University of Cologne

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Unraveling the electronic structure of halide perovskites

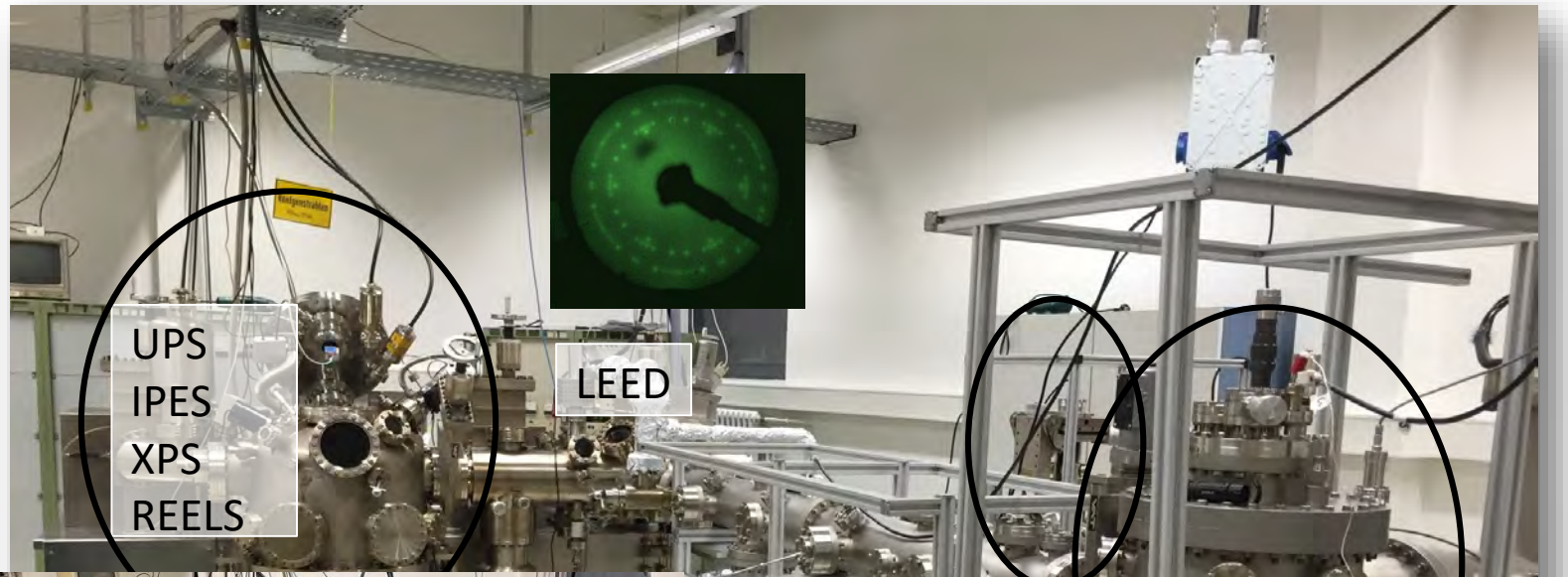
Summer School, Khiva

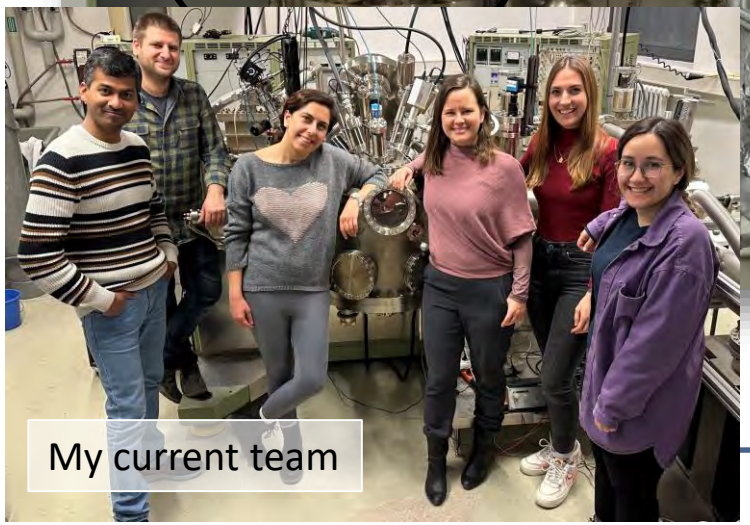
Selina Olthof

Cologne Surface Science Lab

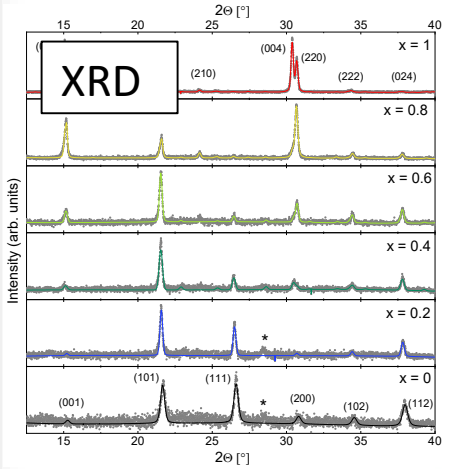
My research focus: determination of the **electronic structure using photoelectron spectroscopy**

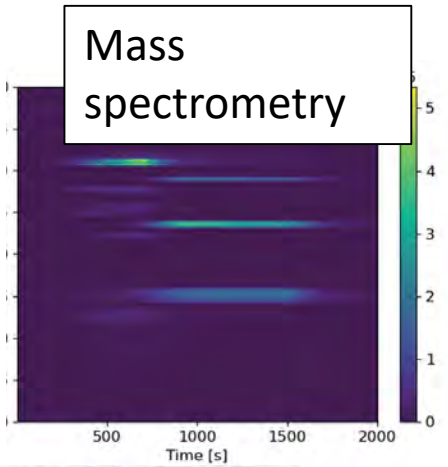
My Surface Science Lab in Cologne

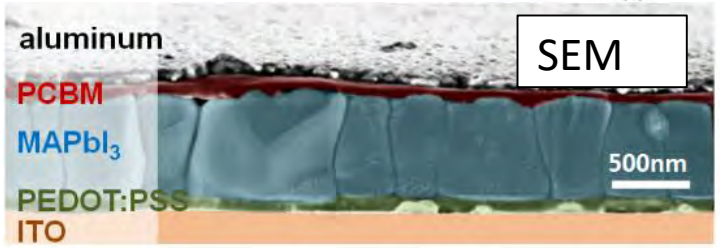




Additional techniques for analysis



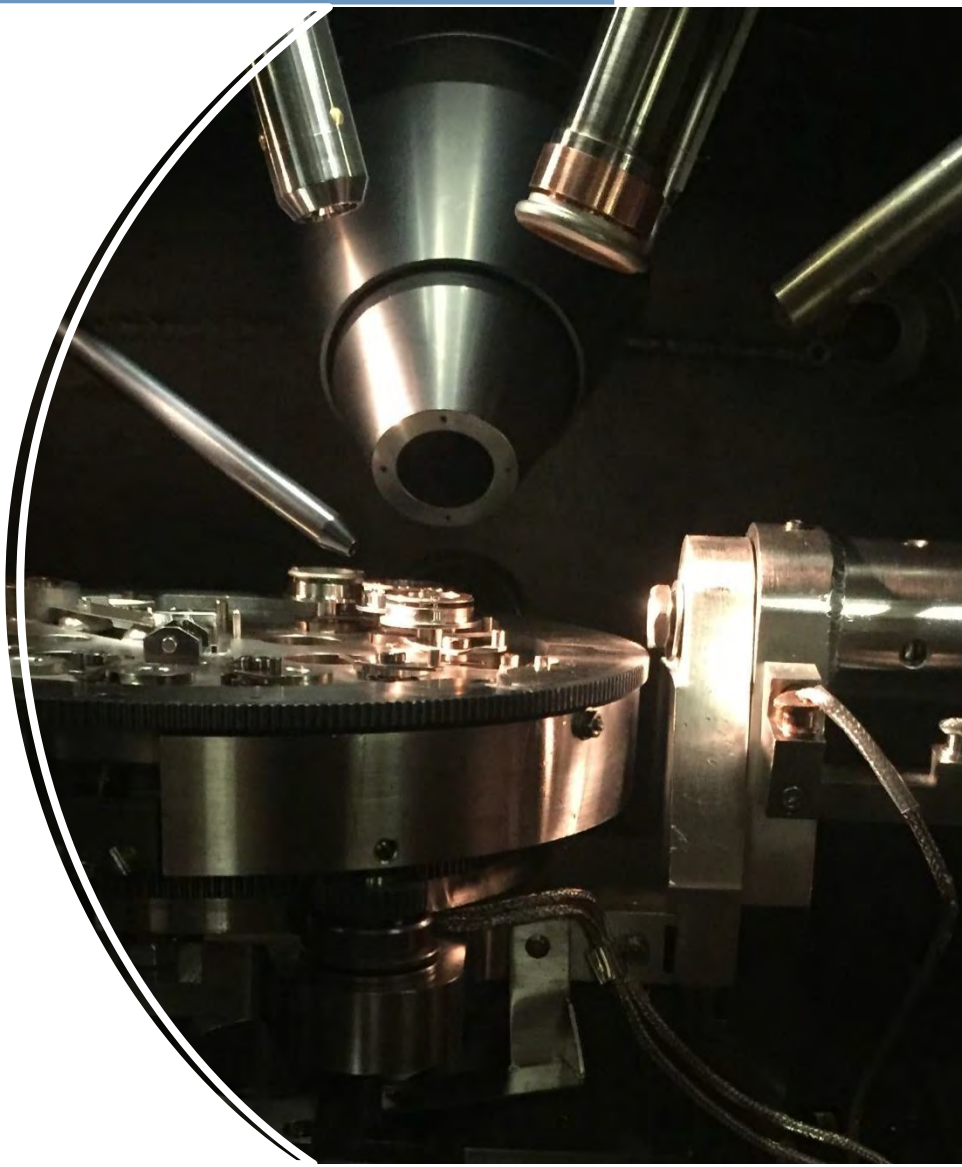




We investigate well-defined materials relevant for thin film optoelectronic applications

Content

1. Introduction halide perovskites
2. Photoelectron spectroscopy (UPS / IPES)
3. Electronic structure of $MAPbI_3$
4. Considerations for measuring
5. Tuning of perovskite composition
6. Energy levels of mixed perovskites

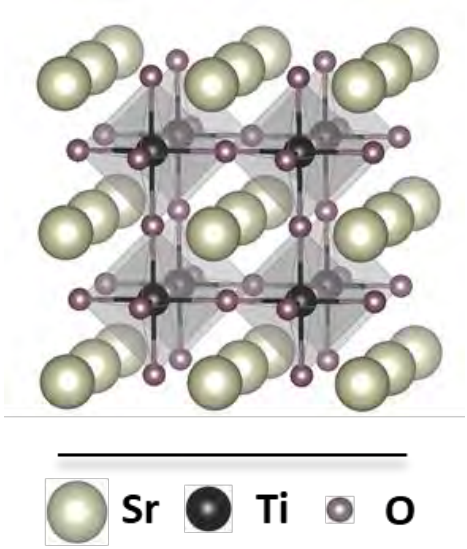


Perovskites

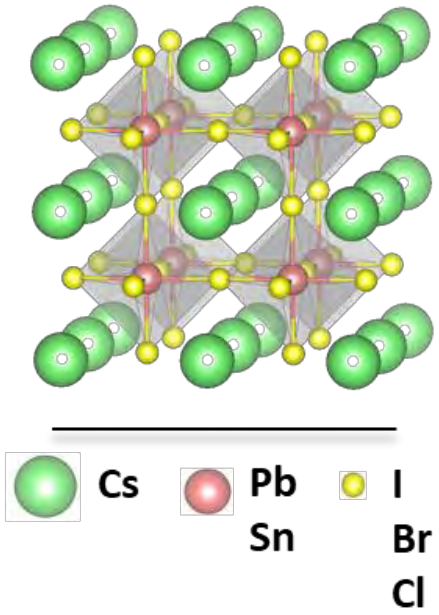
Perovskite: class of compounds with the same crystal structure as $CaTiO_3$

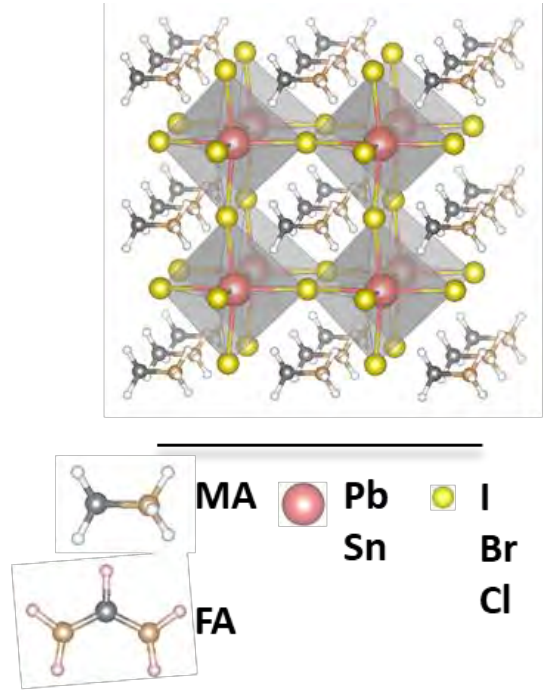
→ Stoichiometry is **ABX_3**:

Most are oxides, e.g. $SrTiO_3$



… but halide compounds exist as well

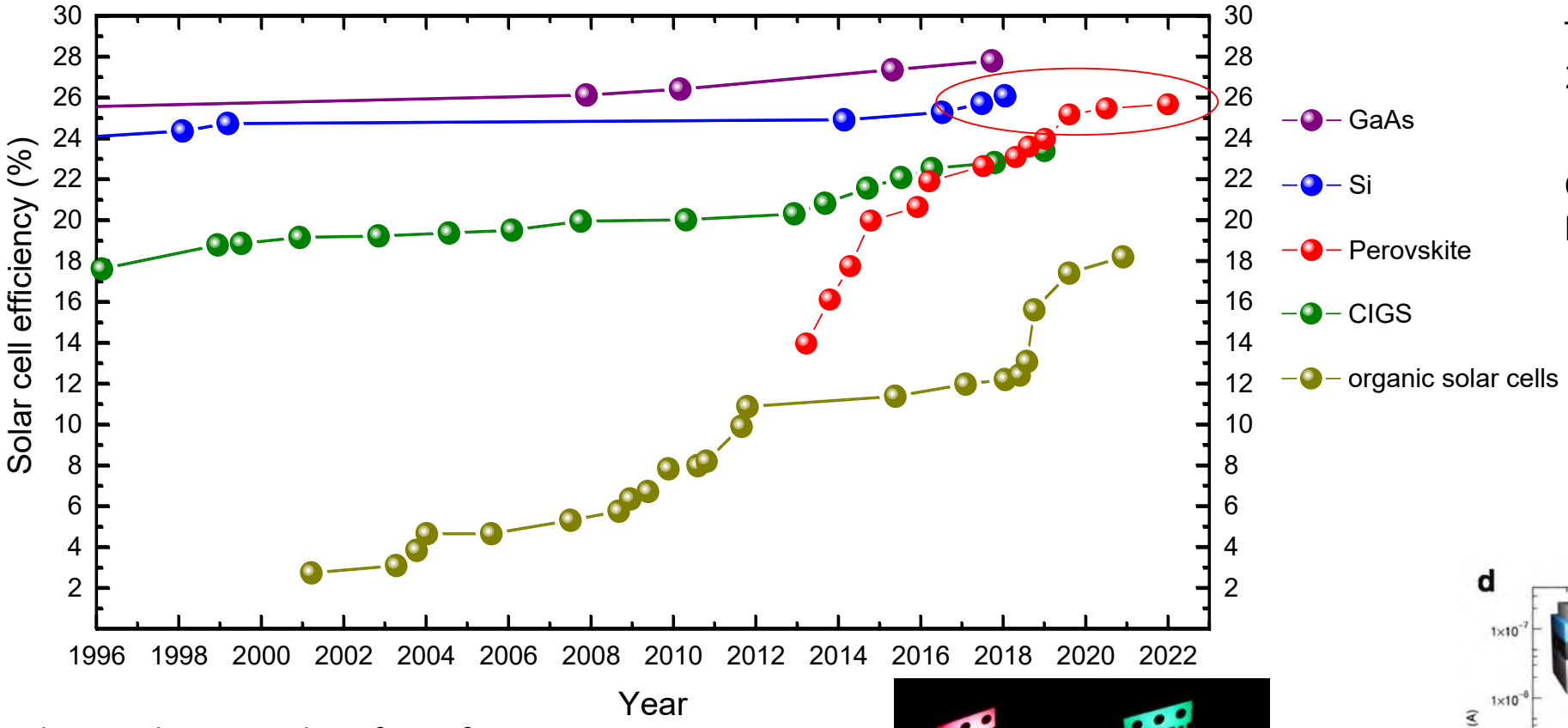




Here the perovskite lattice can be stabilized by Cs
or a small organic cation Methylammonium ("MA" CH_3NH_3) or Formamidinium ("FA", $CH(NH_2)_2$)

Solar cell efficiency chart

Widespread interest today because of overwhelming success in thin film photovoltaics

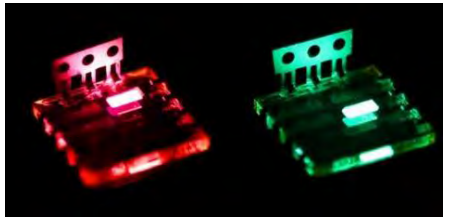


Today : highest certified efficiency 25.7%

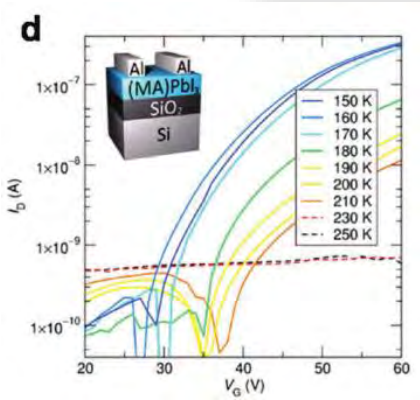
Commercial demonstrators are being developed

Other applications also of significant interest, e.g.

- Light emitting diodes
- (Photo-)transistors, etc.
- X-ray detectors



Tan et al., Nat. Nanotechnol. 9, 687 (2014)



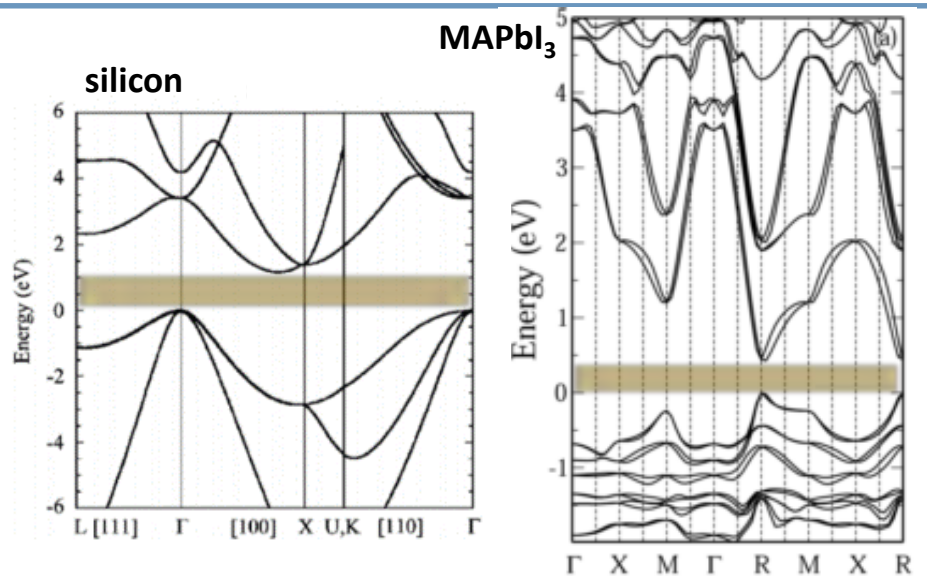
Lobam et al., J Phys Chem Lett 6, 3565 (2015)

Image adapted from Schmidt-Mende, Olthof, Dyakonov, Phys. Unserer Zeit 50, 298 (2019)

Basic properties of halide perovskites

Advantageous properties:

1. Direct band gap
   (with large band dispersion)



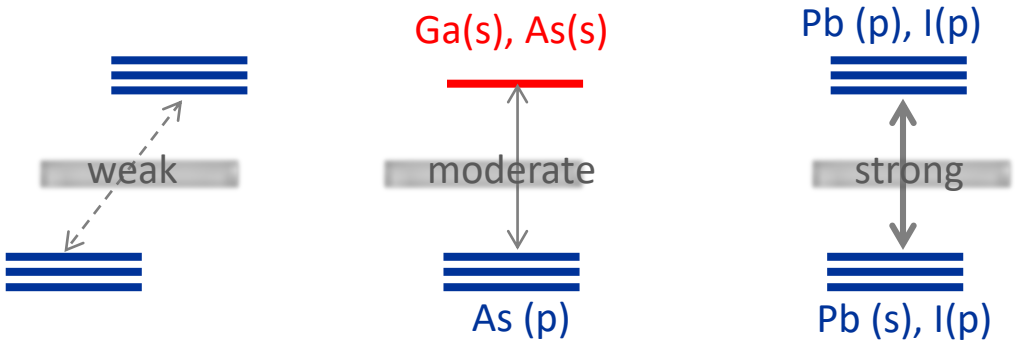
S. Richard et al., Phys. Rev. B 70, 235204 (2004)

Y. He et al., Chem. Mater. 26, 5394 (2014)

Perovskites have a direct bandgap, therefore absorbance higher than in e.g. silicon

Furthermore, perovskites exhibit p⟶p transition

→ Absorbance higher than GaAs



Si
indirect gap

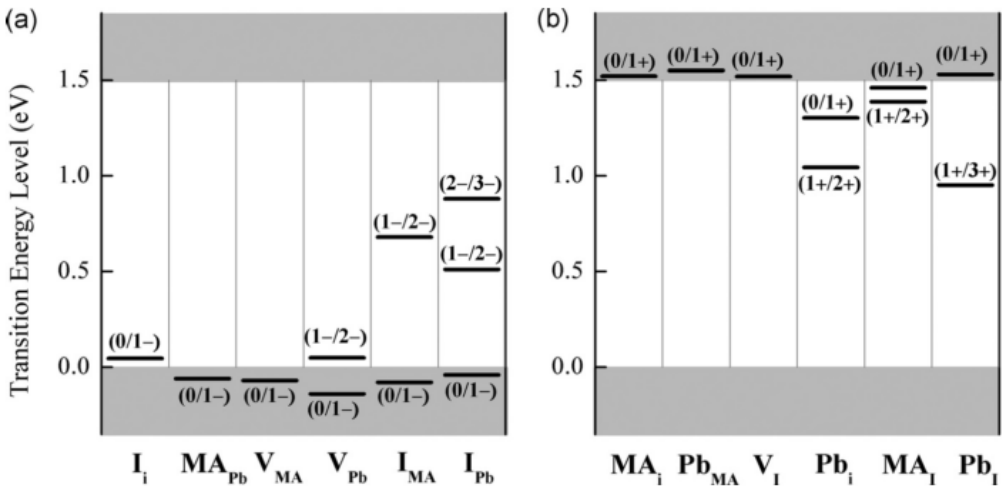
GaAs direct gap
p⟶s transition

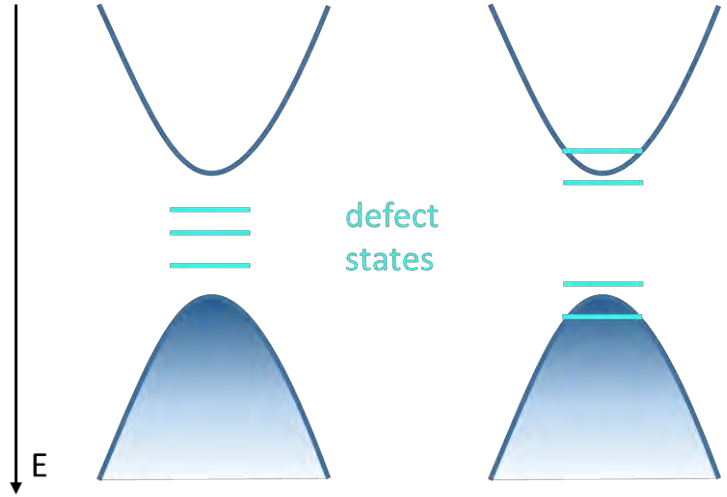
$MAPbI_3$
direct gap

Basic properties of halide perovskites

Advantageous properties:
2. Defect tolerance

For perovskites most defects end up located within the bands





Traps furthermore effectively screened by high dielectric function

→ low losses in photovoltaic performance

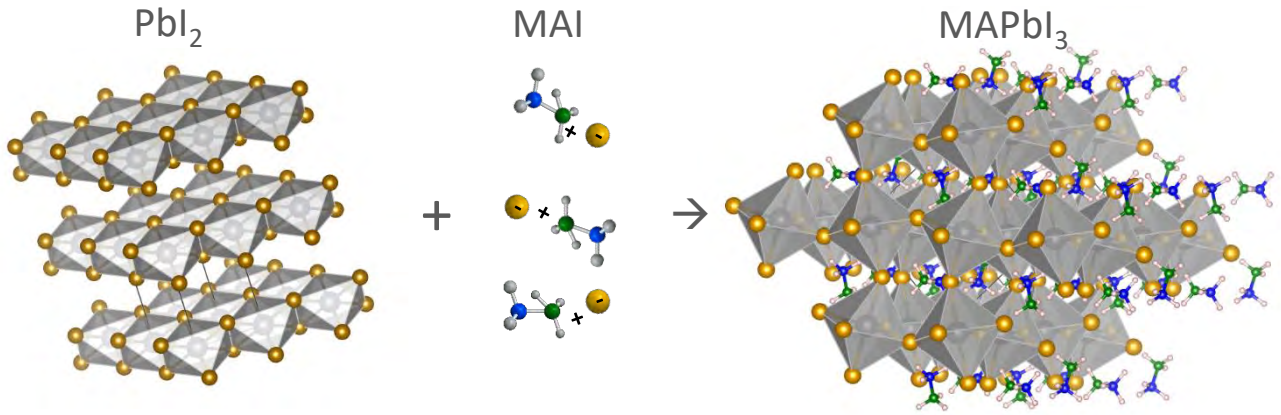
Schmidt-Mende, Olthof, Dyakonov, Phys. Unserer Zeit 50, 298 (2019)

W. Yin et al., Appl. Phys. Lett. 104, 063903 (2014)

Preparation

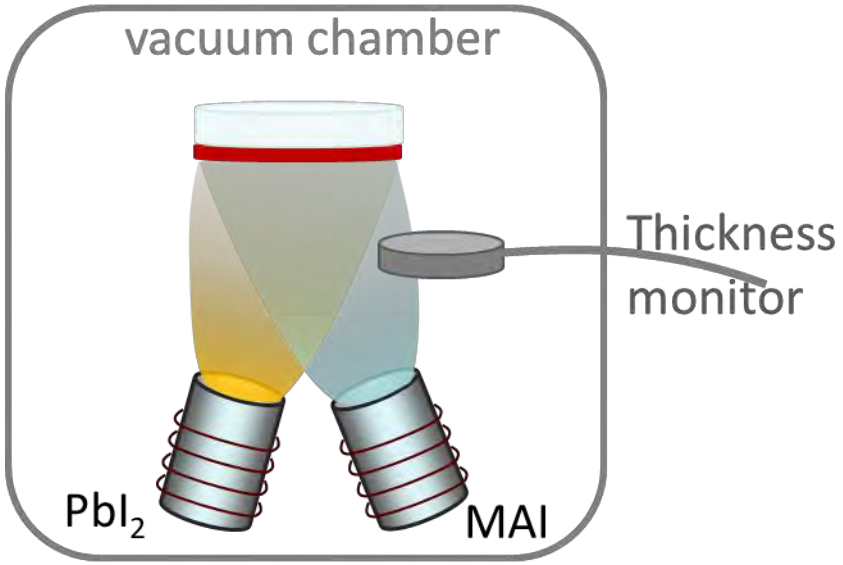
"Easy" preparation via spin coating

- preparation in a glovebox
- moderate temperature (< 150°C) processing
- using low cost materials (e.g. PbI_2, MAI, ...)



Preparation

… or thermal evaporation



- materials heated in crucibles
- via co-evaporated perovskite forms
- thickness control via quartz crystal monitors
- moderate temperatures needed

  MAI 140°C

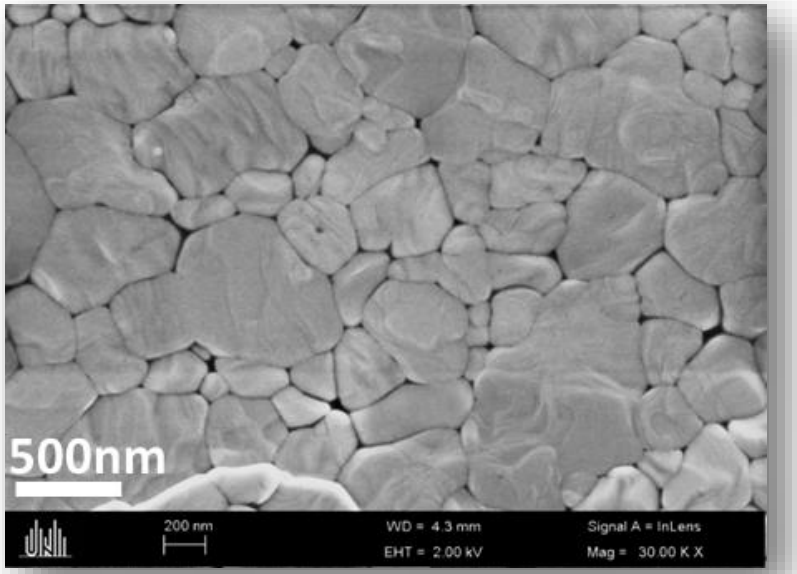
  PbI_2 320°C

  CsBr 520°C

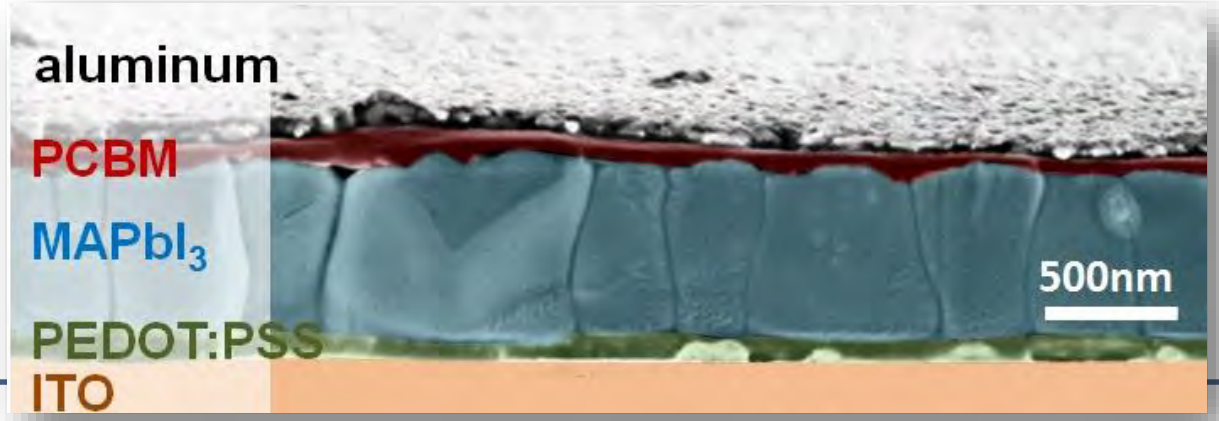
Preparation

This way, thin films with decent crystallinity can be made

Top view



Cross section



Even single crystals of several mm size can be grown within hours close to room temperature:

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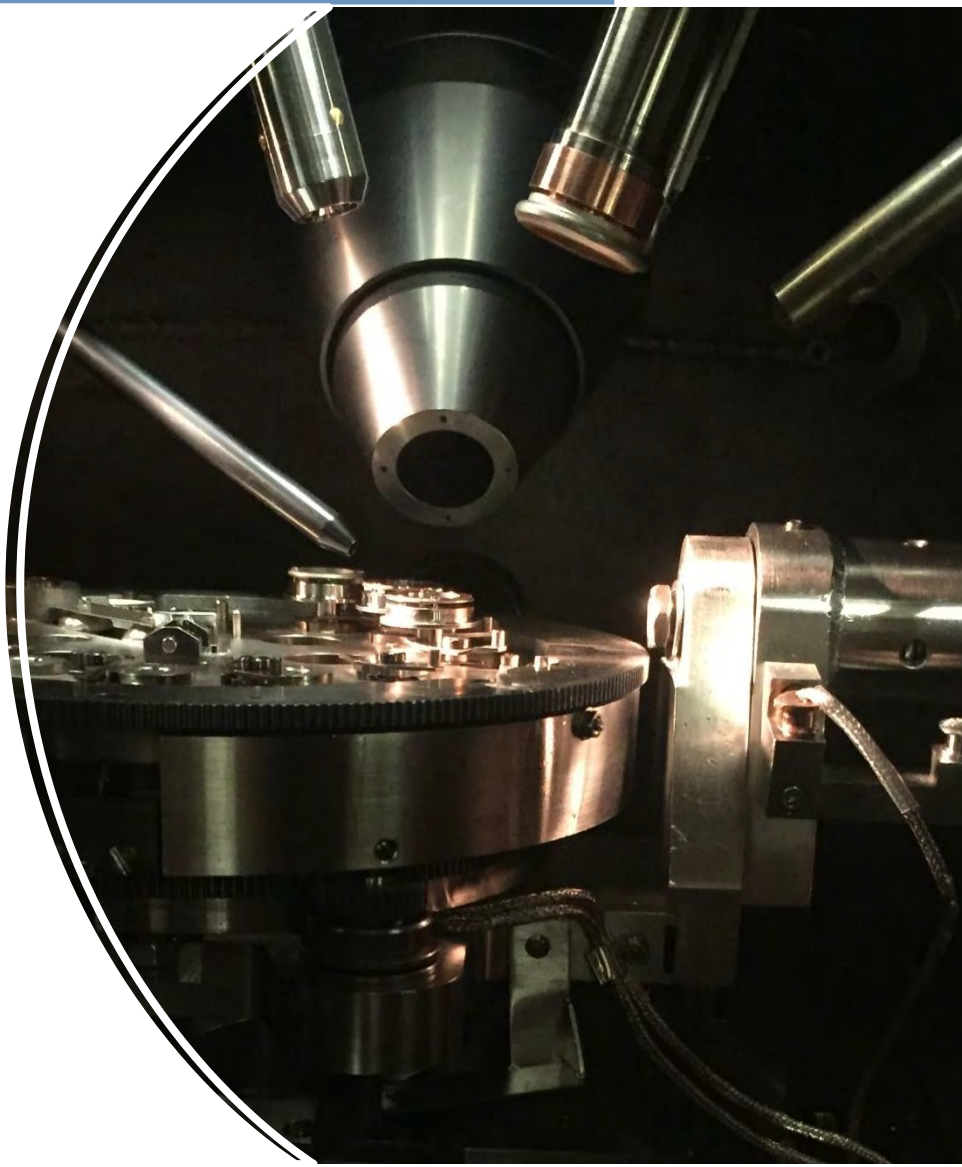
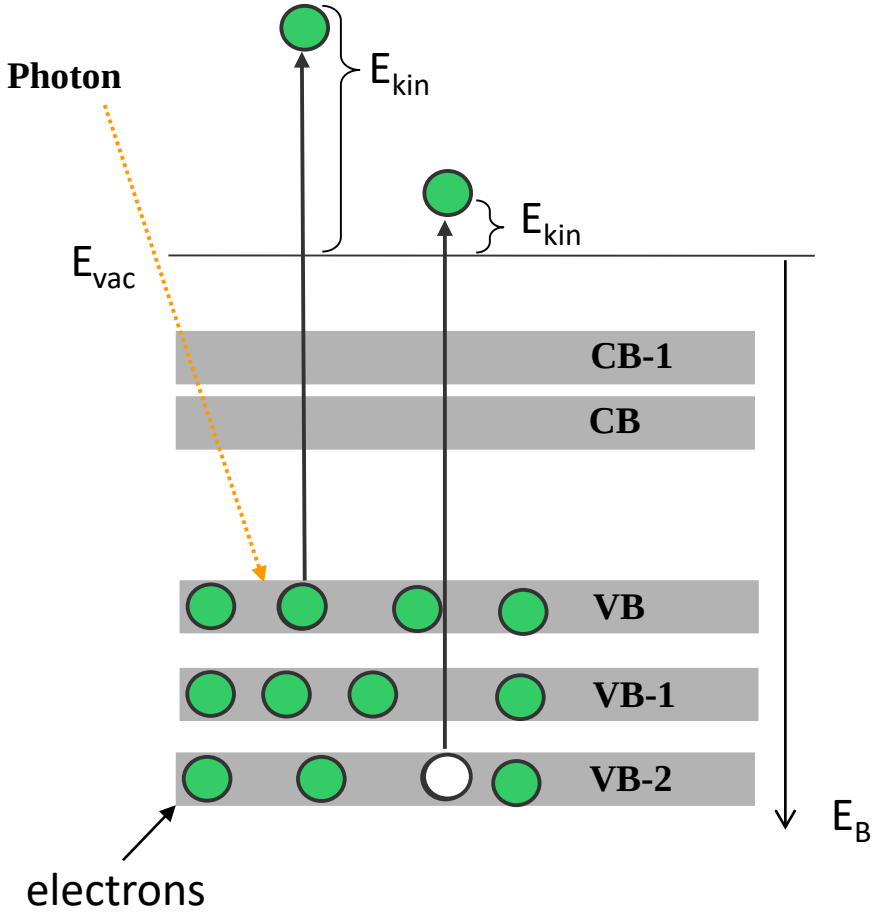


Photoelectron spectroscopy

Basic measurement idea: A photon releases an electron



Sample is illuminated with monochromatic light of specific energy
$E = h\nu$

The kinetic energies of electrons originating from different energy levels will be different – depending on binding energy E_B

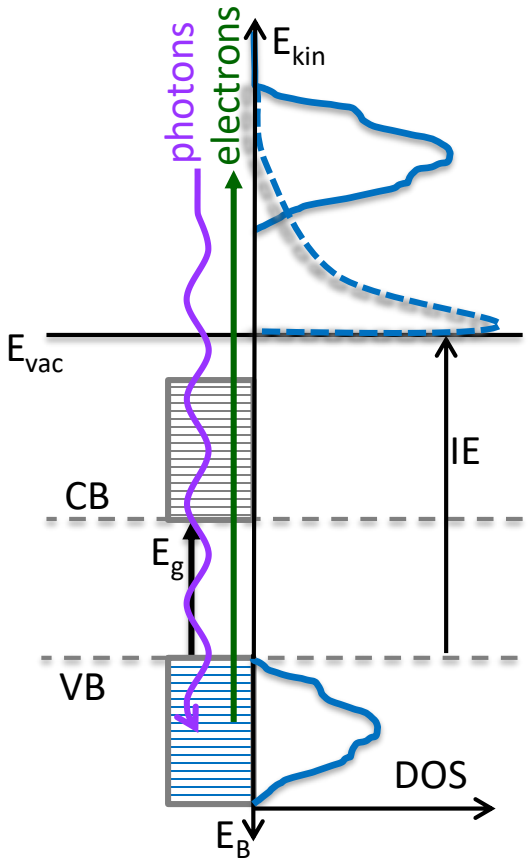
The relation between E_{kin} and E_B is

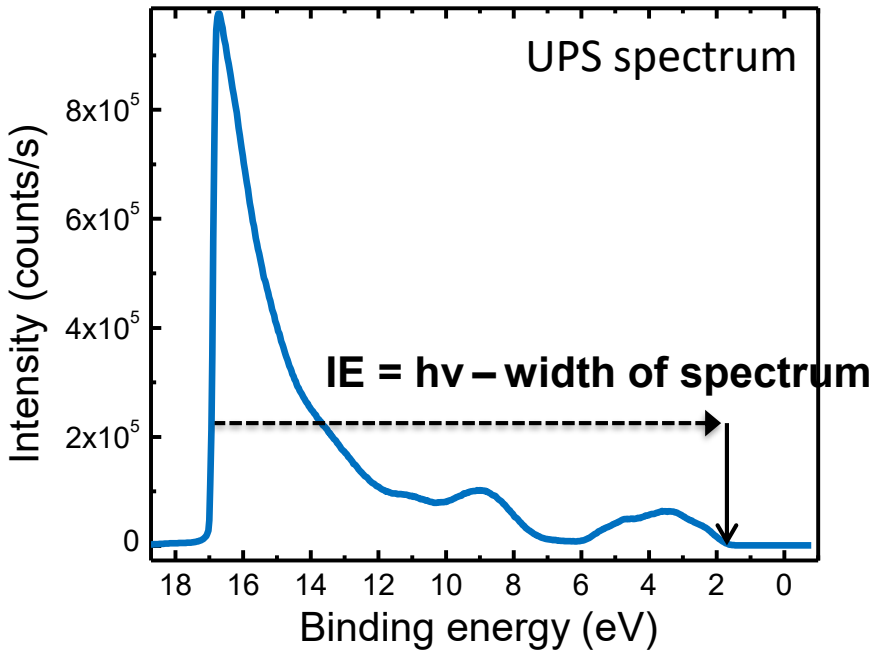
$$E_{kin} = h\nu - E_B$$

UV photoelectron spectroscopy (UPS)

Measurement of occupied density of states:

UPS: Excitation by UV light, e.g. hv = 21.22eV



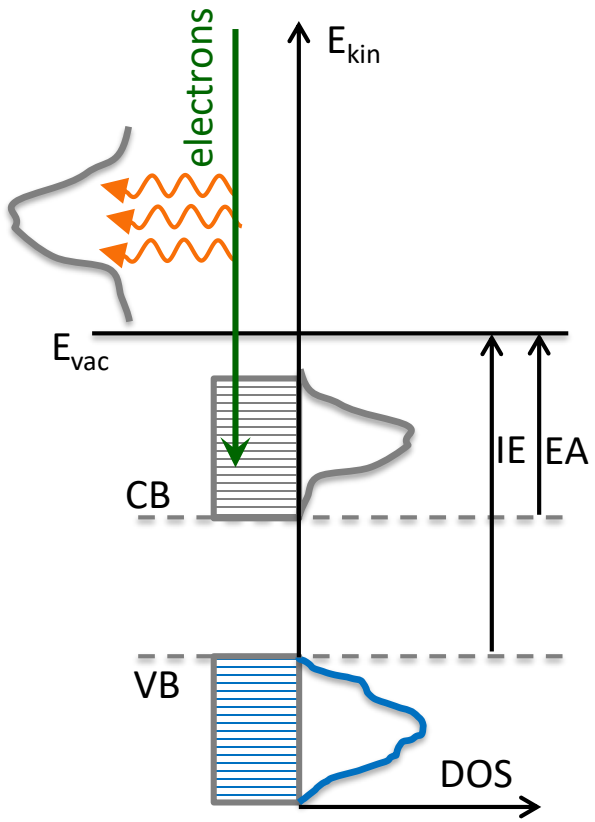


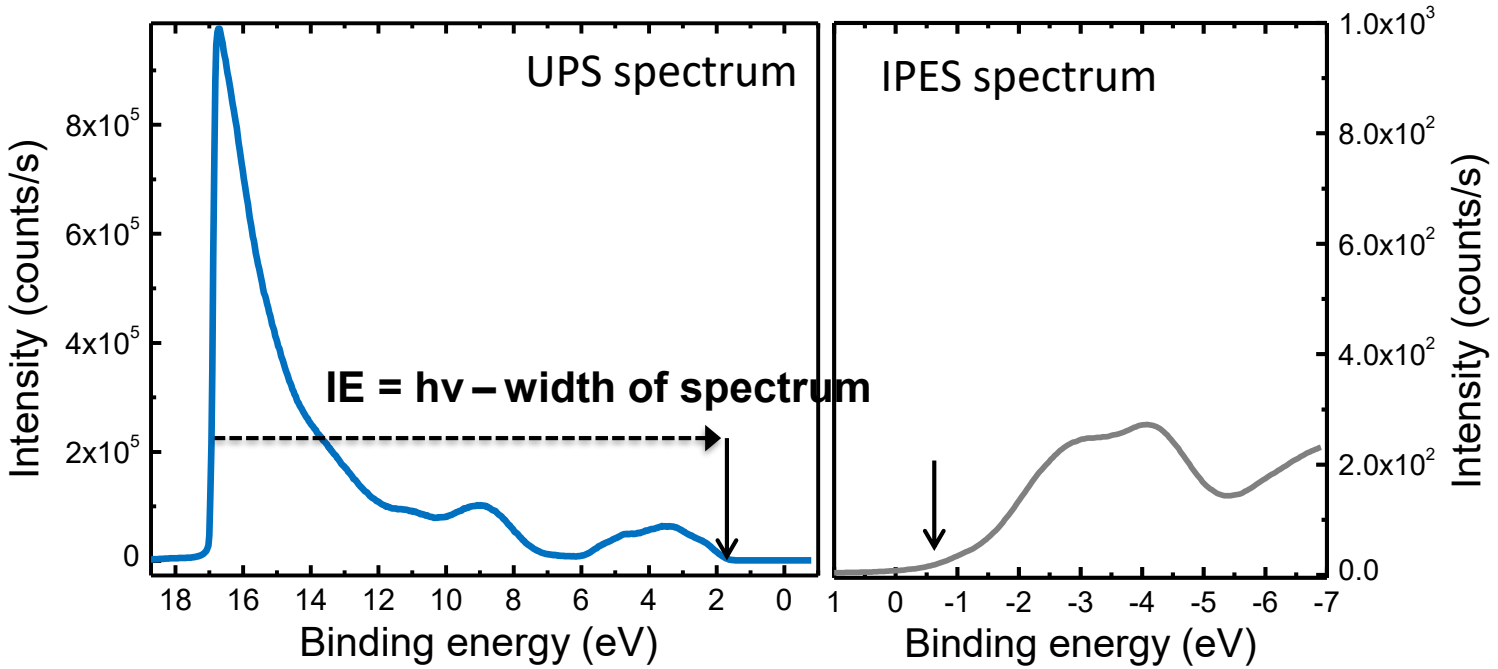
E_{vac}: Vacuum level

IE: Ionization energy

Inverse photoelectron spectroscopy (IPES)

Measure unoccupied density of states:
IPES: Electrons with energy ~ 5 – 15 eV shot onto sample





EA: Electron affinity

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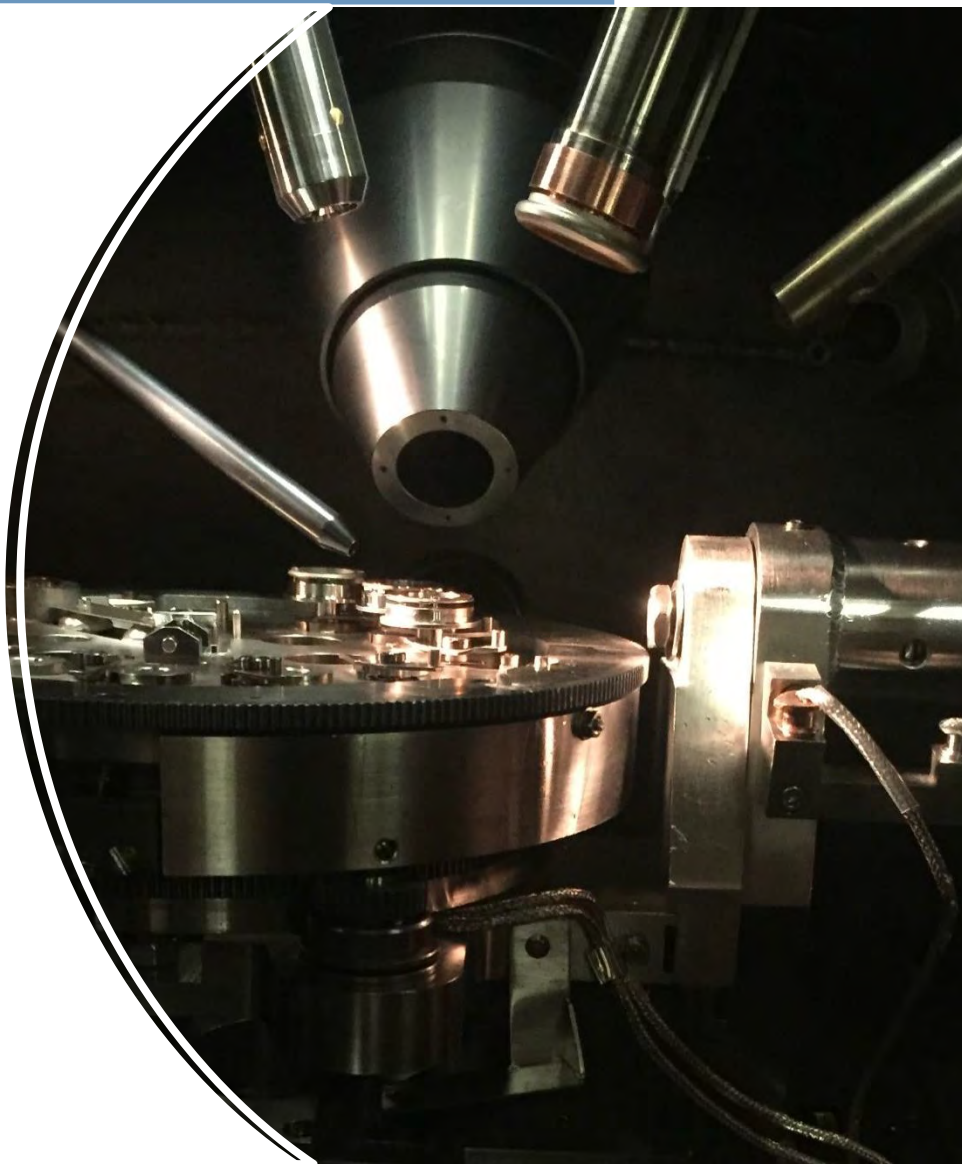
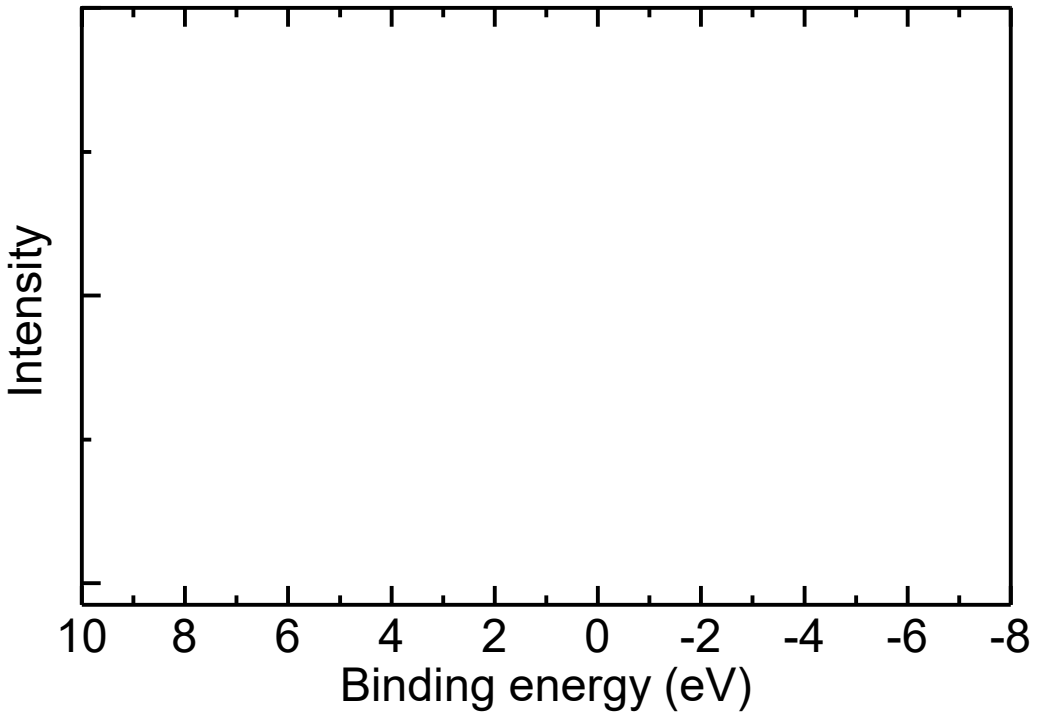
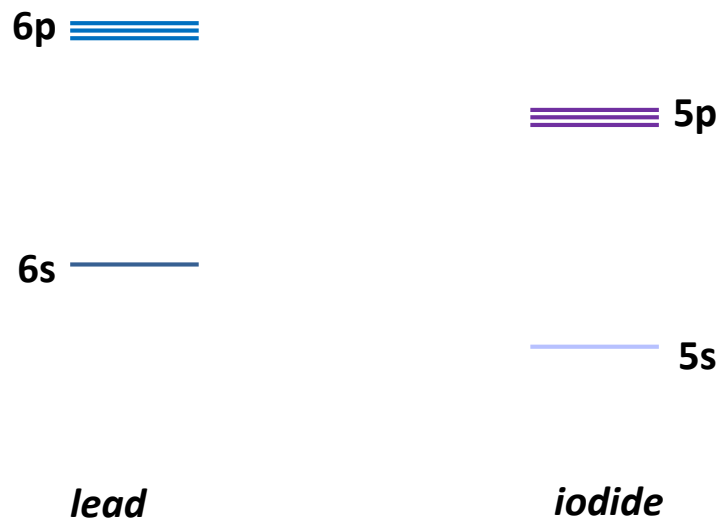


Electronic Structure of $MAPbI_3$

Density of states



Energy levels in $MAPbI_3$:



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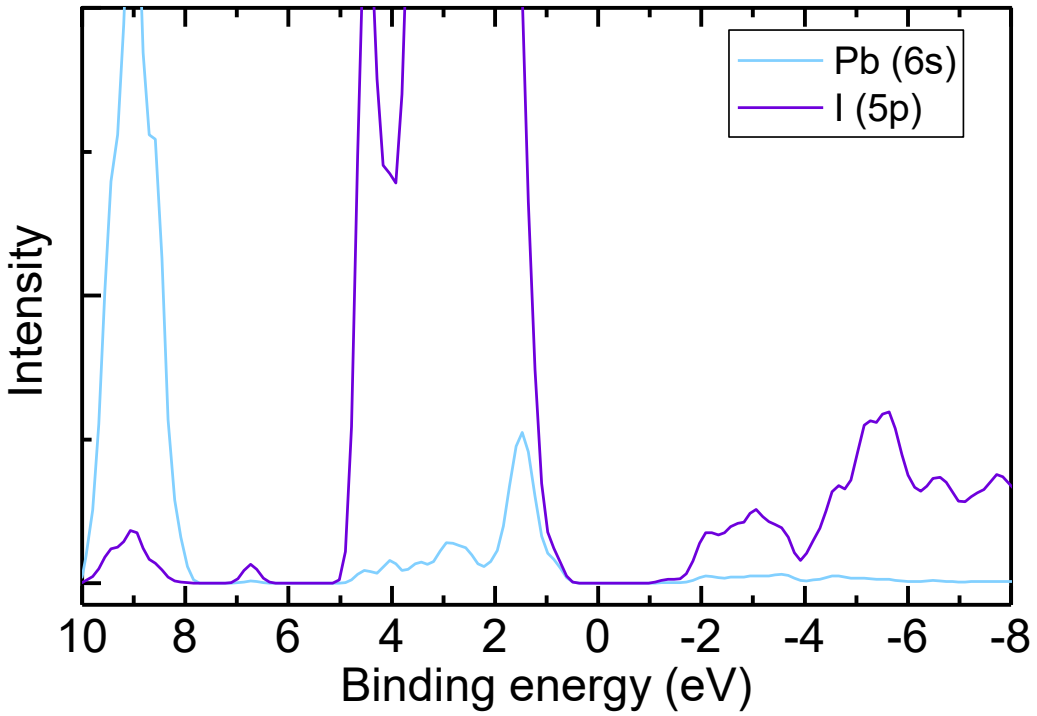

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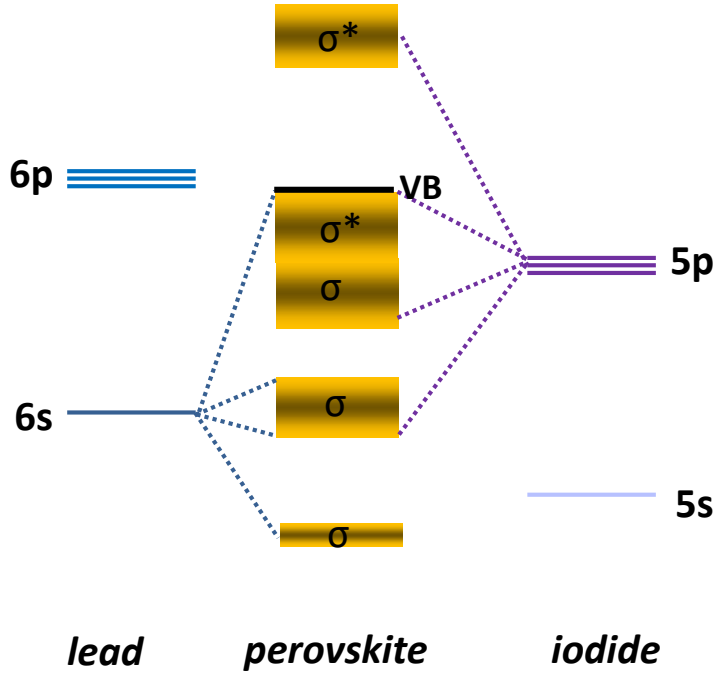
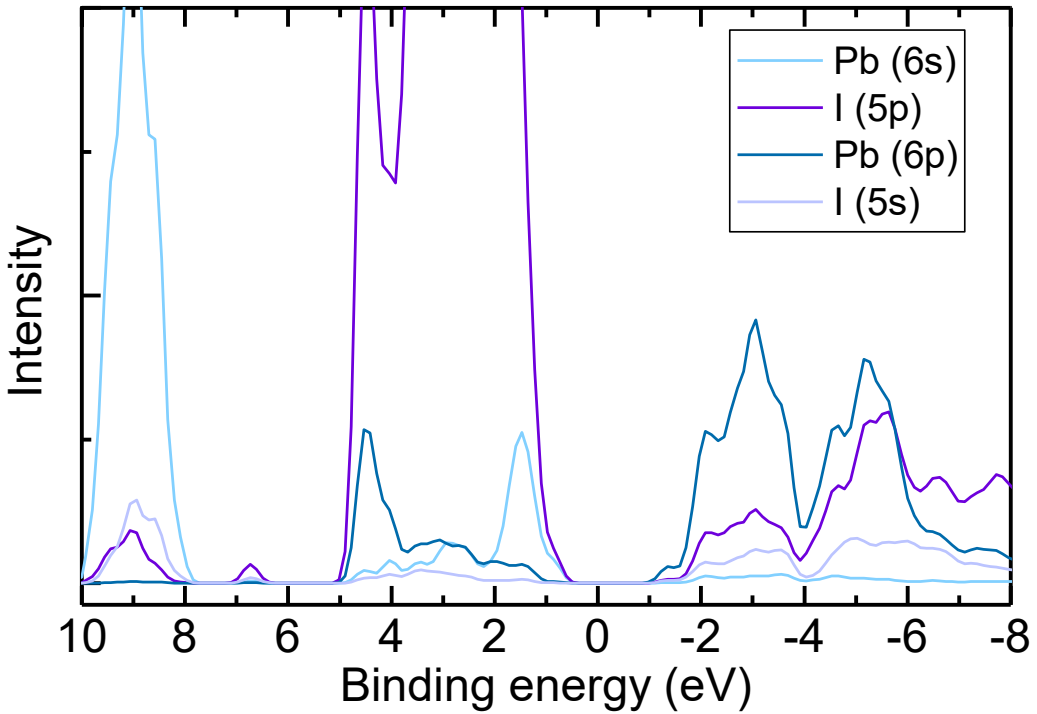


DFT calculations by S. Tao, University Eindhoven

Electronic Structure of $MAPbI_3$

Density of states



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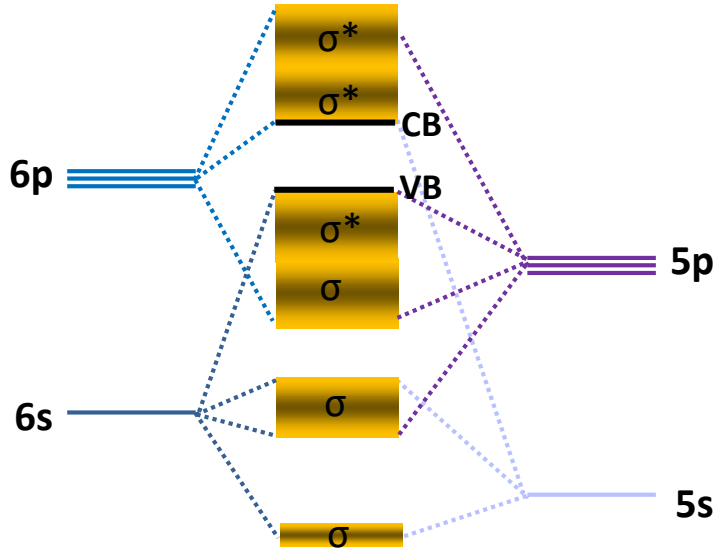
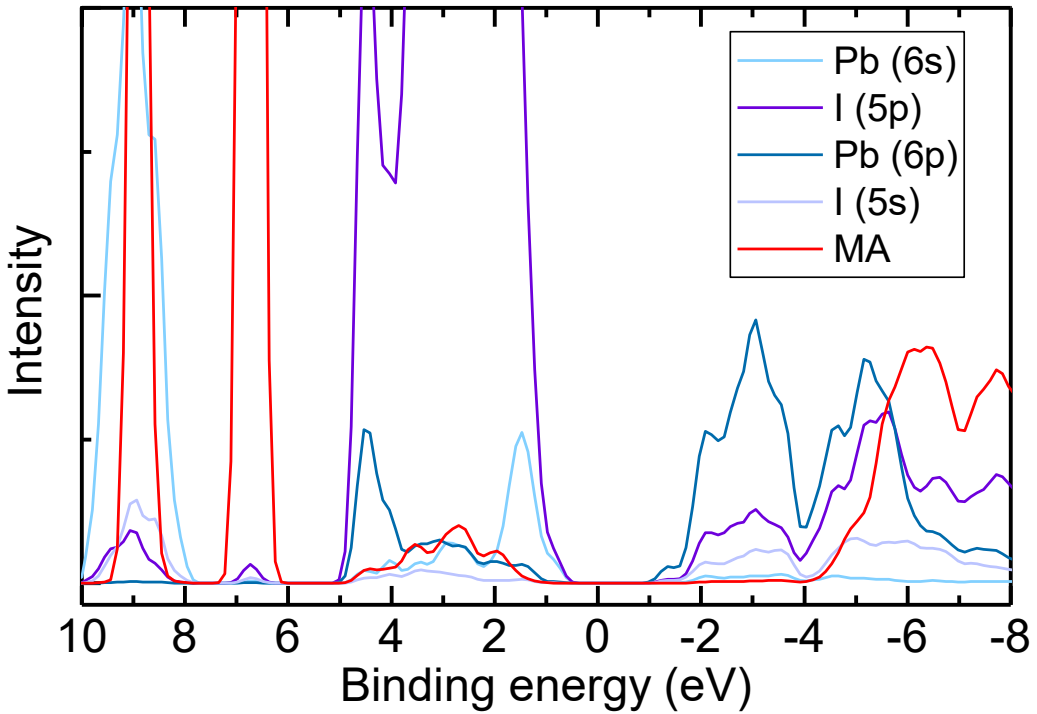


lead ***perovskite*** ***iodide***

DFT calculations by S. Tao, University Eindhoven

Electronic Structure of $MAPbI_3$

Density of states



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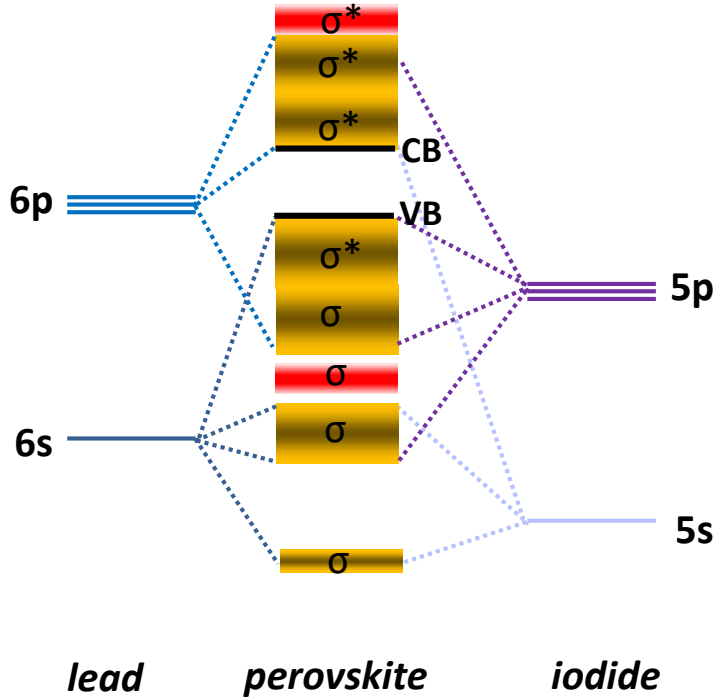
Energy levels in $MAPbI_3$:



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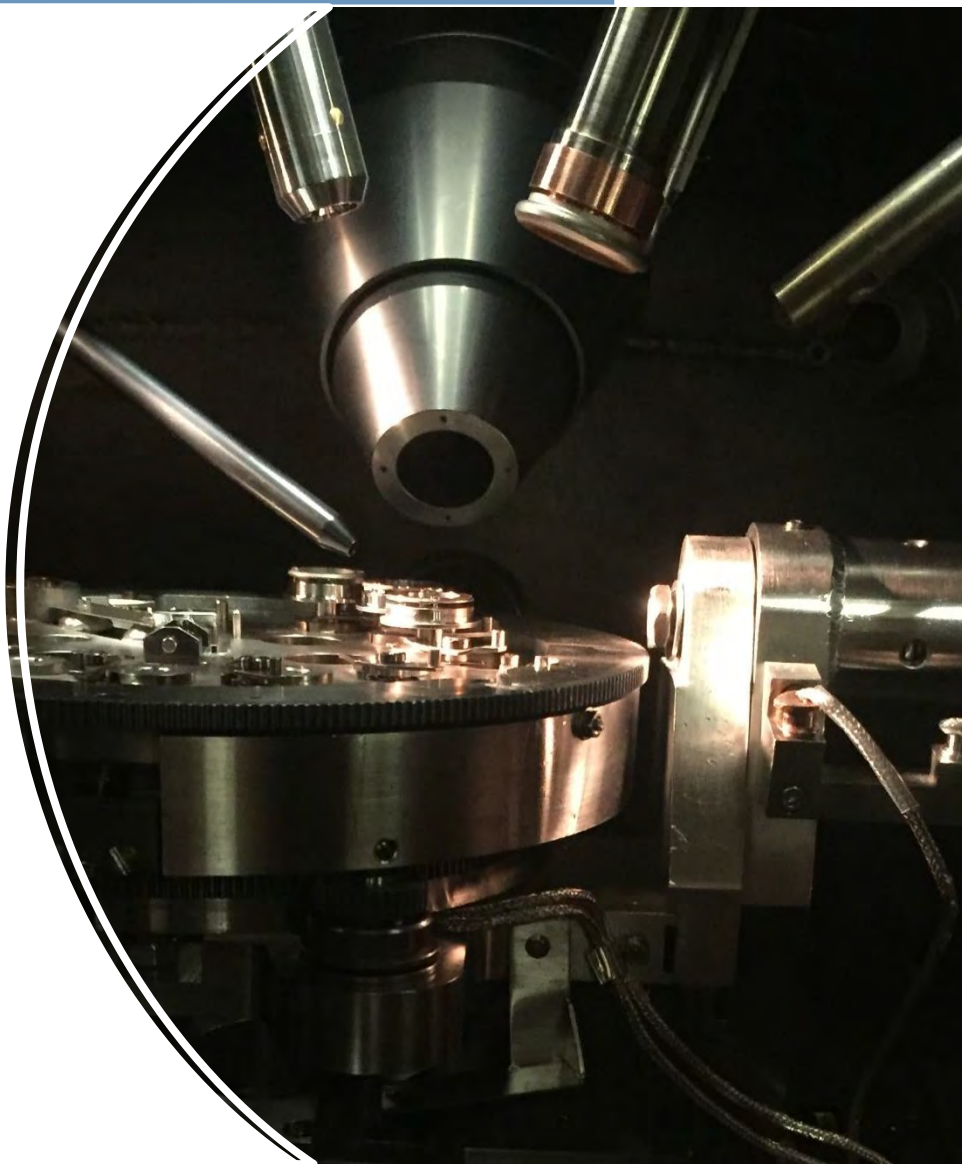
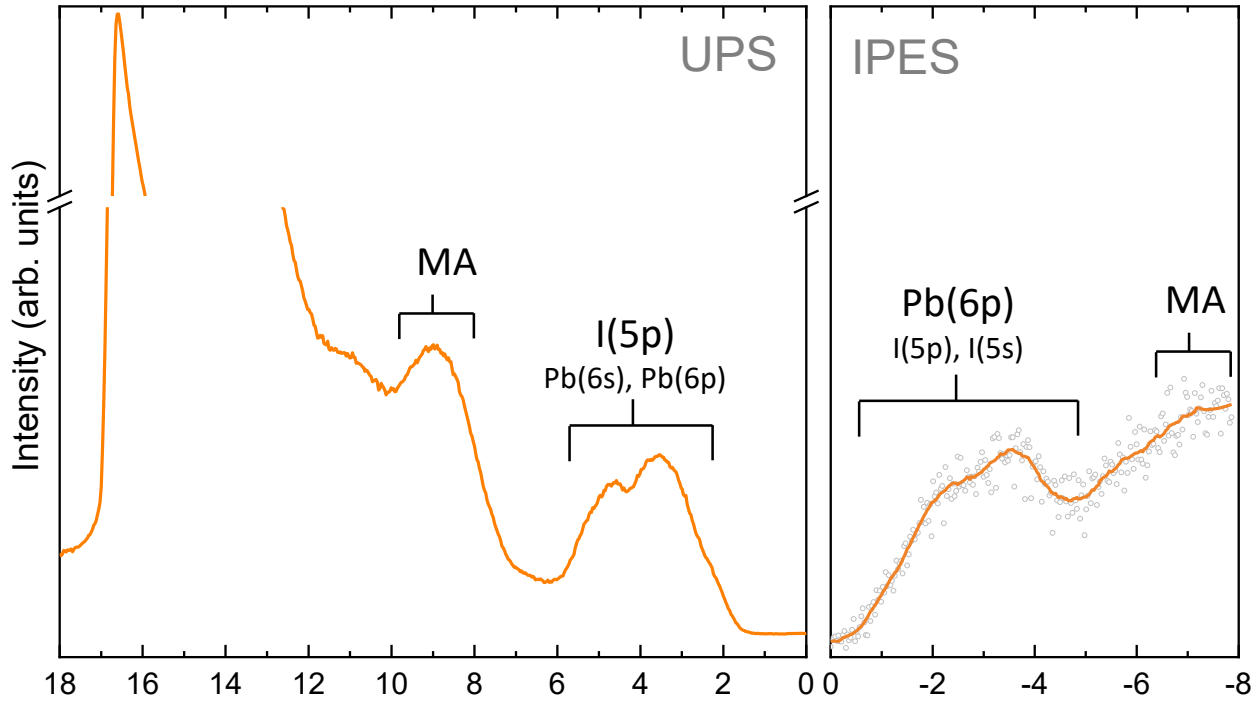
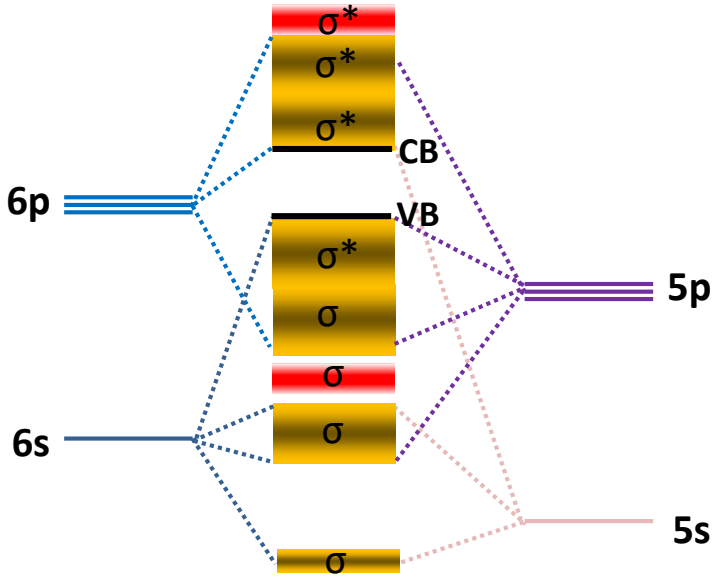


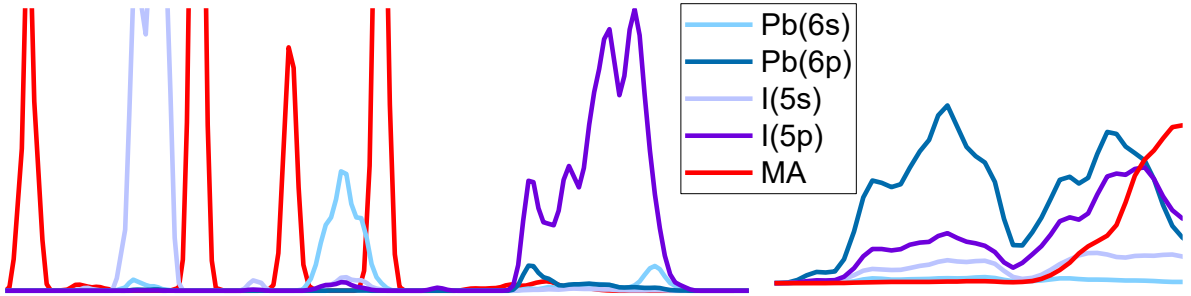
Electronic Structure of $MAPbI_3$

UPS / IPES measurement $MAPbI_3$:



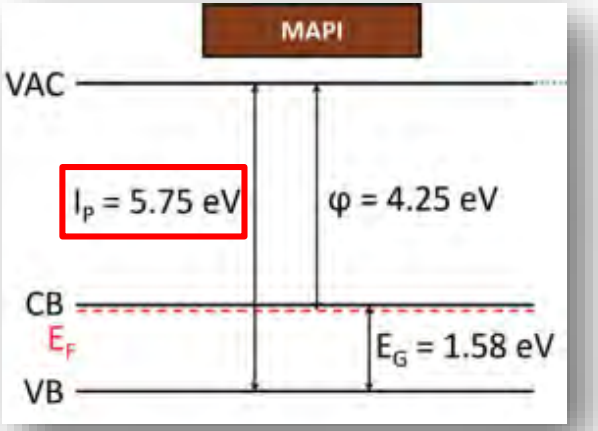


DFT pDOS

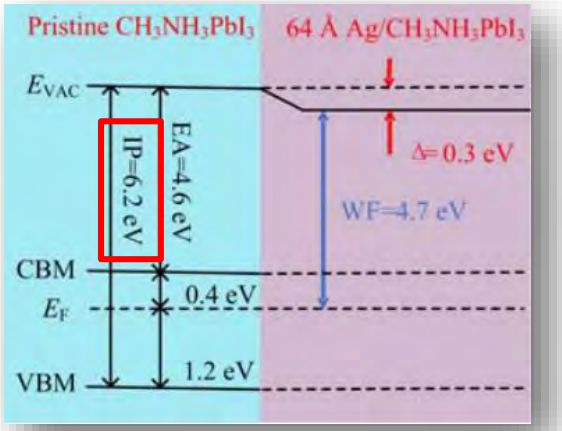


Emara et al., Adv. Mater. 2016, 28, 553 (2016)

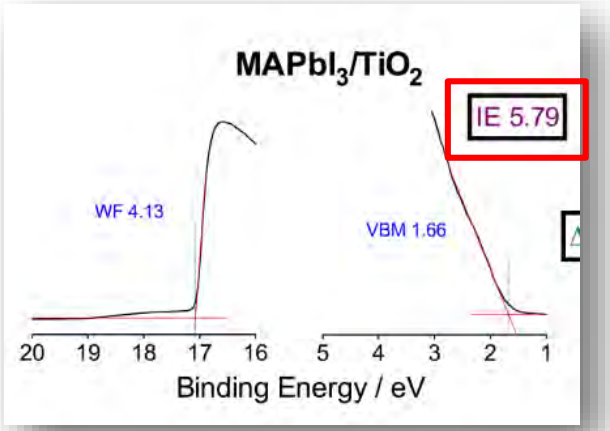
$MAPbI_3$ – reported values



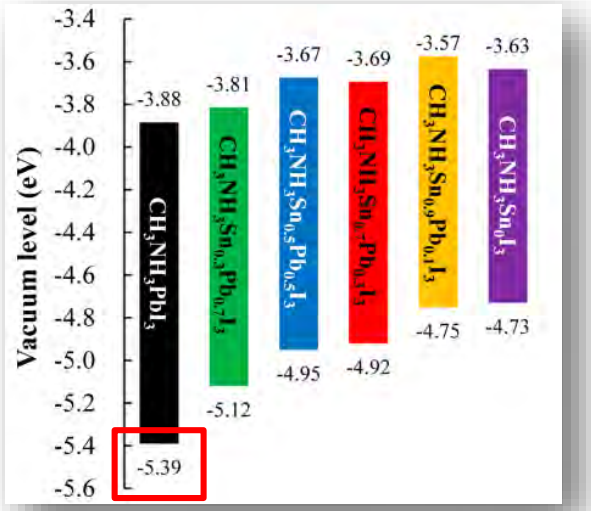
T. Hellmann et al. J. Mater. Chem. C 7 (2019) 5324



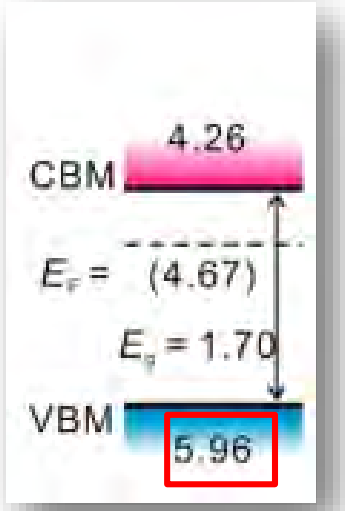
X. Li et al. Chinese J. Chem. Phys. 32 (2019) 299



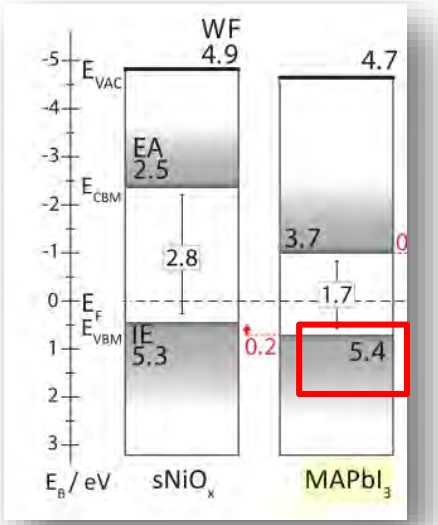
J.-P. Correa-Baena et al. Energy Environ. Sci. 8 (2015) 2928



Y. Ogomi et al. J. Phys. Chem. Lett. 5 (2014) 1004



C. Li et al. ACS Appl. Mater. Interfaces 8 (2016) 11526



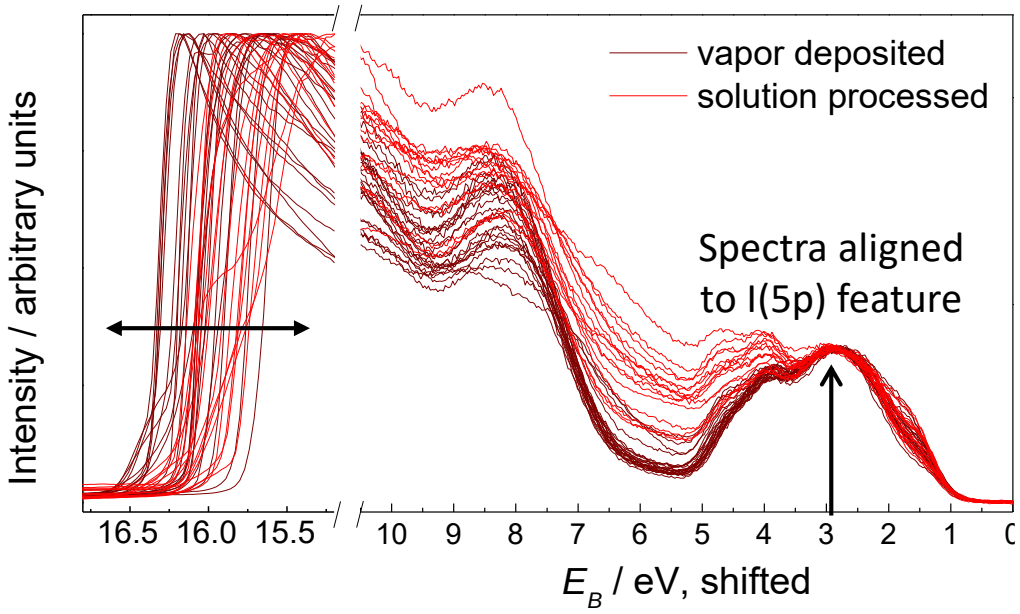
P. Schulz et al. Adv. Mater. Interfaces 2 (2015) 1400532

Values range from 5.39 eV to 6.2 eV

Deviation of reported energy level values

Reason 1:
Film / surface composition plays a role

40 *evaporated* and *solution processed* $MAPbI_3$ samples:

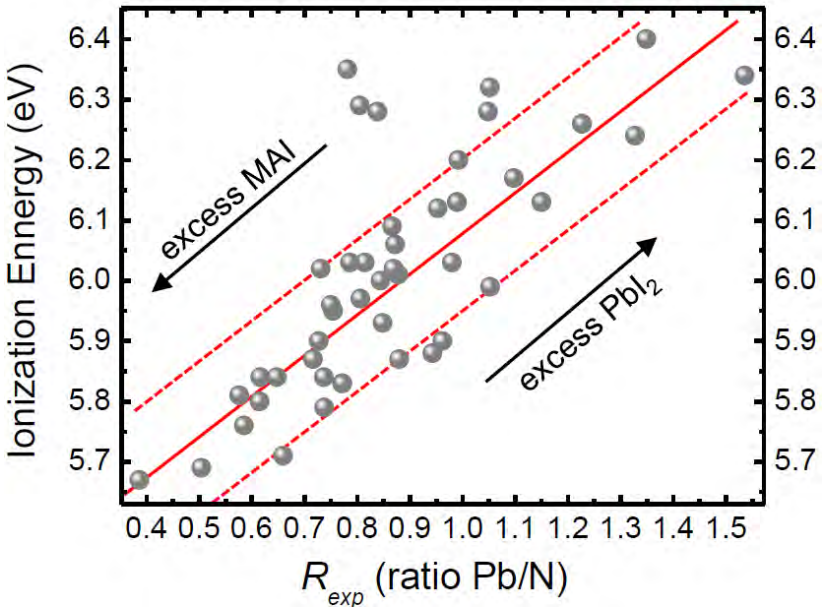


→ Overall shape of the density of states very similar
→ Onset (VB) looks identical – no gap or trap states
→ BUT: strong variations in the high binding energy cutoff by ~1eV
→ Ionization energy varies!

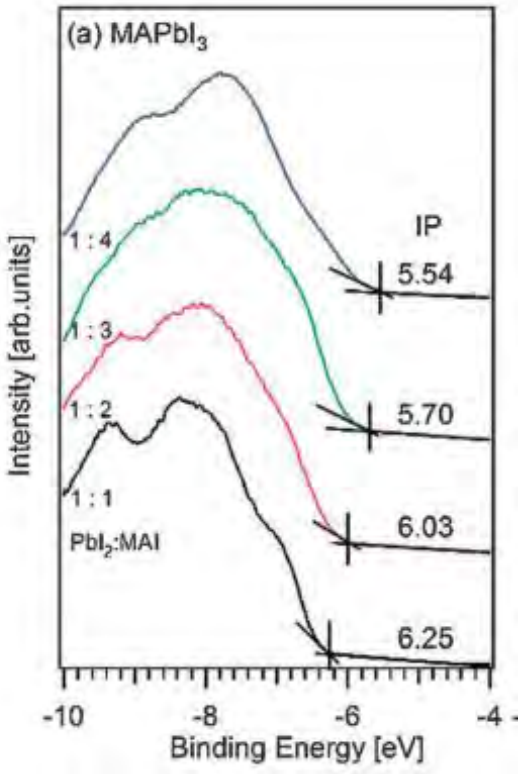
J. Emara et al., Adv. Mater. 28, 553 (2016)

Deviation of reported energy level values

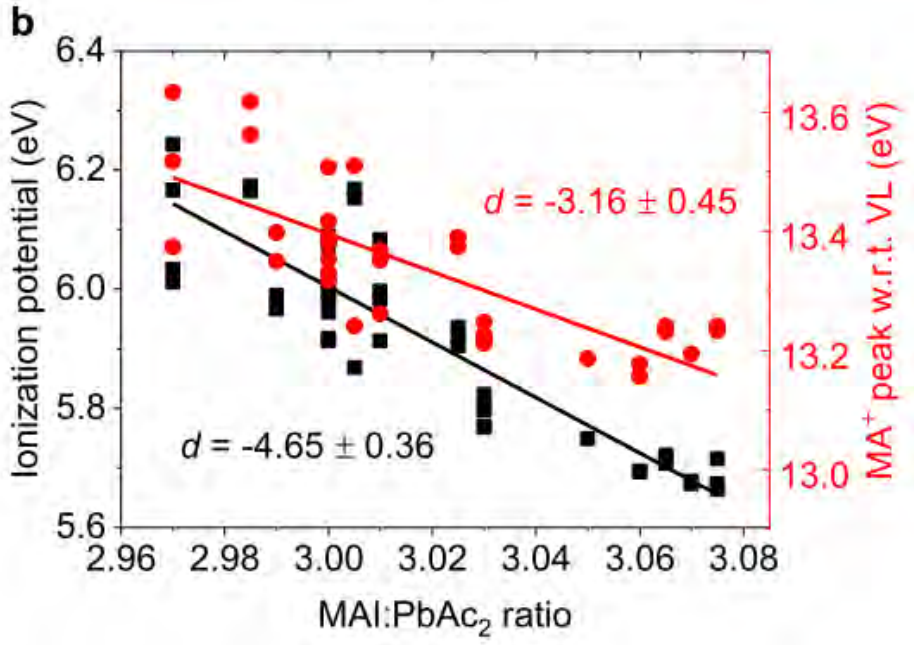
Reason 1:
Film / surface composition plays a role



J. Emara et al., Adv. Mater. 28, 553 (2016)



T. G. Kim et al., Phys. Chem. Chem. Phys. 17 (2015)



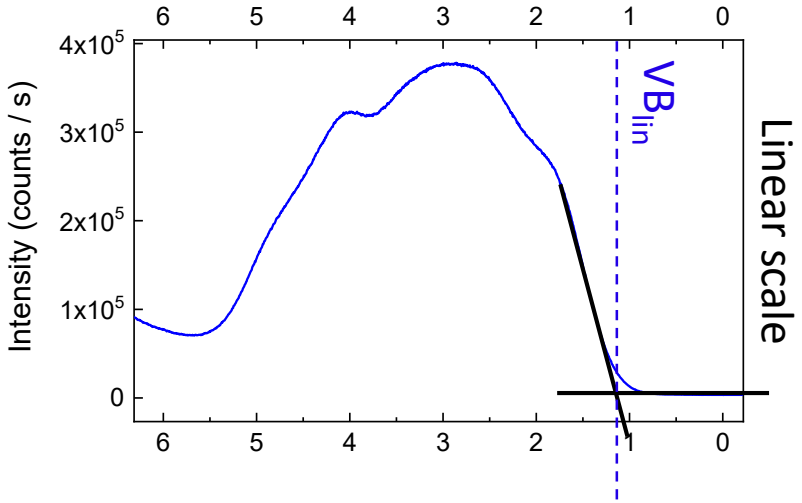
P. Fassl et al. Energy Environ. Sci. 11 (2018) 3380

(Un-)intentional changes in composition have severe impact on observed energy level positions

Deviation of reported energy level values

Reason 2:
Data evaluation

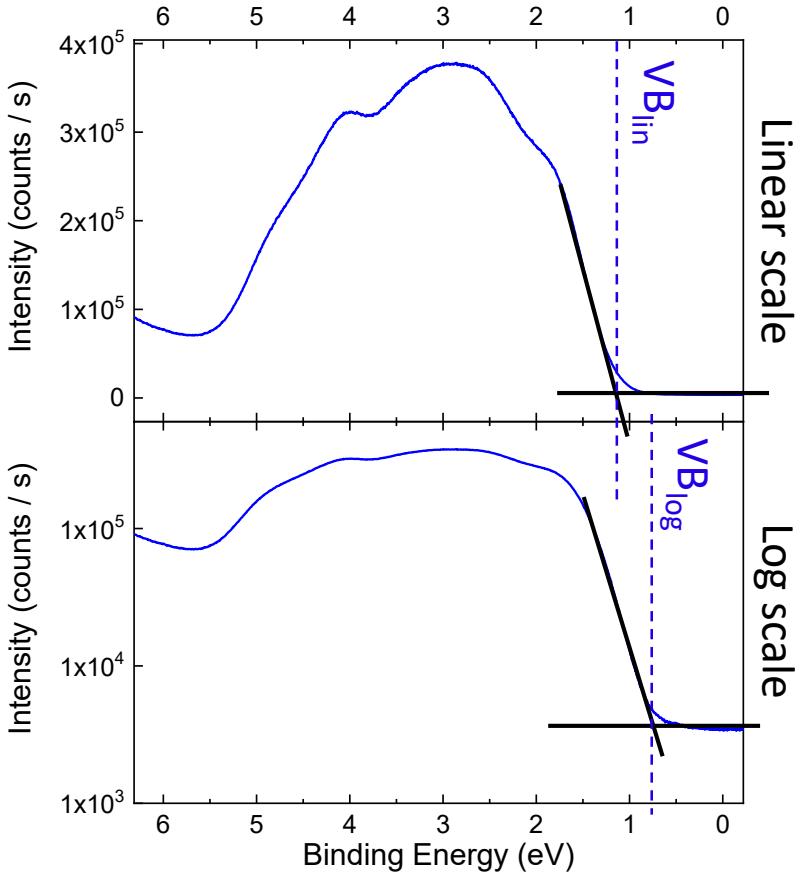
Valence band of $MAPbI_3$:



Deviation of reported energy level values

Reason 2:
Data evaluation – some researchers look at the data in a logarithmic scale

Valence band of $MAPbI_3$:

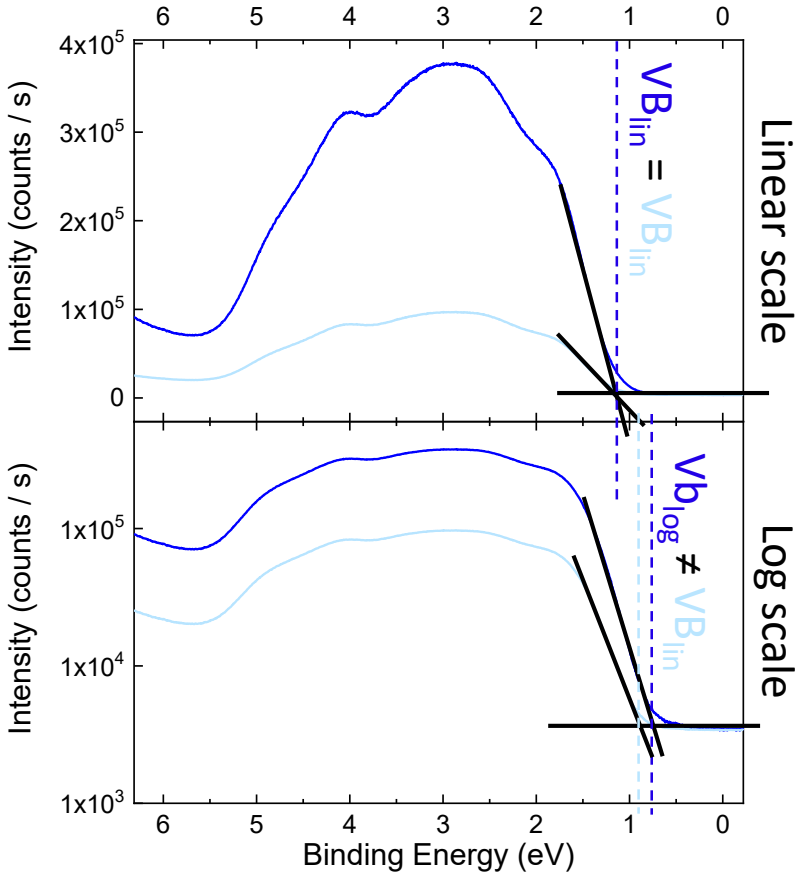


Log scale value could be device relevant as density of states at VB is rather low.

Deviation of reported energy level values

Reason 2:
Data evaluation – some researchers look at the data in a logarithmic scale

Valence band of $MAPbI_3$:



But evaluating log spectra is not trivial

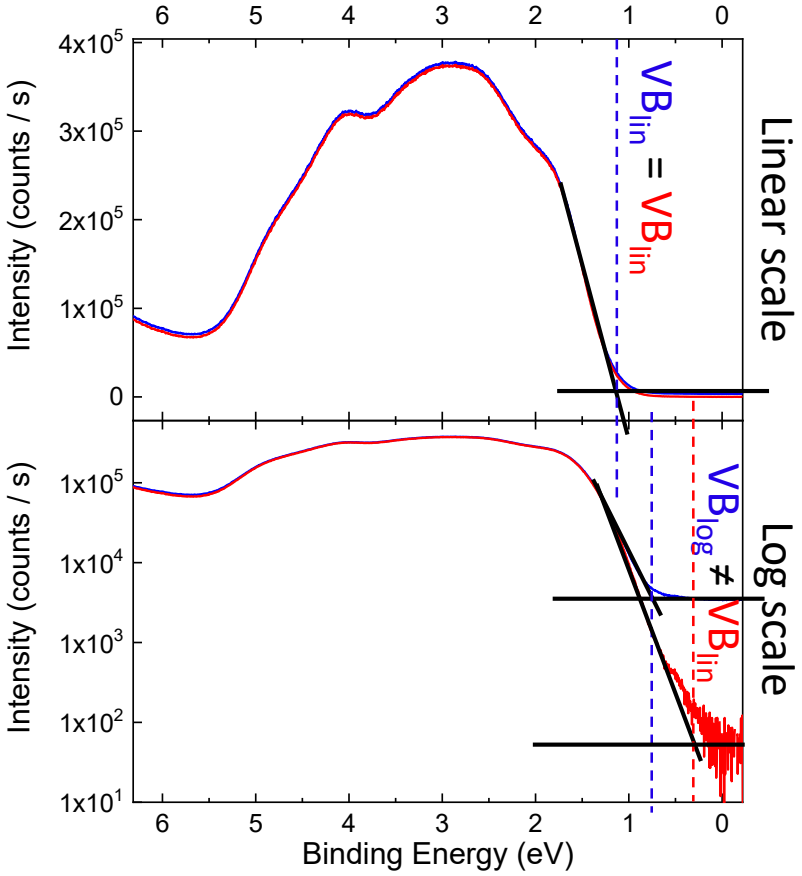
1. Effect of signal intensity

Olthof, APL Mater. 4, 091502 (2016)

Deviation of reported energy level values

Reason 2:
Data evaluation – some researchers look at the data in a logarithmic scale

Valence band of $MAPbI_3$:



But evaluating log spectra is not trivial

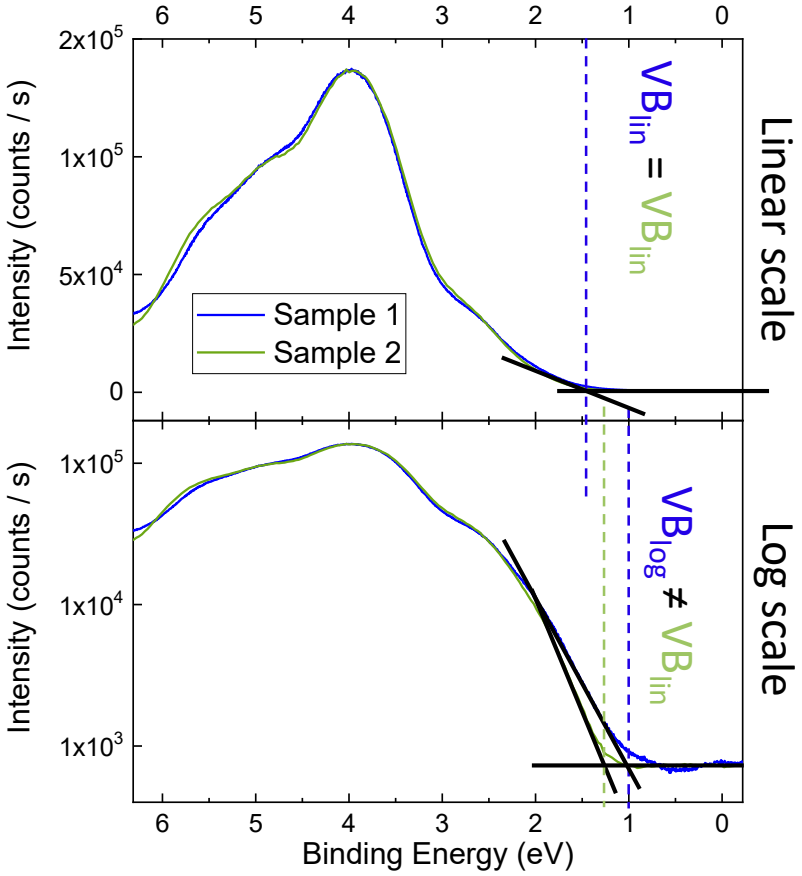
1. Effect of signal intensity
2. Effect of background intensity

Olthof, APL Mater. 4, 091502 (2016)

Deviation of reported energy level values

Reason 2:
Data evaluation – some researchers look at the data in a logarithmic scale

Valence band of $CsPbBr_3$:



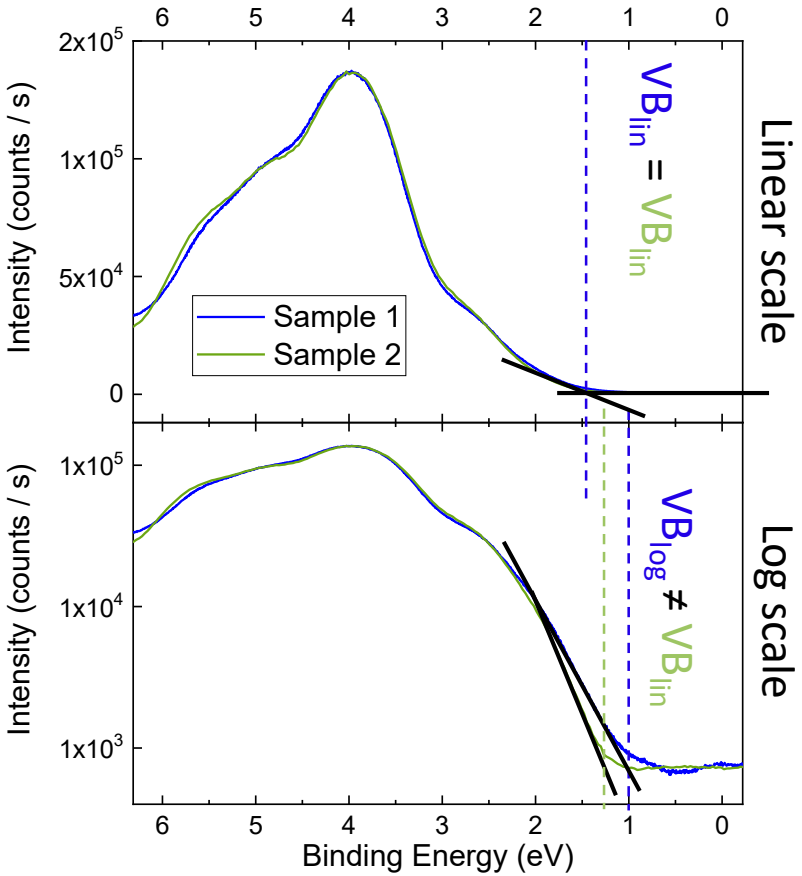
But evaluating log spectra is not trivial

1. Effect of signal intensity
2. Effect of background intensity
3. Effect of unknown gap states

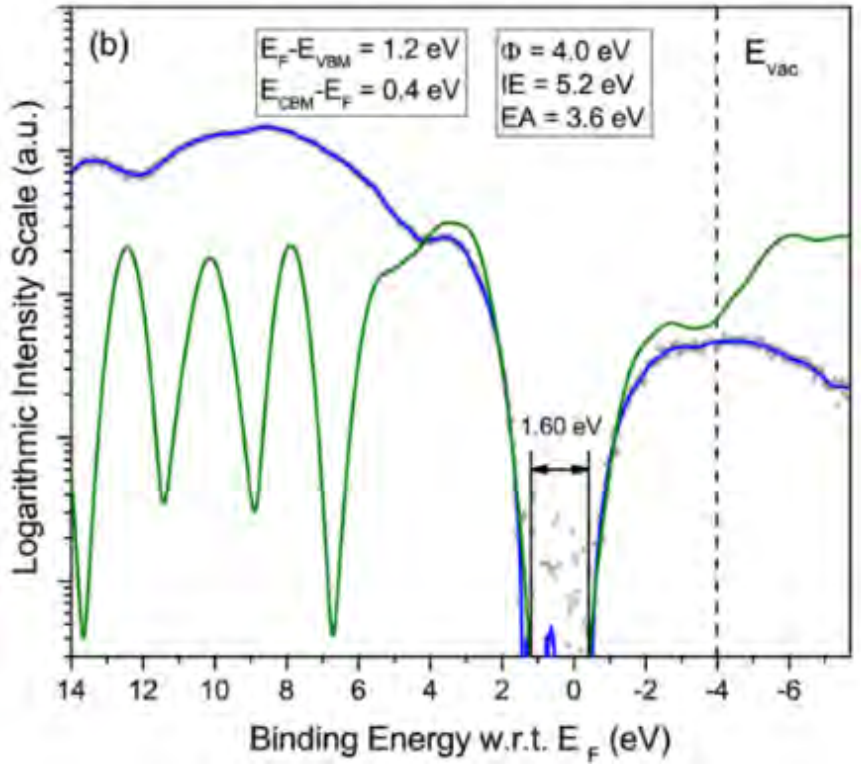
Deviation of reported energy level values

Reason 2:
Data evaluation – some researchers look at the data in a logarithmic scale

Valence band of $CsPbBr_3$:



Advisable to correlate measurement with DFT calculated spectra:



J. Endres, D.A. Egger, M. Kulbak, R.A. Kerner, L. Zhao, S.H. Silver, G. Hodes, B.P. Rand, D. Cahen, L. Kronik, and A. Kahn, J. Phys. Chem. Lett. 7, 2722 (2016).

Content

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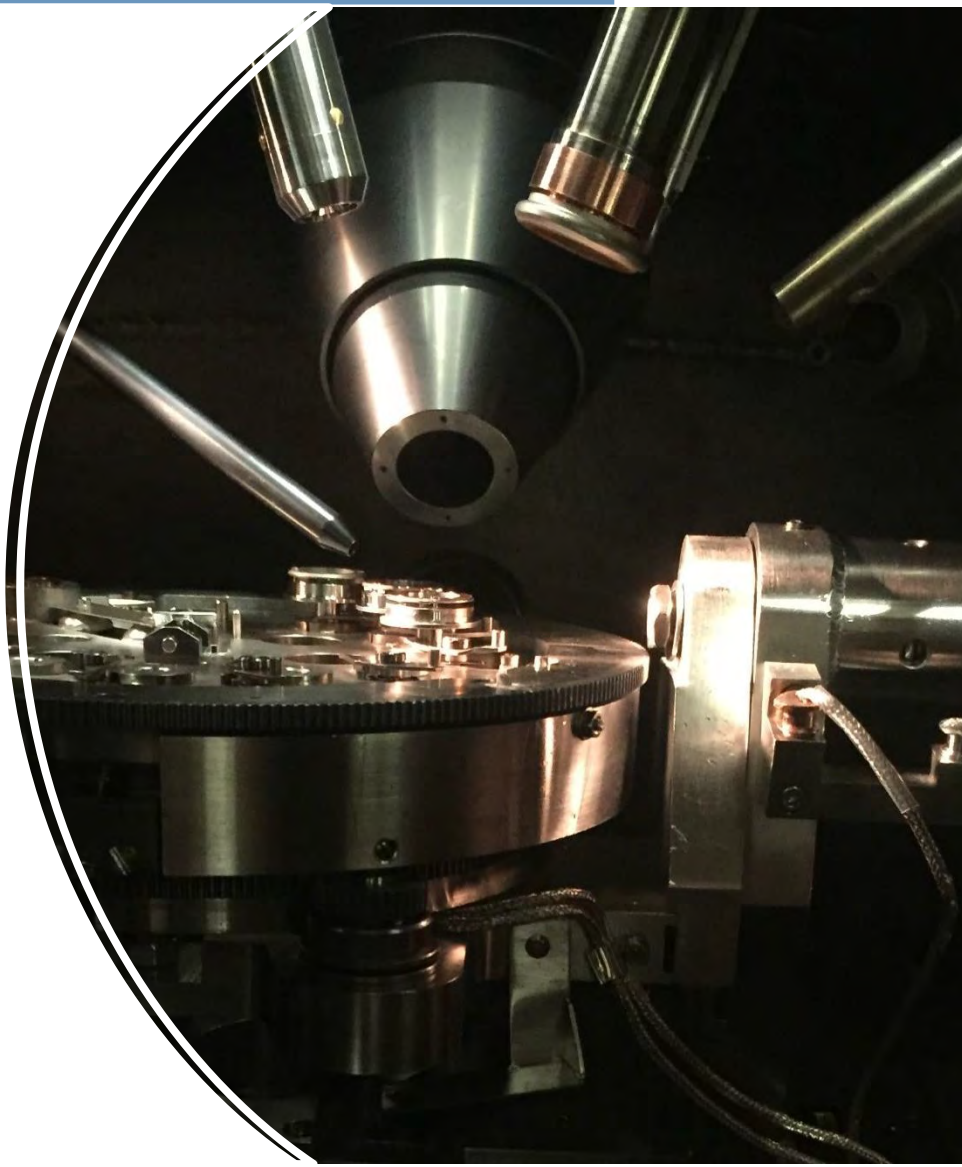
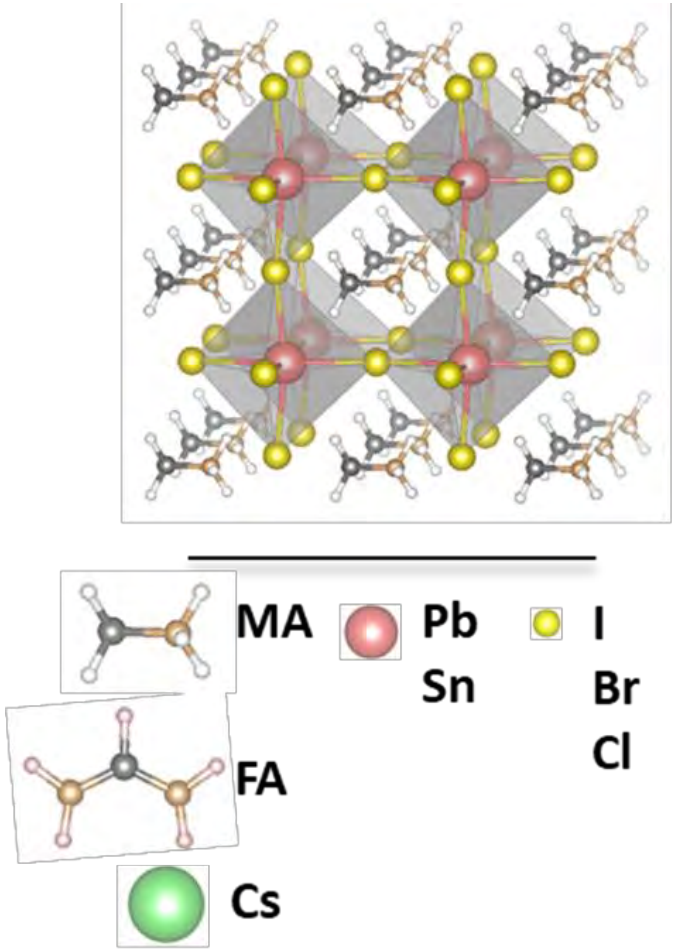
4. Considerations for measuring
5. **Tuning of perovskite composition**
6. Energy levels of mixed perovskites

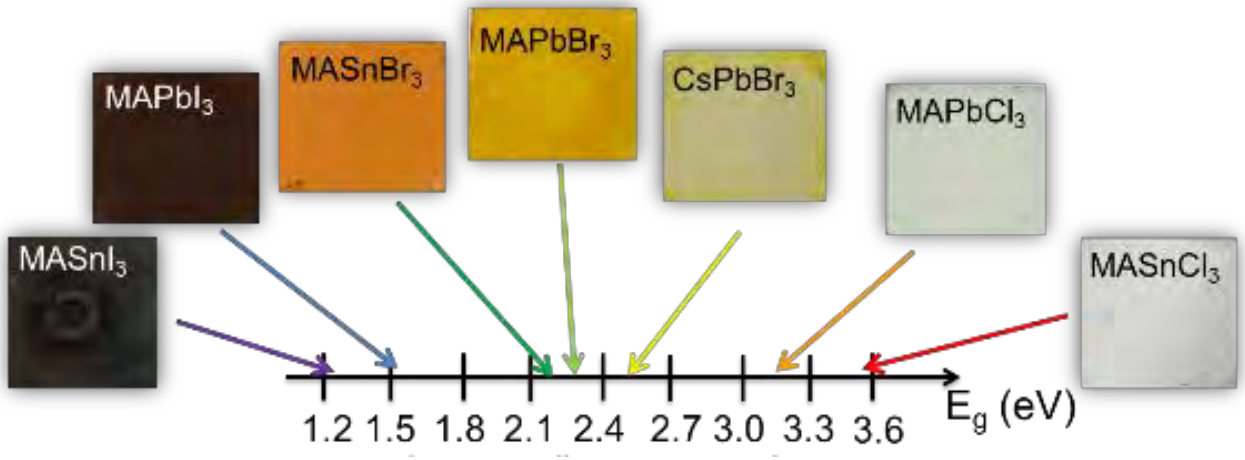


Variation of composition

Our study covers all 18 possible “pure” 3D Pb or Sn based perovskites



Band gap

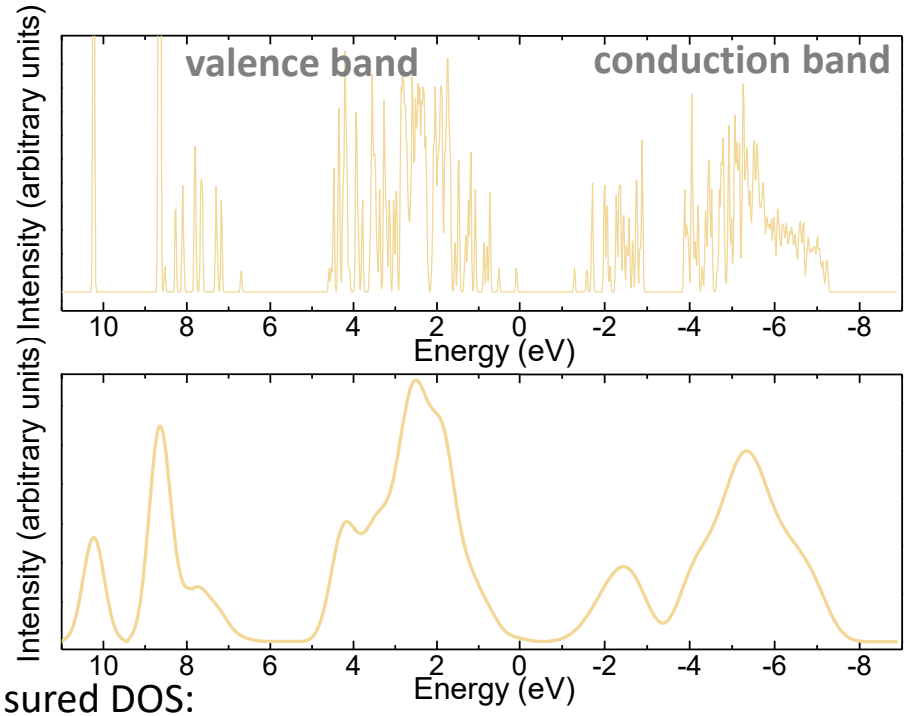


→ How do energy levels change with composition?

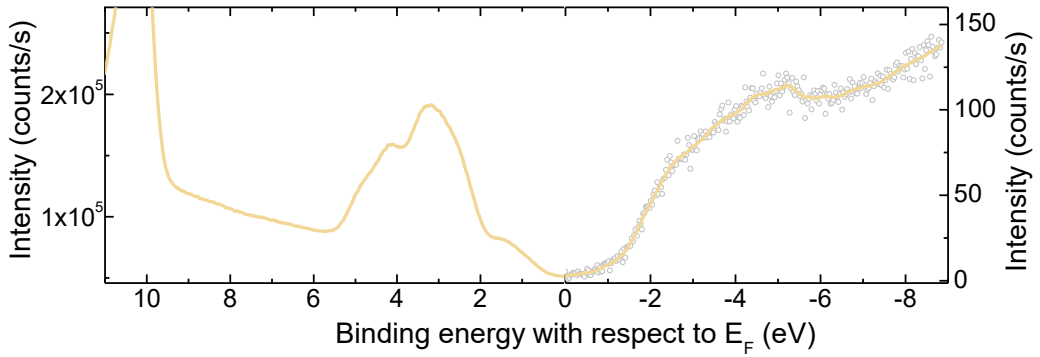
Variation of composition – electronic structure

Our procedure to compare VB and CB trends: example $CsSnI_3$

Calculated DOS:



Measured DOS:

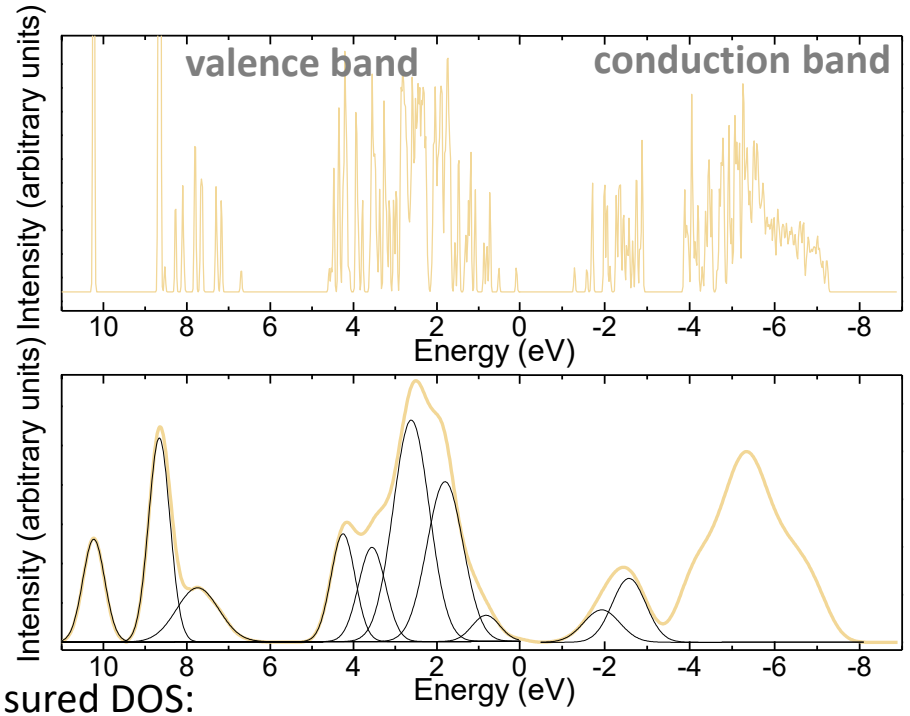


1. Calculate DOS by DFT *(S. Tao, Eindhoven)*
2. Broaden DOS according to experiment

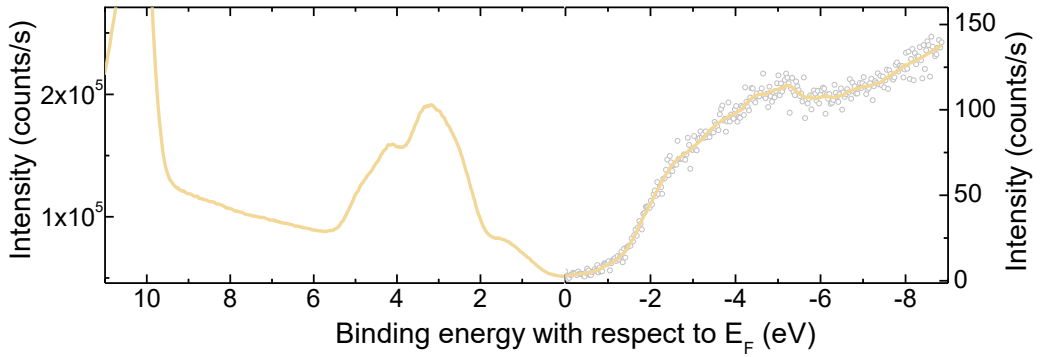
Variation of composition – electronic structure

Our procedure to compare VB and CB trends: example $CsSnI_3$

Calculated DOS:



Measured DOS:

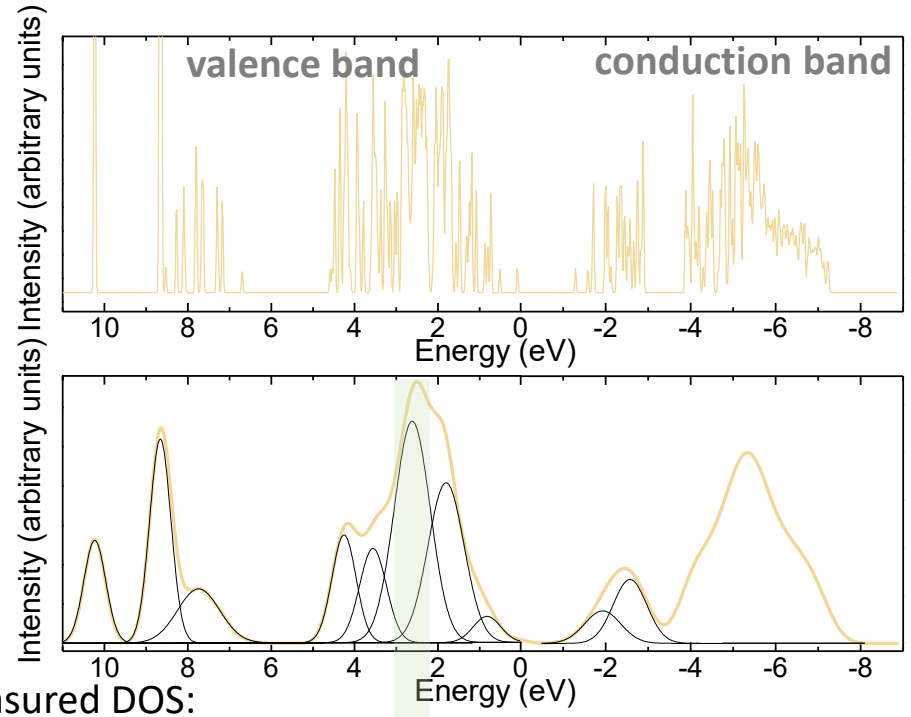


1. Calculate DOS by DFT
2. Broaden DOS according to experiment
3. Fit Gaussian peaks into DOS

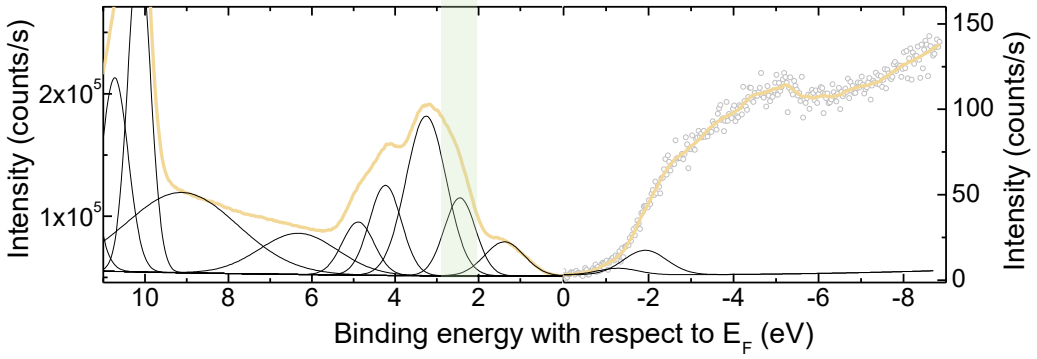
Variation of composition – electronic structure

Our procedure to compare VB and CB trends: example $CsSnI_3$

Calculated DOS:



Measured DOS:

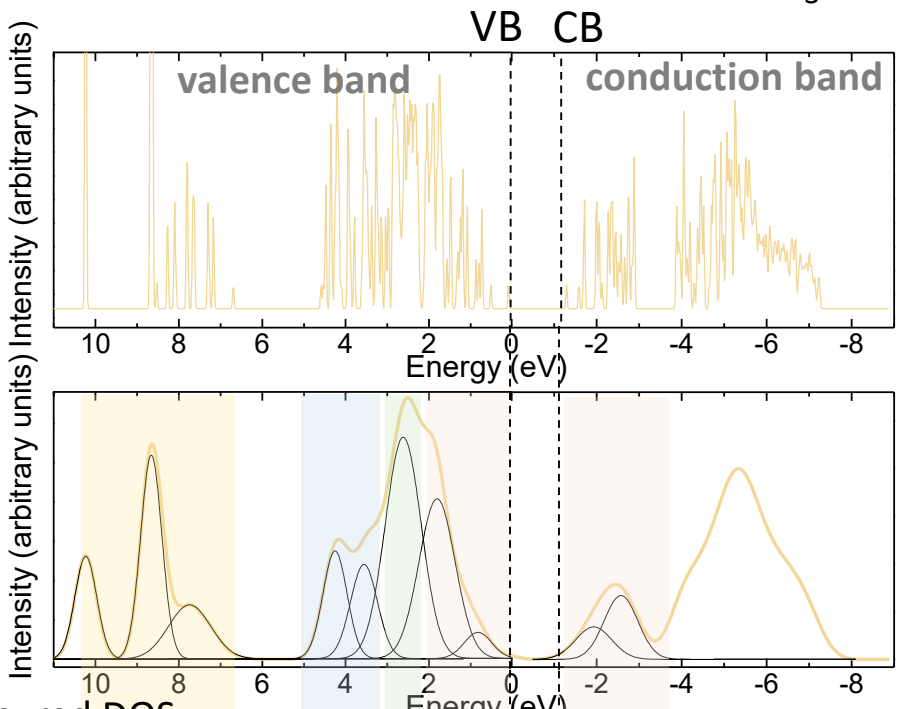


1. Calculate DOS by DFT
2. Broaden DOS according to experiment
3. Fit Gaussian peaks into DOS
4. Fit same peaks into experiment
5. Align DFT and experiment

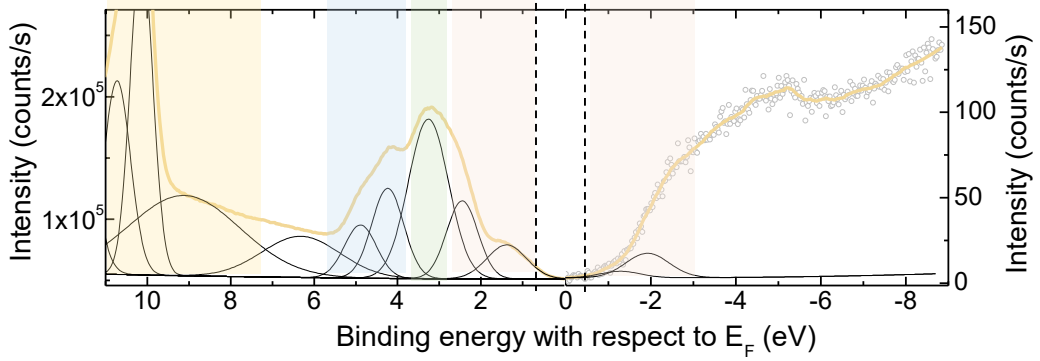
Variation of composition – electronic structure

Our procedure to compare VB and CB trends: example $CsSnI_3$

Calculated DOS:



Measured DOS:



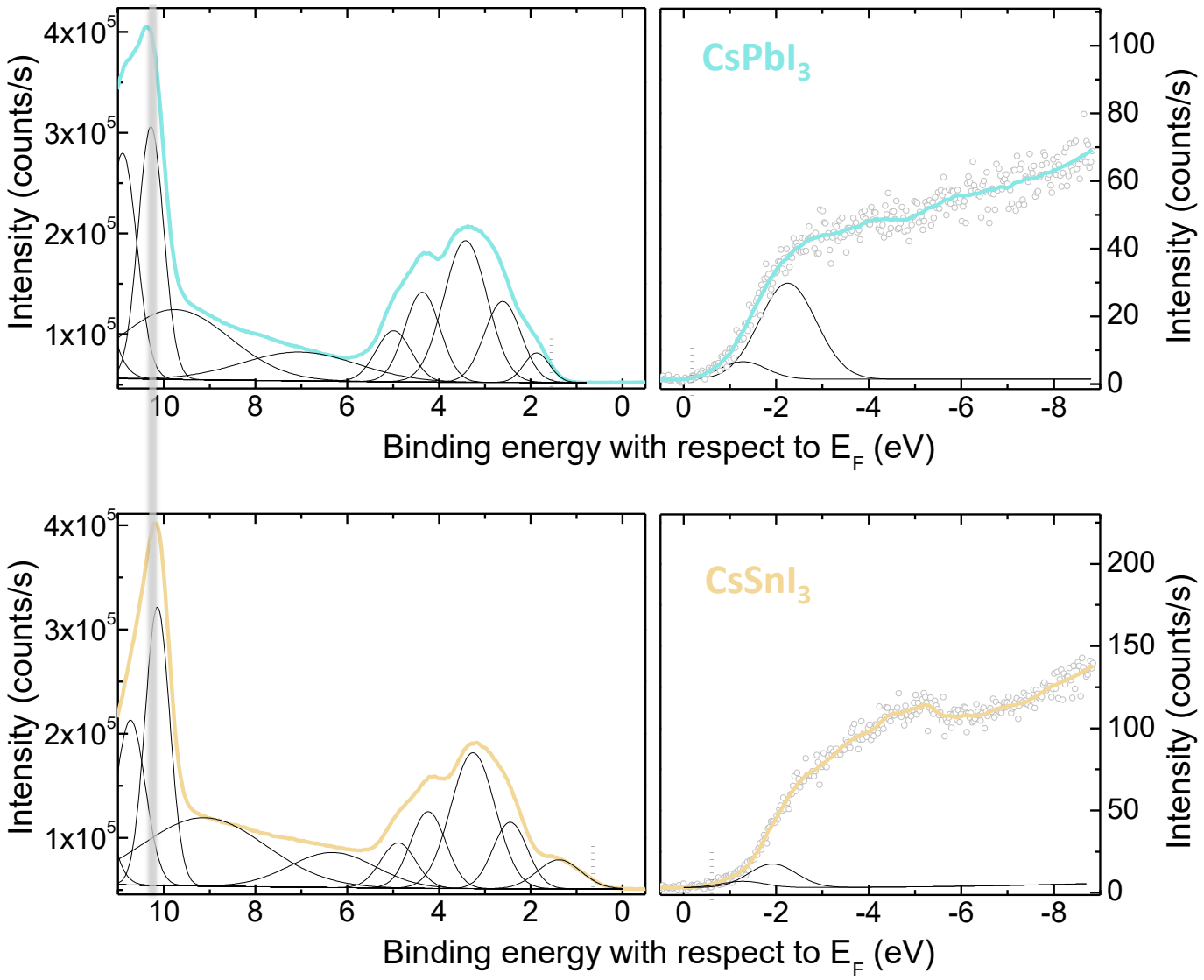
1. Calculate DOS by DFT
2. Broaden DOS according to experiment
3. Fit Gaussian peaks into DOS
4. Fit same peaks into experiment
5. Align DFT and experiment
6. Determine VB and CB onset

Variation of composition – electronic structure

Change of metal cation: $CsXI_3$

Metal: Pb → Sn

Opt. band gap: 1.72 → 1.25 eV



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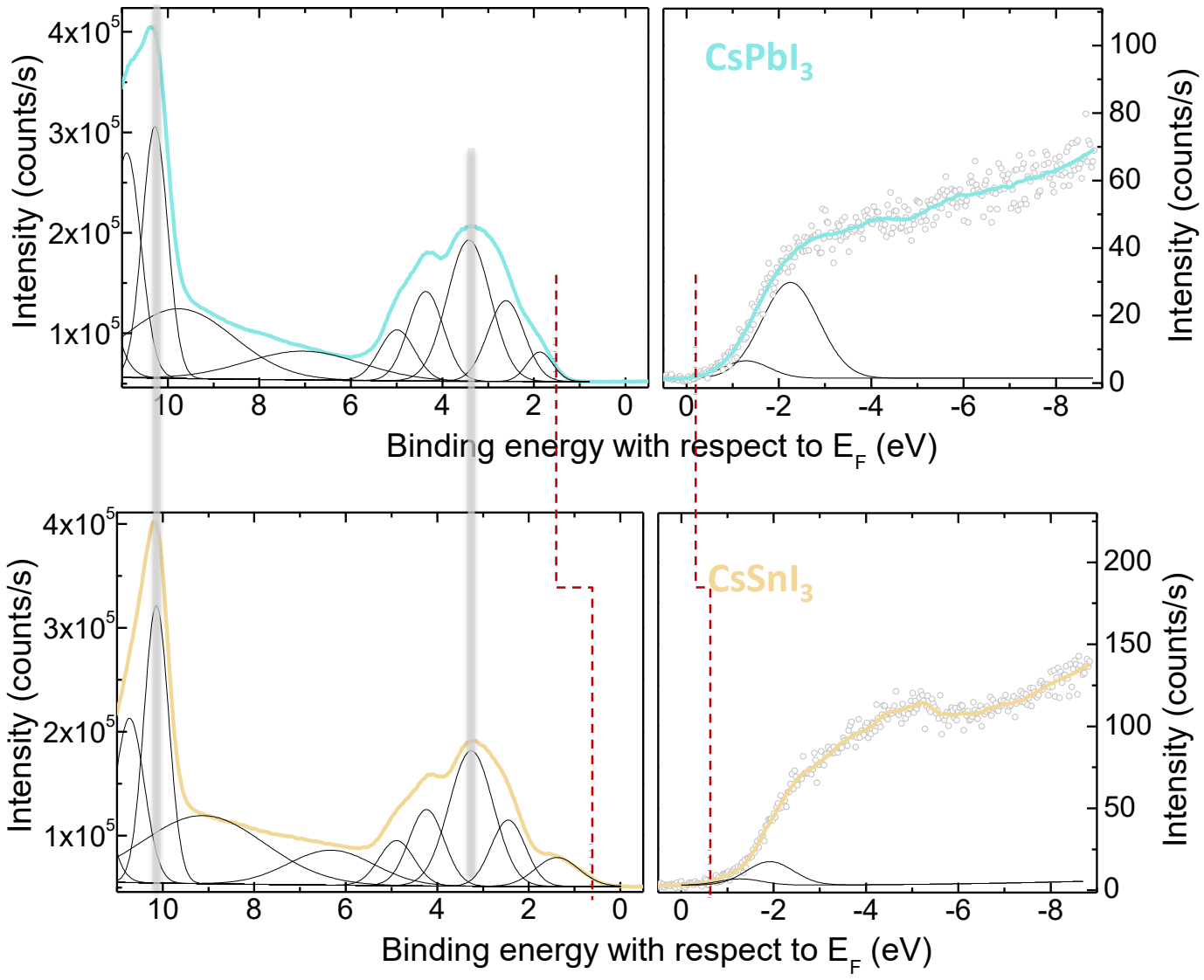


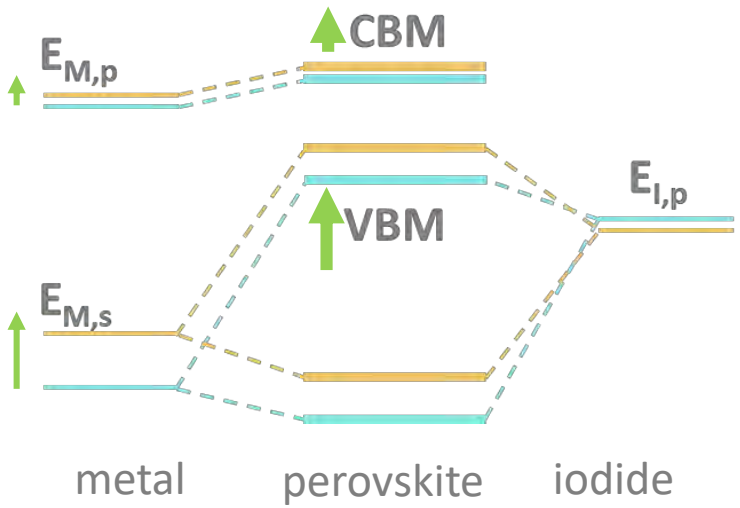
Variation of composition – electronic structure

Change of metal cation: Cs ***X*** I_3

Metal: Pb → Sn

Opt. band gap: 1.72 → 1.25 eV

Tight binding model

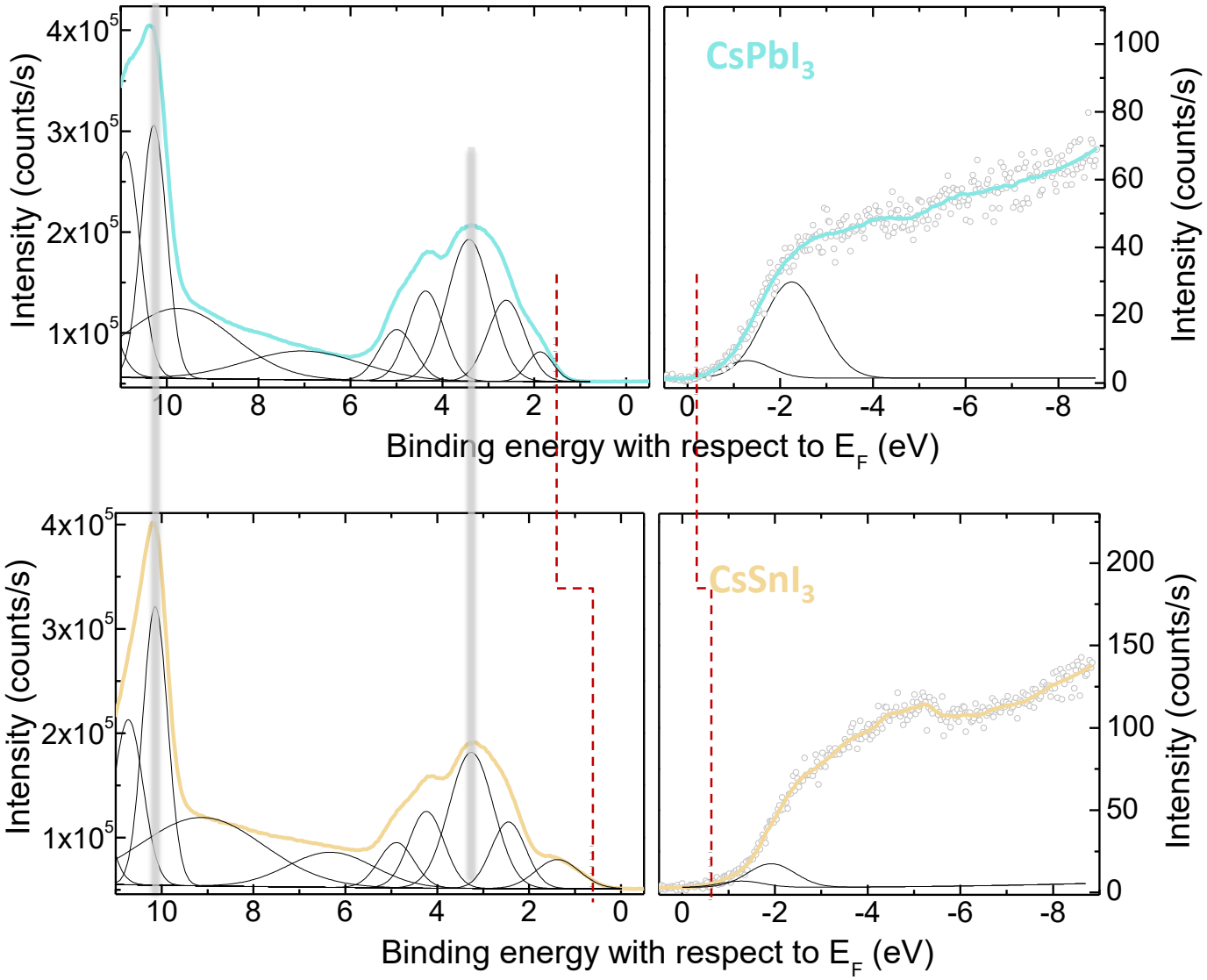


VBM: Sn has higher lying s-state (smaller electronegativity) than Pb

→ VBM shifts up

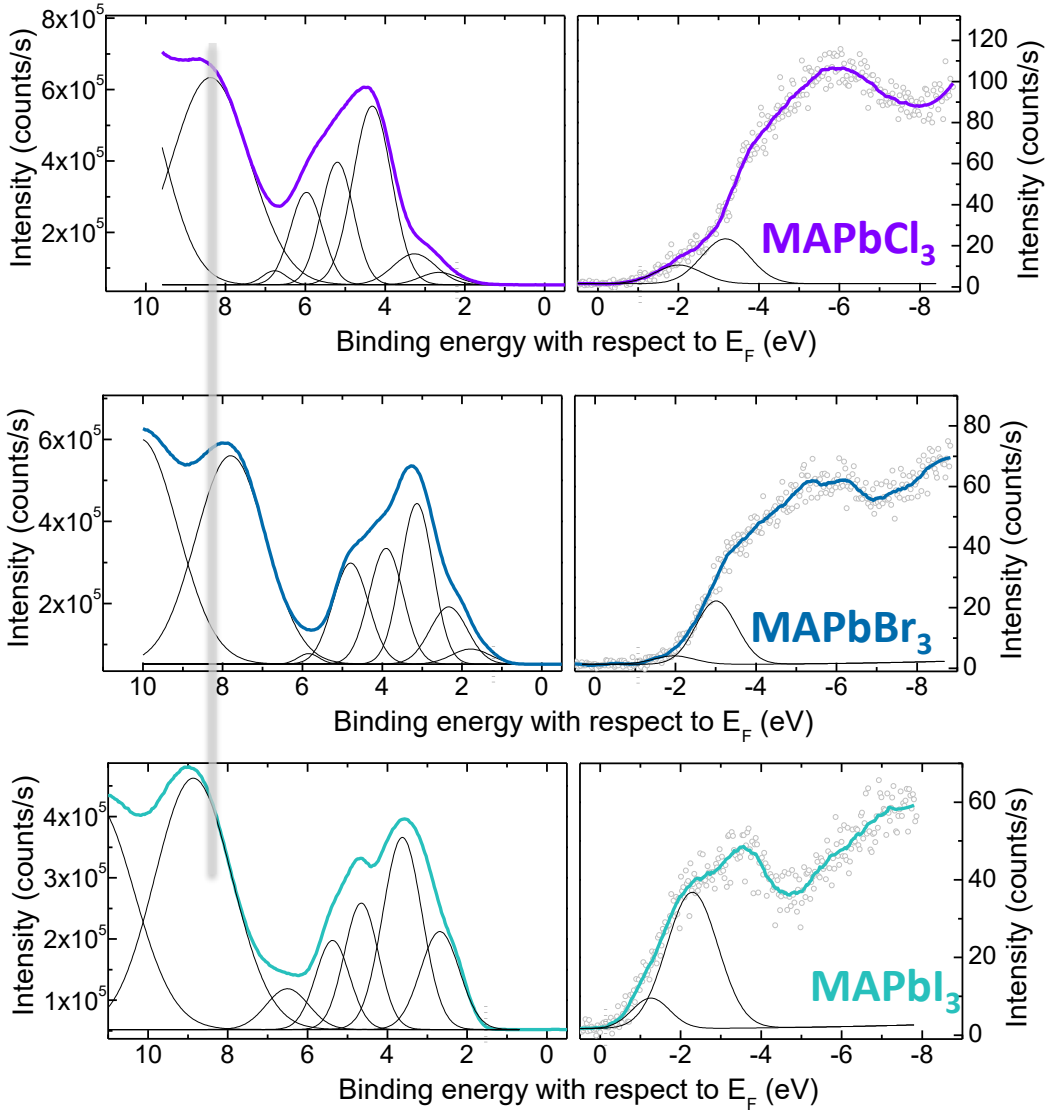
CBM:

Metal p-states rather similar



Variation of composition – electronic structure

Change of halide anion: MA Pb $\mathbf{X_3}$
Halide: Cl → Br → I
Opt. band gap: 3.04 → 2.29 → 1.59 eV



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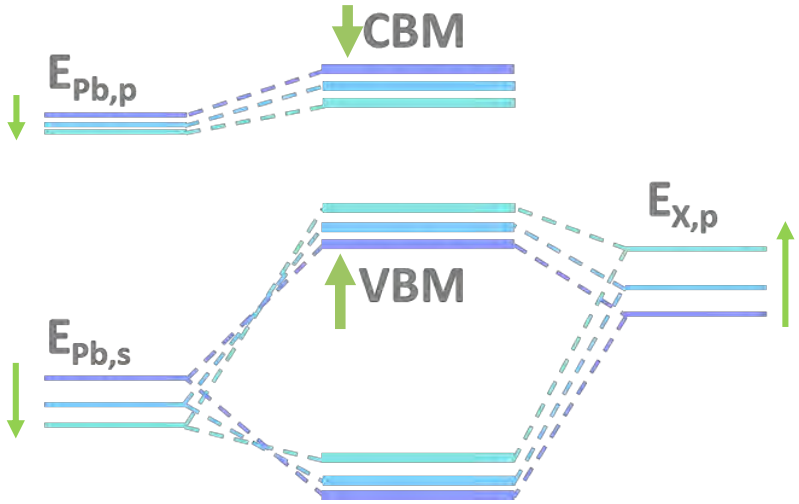
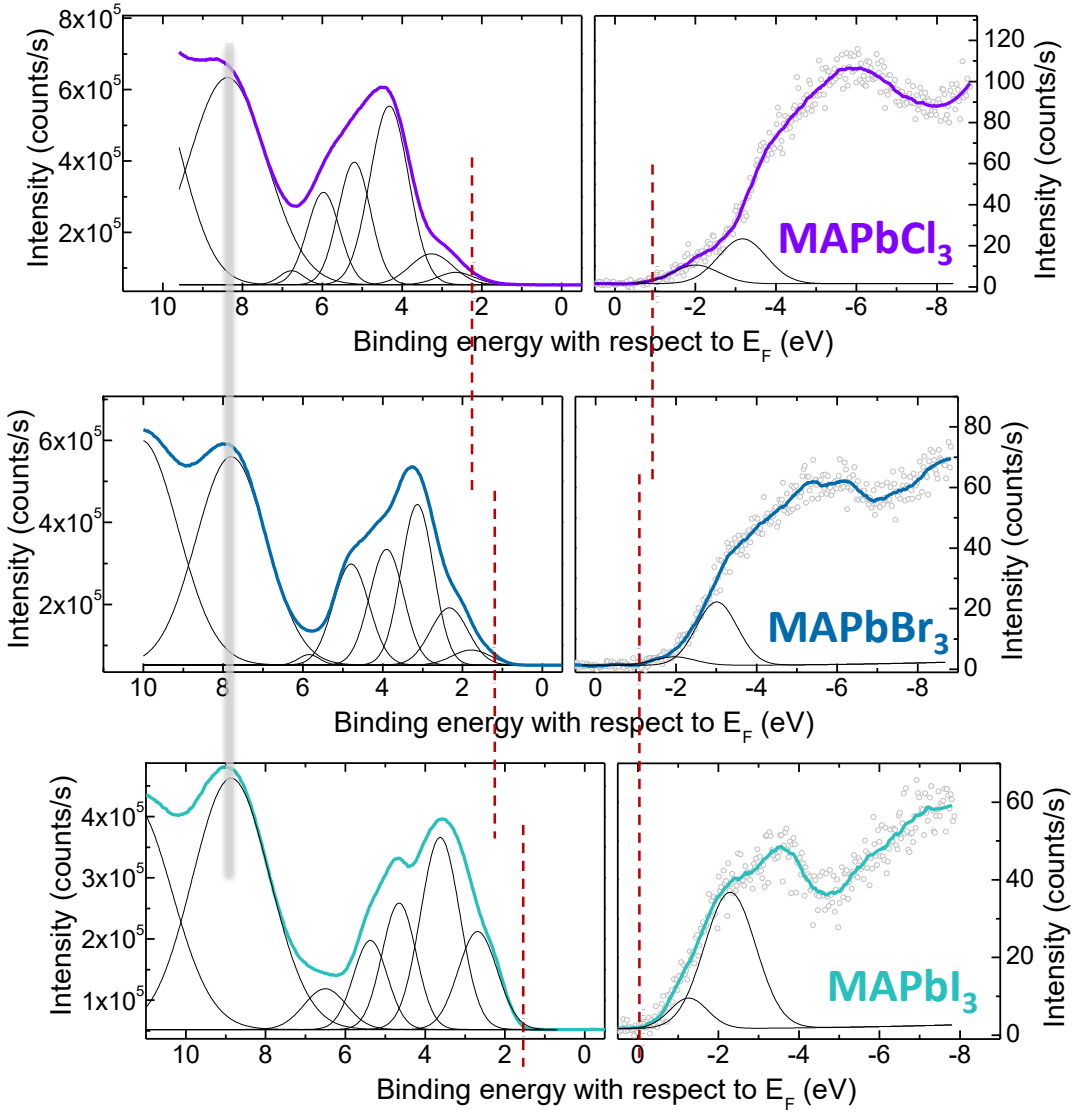
Opt. band gap: 3.04 → 2.29 → 1.59 eV



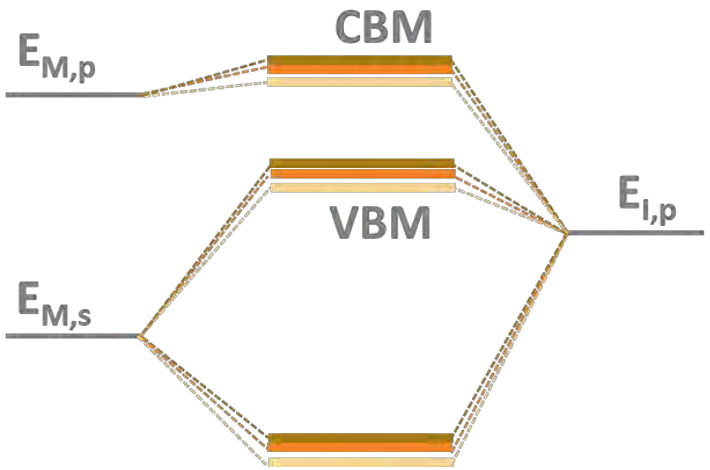
VBM dominated by halide p level (electronegativity)

CBM changes less, is due to the shifts in Pb p-state due to confinement effects

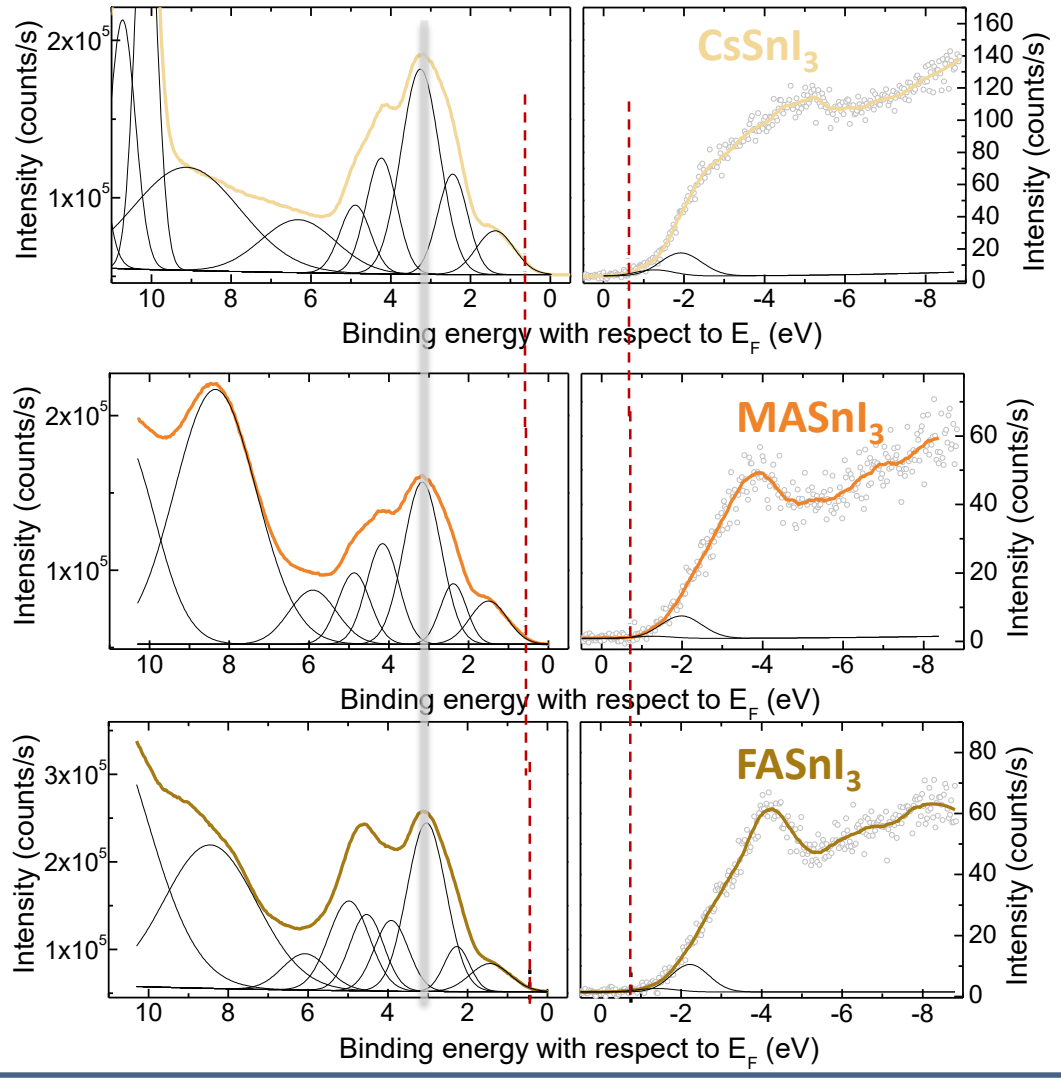


Variation of composition – electronic structure

Change of size of the stabilizing cation ***X*** Sn I_3:
Organic cation: Cs → MA → FA
Opt. band gap: 1.25 → 1.24 → 1.24eV



→ IE and EA similar
(not true if lattice distortion is present)

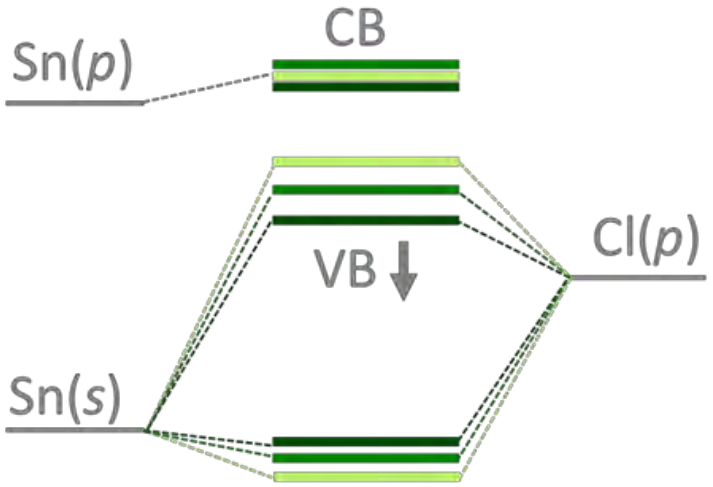


Variation of composition – electronic structure

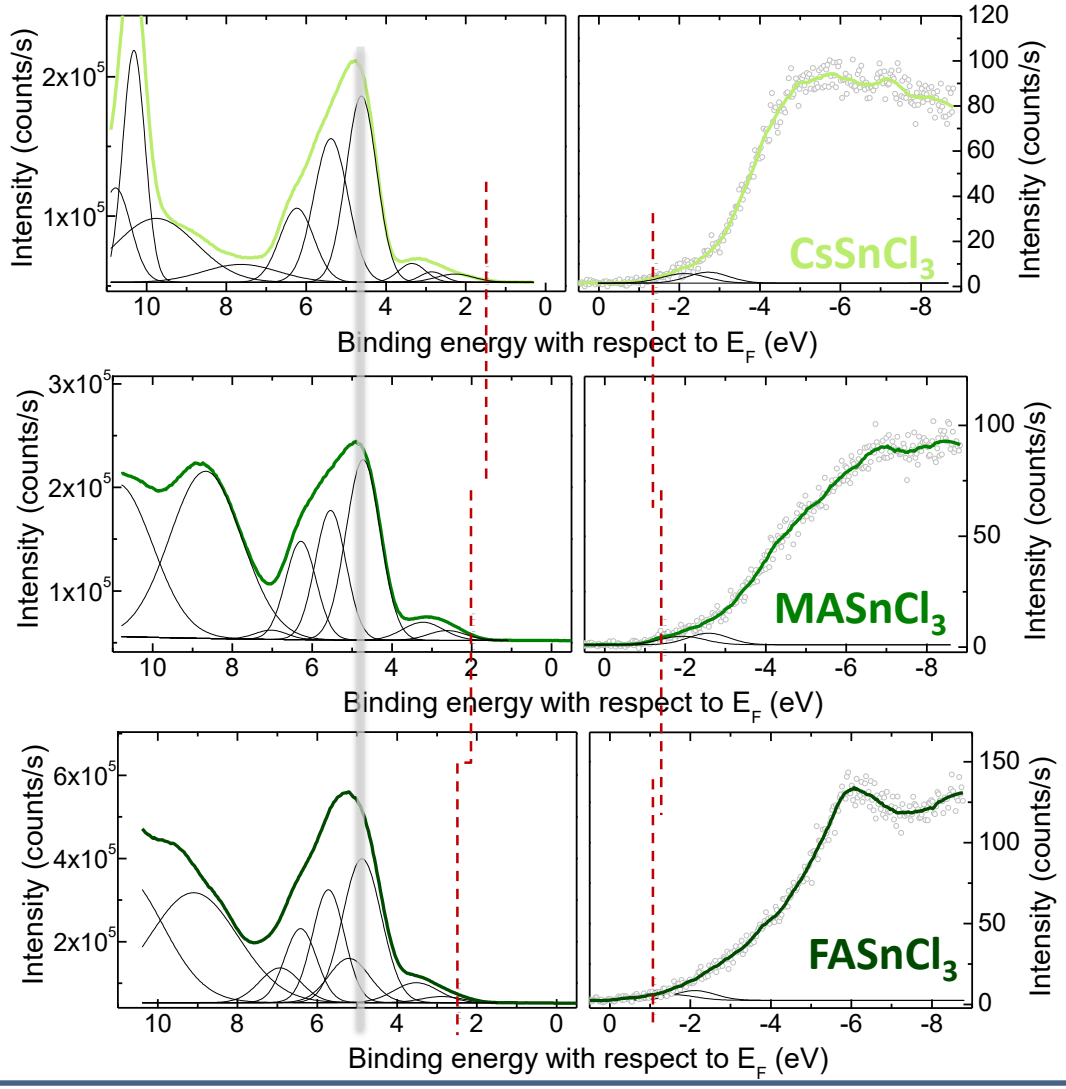
Change of size of the stabilizing cation ***X*** $Sn Cl_3$:

Organic cation: Cs → MA → FA

Opt. band gap: 2.88 → 3.5 → 3.55 eV

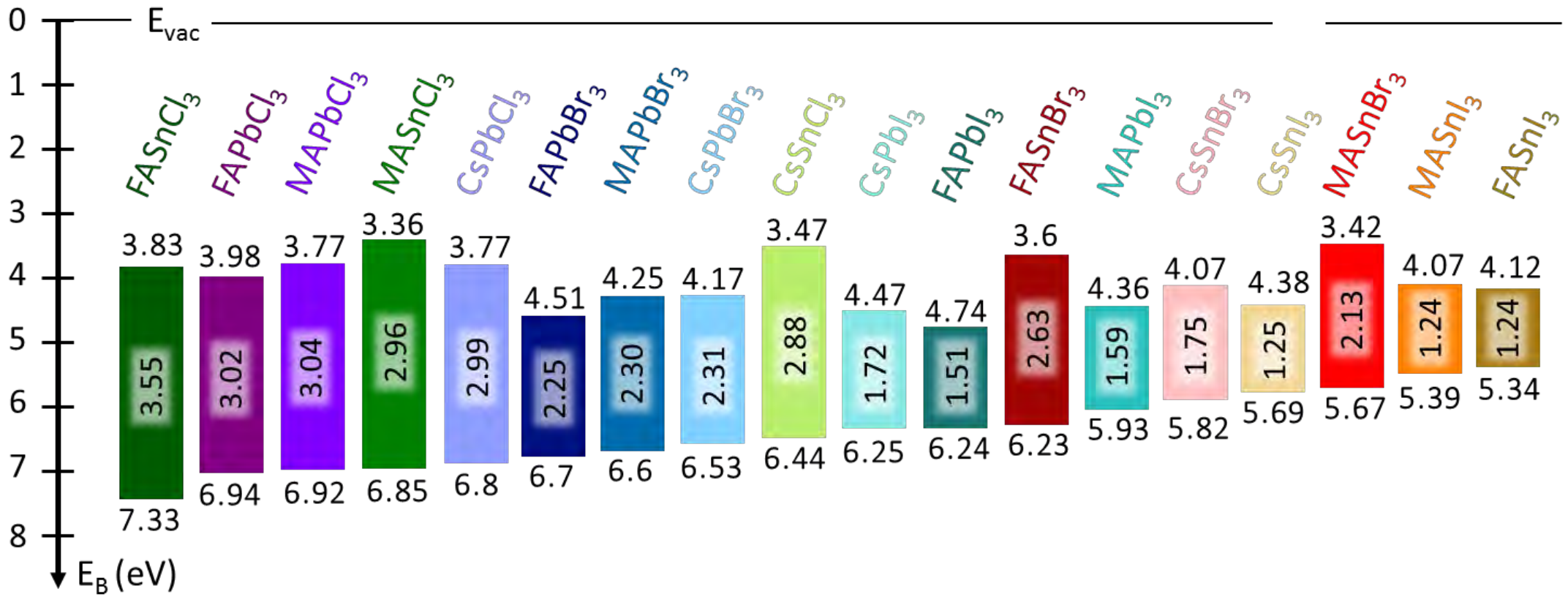


→ lattice distortion affects VB more than CB



Energy levels - overview

Summary of energy level measurements



Tao, Brocks, Olthof et al., Nat. Commun. 10 (2019) 2560

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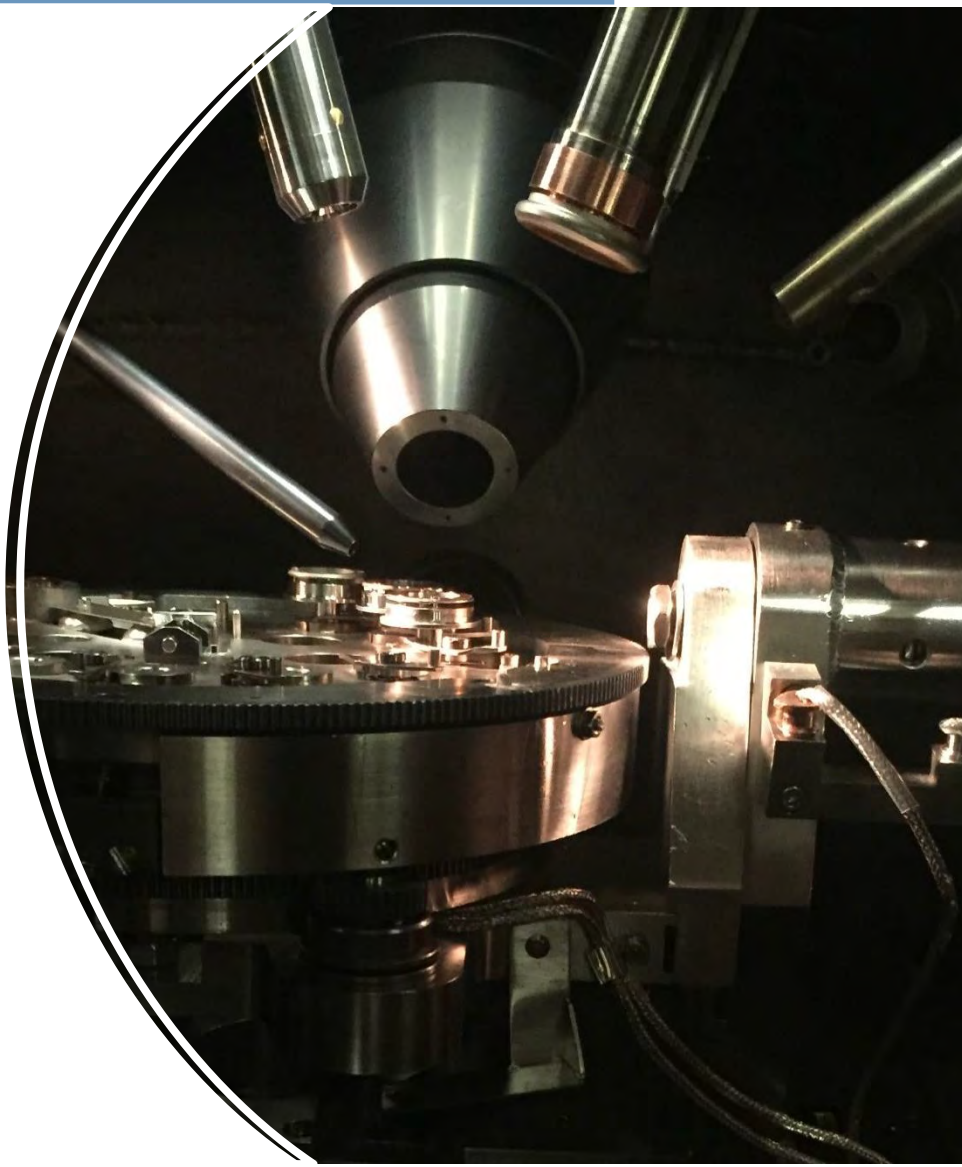
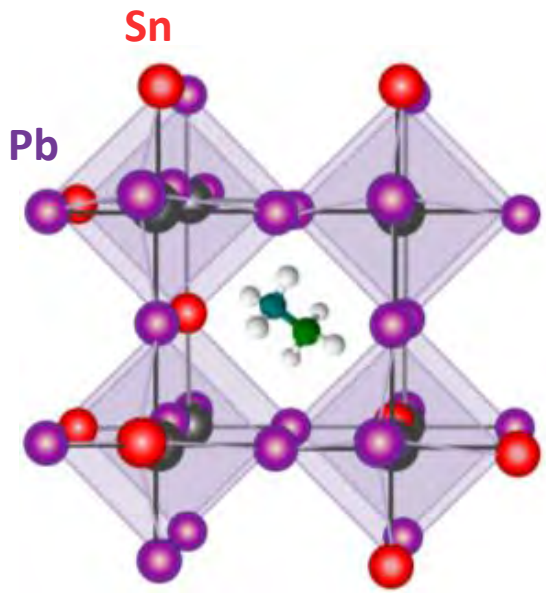
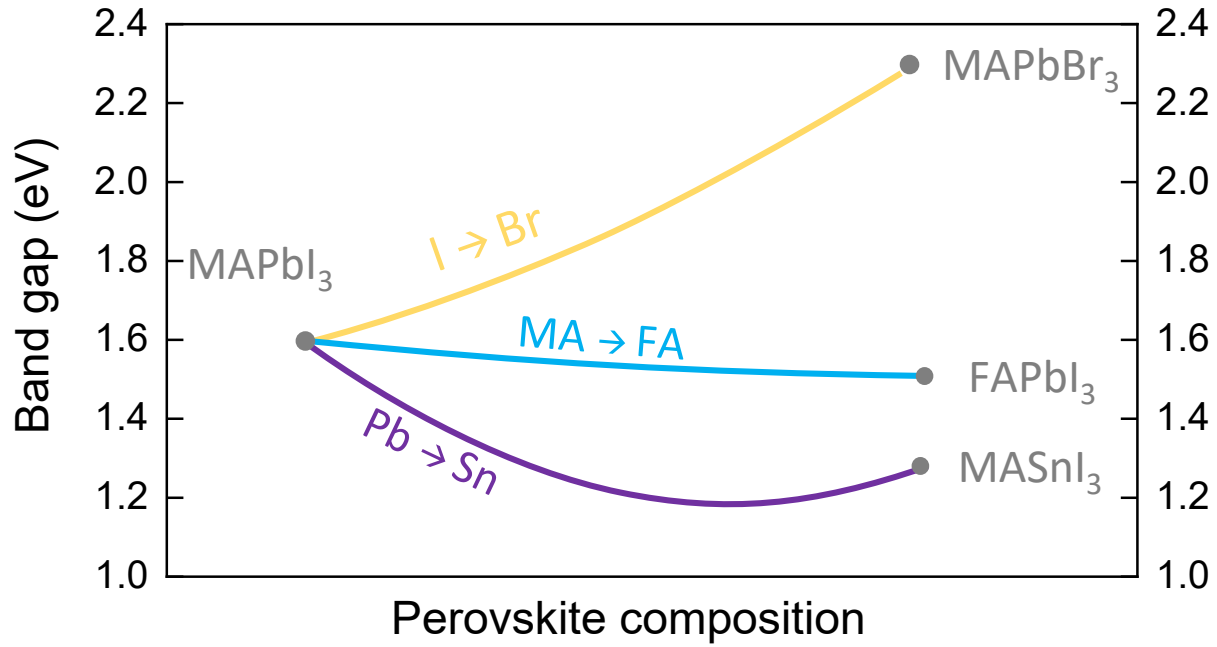


Mixed perovskite structures

It is also possible to prepare mixed perovskites structures



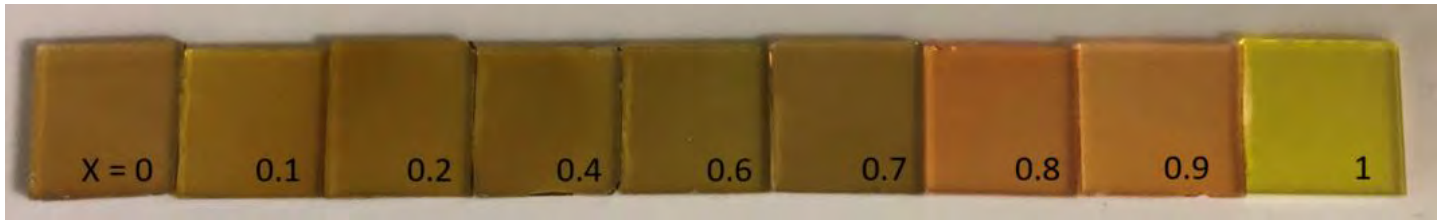


→ these allow for a gradual tuning of the electronic structure

APL Mater., 9, 109202 (2021)

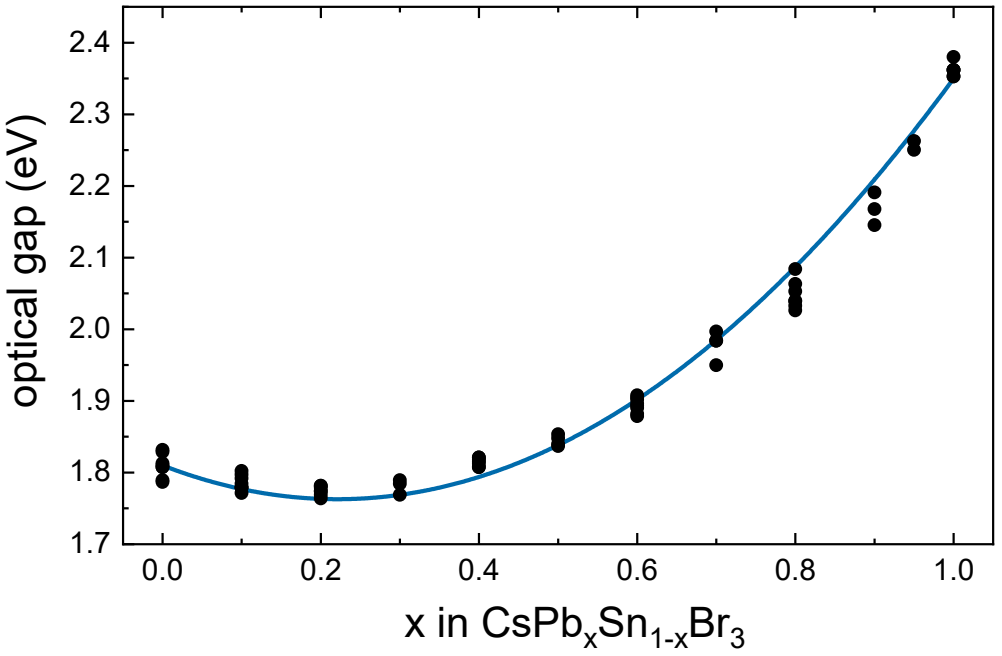
Mixed perovskite structures

Mixed perovskite $CsPb_xSn_{1-x}Br_3$

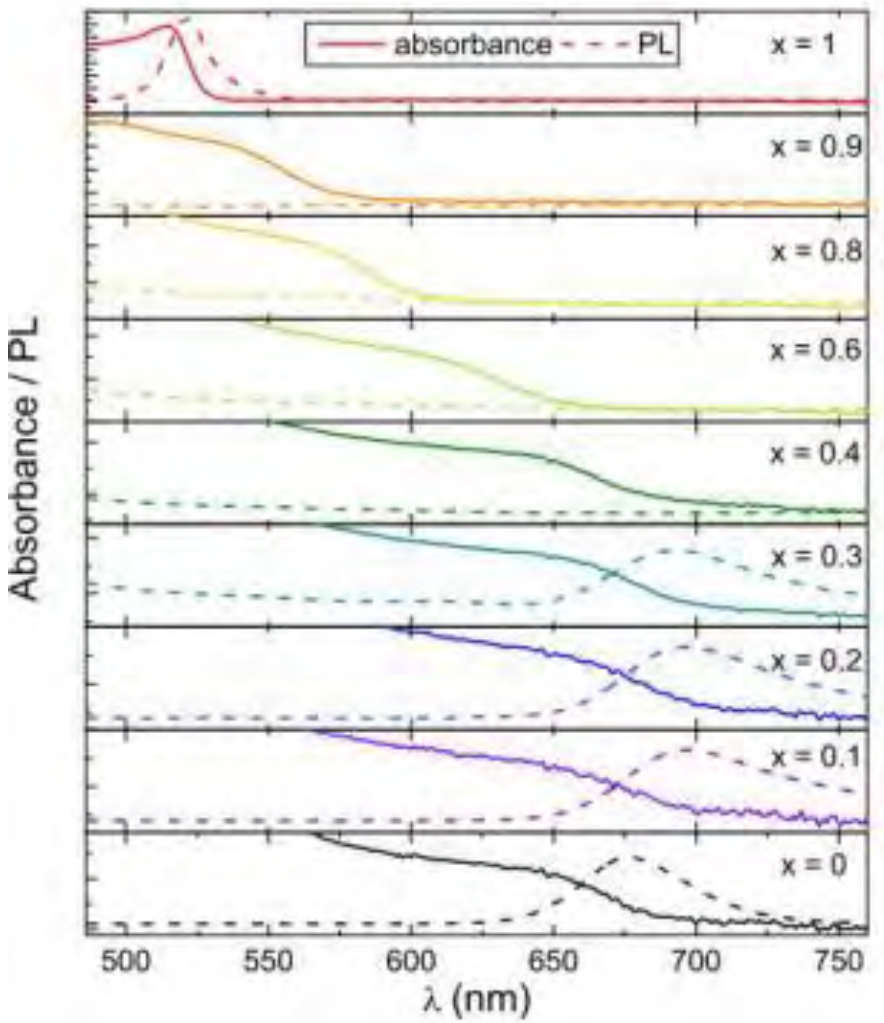


→ band gap can be tuned

Optical gap:



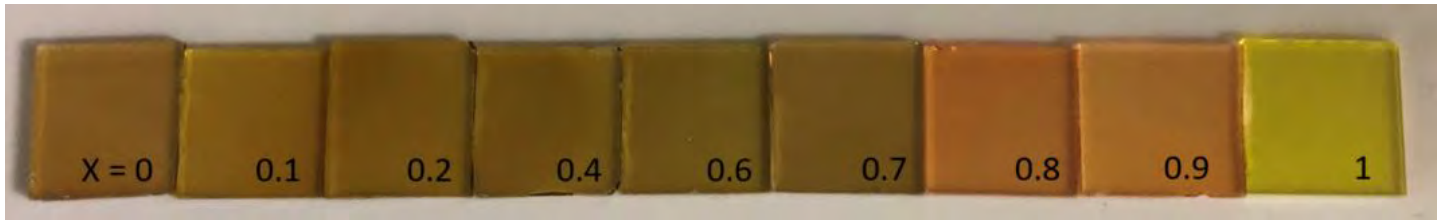
- slight band gap narrowing for high Sn content
- total change in bandgap by ~ 600 meV



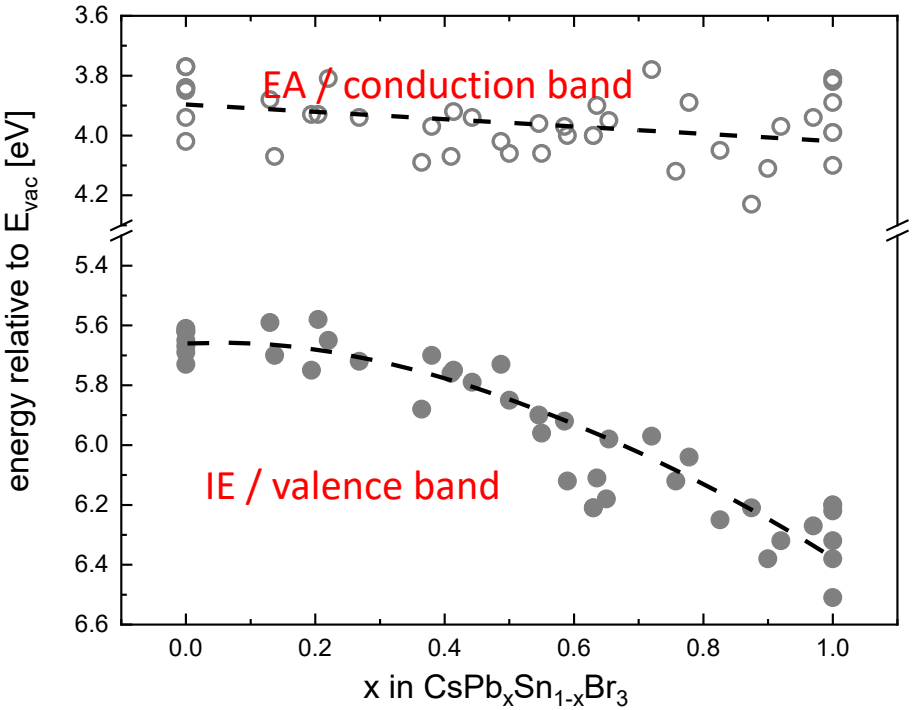
ACS Appl. Mater. Interfaces, 13, 4203 (2021)

Mixed perovskite structures

Mixed perovskite $CsPb_xSn_{1-x}Br_3$



UPS /IPES measurements:

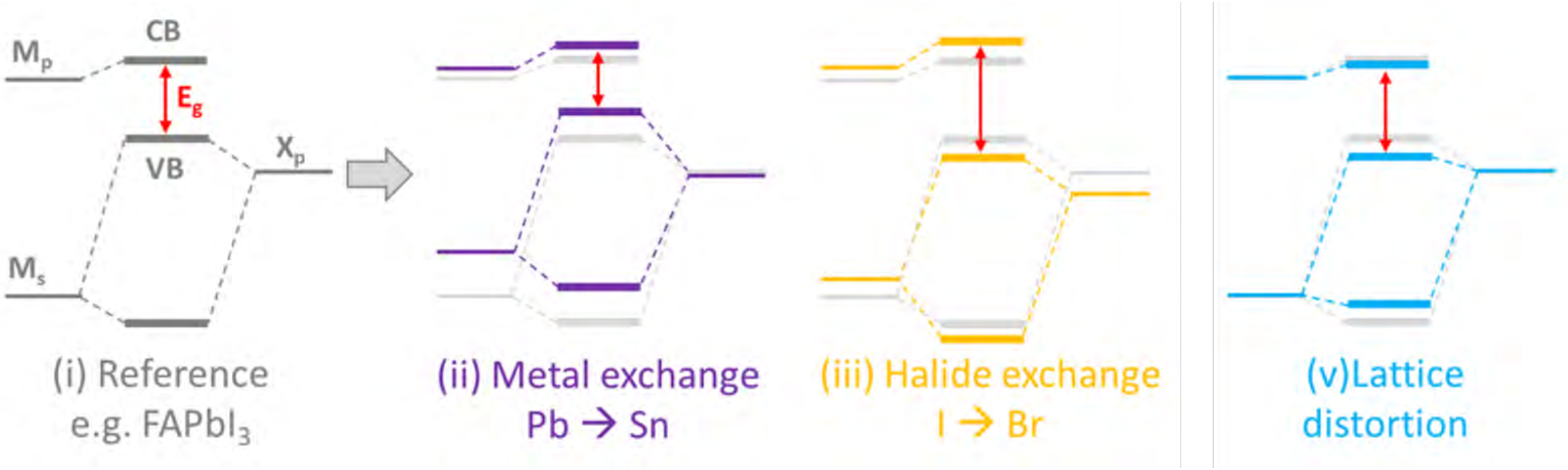


- Conduction band is barely changing
- Change in band gap is due to the VB moving downward

ACS Appl. Mater. Interfaces, 13, 4203 (2021)

Effects on electronic structure

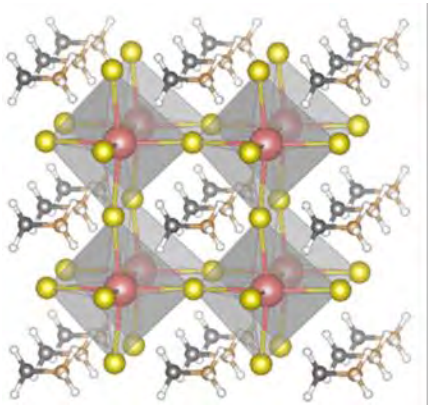
Summary of effects on electronic structure



→ Usually the valence band is more affected

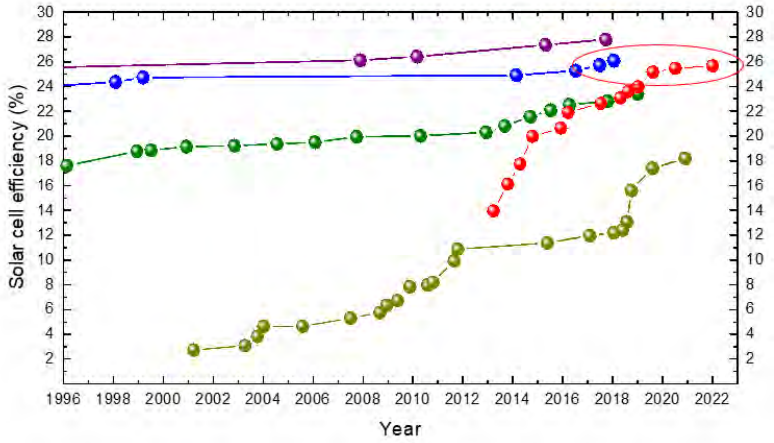
APL Mater., 9, 109202 (2021)

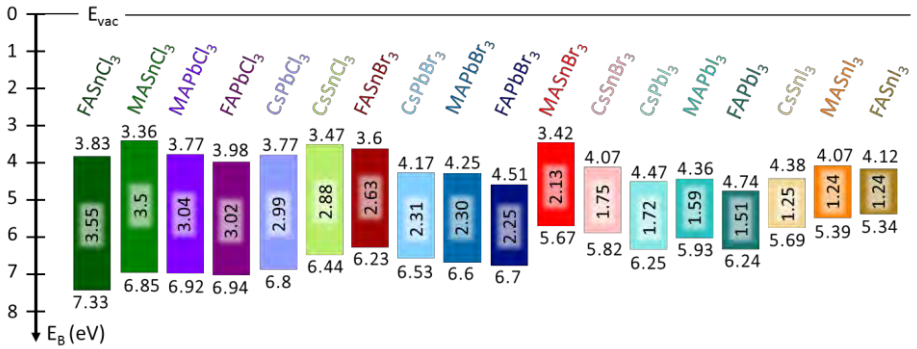
Take home messages



Halide perovskite is a fascinating class of materials…

… with huge potential for optoelectronic application





Electronic structure can be widely tuned by mixing / changing composition