

## Supporting Information

### Insights into the evaporation behaviour of FAI: material degradation and consequences for perovskite preparation

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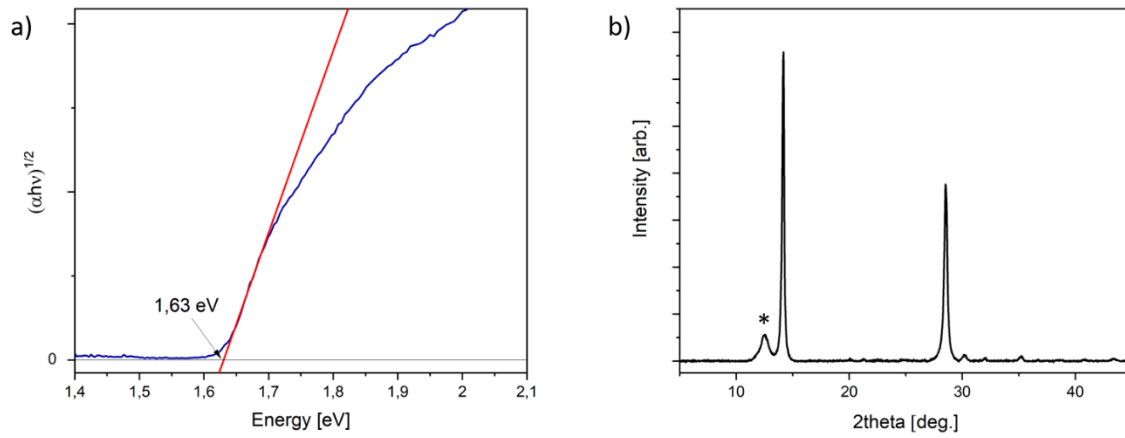
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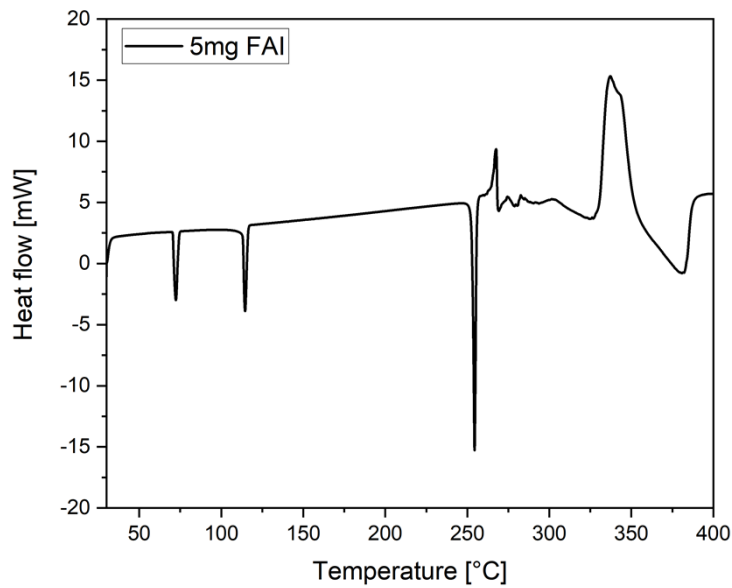
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Keywords: Perovskite, vacuum deposition, thermal evaporation, solar cell, degradation FAI

Methanol Acetone  
 - 1e-6 Ethanol Diethylether



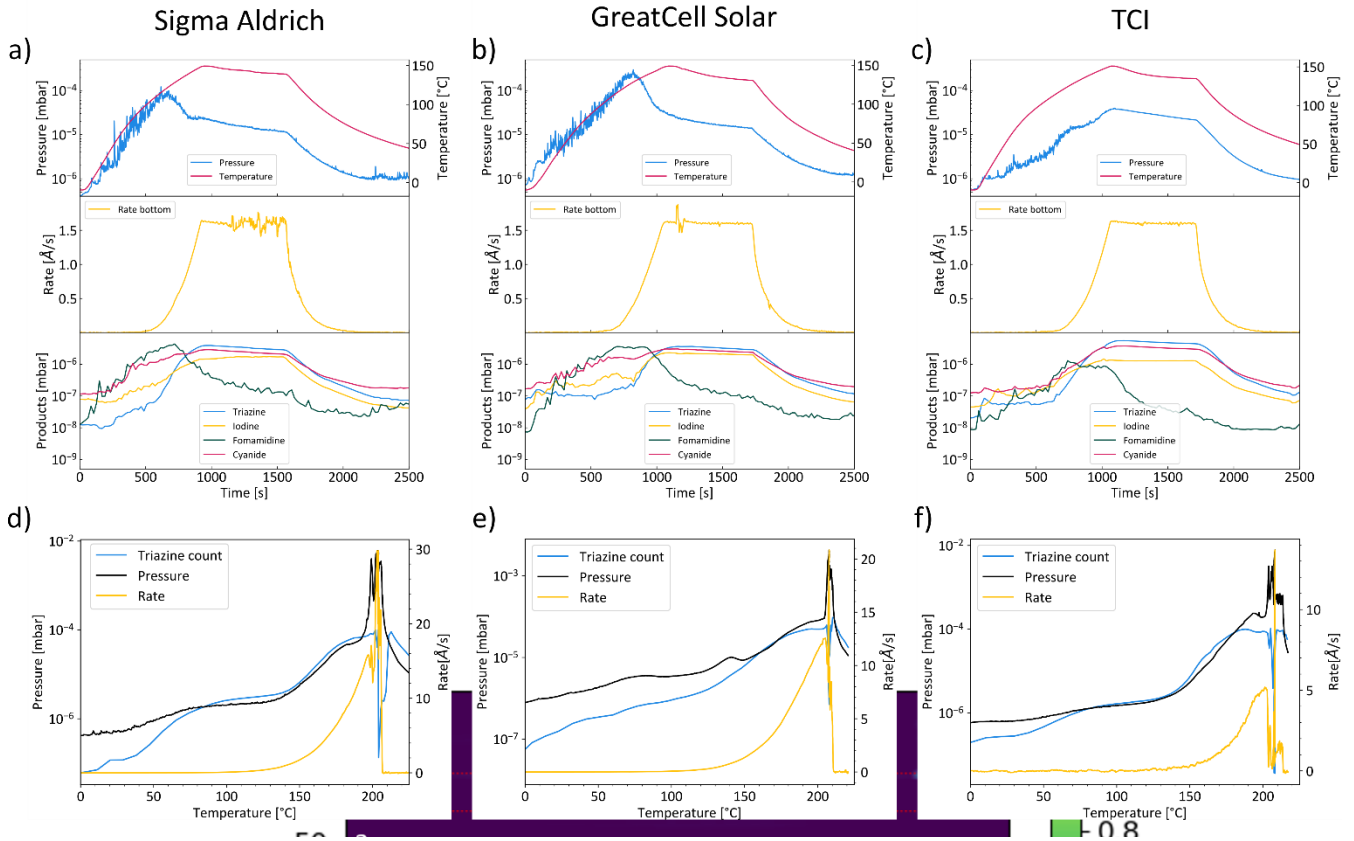
**Figure S1:** Characterization of Perovskite layer embedded in solar cell structure in Figure 1: a) Tauc-plot from UV-VIS measurement with linear fit (red) to determine the bandgap, b) XRD-diffractogram of  $\text{FA}_{0.7}\text{Cs}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$  with the characteristic perovskite peaks at  $14^\circ$  and  $28^\circ$ , at  $12.6^\circ$  a surplus of  $\text{PbI}_2$  is detected(\*)



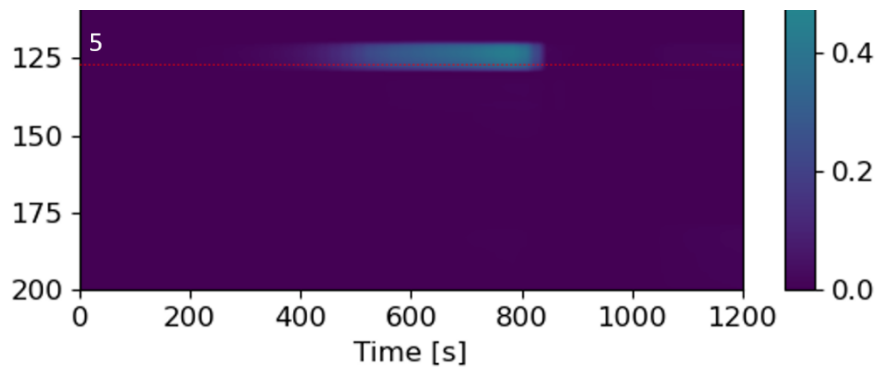
**Figure S2:** Differential scanning calorimetry measurement of 5mg FAI in argon atmosphere

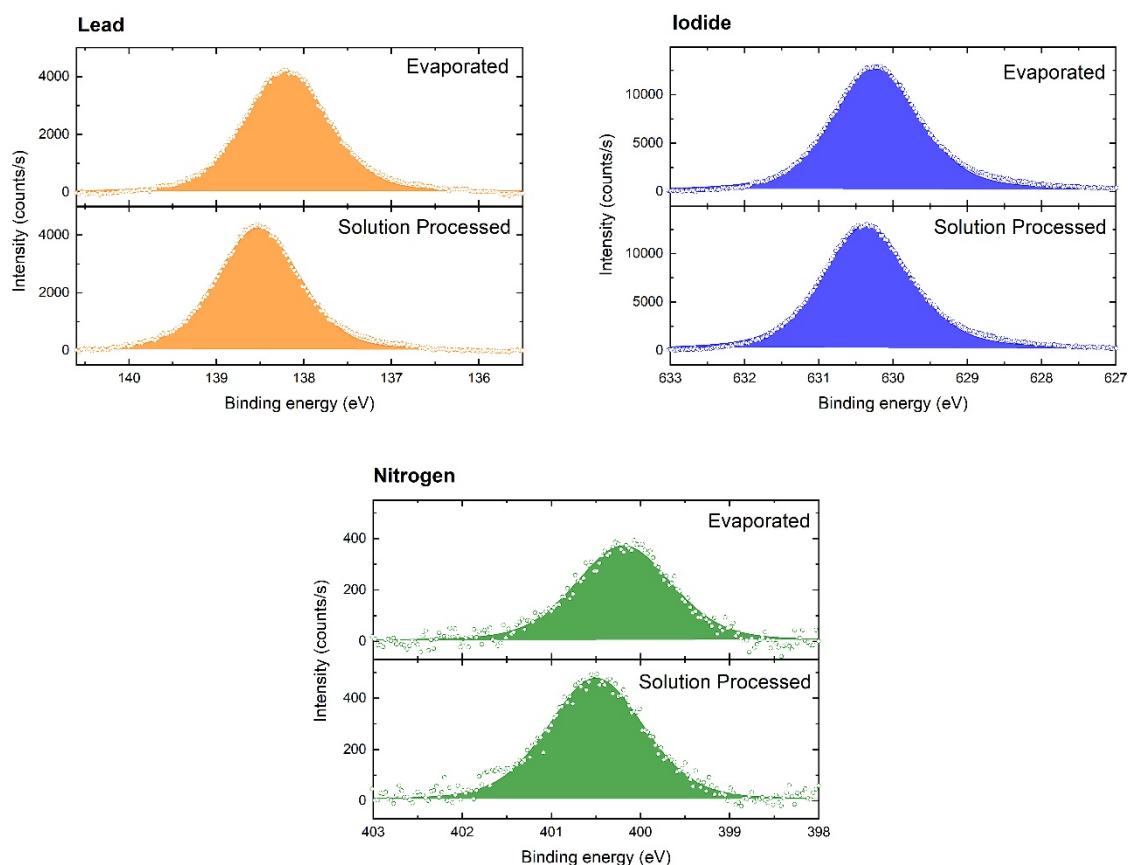
**Figure S4:** Contour plot of mass spectrum signal during a degradation experiment, the main observed reaction educts and products are marked: 1) hydrogencynaide, 2) formamidine, 3) fragment of sym-triazine, 4) sym-triazine, 5) hydrogen iodide/iodide

**Figure S3:** Mass spectrum at  $t=500s$  during the outgassing process. The main outgassing molecules are marked with red lines



**Figure S5:** Evaporation properties of FAI from different vendors; a), b), c): Outgassing behaviour of materials from different suppliers. A) b) show very similar behaviour, which leads to the assumption that the material is from the same production line, c) shows a lower increase in pressure in the beginning, which originates from a finer milled powder. d), e), f): Degradation behaviour of the same materials in dependence of the source temperature. All materials degrade at the same temperature of 205 °C.

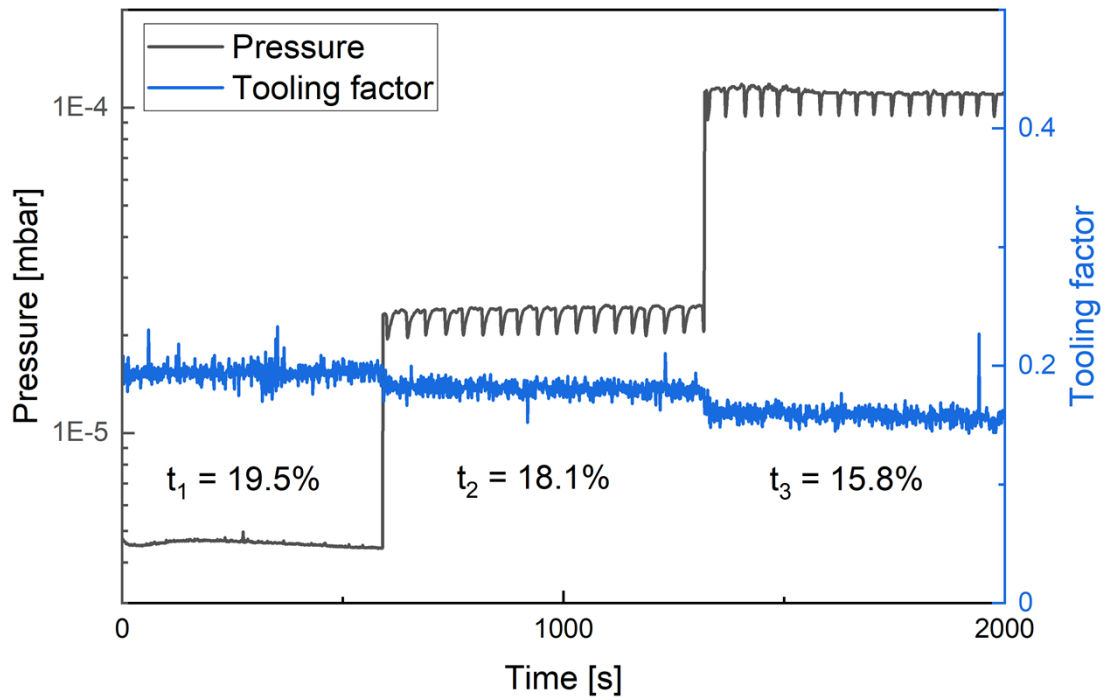




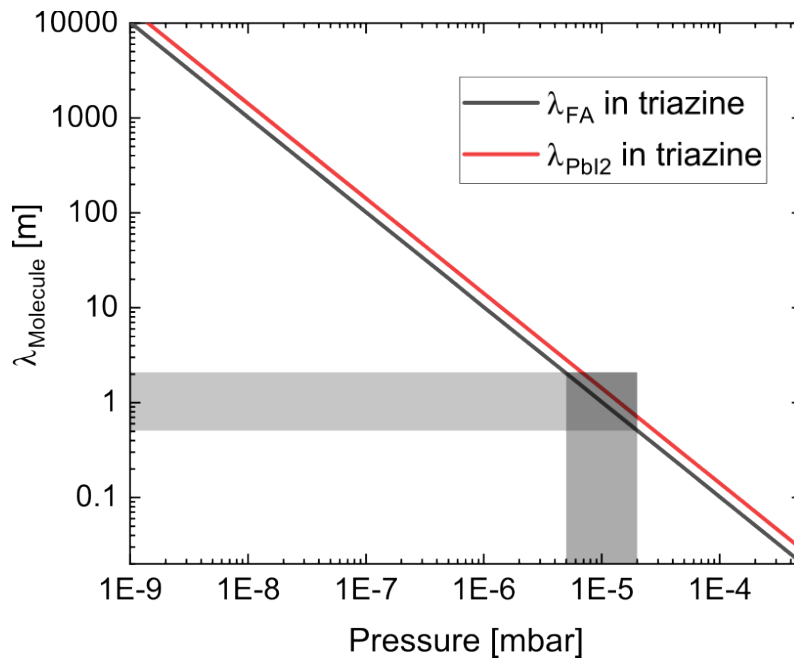
	Area lead	Area iodide	Area nitrogen	composition
Evaporated	344	936	322	$N_{0.9}Pb_{12.7}$
Solution	345	941	413	$N_{1.2}Pb_{12.7}$

**Figure S6:** Comparison of XPS core level peaks of  $Pb4f_{7/2}$ , Iodide  $3d_{3/2}$  and  $N1s$  belonging to evaporated and solution-processed  $FAPbI_3$  films. The evaporated film was prepared in the second evaporation setup using the optimized molar co-evaporation ratio of 3.5 : 1 (FAI to  $PbI_2$ ). The solution-processed film was prepared in a nitrogen glovebox by spin coating technique using 1M  $FAPbI_3$  solution in DMF and chlorobenzene antisolvent. The substrate was at last annealed at 140 °C.

XPS measurements of evaporated and solution processed  $FAPbI_3$  films have been compared, to determine whether degradation products of FAI are incorporated into the evaporated perovskite film. As shown in Figure S8, the specific core level features are rather similar in intensity as well as shape (Voight fits have same FWHM and L:G ratio). No additional chemical species for the core level signals of Pb, I and N are present. Therefore, it can be concluded that no substantial amount of the degradation products is incorporated in the film. The only difference is a slightly smaller nitrogen signal in the evaporated film. This is most likely related to the fact that FA molecules are more affected by the background pressure and are scattered away before reaching the sample position as discussed in the main text.



**Figure S7:** Determination of the tooling factor  $t$  at different background pressures, periodic pressure variations originate from the open pressure inlet



**Figure S8:** Free mean path  $\lambda_{\text{Molecule}}$  for FA and  $\text{Pbl}_2$  according to Formular (1), the relevant pressure region marked in gray

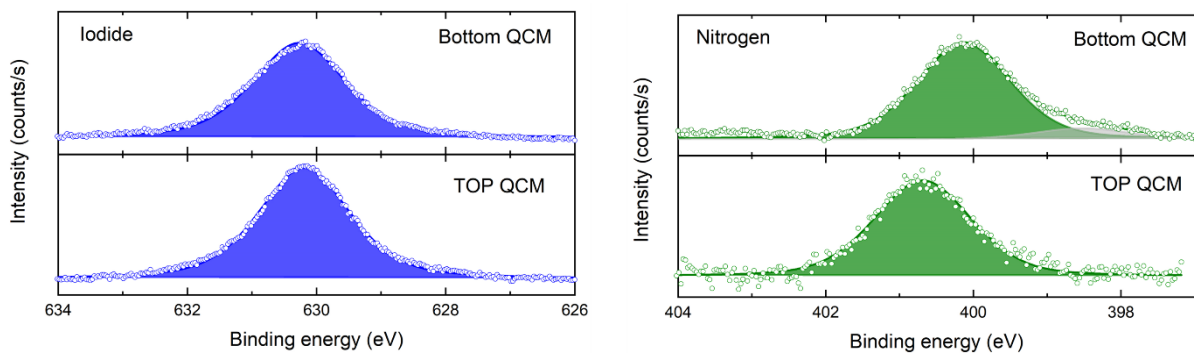
From the thermodynamic description of a classical gas:

$$P_{\text{Molecule}} = \frac{n_{\text{Molecule}} RT_{\text{Evaporation}}}{V}$$

With  $n_{\text{Molecule}} = 1,3 \cdot 10^{-10}$  Mol/s derived from  $R_{\text{Deposition}} = 1 \text{ \AA/s}$ , with  $\rho_{\text{FAI}} = 2,2 \text{ g/cm}^3$  and  $M_{\text{FAI}} = 172 \text{ g/mol}$  and  $T_{\text{Evaporation}} = 400 \text{ K}$ . The volume  $V$  is assumed to be the volume of gas molecules

with  $\bar{v}_{\text{FAI}} = \sqrt{\frac{8 k_B T_{\text{Evaporation}}}{\pi M_{\text{FAI}}}} = 220 \text{ m/s}$  and the surface  $A = 1 \text{ cm}^2$ . For  $P_{\text{Molecule}}$  this results in a pressure of  $1,95 \cdot 10^{-5} \text{ Pa}$  on the substrate.

For the estimation of the pressure above the crucible, the mass of the crucible was measured before and after an evaporation of  $1 \text{ \AA/s}$  for 1 h, which results in weight loss of 69 mg and thus a mass flow of  $n_{\text{Molecule}} = 1,1 \cdot 10^{-7} \text{ Mol/s}$ . With the same assumptions above, a pressure of  $1,7 \cdot 10^{-2} \text{ Pa}$  above the crucible can be estimated.



**Figure S9:** Comparison of XPS core level peaks of Iodide  $3d_{3/2}$  and N1s belonging to FAI evaporated bottom and top QCMs.

The bottom QCM and top QCM after an FAI deposition were investigated with XPS (see above). As expected, signals related to FAI (N and I) were received, and it was seen that both QCMs had similar N and I signals with an N to I ratio of  $\sim 2$ . The only difference detected was a considerably small additional signal of N at lower binding energy that could be coming from a degradation product. However, it is important to state that the signal of this species was not detected in the perovskite film (Figure S8) hence it can be said that it is not incorporated in the final FAPI film.

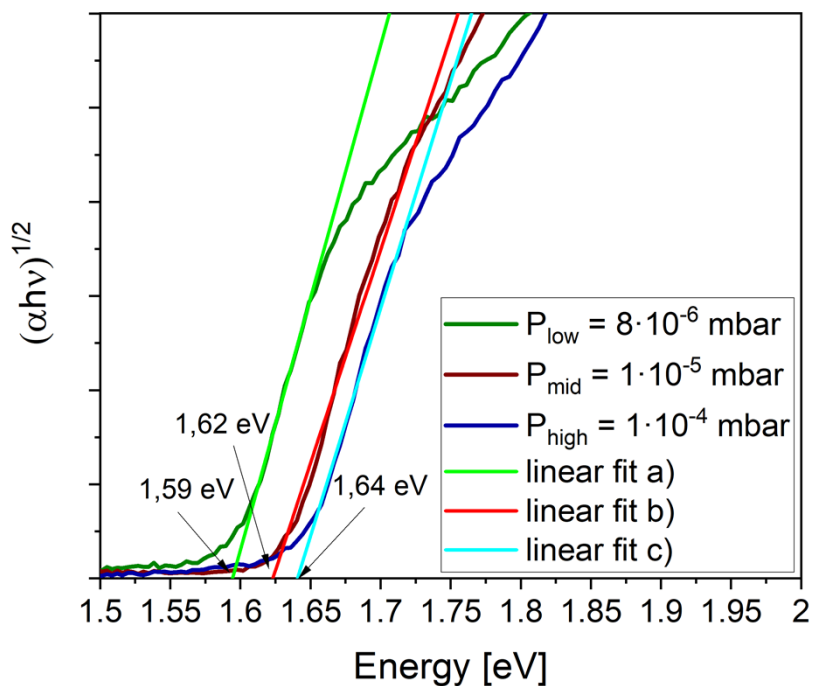


Figure S10: Tauc plot from absorption measurements of  $\text{FA}_x\text{Cs}_{1-x}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$  prepared at different background pressures

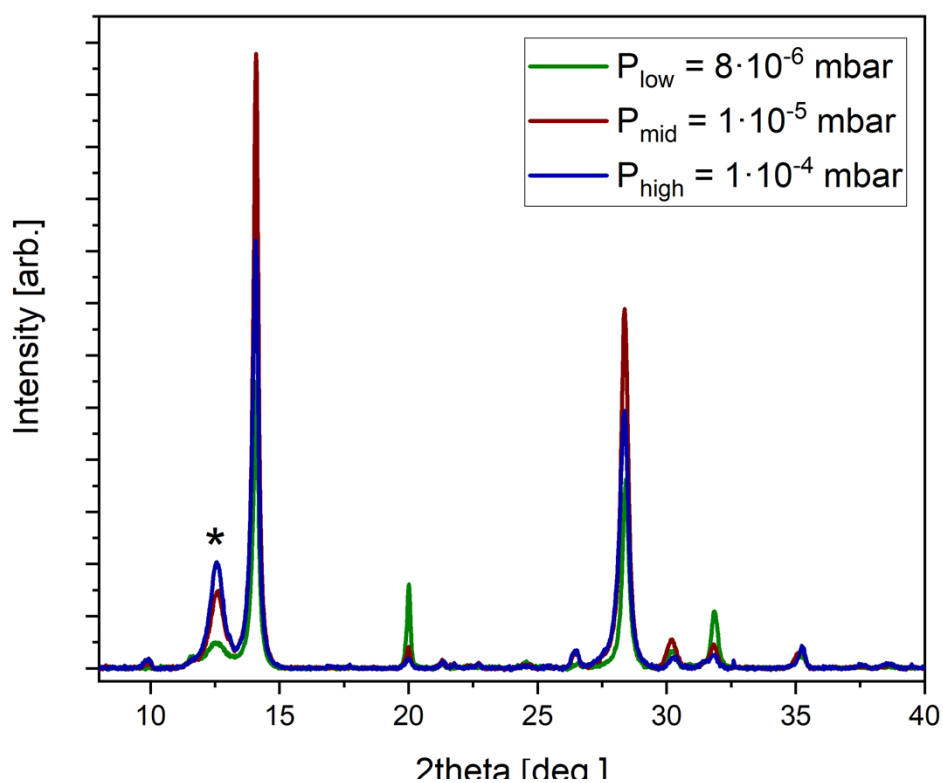


Figure S11: XRD diffractogram of films prepared at different pressures,  $\text{PbI}_2$  peak ( $12.6^\circ$ ) highlighted with star (\*)