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$BaZrS_3$ Chalcogenide Perovskite Thin Film Grown by Reactive Sputtering

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Outline

- Motivation

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Outline

- Motivation
- Co-sputtering

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- Co-sputtering
- Sequential sputtering

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Outline

- Motivation
- Co-sputtering
- Sequential sputtering
- Conclusions

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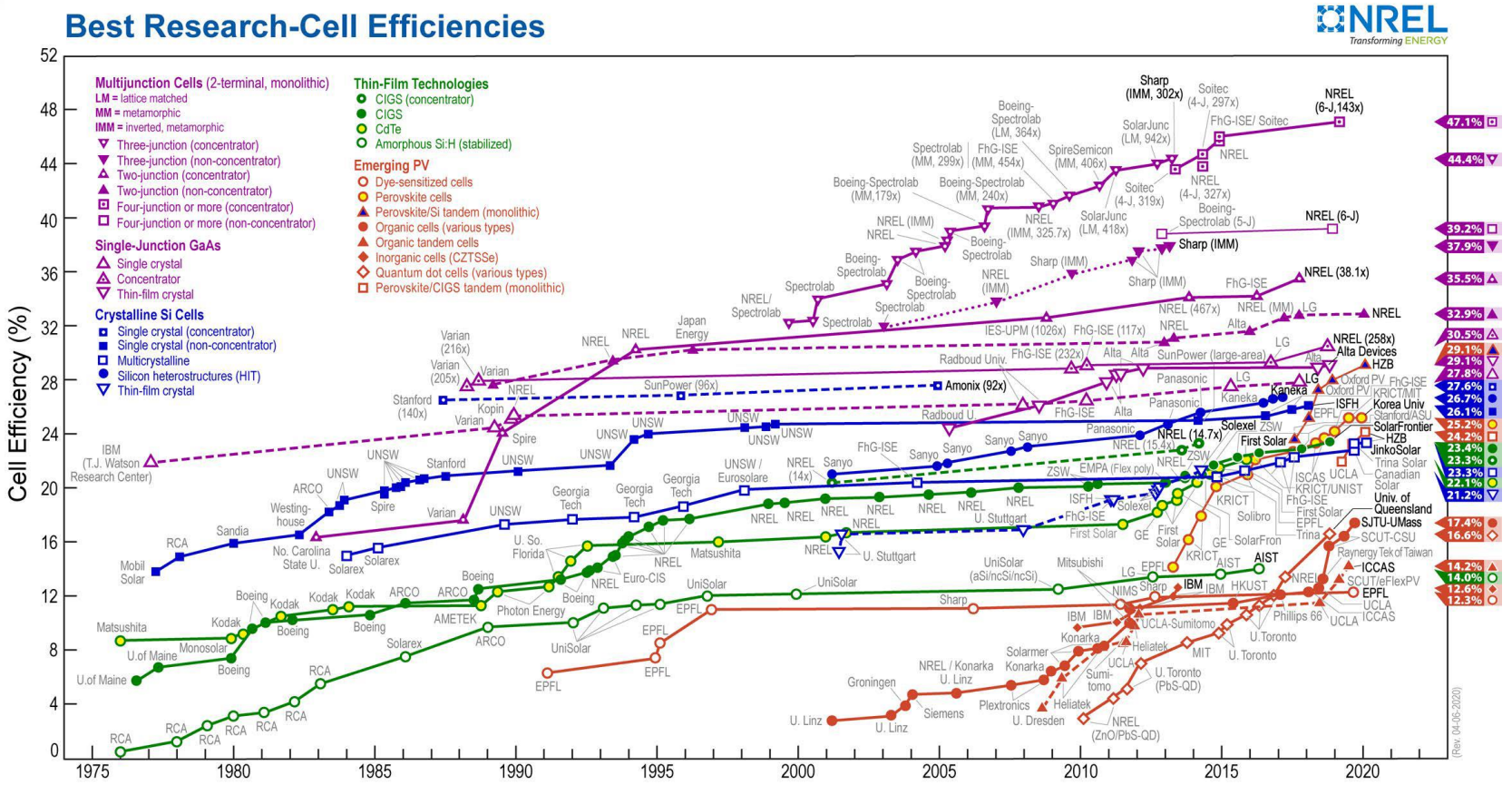
Motivation



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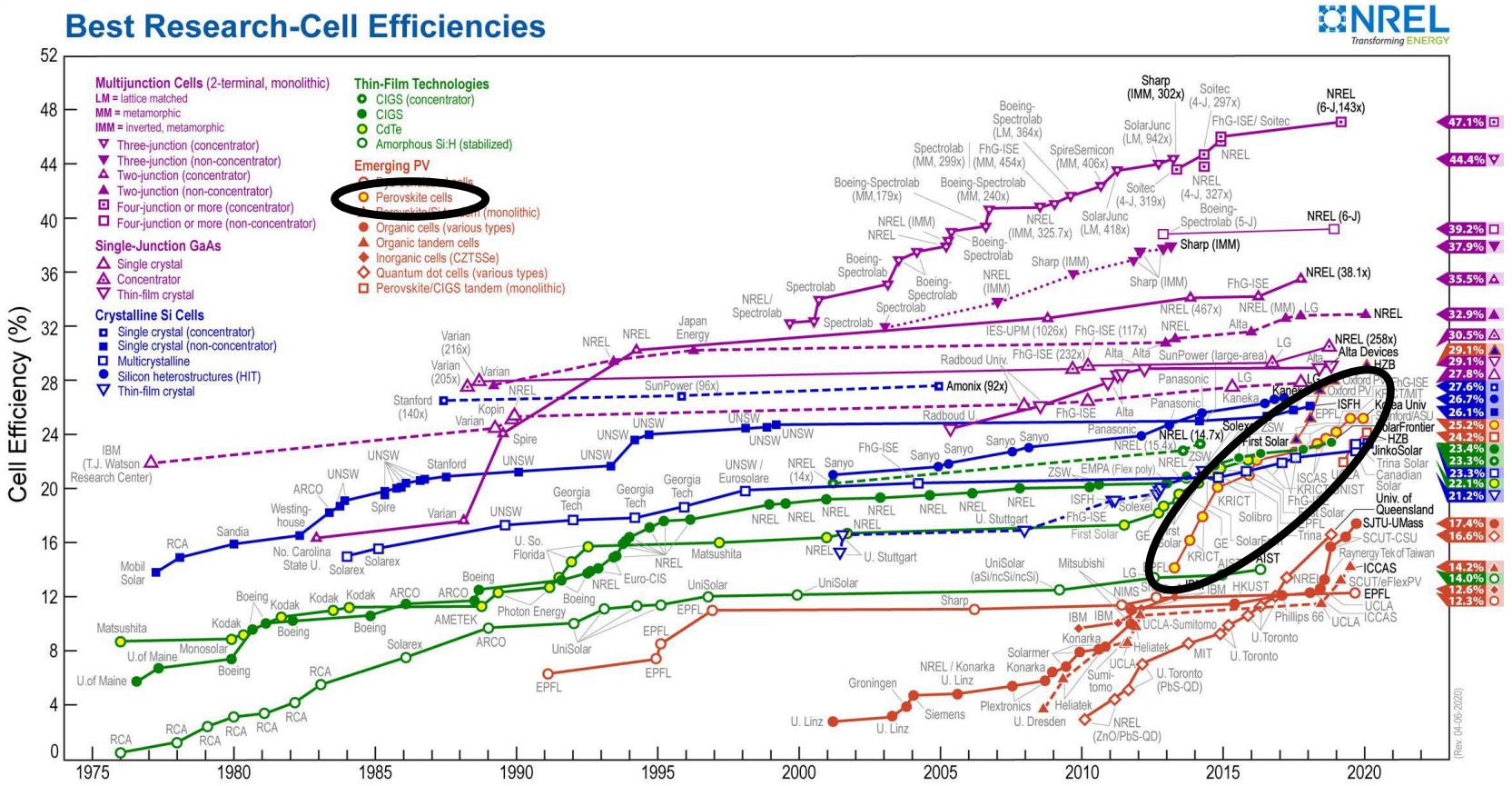
Motivation



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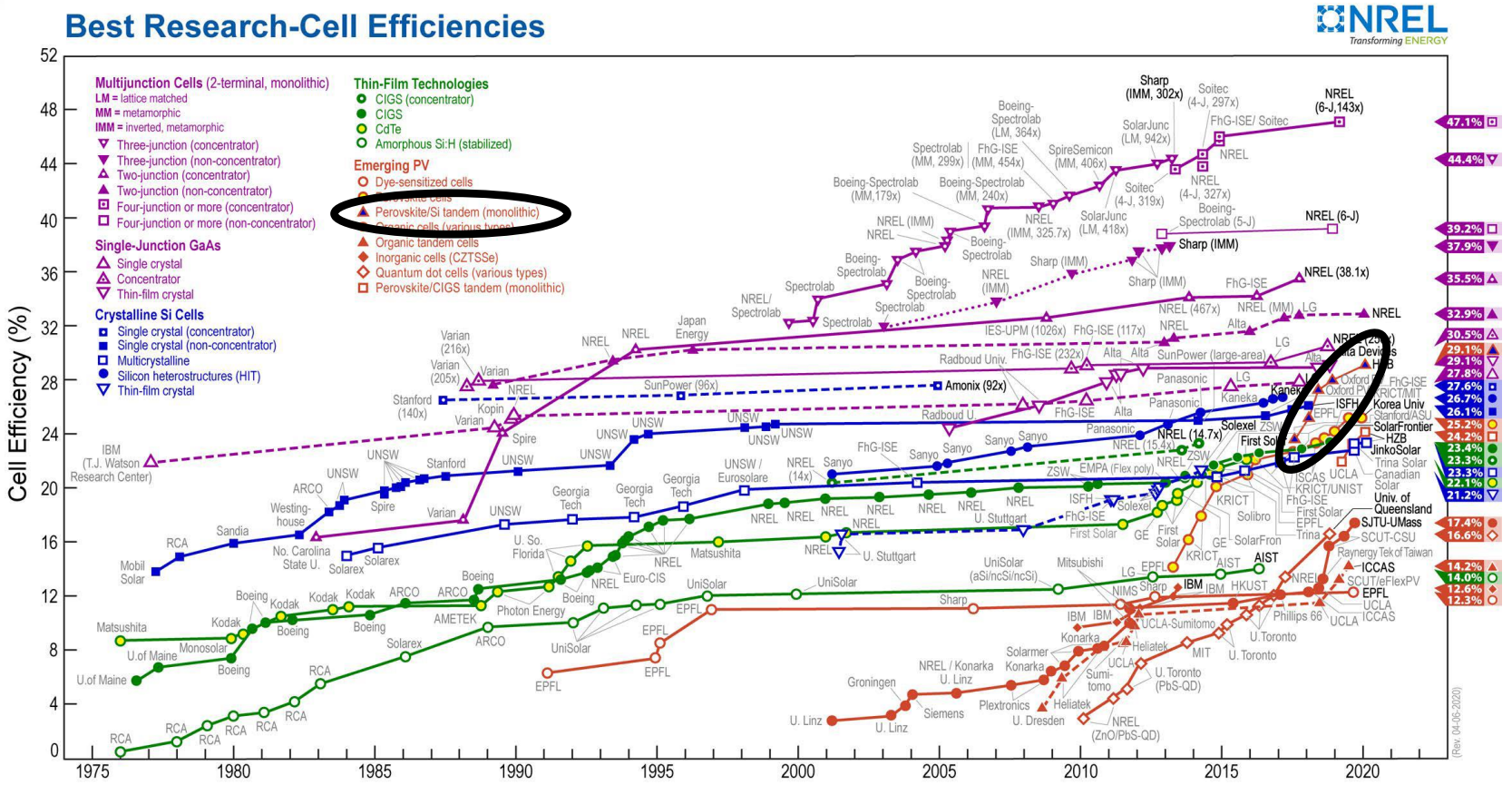
Motivation



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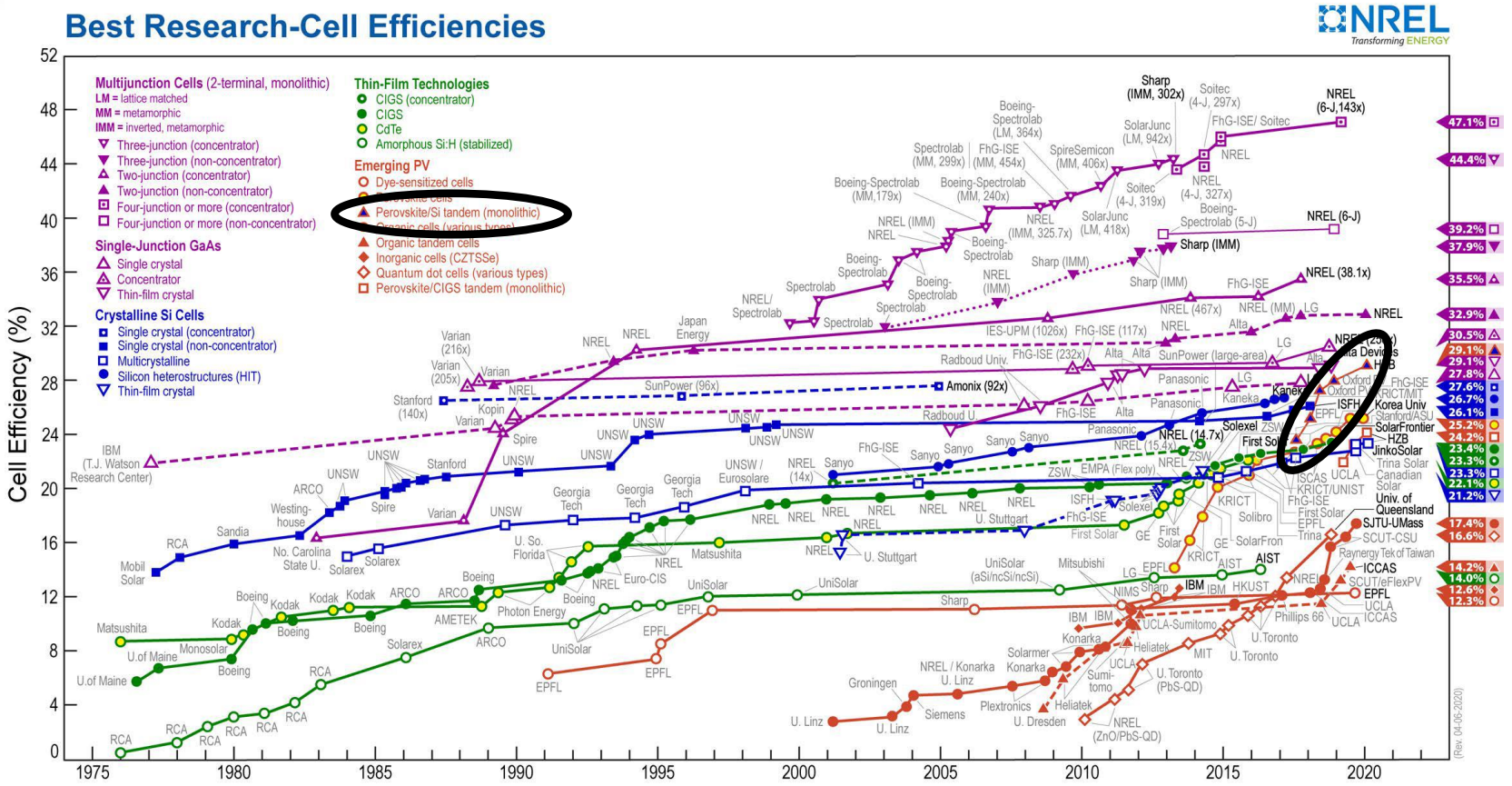
Motivation



<u>Concerns:</u> toxicity (Pb) and stability

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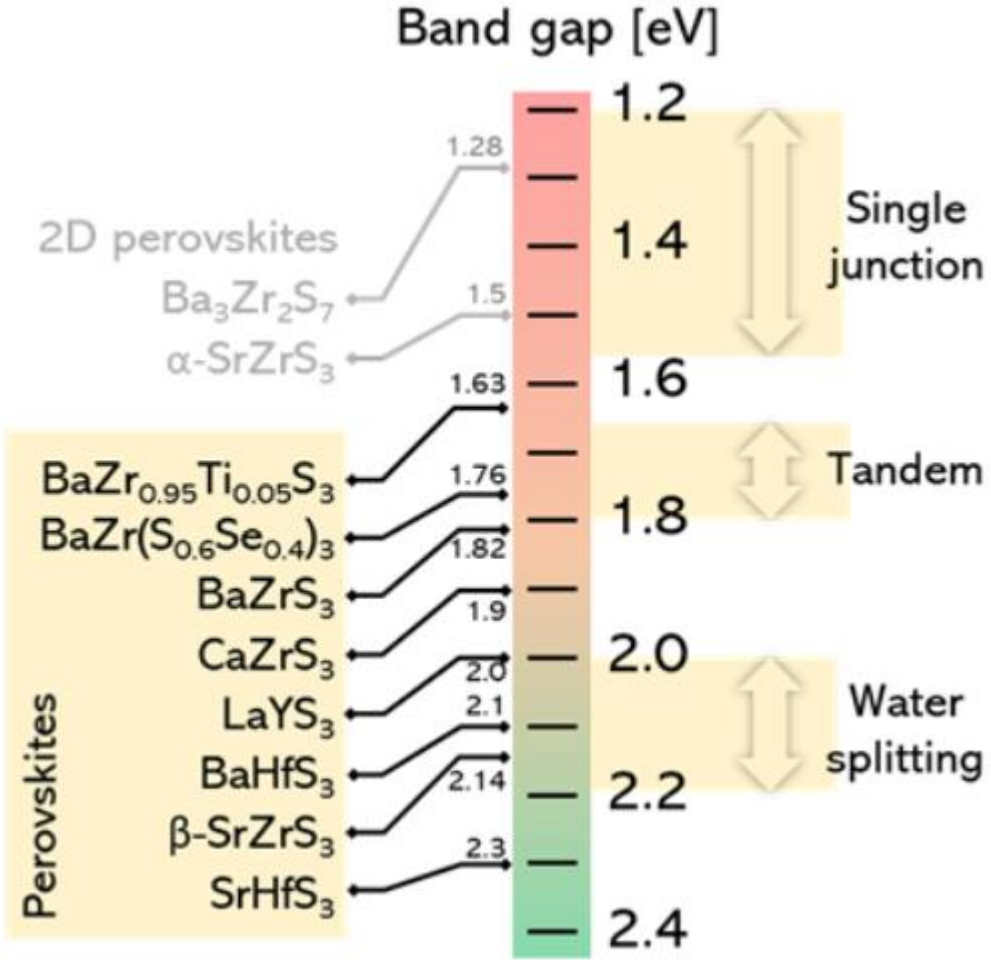
Chalcogenide Perovskites



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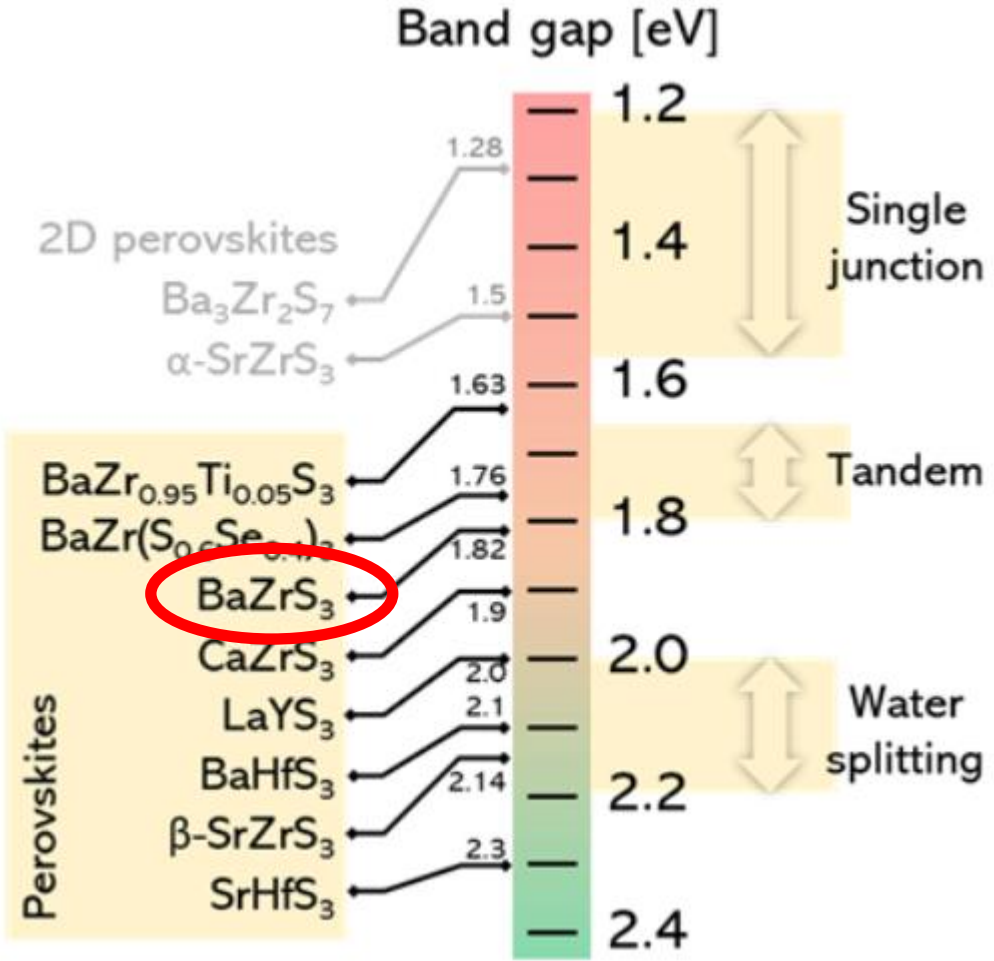
Chalcogenide Perovskites



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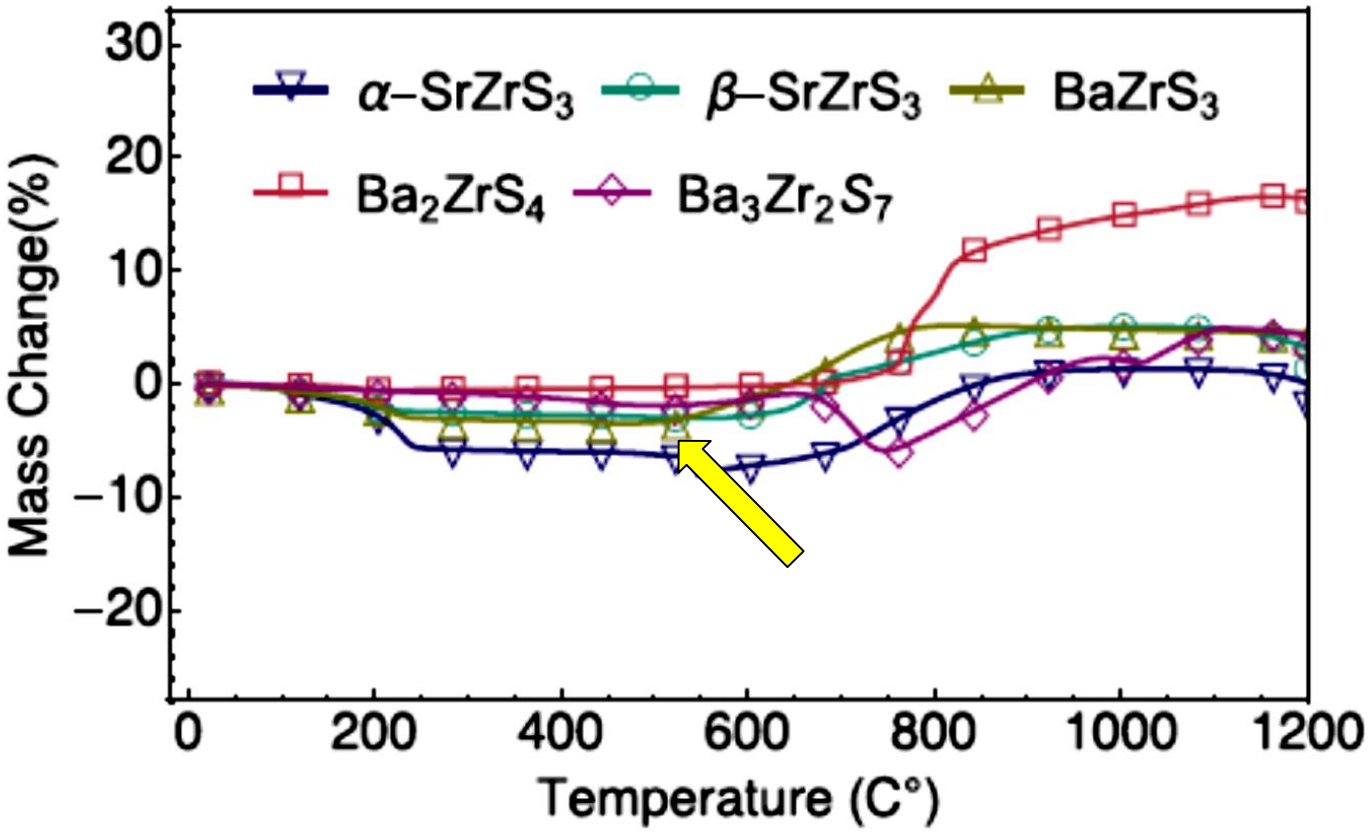
$BaZrS_3$ - Stability

Heating in air - TGA



Niu S., *J. Mater. Res.*, Vol. 33, No. 24, 2018, pp. 4135-4143

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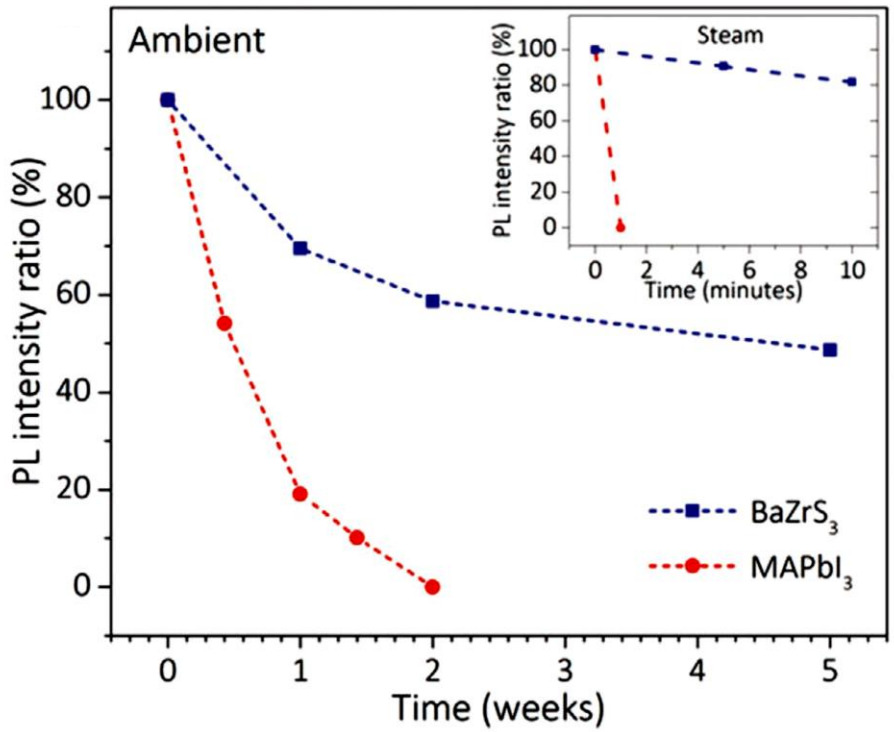
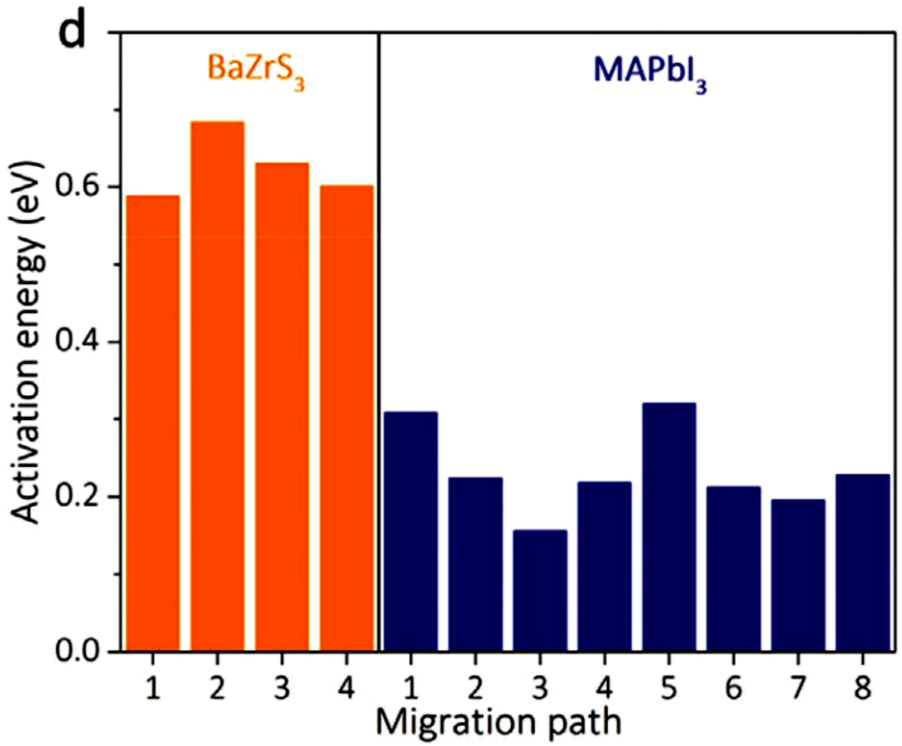
$BaZrS_3$ - Stability

High energy barrier for anion diffusion → Reason for high stability?

V_I migration rates in $MAPbI_3$ are about **seven orders of magnitude** higher than those of V_S in $BaZrS_3$





Gupta T., *Adv. Funct.* Mater. 2020, 2001387

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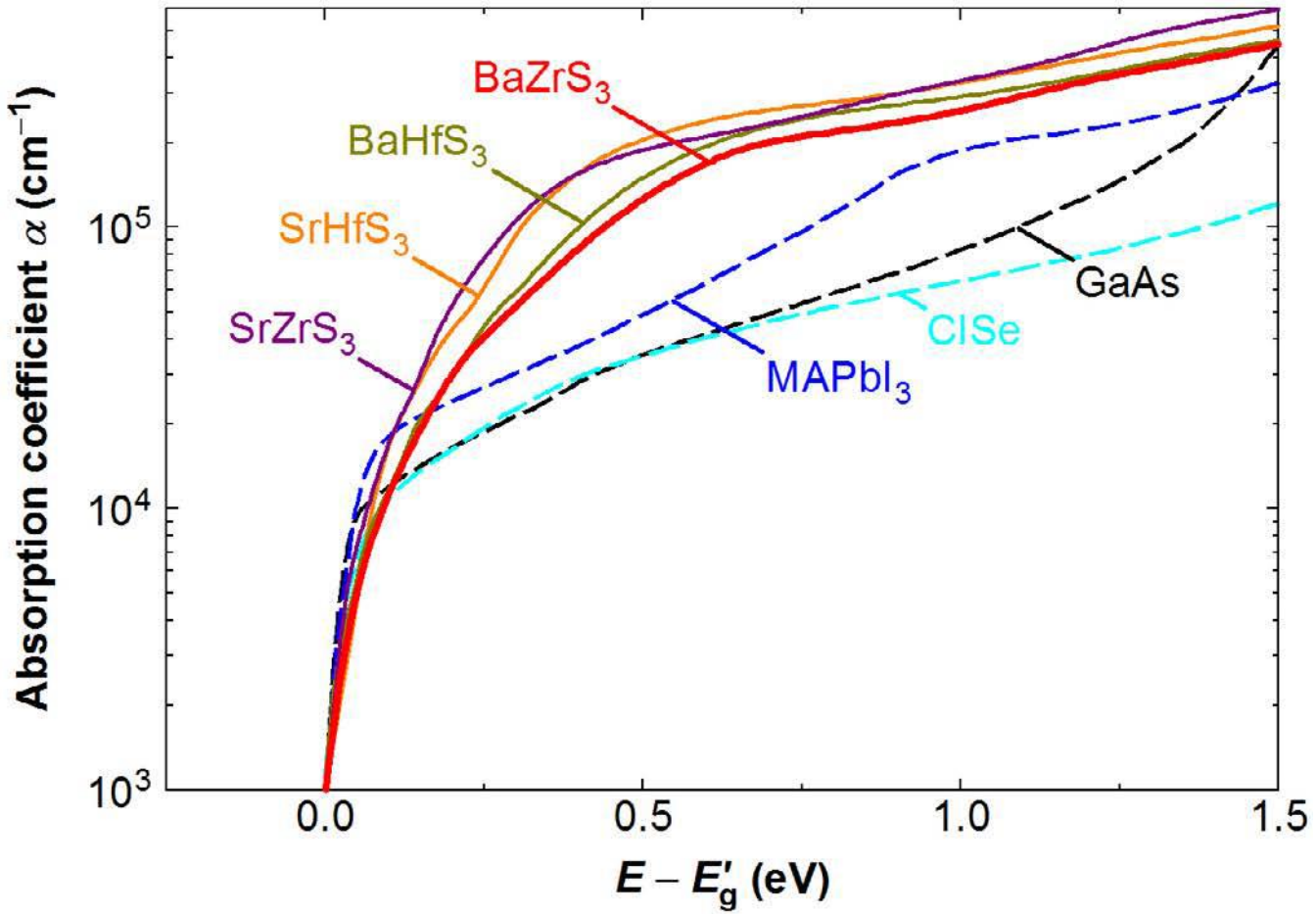
Strong Band-Edge Absorption

Nishigaki Y., *Sol.Rrl*, 1900555 (2020)



$\alpha > 10^5$ cm^{-1} near band edge

Highest among all known solar absorber layers

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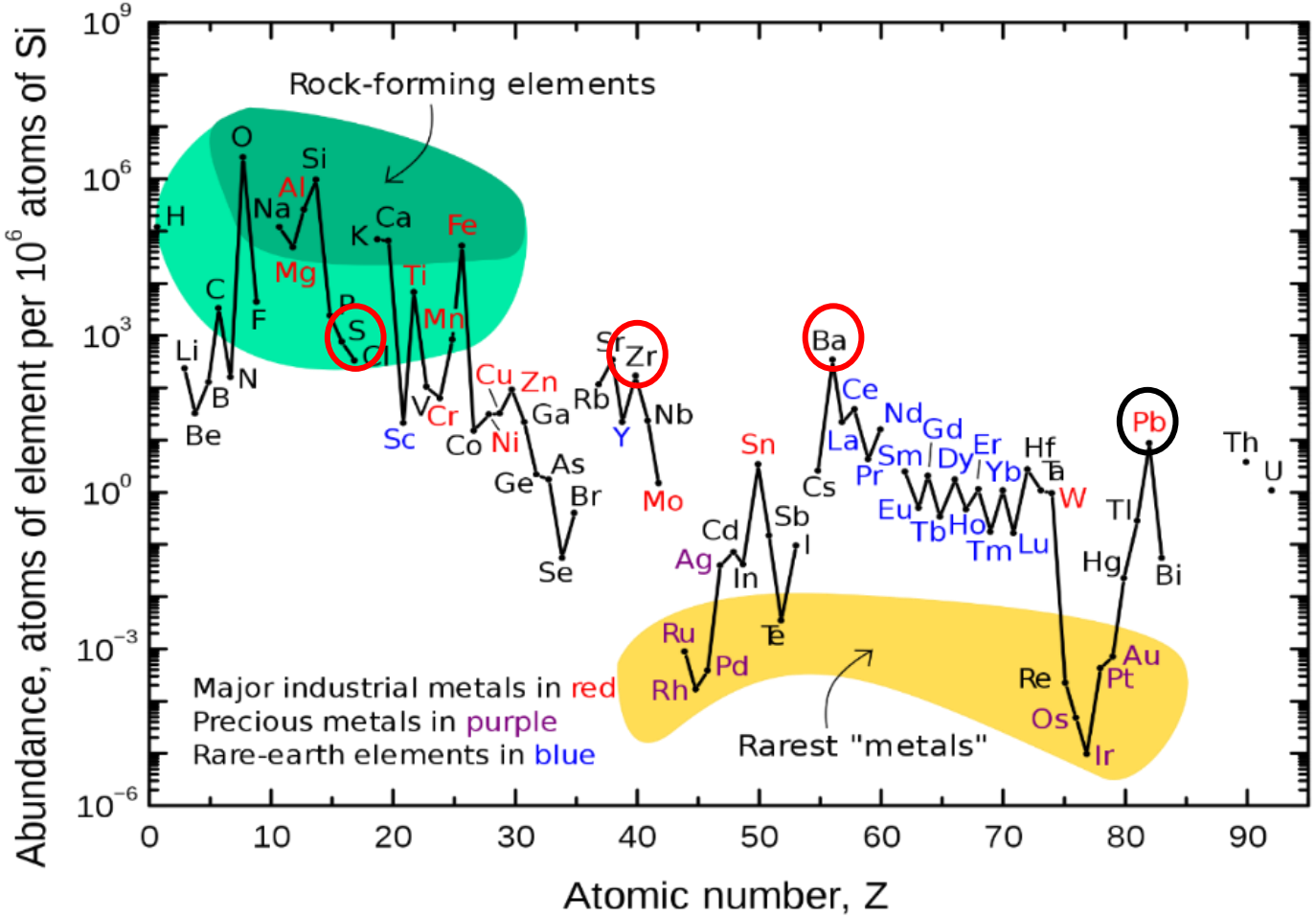
Elements abundance in Earth's crust



- Ba, Zr, S among the 18 most abundant elements
- Less toxic and more abundant than Pb

Haxel G. B., USGS Fact Sheet 087-02

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Co-Sputtering

Deposition

Heating

<u>1st step</u>
RT
BaS target
Zr target
H_2S atmosphere
Amorphous film

<u>2nd step</u>
ex-situ in RTP
60 s
N atmosphere
650 – 1000 °C
Crystalline film
200 – 400 nm

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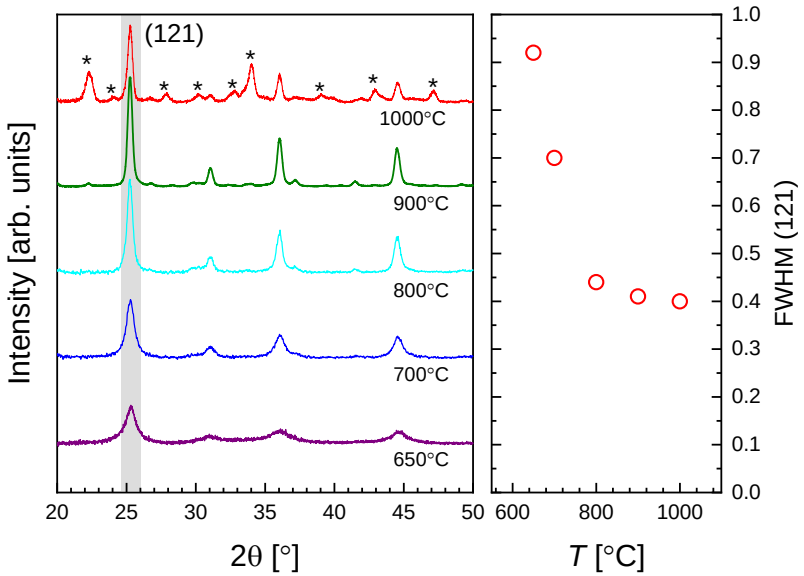
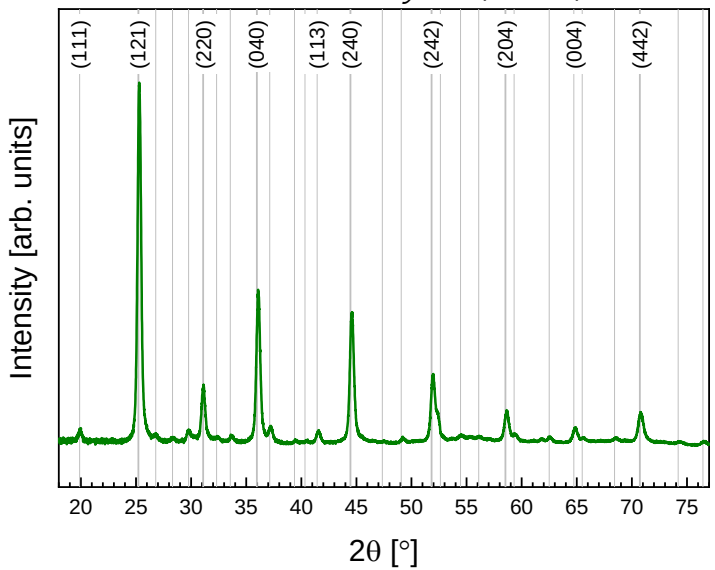
X-Ray Diffraction



Clearfield A., *Acta Cryst.* (1963), 16, 134



- XRD for each heating temperature
- Pattern quality improves with increasing temperature

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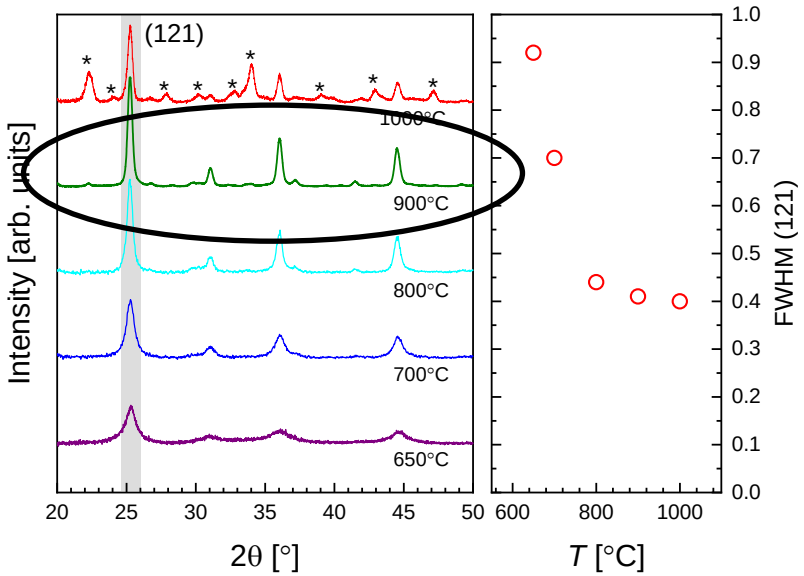
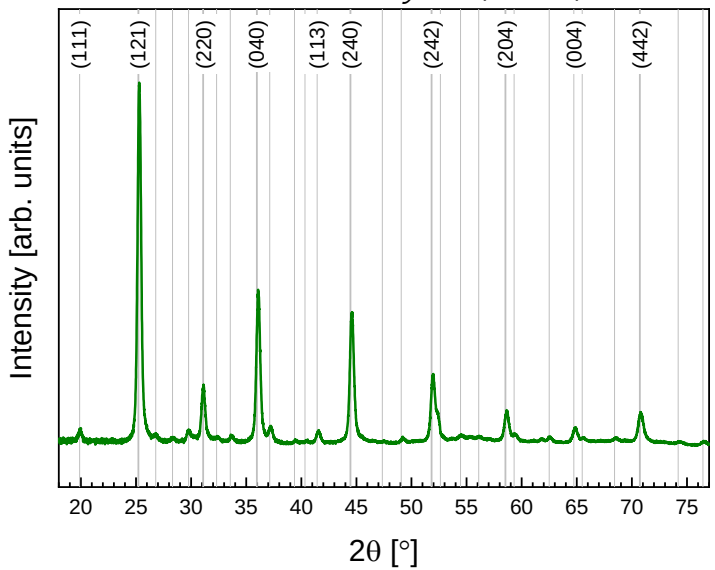
X-Ray Diffraction



Clearfield A., *Acta Cryst.* (1963), 16, 134



- Optimum temperature: 900 °C
- Perfect agreement with the reference pattern
- Dominant crystalline phase: $BaZrS_3$
- ZrO_2 in some cases

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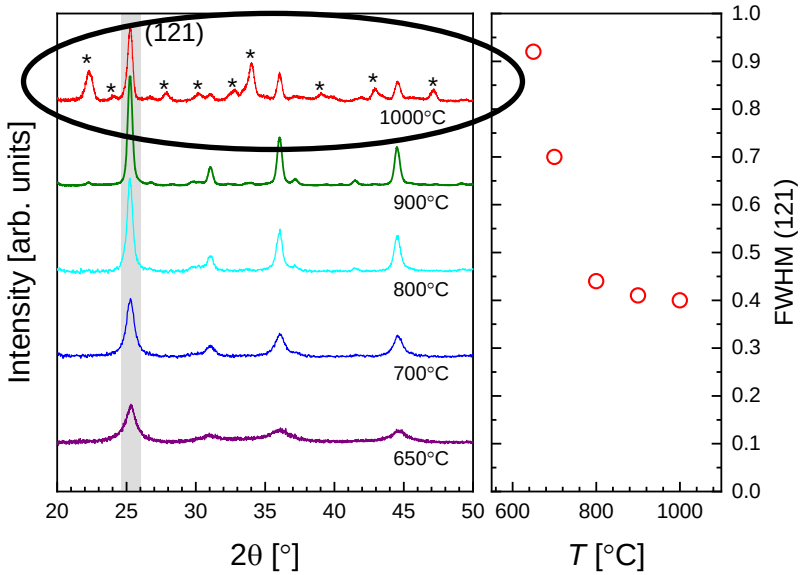
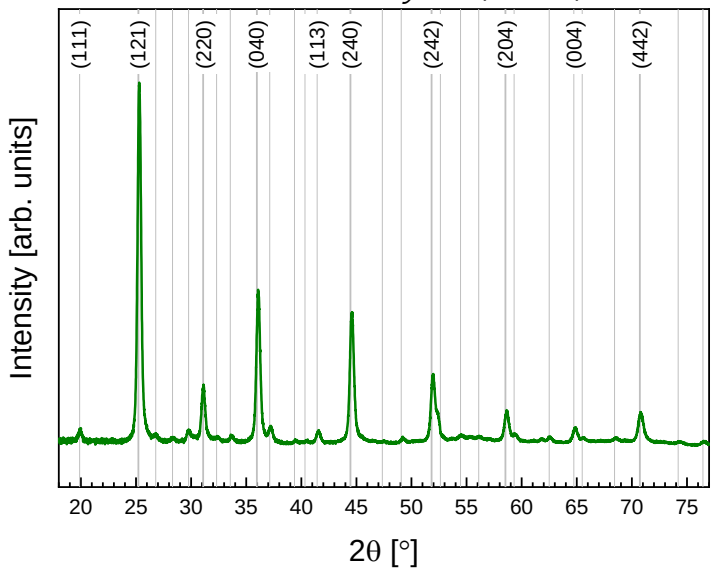
X-Ray Diffraction



Clearfield A., *Acta Cryst.* (1963), 16, 134



- Appearance of other phases at 1000 °C → Decomposition
- High thermal stability

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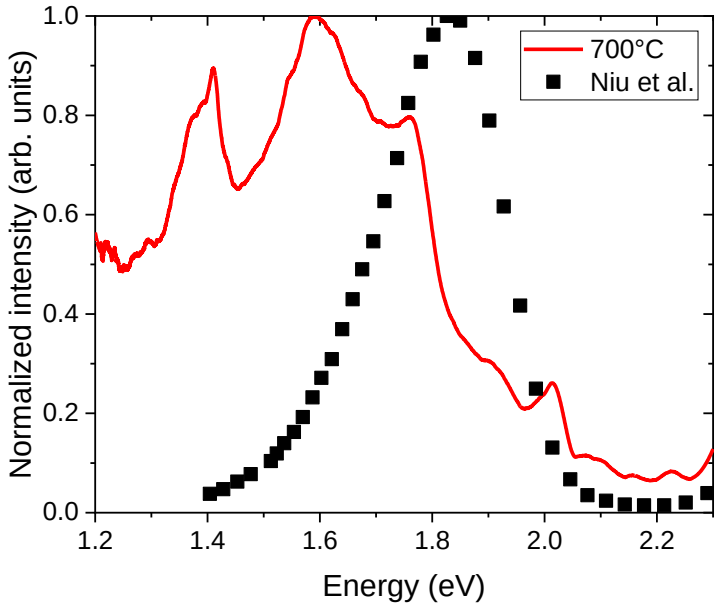
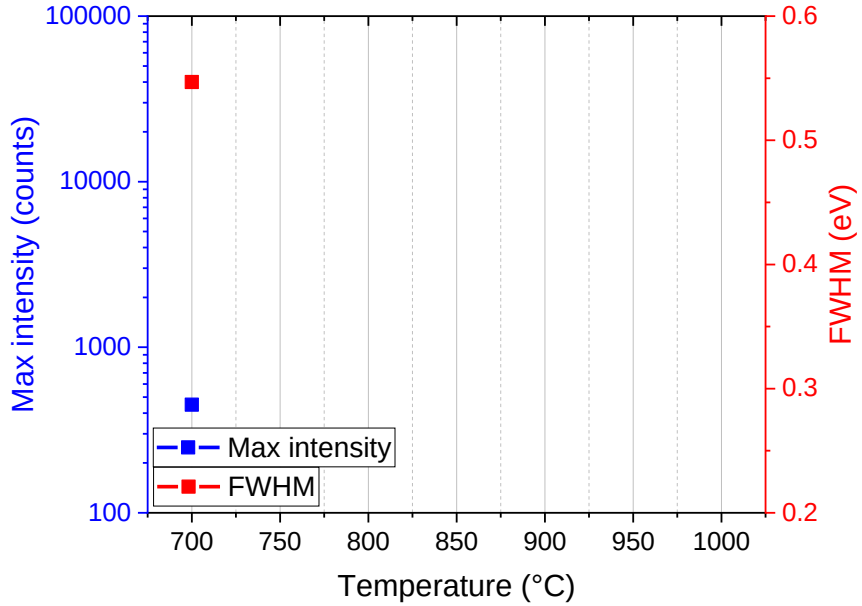
Photoluminescence

Reference from powders (60 h combustion)
Niu, S., *Adv. Mater.* 2017, *29* (9), 1604733





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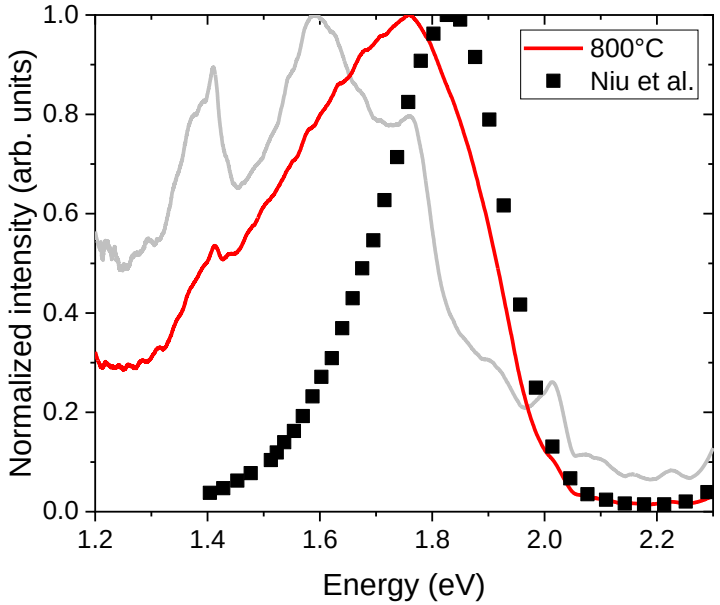

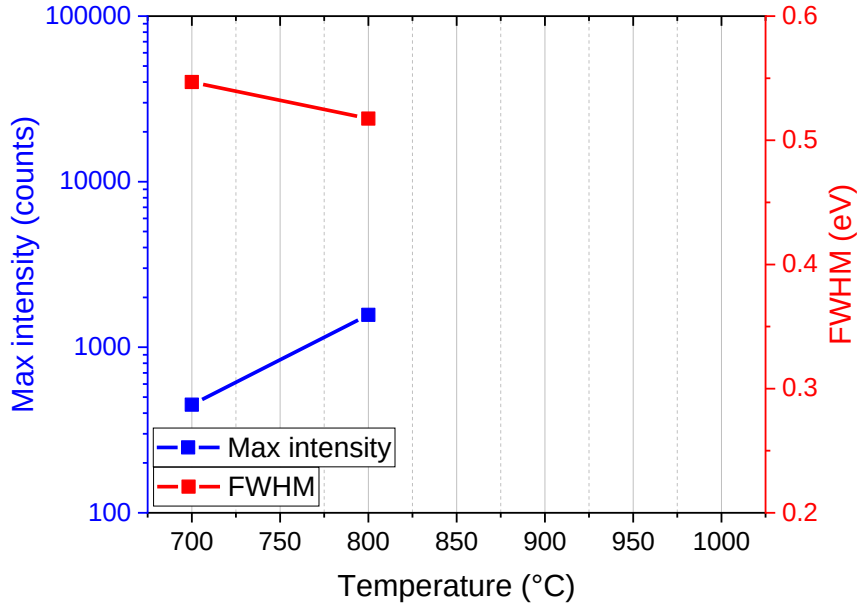

Main peak becomes narrower, higher, and moves towards higher energies

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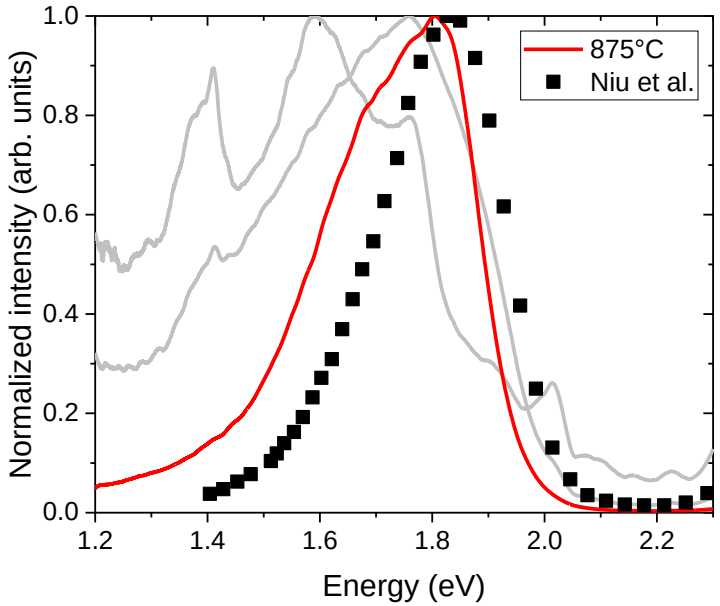
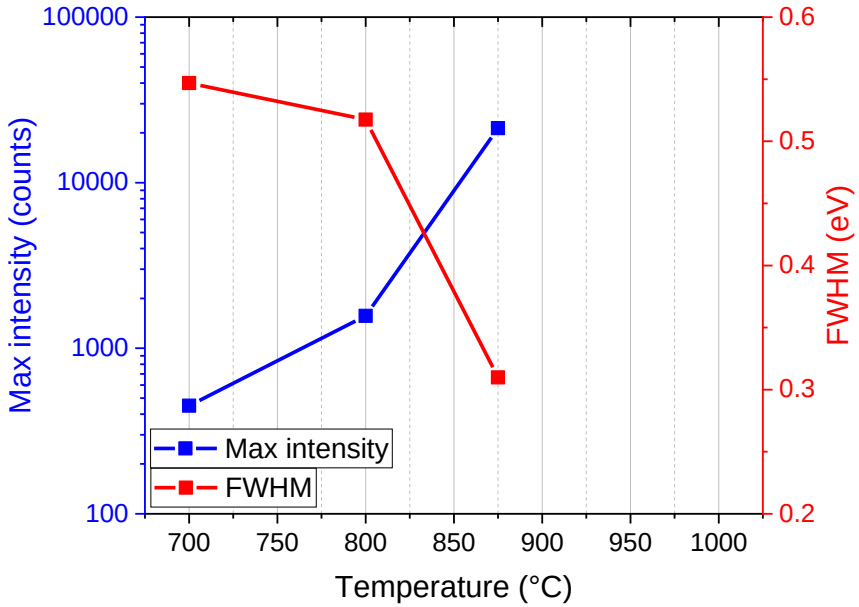
Reference from powders (60 h combustion)
Niu, S., *Adv. Mater.* 2017, *29* (9), 1604733





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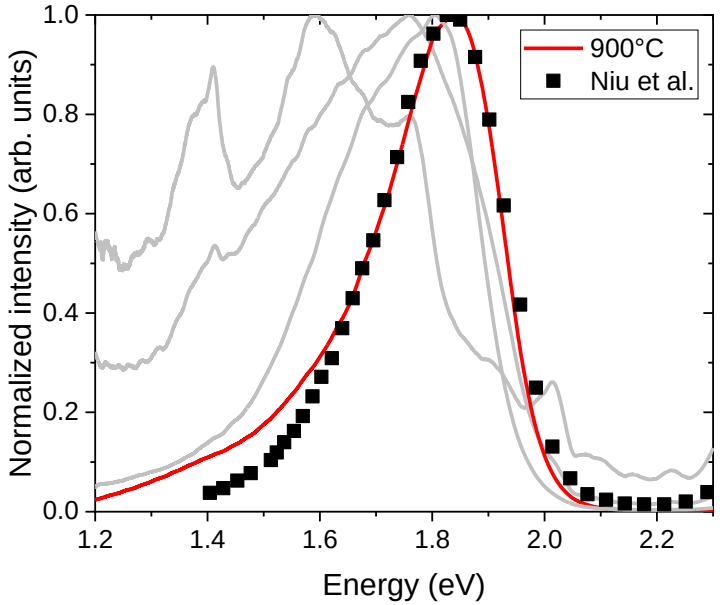

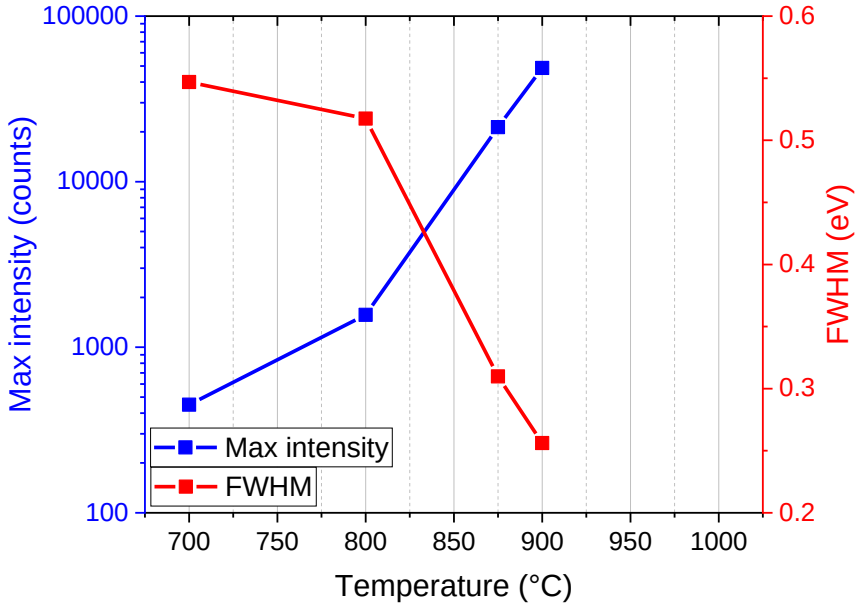

Good agreement with literature at 900 °C

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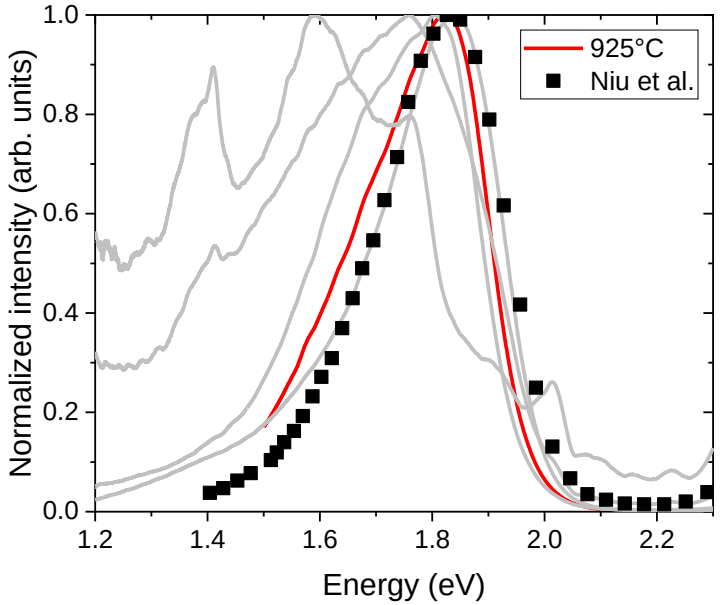
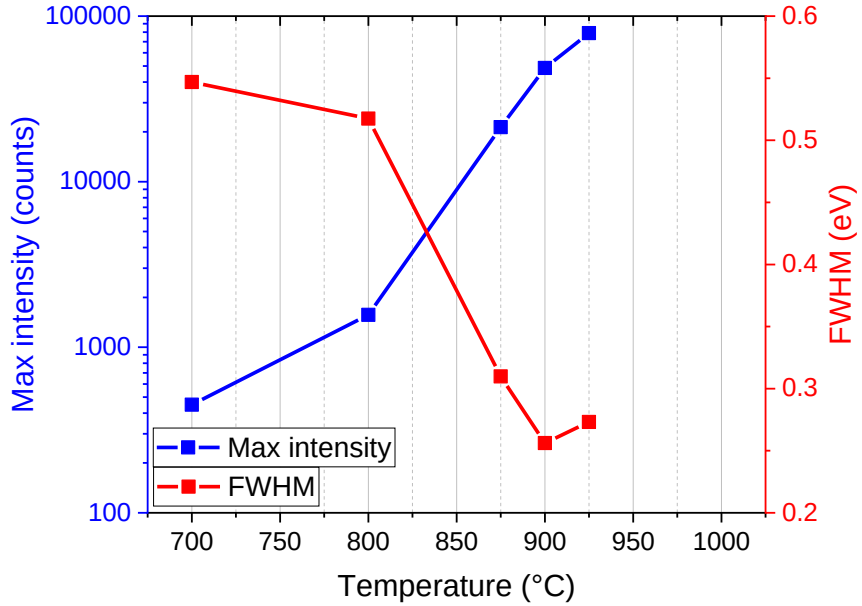
Niu, S., *Adv. Mater.* 2017, *29* (9), 1604733





Reversed trend above 900 °C

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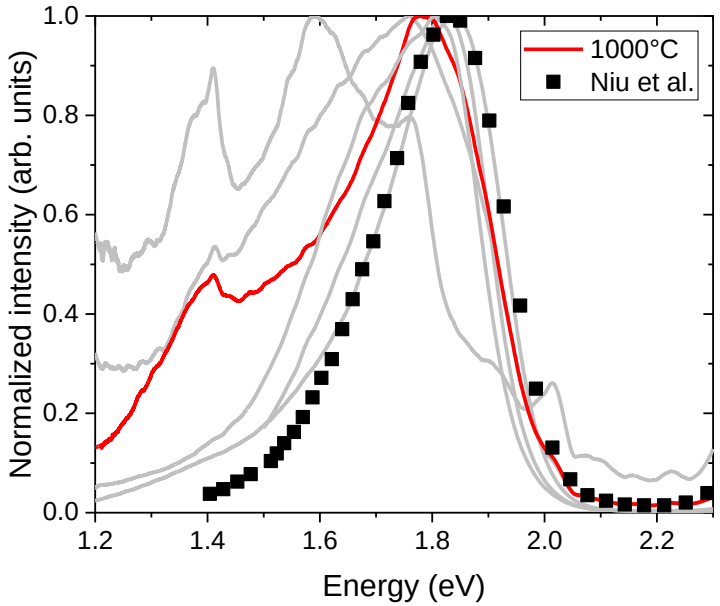
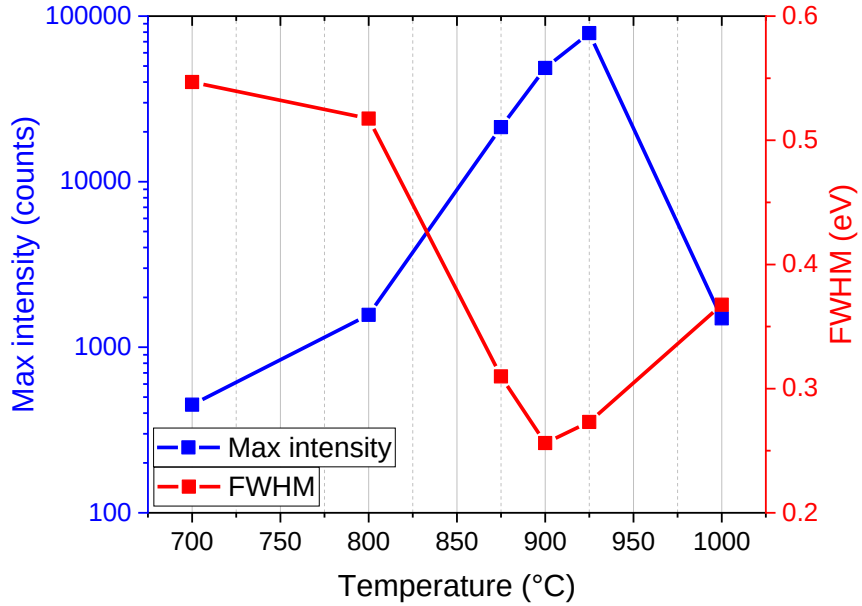
Photoluminescence

Reference from powders (60 h combustion)
Niu, S., *Adv. Mater.* 2017, *29* (9), 1604733





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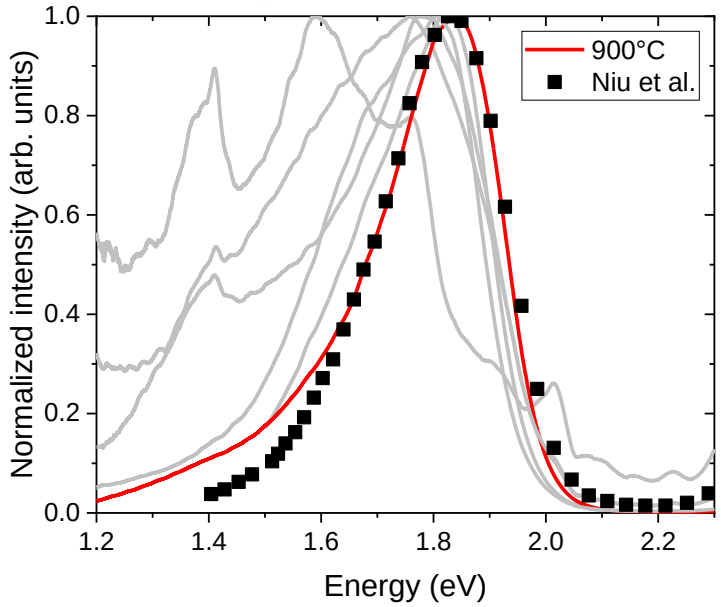
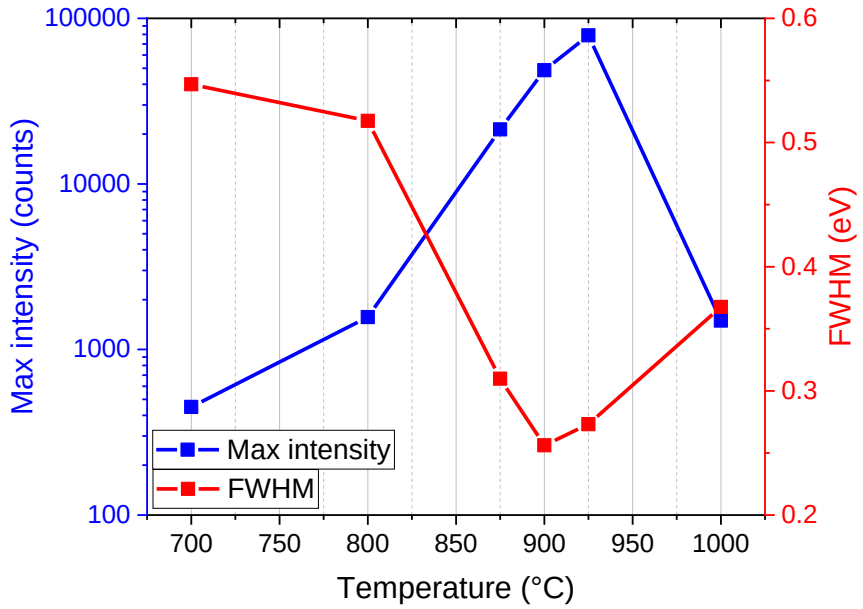
Photoluminescence



- Best temperature in terms of PL: 900 °C (as for XRD)
- Bandgap: ~ 1.84 eV → Tandem cells
- Quality comparable with the reference from powders (60 h combustion)



Comparotto C. et al.,
ACS Appl. Energy Mater. 2020, 3, 3, 2762–2770

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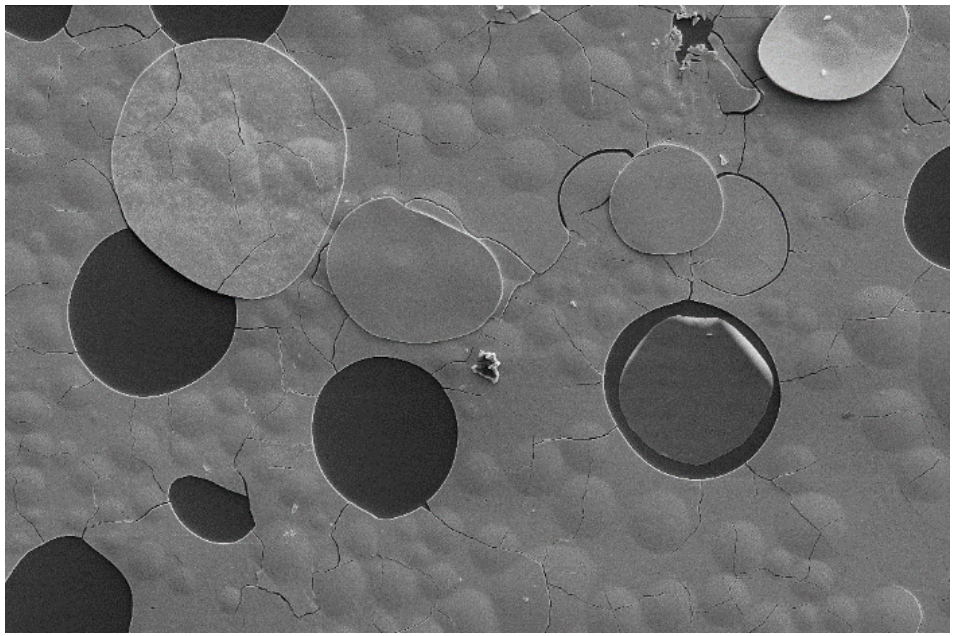
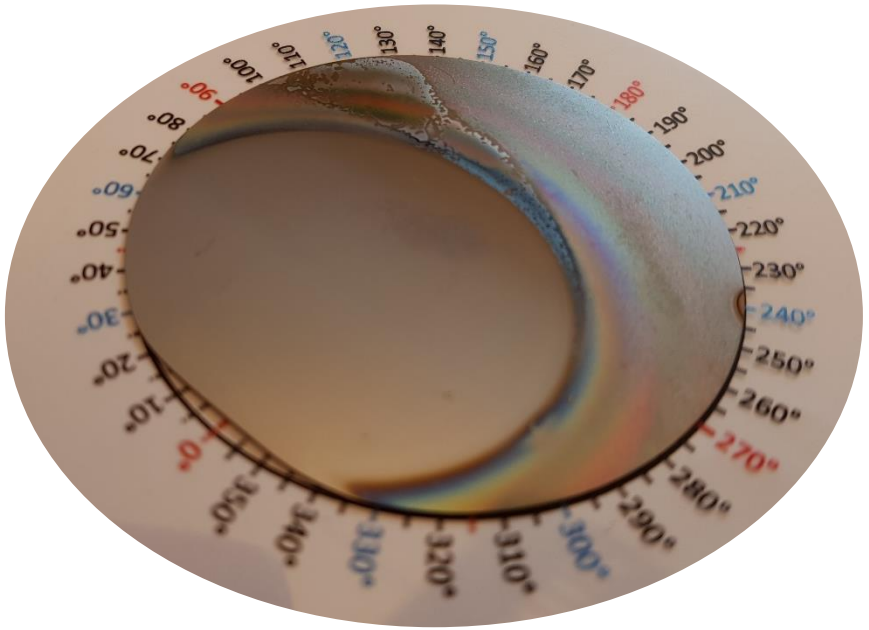
Morphology

Microscopic: Stress, Adhesion



Macroscopic: Resputtering



- Limited range of flows, power, and pressure in current sputtering system
- Explore new sputtering route

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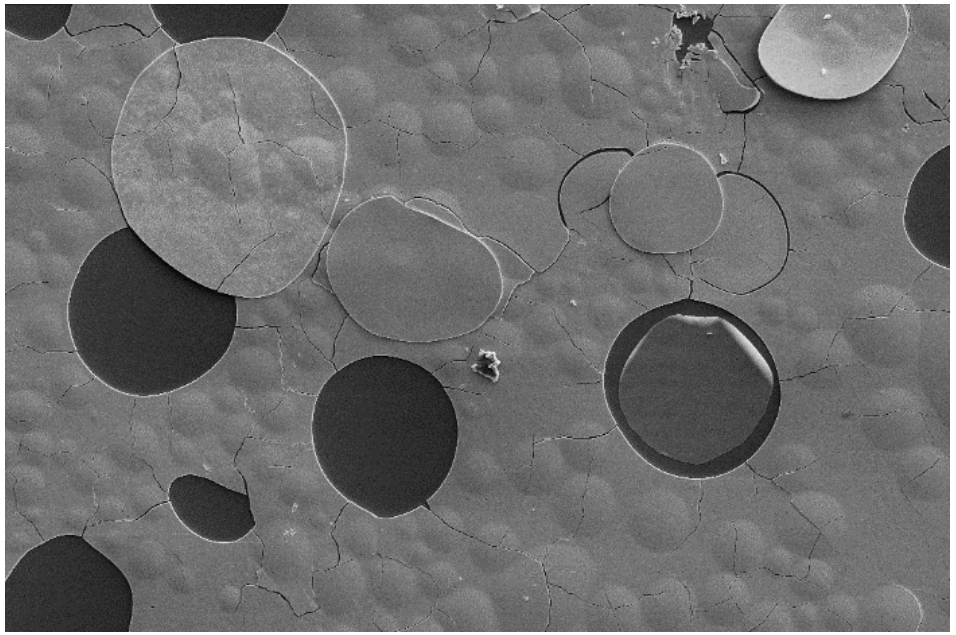
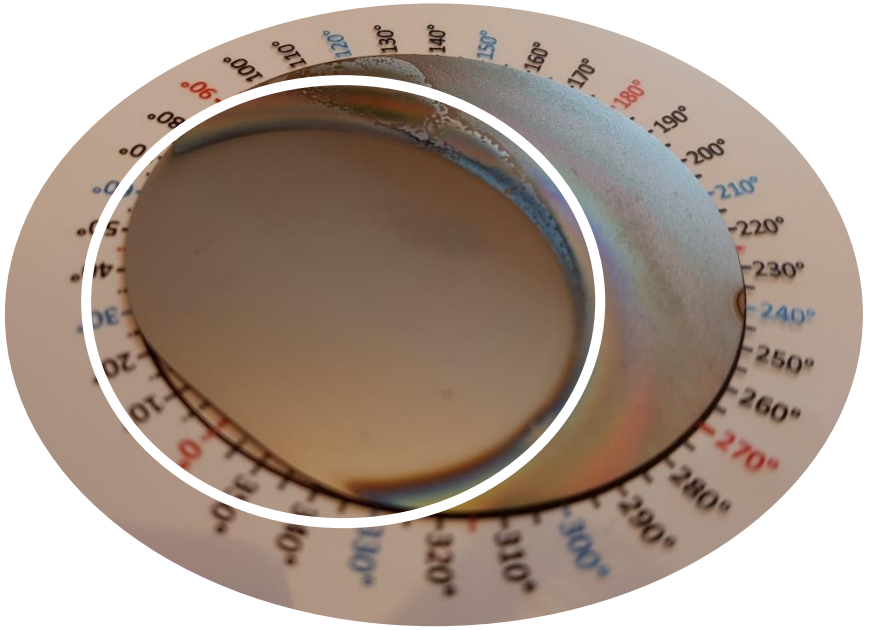
Morphology

Microscopic: Stress, Adhesion



Macroscopic: Resputtering



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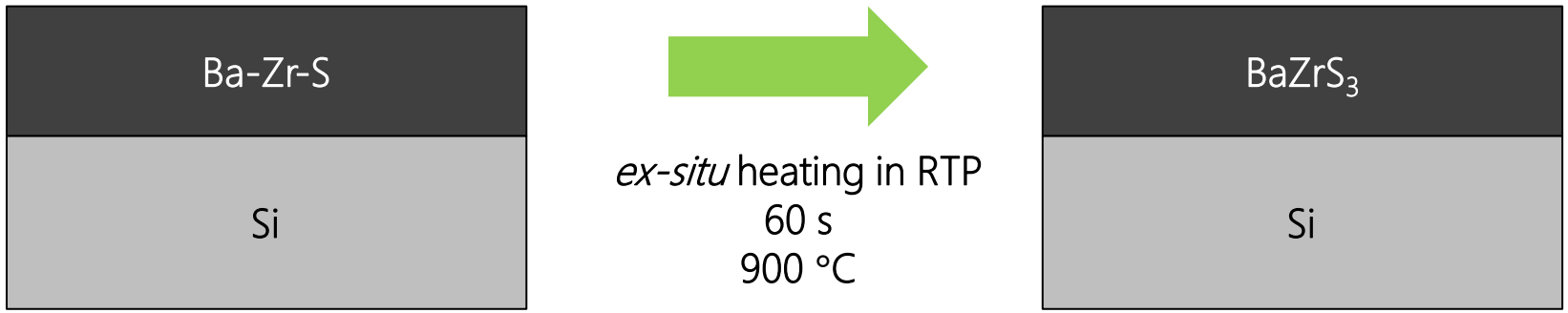
Co-Sputtering

Co-sputtering



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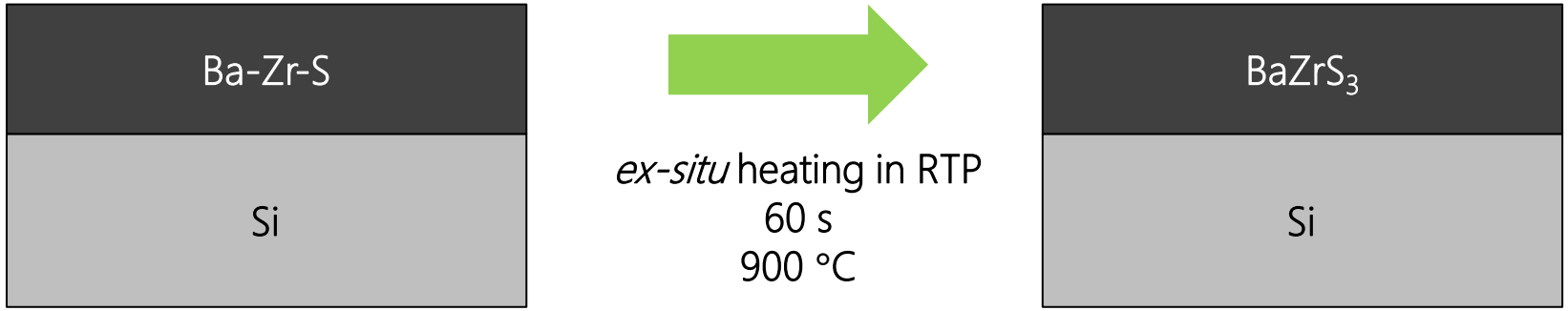
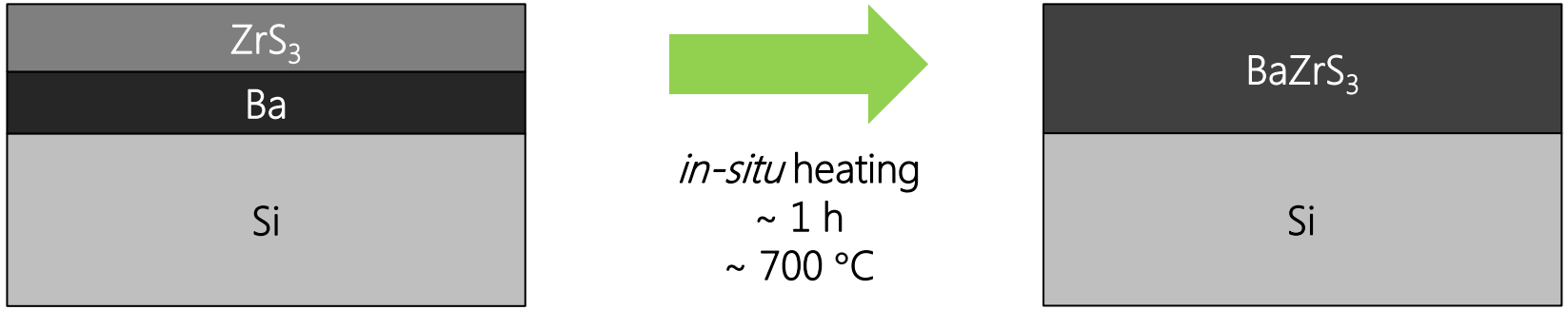
Sequential sputtering

Co-sputtering



Sequential sputtering



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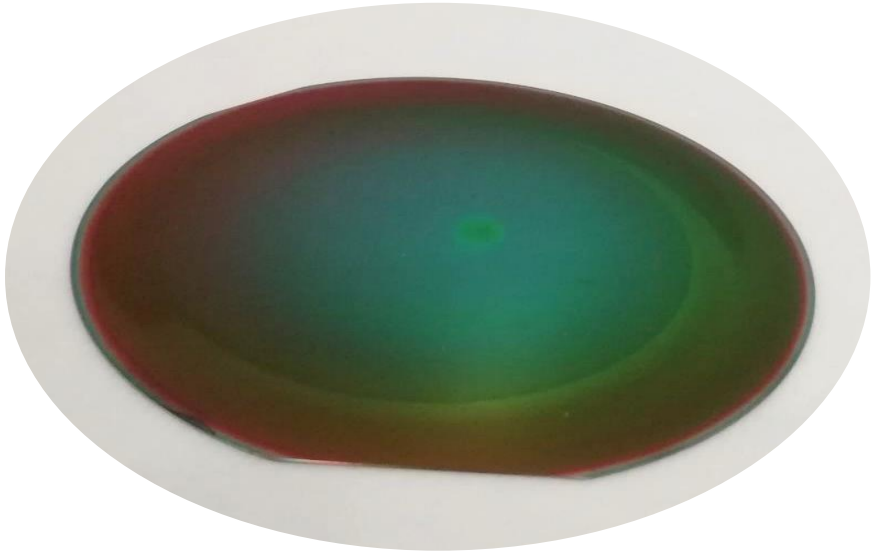
Homogeneous deposition



<u>Co-sputtering</u>

BaS + H_2S → Resputtering

<u>Sequential sputtering</u>

Ba + Ar → No resputtering

➢ Negative S ions?

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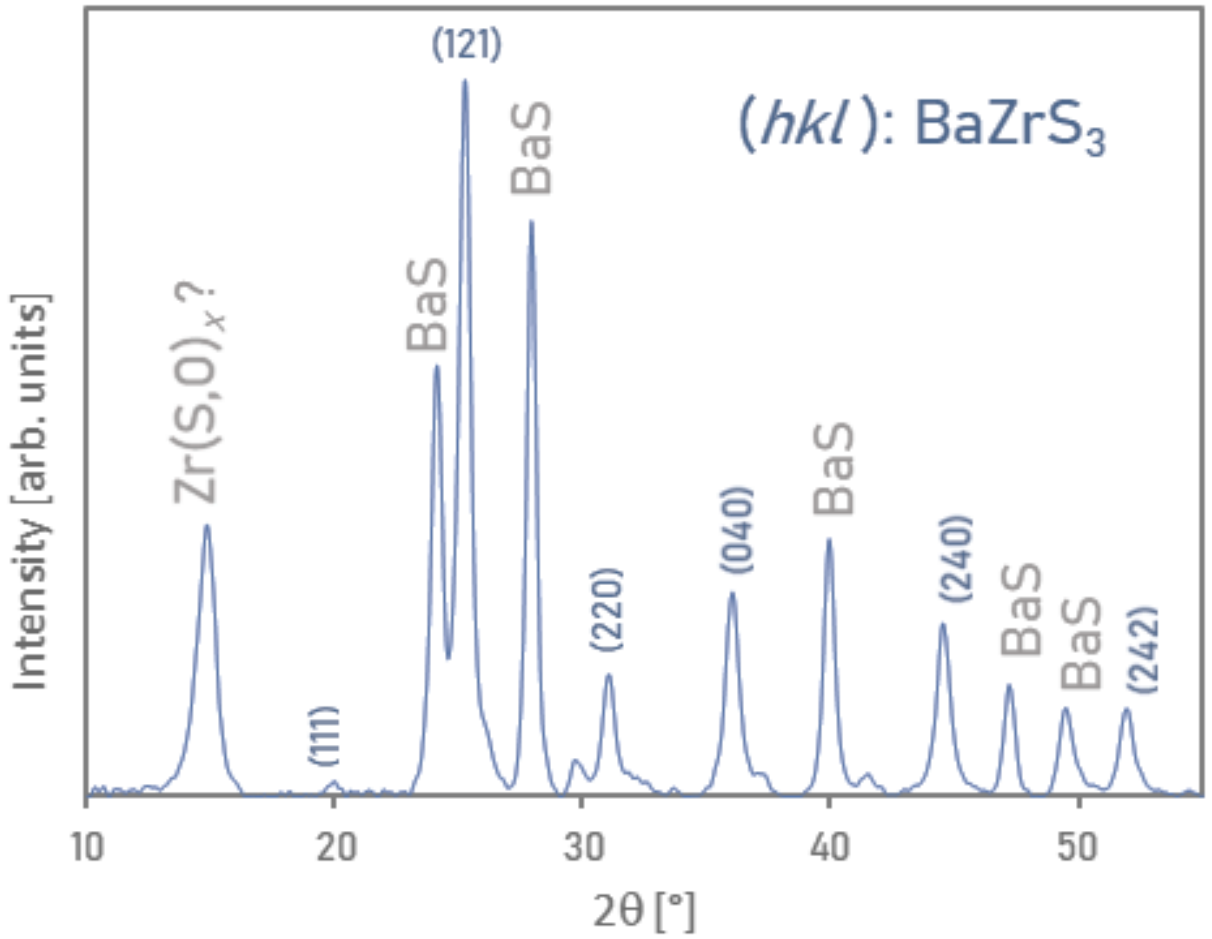
X-Ray Diffraction



Presence of:

- $BaZrS_3$
- BaS
- Zr(S,O)?

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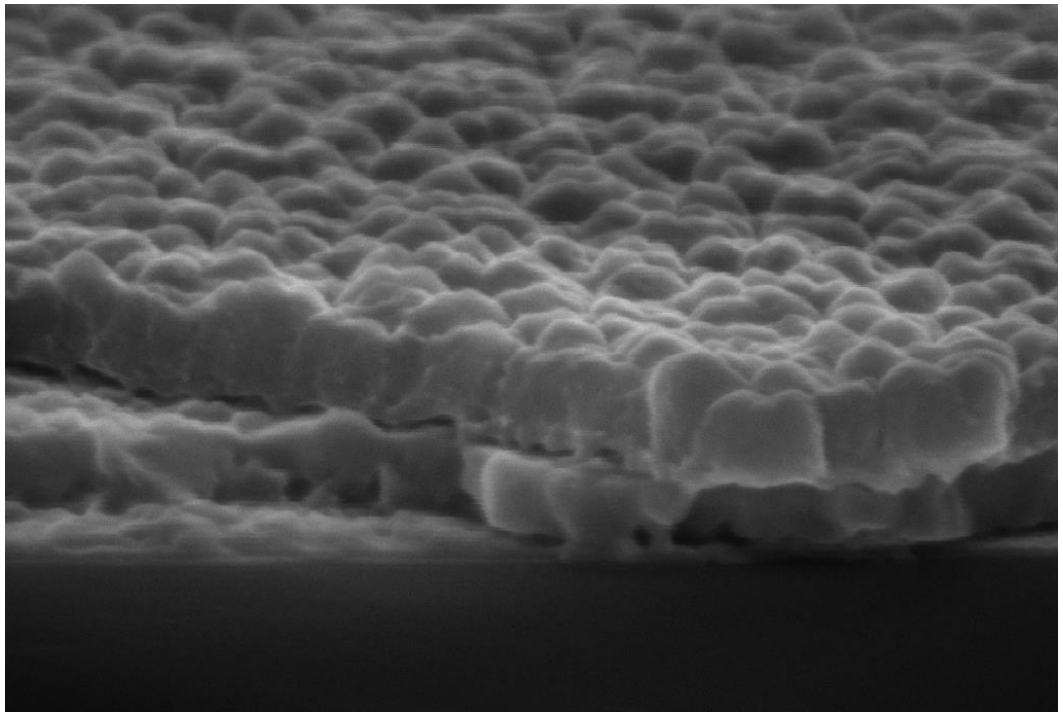
Ion Beam Analysis

$BaZrO_{0.15}S_{0.85}$

BaS + impurities



Layer	Ba (at%)	Zr (at%)	S (at%)	O (at%)
Top	19	20	50	10
Bottom	44	2	39	10
Stoichimetric $BaZrS_3$	20	20	60	0

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Conclusions

- $BaZrS_3$ possesses the right properties for perovskite/Si tandem cells → Thin films
- Co-sputtering
  - Fabrication of $BaZrS_3$ thin films of good crystalline quality
  - Inhomogeneity
  - High formation temperature (900 °C)
- Sequential sputtering (very recent)
  - Homogeneous film
  - Formation of a $BaZrO_{0.15}S_{0.85}$ film at ~ 700 °C
  - Sluggish reaction → Need of relatively high temperature (e.g. compared to other chalcogenides)
  - High thermal stability

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Acknowledgements

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RIF14-0053

Vetenskapsrådet

2017-04336

Göran Gustafsson Foundation

grant no. 1927

STandUPforENERGY

Thank you for your attention!