# The $FA_{1-x}MA_xPbI_3$ System: Correlations among Stoichiometry Control, Crystal Structure, Optical Properties, and Phase Stability

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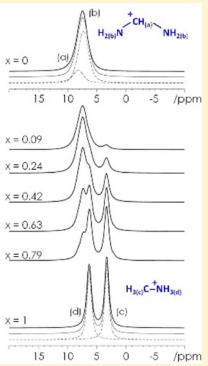
Supporting Information

**ABSTRACT:** The $FA_{1-x}MA_xPbI_3$ solid solution has been carefully investigated in terms of the MA/FA stoichiometry, crystal structure, and optical properties. This work allowed for the determination of reliable correlations between the amount of protonated amine and the physicochemical properties. The deleterious effect of aging on the mixed MA/FA composition was observed by diffraction and optical measurements, showing progressive phase separation within the samples.




## INTRODUCTION

Mixed methylammonium/formamidinium (MA/FA) lead halide hybrid perovskites have recently attracted significant interest because of the very high efficiencies of perovskite solar cells (PSCs) employing such semiconductor layers, which exhibit strong band-gap photoabsorption.[1−4] One of the reasons for using these mixed systems is the need to stabilize the black phase ($\alpha$) of formamidinium lead iodide (FAPI) at room temperature. In fact, at room temperature, $FAPbI_3$ crystallizes in a hexagonal yellow phase ($\delta$-phase) in the space group $P6_3mc$, whereas the perovskite $\alpha$-phase, with an optimal band gap of about 1.47−1.49 eV, is achieved by crossing the phase transition above 165 °C.[5] The black $\alpha$-phase crystallizes in a cubic symmetry with space group $Pm\bar{3}m$. Interest in the use of FAPI-based perovskites is also related to the facts that (i) the larger FA cation leads to more symmetric perovskites than for the $MAPbI_3$ (MAPI) phase (which is tetragonal at room temperature), (ii) the smaller band gap of FAPI allows for near-IR absorption, and (iii) perovskites containing FA cations have improved stability.[6] Most of the solid solutions investigated so far are based on FAPI systems with partial substitution of Br for the I halogen and mixed MA/FA lead iodides.[1−6] The present work focuses on the latter system.

The $FA_{1-x}MA_xPbI_3$ system has been the subject of a number of studies in the past few years reporting very high efficiencies for PSCs employing such phases.[2,3,6−8] For example, Pellet et al.[2] explored several compositions of the $FA_{1-x}MA_xPbI_3$ system using samples prepared in the form of films by infiltrating $TiO_2$ with $PbI_2$, dripping these films in mixed FAI and MAI solutions, and then performing a thermal treatment. According to the observed XRD patterns, each of the samples still contained a significant amount of $PbI_2$, no lattice parameters were provided, and only relative shifts from the peaks of FAPI were reported. In addition, the starting FAPI sample consisted of a mixture of $\alpha$ and $\delta$ phases with a band-gap value, $E_g$, for pure FAPI reported to be 1.530 eV, which is higher than most of the values reported in the current literature (about 1.48 eV). Moreover, the $E_g$ values reported for phases with very different *nominal* stoichiometries, such as $FAPbI_3$ and $FA_{0.4}MA_{0.6}PbI_3$, were the same.[2] Such anomalous trends might be due to the peculiar growth kinetics of the films prepared by the reported method, leading to a difference between the nominal and real compositions. In the work of Binek et al., XRD investigation on powdered samples revealed the stabilization of the cubic phase of FAPI when the amount of FA was greater than 20%, whereas for lower stoichiometries, the solid solution maintained the tetragonal symmetry of MAPI.[6] The authors also reported no lattice shrinkage upon the replacement of about 13% of the FA with MA and confirmed the stabilization of the $\alpha$-phase induced by MA doping already at relatively low amounts. Moreover, in ref 6, for all of the levels of MA doping in $\alpha$-FAPI (5%, 10%, and 15% MA), the band gap remained the same, at about 1.52 eV.[6] A very recent work by Jacobsson et al. presented a comprehensive investigation of the $FA_{1-x}MA_xPbI_3$ system.[3] In that case, the band-gap value of FAPI was reported

to be 1.52 eV, the trend of the cell volume as a function of MA content did not follow a linear trend (as predicted by Vegard's law for solid solutions), and no information was provided on the real stoichiometries of the prepared films. It is surprising to see how large the spread is in the reported results for the $FA_{1-x}MA_xPbI_3$ system in terms of the crystal structure and optical properties. Some of the discrepancy might arise from the presence of powdered and thin-film samples and, for the latter, from the fact that their preparation by means of different routes can lead to compositions that differ from the nominal ones. Another relevant point might be the actual phase stability of FA-rich phases. Concerning this last point, the literature does not provide any information about the time stability of the $\alpha$-phase within the $FA_{1-x}MA_xPbI_3$ system. It is well-known that the pseudocubic black phase of pure FAPI can be stabilized at room temperature after a thermal treatment of the hexagonal phase above 165 °C, but that this phase, being a metastable phase, progressively converts to the yellow phase with time.[5] A very recent work addressed the structural behavior of this solid solution and found that the cubic perovskite phase is stable up to $x = 0.8$, whereas the mixed phase is tetragonal for higher stoichiometries. No information has been provided about the phase stability of mixed phases, even though express mention is made of the fact that pure FAPI is not stable in the perovskite phase.[9]

Considering the significant interest in the $FA_{1-x}MA_xPbI_3$ mixed system related to the high efficiencies of the PSCs employing such materials as absorbers, in the present article, we report a detailed investigation of the crystal structure, optical properties, and phase stability of this solid solution as a function of $x$ carried out on samples with well-defined cation stoichiometries (i.e., $x$ values), as determined by NMR spectroscopy.

## EXPERIMENTAL METHODS

**Material Preparation.** Samples of general formula $FA_{1-x}MA_xPbI_3$ were synthesized according to a general procedure that we developed previously.[10,11] In a typical synthesis, a proper stoichiometric amount of lead acetate is dissolved in excess HI under continuous mechanical stirring under a nitrogen atmosphere. Then, the solution was heated to 100 °C, and the corresponding amines (methylammonium and/or formamidinium in water, 40 wt %) were added in the correct stoichiometric amounts. The solution was then cooled to 46 °C at 1 °C/min, until the formation of a precipitate, which was immediately filtered and dried under a vacuum at 60 °C overnight. All reagents were purchased from Sigma-Aldrich in pure form and were used without any further purification.

**X-ray Diffraction.** The crystal structures of the samples were characterized by room-temperature Cu-radiation Powder X-ray diffraction (XRD) on a Bruker D8 diffractometer. Scans were performed in the 10−90° range, with a step size 0.02° and a counting time of 8 s/step. Data were fitted by the Rietveld method using the FullProf suite of programs.[12]

**Diffuse Reflectance Measurements.** The optical diffuse reflectance spectra of the different perovskites were measured from 0.8 to 4.5 eV (250−1500 nm, in steps of 1 nm) on a Varian Cary 6000i spectrophotometer equipped with an integrating sphere. For this type of measurement, polycrystalline powders were compacted into pellets of about 10 mm in diameter, and reflectance spectra were calibrated using a standard reference disk.

**NMR Spectroscopy.** $^1$H solid-state NMR room-temperature spectra were acquired on a 9.4 T ($^1$H = 400.16 MHz) Bruker Avance III spectrometer with the use of TopSpin 3.1 software; spectra were collected with a 4-mm magic-angle-spinning (MAS) probe under 8 kHz spinning conditions. $^1$H quantitative one-pulse experiments were performed with a pulse length of 4.65 $\mu$s, a recycle delay of 120, and 16 scans. The pulse length and recycle delay were carefully calibrated before the acquisition of the final spectra to ensure the full relaxation of the magnetization and to fulfill the conditions for quantitative data acquisition. Chemical shifts are referred to tetramethylsilane (TMS) using adamantine as a secondary standard. The analysis of the obtained data was performed using the DMFit program.[13]

**Differential Scanning Calorimetry (DSC).** DSC measurements were performed in a Q2000 apparatus from TA Instruments by heating about 25 mg of powder from −90 to 200 °C in Al open crucibles under a flux of nitrogen.

## RESULTS AND DISCUSSION

Samples synthesized according to the experimental procedure were first investigated by solid-state $^1$H NMR spectroscopy to determine their *actual* FA/MA ratios. $^1$H MAS spectra for the whole $FA_{1-x}MA_xPbI_3$ series are reported in Figure 1, together with the corresponding attributions and the best fits for the two end members.

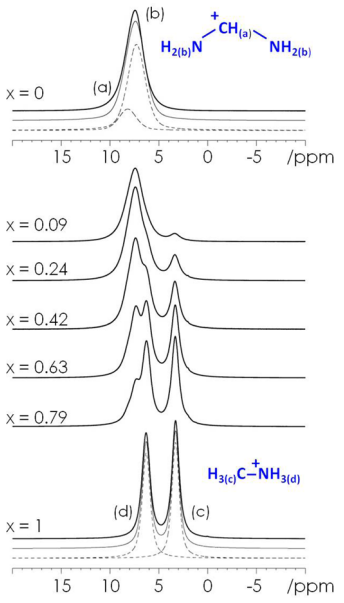



**Figure 1.** Solid-state NMR spectra of the $FA_{1-x}MA_xPbI_3$ solid solution. Dashed lines represent fit contributions, and the light solid line represents the overall best fit to the experimental spectra.

The spectrum of the FAPI composition presents two peaks at 7.53 and 8.87 ppm with a relative ratio of 4:1, and these signals can be attributed to the $-NH_2$ and $-CH$ protons, respectively. Similar chemical shifts were observed for the NMR signal (liquid) of the $HC(NH_2)_2I$ and FAI precursors used for the synthesis of FAPI.[7,14] Similarly, the attribution of the MAPI composition was made considering the presence of the two resonances at 6.22 and 3.28 ppm with a ratio of 1:1. These two signals have been previously correlated with the $-NH_3^+$ and $-CH_3$ protons, respectively, of the series $MAPbX_3$ (X = I, Br, Cl).[15] The signals of the two MA and FA species were only

partially overlapping, and at the experimental MAS speed (8 kHz), the observed lines were sufficiently sharp and the acquisition parameters (pulse length and recovery delay) were optimized to obtain fully relaxed signals. Under these conditions, the quantitative analysis of the mixed samples was possible, and the results are reported in Table 1.

**Table 1. Nominal Composition and Composition Determined from Analysis of $^1$H NMR Spectra for the $FA_{1-x}MA_xPbI_3$ Series**[a]

| FA/MA ratio | |
|---|---|
| nominal | NMR-determined |
| 1.0:0.0 ($x$ = 0, pure FAPI) | 1.0:0.0 |
| 0.8:0.2 | 0.91:0.09 |
| 0.7:0.3 | 0.76:0.24 |
| 0.5:0.5 | 0.58:0.42 |
| 0.3:0.7 | 0.37:0.63 |
| 0.1:0.9 | 0.21:0.79 |
| 0.0:1.0 ($x$ = 1, pure MAPI) | 0.0:1.0 |

[a]Best-fit error < 5%.

Analysis of the NMR data revealed that the actual compositions of the samples were slightly different from the nominal compositions used for the synthesis (see the Experimental Methods section), as the MA amount was always slightly overestimated. This result suggests that proper control of the actual MA/FA ratio for this and related systems is a key aspect to be checked after material synthesis, also considering that most of the synthetic procedure is carried out in solution by dripping methods where a proper control of precursor stoichiometry might be hard to achieve. A possible origin of the difference between the nominal and measured stoichiometries might be the different solubilities/reactivities of the MA and FA precursors in solution.

$^1$H and $^{13}$C solid-state NMR techniques have been exploited for the study of the phase transitions between different polymorphs for MA lead halide perovskites series,[15] whereas $^1$H liquid NMR data for mixed MA/FA iodide precursors have been presented to confirm the alloying of MA and FA in MA-stabilized FAPI.[14] Nevertheless, to our knowledge, this is the first time that $^1$H solid-state NMR spectroscopy has been used to address the problem of the quantitative determination of mixed FA/MA compositions. Based on the NMR results, the $x$ values in the $FA_{1-x}MA_xPbI_3$ solid solution (within the estimated standard deviations) were 0, 0.09, 0.24, 0.42, 0.63, 0.79, and 1.0.

The X-ray diffraction (XRD) patterns of all of the samples investigated in the present work are reported in Figure 2.

All of the samples were single-phase, and for those from $x$ = 0 to $x$ = 0.79, the unit cell was in agreement with the crystal structure of the $\alpha$-phase (black perovskite) of the FAPI end member. In the inset of Figure 2, the XRD pattern of FAPI is compared with the literature reference pattern using the $Pm\bar{3}m$ space group, and this black sample was obtained by annealing the yellow, as-synthesized, FAPI sample at 185 °C for 1 h. On the other hand, MAPI has a diffraction pattern consistent with the reported tetragonal structure in the $I4mc$ space group.[10] The reported patterns show similar peak shapes and small full width at half-maximum (fwhm) as well, indicating good crystallinity of the phases. Small intensity variations are due to possible preferential orientation effects during sample preparation.

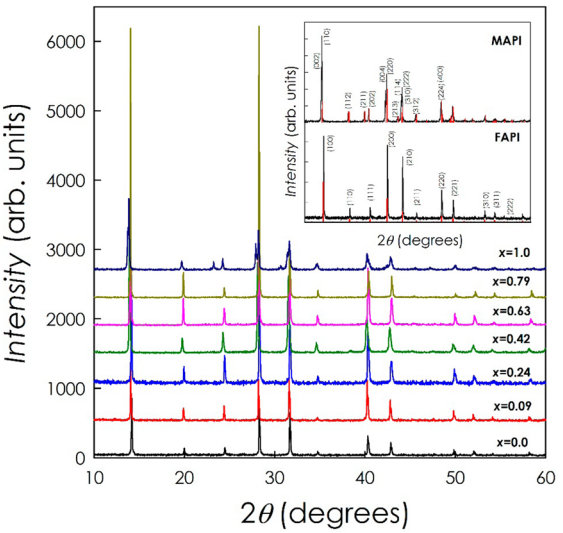



**Figure 2.** XRD patterns for samples of the $FA_{1-x}MA_xPbI_3$ solid solution. Patterns are vertically shifted to clarify viewing. Inset: XRD patterns of the two end members of the solid solution, namely, FAPI and MAPI, together with the reflection positions from the literature patterns and Miller indices (red vertical bars).

It is interesting to observe that even a small amount of the larger FA cation (ionic radii have been estimated to be 253 and 217 pm for FA and MA, respectively[16]) in the solid solution, as in the $x$ = 0.79 sample, gave rise, at the end of the synthesis, to a sample with the cubic crystal structure. Moreover, for the low-MA-containing samples, black perovskite samples were obtained at the end of the synthesis without the need for any thermal treatment, as in the case of the pure FAPI sample. This means that very low MA contents, such as in the $x$ = 0.09 sample, are already able to destabilize the hexagonal phase. However, as shown later in the text, for small $x$ values, the perovskite phase is not stable with time. By using the effective radii of the organic cations, $r_{eff}$ = 217 pm for MA and $r_{eff}$ = 253 pm for FA, to calculate a tolerance factor, it was found that $\alpha$ = 0.91 for $MAPbI_3$ versus 0.98 for $FAPbI_3$.[9] Both values should give a perovskite structure that can be observed for 0.81 < $\alpha$ < 1.01, which is not the case for $\delta$-$FAPbI_3$. It is clear that the spherical approximation used to estimate the effective radii of the organic cations is too simplistic in the present case and that the shape and hydrogen-bonding capabilities of each organic species play crucial roles in the definition of the structural properties of these hybrid perovskites.[9]

Panels a and b of Figure 3 show the trends in the cell volume ($V$) and cubic lattice parameter, respectively, of the $FA_{1-x}MA_xPbI_3$ solid solution, as obtained from Rietveld refinement of the diffraction data, as a function of the $x$ value. The data are reported as cell volumes per formula unit, considering that the $Pm\bar{3}m$ and the $I4mc$ space groups have different $Z$ values. In the Supporting Information are reported the values of $a$ and $V$ as obtained from the Rietveld refinement of the patterns, together with an illustrative refined pattern.

Figure 4 shows the differential scanning calorimetry (DSC) measurements for all of the samples except MAPI between −90 and 200 °C (from −90° to 100 °C for MAPI), showing the well-known tetragonal-to-cubic phase transition for MAPI at about 57 °C and the hexagonal-to-cubic phase transition for the

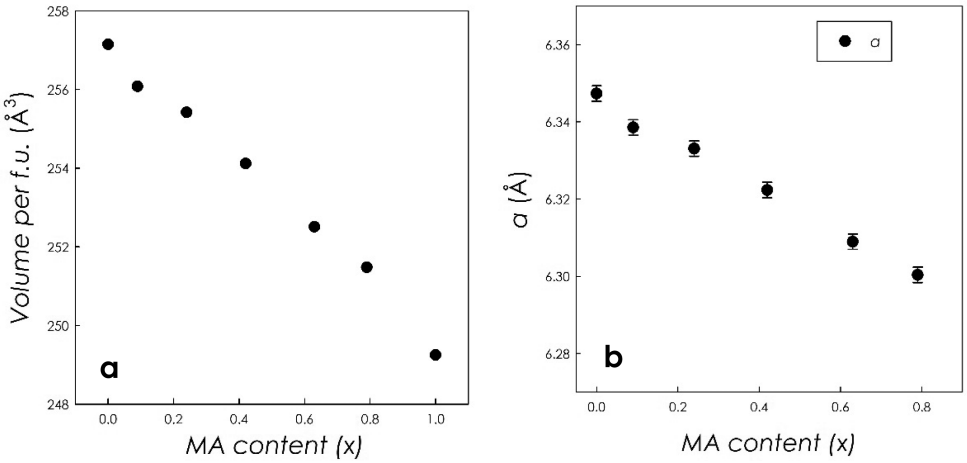



**Figure 3.** (a) Cell volume and (b) cubic lattice parameter of the $FA_{1-x}MA_xPbI_3$ solid solution as functions of $x$.

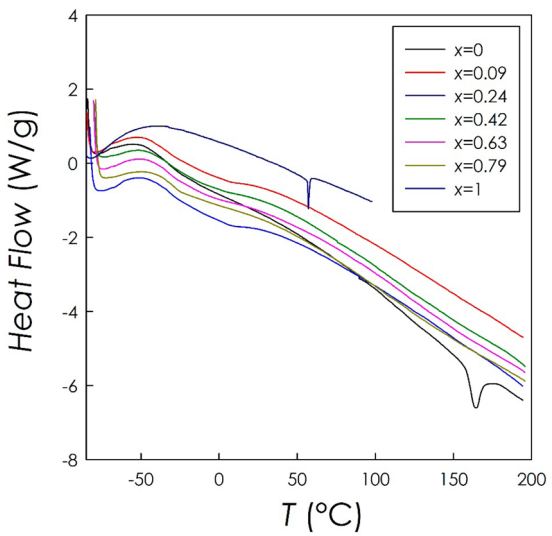



**Figure 4.** DSC measurements of samples of the $FA_{1-x}MA_xPbI_3$ solid solution. Data for MAPI have been shifted by +1 to clarify the view of the peak corresponding to the tetragonal-to-cubic phase transition.

as-prepared yellow FAPI at about 165 °C. As expected and in agreement with the XRD results, none of the intermediate compositions present any peaks in the investigated temperature range because the perovskite phase was stabilized by the doping. The results for the thermal stability of the $FA_{1-x}MA_xPbI_3$ solid solution, determined by means of DSC and not yet reported in the current literature, indicate that the absence of phase transitions is a beneficial aspect of the use of these mixed phases.

Returning to the data of Figure 3, one can see that linear decreases of both the cell volume (Figure 3a) and the cubic $a$ lattice parameter (Figure 3b) occurred with increasing amount of the smaller MA cation in the solid solution (about 3% volume shrinkage). This behavior is consistent with Vegard's law of solid solution formation, which could be anticipated for this system but which is confirmed by the present structural data, DSC data, and optical absorbance results (see later in the text). Other recent literature results based on thin films have indicated slightly different trends. A nonlinear trend, for example, was found in ref 3, where, for example, the $x$ = 0 and 0.2 samples had the same cell volume and a significant decrease of $V$ was found for the $x$ = 0.8 sample. Binek and co-workers considered the doping of the FAPI phase with 5%, 10%, and 15% MA cation, and their mixed samples, after synthesis, were rich in the hexagonal FAPI phase for all doping levels, a with reduction in the amount of this phase with increasing methylammonium doping.[6] In their article, they indicated no shrinkage of the unit cell upon the replacement of FA with MA, even for stoichiometries up to about $x$ = 0.13. It is important to emphasize that, in both of the works cited here, the thin-film samples were prepared by immersion of the substrate in mixed FAI/MAI solutions and cannot be directly compared to the powdered samples prepared and characterized by the synthetic method used in the present work. In particular, whereas the synthetic approach used herein provides strict control over the stoichiometry, the earlier methods can lead to phases with different stoichiometries. However, the results reported in this work can be used as a reference to rationalize the results obtained for thin films.

The stability as a function of time of FAPI (black) perovskites is well-known and was investigated previously.[6] In general, once the $\alpha$-phase has been stabilized by thermal annealing at about 180−185 °C, this phase remains stable in the black form for several days with the progressive formation of the yellow hexagonal phase, which is usually observed after 10 days regardless of storage in a vacuum or inert gas.[6] However, no data are actually available on the time stability of mixed MA/FA systems, which are considered to be very efficient absorbers for use in PSCs. Figure 5 reports the XRD patterns of the $x$ = 0 (FAPI), $x$ = 0.09, and $x$ = 0.24 samples immediately after synthesis and after 10 days of storage in a glovebox and in dark glass containers (aged samples). The blue vertical bars in the plot correspond to the reference pattern for the black $\alpha$-FAPI, whereas the orange vertical bars correspond to the hexagonal $\delta$-FAPI reference pattern.

FAPI developed a remarkable amount of hexagonal phase after the considered time frame, in agreement with previous data. $FA_{0.91}MA_{0.09}PbI_3$ also developed a significant fraction of the $\delta$-phase, whereas for $FA_{0.76}MA_{0.24}PbI_3$, the amount of the $\delta$-phase was very small. For stoichiometries with $x$ > 0.24, no traces of the hexagonal phase were detected. It should be noted that these preliminary results are related to optimal storage conditions and relatively short-time evaluations after synthesis. However, this evidence strongly suggests that, whereas the complete substitution of FA by MA (or other cations) directly

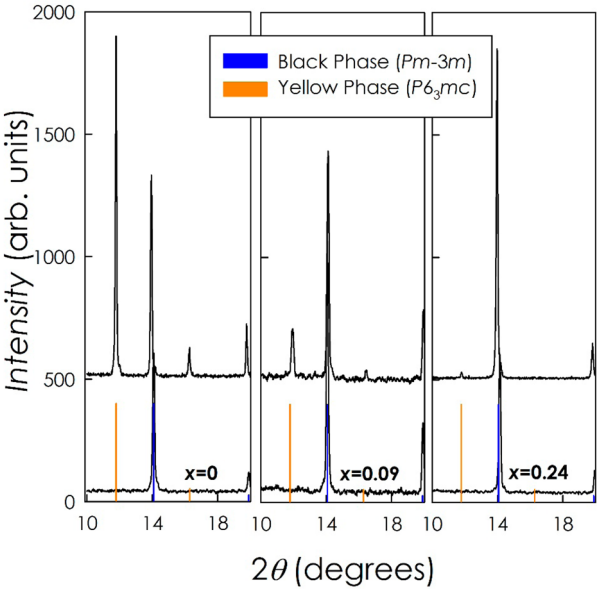



**Figure 5.** XRD patterns of the $x$ = 0, 0.09, and 0.24 samples of the $FA_{1-x}MA_xPbI_3$ solid solution (bottom) immmediately after synthesis and (top) after 10 days of storage. Orange and blue vertical bars correspond to the reference patterns of the hexagonal and cubic structures, respectively, of FAPI.

stabilizes the (cubic) perovskite phase at room temperature after the synthesis, care must be taken when considering the stability of MA/FA mixed phases. In fact, in this work, we have shown that the time stability of cubic FAPI-based lattices stabilized by low cation replacement might be poor. This suggests that other mixed systems such as Cs-doped and I-/Br-doped FAPI perovskites should be re-evaluated concerning their phase stability with time.[17,18]

For the samples investigated in this work, optical measurements were carried out to define the band-gap values as a function of (real) stoichiometries. The vis−NIR diffuse reflectance spectra and the trends in the band gaps as functions of $x$ are reported in panels a and b, respectively, of Figure 6. [The $x$ = 0 (FAPI) values refer to the cubic "black" phase.] The $E_g$ values were obtained from the extrapolation of the linear part of $[F(R)h\nu]^2$, where $F(R)$ is the Kubelka−Munk function $F(R) = (1 - R)^2/2R$.[19,20]

FAPI perovskite was found to have a band-gap value of about 1.48 eV, in agreement with the literature, and with increasing amount of MA, the $E_g$ value increased to about 1.53 eV (again in agreement with previously reported values), thus indicating a relatively small shift with MA substitution for FA in the $FA_{1-x}MA_xPbI_3$ solid solution.[1,4,7]

Figure 6c reports the evolution of the diffuse reflectance spectra of aged samples, analogous to those presented in Figure 5 for the XRD characterization. It can be observed that, for $x$ = 0 and 0.09, the spectra showed a shift of the band gap to higher values when the samples were left under optimal storage conditions for several days. On the other hand, for the sample with $x$ = 0.24 and greater, there was no shift of the band gap (the dotted curve is exactly superimposed on the solid curve for the as-prepared sample), suggesting a greater stability of the material, at least in this time frame. The results for the optical measurements of aged samples are in very good agreement with the phase separation observed for the aged samples by means of XRD: The samples exhibiting a shift to higher values of $E_g$ are the same as those showing the separation of the hexagonal $\delta$-phase with time (see Figure 5). This agreement clearly indicates that the time variation of the optical properties of the samples within the $FA_{1-x}MA_xPbI_3$ solid solution can be directly correlated with the phase stability of the same samples and that this change in the absorption properties might have a crucial effect on the performance of PSCs employing such materials as absorbing layers. It should be noted that, for low $x$ values, the degradation was found to be very fast (within a few days under optimal storage conditions) and that, for samples with higher $x$ values, the same behavior might also occur at longer times. Further investigation in this regard is strongly needed for most of the mixed doped systems of hybrid perovskites. Finally, based on the observation of an increase in band-gap values due to phase separation within the samples, it can be suggested that literature data where the band-gap values for FAPI samples are reported to be very high and on the order of 1.53−1.55 eV might be due to significant phase separation occurring within the samples.

## CONCLUSIONS

In this work, we have deeply investigated the $FA_{1-x}MA_xPbI_3$ system, defining its crystal structure, phase stability, and optical properties as functions of the actual $x$ values determined by means of solid-state NMR spectroscopy. The collected results confirm the formation of a solid solution within this mixed system. By properly controlling the relative MA and FA amounts, we obtained reliable evidence of structural changes occurring upon doping. In addition, we characterized the time stability of mixed systems, highlighting a phase separation

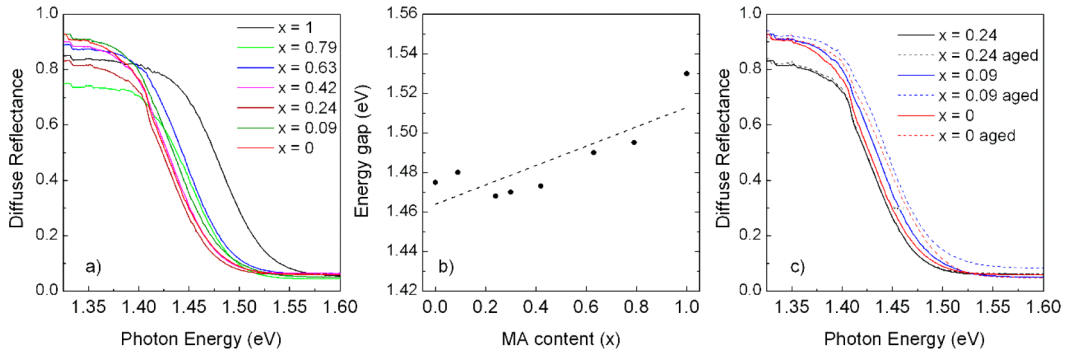



**Figure 6.** (a) Diffuse reflectance spectra for the $FA_{1-x}MA_xPbI_3$ solid solution; (b) trend in the energy gap as a function of $x$ for the $FA_{1-x}MA_xPbI_3$ solid solution; and (c) diffuse reflectance spectra of as-prepared and aged samples for $x$ = 0 (FAPI), 0.09, and 0.24.

phenomena in aged samples leading to the formation of the δ-phase. The optical properties were also found to scale with the real $x$ values, and the time degradation of the samples resulted in an increase of the band-gap values due to the phase separation observed by diffraction. These results, providing a reliable definition of structure−property correlations in the $FA_{1-x}MA_xPbI_3$ system for well-defined doping levels, demonstrate the significant stability issue of such mixed systems that could also be a key issue for other mixed systems based on FAPI perovskite. These effects might, in turn, have detrimental effects on the performance of PSCs based on these materials as active layers.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b01250.

Table reporting the structural data for the $FA_{1-x}MA_xPbI_3$ solid solution ($x$ = 0, 0.09, 0.24, 0.42, 0.63, 0.79, and 1.0) as determined from the Rietveld refinement of the patterns and illustrative refined pattern for FAPI (PDF)

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### Notes

The authors declare no competing financial interest.

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