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# XRD and phase transition study of organohalide perovskites thin films and microwires

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We have performed the structural study of the bulk $MAPbI_3$ samples (powder and polycrystalline micro−wires) and $MAPbI_3$:Cl films grown on compact $TiO_2$, poly(3,4-polyethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS), commercial fluorine doped $SnO_2$ (FTO) and bare glass for comparison.

In the case of films, we registered diffraction patterns in $\theta$–$2\theta$ configuration (*chi-gamma* scan) and rocking curves for different reflections, as well as in a configuration with the transferred momentum almost parallel to the surface (*delta* scan) at room temperature (RT). Unlike the case with films, powder or micro−wires were mounted into glass capillaries and scanned ($\theta$–$2\theta$ scans) from RT to 100 K.

## 1. MAPbI3:Cl films at RT

The perovskite films show a strong *hh*0 preferential orientation for any of the evaluated substrates (Fig. 1). The fraction of preferentially oriented grains increases on smoother substrates like PEDOT:PSS.[1]

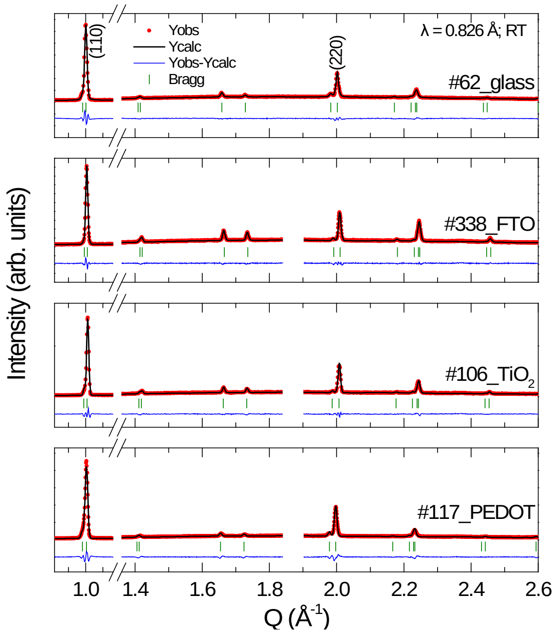


**Figure 1**. *Le Bail* profile fits (solid line) of SXRD data (circles) of $MAPbI_3$ films on glass, glass/FTO, glass/FTO/$TiO_2$ and glass/FTO/PEDOT:PSS at RT. Tick marks indicate the position of allowed reflections in *I*4*cm*.

Besides, the chemical nature and reactivity of the substrate have an important influence on the crystallite sizes and the lattice parameters through the chlorine content as well as by the incorporation of oxygen and probably iodine vacancies in the MAPbI3:Cl films during the synthesis.[1]

## 2. Low temperature phase in bulk $MAPbI_3$ samples: powder and polycrystalline micro−wires.

It can be seen that $MAPbI_3$ undergoes a series of not clearly established structural phase transitions between pseudocubic, tetragonal and orthorhombic phases as a function of the temperature (Fig. 2).

The polycrystalline micro−wires sample is pseudocubic at room temperature (RT). At temperatures slightly lower than RT, the pseudocubic symmetry transforms to tetragonal and then to orthorhombic at about 150 K. It is important to notice that the tetragonal phase remains present up to the complete transformation at ~100 K (Fig. 2). However, the powder sample is tetragonal at RT and it then changes into orthorhombic at around 150 K. The coexistence of the tetragonal and orthorhombic phases is observed in almost the same temperature range.

Data are still undergoing analysis, but this complex scenario (polymorphism or phase separation) probably requires further experiments.

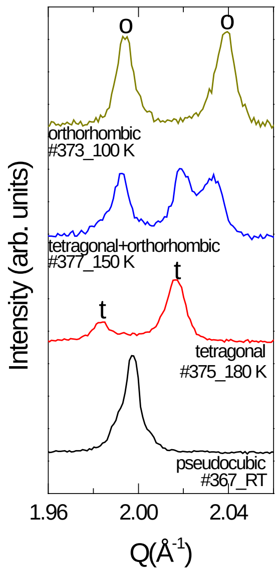


**Figure 2**. Thermal evolution of the SXRPD (λ= 0.826 Å) profiles for the $MAPbI_3$ polycrystalline micro−wires sample in the temperature range 100−298 K. O and T marks are used to identify the presence of the tetragonal and orthorhombic phases.

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[1] E. Climent-Pascual, B. Clasen Hames, J.S. Moreno-Ramírez, A. Luis Álvarez, E.J. Juarez-Perez, E. Mas-Marza, I. Mora-Seró, A. de Andrés and C. Coya, "Influence of the substrate on the bulk properties of hybrid lead halide perovskite films", *J. Mater. Chem. A*, 2016, **4**, 18153-18163.