Mixed-halide hybrid perovskite semiconductors have attracted tremendous attention as a promising candidate for efficient photovoltaic and light-emitting devices. However, these perovskite materials may undergo phase segregation under light illumination, thus affecting their optoelectronic properties. Here, photoexcitation induced phase segregation in triple-cation mixed-halide perovskite films that yields to red-shift in the photoluminescence response is reported. It is demonstrated that photoexcitation induced halide migration leads to the formation of smaller bandgap iodide-rich and larger bandgap bromide-rich domains in the perovskite film, where the phase segregation rate is found to follow the excitation power-density as a power law. Results confirm that charge carrier lifetime increases due to the trapping of photoexcited carriers in the segregated smaller bandgap iodide-rich domains. Interestingly, these photoinduced changes are fully reversible and thermally activated when the excitation power is turned off. A significant difference in activation energies for halide ion migration is observed during phase segregation and recovery process. Additionally, the emission linewidth broadening is investigated as a function of temperature which is governed by the exciton–optical phonon coupling. The mechanism of photoinduced phase segregation is interpreted based on exciton–phonon coupling strength in both mixed and demixed (segregated) states of perovskite films.

1. Introduction

Over the past few years, organic–inorganic halide perovskites have attracted tremendous attention as a promising material for low-cost preparation and highly efficient photovoltaic and light-emitting devices. These hybrid perovskite materials show unique optoelectronic properties such as high absorption coefficient, long carrier diffusion length, and small exciton binding energy. To date, various combinations and ratios of monovalent inorganic cations (such as formamidinium (CH(NH2)2+ = FA), methylammonium (CH3NH3+ = MA), Cs, and Rb) and halide anions (I− and Br−) have been used for bandgap tuning as well as a means of improving efficiency and stability of perovskite photovoltaic devices. One of the most influential improvement was the incorporation of cesium cations in perovskite structure to fine-tune Goldschmidt tolerance factor toward more structurally stable black phase perovskite with improved performance of photovoltaic devices. Therefore, triple-cation based mixed-halide perovskites (Cs, FA, MA) Pb(I1−xBrx)3 have been found more suitable for solar cell application. Unfortunately, even such most advanced perovskite materials still suffer from instabilities of the bandgap when subjected to photoexcitation under continuous light illumination. As originally reported by Hoke and coworkers, MAPb(I1−xBrx)3 undergoes reversible halide phase segregation under light illumination into separate iodide- and bromide-rich domains within the

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parent phase.\[6\] In recent years, it is commonly reported that light-induced phase segregation process in mixed halide MAPb\(_{1-x}\)Br\(_x\)\(_3\) and CsPbBr\(_{1-x}\)I\(_x\)\(_3\) perovskites is initiated by segregation of iodine ions which causes a red-shift in the photoluminescence (PL).\[7,8\] On the other hand, phase segregation can also induce a PL blue-shift as reported in CsPbBr\(_{1.12}\)I\(_{0.88}\) nanocrystals subjected to photoexcitation and external electrical biasing.\[7\] Furthermore, other reports suggest that variation of energy bandgap of mixed halide perovskite could also be due to lattice distortion as light illumination could generate lattice expansion or contraction.\[9-11\] Therefore, the existing literature on phase segregation is often subject to controversy.

Another puzzling feature under debate in hybrid perovskites is the unusual long carrier lifetime. Several mechanisms have been proposed to explain the long carrier lifetime of perovskite materials, such as large polarons formation, Rashba effect and photon recycling.\[12\] Moreover, recombination of excited charge carriers through trap-mediated channels also influences the rate of halide segregation and recombination lifetime.\[13\] The nature of trap states and trapped carrier type (electrons or holes) in segregated domains are not yet entirely understood although it was reported that electrons are more likely to be trapped than holes.\[14,15\] Such existing reports imply that excited charge carriers trapping in trap-states and corresponding energy levels within the bandgap could alter the phase segregation dynamics. Recently, it was also demonstrated that excited charge carriers could couple with the perovskite lattice to create a polaron,\[16-18\] which could promote the halide ion segregation. A strong exciton–phonon coupling is expected in such soft and ionic hybrid perovskite materials at room temperature.\[19,20\] Eventually, the Cs cation-based mixed halide perovskite (partially exchanging FA cation with Cs) unveils lower electron–phonon coupling strength and exhibits high structural stability against photoinduced phase segregation.\[18\] Therefore, it is interesting to study the role of exciton–phonon coupling in triple-cation mixed halide perovskite (TC-MHP) films during phase segregation process and the role of trapped charge carrier under photocexcitation.

In the present study, we have explored different aspects of photocexcitation induced phase segregation in triple-cation mixed-halide (MA\(_{0.17}\) FA\(_{0.83}\)\(_{0.05}\) Cs\(_{0.05}\) Pb\(_{0.81}\) Br\(_{0.19}\))\(_3\) perovskites (TC-MHP) films and quantitatively rationalized the spectroscopic processes that occur during phase segregation and recovery processes. We demonstrate the laser power dependent evolution of segregated halide domains and their kinetics with laser exposure time. We performed time-correlated single photon counting (TCSPC) measurements along with low-temperature PL studies to read the nature of photoexcited carriers trapping states in phase segregated domains, revealing their role in long decay lifetime. We discuss the emission linewidth broadening with rising temperature, which is governed by exciton–optical phonon coupling in both segregated and remaining nonsegregated domains of TC-MHP film. Additionally, recovery kinetics of phase-segregated films is studied under dark at different temperatures and activation energies of halide ion migration are derived.

2. Results and Discussion

2.1. Photocexcitation Induced Phase Segregation

The TC-MHP perovskite film shows high optical absorbance and exhibits the direct band gap (\(E_g\)) of \(\approx1.625\) eV, calculated using the Tauc’s relation as presented in Figure S1 (Supporting Information). The surface morphological properties of TC-MHP film is also presented in Figure S2 (Supporting Information): a SEM image shows the uniformly distributed nanostructure with average grain size of \(\approx175\pm50\) nm. We have performed laser power dependent PL measurements at room temperature (296 K) to provide insight into the photoexcitation induced spectroscopic variation in TC-MHP film in terms of carrier trap-states and recombination dynamics. Figure 1a shows the normalized PL spectra as a function of laser power density (\(P_{\text{exc}}\)). With increasing excitation power density, a continuous red-shift of about \(\approx58\) meV is observed in emission peak: it goes from 1.625 eV (1 mW cm\(^{-2}\)) to 1.566 eV (840 mW cm\(^{-2}\)), concurrent with the increase in PL emission intensity (\(I_{\text{em}}\)). In Figure 1b, data clearly shows that PL intensity increases as a power law of excitation power, with an exponent \(\approx3/2\) (i.e., \(I_{\text{em}} \propto P_{\text{exc}}^{3/2}\)) for power-densities up to 380 mW cm\(^{-2}\). Generally, in the case of free excited carrier recombination, \(I_{\text{em}}\) grows linearly with \(P_{\text{exc}}\) (i.e., \(I_{\text{em}} \propto P_{\text{exc}}\)). In present case, this possibility is readily excluded at room temperature, because excitonic feature is not observed in the absorption spectrum (Figure S1, Supporting Information). The unusual \(\approx3/2\) power low PL response points the participation of intra-gap states in recombination process that act as traps for electrons or holes. Therefore, superlinear growth of PL intensity suggests that photogenerated carrier trapping at available defects or traps sites competes with bimolecular electron/ hole recombination process in TC-MHP film.\[21,22\] At higher excitation power-density (above 380 mW cm\(^{-2}\)), the power law changes from superlinear to sublinear owing to the fact that trap-mediated recombination process is dominated by bimolecular recombination process controlled with Auger losses. Therefore, at higher excitation power-density, the saturation in \(I_{\text{em}}\) is attributed to the saturation of radiative bimolecular recombination centers, as Auger losses starts playing a key role in recombination process.

Figure 1c shows the red-shift and broadening in PL emission linewidth as a function of excitation power-density which confirms the participation of low energy sub-bandgap states in recombination process. To further confirm the photocexcitation induced red-shift in PL emission, time dependent PL measurements were performed at given excitation power-densities and shown in Figure S3a–f (Supporting Information). At low-excitation power-density (1 mW cm\(^{-2}\)), the position of PL spectrum remains unchanged and shows significant increment in PL intensity over exposure time. The increase in PL intensity might be related to the filling of existing nonradiative traps sites in TC-MHP film. At higher excitation power-densities, results show the red-shift and an increase in PL intensity with exposure time, indicating the formation of low-energy sub-bandgap states and filling of existing trap sites.\[23\] The laser-induced heating possibility is safely ruled out here since temperature dependent PL emission exhibit blue-shift with increasing temperature.
(discussed in later section). It is observed that increasing excitation power leads to faster shifting of PL emission peak (Figure S3, Supporting Information). In particular, it is noted that photoexcited TC-MHP film shows red-shifted PL emission at ≈1.564 eV which corresponds to the standard PL emission from FAPbI$_3$ perovskite. It confirms that the magnitude of redshift is related to the evolution of localized low-bandgap energy states, which might be related to halide ion migration and iodide-rich perovskite phase. Therefore, it establishes the possibility of photoexcitation induced halide ion migration and formation of smaller-bandgap iodide-rich perovskite domains in TC-MHP film that yields red-shift in PL emission.

Figure 1d shows the redshift in peak position as a function of time at given excitation power densities. Peak position values are extracted using PL emission data (Figure S3, Supporting Information) fitted with Gaussian–Lorentzian (Voigt) function. The first order phase segregation rate constant ($k_{seg}$) is calculated from subsequent fitting of exponential red-shifting curves at different excitation power densities. It is found that at excitation power $P_{exc} \leq 1$ mW cm$^{-2}$, PL emission peak remains stable at a position of ≈1.624 eV and reveals that no phase segregation occurs up to long exposure time. At $P_{exc} = 5$ mW cm$^{-2}$, PL peak shifts slowly in exponential manner and shows ≈20 meV red-shift after 140 min illumination; the corresponding $k_{seg}$ value is found to be $0.21 \times 10^{-3}$ s$^{-1}$. The PL emission peak shifts faster with increasing excitation power-density and exhibits higher $k_{seg}$ value. The maximum redshift in PL emission peak is about ≈56 meV for $P_{exc} = 84$ mW cm$^{-2}$ and no further shift is observed at higher $P_{exc}$ value. The $k_{seg}$ value increases in a nonlinear fashion with increasing $P_{exc}$ from $0.21 \times 10^{-3}$ s$^{-1}$ for $P_{exc} = 5$ mW cm$^{-2}$ to $8.92 \times 10^{-3}$ s$^{-1}$ for $P_{exc} = 840$ mW cm$^{-2}$. Therefore, high $k_{seg}$ value corresponds to faster exponential growth of iodide-segregated domains. It is interesting to note that $k_{seg}$ in TC-MHP shows lower propensity for halide segregation than the reported MA-based mixed halide perovskite with a similar halide composition range ($0.2 < x < 0.5$).[8,13] Furthermore, a relationship between PL-redshift and halide composition variation is established using nonlinear bandgap variation as a function of halide composition ratio (Br, $x = 0–1.0$) under Vegard’s law expression and presented in Figure S4 (Supporting Information). The PL-emission values of mixed and segregated domains are used to fit the nonlinear bandgap variation curve as a function of
bromide concentration. Result shows that PL-redshift follows the nonlinear decrease in bandgap value with reduction in Br-concentration (enrichment in iodide) in TC-MHP film. It confirms that photoexcitation induces halide composition changes due to halide ion migration and leads to formation of segregated halide domains in TC-MHP film. Moreover, PL emission broadening during phase segregation may also occur due to the change in halide composition (decrease in bromide and enrichment of iodide content) as interpreted from Figure 1c. However, the PL width broadening with varying halide composition may also include other complex phenomena such as increased lattice disorder (due ion migration and related point defects). Furthermore, threshold excitation density of phase segregation \( P_{\text{th}}^{\text{seg}} \) is also calculated using different laser power densities at two different temperatures and found to be \( \approx 2.0 \text{ mW cm}^{-2} \) at 296 K and \( \approx 1.5 \text{ mW cm}^{-2} \) at 330 K (Figure S5, Supporting Information). In comparison to 296 K, the observed low \( P_{\text{th}}^{\text{seg}} \) value at 330 K reveals that lower-excitation density input is required for initiating the phase segregation process at higher temperature (faster segregation rate). The estimated \( P_{\text{th}}^{\text{seg}} \) value of TC-MHP is about 100 times higher as compared to reported values of \( \approx 30 \text{ and } \approx 40 \mu \text{W cm}^{-2} \) for MAPb(I\(_3\)Br\(_{0.3}\)) at 300 K,[6,26] which is meaningful as triple cation perovskites were developed for their increased robustness as compared to single cation perovskites.

2.2. Phase Segregation and Carrier Lifetime

To better understand the phase segregation process and gain an insight into the charge-carrier trapping dynamics in photoexcited TC-MHP film, we performed TCSPC measurements. Figure 2 shows the PL decay curves of red-shifted PL emission on a semi-logarithmic scale measured just after the laser excitation at different power-densities. The exponential fit of PL decay spectra measured on red-shifted PL emission position after light soaking of different excitation power-densities at room temperature (296 K) with fitted exponential decay curves. Inset: Lifetime components as a function of PL emission position.

![Figure 2](image_url)
that estimated difference in the conduction band energies for MAPbI₃ and MAPbBr₃ is significantly low (≈ 0.09 eV) while, the remaining difference in bandgap energy is mainly due to larger offset in their valence band energies (≈ 200 meV). Therefore, valence band alignment of iodide-rich domains would act as a major energy barrier for holes to move from the iodide-rich phase back to remaining mixed phase and/or bromide-rich domains. Thus, slow release of trapped charge carriers (mainly holes) from smaller-bandgap iodide-rich domains are likely to contribute in slower recombination and responsible for long carrier lifetime in phase segregated TC-MHP film.

2.3. Activation Energies of Halide Ion Migration and Recovery Kinetics under Darkness

The recovery kinetics of phase segregated TC-MHP film is studied under darkness at different temperatures. Initially, TC-MHP film is illuminated at high excitation power-density (840 mW cm⁻²) to achieve the phase segregated stage; then recovery process in PL emission is monitored at different time intervals using very low excitation power-density (<1 mW cm⁻²). Results reveal that phase segregation is reversible under darkness with nearly complete recovery of original PL emission spectra. In recovery process, PL emission peak recover back to original position as a function of time concurrently with decrease in PL intensity. It confirms the reduction of existing low-bandgap trapping sites of iodide rich domains due to remixing of halide ions under dark. The first-order phase segregation and recovery rate constants are determined from exponential fits of PL peak positions as a function of time and shown in Figures S6 and S7 (Supporting Information). During photo-induced segregation process, the slowest segregation rate constant (kₗ₀ = 0.29 × 10⁻³ s⁻¹) is observed at lower temperature (250 K). By contrast, increasing temperature leads to fastest segregation rate as extracted values are kₗ₀ = 0.81 × 10⁻³, 1.28 × 10⁻³, 2.39 × 10⁻³, 8.92 × 10⁻³, and 20.29 × 10⁻³ s⁻¹ for 260,

Figure 3. Spectroscopic observation of halide phase segregation in triple-cation mixed-halide (MA₀.₁₇ FA₀.₈₃)₀.₉₅Cs₀.₀₅ Pb(Ι₀.₈₃ Br₀.₁₇)₃ perovskite film. a) Time dependent red-shift in PL emission and evolution of PL spectra from iodide-rich domains under continuous wave excitation (Pₑₓc = 840 mW cm⁻²). b) Time dependent evolution of PL spectra from bromide-rich domains under continuous wave excitation (Pₑₓc = 840 mW cm⁻²). c) A comparative analysis of PL decay spectra from initial mixed stage and segregated iodide and bromide-rich domains. Inset: PL decay spectrum from bromide-rich domains shows faster decay time. d) Schematic illustrating the reversible phase segregation process where carrier trapping and recombination in segregated smaller bandgap iodide-rich domain generates red-shifted PL emission.
270, 280, 296, and 310 K, respectively. Similar trends in recovery rate constants are observed at different temperatures under darkness. In Figure 4a, results confirm that recovery dynamics is highly temperature sensitive. However, the overall recovery process in dark occurs on a much slower timescale than the photoinduced phase segregation process at a given temperature. At room temperature (296 K), segregated TC-MHP film recovers itself completely in 10 h under dark. Moreover, increase in temperature leads to faster recovery of segregated films as ≈5 h at 310 K, 2.5 h for 320 K and less than 2 h at 330 K, respectively. Similarly, the corresponding recovery rate constant \( k_{\text{rec}} \) is increased from \( 1.32 \times 10^{-4} \) to \( 6.32 \times 10^{-4} \) s\(^{-1} \), as film temperature raised from 296 to 330 K. However, decreasing temperature below 270 K, the recovery kinetics is almost frozen since the PL emission recovers in ≈24 h at 270 K with an very slow rate \( k_{\text{rec}} = 0.54 \times 10^{-4} \) s\(^{-1} \). Thus, decrease in temperature leads to reduction of halide ion mobility in TC-MHP film. Similar results are reported by our co-workers that ionic conduction is frozen below 263 K in MAPbI\(_3\) perovskite based solar cells.[31]

The activation energy of halide ion movement is estimated in two different photoexcitation induced phase—segregation \( (E_a^{\text{Seg}}) \) and dark-recovery \( (E_a^{\text{Rec}}) \) processes. In Figure 4b, an Arrhenius plot is constructed from the natural log of the rate constants \( (\ln k) \) obtained at different temperatures versus 1000/T, using the following Arrhenius equation

\[
\ln(k) = - \frac{E_a}{RT} + \ln(A)
\]

where \( E_a \) is the activation energy, \( R \) is the universal gas constant, and \( A \) is a pre-exponential factor. Activation energies of halide ion movement in two different processes are calculated by least square fitting of linear data points and reveal that activation energy in phase segregation process \( E_a^{\text{Seg}} \) is \( 0.46 \pm 0.02 \) eV which is found to be higher than in case of recovery process, \( E_a^{\text{Rec}} \approx 0.31 \pm 0.03 \) eV. Indeed, these calculated \( E_a \) values are consistent with the reported values of forward photosegregation activation energies of order ≈0.27–0.28 eV for MAPb\(_{(1-x)\text{Br}_x}\).[6,24] Moreover, the calculated \( E_a \) values are also consistent with prior studies of halide ion motion, where activation energies of halide vacancy Br\(^-\) \( (\Gamma^-) \) have been reported in between 0.09 and 0.27 eV (0.08 and 0.58 eV), respectively.[6,26,32,33] The differences in reported activation energy may in part be due to different local stoichiometry of perovskite structure (different halide concentration and incorporation of different cations) which influences the halide ion mobility. In present case, two different \( E_a \) values confirm the two different halide ion migration mechanisms of both phase segregation and recovery processes. The high \( E_a^{\text{Seg}} \) value in phase segregation process indicates that a high activation energy is required to alter the lead—halide bonds for initiating halide ion migration. On the other hand, comparably low \( E_a^{\text{Rec}} \) value in recovery process may be due to the fact that back-diffusion of halide ions is driven by halide concentration gradient[13] or entropically driven intermixing[34,35] to return the perovskite into a homogeneous condition. In other possible way, once the trapped charge carriers have recombined, the created local electric field vanishes and then the halide ions start back-diffusion to fill the vacancies left in the original position.

2.4. Low-Temperature Dynamics and Role of Exciton–Phonon Coupling

The temperature dependent PL measurements are performed for in-depth understanding of mixed and demixed stage (segregated phases) in TC-MHP film over a range of temperature \( (T = 300–10 \text{ K}) \). Figure 5a shows the temperature-dependent PL spectra of mixed stage (parent phase), on a semilogarithmic scale measured at low excitation power-density \(<1 \text{ mW cm}^{-2}\) and exhibits a single emission peak with low energy asymmetry at low-temperature (10 K). The low-energy asymmetry in PL emission is related to presence of bound excitons and shallow energy levels by iodine interstitials defects.[36,37]

\[
E_a^{\text{Seg}} = 0.46 \pm 0.02 \text{ eV}
\]

\[
E_a^{\text{Rec}} = 0.31 \pm 0.03 \text{ eV}
\]
Figure 5b shows the semilog scale temperature dependent PL spectra of demixed stage measured at high power-density (840 mW cm\(^{-2}\)). For demixed stage dynamics, first sample was illuminated at high power (840 mW cm\(^{-2}\)) at room temperature to create phase segregated domains and then cooled down to 10 K under continuous photoexcitation. In Figure 5b results show the presence of two emission peaks located at 1.574 and 1.534 eV at 10 K, where, low-energy emission peak (LE-peak) is related to iodide-rich phase and high-energy emission peak (HE-peak) corresponds to remaining mixed halide phase. Figure 5c shows the blue-shift response of PL emission in both mixed and demixed stages as a function of temperature. In mixed stage, PL emission peak experiences a blue-shift of 18 meV as rising the temperature from 10 to 80 K, while after phase transition to tetragonal phase, the PL peak exhibits a blue-shift of 24 meV when rising temperature from 150 to 300 K. In demixed stage, HE-peak follows the similar response and exhibits the blue-shift of \(\approx 15\) and \(\approx 25\) meV in orthorhombic (10–80 K) and tetragonal phase (150–300 K), respectively. However, LE-peak (iodide-rich domain) in demixed stage shows blue-shift of \(\approx 18\) meV in orthorhombic phase and large blue-shift of \(\approx 45\) meV in tetragonal phase when temperature goes from 150 to 300 K.

Furthermore, we carefully examine the temperature dependent PL linewidth broadening to study the contributions this behavior of perovskites is related to the thermal expansion of the lattice and stabilization of valence band energy.\(^{[38]}\) The response character of blue-shift with temperature changes near \(T \approx 150\) K in both stages, reveals the standard phase transition from orthorhombic to tetragonal phase in TC-MHP film. In mixed stage, PL emission peak experiences a blue-shift of 18 meV as rising the temperature from 10 to 80 K, while after phase transition to tetragonal phase, the PL peak exhibits a blue-shift of 24 meV when rising temperature from 150 to 300 K. In demixed stage, HE-peak follows the similar response and exhibits the blue-shift of \(\approx 15\) and \(\approx 25\) meV in orthorhombic (10–80 K) and tetragonal phase (150–300 K), respectively. However, LE-peak (iodide-rich domain) in demixed stage shows blue-shift of \(\approx 18\) meV in orthorhombic phase and large blue-shift of \(\approx 45\) meV in tetragonal phase when temperature goes from 150 to 300 K.
of charge-carrier interactions with phonons in both mixed and
demixed stages using Segall’s expression[39]

\[ \Gamma = \Gamma_{\text{inh}} + \Gamma_{\text{ac}} + \Gamma_{\text{LO}} + \Gamma_{\text{imp}} \] (2)

\[ \Gamma = \Gamma_{\text{inh}} + \gamma_c T + \frac{\gamma_{LO}}{\exp(h\omega_{LO}/k_B T) - 1} \] (3)

where \( \Gamma_{\text{inh}} \) is the inhomogeneous broadening contribution that
arises from scattering due to exciton–exciton interactions and
crystal disorder, and is temperature independent. In expression
(2), \( \Gamma_{\text{ac}} \) and \( \Gamma_{\text{LO}} \) are the homogeneous broadening terms resulting
from acoustic and longitudinal optical (LO)-phonon (Fröhlich)
scattering with charge carrier–phonon coupling strength of \( \gamma_c \)
and \( \gamma_{LO} \), respectively. Acoustic phonons, whose energy is much
smaller than \( k_B T \), mainly relate to the deformation potential
interaction which is linearly dependent on temperature. The
exciton LO-phonon coupling (Fröhlich coupling) coefficient is
associated with Bose–Einstein distribution of the LO-phonons,
where \( h\omega_{LO} \) is the optical phonon energy of weakly dispersive
LO-phonon branch. The FWHM of emission peaks are plotted as
a function of temperature along with the least square fitting
using Equation (3). The inset of Figure 5d demonstrates the
typical PL linewidth broadening pattern with temperature asso-
ciated with different scattering mechanisms. Result makes it
apparent that Fröhlich coupling to LO-phonons is the predomi-
nant cause of linewidth broadening with rising temperature.
Therefore, the scattering term from ionized impurities (\( \Gamma_{\text{imp}} \)) is
excluded in Equation (3) for the rest of the analysis. In mixed
stage, the calculated exciton LO-phonon coupling strength is
\( \approx 14.82 \text{ meV} \) with LO-phonon energy of \( \approx 22.8 \text{ meV} \). In demixed
stage, HE-peak follows a similar response of linewidth broad-
ening with increasing temperature; the corresponding coupling
strength and LO-phonon energy are \( \approx 38.86 \text{ and } 86 \text{ meV} \), respec-
tively. On the other hand, LE-peak shows large broadening in
linewidth with temperature and the corresponding Fröhlich cou-
pling strength and LO-phonon energy are \( \approx 46.70 \text{ and } 168 \text{ meV} \), respec-
tively. Therefore, strong exciton LO-phonon coupling is
observed in LE-peak of demixed stage, which may be due to the
strong interaction of phonons with long lived charge carriers
trapped in low energy iodide-rich domains.

3. Discussion

In the different scenario of photoexcitation induced phase seg-
regation in mixed halide perovskite, excited-charge carriers play
a main role either caused by light illumination[40,41] or by elec-
trical injection.[7,42–45] In present case, photoexcited phase seg-
regation would be initiated by charge separation arising from the
carrier trapping on surface defects sites and at the grain bound-
aries (e.g., electrons and leaving behind holes) which attribute
to the formation of local electric fields.[13,46–47] Furthermore, ion
migration induced segregated domains having a significant
offset in valence band and conduction band energies create a
degree of charge separation between the randomly distributed
segregated domains and remaining mixed halide phase, which
thus establishes a local electric field in the film. The high bar-
rrier in valence-band energies between both iodide-rich domains
and mixed halide perovskite act to draw holes away from the
electrons. Thus photoexcitation induced local electric field
promotes the degree of halide segregation and charge separa-
tion by further trapping of excited carriers into smaller-energy
bandgap iodide-rich domains in a feedback loop. The phase
segregated halide domains are stabilized under photoexcita-
tion when a steady state is reached. A high Fröhlich coupling
is observed in these iodide-rich domains due to strong interac-
tion of soft ionic lattice with long lived excited charge carriers.
It is reported that segregated halide clusters are stabilized by
the presence of a photogenerated trapped polaron in the hybrid
perovskites.[18] Therefore, high exciton LO-phonon coupling in
iodide-rich domains induces sufficient polaronic strain which is
able to locally change the free energy for halide demixing
and leads to stabilize the segregated domains under photoex-
citation. Eventually, concentration gradient of halide ions and
limited tunneling of photoexcited charge carriers into iodide-
rich domains are also limits to the further growth of segregated
domains under photoexcitation.

4. Conclusions

In summary, our findings provide new insights into the halide
ion migration and phase segregation effect in triple-cation
mixed-halide perovskite film when subjected to photoexcitation.
We demonstrate that laser-excitation induced phase segrega-
tion in TC-MHP film leads to formation of smaller-bandgap
iodide-rich and larger-bandgap bromide-rich domains where
iodide-rich domains efficiently traps the photoexcited-carriers,
revealing their dominant role in the origin of unusual long
carrier lifetime (larger than 1 \( \mu \)s). Moreover, we found that
phase segregation process is fully reversible under darkness
and recovery rate increases with rising temperature. It is also
shown that activation energy of halide ion migration is higher
during photoexcitation induced phase segregation process as
compared to recovery process under darkness. In addition, tem-
perature-dependent PL studies have been performed for better
understanding of exciton–phonon coupling in both mixed
and demixed (segregated) states. A high Fröhlich coupling is
observed in the segregated iodide-rich domains as compare to
demixed (parent) phase due to strong coupling of phonons with
long lived trapped charge carriers. Thus, high coupling strength
in segregated iodide-rich domains may be responsible for the
limited growth and stabilization of segregated halide domains
under photoexcitation. These findings will help to understand
the key issues of phase segregation in the mixed halide perov-
skite materials for the development of efficient solar cells and
optoelectronic devices.

5. Experimental Section

The triple-cation mixed halide hybrid perovskite thin films (thickness
\( \approx 380 \text{ nm} \)) were prepared using spin coating technique on glass
substrates. At first, for the materials’ synthesis, the \( (\text{MA})_{0.37} \text{FA}_{0.63}\)
\( \text{PbI}_2(0.83) \text{Br}_{0.17})_3 \) perovskite precursor solution was prepared by dissolving
\( \text{PbI}_2 (1.1 \text{ m}) \), \( \text{FAI} (1.0 \text{ m}) \), \( \text{PbBr}_2 (0.2 \text{ m}) \), \( \text{MABr} (0.2 \text{ m}) \) in a 44 wt%
mixture of anhydrous \( N,N \)-dimethylformamide (DMF) and dimethyl
sulfoxide (DMSO). The solution was kept on stirring and then 42 \( \mu \)L
(5 vol%) of CsI (1.5 m in DMSO) was added in the resultant solution at room temperature. The precursors of FAI and PbI₂ were purchased from Sigma Aldrich; MABr from Solaronix; PbI₂ and CsI from Alfa Aesar. Before thin film coating, glass substrates were initially cleaned in deionized water, acetone, 2-propanol sequentially by ultrasonication followed by drying in dry nitrogen gas. In general, a dynamic dispense is preferred in synthesis process as it is a more controlled process that produces less substrate-to-substrate variation. The precursors of FAI and PbI₂ were purchased (5 vol%) of CsI (1.5 m in DMSO) was added in the resultant solution at room temperature. The precursors of FAI and PbI₂ were purchased from Sigma Aldrich; MABr from Solaronix; PbI₂ and CsI from Alfa Aesar. Before thin film coating, glass substrates were initially cleaned in deionized water, acetone, 2-propanol sequentially by ultrasonication followed by drying in dry nitrogen gas. 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The surface morphology measurement of prepared TC-MHP films was carried out using field-emission scanning electron microscopy (FE-SEM, JSM-7000 F) at CNRS-CSNSM, Orsay. The UV-visible absorption measurements were performed using Cary 5000 UV-VIS-NIR double beam spectrophotometer. Photoluminescence spectroscopy studies on mixed halide perovskite sample were performed in reflection geometry with a Horiba-JY Quantamaster spectrometer equipped with a R13456 photomultiplier (Hamamatsu) detector. A continuous-wave fiber-coupled laser diode (MDL-III-454 nm/90-800 mW) from CNI was used; it had a wavelength of $\pm 454 \pm 5$ nm at different excitation powers and was focused on the sample on a spot size of $\pm 1.75$ mm diameter. The TCSPC measurements were carried out using NanoLED source (Horiba), which had an excitation of 482 nm and was pulsed at 25 kHz. For low-temperature measurements the samples were glued with silver paste in an optical closed-cycle cryostat from ARS Instruments equipped with two quartz windows.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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