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HyPerCells

HZB Helmholtz Zentrum Berlin

Universität Potsdam

Stabilizing the cubic phase of the triple cation hybrid perovskite $(FA_{1-x}MA_x)_{1-y}Cs_yPbI_3$ solid solution

At present, the rapidly rising solar conversion efficiencies are standard for solar cells with hybrid perovskite absorber layers, for which methylammonium lead triiodide ($MAPbI_3$) and formamidinium lead triiodide ($FAPbI_3$) are promising candidates.[1] Nevertheless, further optimization is necessary because the long term stability of these perovskites is a crucial problem. Unfortunately, the desired cubic modification of $FAPbI_3$ is unstable and transforms to a non-perovskite hexagonal room temperature modification[2], which is not suitable as absorber layer in solar cells. Our approach is to stabilize the favorable high temperature cubic perovskite modification at room temperature by partially substituting FA by MA or Cs and systematically study the $(FA_{1-x}MA_x)_{1-y}Cs_yPbI_3$ solid solution with regard to miscibility and phase stability.

Crystallographic information

$FAPbI_3$ [3]
► perovskite type structure

A: formamidinium $[HC=(NH_2)_2^+=FA^+]$; B:$[Pb^{2+}]$; [X = I]

► cubic modification (**desired α-phase**)

space group $P\,4/m\,\overline{3}\,2/m$ with a = 5.931 Å (at RT)

► hexagonal modification (**undesired δ-phase**)

space group $P\,6_3\,m\,c$ with a = 8.660 Å c = 7.902 Å (at RT) [2]

► phase transitions: $Pm\overline{3}m \overset{165°C}{\longleftrightarrow} P\,6_3\,m\,c \overset{>-123°C}{\longleftrightarrow} P3$

$MAPbI_3$ [4]
► tetragonal modification

space group $I\,4/m\,2/c\,2/m$ with a = 8.879 Å, c = 12.689 Å
A: methylammonium $[CH_3NH_3^+=MA^+]$; B:$[Pb^{2+}]$; [X = I]

α-$FAPbI_3$:

$MAPbI_3$:
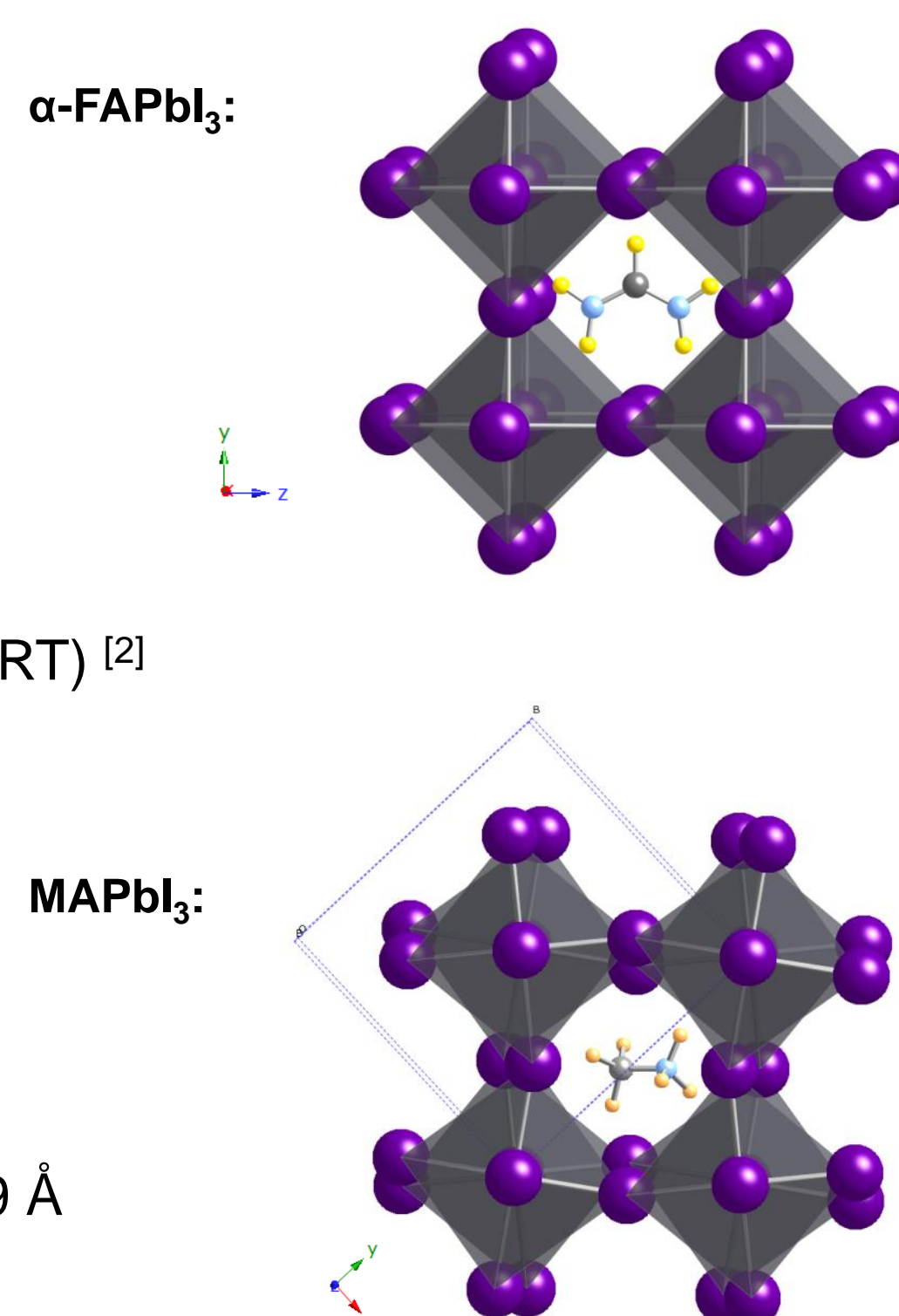
Synthesis of powder samples

$$((1-x)\cdot FAI + x\cdot MAI)_{1-y} + (CsI)_y + PbI_2 \xrightarrow{GBL,\ DMF,60\ °C} (FA_{1-x}MA_x)_{1-y}Cs_yPbI_3$$

Dissolving precursors
1. 1:1 and 5:4 molar mixtures of precursors in a solvent mixture of γ-butyrolactone (GBL) and dimethylformamid (DMF)[5]

Homogenizing
2. stirring the solution at 60°C until the precursor powders were completely dissolved

Evaporation
3. transfering the hot solution into a petri-dish and evaporation of the solvent at 100-110°C

Annealing
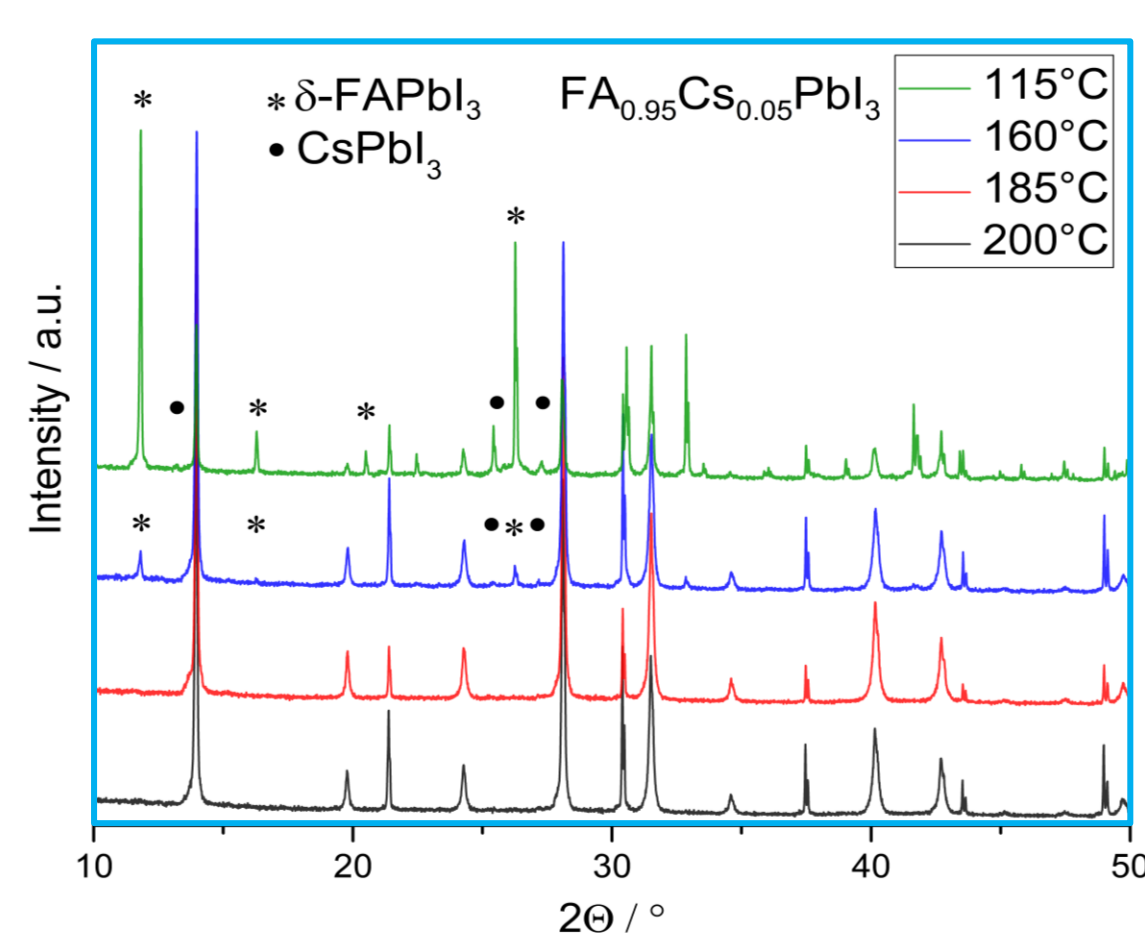4. annealing of the dry powder at selected temperatures of 115°, 165°, 185° and 200°C

temperature controller 60 °C

thermometer

Heat-on-block

magnetic stirrer with hotplate
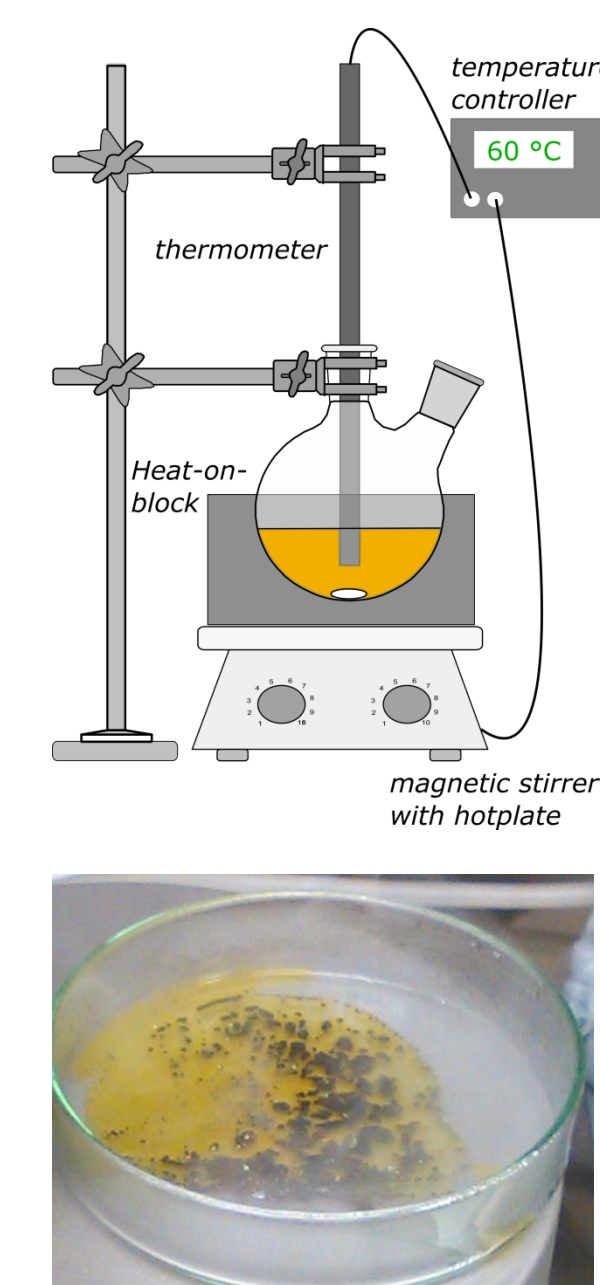
Binary compounds
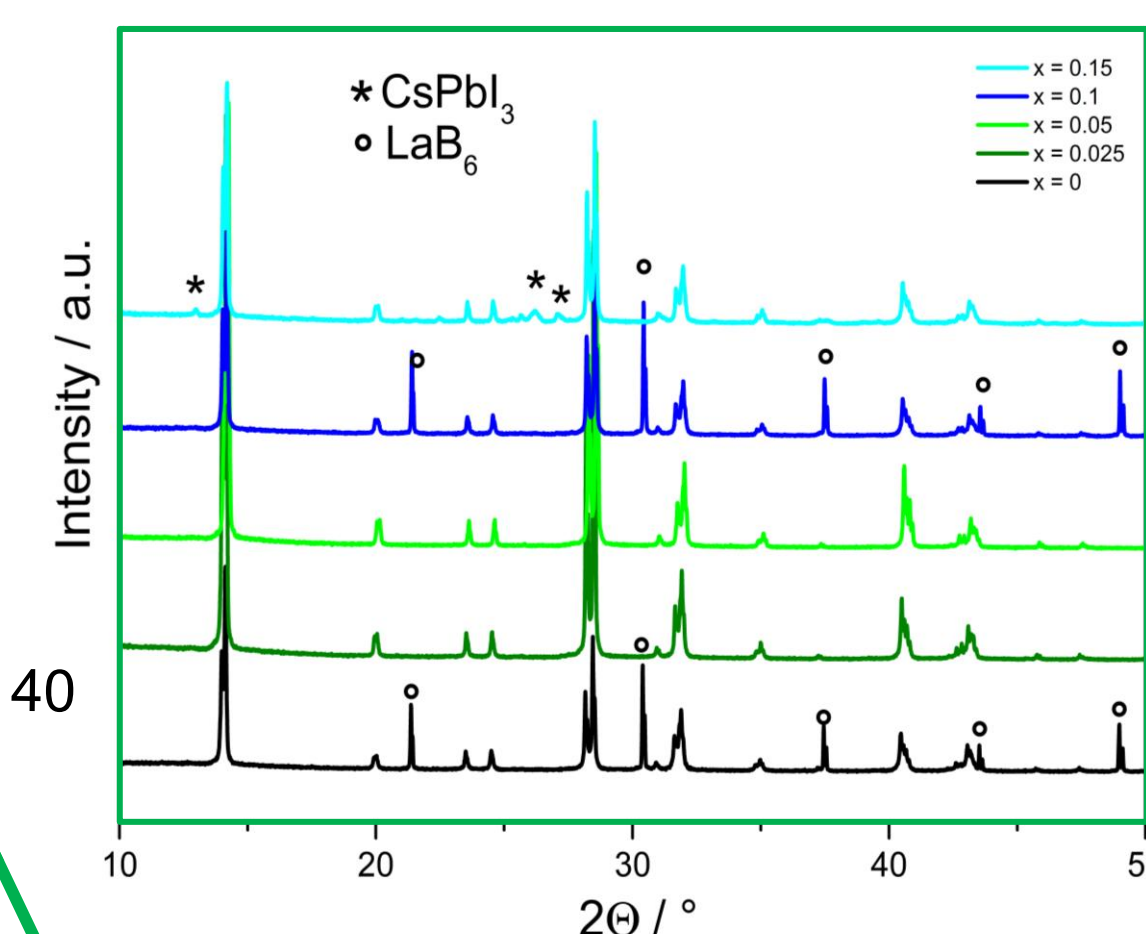
$FA_{1-x}Cs_xPbI_3$ solid solution

► annealing procedure applyed on samples with 5:4 molar ratio leads to increased stability

► Cs can be incorporated into the crystal structure of $FAPbI_3$ up to x<0.1
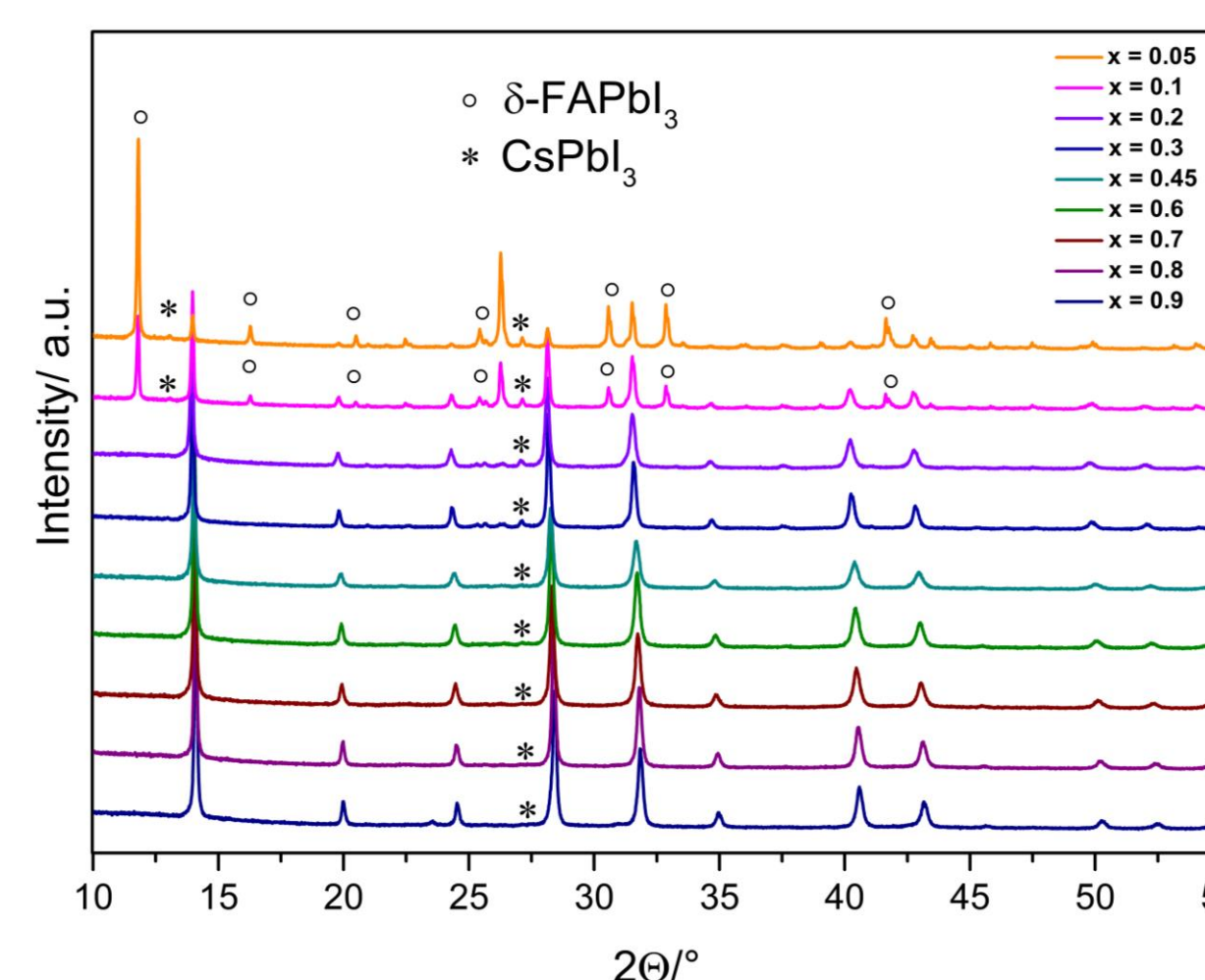
► studies were performed by M. Cherasse

$MA_{1-x}Cs_xPbI_3$ solid solution

► solid solution stable up to x = 0.1 (10%) Cs in $MA_{1-x}Cs_xPbI_3$ (1:1 molar ratio)

► these studies were performed as part of a master thesis of S. Binet

CsPbI₃

**$(FA_{1-x}MA_x)_{1-y}Cs_yPbI_3$ solid solution**

$(FA_{1-x}MA_x)_{0.9}Cs_{0.1}PbI_3$

δ –phase | stabilized cubic phase | tetragonal phase

FAPbI₃ | **MAPbI₃**

10 20 30 40 50 60 70 80 90

$FA_{1-x}MA_xPbI_3$ solid solution

► $FA_{1-x}MA_xPbI_3$ shows complete miscibility

► δ-phase of $FAPbI_3$ disappears in samples with x = 0.2

► powder X-ray diffraction data obtained from Bruker D8, Cu K$_α$-radiation

Ternary phase system

$(FA_{1-x}MA_x)_{0.9}Cs_{0.1}PbI_3$ solid solution

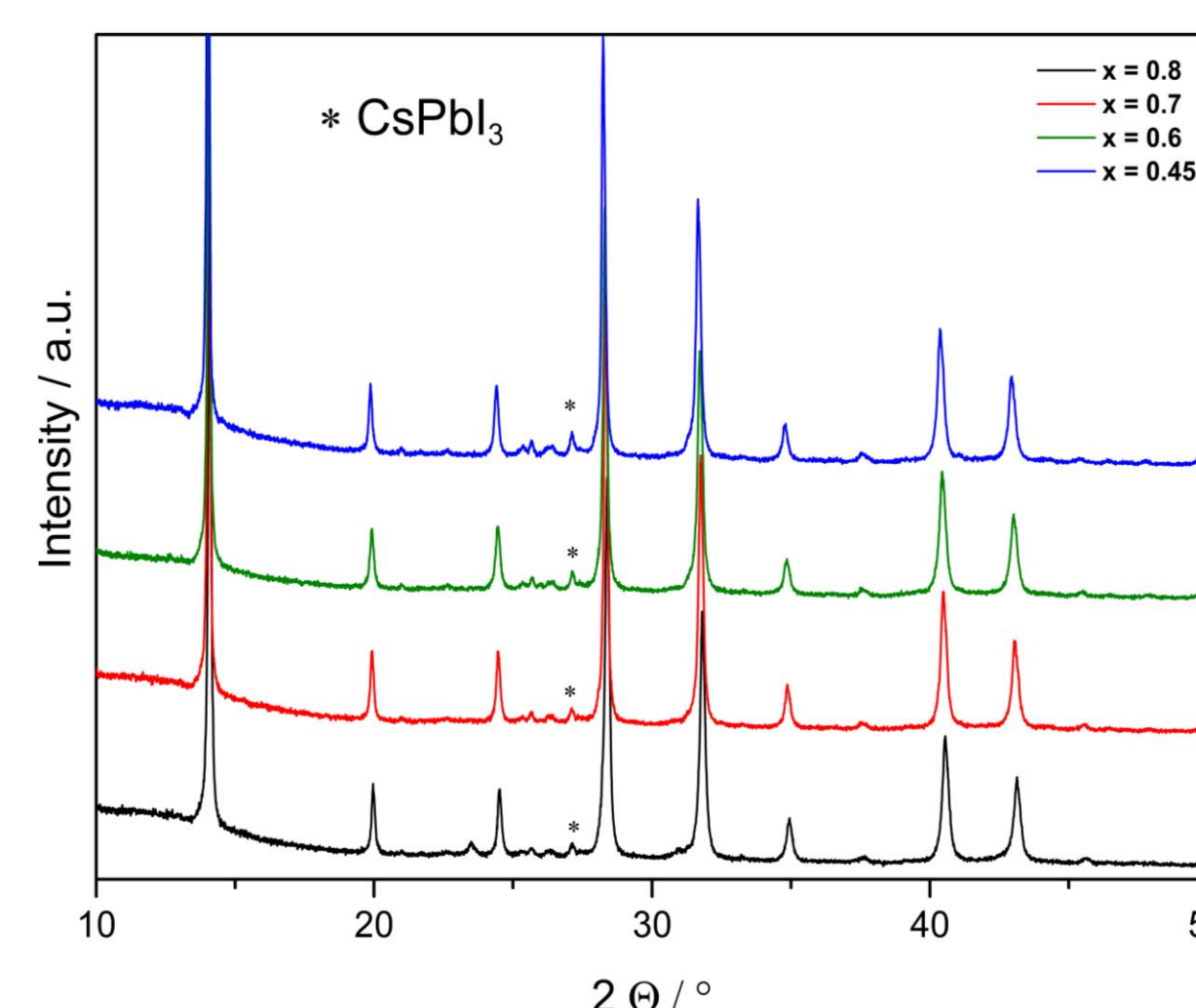► δ-phase of $FAPbI_3$ is not present in samples with x ≤ 0.2 in $(FA_{1-x}MA_x)_{0.9}Cs_{0.1}PbI_3$

► $CsPbI_3$ secondary phase indicating an incomplete cesium incorporation in the crystal structure of $(FA_{1-x}MA_x)_{0.9}Cs_{0.1}PbI_3$

► $CsPbI_3$ phase indicating solubility limit of cesium in $(FA_{1-x}MA_x)_{1-y}Cs_yPbI_3$: x < 0.1
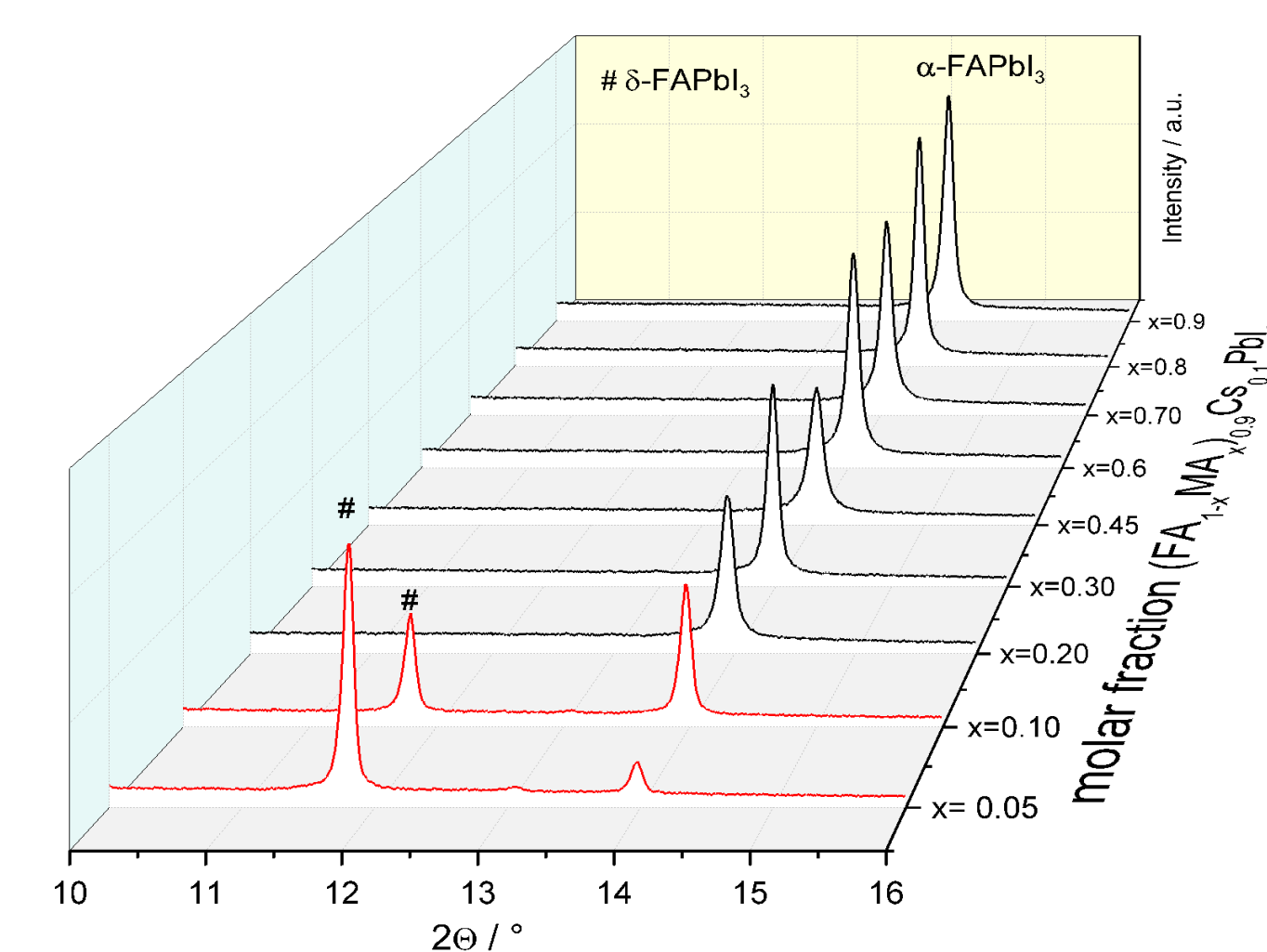
long term stability
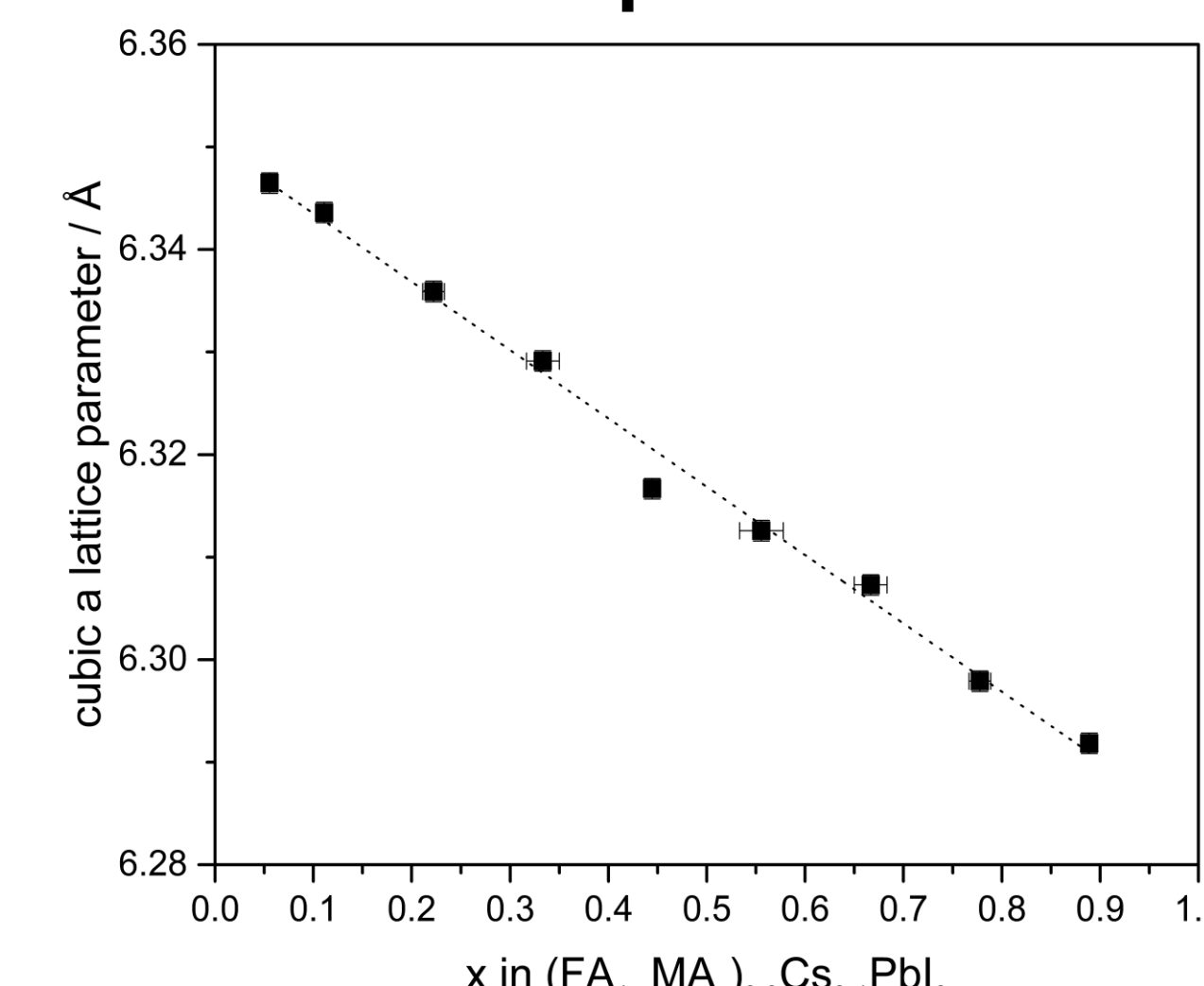

lattice parameters

► long-term stability of samples proven after 6 months of storage in N_2 atmosphere (left figure)

► cubic a lattice parameter obtained from LeBail profile fitting of the XRD data of the complete $(FA_{1-x}MA_x)_{0.9}Cs_{0.1}PbI_3$ series

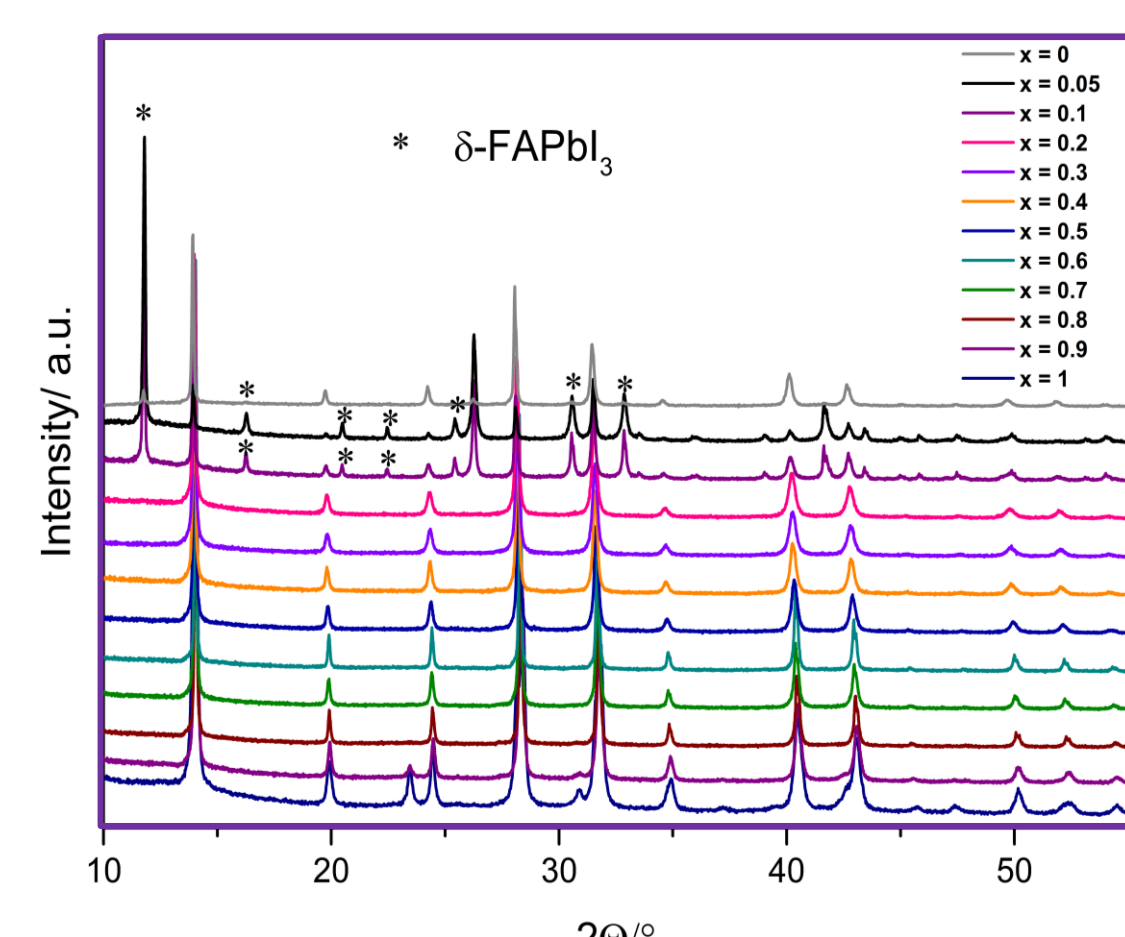► linear dependence of lattice parameters from composition (dotted line), following Vegard's law (right figure)

Conclusion and Outlook

► Substitution of FA by MA in $FA_{1-x}MA_xPbI_3$ hinders formation of δ-phase for x = 0.2, Cs is less suitable to stabilize the cubic high temperature modification of $FAPbI_3$.

► $(FA_{1-x}MA_x)_{0.9}Cs_{0.1}PbI_3$ solid solution shows a long-term stability of >6 months.

► Linear dependence of lattice parameters from composition of $(FA_{1-x}MA_x)_{0.9}Cs_{0.1}PbI_3$ revealed, proving that the solid solution follows Vegard's law.

► Additional synthesis of $(FA_{1-x}MA_x)_{0.9}Cs_{0.1}Pb(I,Br)_3$ solid solution with variation of halides $(FA_{1-x}MA_x)_{0.9}Cs_{0.1}Pb(I,Br)_3$ for bandgap tuning.

► Further studies on the effect of annealing temperatures and stoichiometry to hinder the formation of the δ-phase in $(FA_{1-x}MA_x)_{1-y}Cs_yPbI_3$ compositions.

► Analysis on the influence of Cs doping on bandgap and structure.

[1] Y. Zhang *et al.*, ACS Energy Lett., **2017**, 2, 802–806.

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[3] M. Weller *et al.*, J. Phys. Chem. Lett., **2015**, 6, 3209–3212.

[4] A. Franz *et al.*, Cryst. Res. Technol., **2016**, 51, 534–540.

[5] P. Fedeli *et al.*, J. Phys. Chem. C, **2015**, 119, 37, 21304–21313.