# Imprint-induced grain growth in perovskite layers

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Recent work on methyl ammonium based halide perovskites has demonstrated their capability as active materials for lasers [1] or solar cells [2]. However, solution-processed polycrystalline layers, which are obtained by spin coating, are rough and may exhibit structural defects, such as holes. It could be demonstrated that thermal nanoimprint is well suited to improve the quality of these layers. The perovskite layers are flattened, holes are less prominent and especially the crystal grains have grown. Most commonly, the quality of the layers is characterized for control purposes and with respect to the application envisaged (e.g. by XRD, PL, ASE). The physics underlying the crystal grain growth during the imprint process has not been studied yet [3].

The present investigation intends to close this apparent gap. Therefore we ‘simulate’ specific situations during the imprint process as marked in Fig. 1, however, with an increased process time to amplify the effect. The imprint is performed with flat stamps (planar hot pressing, PHP). The stamp is substantially smaller than the sample, which allows us to characterize the impact of the temperature with and without pressure under exactly the same conditions (see insert). In a further experiment we study the layers after annealing under a nitrogen atmosphere.

Previous experiments have shown that the perovskites change their morphology already during the long heat-up time [3]. Since the ‘simulation’ asks for an experiment without a misleading heat-up, the imprint system is not loaded with the sample before the imprint temperature is reached (hot loading, HL).

The simulation at room temperature (RT) demonstrates the effect of pressure, only (Fig. 2). Obviously, the imprinted layer is compressed but no grain growth is observed. The simulation at reduced temperature (Fig. 3) documents a grain growth for the imprinted part, only. This means that grains under pressure are stimulated to grow at a temperature that would not be sufficient for grain growth without pressure. The simulation at a typical imprint temperature (Fig. 4) results in a layer with similar grain sizes in the imprinted and the annealed part. Here, the impact of temperature is stronger than the one of pressure.
The simulation results allow to develop a perception of what happens during the imprint process as sketched in Fig. 5. As soon as the imprint pressure is applied the perovskite layer is compressed. With increasing temperature the static pressure induces a grain growth during the heat-up phase. However, the higher the temperature the more it dominates the grain growth.
To further substantiate this view we will discuss it with theoretical concepts in mind. The necessary link is derived from the annealing experiment shown in Fig. 6, which shows a uniform growth of the grains with time, however, at an elevated temperature, only. Such a behavior indicates a ‘normal’ grain growth [4]. We anticipate that the theory is able to provide arguments for the dominance of pressure or temperature in the different temperature regimes.

[1] N. Pourdavoud et al, Adv. Mater. Technol. 3, 1700253 (2018); Adv. Mater. 29, 1605003 (2017).
[2] J. Xiao et al, J. Mater. Chem. A 3 , 5289 (2015).
[3] L. Dimesso et al, J. Mater. Sci. 54 , 2001 (2019); A. Mayer et al, JVST B 35, 06G803 (2017).
[4] H.V. Atkinson, Acta. Metall. 3, 469-491 (1988); M. Hillert, Acta. Metall. 13, 227-238 (1965)

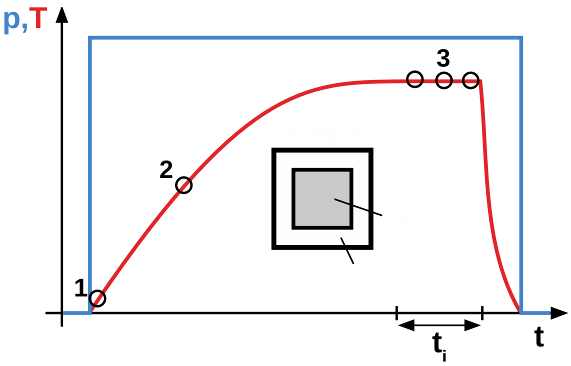


*Figure 1. Typical imprint procedure used for PHP of $MAPbBr_3$* – p = 100 bar, $T_i$ = 150°C, $t_i$ = 5 min, heat-up time 20 min. The labels refer to specific situations characterized in Fig. 2 – 4.

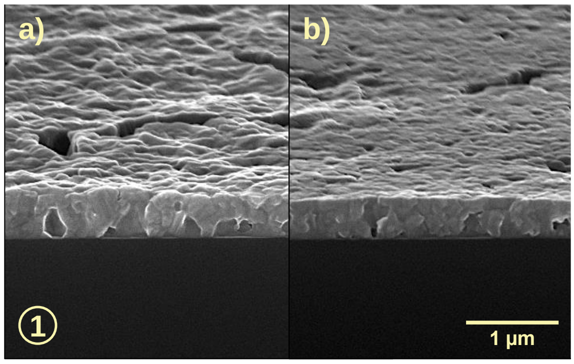


*Figure 2. Simulation of the impact of pressure* – a) annealed part, b) imprinted part (HL, 100 bar, RT, 60 min).

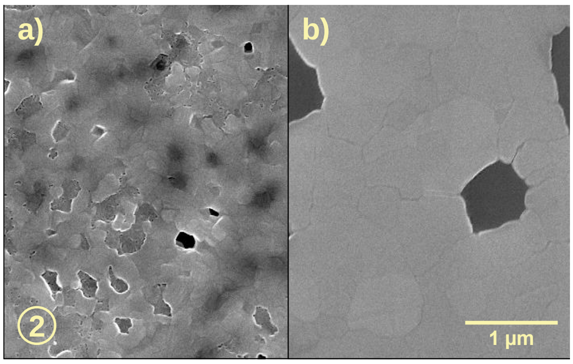


*Figure 3. Simulation of the impact of a reduced temperature* – a) annealed part, b) imprinted part (HL, 100 bar, 75°C, 60 min).

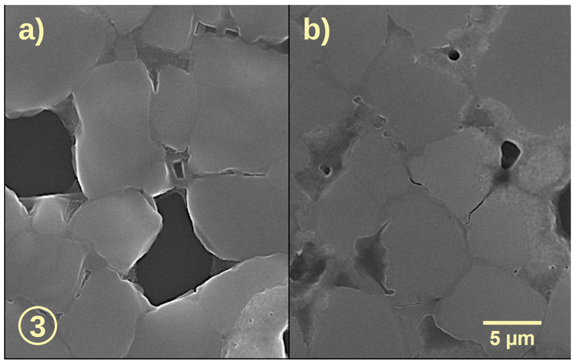


*Figure 4. Simulation of the impact of a typical imprint temperature* – a) annealed part, b) imprinted part (HL, 100 bar, 150°C, 5 min).

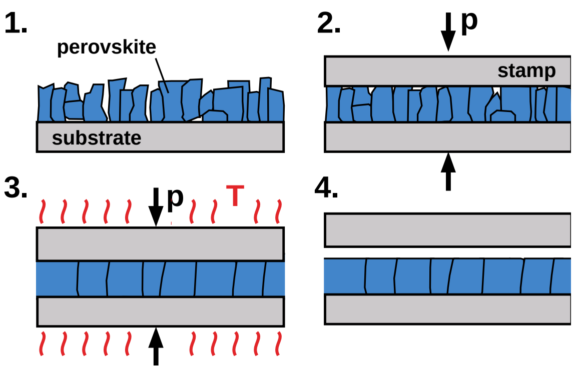


*Figure 5. Perception developed from the simulation experiments* – 1. Pristine layer, 2. compression, 3. grain growth, 4. final layer

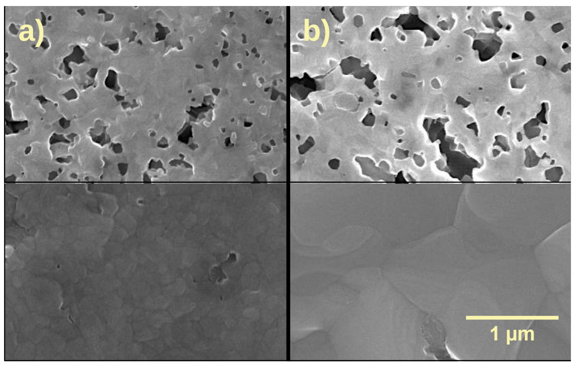


*Figure 6. Pure annealing experiment* – 75°C (top) / 125°C (bottom)*;* a) 1 min, b) 20 min.(nitrogen atmosphere)