of substitutional impurities in order to obtain miscibility at 1000 K. In our case the experimentally found photo-striction effect can be transferred into a de-mixing tendency: if the self-trapping effect is the cause,  $(I-I)^*$  takes the role of the impurity substituting for  $(I-I)$ . However, the above consideration is too crude to be quantitatively applied in our case, let alone the fact that the decisive materials parameters are not known.

Having considered the consequences of holes being trapped and of the formation of higher order defects, one question that arises naturally concerns the potential role of electrons in the de-mixing process. Given the fact that the conduction band edge decreases when increasing the iodide content [13a, 27a, 32], it is reasonable to assume that electrons will also locate themselves in I-rich domains [44]. Since the conduction band in MAPbI<sub>3</sub> is predominantly formed by Pb-orbitals, e<sup>-</sup>-trapping on Pb<sup>2+</sup> would favor localization within the already formed I-rich domains and contribute to the de-mixing tendency. Further interactions with I interstitials would make the balance more favorable (see below). The formation of Pb<sup>0</sup> has been reported in mixed halide perovskites under illumination [45]. However, the aggregation tendency of Pb<sup>0</sup> is expected to be lower than that of I<sup>0</sup> due to its larger size. Yet the interaction of I<sup>0</sup> and Pb<sup>+</sup> or even Pb<sup>0</sup> in the I-rich domains might play an important but underrated role here. In the limit of a symmetrical situation, one would assume interstitial (PbI)<sup>+</sup> or PbI<sub>2</sub> molecules. The excitation could be then solely written in terms of trapped defects, e.g. as



Such massive trapping might also have important consequences on the charge carrier life-times in these materials [46]. Pb–I interactions could influence the extent to which iodide vacancies are mobile, rather than associated with the iodine interstitial. Testing these possibilities via spectroscopic methods will clarify the extent to which such defect formation routes are favorable and elucidate their contribution to the phase behavior, but also to the charge carrier dynamics of hybrid perovskites. Such investigation also requires further theoretical work to understand self-trapping effects in photo-active ionic materials [47].

From the point of view of applying mixed halide perovskites to optoelectronic devices, it is highly desirable to find ways to reduce the rate of (or even completely suppress) photo de-mixing. Partially replacing A cation [4a, 48] and passivating the surfaces and grain boundaries of films with halide species [3c, 49] showed a kinetic reduction of the de-mixing process. Developing strategies that can extend this rate reduction to time scales comparable to the lifetime of devices appears challenging, given the significant ionic transport in these compounds. The most promising approach would be to make mixed halide perovskites thermodynamically stable under the operational light intensity and temperature range required for their application in solar cells or other optoelectronic devices. From a thermodynamic viewpoint, in order to suppress the critical temperature of the mixture under light below typical device operational temperatures, it is necessary to vary the energetic contributions to the overall free energy of the mixed and the de-mixed situations. One way to increase the free energy of the mixture in the de-mixed state is nanosizing the grains of the mixed halide perovskites (as shown in figure 2 and discussion above). While this can solve the phase stability issue, the performance of perovskite nanocrystal-based devices can be sub-optimal compared to the case where films with larger grains are used [24, 50]. Besides the changes in the kinetics of ion transport mentioned above, compositional engineering can also be explored to increase the free energy associated with the products of the photo de-mixing process. Some recent demonstrations (e.g. suppressed photo de-mixing upon Cl incorporation into the lattice [51]) show that such approach may have promise for future developments. Finally, further research aimed at correlating the factors discussed here with the mixed-halide perovskite phase diagram under light will generate new guidelines for the design of phase stable devices.

In this perspective, we considered the various energetic contributions that have been discussed to date to drive photo de-mixing in mixed halide perovskites: photostriction and strain effects, hole stabilization due to high valence band edge in I-rich environment compared with the mixed phase, hole stabilization by ionic defect formation and structure relaxation. We have particularly emphasized the latter optoionic effect, and its potential consequences for different halide compositions. A comprehensive understanding of the origin of photo de-mixing in mixed halide perovskites is emerging. Further experimental and theoretical effort is needed to clarify the role of electronic charge transfer and trapping processes involving holes, and potentially electrons too. Finally, determining the relevant defect formation routes in mixed halide perovskites under

illumination is a key step towards the advance in the phase engineering of these materials and in the optimization of their electronic charge carrier dynamics.

### Data availability statement

No new data were created or analysed in this study.

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