Optimization of optoelectrical properties of DC magnetron-sputtered Cu_2ZnSnS_4 absorber layer

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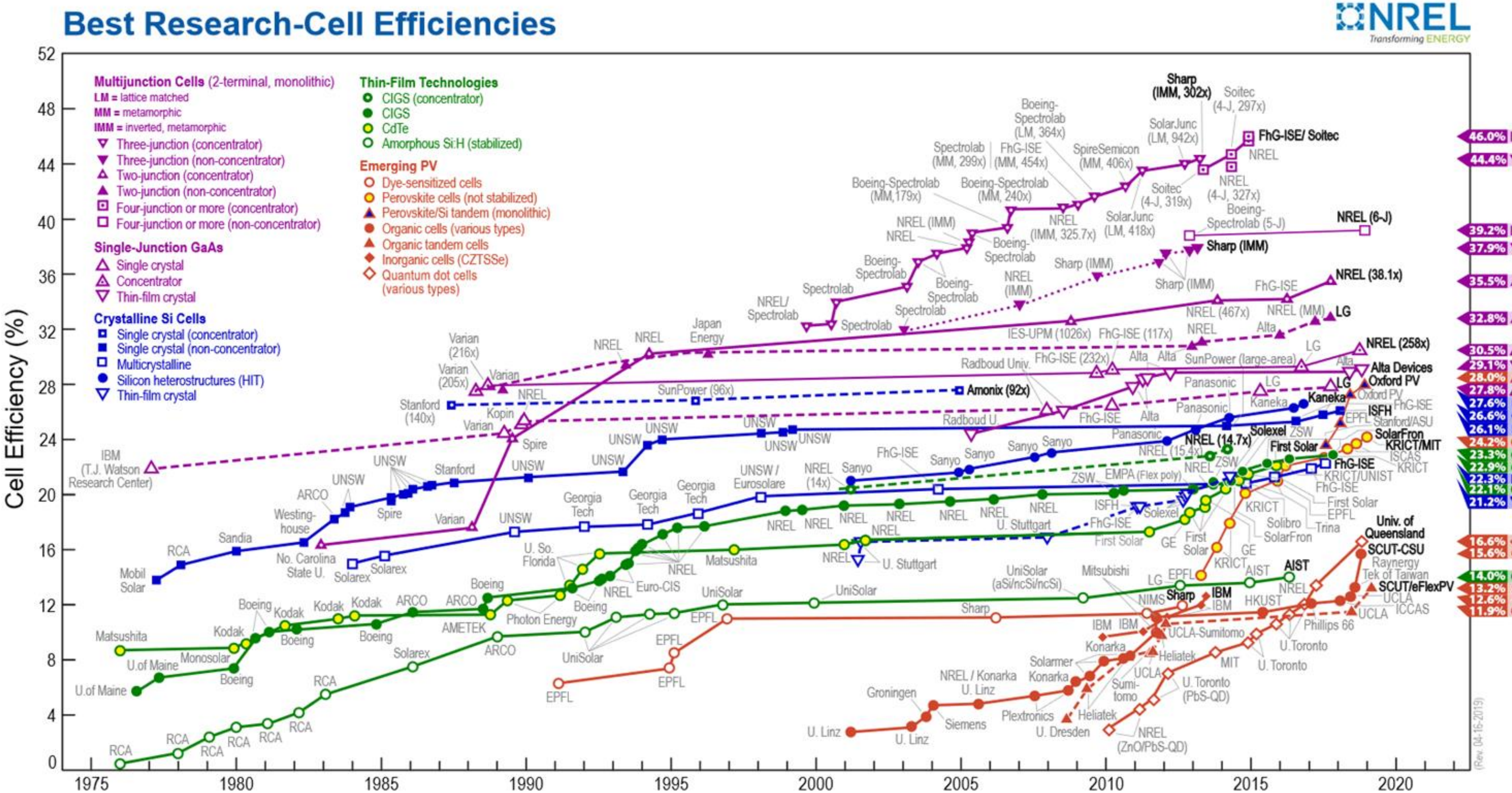
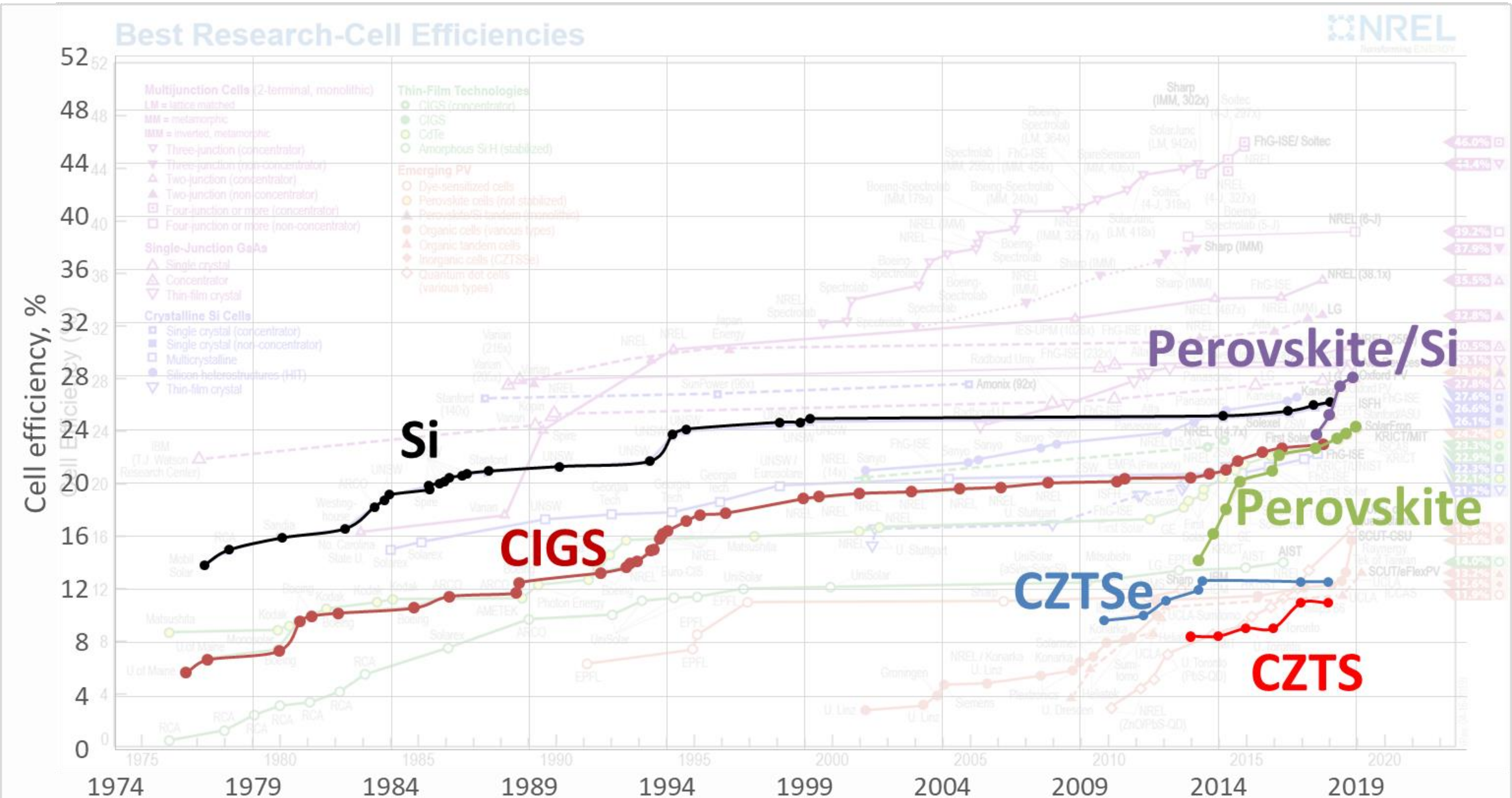
[3] IMAP, UC Louvain, Place Sainte Barbe 2, 1348, Louvain-la-Neuve, Belgium


Best Research-Cell Efficiencies
NREL Transforming ENERGY
Cell Efficiency (%)
Multijunction Cells (2-terminal, monolithic)
LM = lattice matched
MM = metamorphic
IMM = inverted, metamorphic
Three-junction (concentrator)
Three-junction (non-concentrator)
Two-junction (concentrator)
Two-junction (non-concentrator)
Four-junction or more (concentrator)
Four-junction or more (non-concentrator)
Single-Junction GaAs
Single crystal
Concentrator
Thin-film crystal
Crystalline Si Cells
Single crystal (concentrator)
Single crystal (non-concentrator)
Multicrystalline
Silicon heterostructures (HIT)
Thin-film crystal
Thin-Film Technologies
CIGS (concentrator)
CIGS
CdTe
Amorphous Si:H (stabilized)
Emerging PV
Dye-sensitized cells
Perovskite cells (not stabilized)
Perovskite/Si tandem (monolithic)
Organic cells (various types)
Organic tandem cells
Inorganic cells (CZTSSe)
Quantum dot cells (various types)
FhG-ISE/ Soitec
NREL (6-J)
Sharp (IMM)
NREL (38.1x)
LG
NREL (258x)
Alta Devices
Oxford PV
Amonix (92x)
NREL (14.7x)
Solexel
First Solar
SolarFron
KRICT/MIT
FhG-ISE
Univ. of Queensland
SCUT-CSU
SCUT/eFlexPV
AIST
46.0%
44.4%
39.2%
37.9%
35.5%
32.8%
30.5%
29.1%
28.0%
27.8%
27.6%
26.6%
26.1%
24.2%
23.3%
22.9%
22.3%
22.1%
21.2%
16.6%
15.6%
14.0%
13.2%
12.6%
11.9%
(Rev. 04-16-2019)



…

5.5% by magnetron sputtering A. Fairbother et al. 2013

9.2% by co-sputtering K. Sun et al. 2016

11% by sputtering Cu/ZnS/Sn + RTP C.Yan et al. 2018

Context

- SCAPS simulation
- CZTS fabrication
- Material characterization
- Optoelectrical characterization
- Conclusions

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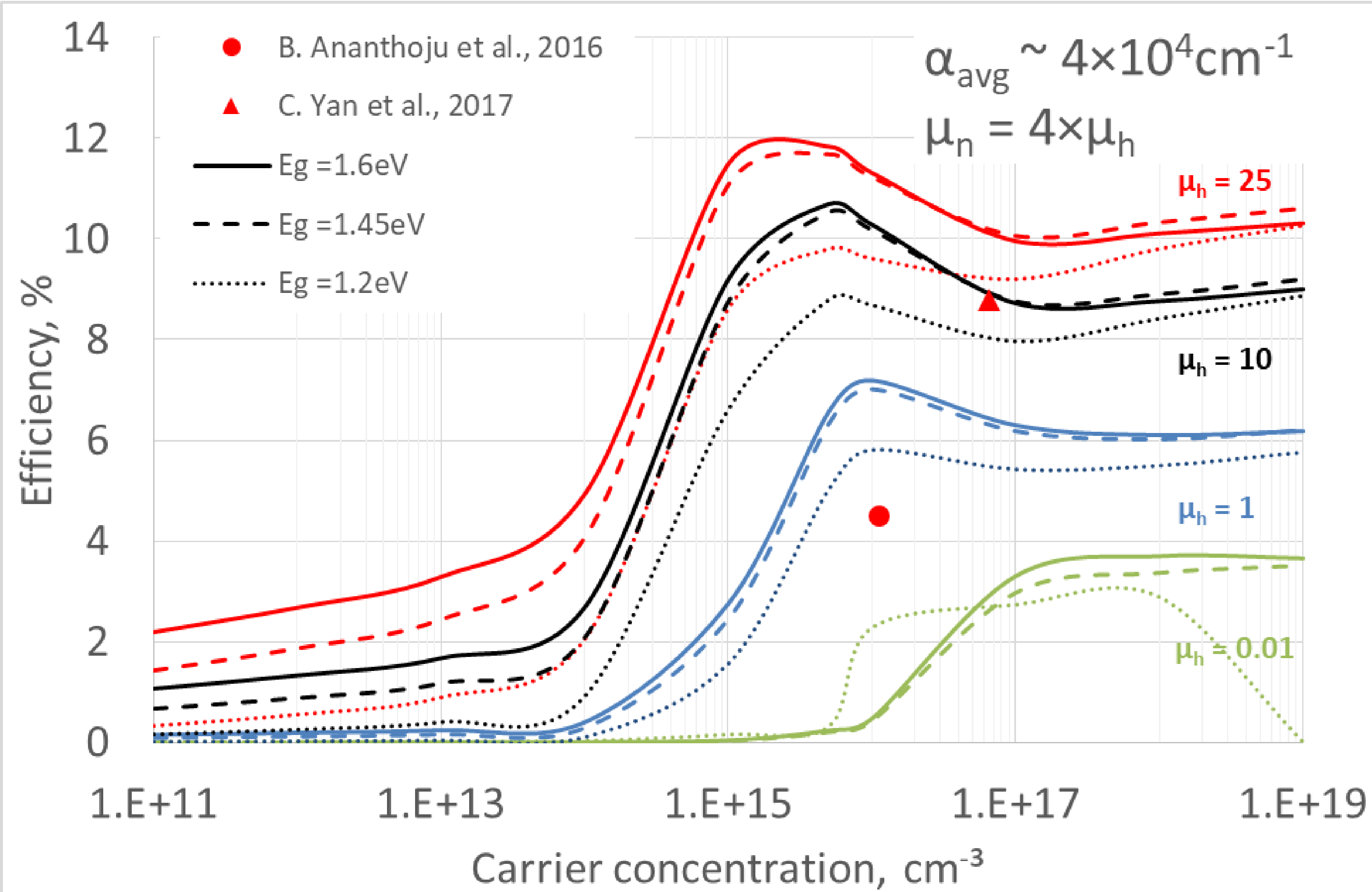
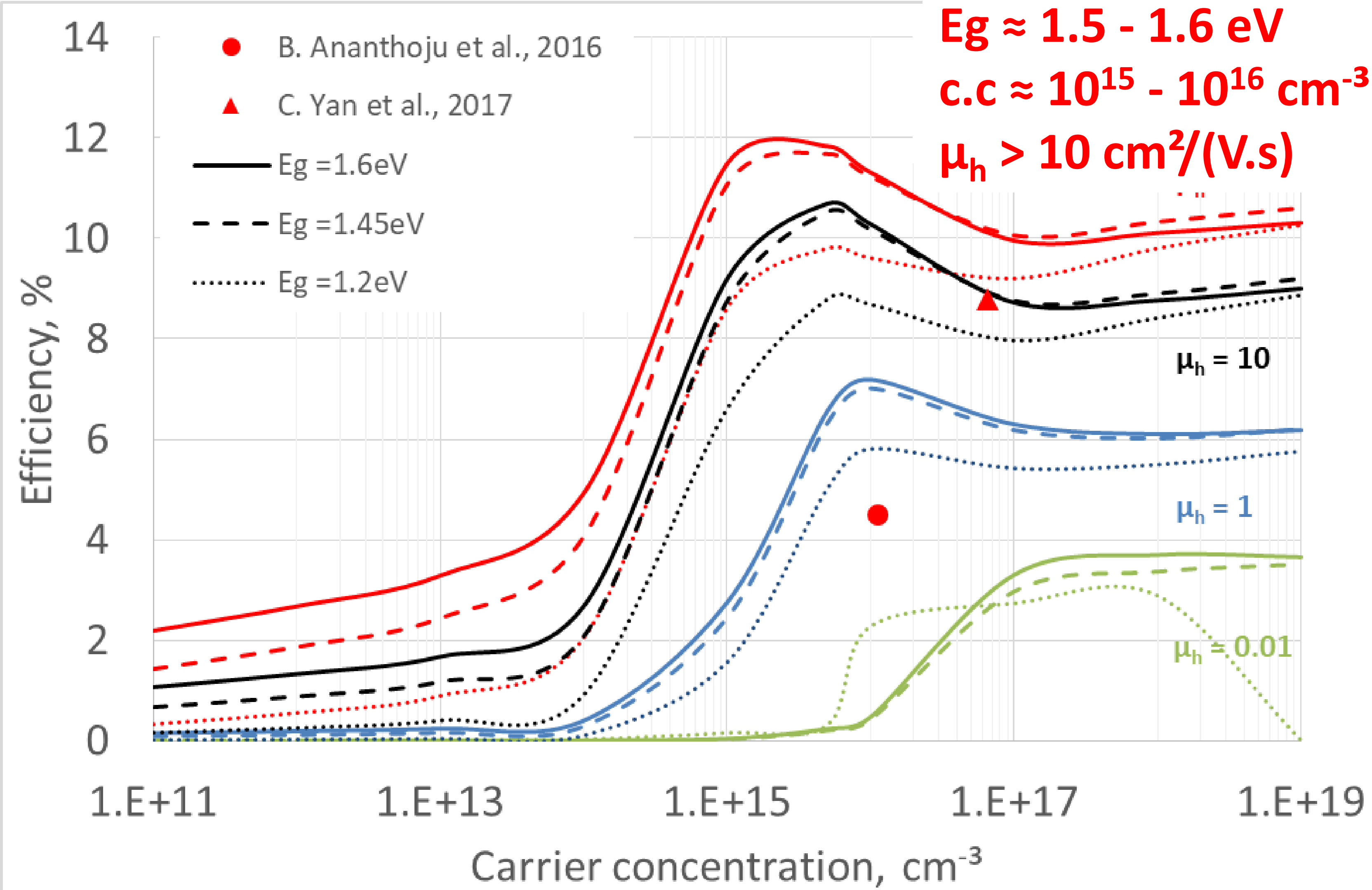
Results of SCAPS* simulations:



* Solar cell CAPacitance Simulator http://scaps.elis.ugent.be

Results of SCAPS* simulations:



Eg ≈ 1.5 - 1.6 eV

c.c ≈ 10^{15} - 10^{16} cm^{-3}

μ_h > 10 $cm^2/(V.s)$

* Solar cell CAPacitance Simulator http://scaps.elis.ugent.be

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DC magnetron sputtering + RTP in AS-ONE

Processing conditions:

- Deposition parameters*
- Ratios
- Stack thickness
- Stack ordering*
- Pre-annealing

Material properties:

- Ratios or Composition
- Crystallinity
- CZTS (k) phase

Opto-electrical properties:

- Efficiency
- Band gap
- Absorption
- Urbach energy
- Carrier concentration
- Mobility

** M. Zhukova et al. PVSEC 2017 conference proceedings*

DC magnetron sputtering + RTP in AS-ONE

Correlation ?

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Processing conditions:
- Deposition parameters*
- Ratios
- Stack thickness:

Small, Medium, Large
- Stack ordering*
- Pre-annealing

Material properties:
- Ratios or Composition
- Crystallinity
- CZTS (k) phase

Opto-electrical properties:
- Efficiency
- Band gap
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- Urbach energy
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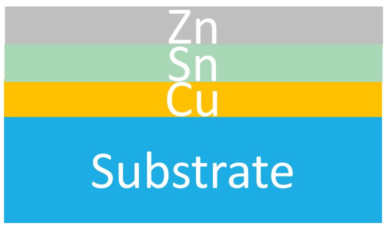
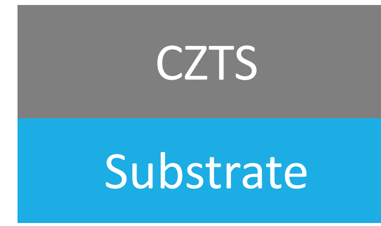
** M. Zhukova et al. PVSEC 2017 conference proceedings*

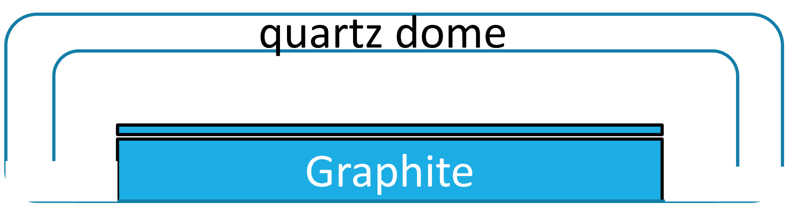
Different RTP in AS-ONE

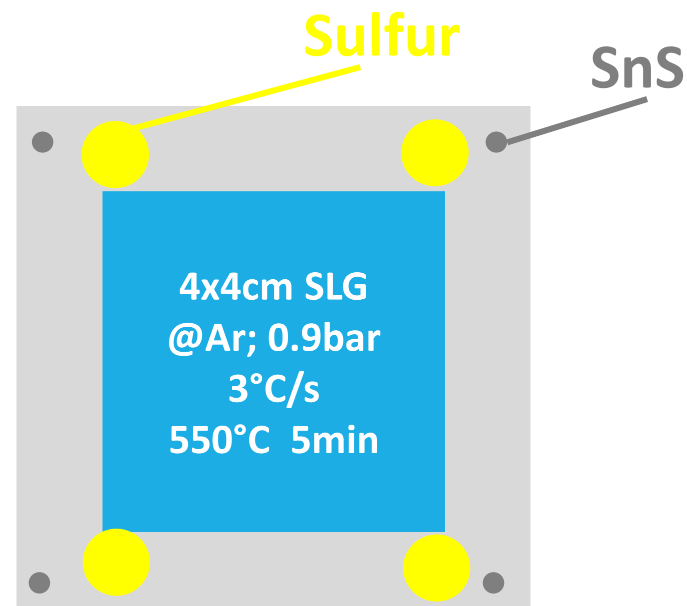
Small, Medium, Large



RTP 1 with S~100mg

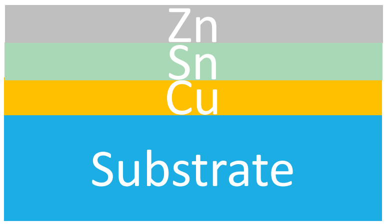






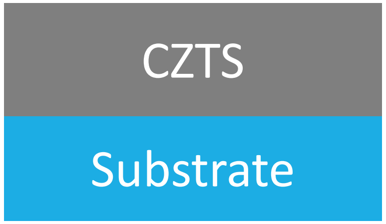
Different RTP in AS-ONE

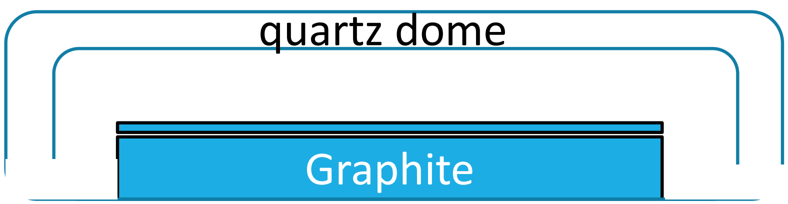
Small, Medium, Large

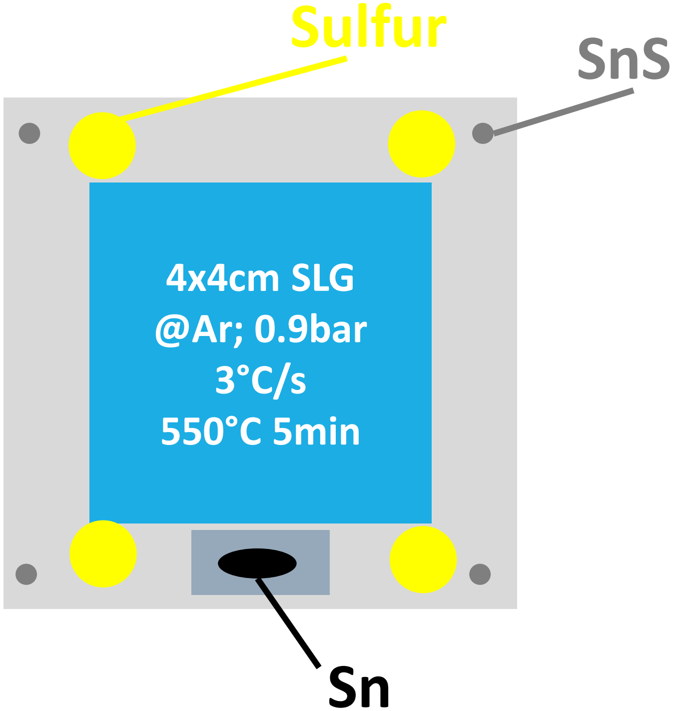


RTP 1 with S~100mg

RTP 2 with S~100mg Sn~10mg*

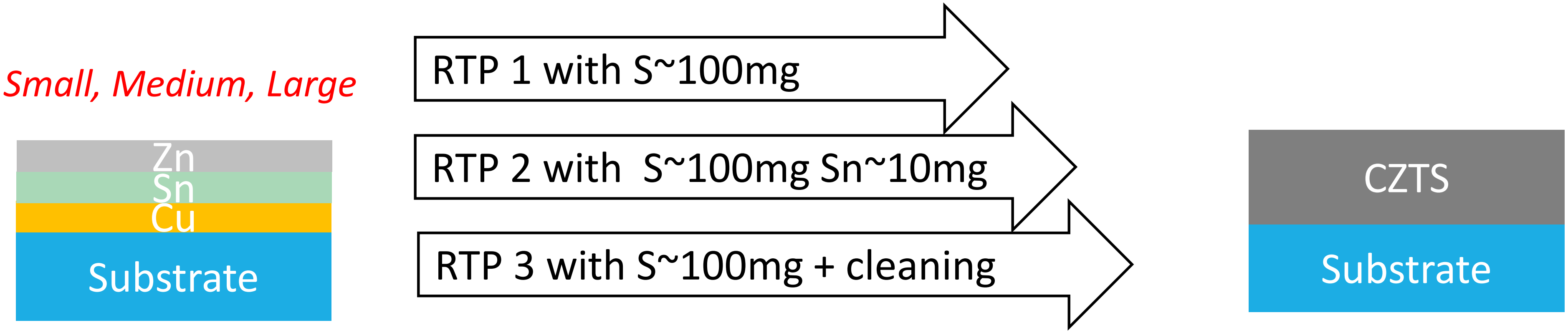


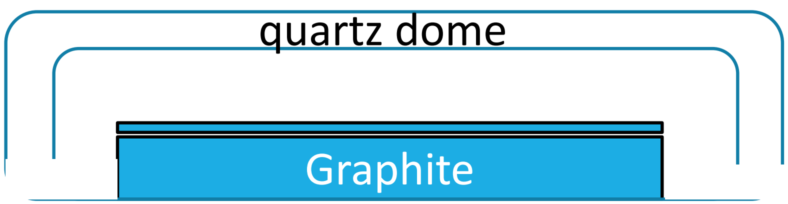


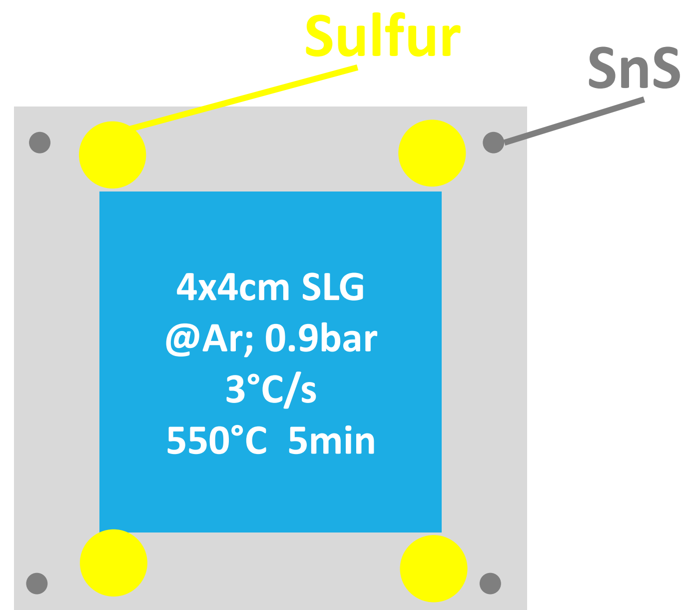


* *M. Zhukova et al. 8th EU Kesterite workshop 2017 (non-published)*

Different RTP in AS-ONE

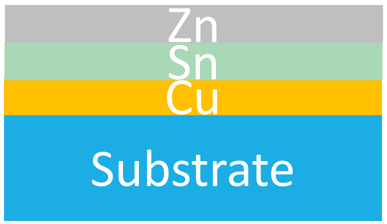






Different RTP in AS-ONE

Small, Medium, Large

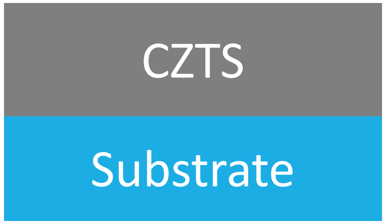


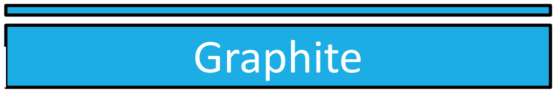
RTP 1 with S~100mg

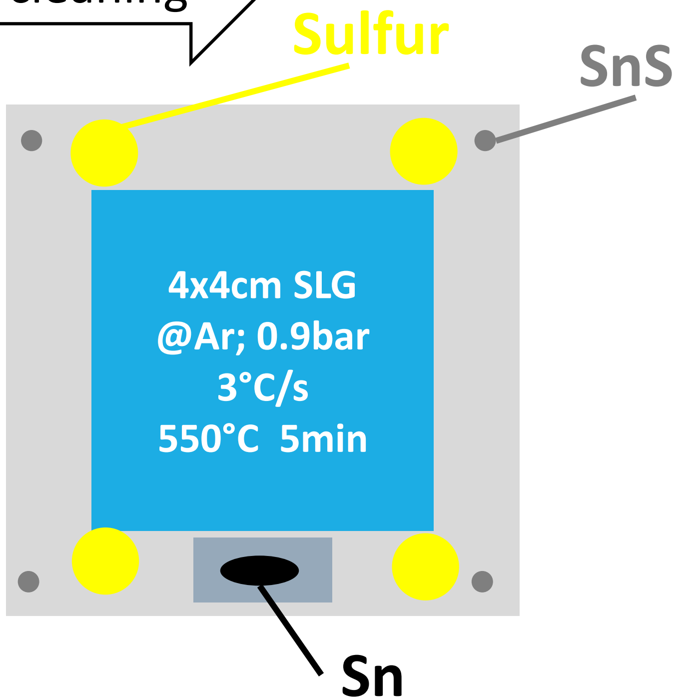
RTP 2 with S~100mg Sn~10mg

RTP 3 with S~100mg + cleaning

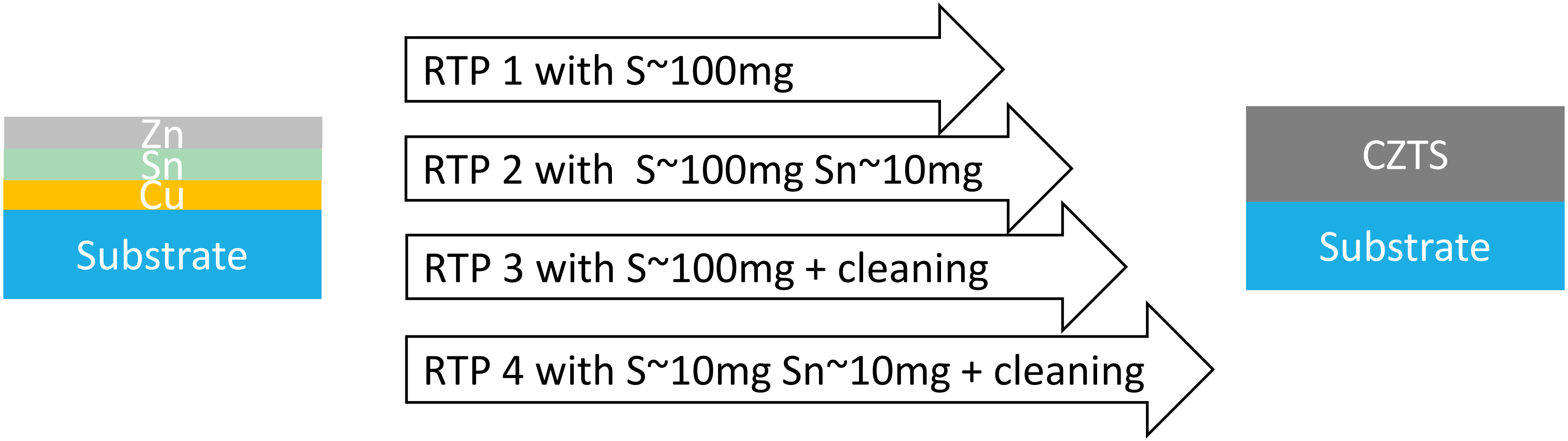
RTP 4 with S~10mg Sn~10mg + cleaning







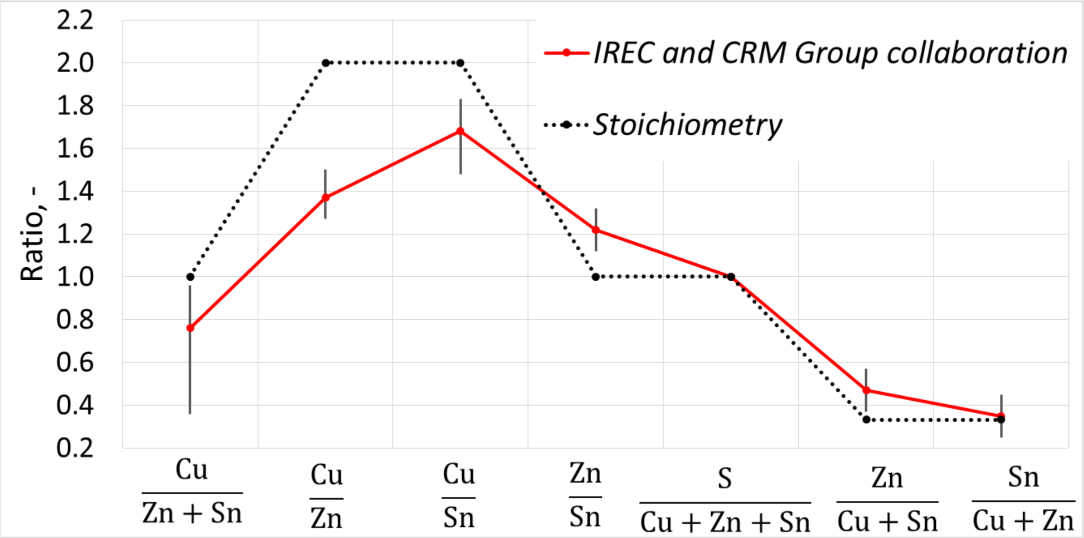
List of samples



Groups:	Final CZTS thickness, µm:	RTP 1	RTP 2	RTP 3	RTP 4
Small	1	S1	S2	S3	S4
Medium	1.5	M1	M2	M3	M4
Large	2	L1	L2	L3	L4

List of samples

at.%	Stoichiometry	Ref*
Cu	25	21.5
Zn	12.5	15.6
Sn	12.5	12.8
S	50	50



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* *IREC and CRM Group collaboration*

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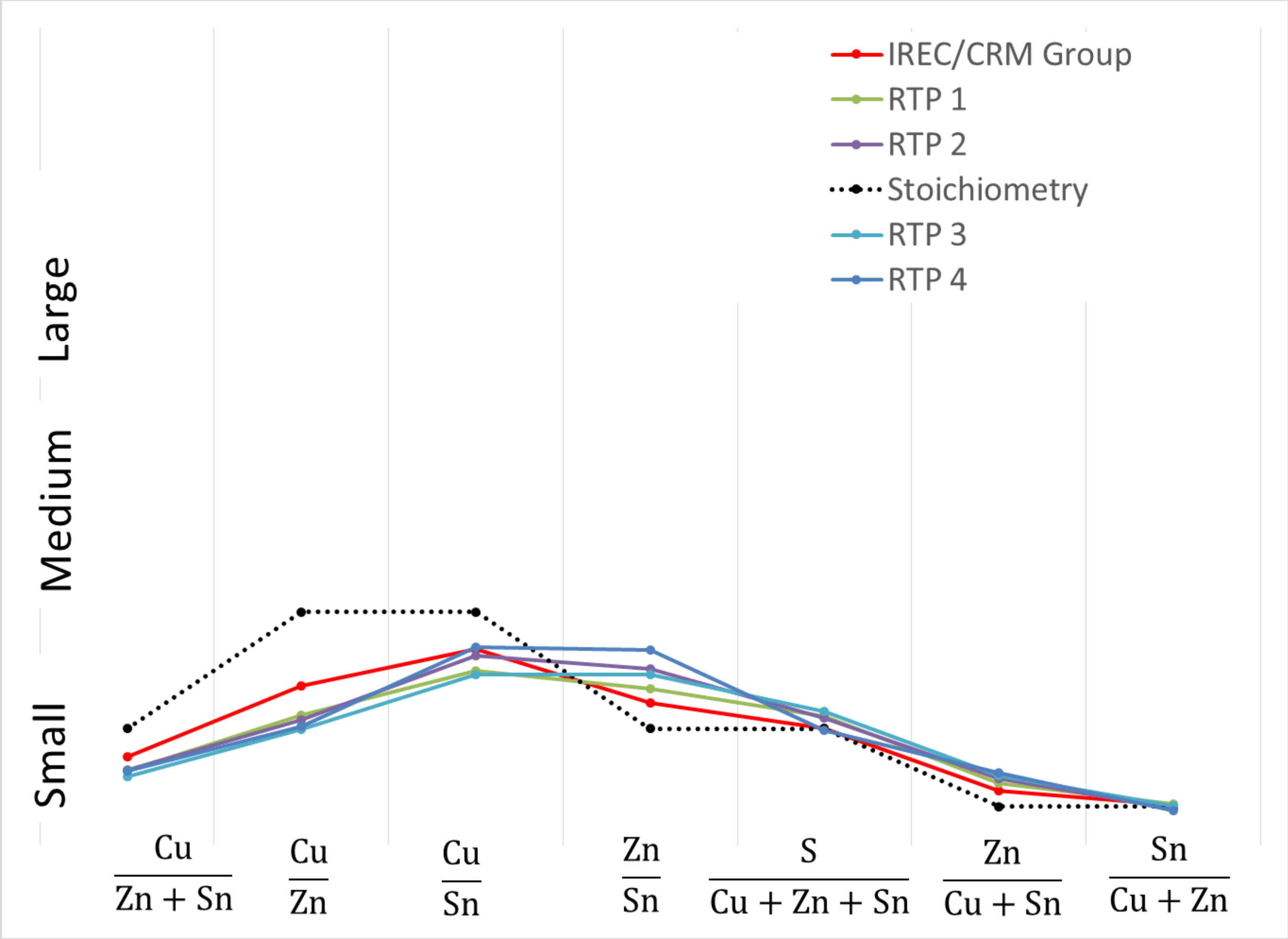
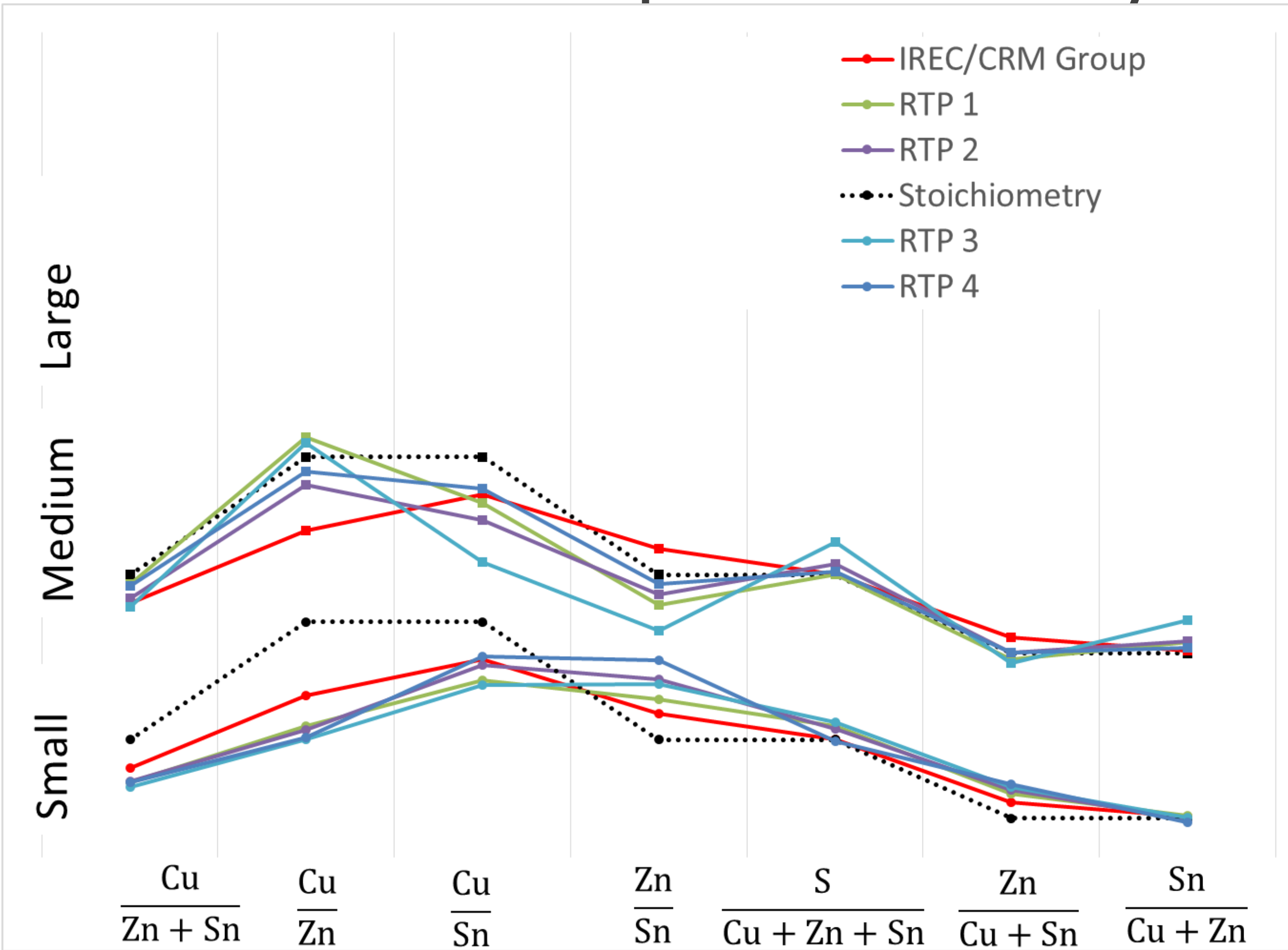
Results of composition by EDX



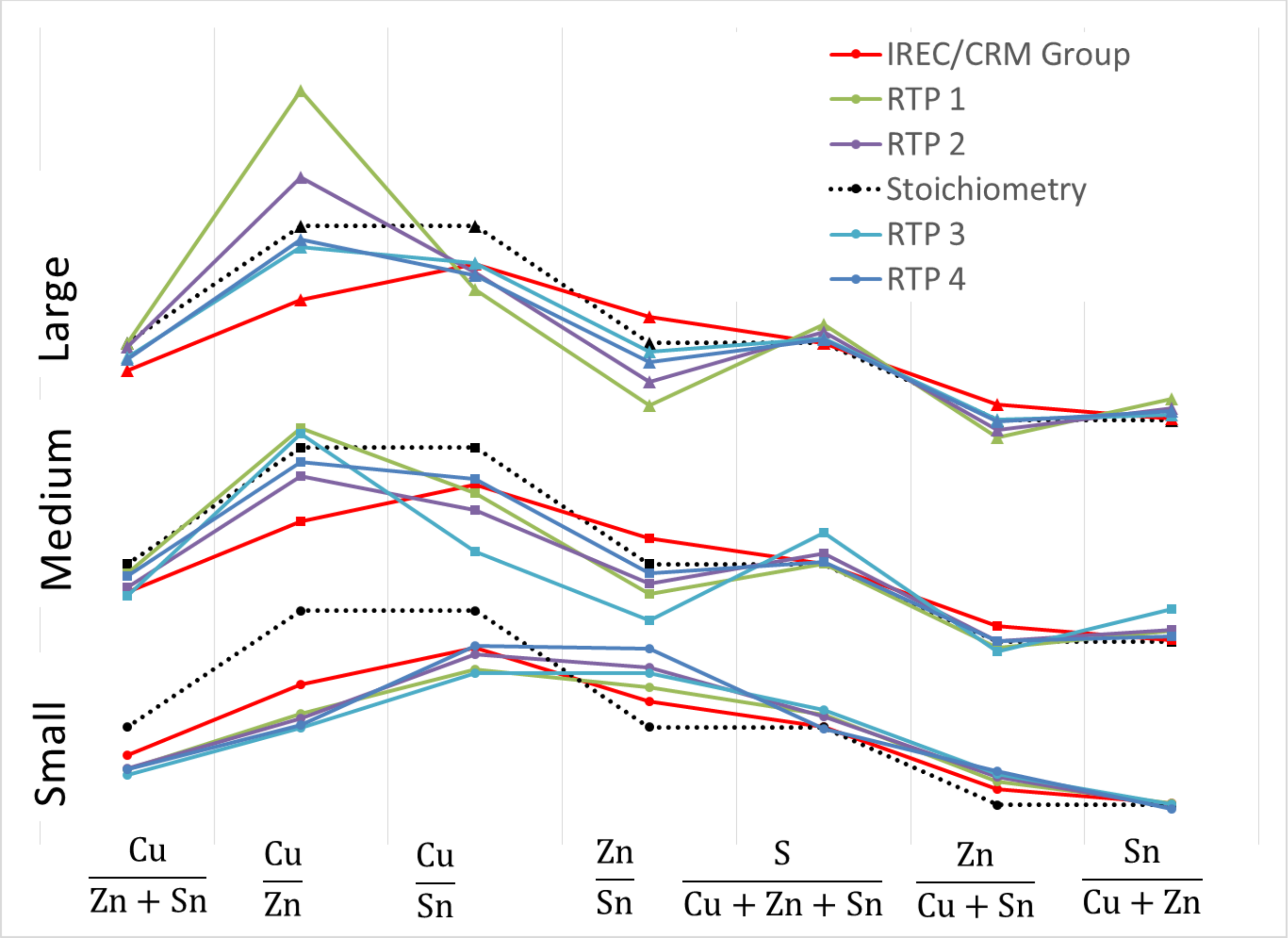
- Small: Cu-poor, Zn-rich

Results of composition by EDX



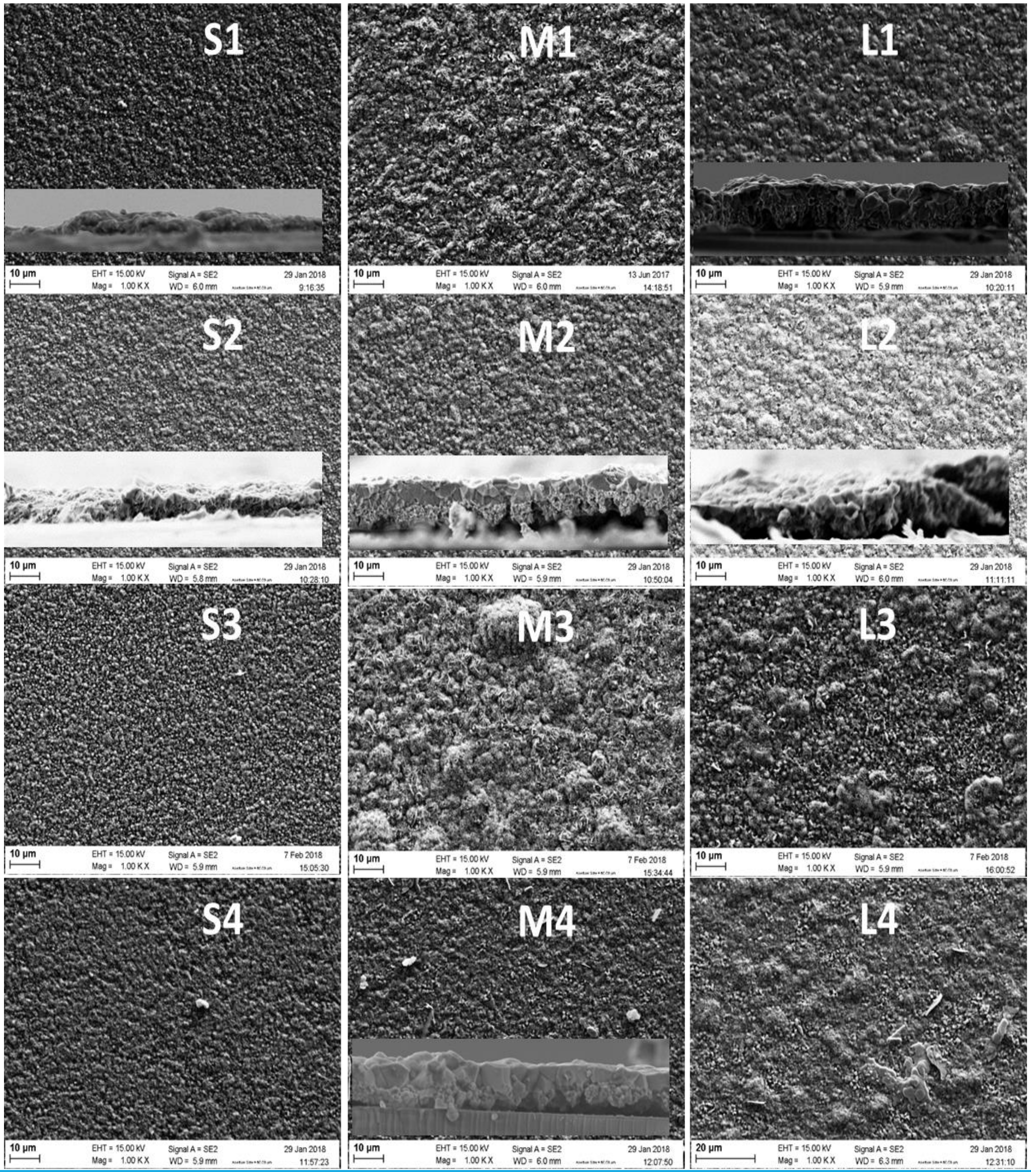
- Small: Cu-poor, Zn-rich
- Medium: Cu-correct, Zn-poor

Results of composition by EDX



- Small: Cu-poor, Zn-rich
- Medium and Large: Cu-correct/rich, Zn-poor

Results of morphology by SEM

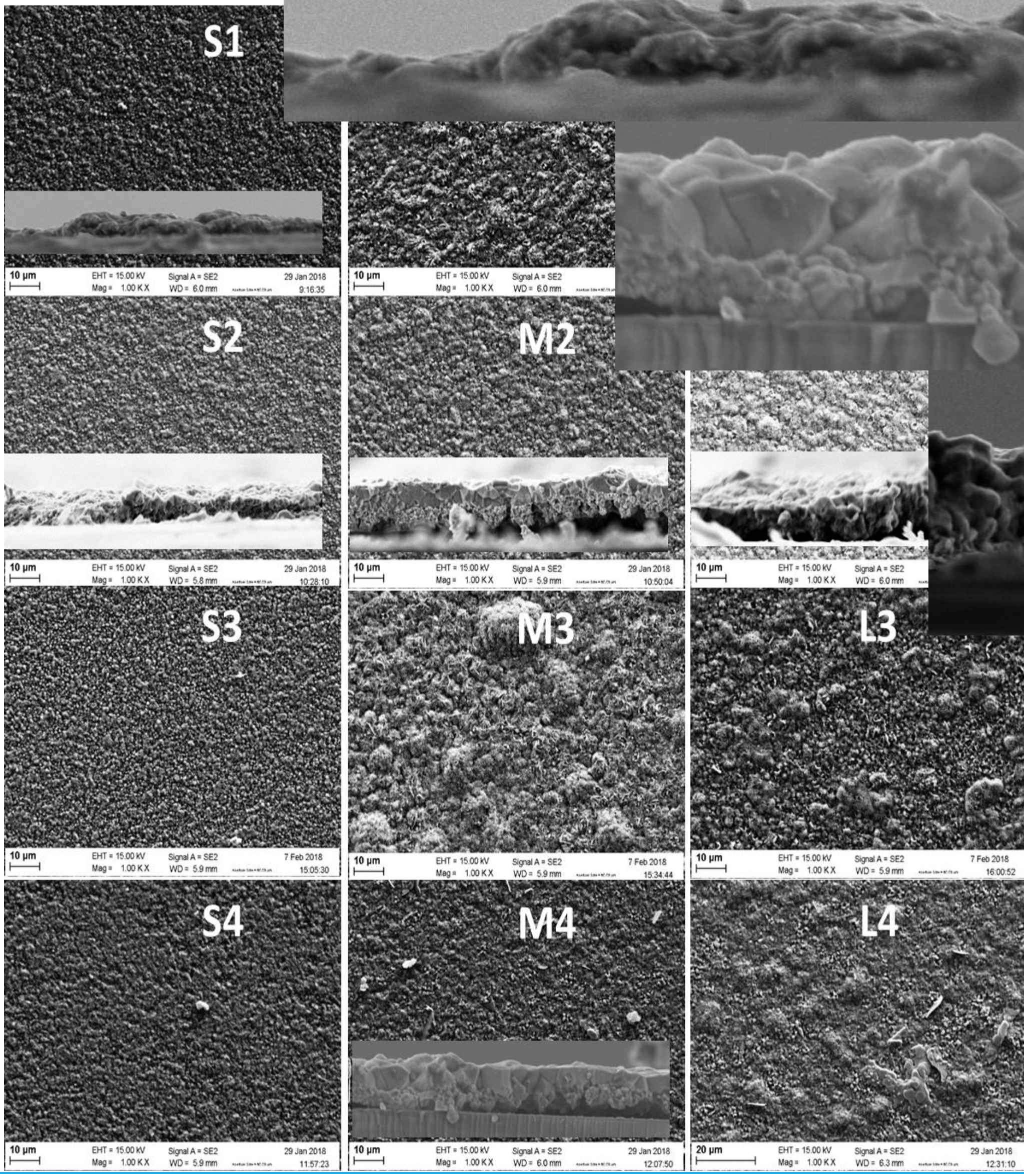


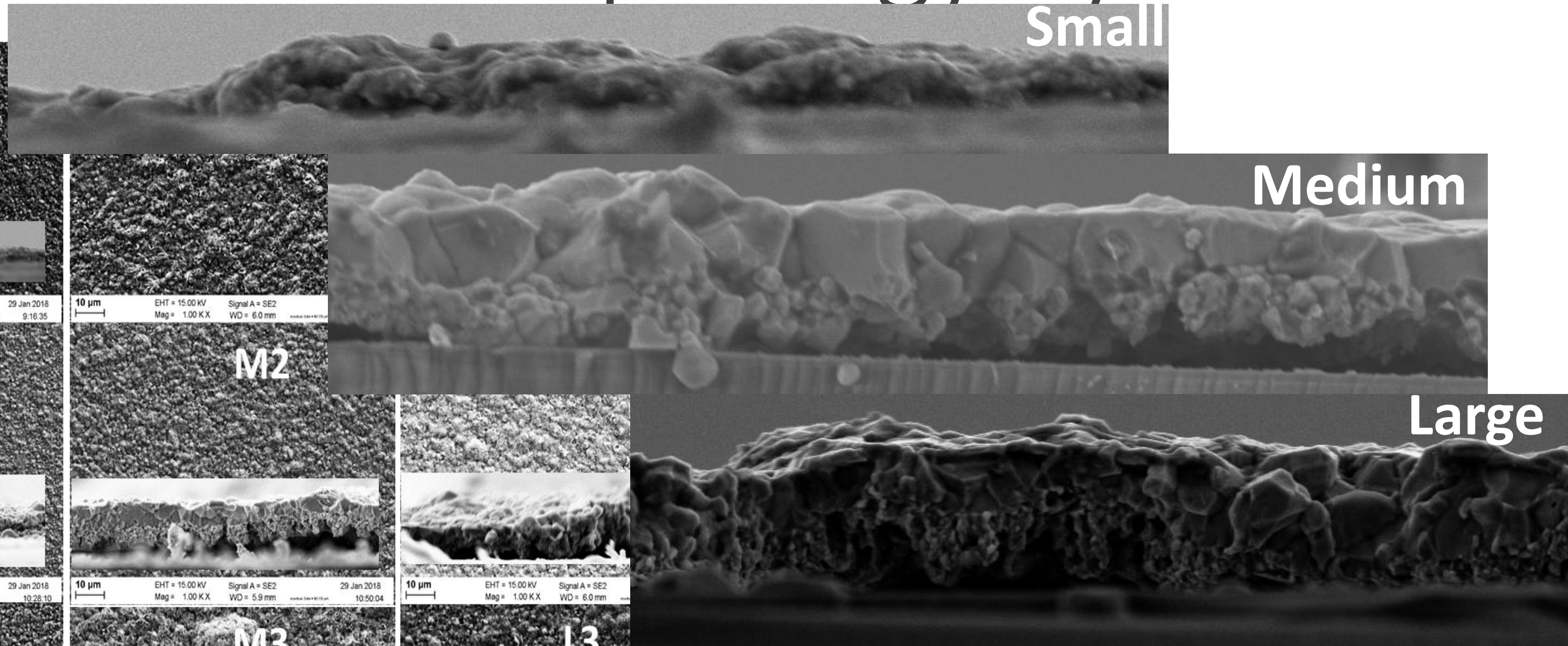
➔ Rough

➔ Different textures

➔ Thickness Small ~ 1 µm
Medium ~ 1.5 µm
Large ~ 2 µm

Results of morphology by SEM





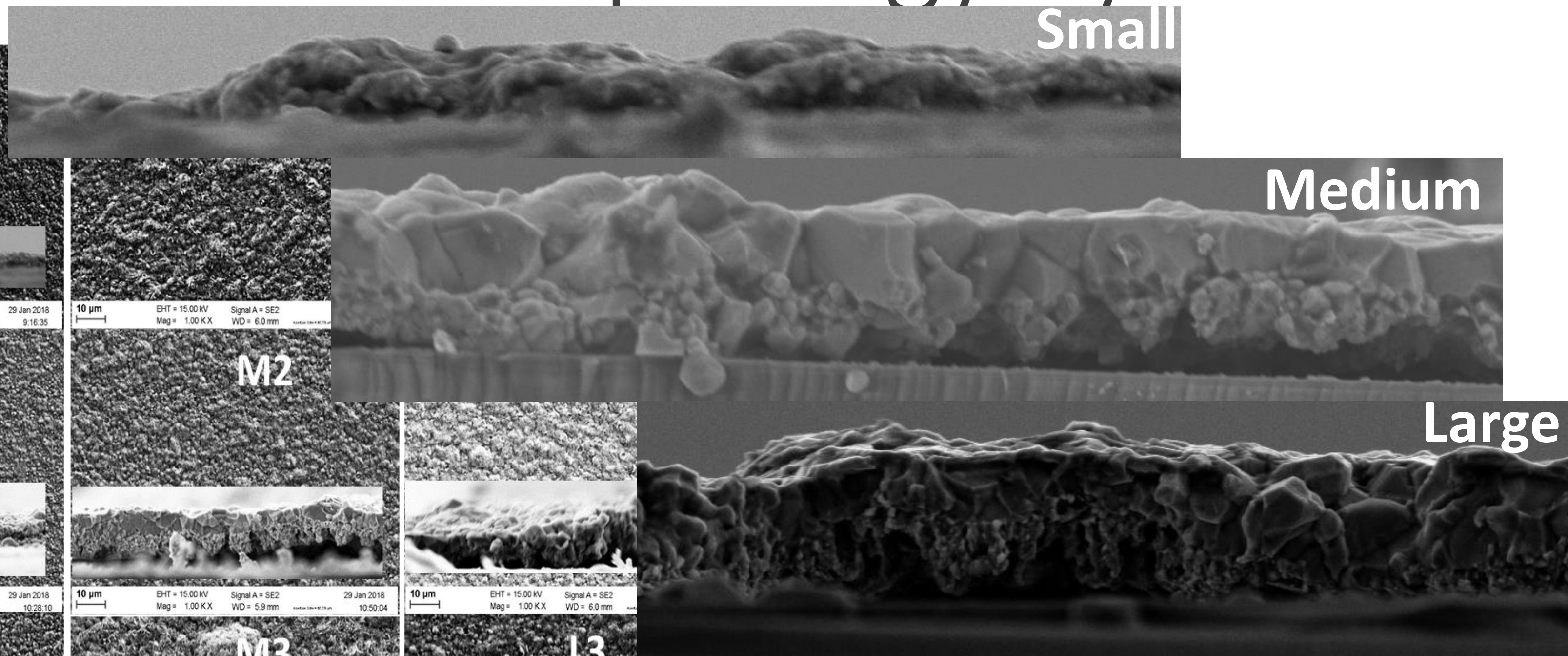
➔ Grain size

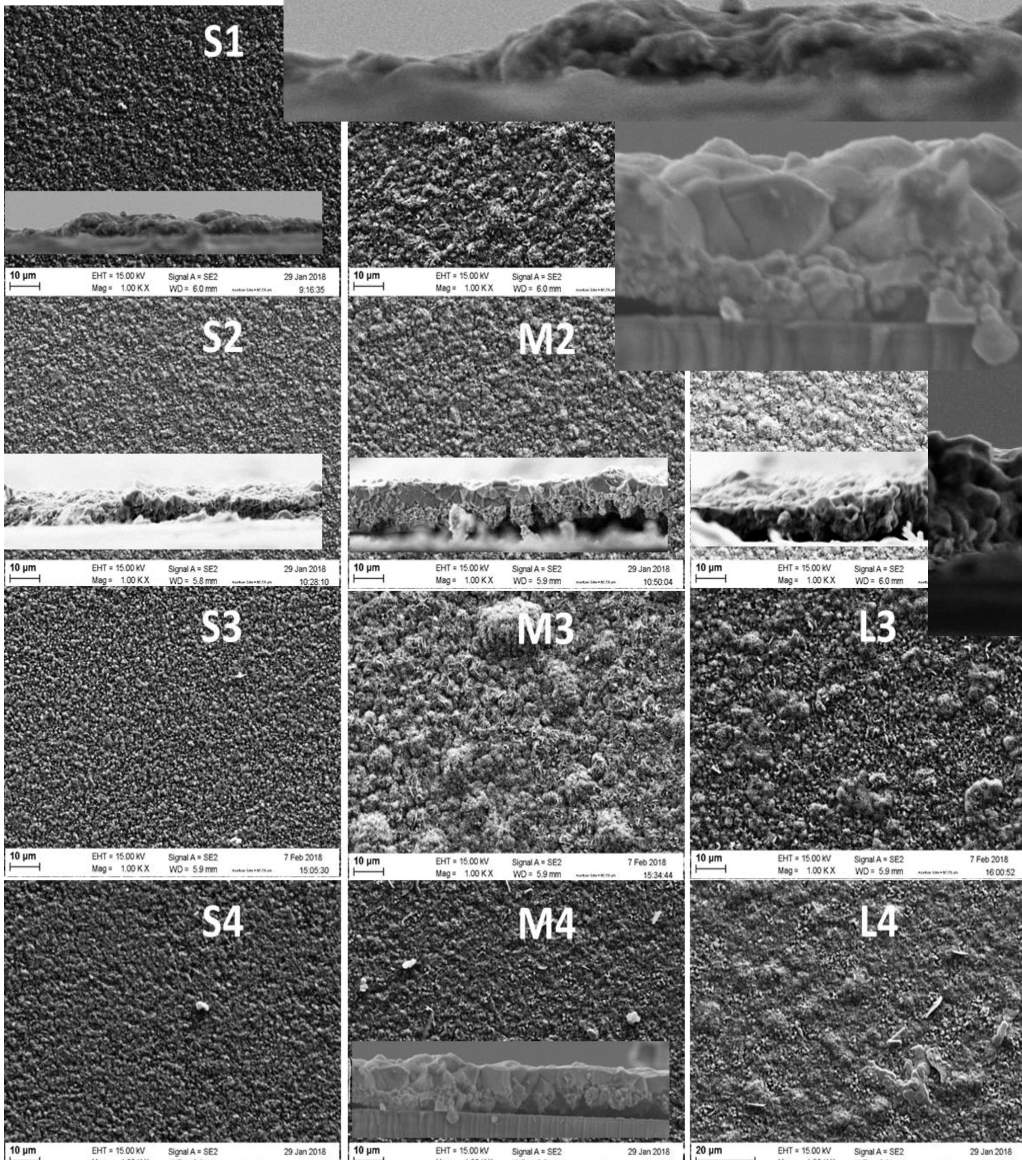
Small ~ 10 nm

Medium ~ 100-800 nm

Large ~ 50 - 600 nm

Results of morphology by SEM





➔ Grain size

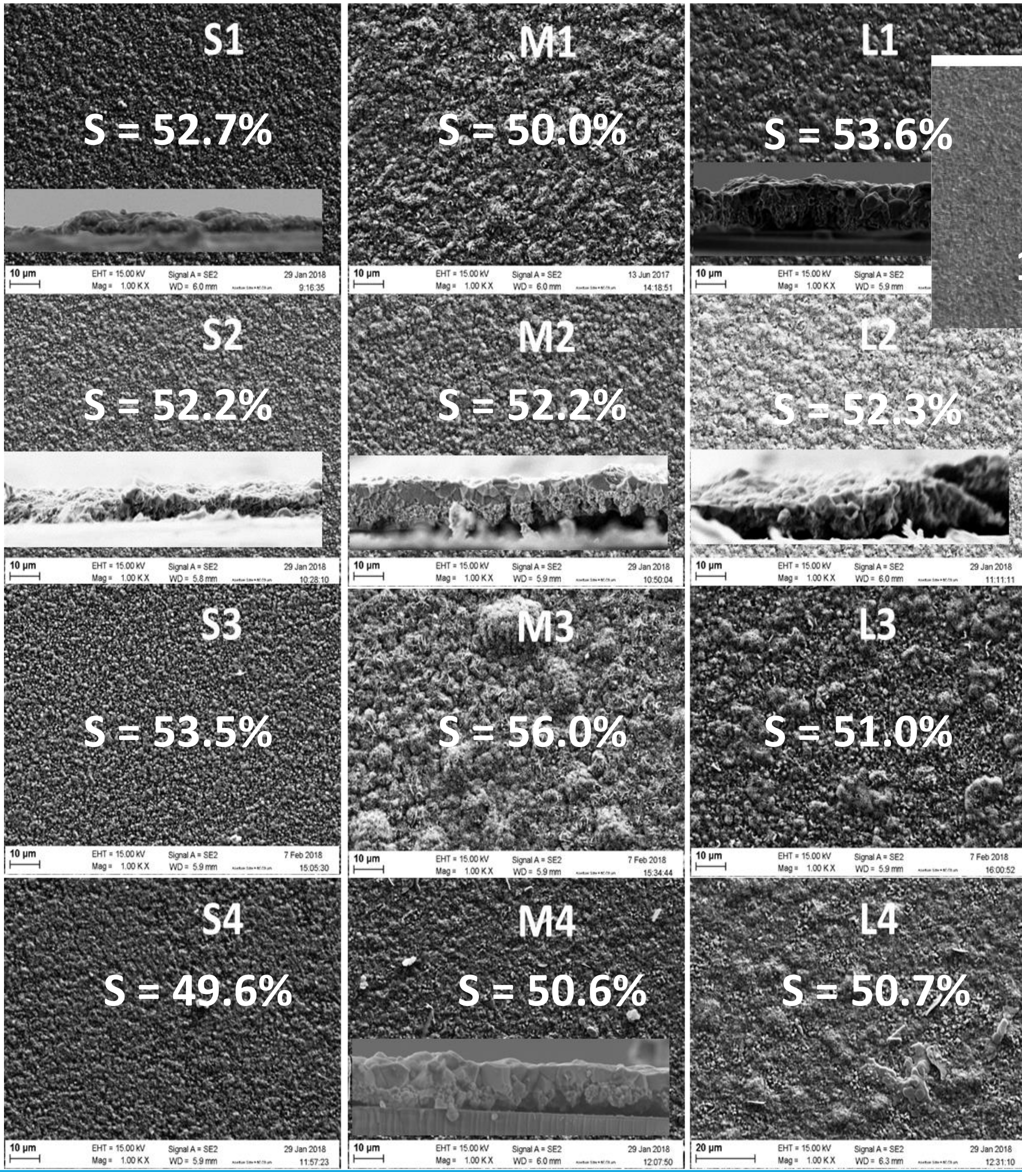
Small ~ 10 nm

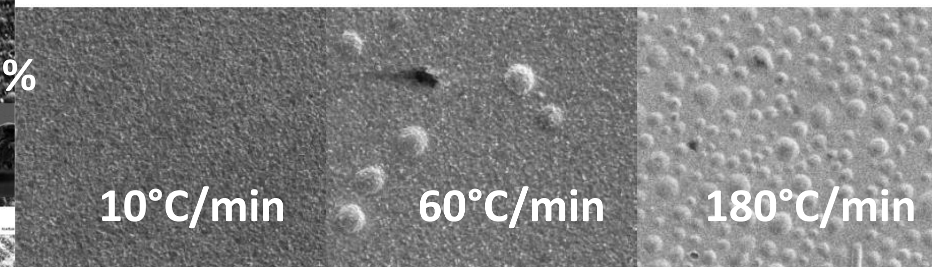
Medium ~ 100-800 nm

Large ~ 50 - 600 nm

➔ Voids/ Bubbles

Results of morphology by SEM

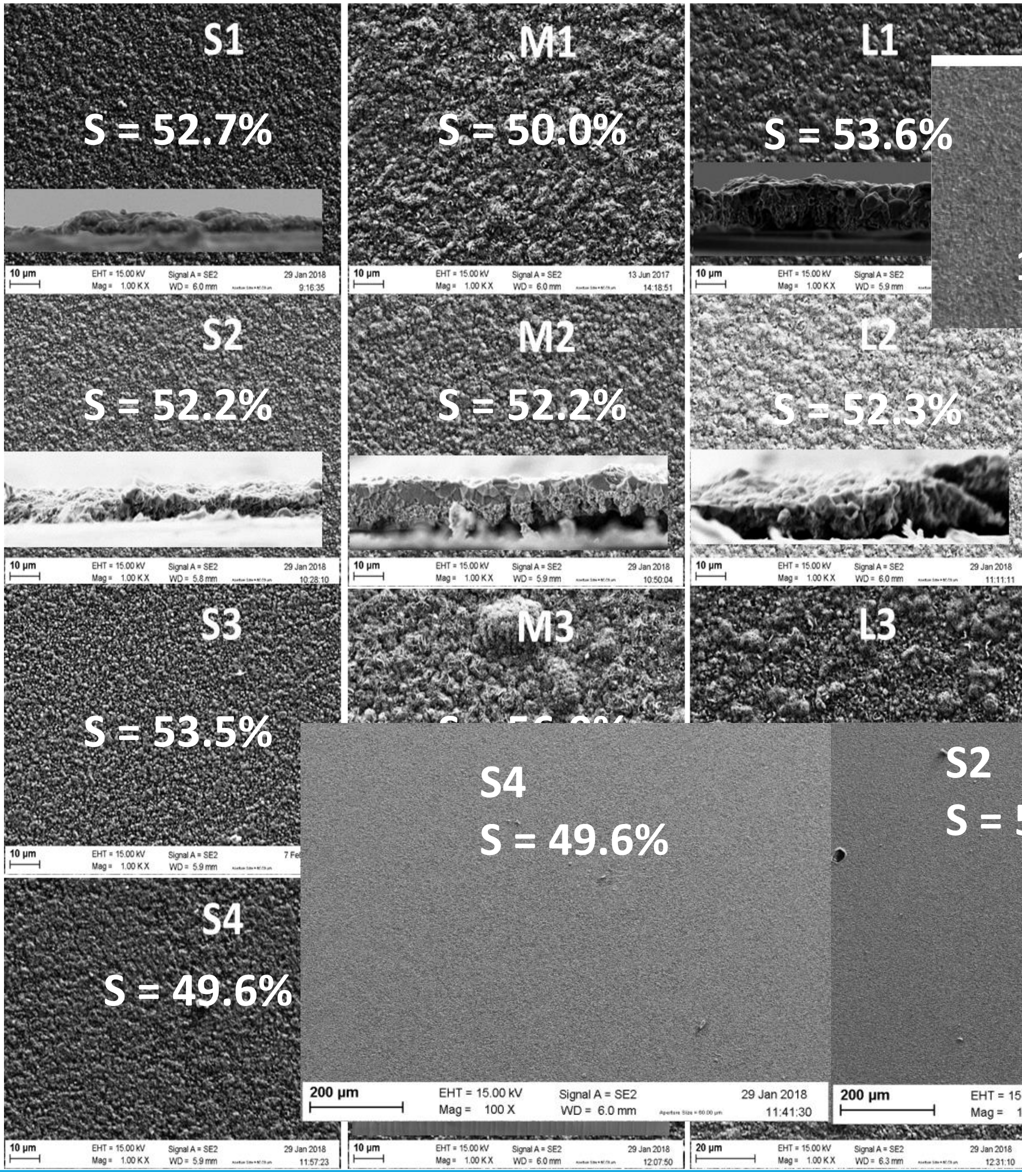


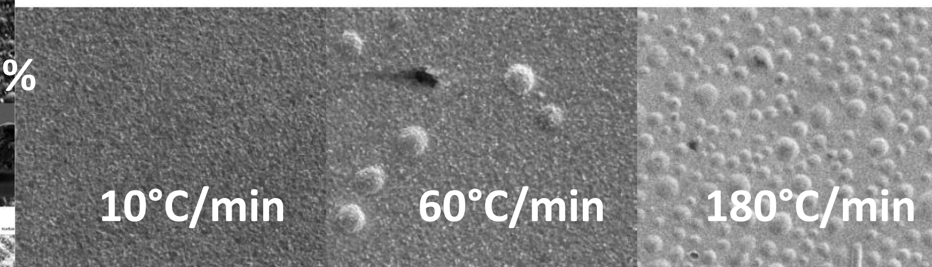


** Chang Yan et al. 2018 Cu2ZnSnS4 solar cells with over 10% power conversion efficiency enables by heterojunction heat treatment Nature Energy 2018 764-772*

Or by SnO2 at E1.6 M. Gansukh et al. Oxide route for CZTS solar cells by Pulsed Laser Deposition (E symposium EMRS 2019 talk Monday 25 May)

Results of morphology by SEM





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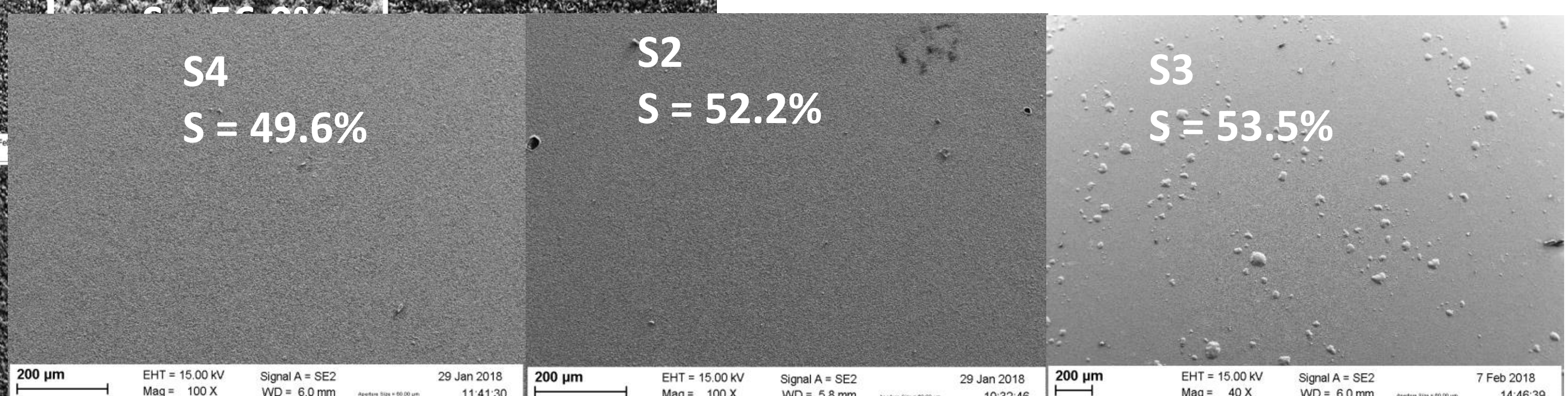
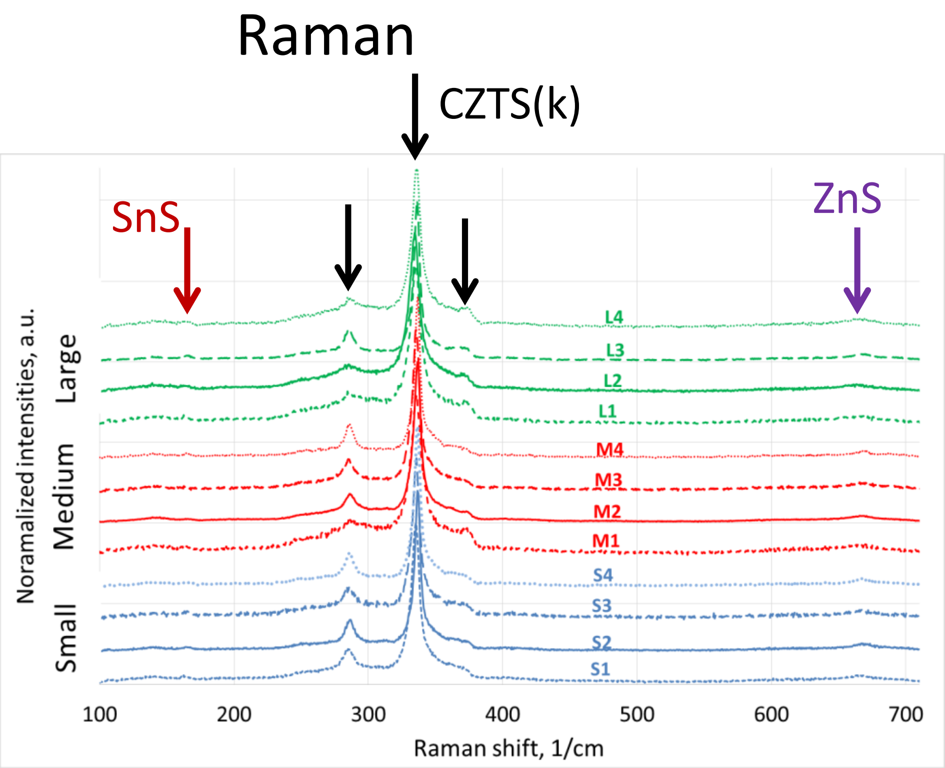
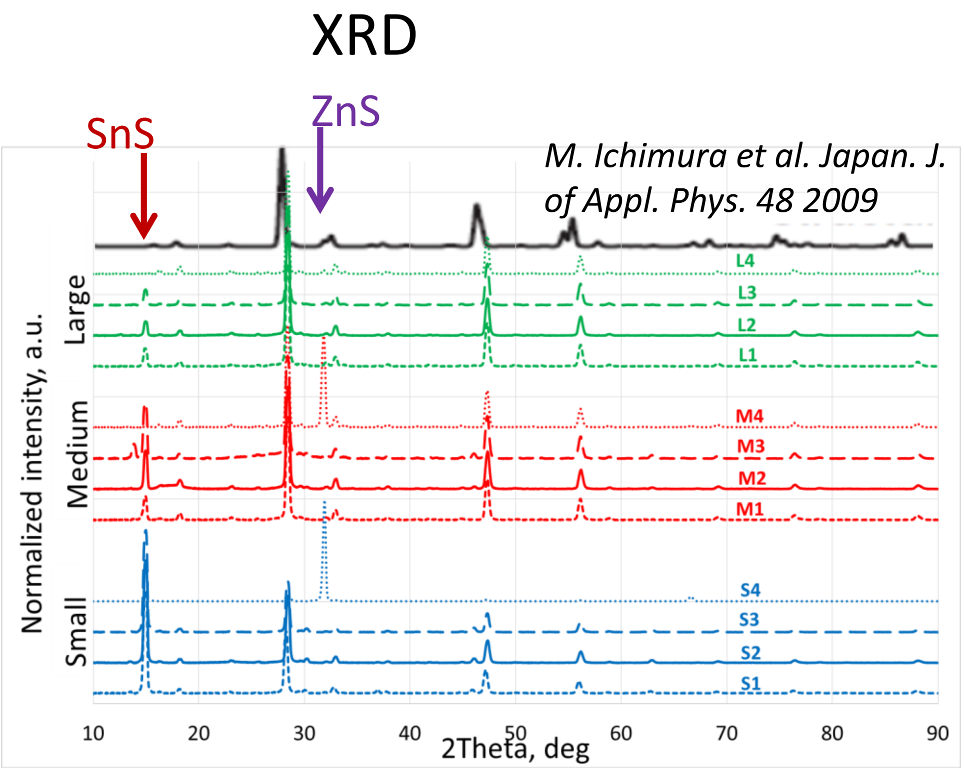


Results of crystal structure





- ➔ CZTS (k) phase is present in all samples
- ➔ Secondary phases SnS, ZnS
- ➔ XRD needs quantitative analysis

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- **Optoelectrical characterization**
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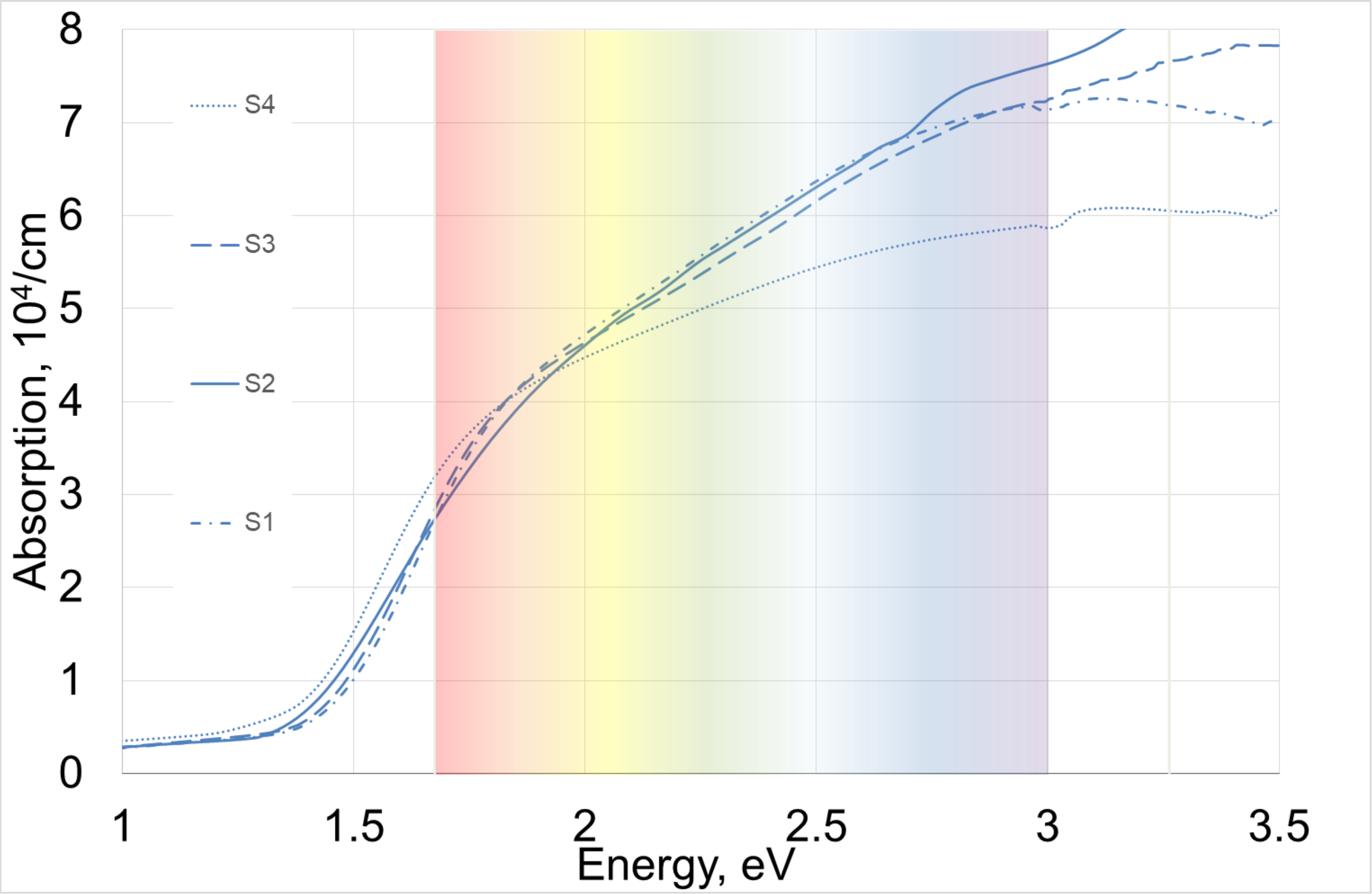
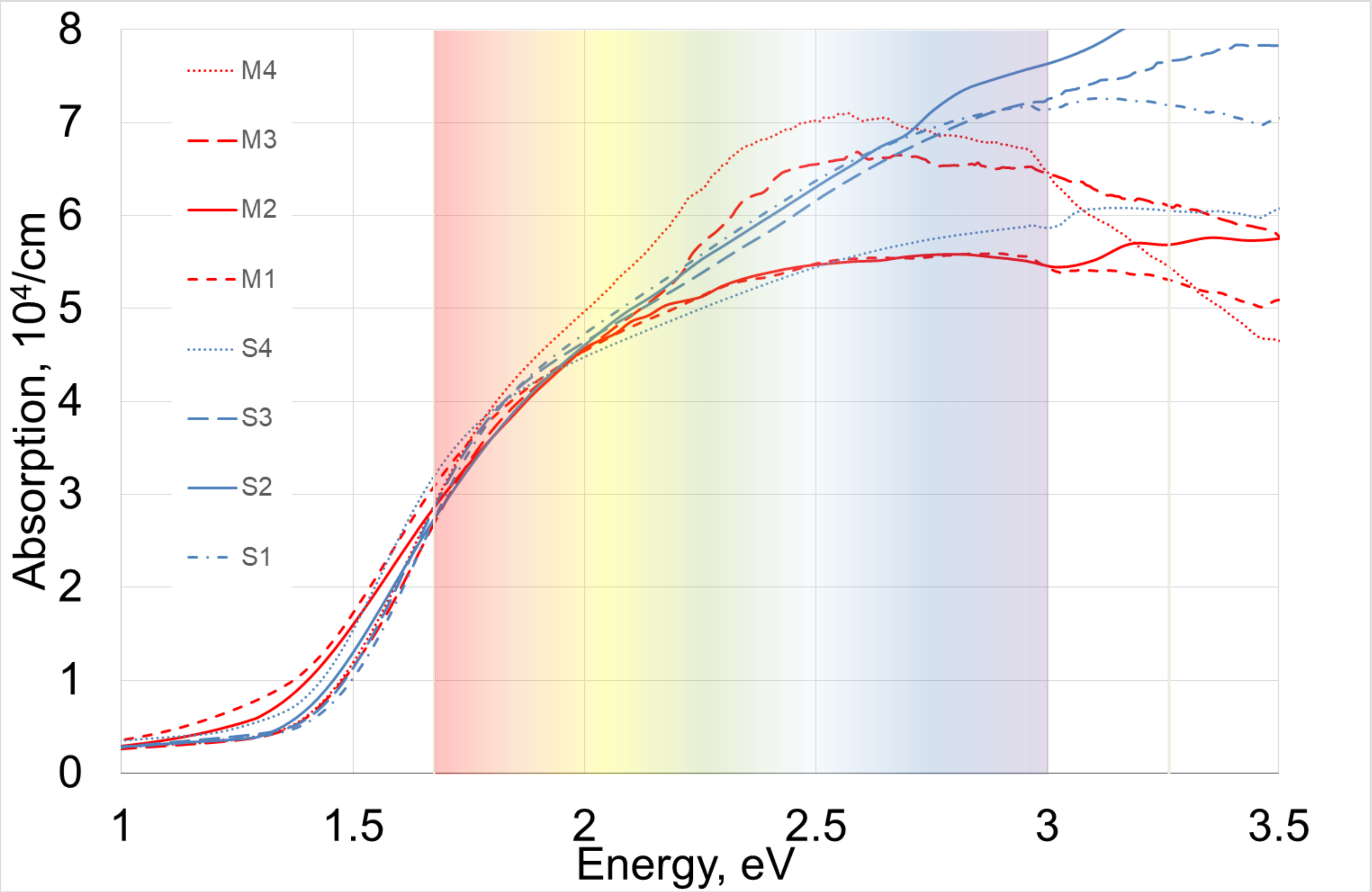
Results by UV-vis spectroscopy



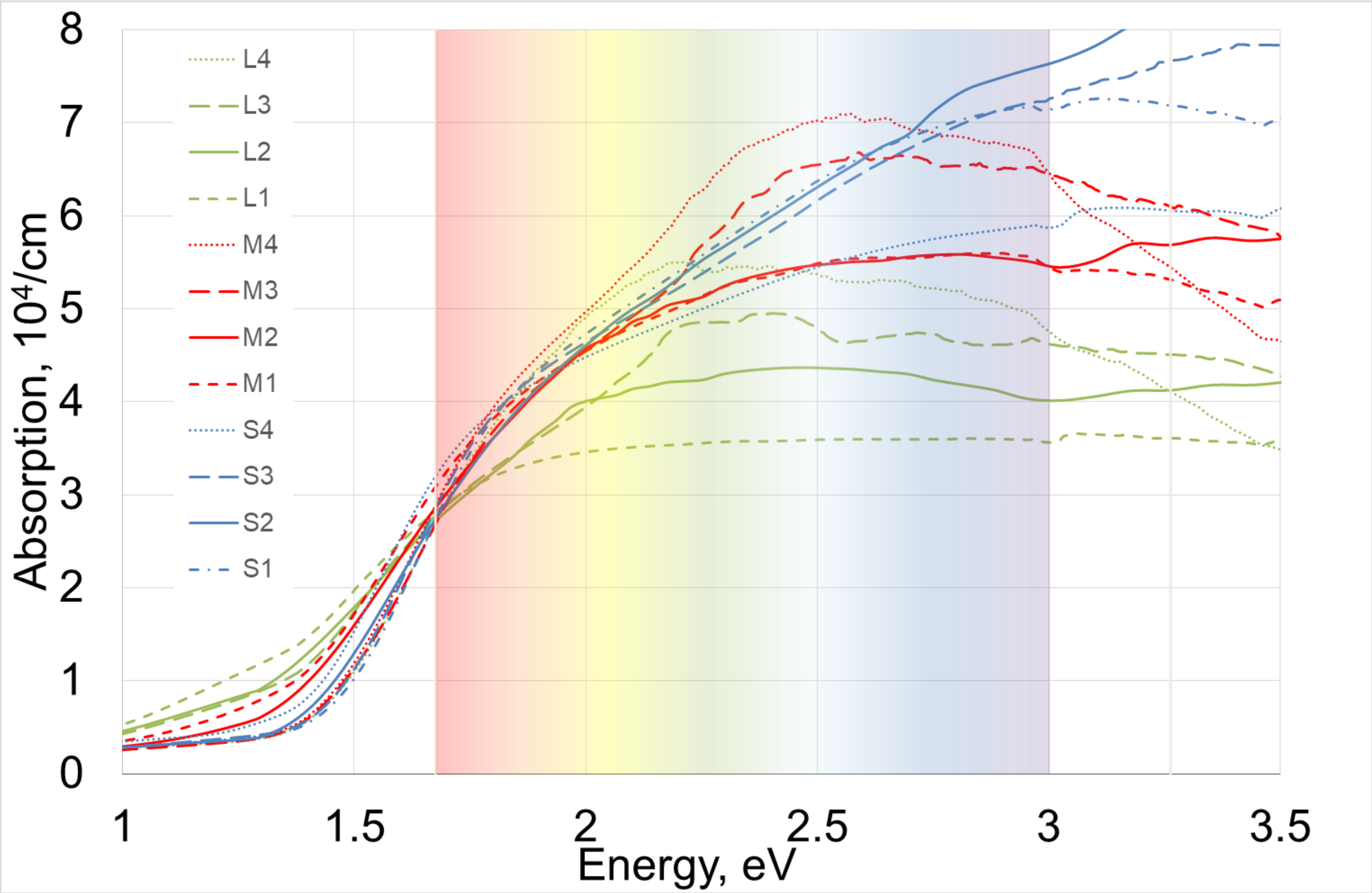
- α (S) in visible spectrum range

Results by UV-vis spectroscopy



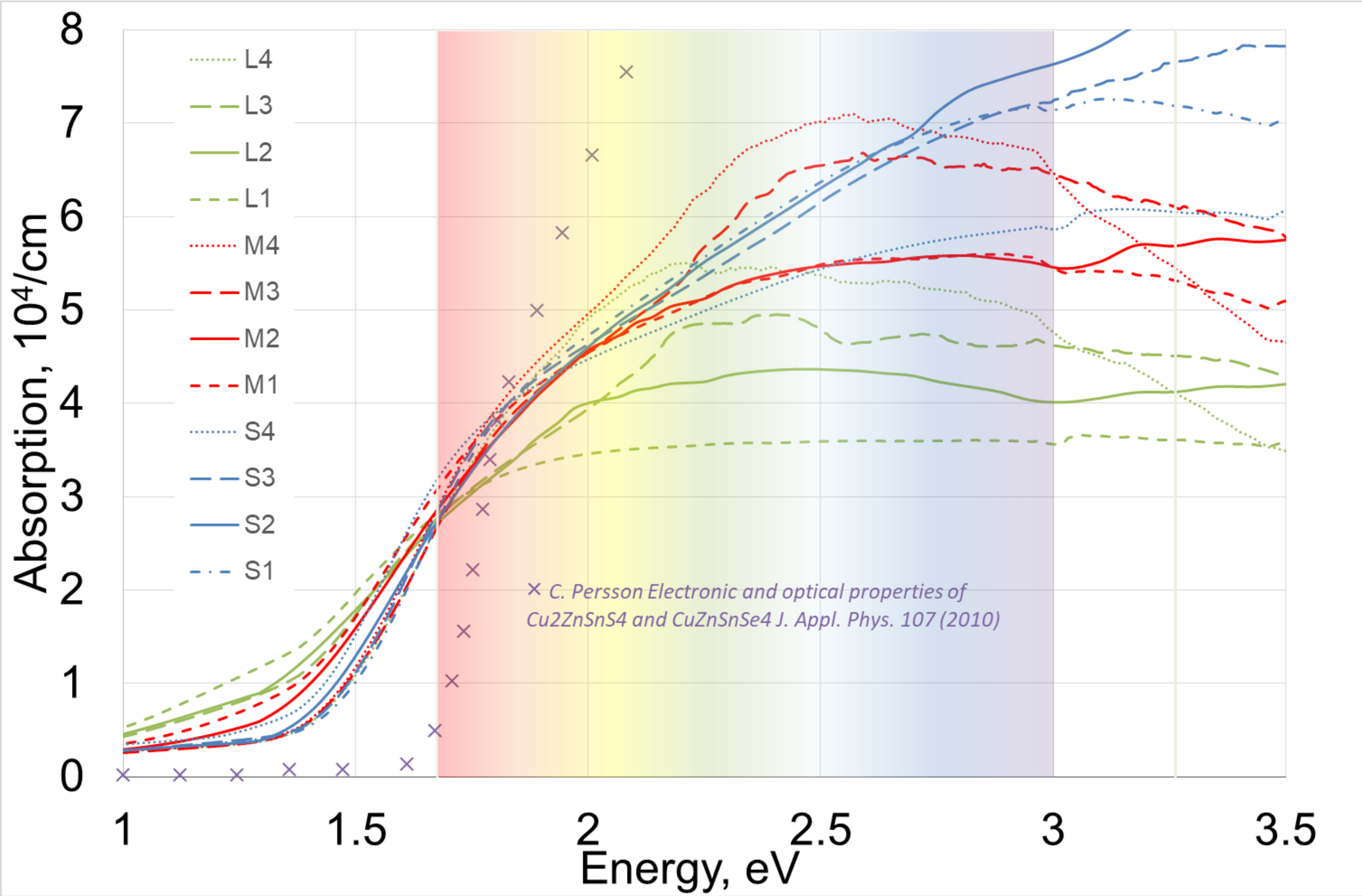
- α (S) > α (M) in visible spectrum range

Results by UV-vis spectroscopy



- α (S) > α (M) > α (L) in visible spectrum range

Results by UV-vis spectroscopy



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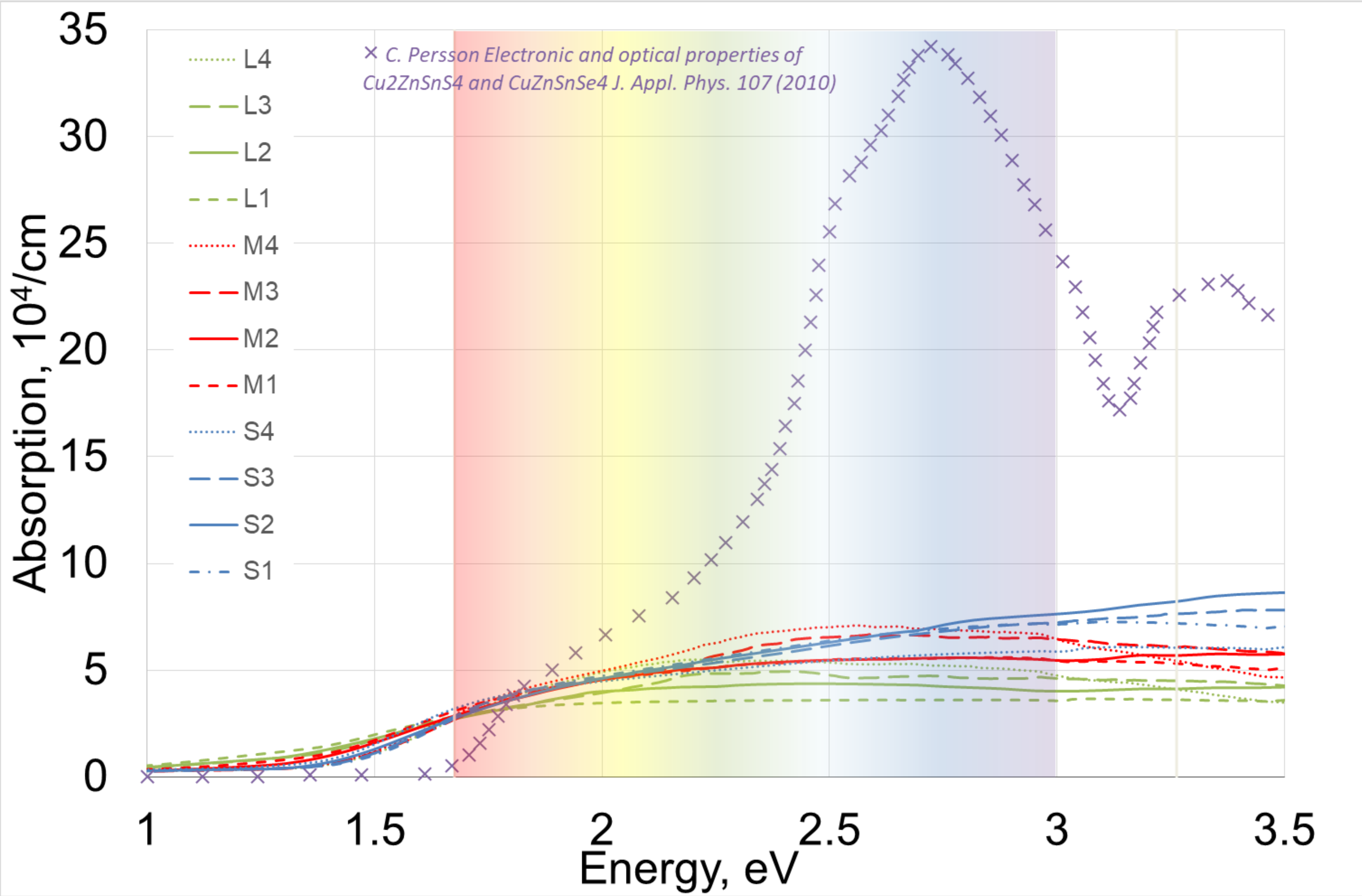

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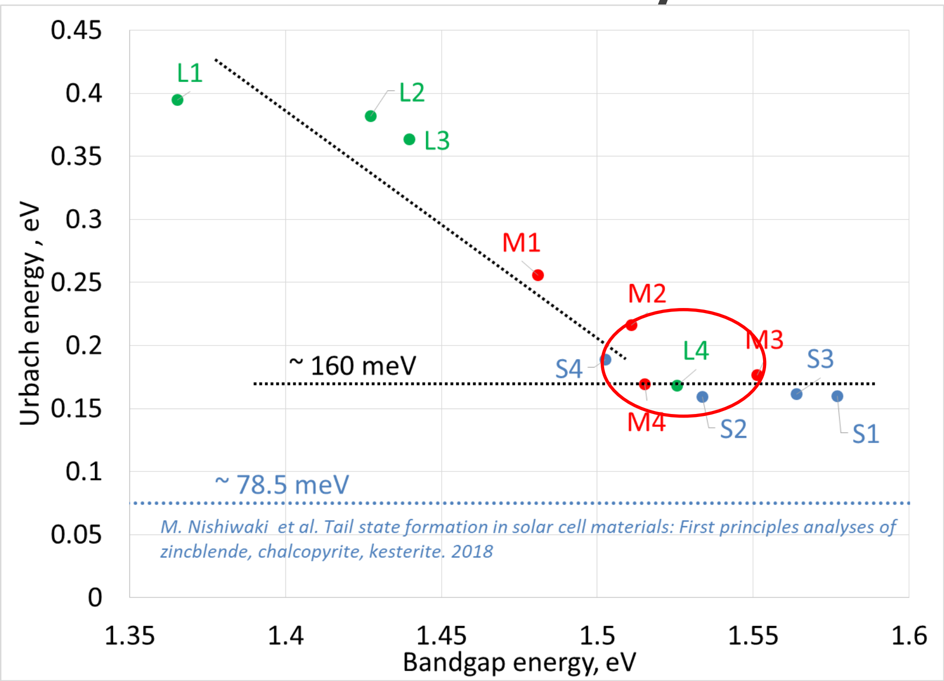
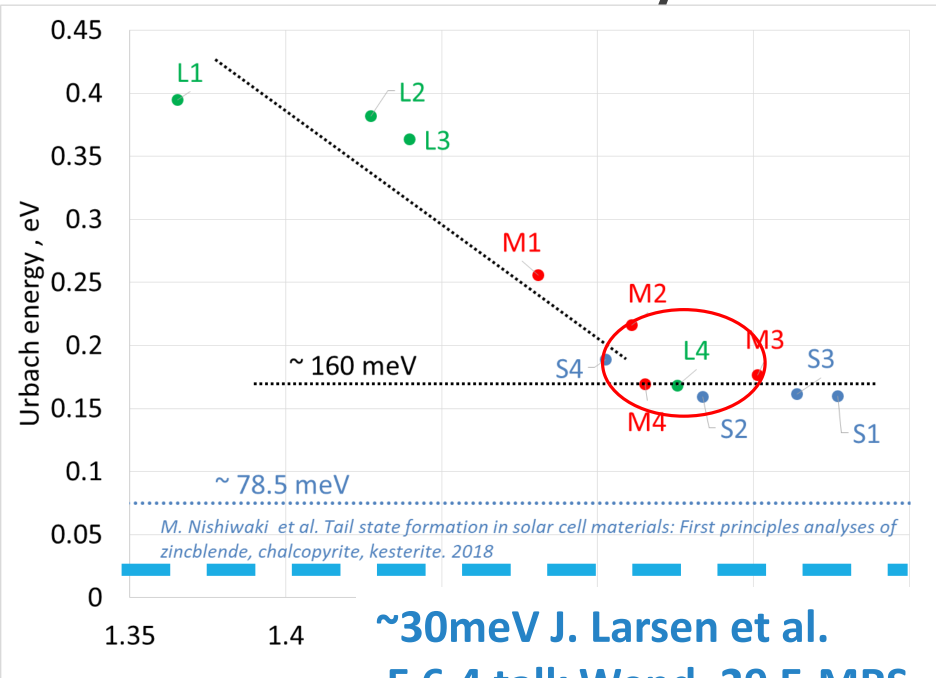


- E_G, E_U (Small) < E_G, E_U (Medium) < E_G, E_U (Large)

Results by UV-vis spectroscopy



~30meV J. Larsen et al.
E 6.4 talk Wend. 29 E-MRS

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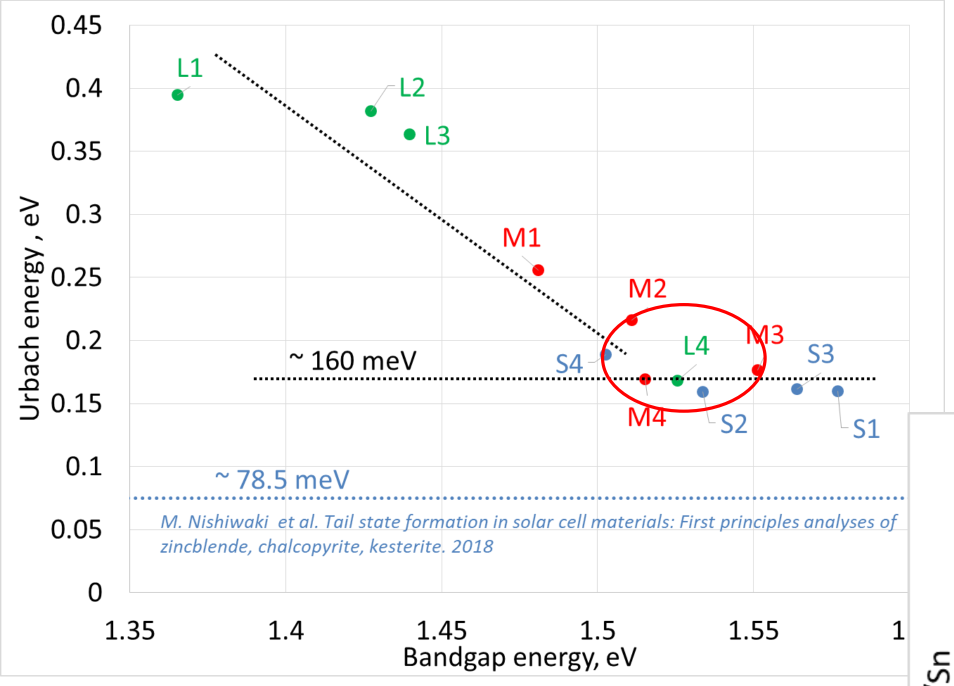
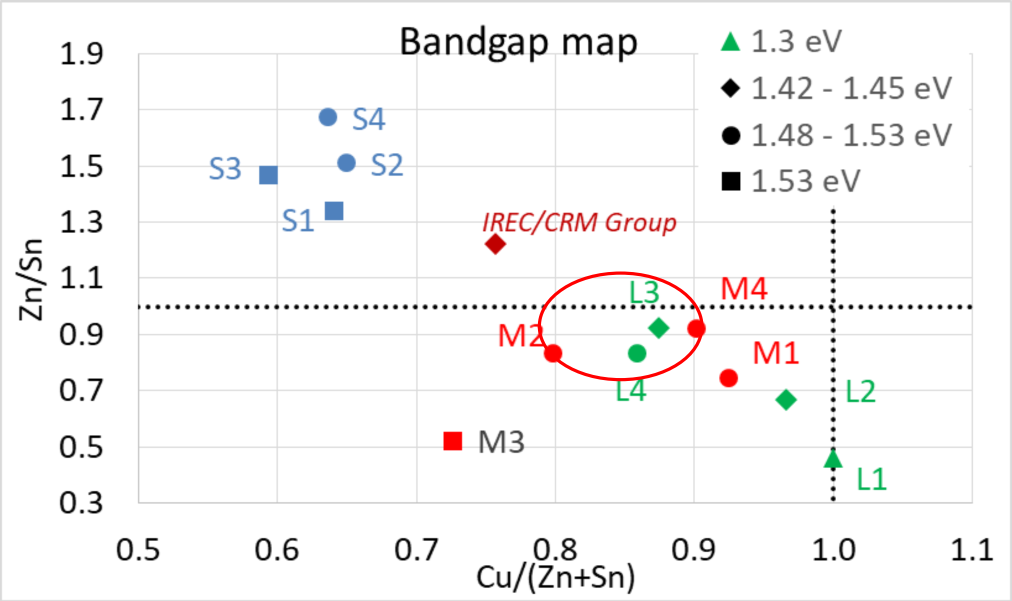
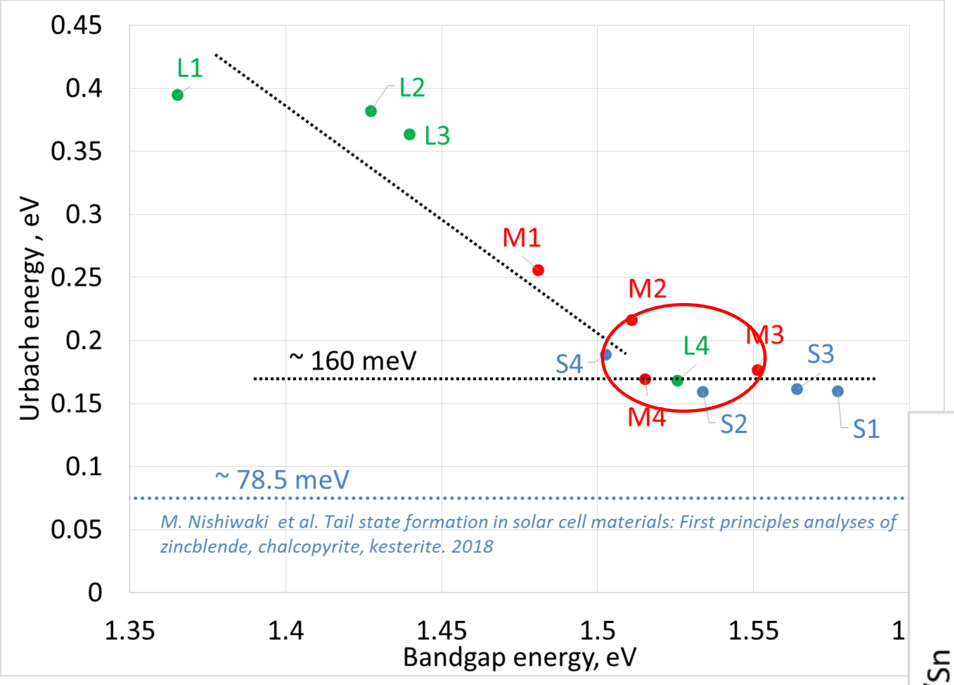
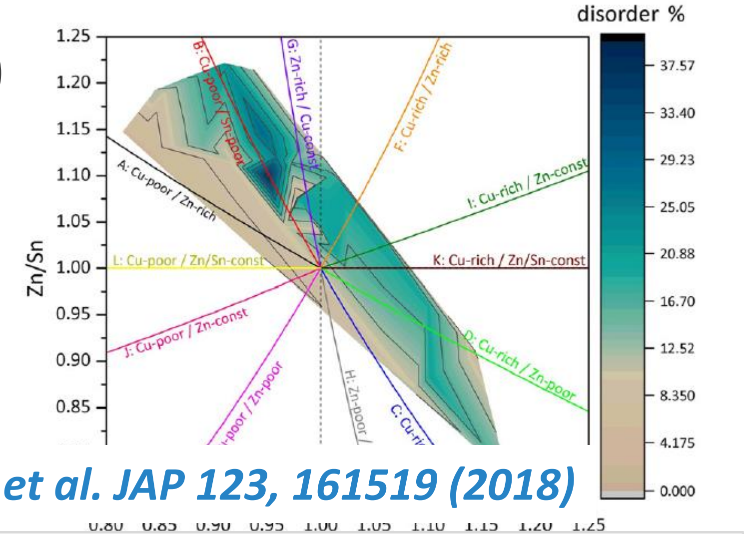




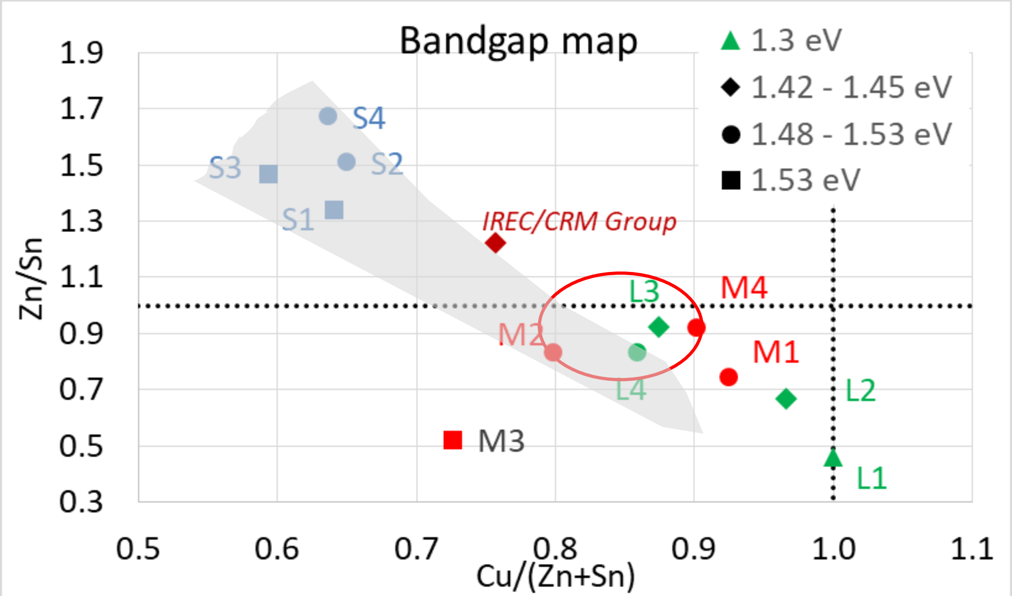
- E_G, E_U (Small) < E_G, E_U (Medium) < E_G, E_U (Large)
- Band gap decreases with Cu/Sn increases

Results by UV-vis sp





Gurieva et al. JAP 123, 161519 (2018)



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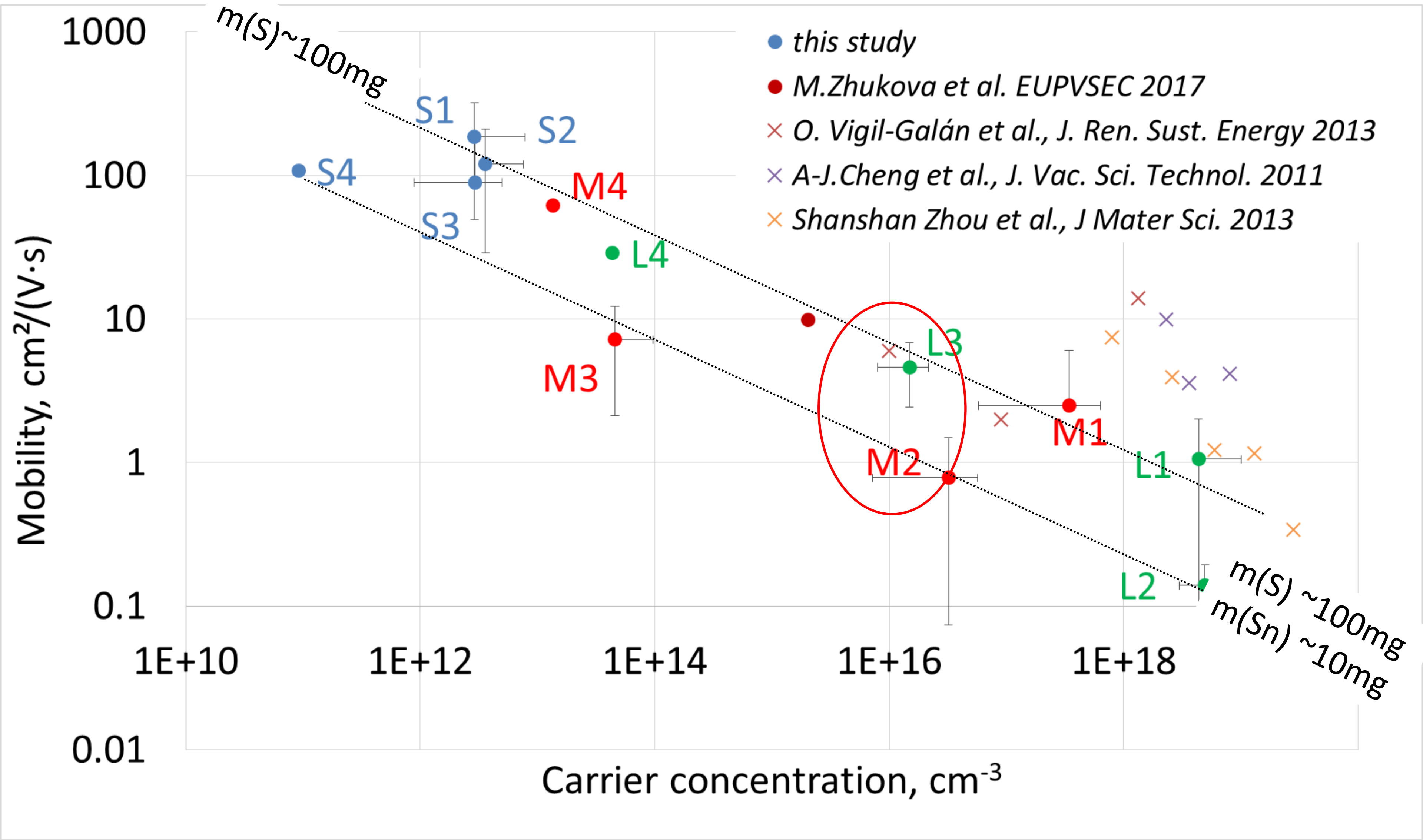
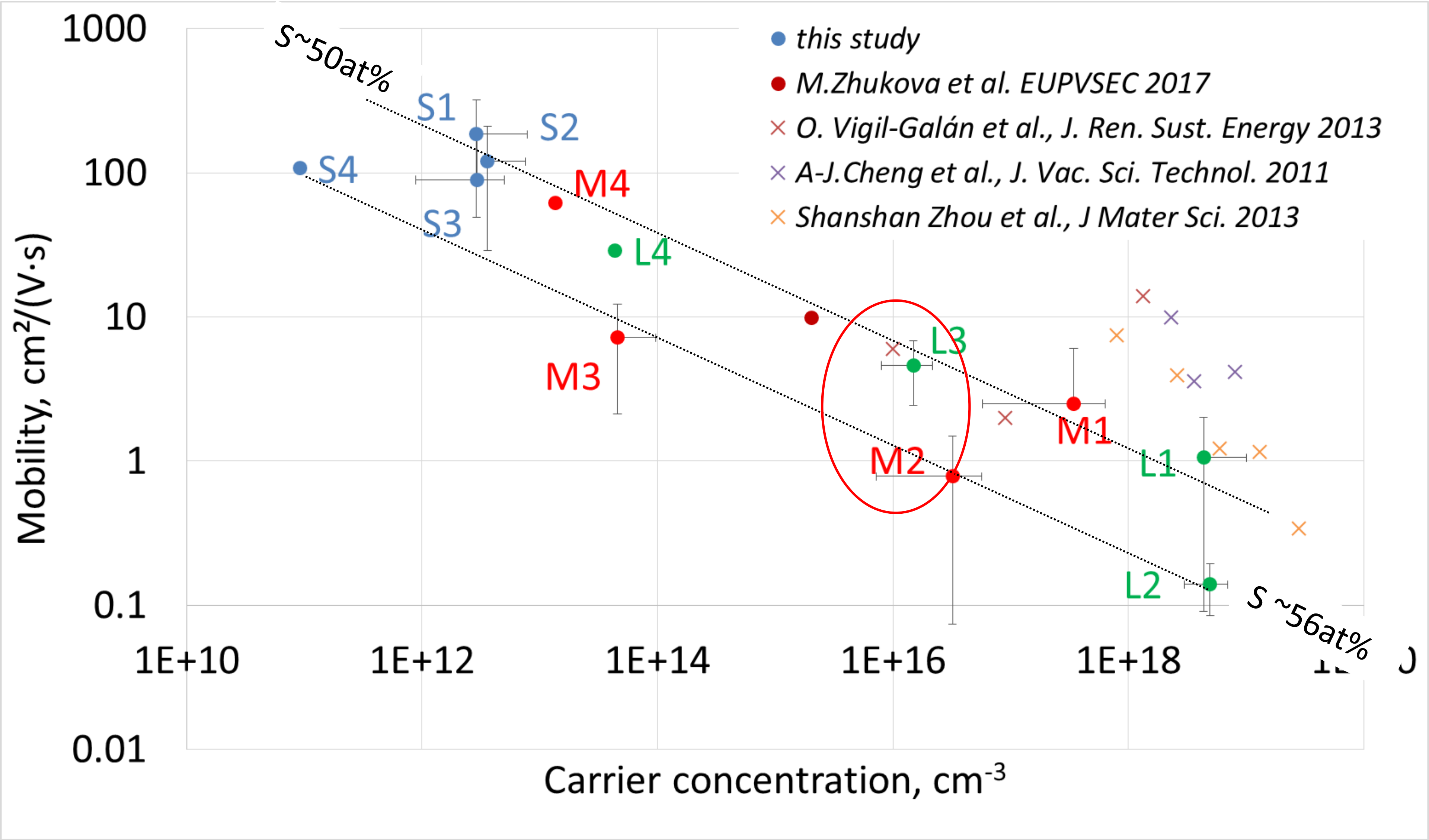
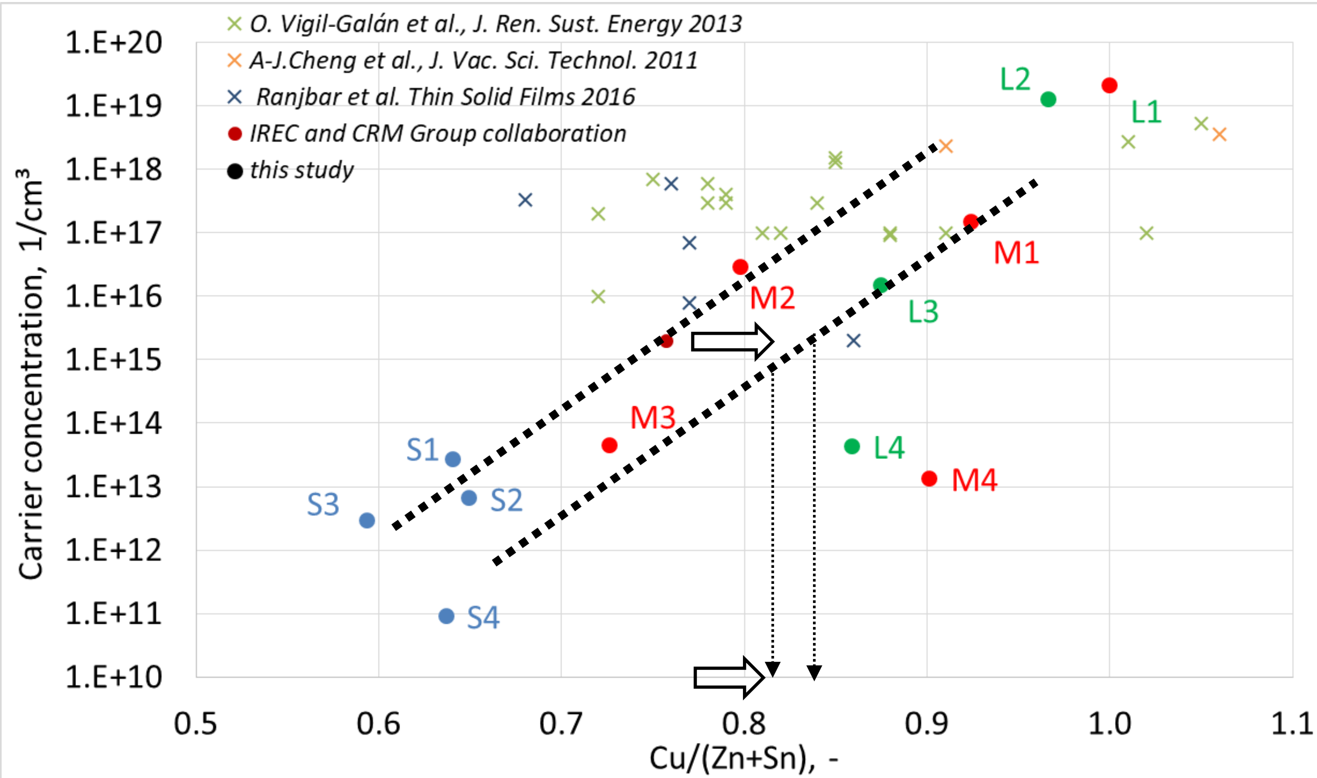
Results by Hall measurement



Results by Hall measurement



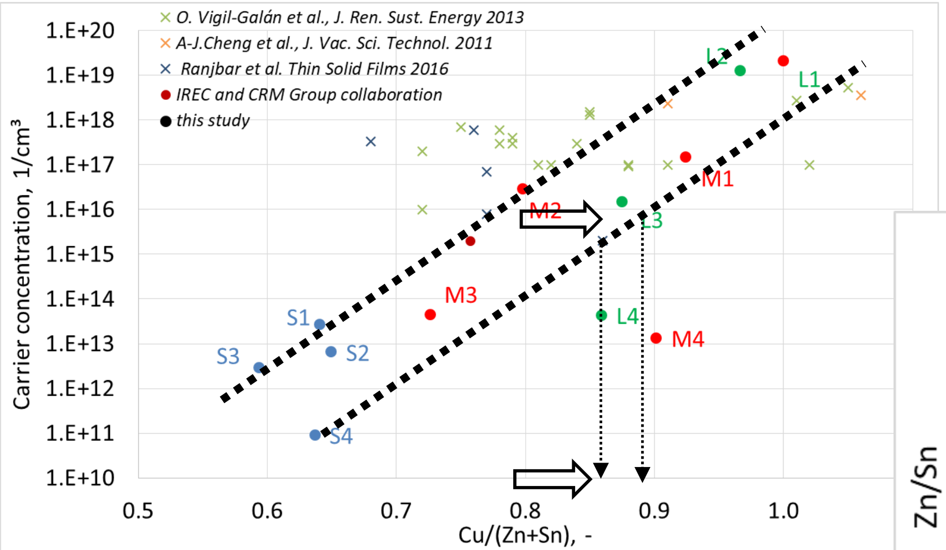
Correlation with composition

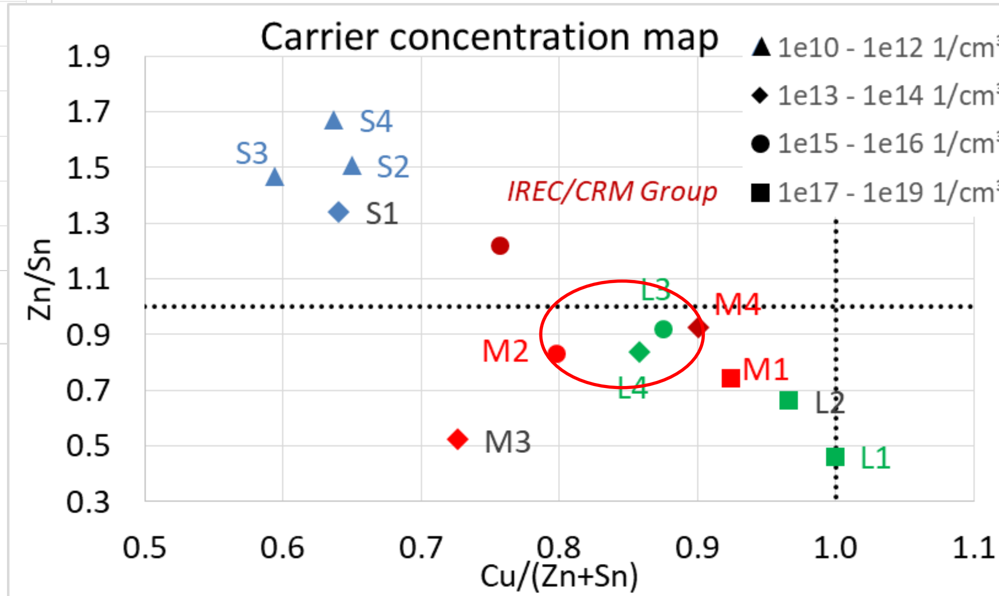


➔ Copper concentration impacts the carriers density

** Liyuan Zhang et al. Chemical Composition Dependence of Cu2ZnSnS4 Absorbers Fabricated by Sulfurization of Thermal Evaporated Metal Precursors and Solar Cell Performance MRS 2015*

Correlation with composition





➔ Copper concentration impacts the carriers density

➔ Optimum shift to less Cu-poor, less Zn-rich

Outline

- SCAPS simulation
- CZTS fabrication
- Material characterization
- Optoelectrical characterization
- Conclusions

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Conclusions and perspectives

- Simulation predicts:

  Efficiency >10 %

  E_G > 1.5 eV

  $\alpha > 4\times10^4$ cm^{-3}

  c.c ~ 10^{15} -10^{16} cm^{-3}

  μ_h > 10 cm²/(V.s)

at.%	Stoichio metry	Ref*	New
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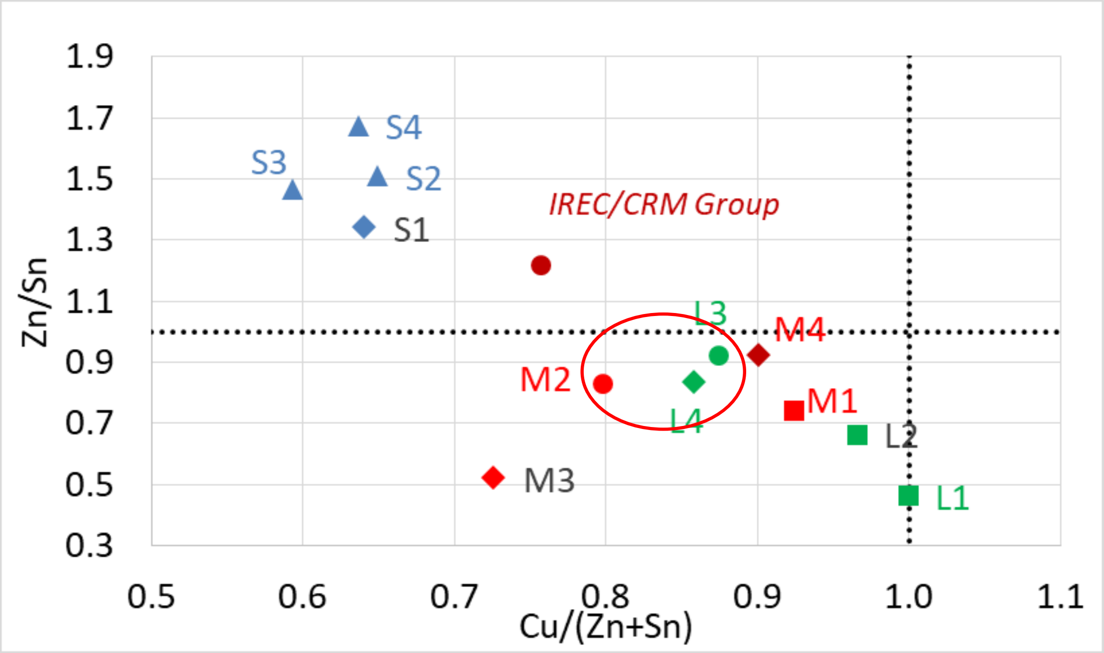
Zn	12.5	15.6	12
Sn	12.5	12.8	13.9
S	50	50	51.5



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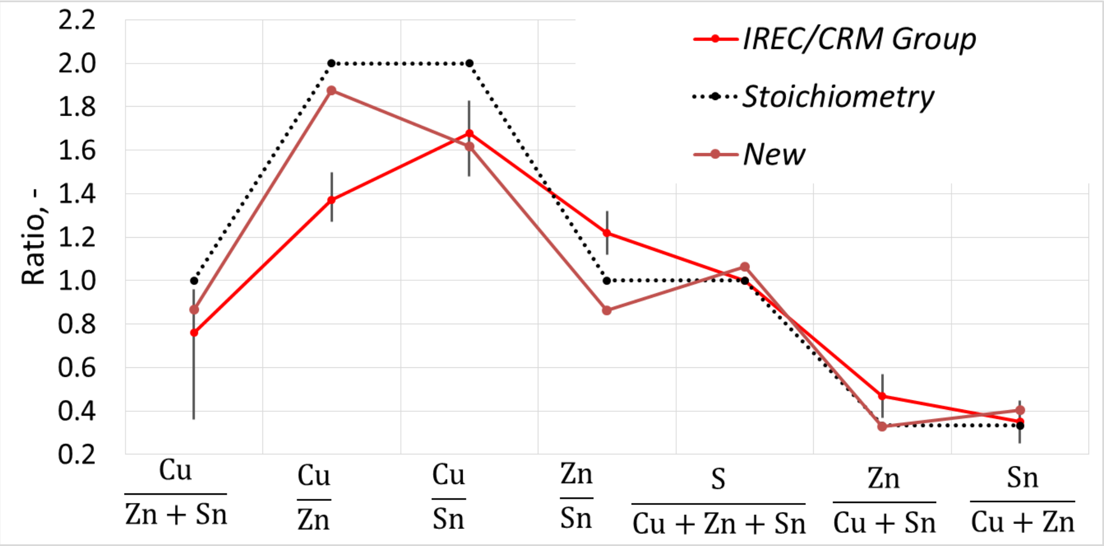
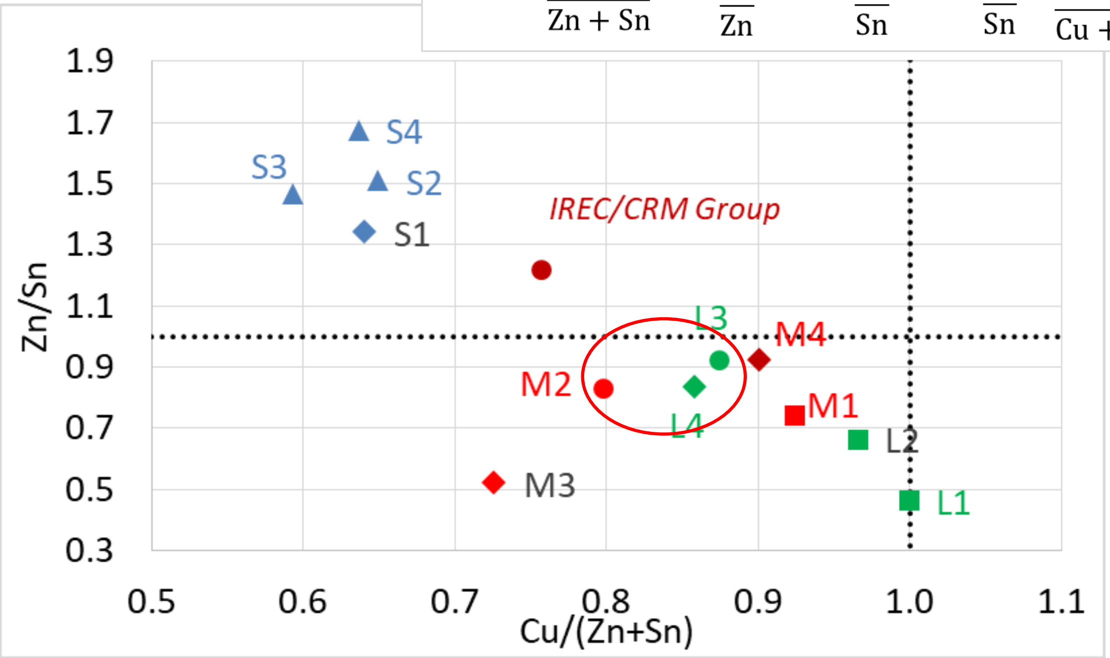
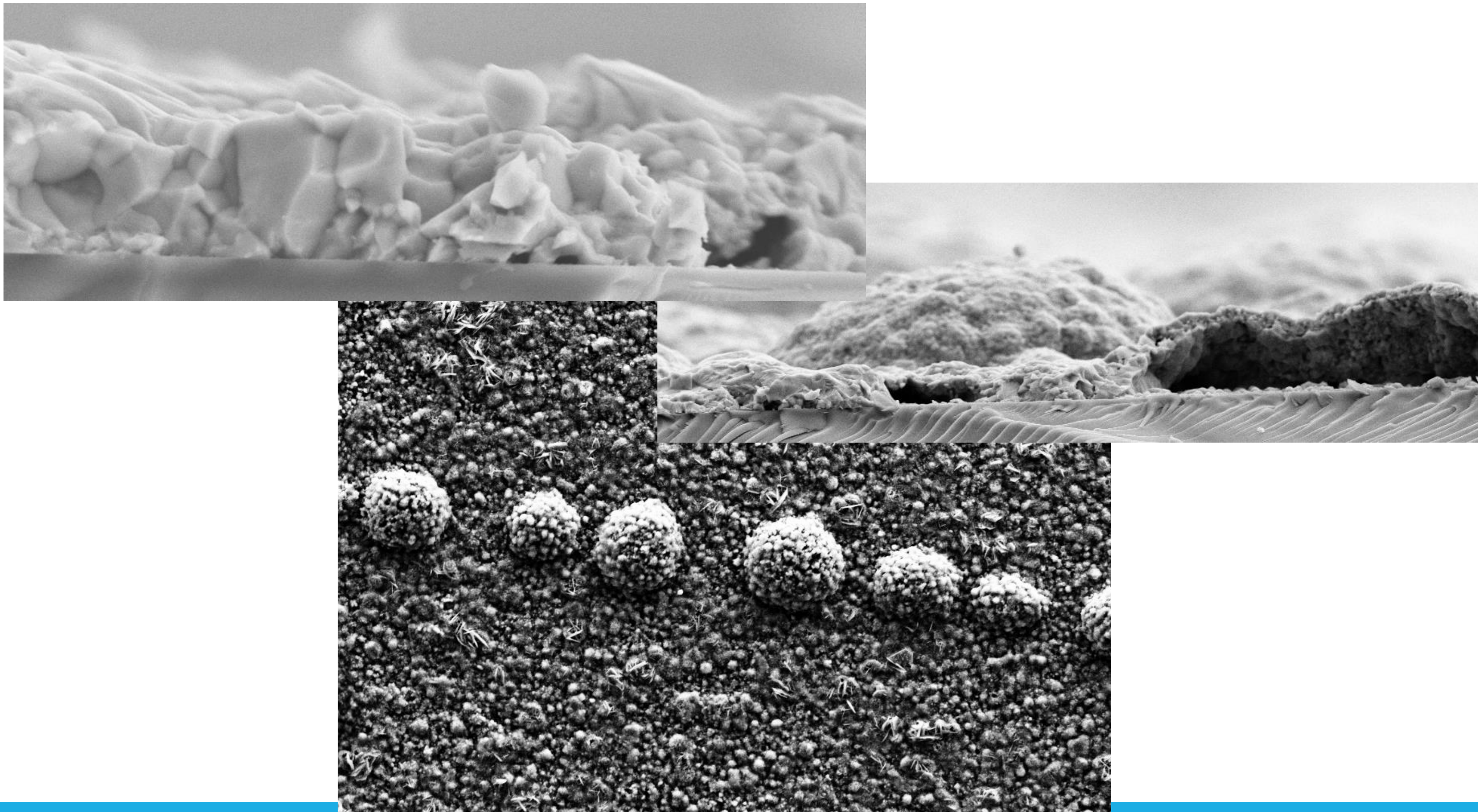




Thank you!



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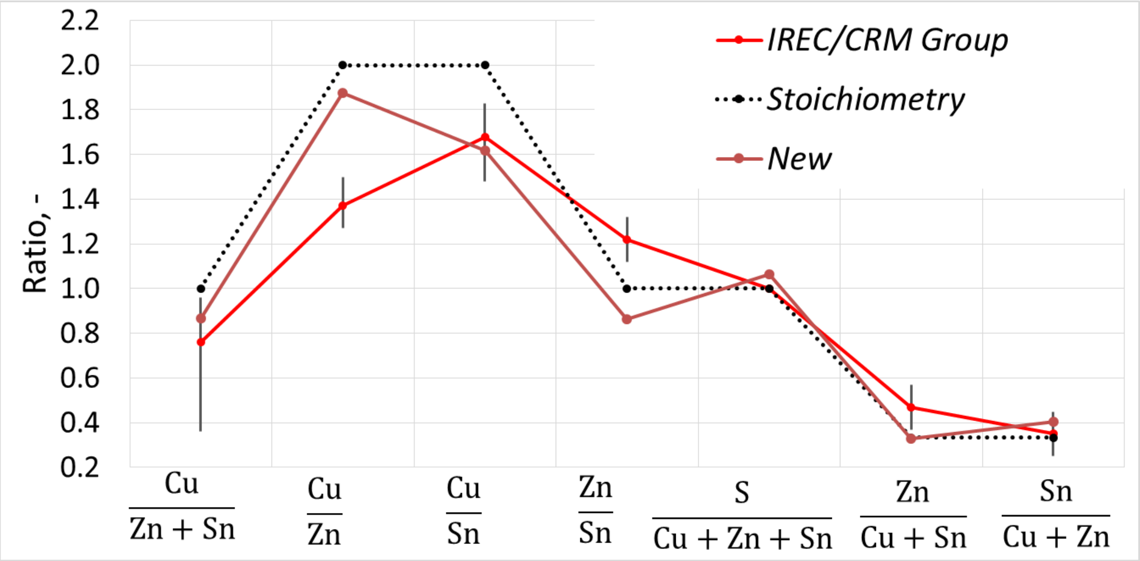

- Precursor thickness as well as RTP conditions impact on the final CZTS layer
- The absorption is about 4×10^4 cm^{-3}
- Cu~22.5at% poor Zn~12at% rich composition is distinguished as an optimum based on optoelectrical properties

at.%	Stoichiometry	Ref*	New
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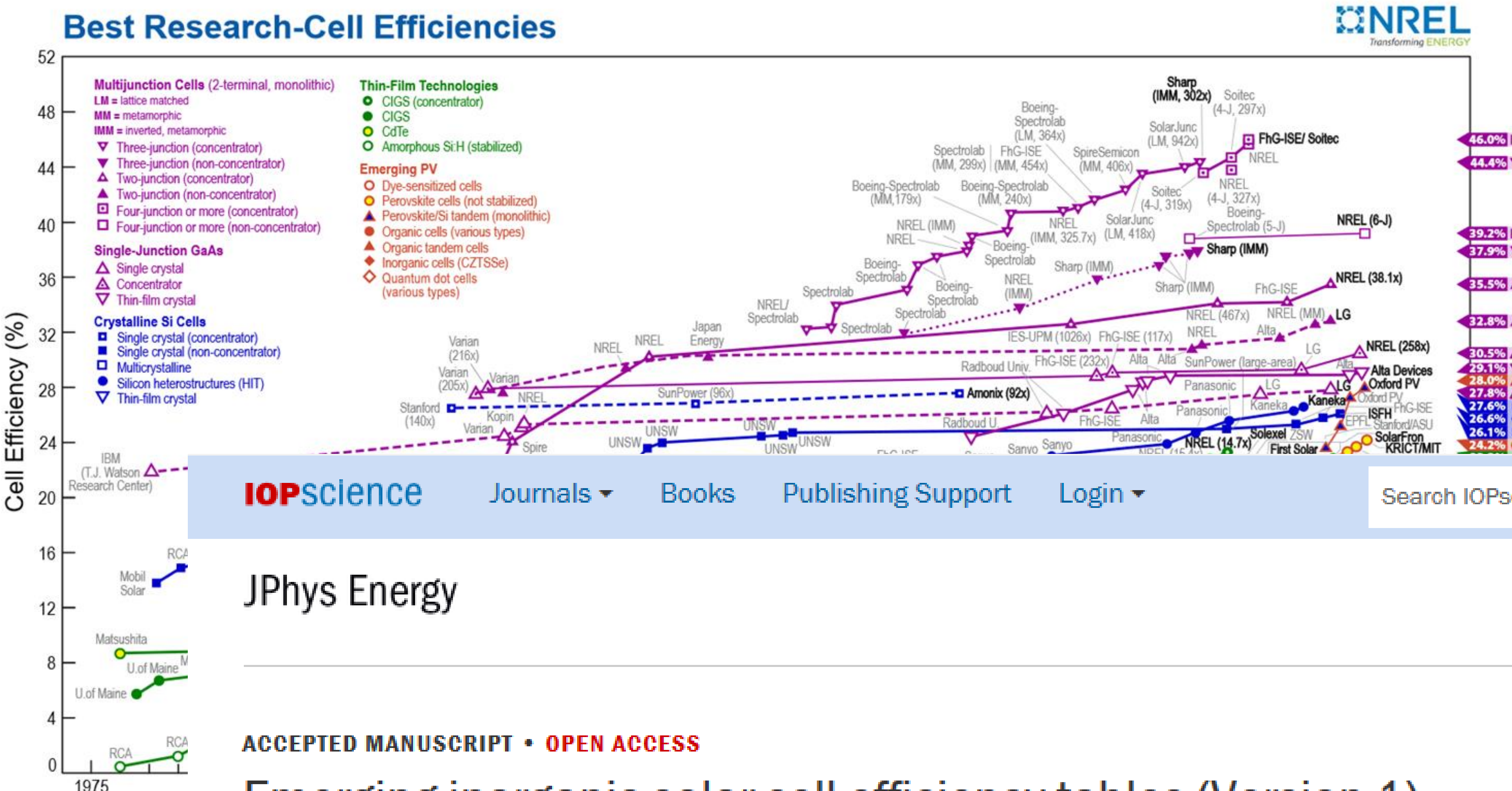

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Emerging inorganic solar cell efficiency tables (Version 1)

Lydia Helena Wong[1], Andriy Zakutayev[2], Jonathan Douglas Major[3], Xiaojing Hao[4], Aron Walsh[5], Teodor K. Todorov[6] and Edgardo Saucedo[7]

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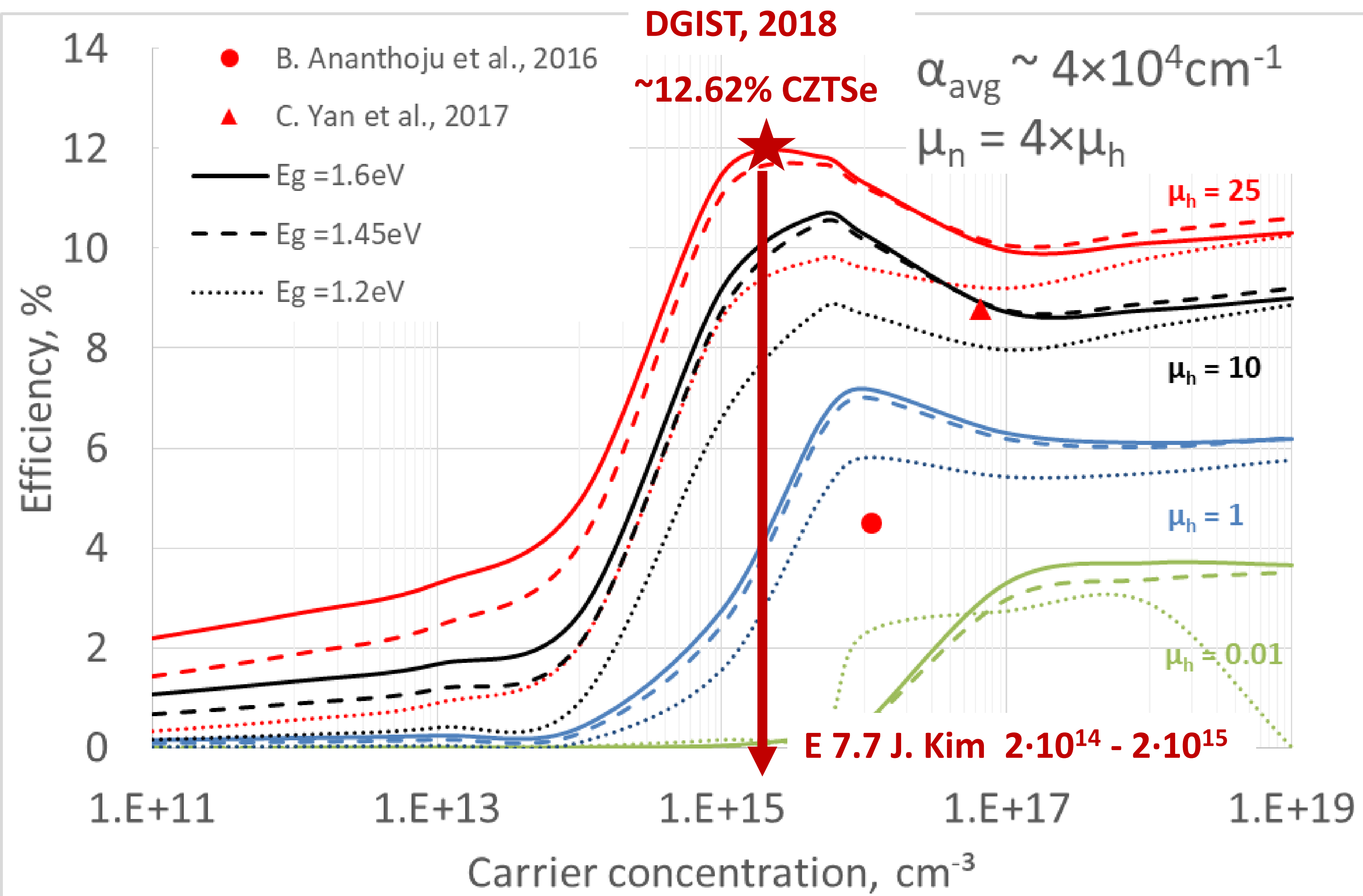
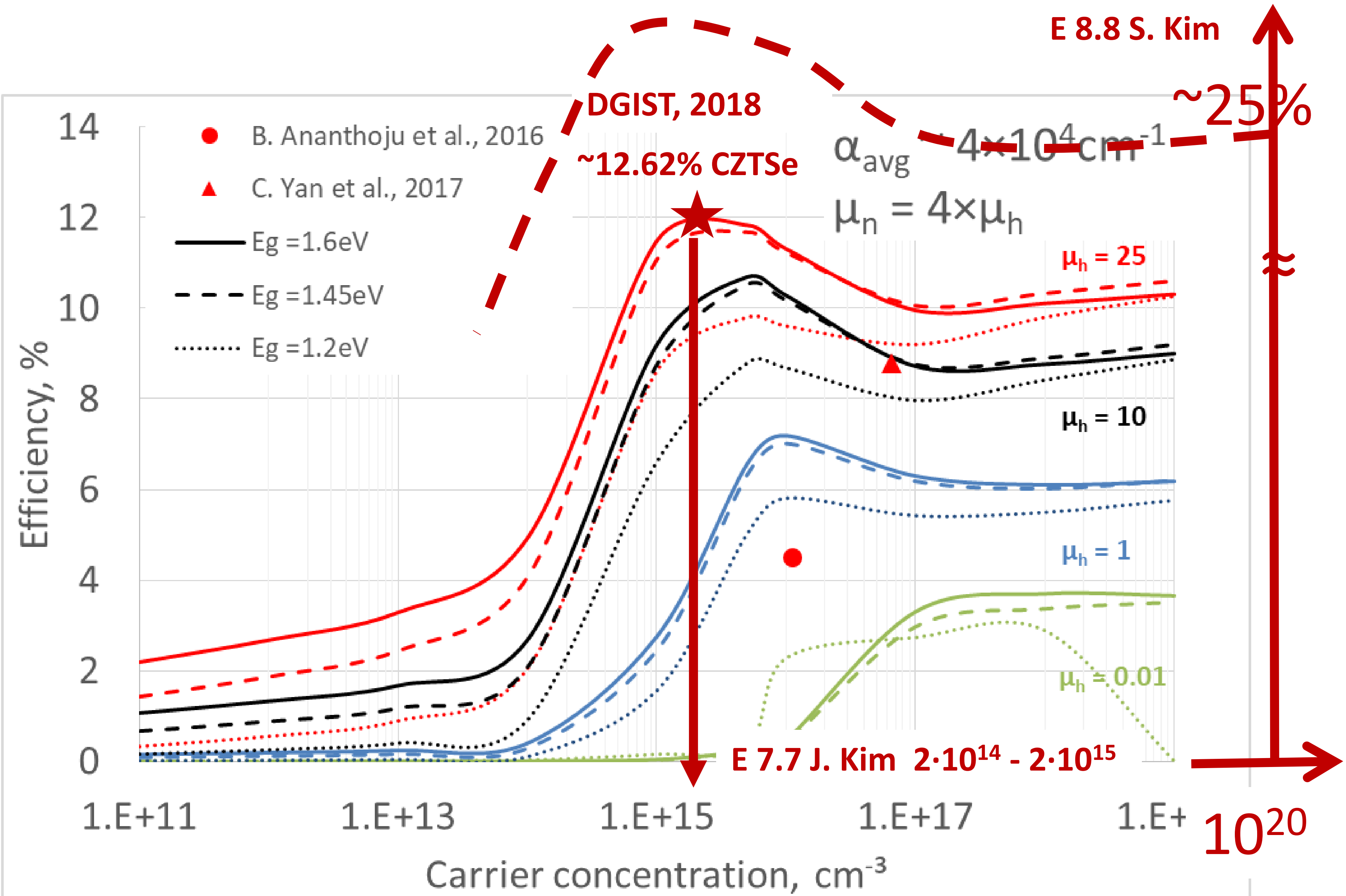
Results of SCAPS* simulations:



* Solar cell CAPacitance Simulator http://scaps.elis.ugent.be



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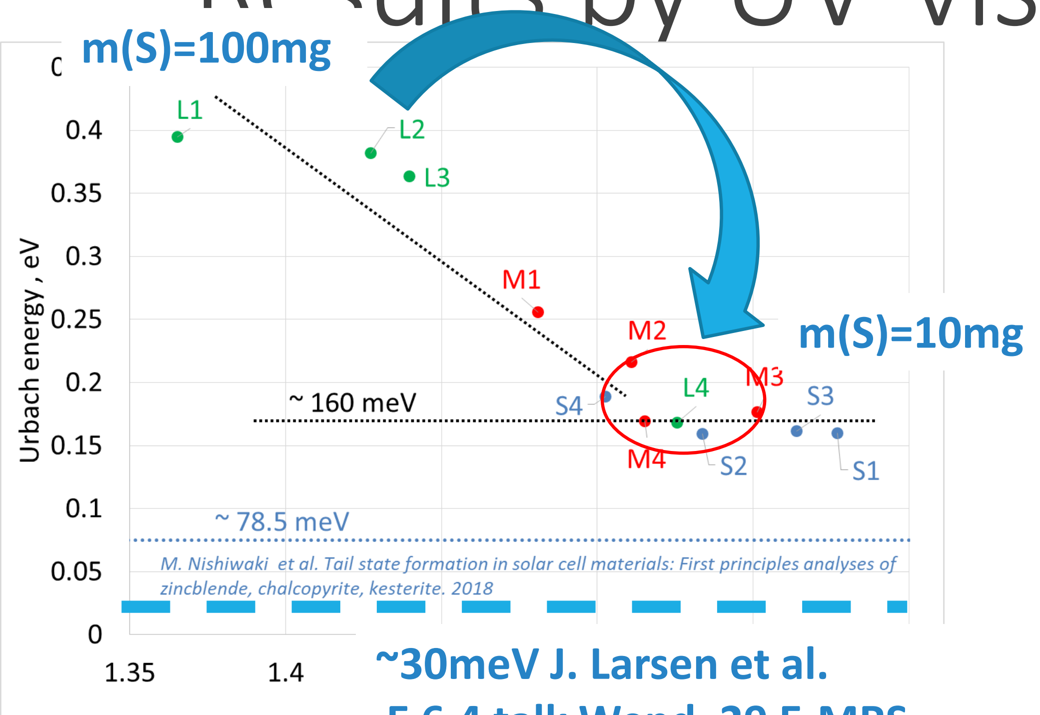
Results by UV-vis spectroscopy



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E 6.4 talk Wend. 29 E-MRS

- E_G, E_U (Small) < E_G, E_U (Medium) < E_G, E_U (Large)