Probing the local environments and optical properties in halide perovskites with short-lived radioactive isotopes

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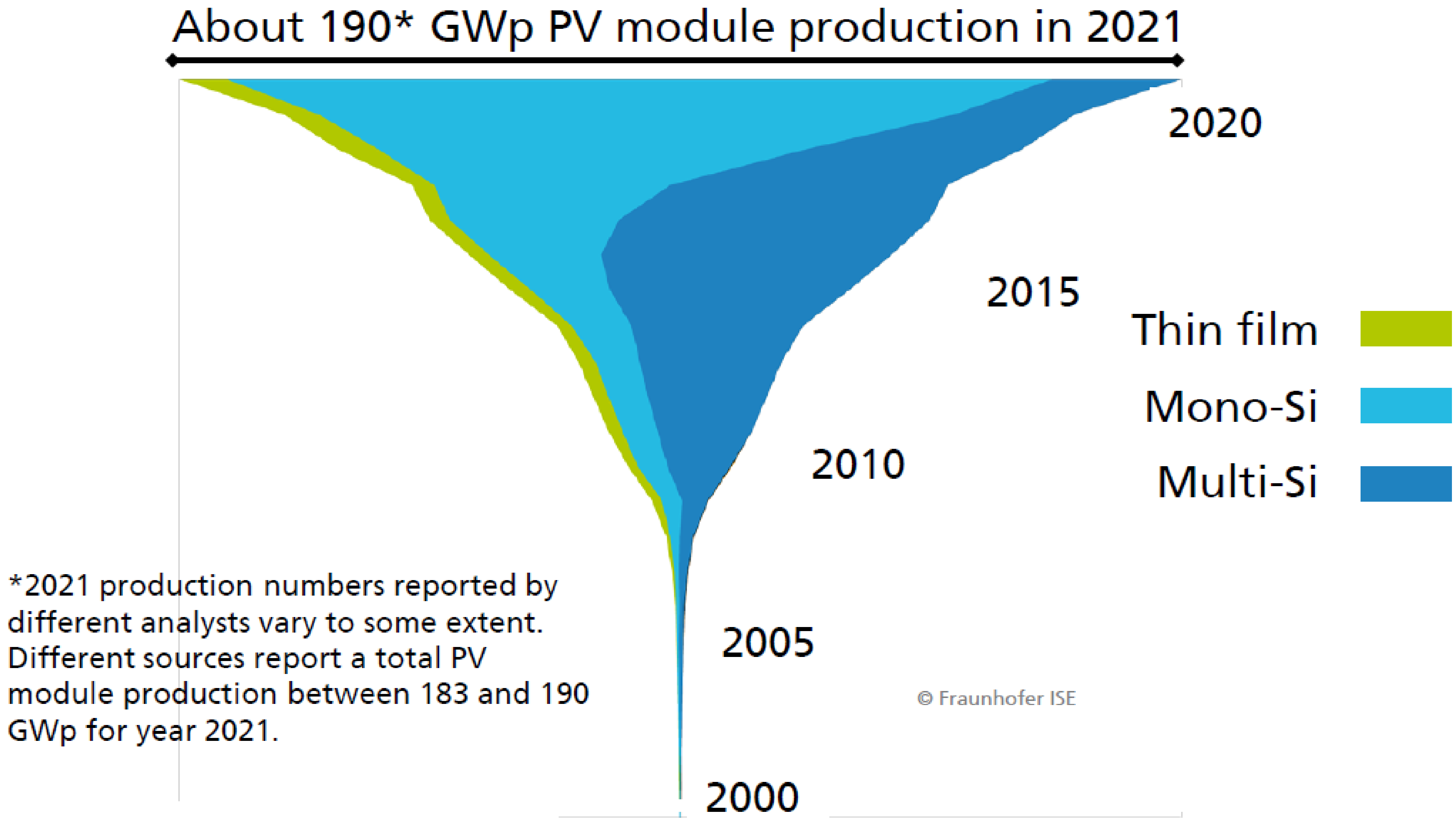
OUTLINE

- ❑ Overview and motivation – perovskites
- ❑ Emission Mössbauer Spectroscopy and radiotracer PL @ ISOLDE
- ❑ Test Measurement + Planned Experiments + Complimentary Studies
- ❑ Expectation and outlook

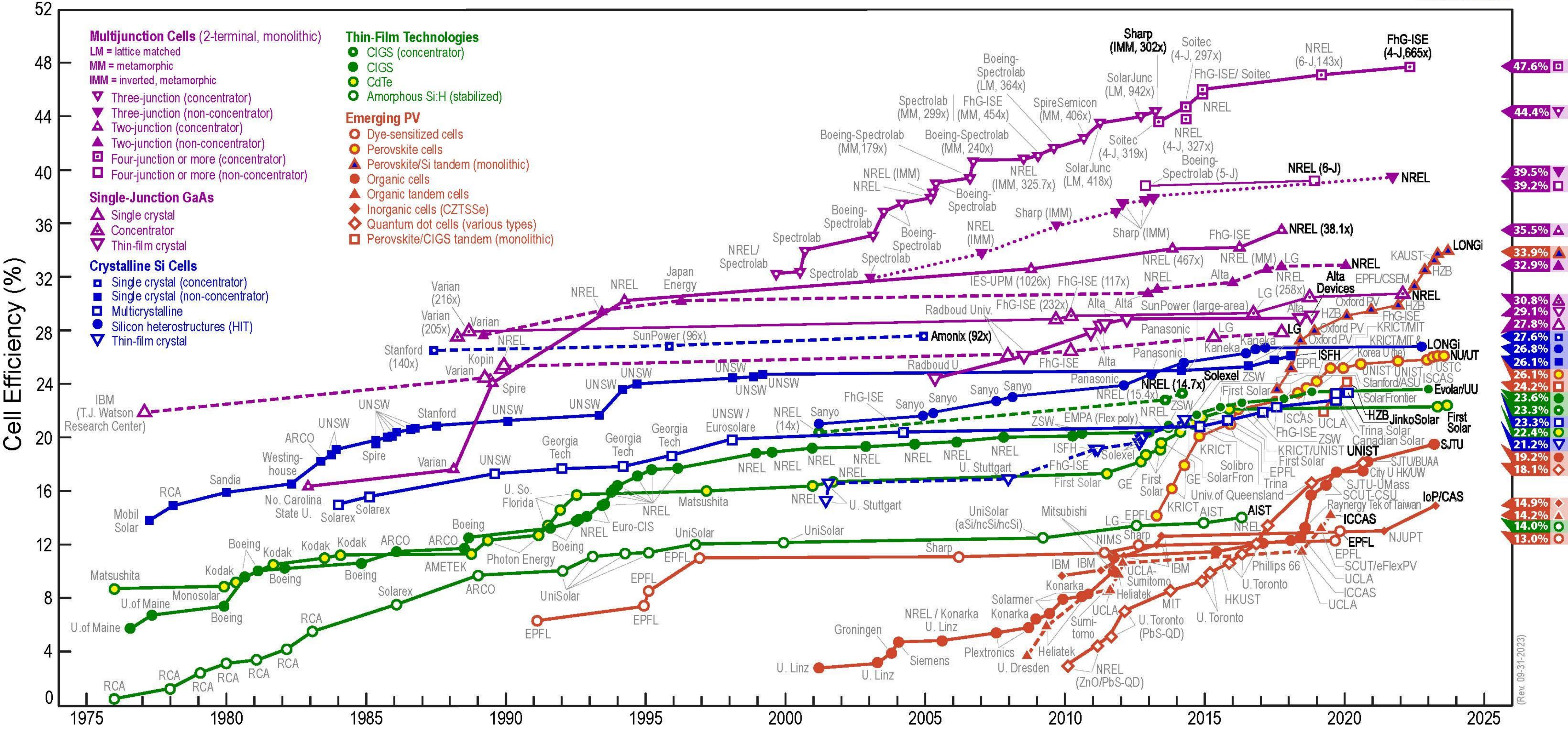
Annual PV Production by Technology - Worldwide (in GWp)



PHOTOVOLTAICS REPORT, Feb 2023

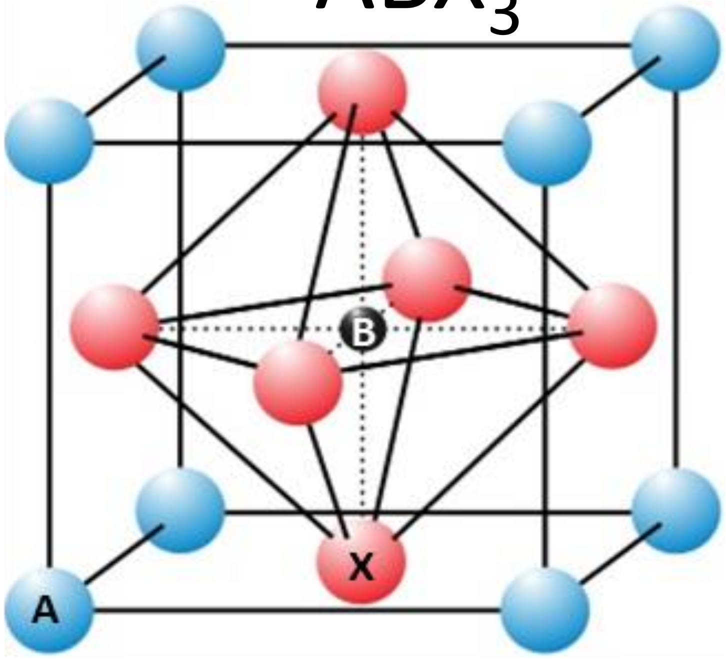
Best Research-Cell Efficiencies

NREL Transforming ENERGY



...to have quantitative control of the optical, electronic (and magnetic) properties of materials

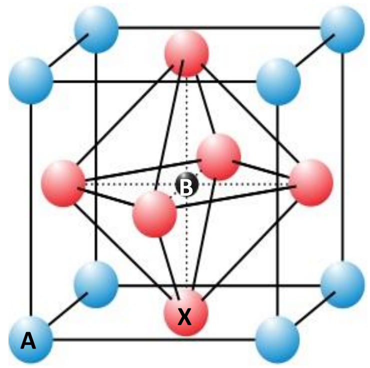
....we should know the....



- ✓ structure of the host material and properties
- ✓ chemical identity of a defect or impurity atom
- ✓ lattice site of an impurity atom
- ✓ interactions between impurity atoms and other defects
- ✓ thermal properties of defects/dopants (diffusion, binding between defects).....

Aim: Ascertain the effect of impurity atoms, lattice sites or defects on the optical properties of perovskite materials.

MOTIVATION: PEROVSKITES - Effects of ion substitution??



ABX_3

- **Organic**: $CH_3NH_3^+$, $CH(NH_2)_2^+$,
- **Inorganic**: Cs^+, Rb^+, or K^+
- **Halide**: Cl^-, Br^-, or I^-
- **Transition Metal**: Pb^{2+}, Ge^{2+}, or Sn^{2+}

- Tolerance factor

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)}$$

- Octahedral factor

$$\mu = \frac{r_B}{r_X}$$

- Charge neutrality

Emission Mössbauer Spectroscopy

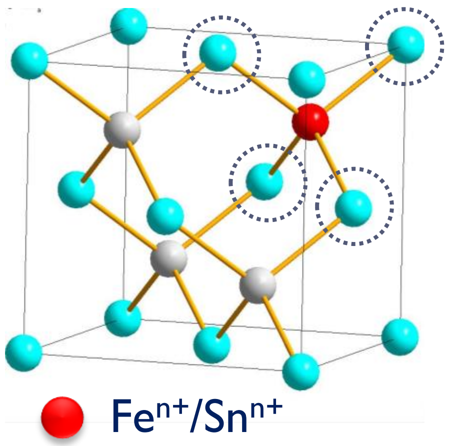
- ❑ Element Specific: $^{119}In^*$ (Sn) and $^{57}Mn^*$(Fe)
- ❑ target Pb substitution with Sn and Fe
- ❑ Aim: investigate the local environment around the probe
  - ✓ lattice sites, charges (and spin) states – [e.g. Sn^{2+}/Sn^{4+}]
  - ✓ Intrinsic/implantation-induced defects and their stability
  - ✓ effect of temperature, laser excitation and power on lattice location, charge states, point defects …..

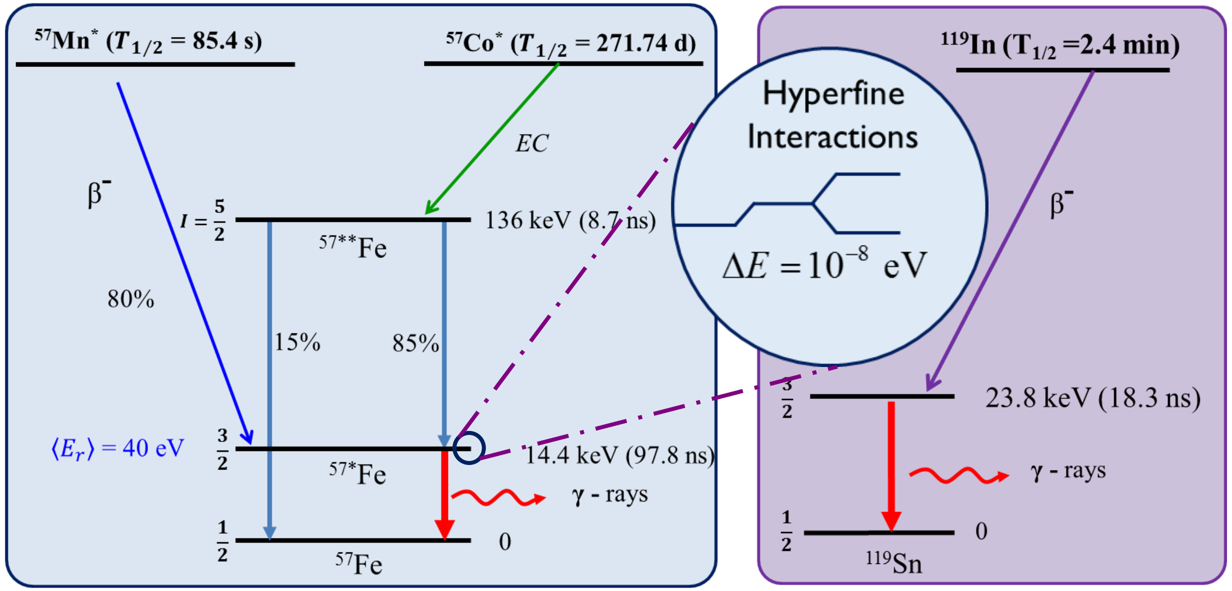
Radiotracer Photoluminescence

- ❑ The technique is not element specific, but the scientific case decides; Sn and Fe,
- ❑ $^{119}Sb^*$ and $^{56}Mn^*$ to correlate atomic-scale characterization from eMS and the effect of dopants/defects, and alloy disorder on luminescence and excitonic states
- ❑ Investigate the role of dopants, radiation damage and defects

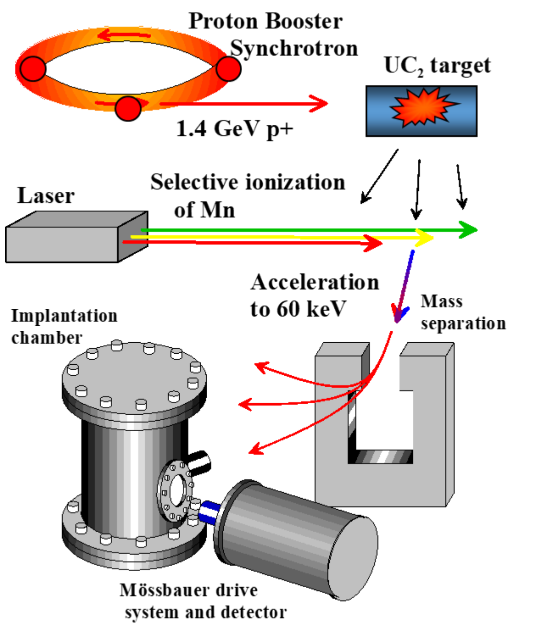
EMISSION MÖSSBAUER SPECTROSCOPY @ ISOLDE

…sensitive to charge density distribution at the nucleus and symmetry around the probe…

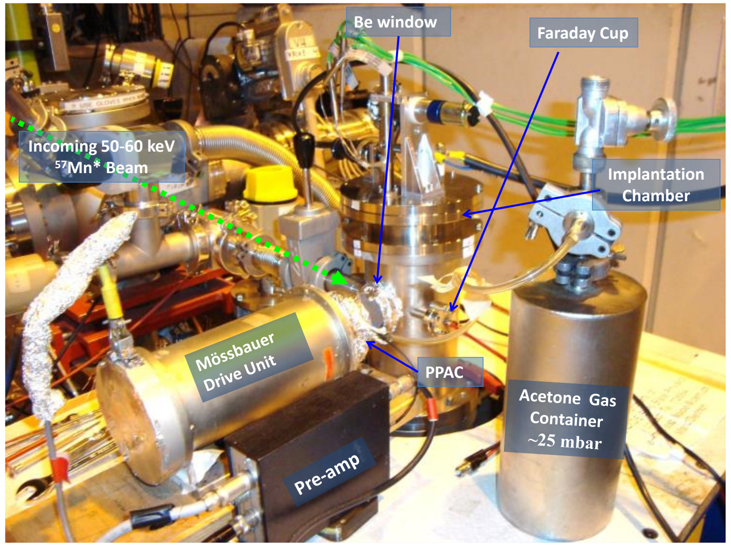


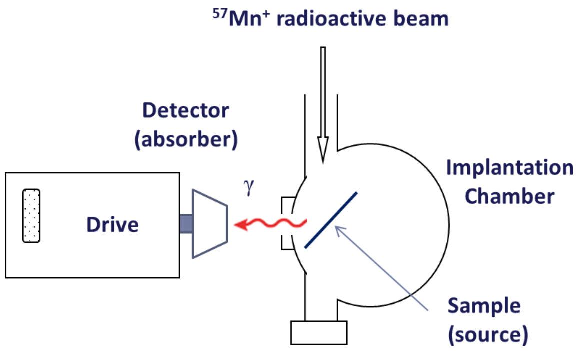


Beam production at ISOLDE



- ✓ Charge and spin state of probe atom: Fe^{n+}, Sn^{n+}
- ✓ Symmetry of lattice site (V_{zz})
- ✓ Binding properties (Debye-Waller factors)
- ✓ Magnetic interactions (ferro/para)
- ✓ Paramagnetic relaxation (~10^7-10^8 Hz) …plus…



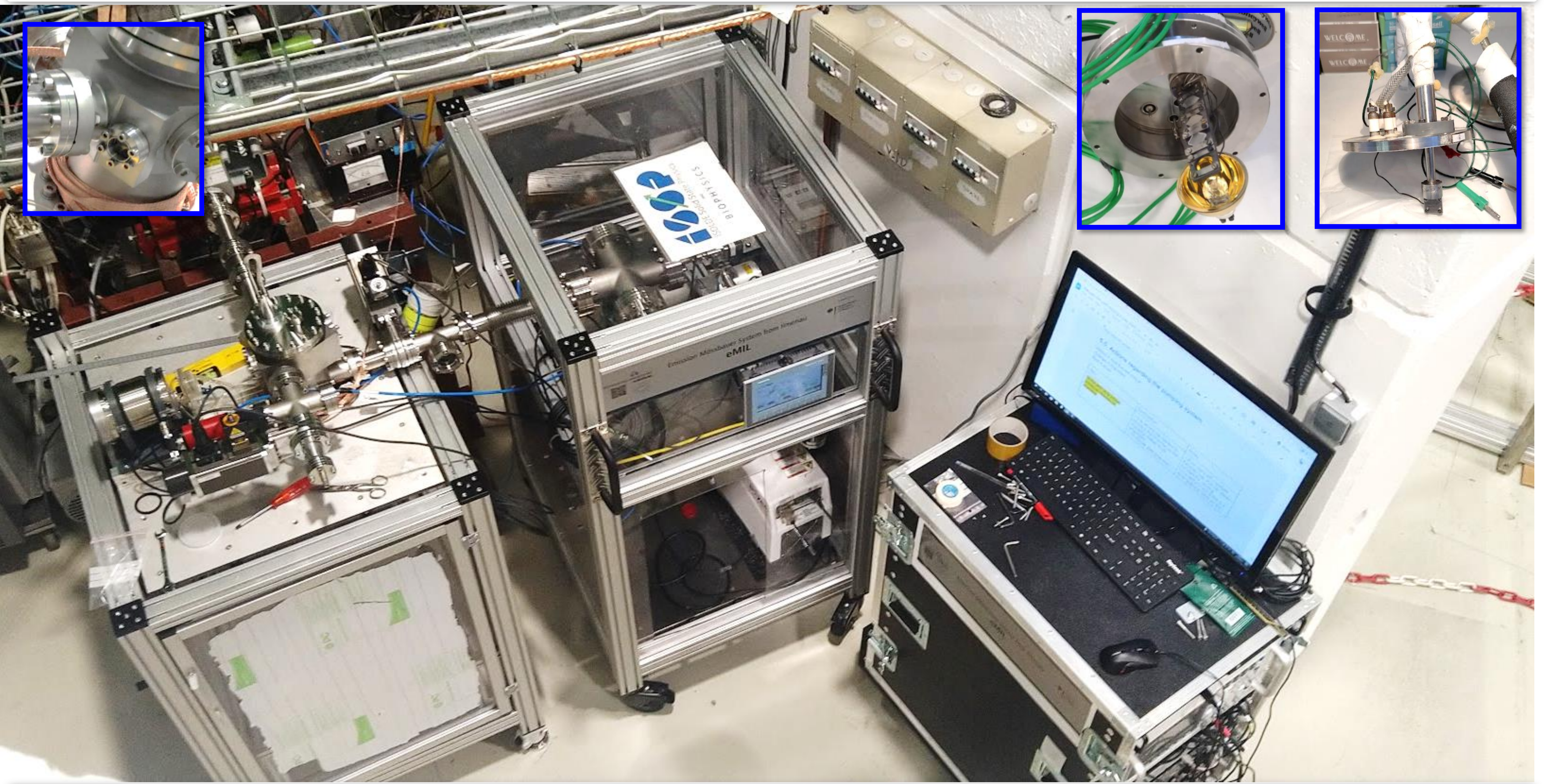


Implantation angle = 30° w.r.t. *c*-axis
Emission angle = 60° w.r.t. *c*-axis
Fluence = ~ 3×10^{12} ions/cm²

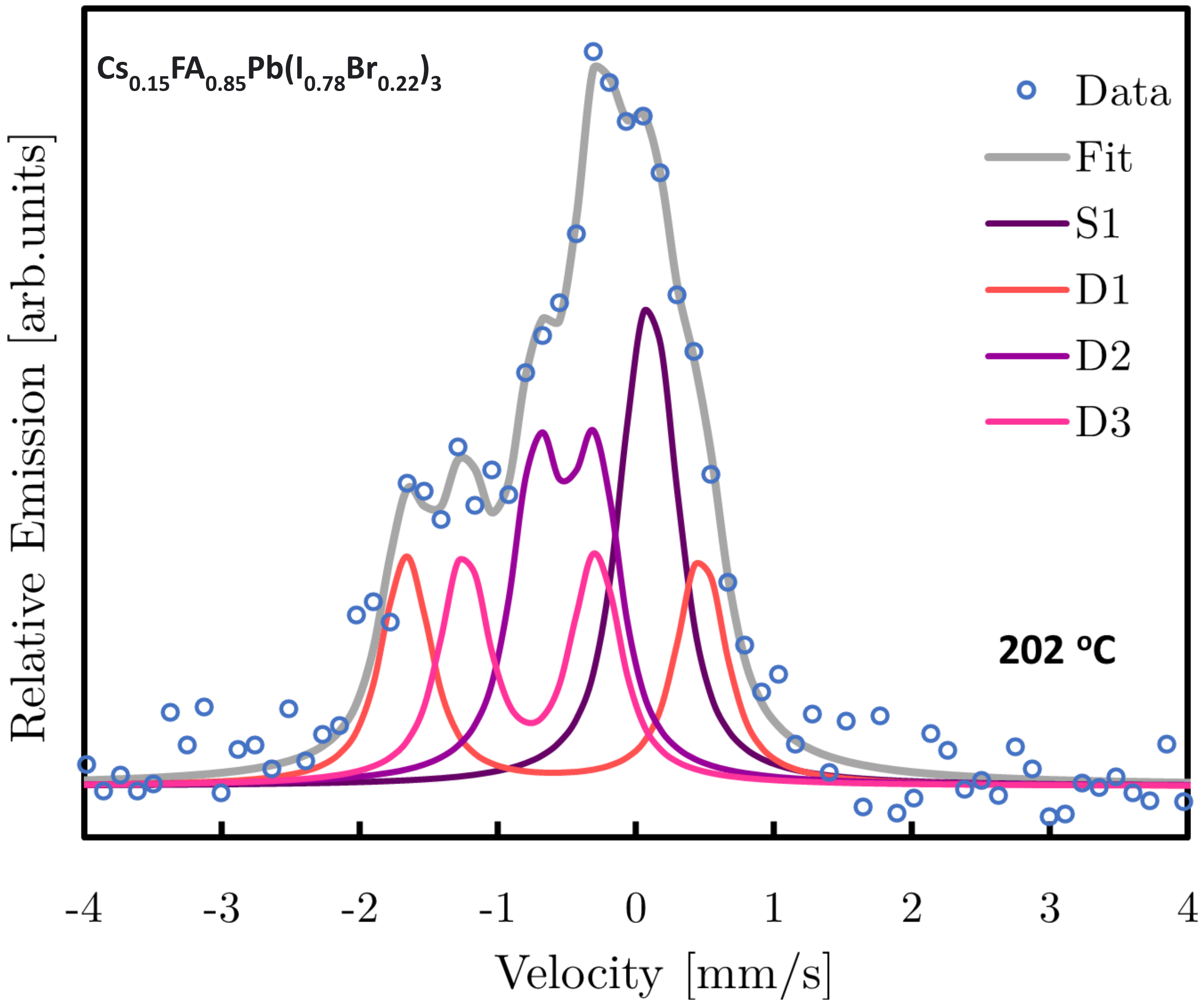
Detect and distinguish up to 4-5 spectral components:

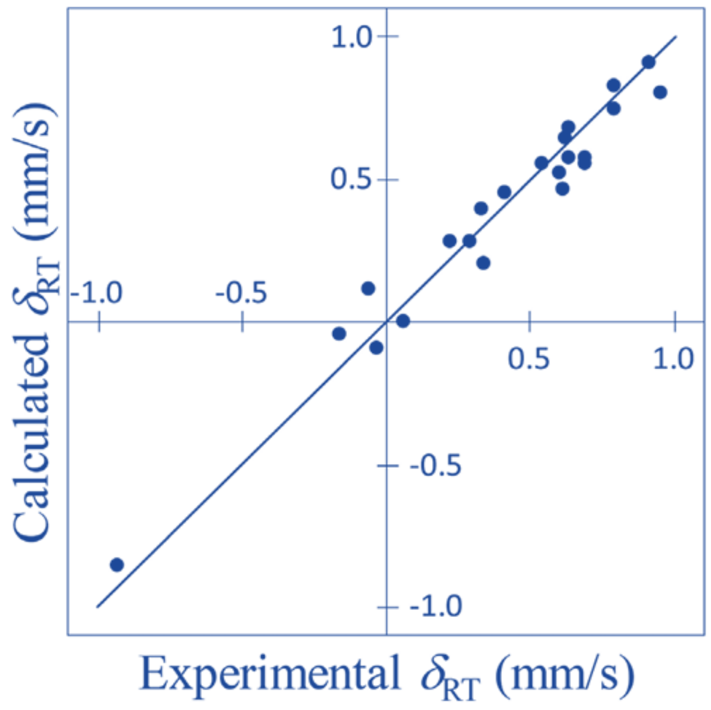
- ✓ substitutional, interstitial, damage, vacancy-defects,…

Emission Mössbauer Spectroscopy @ ISOLDE



Test measurement on hybrid organic-inorganic perovskite

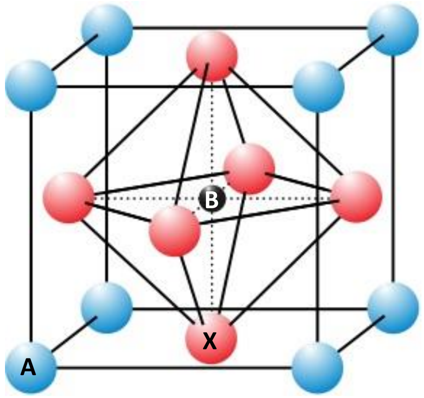




Gunnlaugsson and Masenda, J. Phys. Chem. Solids, 129 (2019).151

Peak	δ (mm/s)	ΔE_Q (mm/s)	Charge state
S1	-0.09	-	?
D1	0.61	2.14	?
D2	0.51	0.43	?
D3	0.77	0.95	Fe^{2+}

Perovskite Samples: Wish-List – Fraunhofer ISE



$CH_3NH_3^+$, $CH(NH_2)_2^+$,

Organic

Cl^-, Br^-, or I^-

Halide

ABX_3

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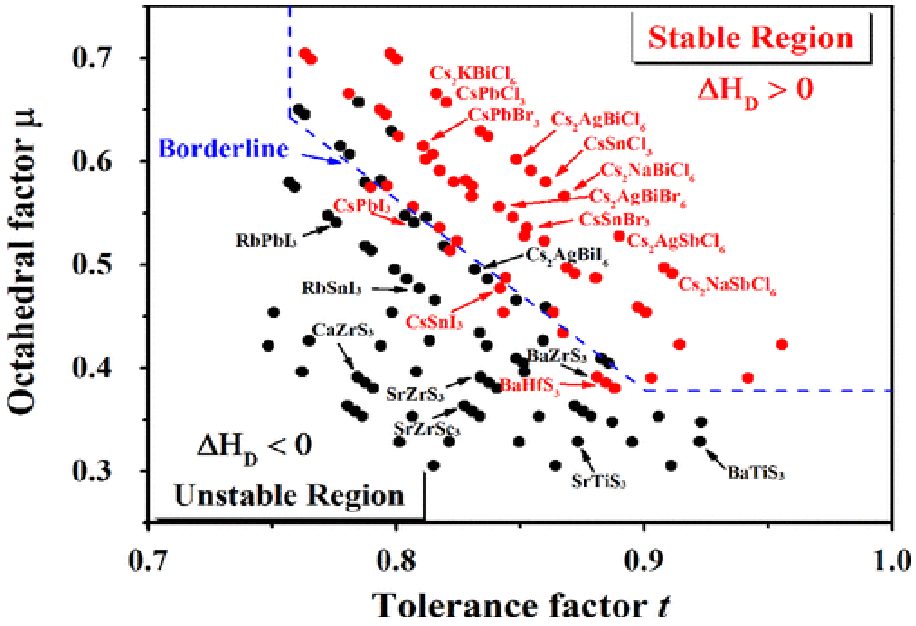
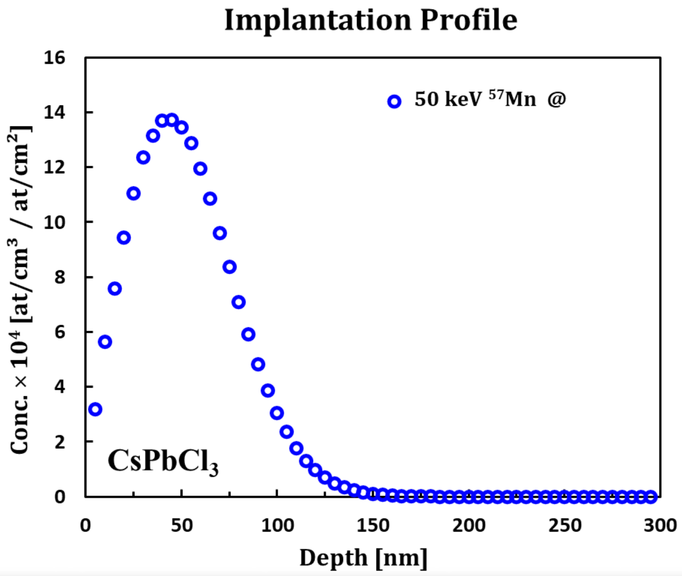
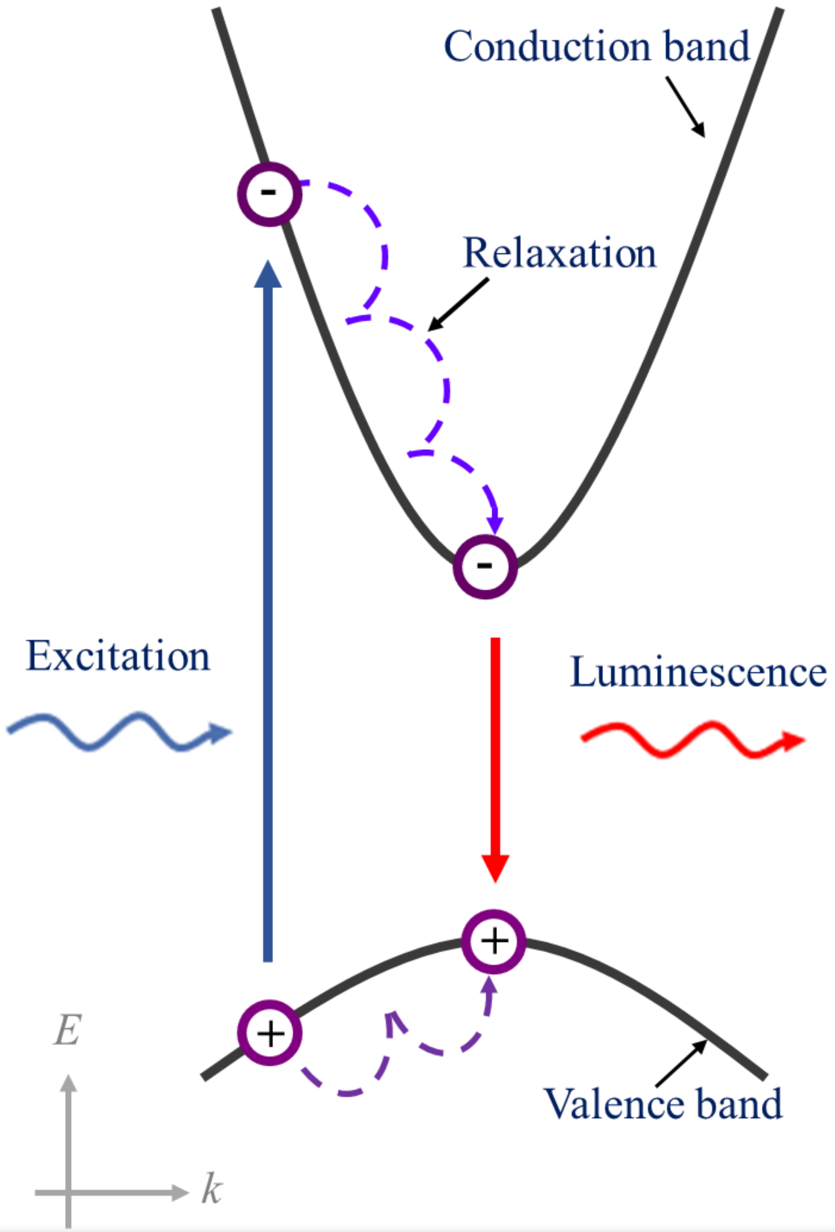


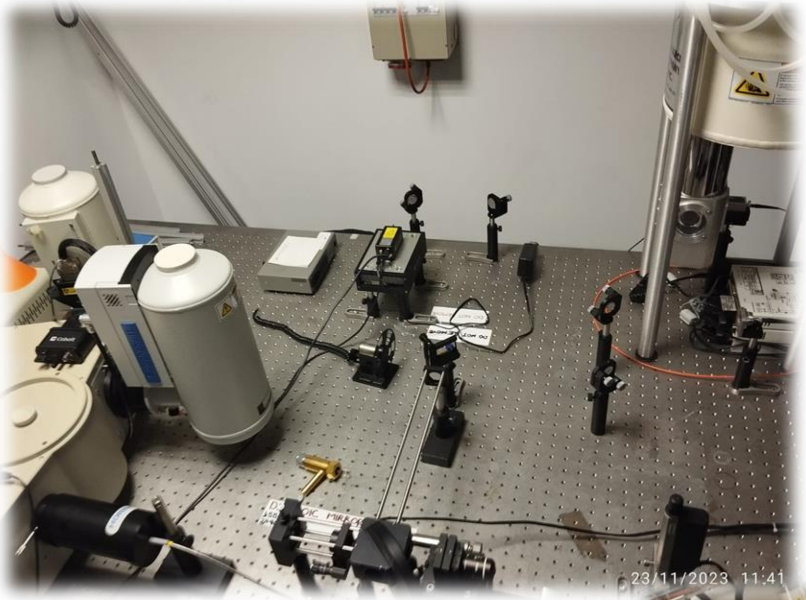
J. Am. Chem. Soc. 2017, 139, 42, 14905-14908



$AB(X_xX'_{1-x})_3$	▪ where X or X′: Cl, Br, and I for $x = 0$, 0.3, 0.5, 0.7, and 1. ▪ starting with A:Cs and B: Pb, Sn or Ge.
$AB_xB'_{1-x}X_3$	▪ where B: Pb and B′: Sn for $x = 0.3$, 0.5 and 0.7. ▪ starting with A:Cs and X: Cl, Br or I.
$A_xA'_{1-x}BX_3$	▪ where A:Cs, Br and A′: FA, MA for $x = 0.3$, 0.5 and 0.7. ▪ starting with B:Pb or Sn and X: Cl, Br or I.

Photoluminescence @ ISOLDE



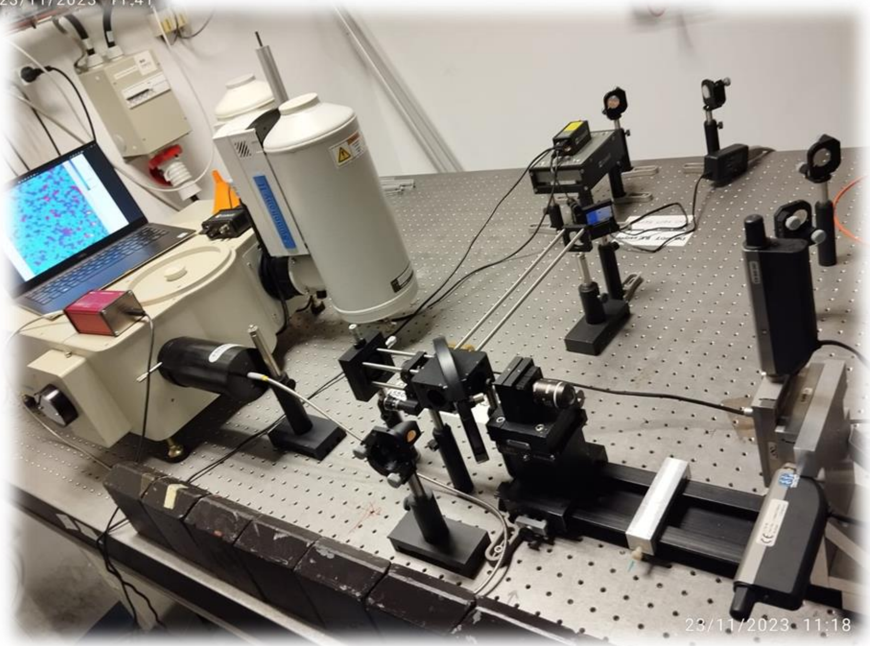


Cryostat
- Janis SHI-950

Excitation sources
- HeCd, 325 nm, 50 mW,
- 450 nm 90 mW,
- Compact 405 nm, 4.50 mW.

Spectrometer
- Horiba iHr500

Detectors
- Horiba CCD3000
- Horiba Symphony II



Planned Experiments

Emission Mössbauer Spectroscopy

[M1+2] Temperature series: 100 – 400 K ($^{57}Mn^*$ and $^{119}In^*$)

- ✓ Extract hyperfine parameters + temperature dependence
- ✓ Annealing of implantation damage, defects and their stability

[M3] eMS with laser excitation – ($^{57}Mn^*$ and $^{119}In^*$)

- ✓ Influence of excitation energy and power on hyperfine interactions

Radiotracer Photoluminescence

[P1] Temperature series: 10 K – 300 K ($^{56}Mn^*$ and $^{119}Sb^*$)

- ✓ Extract peak energies and spectral linewidths

[P2] Power series measurements: 10 K and 300 K – ($^{56}Mn^*$ and $^{119}Sb^*$)

- ✓ Annealing of implantation damage, In-defects and their stability

[P3] Circularly polarized (right- or left-handed)– ($^{56}Mn^*$ and $^{119}Sb^*$)

- ✓ Allows for a wide range of external sample condition

Beam-Time Plans

eMS measurements on inorganic perovskites and alloys; on the X and B sites.

Offline PL on pre-implanted perovskite samples → fluence-dependence before using radioisotopes → PLQE

Radiotracer-PL on eMS-measured samples: Implant + measure offline

eMS and rPL on complex systems

Complimentary: [A] Laboratory- and synchrotron-based techniques

X-ray diffractions (XRD) and scanning electron microscopy, X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), X-ray Absorption Near Edge Spectroscopy (XANES), X-ray absorption fine-structure (XAFS), coherent diffraction imaging (CDI), Bragg CDI and ptychography.

[B]Theory

DFT Calculations/ Simulations

Requested Isotopes and Shifts

Experiment	Isotope	Time (hrs)	Rationale
M1, M3	$^{57}Mn*$	60	**~ 15-20 samples alloyed on different sites, 3 hrs/sample.**
M2,	$^{119}In*$	20	**a few selected alloys (~ 12 samples), 2 hrs/sample.**
P1-P3	$^{56}Mn*$	8	**~ 15-20 samples, collections at SSP and measure offline**
P1-P3	$^{119}Sb*$	10	**~ 15-20 samples, collections at SSP and measure offline**
Calibration	$^{57}Mn*$, $^{119}In*$,	19	**~ 20 % based on past experience**
Contingency	**$^{57}Mn*$, $^{119}In*$,**	**19**	**~ 20 % for exploring new phenomena in detail**

Isotope	$T_{1/2}$	Intensity (Ions/μC)	Activity (MBq)	eMS	PL	Shifts requested
$^{56}Mn^*$	2.6 h	4×10^8	29.6	N	Y	**1.5**
$^{57}Mn^*$	85.4 s	$(2-3) \times 10^8$	online	Y	N	**8**
$^{119}In^*$	2.4 min	$(2-3) \times 10^8$	online	Y	N	**4**
$^{119}Sb^*$	38.2 h	5×10^7	2.50	N	Y	**1.5**
					Total	**15**

- ❑ Identify the lattice sites, defects and annealing behaviours → stability,
- ❑ Establish charge (and spin) states,
- ❑ Ascertain the effect on excitation energy and power of hyperfine interactions,
- ❑ Determine the nature of the energy scale of the disorder potential…

.. gain a deep understanding of the physics that underpins the peculiar functionalities of perovskites…. and their defect intolerance…

…new perspectives for the next generation of photovoltaic, optoelectronic, spintronic devices…

Durban
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- K. Bharuth-Ram

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- Y. Gupta

Geneva
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- J. Schell

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Milan
- R. Mantovan

Oxford
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Reykjavík
- H. P. Gunnlaugsson

Tehran
- A. Mokhles Gerami

Thank You!!!