université PARIS-SACLAY

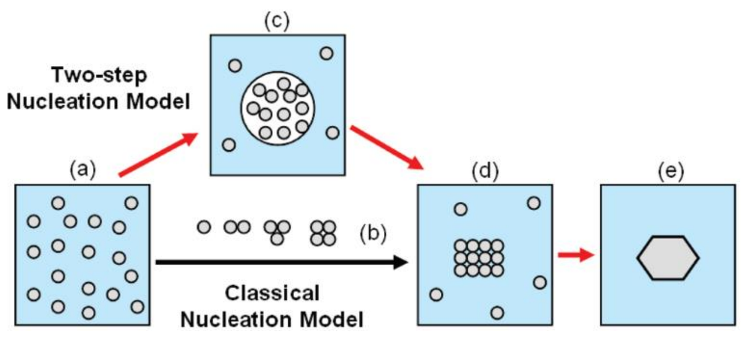
Development of a microfluidic device for the study of plasma-induced nucleation

C. Zindy[1], C. Lafargue[2], J.-F. Audibert[3], A. Salmon[4], A. Brisset[5], R. B. Pansu[2], A. Spasojevic[1]

[1] Laboratoire SPMS, CNRS, CentraleSupélec, Université Paris-Saclay,
[2] Laboratoire LuMIn, CNRS, ENS Paris-Saclay, CentraleSupélec, Université Paris-Saclay,
[3] Laboratoire PPSM, CNRS, ENS Paris-Saclay, Université Paris-Saclay
[4] Laboratoire LGPM, CentraleSupélec, Université Paris-Saclay,
[5] Laboratoire EM2C, CNRS, CentraleSupélec, Université Paris-Saclay,

CONTEXT

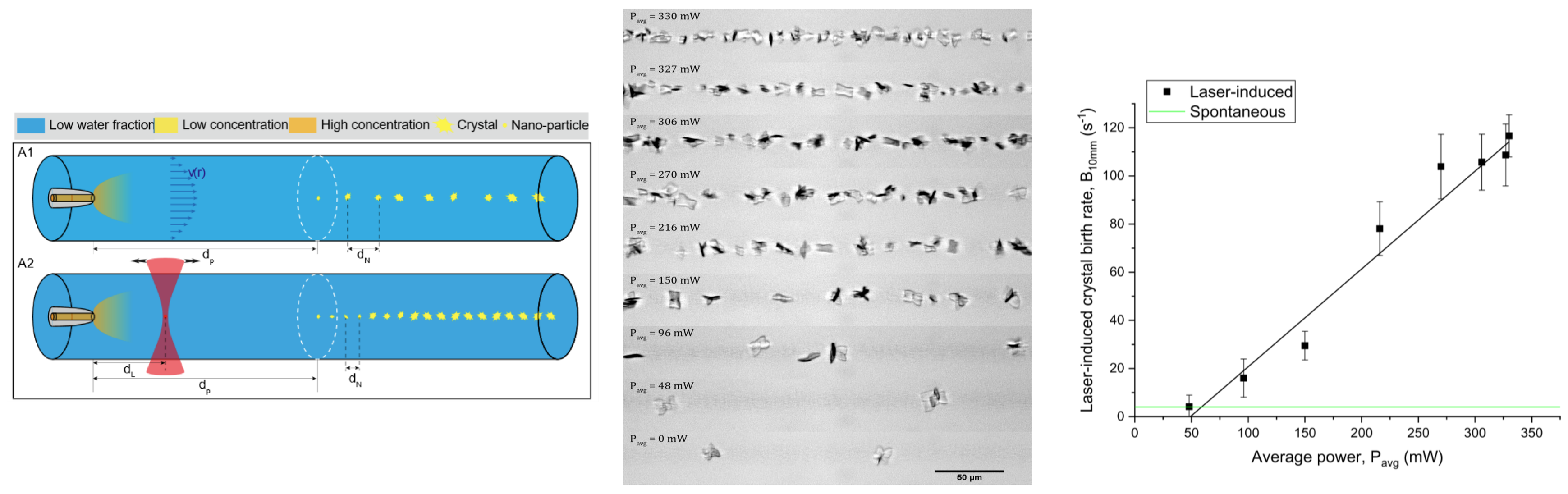
Crystallization is a state transition from a liquid or gas phase to an organized solid structure called crystal. It is widely used in industry as separation and purification process. Two main theories explain its mechanism [1].



Several crystallization techniques such as precipitation, slow evaporation, grinding exist but those don't allow any control on nucleation and don't give any information about where and when nucleation is initiate.
There is a need for **in situ, on-demand and scalable seeding techniques** allowing a high level of polymorph and size distribution controls.

PREVIOUS WORKS

Nucleation can be **triggered by external fields** with a better control over it.
(e.g. laser induced nucleation NPLIN increases the nucleation rate [2])



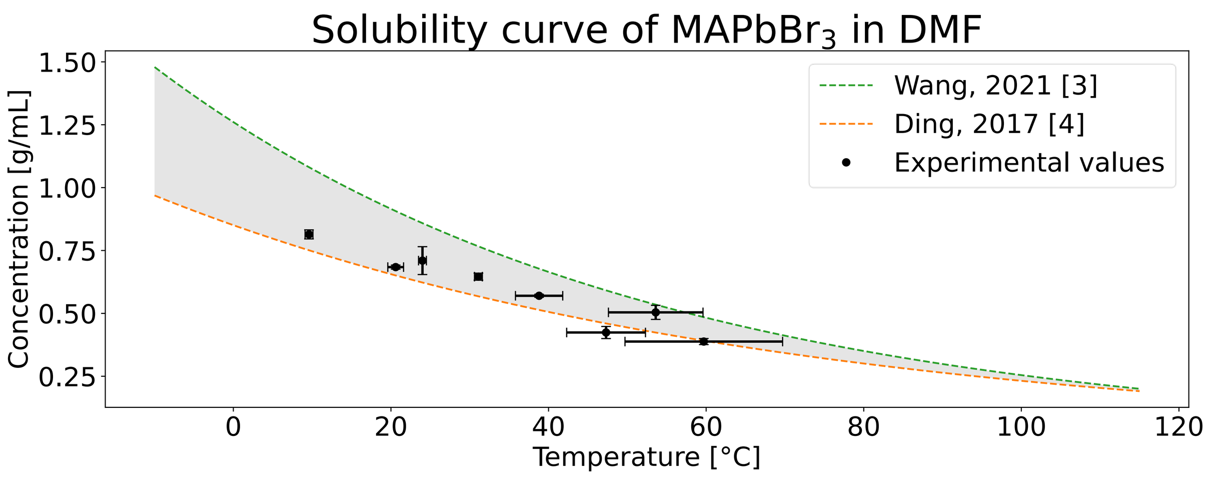
Recent studies in CentraleSupélec show that **cold plasma can induce and control nucleation** with an even greater efficiency.

METHODOLOGY

Nanosecond pulsed discharges will be applied on a solution of supersaturated $MAPbBr_3$ perovskites in N,N-Dimethylformamide (DMF). Nucleation mechanisms will be studied in a microfluidic device by epifluorescence; and several plasma diagnosis. First stages are to characterize the solution and develop the microfluidic system.

SOLUTION CHARACTERIZATION

The **solubility diagram** is necessary to design a crystallization cycle.

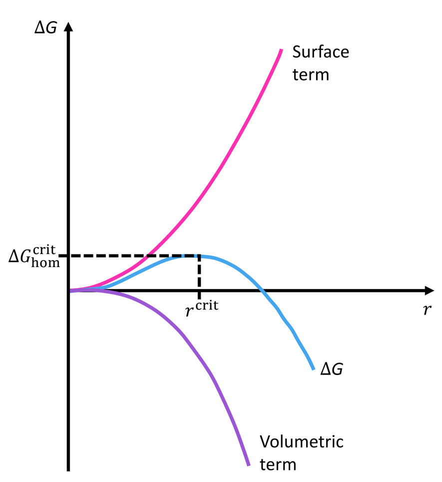


Solubility limit is a key information to control the solution's **supersaturation** (concentration on concentration at solubility).

Gibbs free energy : (energy from supersaturation)

$$\Delta G = -\frac{4\pi r^3}{3V}\Delta\mu + 4\pi r^2\gamma$$

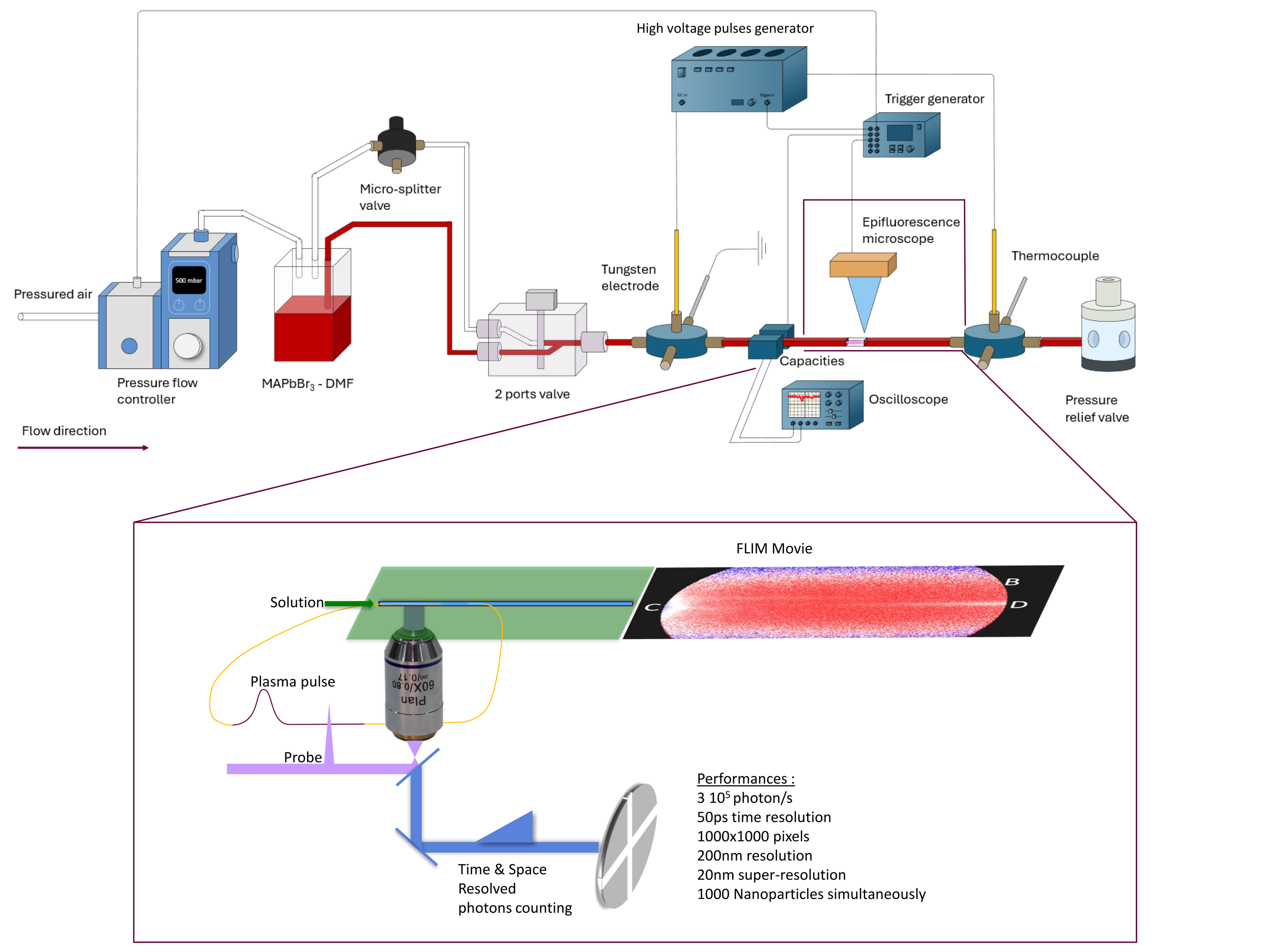
Volumetric term | Surface term



The interfacial energy **γ** between germ and liquid works as a **potential barrier** preventing the formation of the nucleus.

The critical size of a cluster r_{crit} depends on the **supersaturation** of the solution.

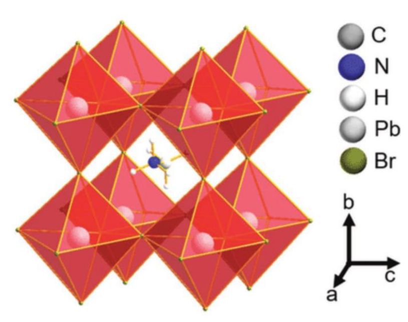
MICROFLUIDIC EXPERIMENTAL SETUP

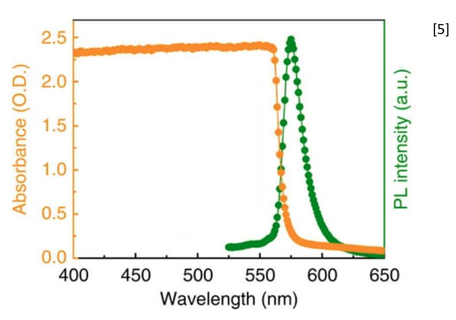


RESULTS

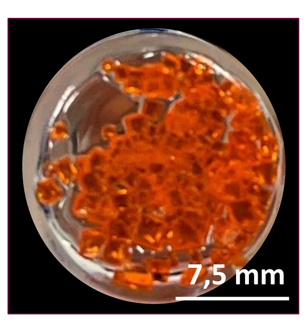
CRYSTALS

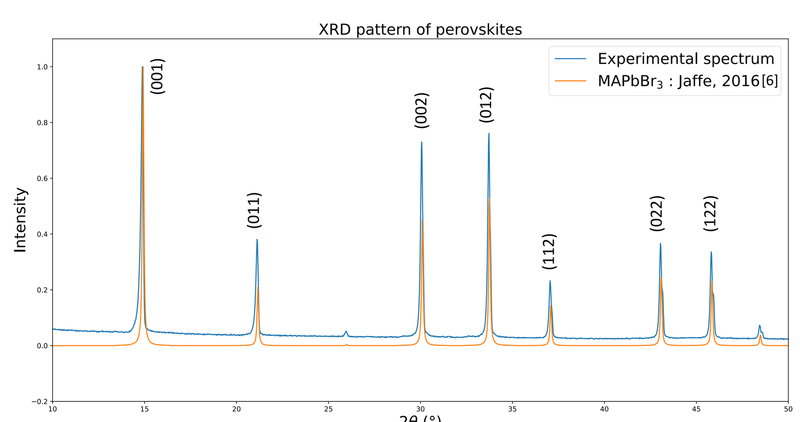
$MAPbBr_3$ ($MA=CH_3NH_3^+$) perovskites are fluorescent in solid form but not when dissolve in DMF.



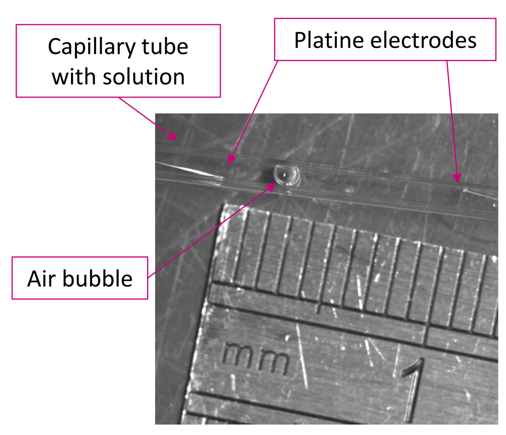


MABr and $PbBr_2$ powders in a DMF solution crystalize as $MAPbBr_3$ perovskites.



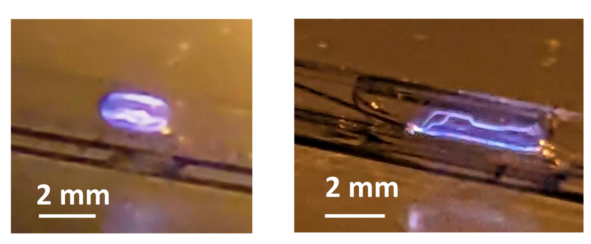


PLASMA

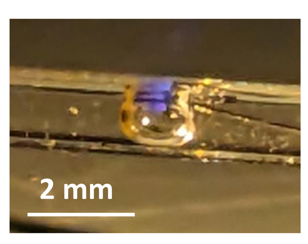


We apply 10 kV nanosecond discharges at 10 kHz in different solutions to trigger plasma discharges.

Solution n°1 :
NaCl : 100 g/L
(20°C)
Bubble size : 2 mm or 7 mm
1 pulse

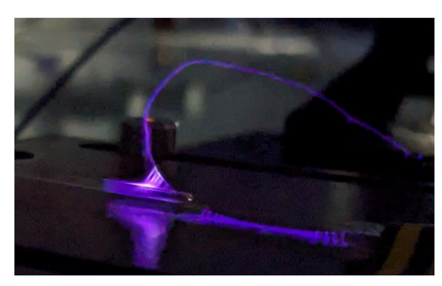


Solution n°2 :
$MAPbBr_3$-DMF : 0,6 g/mL
(S=90%)
Bubble size : 1 mm
30 pulses at 10 kHz



CHALLENGES

- Having a regular bubble train for a future automatization of the process.
- Triggering the plasma discharge with only 1 pulse.
- Reduce electromagnetic plasma radiations.
- We can have a DBD discharge between the electrodes in and outside of the capillary.



ACKNOWLEDGMENTS

ANR INCRYS | ANR-23-CE51-0033

References

1. Erdemir, D. et al., Acc. Chem. Res. 42, 5 (2009) 10.1021/ar800217x
2. Zhang, Z., Laser-Induced Nucleation in a Coaxial Microfluidic Mixer (2019)
3. Wang, H. et al., Mater. Sci. Semicond. Process., 135 (2021) 10.1016/j.mssp.2021.106107
4. Ding, J. et al., J Mater Sci. 52 (2017) 10.1007/s10853-017-0995-8
5. Saidaminov, M. I., et al., Nature Comm., 6(1) (2015) 10.1038/ncomms8586
6. Jaffe, A. et al., ACS Cent. Sci., 2, 4, 201–209 (2016) 10.1021/acscentsci.6b00055