

Rapid crystallization enables controlled and highly stable hybrid perovskite phase transition

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Perovskite hybrid semiconductor materials have an enormous potential for growth across the field with promising applications such as thin-film solar cells. Although device stability is the bottleneck of perovskite solar cell technology, recent advances show a promising way to implement future improvements.

In the field of hybrid perovskite materials, processing methods, compositional engineering, and other approaches need further development to compete with the most stable PV devices, such as silicon solar cells. However, scaling up perovskite solar cells (PSCs) for industrial production is a complex task for this young technology, mainly due to the poor stability of the material. Numerous approaches have been proposed to overcome this problem, and the different strategies can be divided into three categories: 1- chemical passivation; 2- compositional engineering; and 3- new synthesis methods.

The three mentioned strategies focus on removing crystal defects, either from the bulk or from the surface. The selecting layers and the final chosen architecture are also part of the problem to be solved; however, the perovskite attracts the most attention and is also the fundamental component of the cell.

A defect-tolerant perovskite film is less likely to be degraded from interstitial defects and deep traps, causing non-radiative centers, which are significantly related to the crystallization mechanism. Defects can determine the microstrain change in the perovskite lattice during crystal nucleation and growth, which can be further detrimental by external stress factors like humidity, photodegradation, and temperature. These defects will directly affect ion migration, non-radiative recombination, and organic decomposition, which are examples of mechanisms triggering irreversible degradation pathways.

Rapid IR hybrid perovskite crystallization

When a coated wet perovskite film is annealed, the heat provided by an IR pulse is the driving force to reach the supersaturation state by rapidly decreasing the concentration, thereby initiating nucleation and crystal growth. Looking at the specific FIRA case, crystal nucleation and growth can be controlled by the chamber temperature, pulse duration, and pulse number, as shown in Fig. 1a. Once nucleation has occurred, it is followed by the growth of a crystalline phase. The perovskite crystal formation can involve numerous intermediate phases that the growth rate can determine. The highly intense IR pulse causes the rapid evaporation of the solvent and provides the required thermal

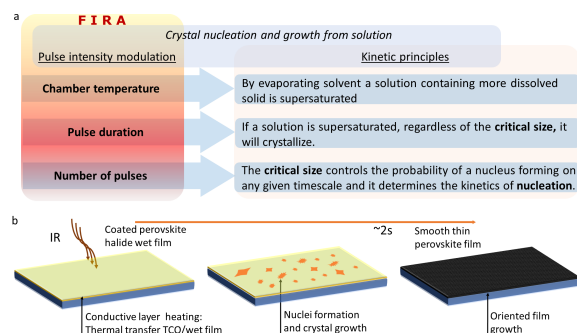


Figure 1: Schematic of the kinetic process in the nucleation and growth of a crystalline perovskite film from a solution and a) its relationship with the IR photonic pulses system, b) the sequential thin film perovskite formation.

activation energy for crystal nucleation and growth [1]. Interestingly, the IR pulse heats the conductive contact, rapidly transferring the thermal energy through the solid/liquid interface, as shown in Fig. 1b, where the thermal diffusion and interfacial energy lead to crystal growth. Then, by adjusting the number of pulses, the heating rate controls how supersaturation is reached and, as a consequence, how the nuclei distribution from tiny clusters defines the final crystal shape.

The experimental investigation of crystal nucleation and growth is complex and challenging for almost all systems. The classical nucleation theory stipulates that the critical nucleus is a sphere. The essential factor is how the total free energy associated with forming an average critical nucleus depends on its size, whatever the shape. However, this is a steady or quasi-steady-state assumption. This analysis cannot apply to non-thermodynamic equilibrium when the temperature changes too fast, as in the case of the FIRA, which is still one of the main challenges for the rate calculations in these processes.

Quasi-infinity steady-state numeric calculations corresponding to non-isothermal conditions must be performed with a non-constant temperature rate. Particularly in perovskite film processing, the calculation of nucleation and growth rates needs to be adapted for specific cases.

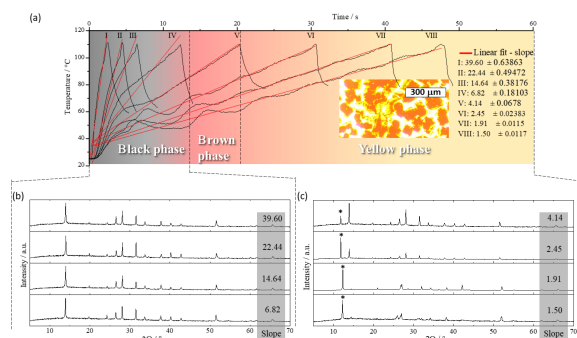


Figure 2: a) Temperature profile of the studied films under different heating rates with their respective linear fitting. Inset: optical image of a film processed with the lowest heating rate. b) and c) X-ray diffraction patterns of the selected films labeled with the respective heating rate-slope. The asterisk over the peaks highlight the δ phase.

The FAPbI₃ case

A phase transformation occurs during heating and cooling at specific temperatures, accompanied by enthalpic and entropic thermodynamic changes. Phase transitions can emerge via different kinetics pathways, for example, when applying rapid thermal annealing and quenching processes at different rates. Accordingly, to the published work [2] it was applied 17 pulse times and respective intensities to the spin-coated FAPbI₃ wet films with the IR photonic annealing method.

The IR pulse incident on the film has an estimated power density of 58.3 W/cm², and rapid cooling was ensured by opening the annealing chamber after light pulsing. A temperature profile of 8 selected annealed films and their respective phase transitions as a function of the heating rates is shown in Fig. 2a. Note that the temperature evolution was measured on the film's surface with an IR pyrometer, and we used the slope of the curve until quenching as a reference for all heating rates for simplification. We identified three main regimes at this step, from black perovskite and mixed brown phases to the yellow non-perovskite phases, denoting the enthalpic and entropic effect on phase transition. The inset of Fig. 2a, indicates an inhomogeneous yellow FAPbI₃ film processed with the lowest

heating rate.

The structural phases of the processed films have been characterized with x-ray diffraction (XRD) as shown in Figures 1b and c, XRD patterns of the perovskite and non-perovskite regimes, respectively. The patterns of the black phase regime evidence the absence of both PbI₂ and other impurities.

FAPbI₃ has been reported as cubic by neutron diffraction at room temperature. Still, many other authors have claimed an alpha cubic phase by XRD characterization without an in-depth structural and symmetry analysis. In geometrical terms, the Pm-3m-I4/mcm phase transition has been widely observed in oxide perovskite materials, such as SrTiO₃, due to lattice instabilities as in perovskite halides where strain can accumulate in the lattice upon substrate cooling.

For the FAPbI₃ IR annealed case, the used refinement model does not accurately match the cubic phase to our processed black films (in terms of peak positions); instead, a tetragonal, primitive unit cell matched the peak position the best. Besides, a small octahedral tilting at room temperature can produce a noncubic structure. Therefore, IR annealing crystallizes a black perovskite photoactive phase (which fits with a tetragonal state) instead of a cubic alpha phase. The nature of this structural phase and its symmetry-related aspects are a strong motivation for further work.

Notes

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References

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