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

*By Ambra Pisanu[a], Chiara Ferrara[a], Paolo Quadrelli[a], Giorgio Guizzetti[b], Maddalena Patrini[b], Chiara Milanese[a], Cristina Tealdi[a], Lorenzo Malavasi[a,]**

[a]Department of Chemistry and INSTM, Viale Taramelli 16, Pavia, 27100 (Italy); Department of Physics and CNISM, Via Bassi 6, Pavia, 27100 (Italy)

Corresponding Author

*Lorenzo Malavasi, email: lorenzo.malavasi@unipv.it; tel. +39 382 987921

Abstract

The $FA_{1-x}MA_xPbI_3$ solid solution has been carefully investigated for what concerns the MA/FA stoichiometry, crystal structure and optical properties. This work allows a reliable correlation between protonated amines amount and physico-chemical properties. The deleterious aging effect of mixed MA/FA composition is demonstrated by diffraction and optical measurements showing the progressive phase separation within the samples.

Introduction

Mixed methylammonium-formamidinium (MA-FA) lead halides hybrid perovskites have recently attracted significant interest in the community due to very high efficiencies shown by the perovskites solar cells (PSC) employing such semiconductor layers which exhibit strong bandgap photoabsorption.[1-4] One of the reasons of using these mixed systems is the need of stabilizing the black phase (α) of formamidinium lead iodide (FAPI) at room temperature (RT). As a matter of fact, $FAPbI_3$, at RT, crystallizes in a hexagonal yellow phase (δ-phase) in the space group $P6_3mc$, while the perovskite α-phase, with an optimal band-gap around 1.47-1.49 eV is achieved by crossing the phase transition above 165°C.[5] The black α-phase crystallizes in a cubic symmetry with space group Pm-3m. The interest in the use of FAPI-based perovskites is also related to the fact that: i) the larger FA cation leads to more symmetric perovskites with respect to $MAPbI_3$ (MAPI) phase (which is tetragonal at room temperature); ii) the smaller band-gap of FAPI allows the near-IR absorption, and iii) perovskites containing FA cation have an 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 object of a certain number of studies in the last few years reporting very high efficiencies for PSC employing such phases.[2, 3, 6-8] Pellet *et al.*, for example, explored several compositions in the $FA_{1-x}MA_xPbI_3$ system on samples prepared in the form of film by infiltrating TiO_2 with PbI_2, dripping such films in mixed FAI and MAI solutions, and then performing a thermal treatment. From their XRD patterns all the samples still contain a significant amount of PbI_2 and no lattice parameters are provided and only relative shifts from the peaks of FAPI are reported. In addition, the starting FAPI shown is a mixture of α and δ phases with the band-gap value E_g reported for pure FAPI being 1.530 eV, which is higher with respect to most of the values reported in the current literature (around 1.48 eV).

Morevoer, the E_g values for phases with very different *nominal* stoichiometries, *e.g.* $FAPbI_3$ and $FA_{0.4}MA_{0.6}PbI_3$, are the same.[2] Such anomalous trends may be due to the peculiar growth kinetics of the films prepared with the reported method leading to a difference between 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 is greater than 20%, while for lower stoichiometries the solid solution keeps the tetragonal symmetry of MAPI.[6] The Authors also report no lattice shrinkage by replacing about 13% of FA with MA and confirm the stabilization of the α-phase induced by MA doping already at relatively low amounts. Moreover, in ref. 6, for all the MA-dopings in the α-FAPI (5, 10, and 15% of MA) the band-gap is the same and around 1.52 eV.[6] A very recent work by Jacobsson *et al*. presents a comprehensive investigation of the $FA_{1-x}MA_xPbI_3$ system.[3] In this case the band-gap value of FAPI is reported to be 1.52 eV and the trend of the cell volume as a function of MA content does not follow a linear trend (as predicted by the Vegards' law for solid solutions) and no information is provided on the real stoichiometries of the prepared films. It is surprising to see how big is the spread in the reported results related to the $FA_{1-x}MA_xPbI_3$ system for what concerns the crystal structure and the optical properties. Some of this discrepancy may come from the presence of powdered and thins films samples and, for the latter, their preparation by means of different routes that may lead to different composition with respect to the nominal ones. Another relevant point may be the actual phase stability of FA-rich phases. Concerning this last point, the actual literature does not provide any information about the time-stability of the α-phase within the $FA_{1-x}MA_xPbI_3$ system. It is well known that the pseudo-cubic 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 progressively converts to the yellow phase with time being a metastable phase.[5] A very recent paper addressed the structural behavior of this solid solution and found that the cubic perovskite phase is stable up to x=0.8 while for higher stoichiometries the mixed phase is tetragonal. No information is provided about the phase stability of mixed phases even though express mention is done to 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 PSC employing such materials as absorbers, in the present work we report a detailed investigation on the crystal structure, optical properties and phase stability of this solid solution as a function of x carried out on samples with a well-defined cation stoichiometry, *i.e.* x-value, as determined by NMR spectroscopy.

Results and Discussion

Samples synthesized according to the experimental procedure have been first of all investigated by solid state NMR ^{1}H spectroscopy in order to determine their *actual* FA:MA content. ^{1}H MAS spectra for the whole $FA_{1-x}MA_xPbI_3$ series are reported in Figure 1 together with the corresponding attribution and the best fit for the two end members.

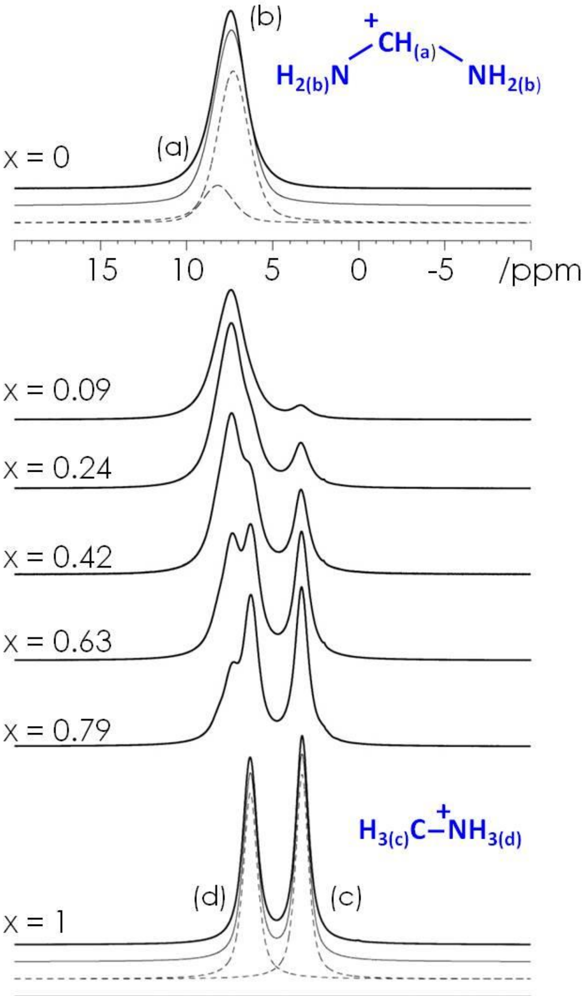

Figure 1. Solid state NMR spectra of the $FA_{1-x}MA_xPbI_3$ solid solution: dashed lines represent fit contributions and the solid light line the overall best-fit to the experimental spectra.

The spectrum of the FAPI composition presents two peaks at 7.53 ppm and 8.87 ppm with relative ratio 4:1 and these signals can be attributed to the –NH_2 and –CH protons, respectively. Similar chemical shifts have been observed for the NMR signal (liquid) of the $HC(NH_2)_2I$ and FAI precursors used for the synthesis of FAPI.[7,10] Similarly, the attribution for the MAPI composition has been made considering the presence of the two resonances at 6.22 and 3.28 ppm with ratio 1:1. These two signals have been previously correlated, respectively, to the –NH_3^+ and – CH_3 protons for the series $MAPbX_3$ (X = I, Br, Cl).[11] The signals of the two MA and FA species are only partially overlapping and under the experimental MAS speed (8 kHz) the observed lines are sufficiently sharp and the acquisition parameters (pulse length and recovery delay) have been optimized to obtain fully relaxed signals. Under these conditions the quantitative analysis of the mixed samples is possible and the results are reported in Table 1.

Nominal ratio FA:MA	NMR determined ratio FA:MA
1 (pure FAPI)	1
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 (pure MAPI)	0

Table 1: Nominal composition and composition determined from analysis of ^1H *NMR spectra for the* $FA_{1-x}MA_xPbI_3$ *series. Best fit error < 5%.*

The analysis of the NMR data reveals that the actual composition of the samples is slightly different with respect to the nominal composition used for the synthesis (see the Experimental) as the MA amount is always slightly overestimated. This result suggests that a proper control of the actual MA/FA ratio on this and correlated systems is a key aspect to be checked after materials' synthesis also considering that most of the synthetic procedure are carried out in solution by dripping methods where a proper control of precursors stoichiometry may be hard to be achieved. Possible origin of this difference between the nominal and measured stoichiometries may come from the different solubility/reactivity of the MA and FA precursors in the solution.

^{1}H and ^{13}C solid state NMR techniques have been exploited for the study of phase transition between the different polymorphs for MA lead halides perovskites series[11] while ^{1}H liquid NMR data for the mixed MA/FA iodide precursors have been presented to confirm the alloying of MA and FA in the MA stabilized FAPI.[10] Nevertheless, to our knowledge, this is the first time the ^{1}H solid state NMR is used to address the problem of quantitative determination for the 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 deviation) are 0, 0.09, 0.24, 0.42, 0.63, 0.79, and 1.0.

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

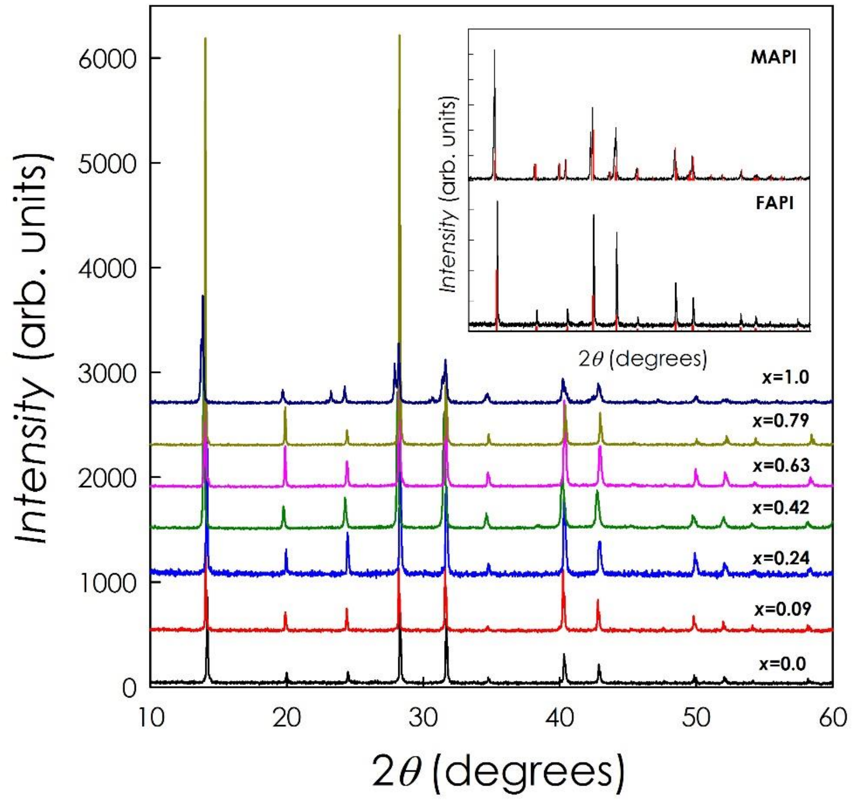

Figure 2. XRD patterns for the samples of the $FA_{1-x}MA_xPbI_3$ solid solution. Patterns are vertically shifted to clarify viewing. Inset: XRD patterns of the two end-members of the solid solution, i.e., FAPI and MAPI, together with the reflection positions from literature patterns (red vertical bars).

All the samples are single phase and from x=0 to x=0.79 the unit cell is in agreement with the crystal structure of the α-phase (black perovskite) of FAPI end member. In the inset of Figure 2, the XRD pattern of FAPI is compared to the literature reference pattern using the *Pm*-3*m* space group and this black sample has been obtained by annealing at 185°C the yellow, as-synthesized, FAPI sample for 1 hour. On the other hand, the MAPI has a diffraction pattern consistent with the reported tetragonal structure in the *I*4*mc* space group.[12] It is interesting to observe that even a small amount of the bigger FA cation (ionic radii for FA and MA have been estimated to be 253 and 217 pm, respectively[13]) in the solid solution, as in the x=0.79 sample, gives origin, at the end of the synthesis, to a sample with the cubic crystal structure. Moreover, for the low-MA containing samples, black perovskite samples are obtained at the end of the synthesis without the need of any thermal treatment as in the case of pure FAPI sample. This means that already very low MA contents, *e.g.* the x=0.09 sample, are able to destabilize the hexagonal phase. However, as it will be shown later in the text, for small x-values the perovskite phase is not stable with time. By using the effective radius of organic cations, MA $r_{eff} = 217$ pm and FA $r_{eff} = 253$ pm, to calculate a tolerance factor, it is found that $\alpha = 0.91$ for $MAPbI_3$versus 0.98 for $FAPbI_3$.[9] Both values should give a perovskite structure which is observed for $0.81 < \alpha < 1.01$, which is not the case for δ-$FAPbI_3$. It is clear that the spherical approximation used to estimate the effective radius for 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]

Figures 3a and b show the trend of the cell volume (V) and cubic lattice parameter of the $FA_{1-x}MA_xPbI_3$ solid solution, respectively, as obtained from Rietveld refinement of the diffraction data, as a function of the x value. The data are reported as cell volume per formula unit, considering that the *Pm*-3*m* and the *I*4*mc* space groups have different Z-values. In the Supporting Information, the differential scanning calorimetry (DSC) measurements on all the samples between -90 and 200°C are also reported showing the well known tetragonal to cubic phase transition for MAPI at about 57°C, and the hexagonal to cubic phase transition for the as-prepared yellow FAPI at about 165°C. As expected, all the intermediate compositions do not present any peak in the investigated T-range since the perovskite phase has been stabilized by the doping. The result of 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, indicates that the absence of phase transitions is a beneficial aspect to the use of these mixed phases.

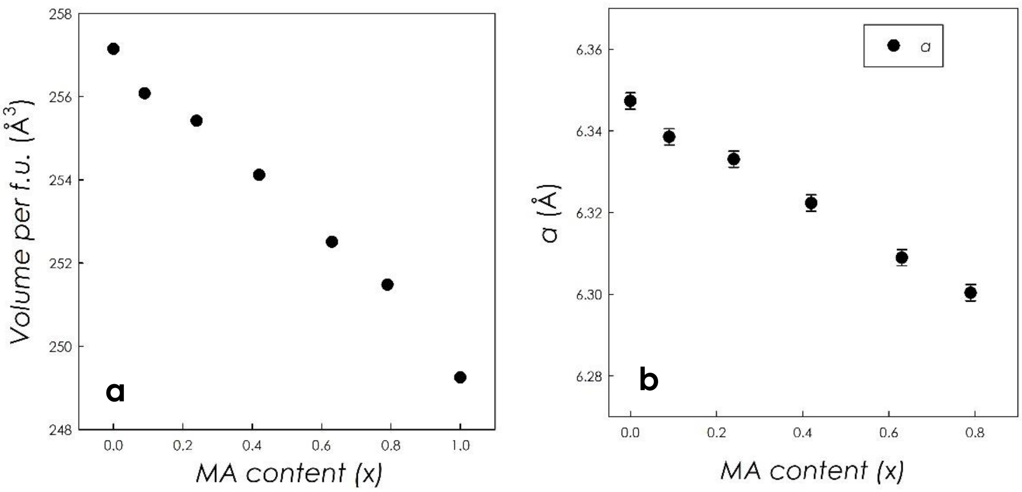

Figure 3. a) Cell volume and b) cubic lattice parameter of the $FA_{1-x}MA_xPbI_3$ *solid solution as a function of x.*

As can be appreciated from Figure 3a, a linear decrease of the cell volume (Figure 3a) and of the cubic *a* lattice parameter (Figure 3b) is found along with the increase of the amount of the smaller MA cation in the solid solution (about 3% volume shrinkage). This behavior is consistent with the Vegard's law of solid solution formation, which may be anticipated in this system but which is confirmed by the present structural data, by the DSC data and by the optical absorbance results (see later in the text). Other recent literature results based on thin films reports slightly different trends. A non-linear trend, for example, is shown in ref. 3 where, for example, x=0 and 0.2 samples have the same cell volume and a significant decrease of V is found for the x=0.8 sample. Binek and co-workers considered the doping of the FAPI phase with 5, 10 and 15% of MA cation and their mixed samples, after the synthesis, were rich in hexagonal FAPI phase for all the dopings, with reduction of such phase by increasing the methylammonium doping.[6] In their paper they indicate no shrinkage of the unit cell by replacing FA with MA, even for stoichiometries up to about x=0.13. It is important to underline that in both the papers the thin film samples have been prepared by immersion of the substrate in mixed FAI/MAI solutions which may not be directly compared to the powdered samples prepared and characterized by the synthetic method used in the present work. In particular, while the synthetic approach used herein provides a strict control over the stoichiometry, those methods may lead to phases with different stoichiometries. However, the results reported in this work may be used as a reference to rationalize the results obtained on thin films.

The stability as a function of time of FAPI (black) perovskites is well known and has been investigated previously.[6] In general, once the α-phase has been stabilized by thermal annealing around 180-185°C, this phase remains stable in the black form for several days with a progressive formation of the yellow hexagonal phase which is usually observed after 10 days regardless of storage in vacuum or inert gas.[6] However, no data are actually available on the time-stability of mixed MA/FA systems which are considered very efficient absorbers employed in PSC. Figure 4 reports the XRD patterns of the x=0 (FAPI), x=0.09 and x =0.24 samples after the synthesis and after 10 days of storage in glove-box and in dark glass containers (ages samples). Vertical blue bars in the plot are relative to the reference pattern for the black α-FAPI while the orange vertical bars refer to the hexagonal δ-FAPI reference pattern, respectively.

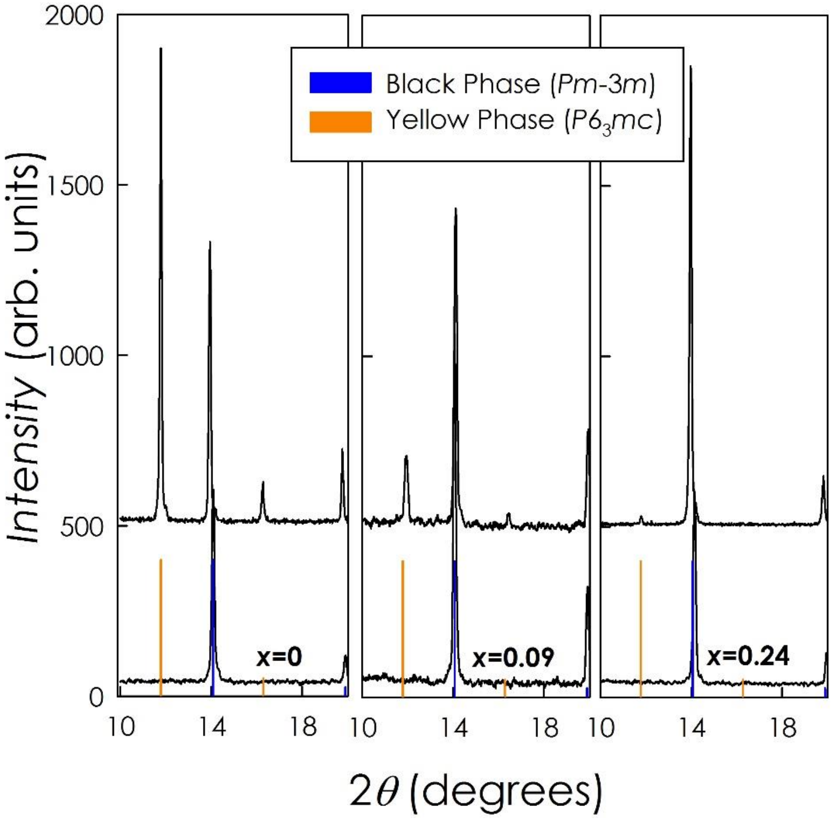

Figure 4. XRD patterns for the x=0, 0.09 and 0.24 samples of the $FA_{1-x}MA_xPbI_3$ solid solution after the synthesis (bottom patterns) and after 10 days of storage (top patterns). Orange and blue vertical bars refer to the reference patterns of the hexagonal and cubic structures of FAPI, respectively.

FAPI develops a remarkable amount of hexagonal phase after the considered time-frame, in agreement with previous data. $FA_{0.91}MA_{0.09}PbI_3$ developed as well a significant fraction of the δ-phase while for $FA_{0.76}MA_{0.24}PbI_3$ such amount is very small. For stoichiometries with $x>0.24$ no traces of hexagonal phase have been detected. It should be noted that these preliminary results are related to optimal storage conditions and for a relatively short-time evaluation after the synthesis. However, these evidences strongly indicate that, while the complete substitution of FA with MA (or other cations) directly stabilizes the (cubic) perovskite phase at RT after the synthesis, care must be taken when considering the stability of MA/FA mixed phases. As a matter of fact, in this paper we have shown that the time-stability of cubic

FAPI-based lattices stabilized by small 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.[14, 15]

On the samples investigated in this work, optical measurements have been carried out in order to define the band-gap values as a function of (real) stoichiometries. Figures 5a and 5b report the vis-NIR diffuse reflectance spectra and the trend of band-gaps as a function of x, respectively (FAPI value refers to the cubic "black" phase). The E_g values have been obtained from the extrapolation of the linear part of $[F(R)\ h\nu]^2$ where F(R) is the Kubelka-Munk function $F(R) = (1-R)^2/2R$.[16, 17]

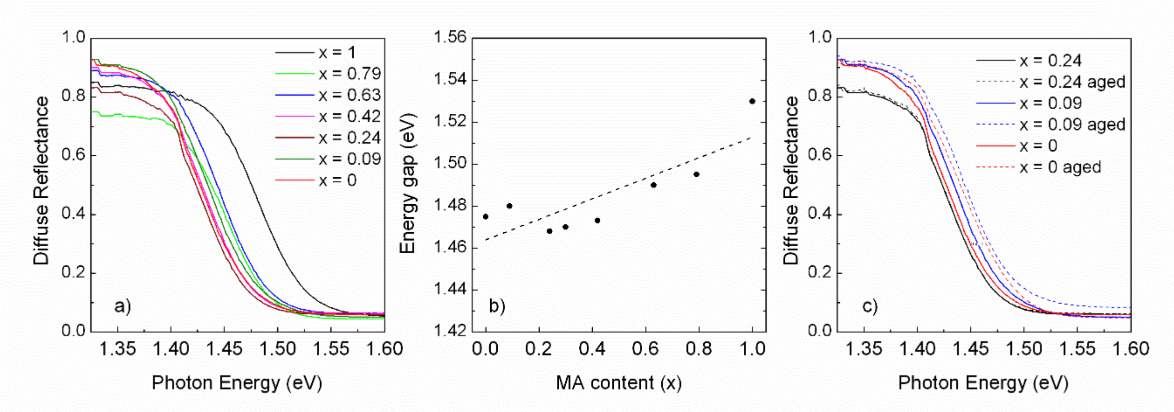

Figure 5. a) Diffuse reflectance spectra for the $FA_{1-x}MA_xPbI_3$ solid solution; b) energy gap trend as a function of x for the $FA_{1-x}MA_xPbI_3$ solid solution; c) diffuse reflectance spectra of as-prepared and aged samples for x=0 (FAPI), 0.09 and 0.24.

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

Figure 5c reports the evolution of the diffuse reflectance spectra on aged samples, analogous to those presented in Figure 4 relative to the XRD characterization. It can be appreciated that for x=0 and 0.09 the spectra show a shift of the band-gap to higher values when the samples is left under optimal storage condition for several days. On the other hand, for the x=0.24 sample and higher, there is no any shift of the band-gap (the dotted curve is exactly superimposed to the solid curve of the as-prepared sample) suggesting, at least in this time frame, a greater stability of the material. The results of the optical measurements for aged samples are in very good agreement with the phase separation observed for the aged sample by means of XRD: those samples showing a shift to higher energies of the E_g are those showing the separation of the hexagonal δ-phase with time (please refer to Fig. 4). This result 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 to the phase stability of the same samples and this change in the absorption properties may have a crucial effect on the performance of PSC employing such materials as absorbing layers. It should be remarked that for low x-values the degradation is very fast (few days under optimal storage conditions) and that such behavior might be present also in samples with higher x-values for longer time. Further investigation in this regard is strongly required for most of the mixed doped systems of hybrid perovskites. Finally, based on the observation of an increase of the band-gap value 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 of the order of 1.53-1.55 eV may be due to a significant phase separation present within the samples.

Conclusions

In this paper we deeply investigated the $FA_{1-x}MA_xPbI_3$ system defining its crystal structure, phase stability and optical properties as a function of actual x-values determined by means of solid state NMR. Collected results confirm the formation of a solid solution within this mixed-system. By properly controlling the relative MA/FA amounts, we could provide reliable evidence of structural changes upon doping. In addition, we defined the time-stability of mixed systems highlighting a phase separation phenomena in aged samples leading to the formation of the δ-phase. The optical properties as well 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-properties correlation in the $FA_{1-x}MA_xPbI_3$ system for well-defined doping levels, put in prominence the stability issue of such mixed systems that could be a key issue also for other mixed systems based on the FAPI perovskite. These effects, in turn, may have detrimental effects on the performance of PSCs based on these materials as active layers.

Experimental Methods

Materials Preparation: Samples of general formula $FA_{1-x}MA_xPbI_3$ were synthesized according to a general procedure we developed.[12,18] In a typical synthesis, a proper stoichiometric amount of Pb acetate is dissolved in an HI excess under continuous mechanical stirring under nitrogen atmosphere. Then, the solution is heated to 100°C and the corresponding amines (methylammonium and/or formamidinium in water, 40wt%) are added in correct stoichiometric amounts. The solution is then cooled down to 46°C at 1°C/min, until the formation of a precipitate, which is immediately filtered and dried under vacuum at 60°C overnight. All the reagents were purchased from Sigma Aldrich in pure form and were used without any further purification.

X-ray Diffraction: The crystal structure of the samples has been characterized by room temperature Cu-radiation x-ray Powder Diffraction (XRD) acquired with a Bruker D8 diffractometer.

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

NMR: ^1H solid state NMR room temperature measurements have been acquired on a 9.4 T (^1H = 400.16 MHz) Bruker Avance III with the use of TopSpin 3.1 software; spectra have been collected with a 4 mm MAS probe under 8 kHz spinning conditions. ^1H quantitative one pulse experiments have been collected with a pulse length of 4.65 μs, recycle delay of 120 s and 16 scans. Pulse lengths and recycle delay have been carefully calibrated before the acquisition of the final spectra to ensure the full relaxation of the magnetization and fulfill the conditions for the quantitative data acquisition. Chemical shifts are referred to TMS using adamantine as secondary standard. The analysis of the obtained data have been performed with the use of DMFit program.[19]

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

Supporting Information

Supporting Information Available: DSC 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).

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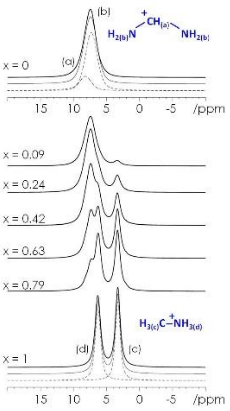

NMR spectroscopy has been used to determined the relative concentration of MA/FA in the $FA_{1-x}MA_xPbI_3$ system.