

# Halide Exchange in Macro-Sized Halide Perovskite Single Crystals

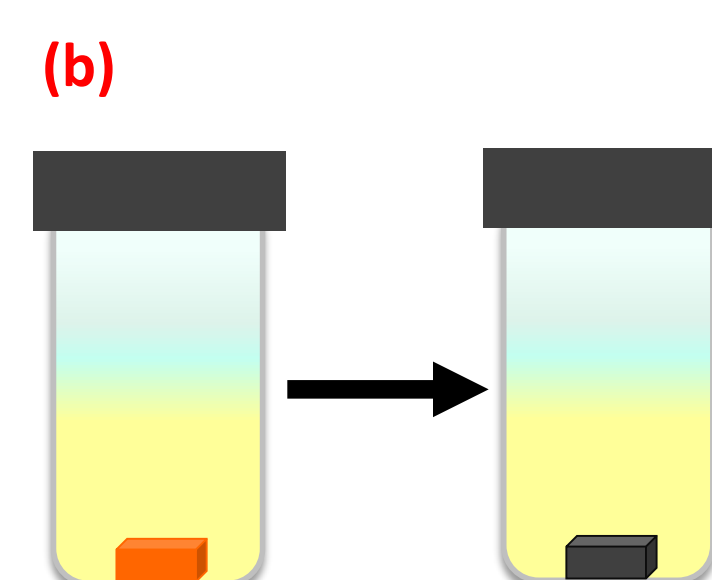
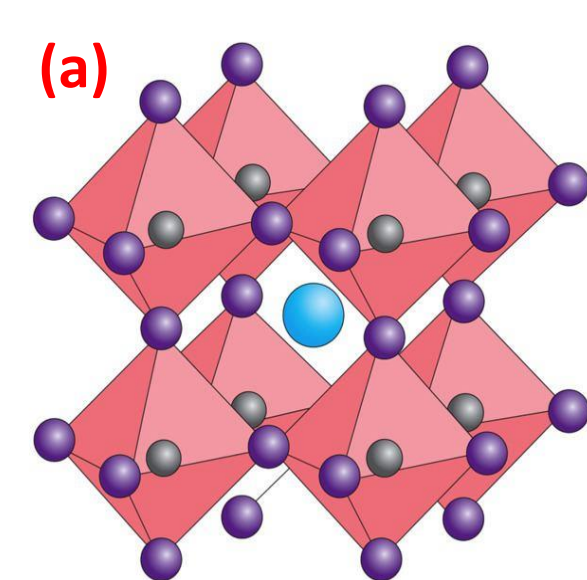
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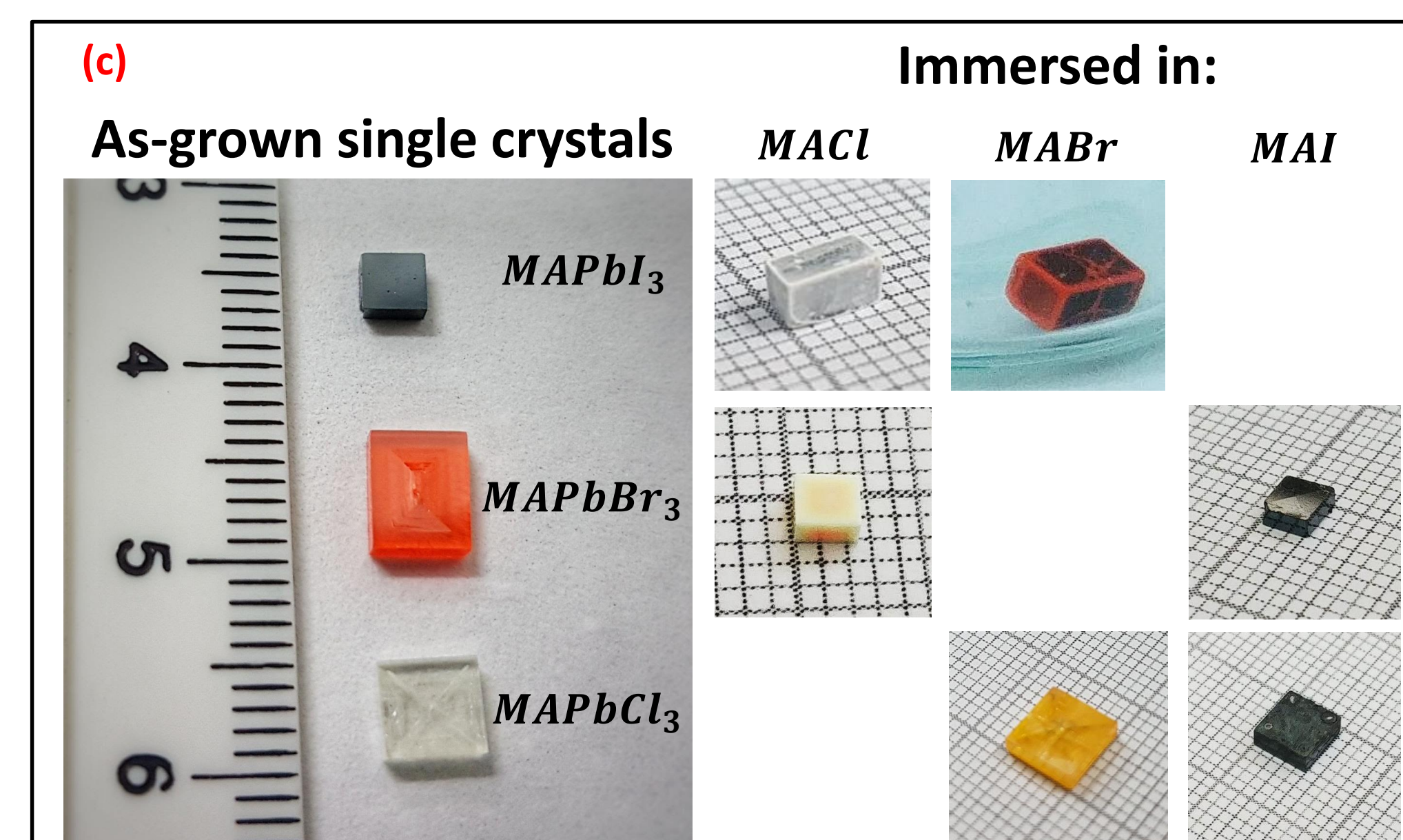
Halide Perovskites, rising star materials in photovoltaics, with the general formula  $ABX_3$ , where  $A$  = methylammonium (MA), formamidinium (FA) or Cs,  $B$  = Pb and  $X$  = halide have remarkable electronic and optical characteristics. The identity of the  $X$  component influences greatly the band gap of the material, and mixed halide compositions have been used for band gap-tuning. We demonstrate halide exchange in mm-sized  $MAPbX_3$  single crystals, achieved by diffusion. In these macro-sized crystals, the effects of surfaces and defects are significantly smaller than in microcrystals and polycrystalline thin films studied previously. Therefore, they are better suited to examine the fundamental exchange process(es), unencumbered by possible grain boundary and surface diffusion effects.

## Halide exchange reaction

- General formula:  $ABX_3$
- $MAPbCl_3$ ,  $MAPbBr_3$  and  $MAPbI_3$  single crystals were grown using various methods <sup>1-3</sup>.
- As-grown single crystals were placed in an “exchange solution” in ambient conditions, in the dark for different time periods (days).
- The “exchange solutions” contain 0.1M  $MAX$  ( $X = Cl$  or  $Br$  or  $I$ ) in isopropanol.

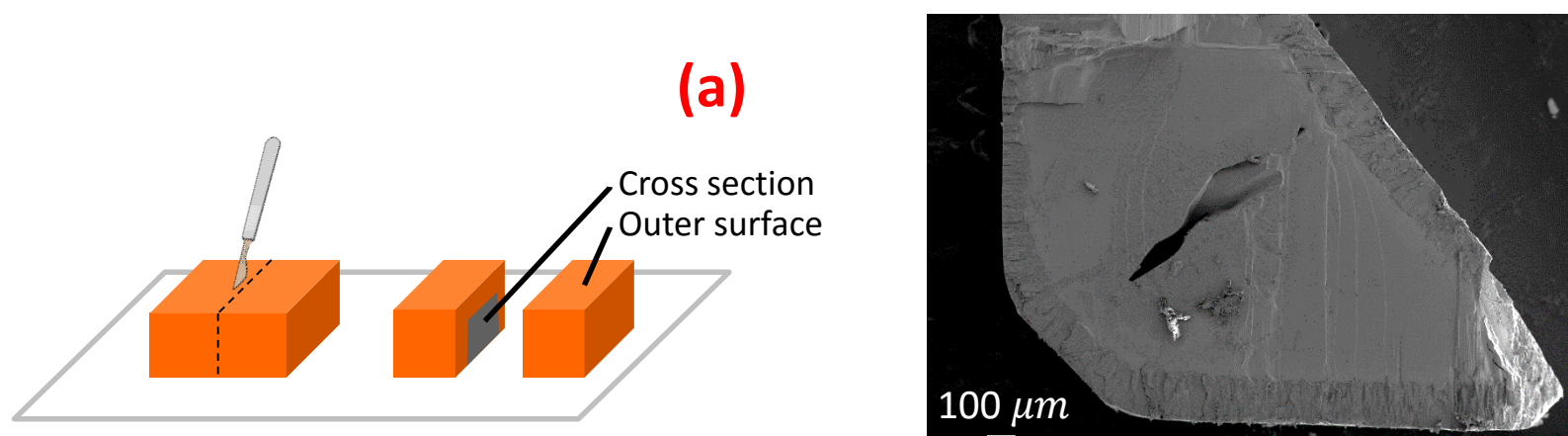


(a) Perovskite crystal structure, (b) Scheme of immersed  $MAPbBr_3$  crystal in a MAI exchange solution, (c) “Before/After” crystals.

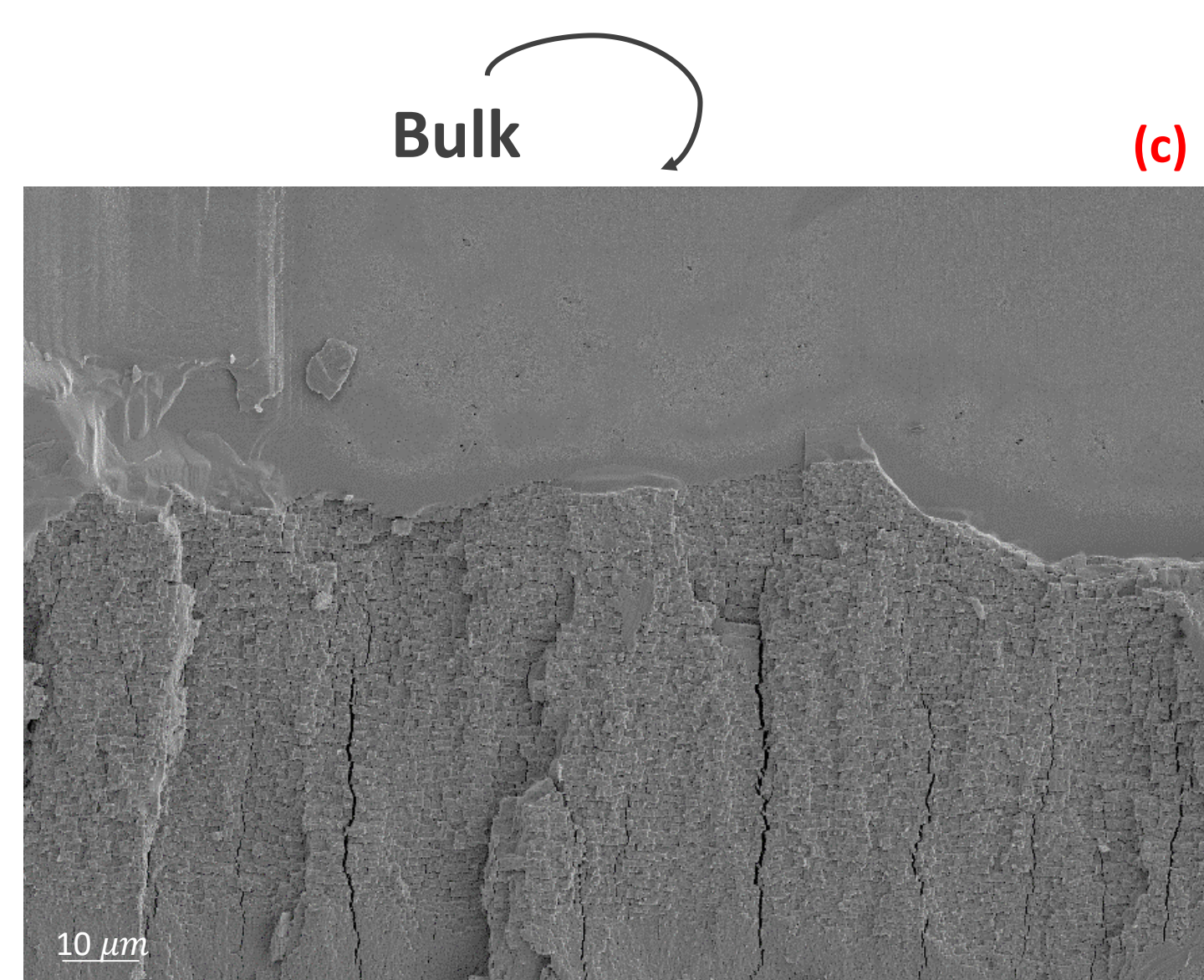


## Morphology change

Scanning Electron Microscope (SEM) images of a cross-section show a distinct morphology change between the bulk of the original single crystal and the exchanged layer close to the surface.



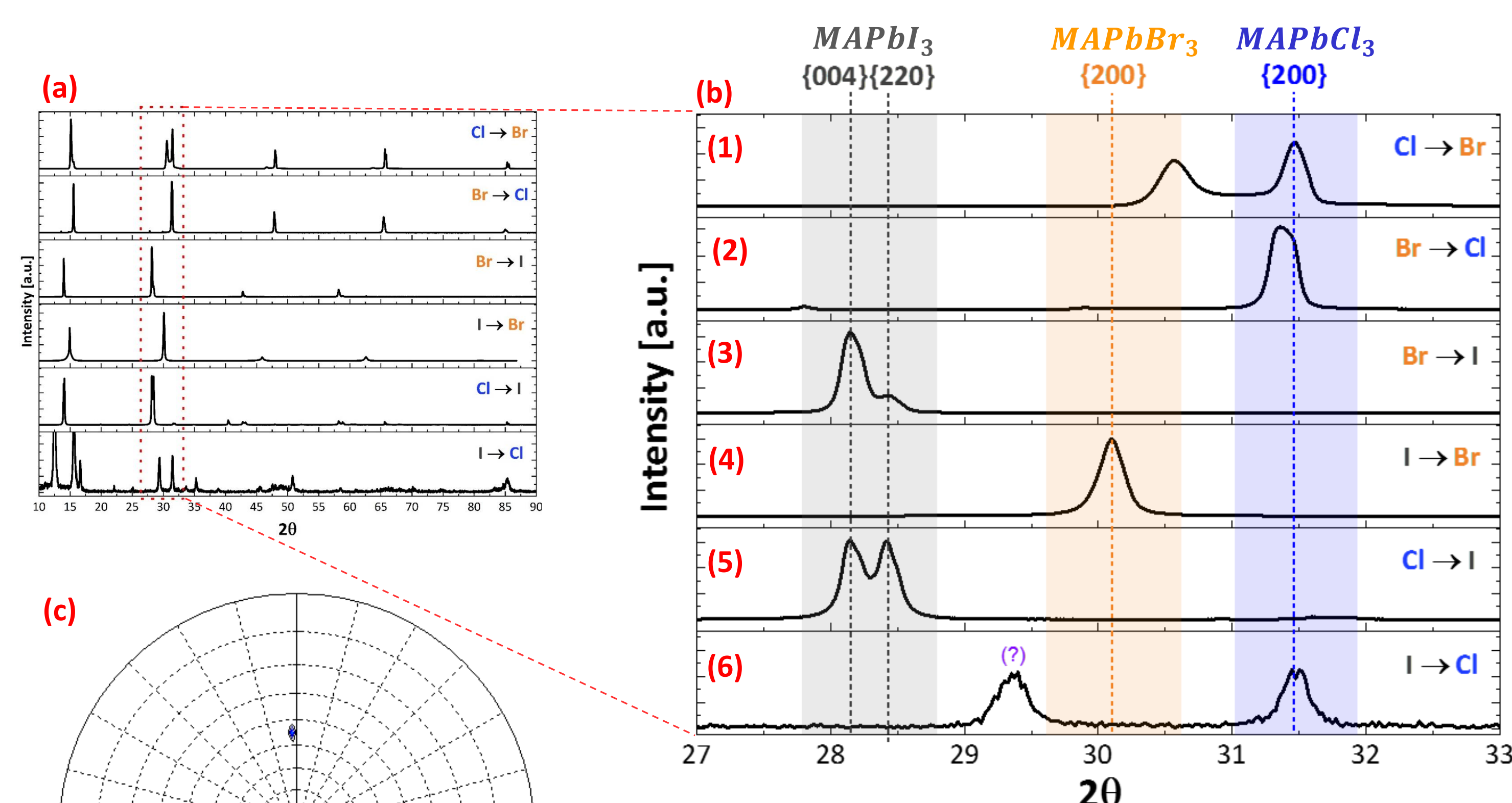
(a) Cross-section scheme of a crystal post exchange. (b),(c) Representative SEM images of a  $MAPbI_3$  crystal immersed in  $MABr$  solution for 1 month.



Surface

## Halide pair determines the crystallinity post substitution

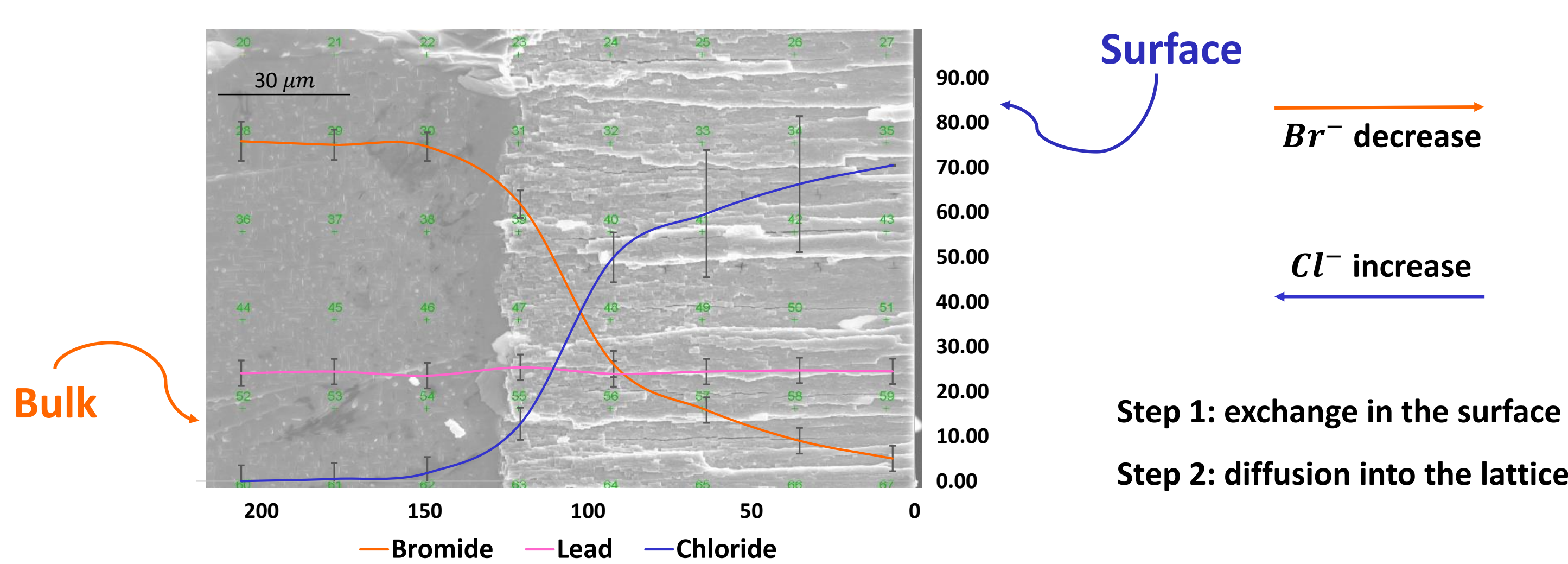
In ambient conditions	$MAPbCl_3$	$MAPbBr_3$	$MAPbI_3$
Symmetry	Cubic	Cubic	Tetragonal
Space group	$Pm\bar{3}m$	$Pm\bar{3}m$	$I4/mcm$



(a),(b) x-ray diffraction (XRD) spectra of crystals post substitution. Colored regions and lines refer to pure  $MAPbI_3$ ,  $MAPbBr_3$ ,  $MAPbCl_3$ . (c)  $\{011\}$  XRD pole figure of  $MAPbCl_3$  crystal immersed in  $MABr$  solution. The orientation of the surface is (001).

- Similar-sized halide pairs (i.e.,  $Br^-$  and  $Cl^-$ ,  $Br^-$  and  $I^-$ , not  $Cl^-$  and  $I^-$ ): high orientation regardless of symmetry and no matter which halide is the in-coming and which is the out-going (spectra 1-4).
- $Cl^-/I^-$ : the crystals do not remain single crystals (spectra 5-6).
- The exchange causes a lattice parameter change and may cause a symmetry change.
- Spectrum 1**: the substituted layer is thinner than the penetration depth of the x-ray, therefore we also see peaks that belong to the bulk single crystal.
- Pole figure** (representative of all similar-sized halide pairs): after the exchange the original crystal remains a single crystal.

## Composition gradient forms in the crystal



Representative SEM image and EDS composition analysis of a cross-section of a  $MAPbBr_3$  crystal soaked in  $MACl$  solution for 6 days. Green crosses represent the measured points.

- Electron Dispersive Spectroscopy (EDS) analysis shows a gradual change in the halide composition of the crystal.
- The composition of the in-coming halide is maximal on the surface of the crystal, and drops as we proceed further into the core of the crystal, and *vice versa* for the out-going halide.
- The ratio between the sum of halides and lead remains approximately 3:1 throughout the sample.

## Acknowledgements

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## Conclusions and future work

- The crystal orientation post exchange is determined by that of the initial crystal.
- Only similar-sized halides exchange results in a single crystal (a topotactic reaction).
- Valuable result when one wishes to achieve a specific composition of halide perovskite crystals/crystallites, using multi-synthesis steps without compromising the degree of crystallinity and orientation.

- Future work**: Determine the diffusion coefficients.

1. Shamsi J, Abdelhady AL, Accornero S, et al. N-methylformamide as a source of methylammonium ions in the synthesis of lead halide perovskite nanocrystals and bulk crystals. - *ACS Energy Lett.* 2016;1(5):1042-1048. doi: 10.1021/acsenerylett.6b00521.  
2. Rakita Y, Meirzadeh E, Bendikov T, et al. CH3NH3PbBr3 is not pyroelectric, excluding ferroelectric-enhanced photovoltaic performance. *APL Mater.* 2016;4(5). Accessed 9 May 2018. doi: 10.1063/1.4949760.  
3. Rakita Y, Bar-Elli O, Meirzadeh E, et al. Tetragonal CH3NH3PbI3 is ferroelectric. *Proc Natl Acad Sci U S A.* 2017;114(28):E5504-E5512. Accessed 21 October 2017. doi: 10.1073/pnas.1702429114.