CZTSSe thin-films and solar cells: effects of Cu-Zn order-disorder transition

Germain Rey

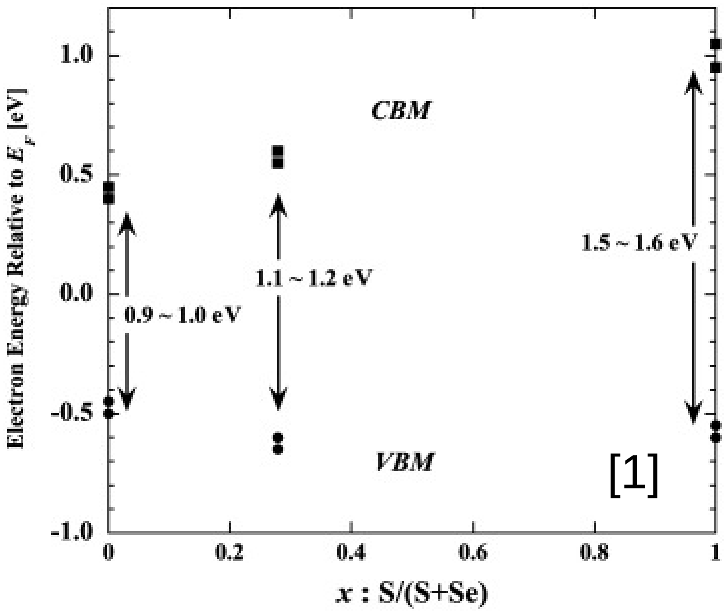
Now at UNSW

Formerly at University of Luxembourg

SPREE Seminar, Sydney, 22th November 2018

Introduction

- CZTS : Cu_2ZnSnS_4
  - Eg = 1.5 eV
- CZTSe : $Cu_2ZnSnSe_4$
  - Eg = 1.0 eV
- CZTSSe : $Cu_2ZnSn(S,Se)_4$
  - Eg = 1.0-1.5 eV

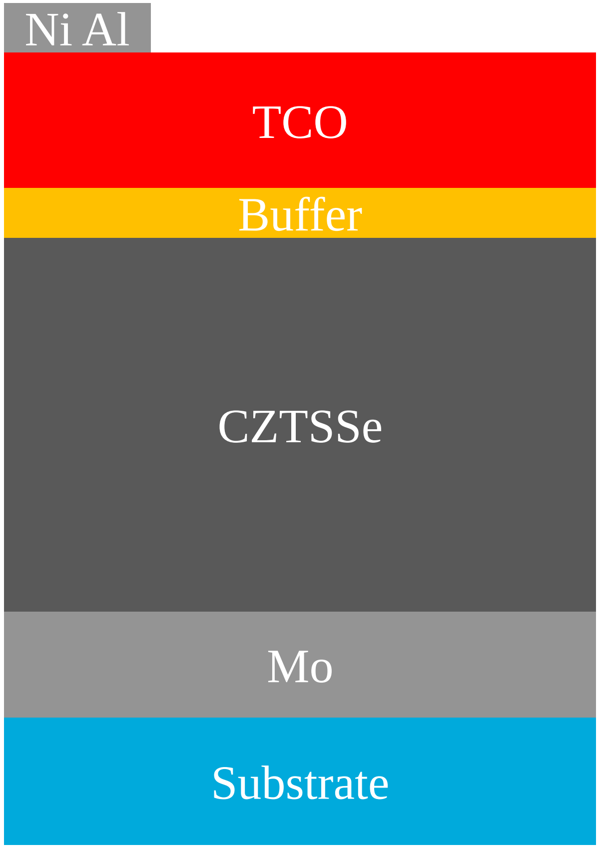


[1] N. Terada *et al.* Thin Solid Films **582** (2015) 166

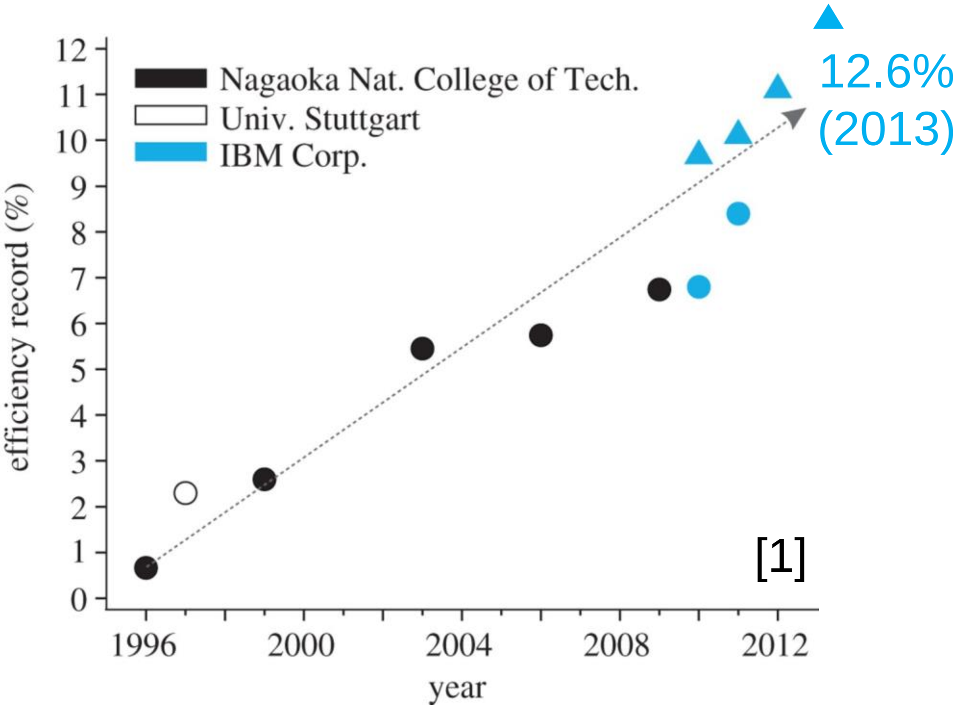
- Large absorption coefficient for hν > Eg
- Non-toxic and abundant metals

Introduction

- Cell structure



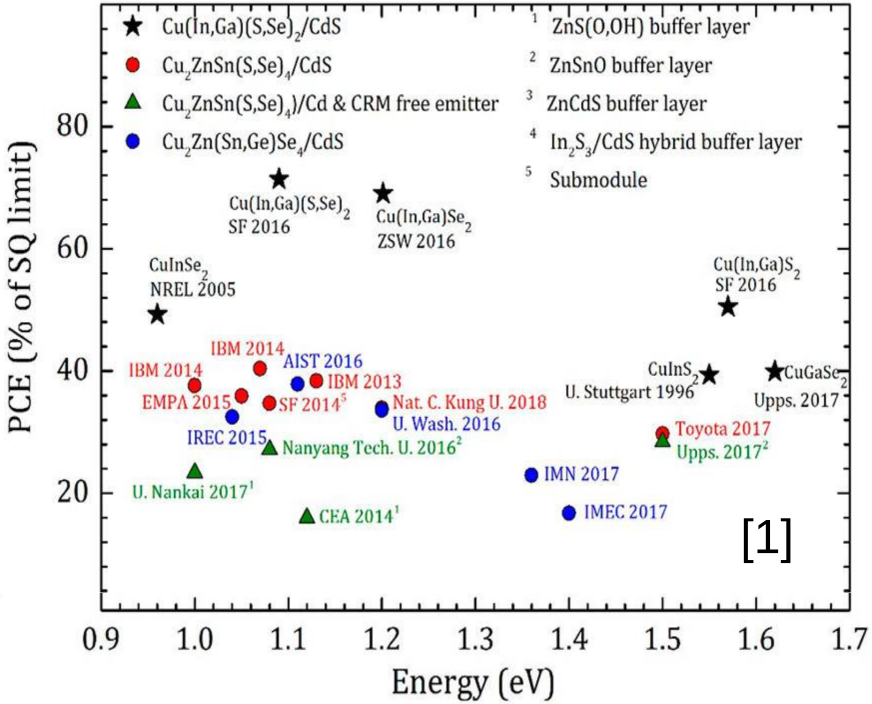
- Efficiency

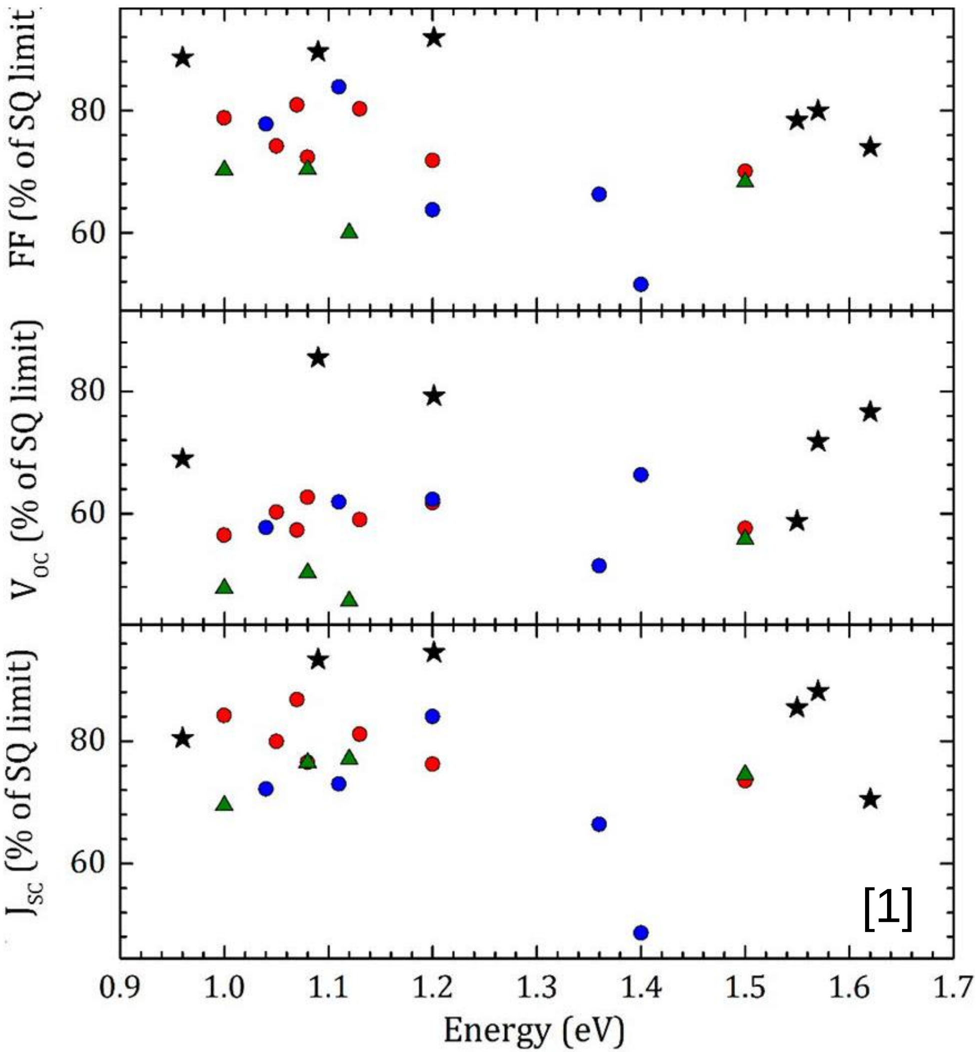


[1] D. B. Mitzi, *et al.* Phil. Trans. R. Soc. A **371** (2013) 20110432

Introduction

- Efficiency limitation

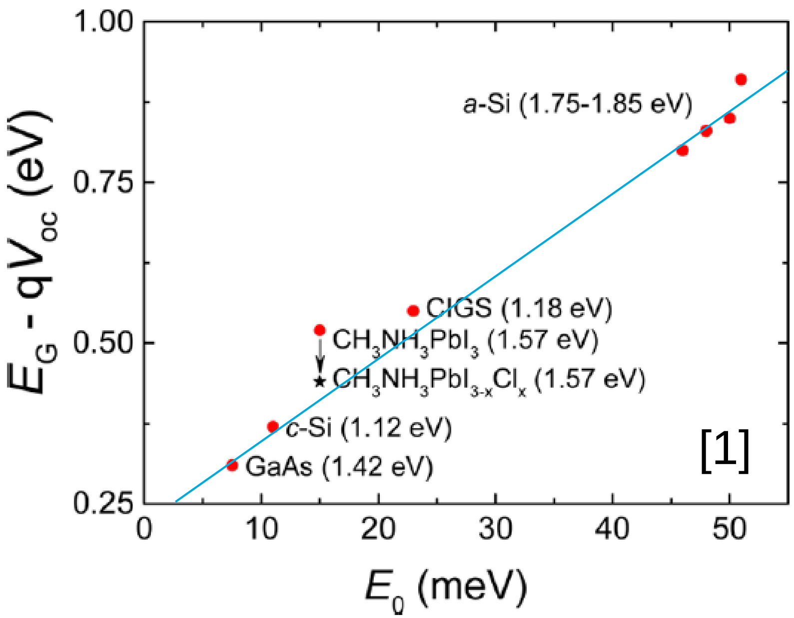


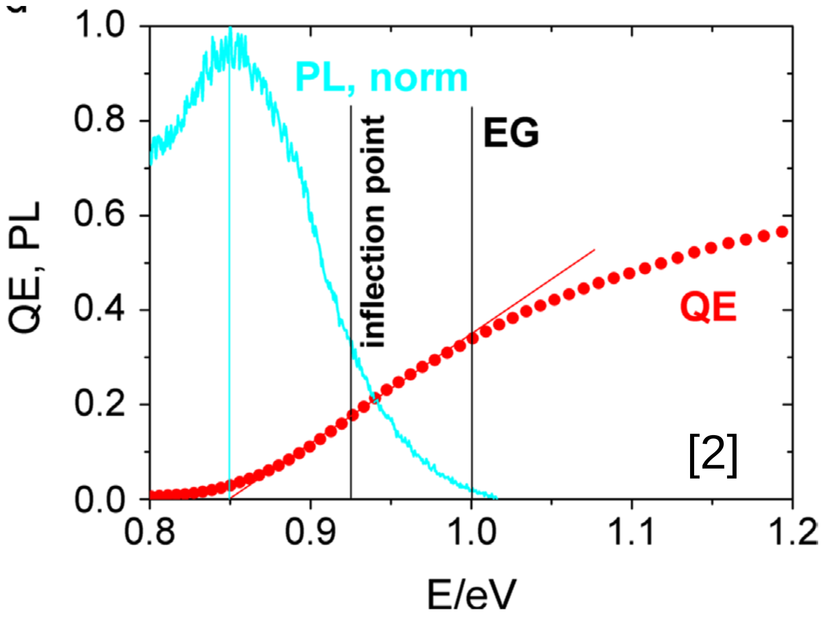


[1] L. Grenet, *et al.* Appl. Ener. Mat. **1** (2018) 2103

Introduction

- Voc and Band-tails



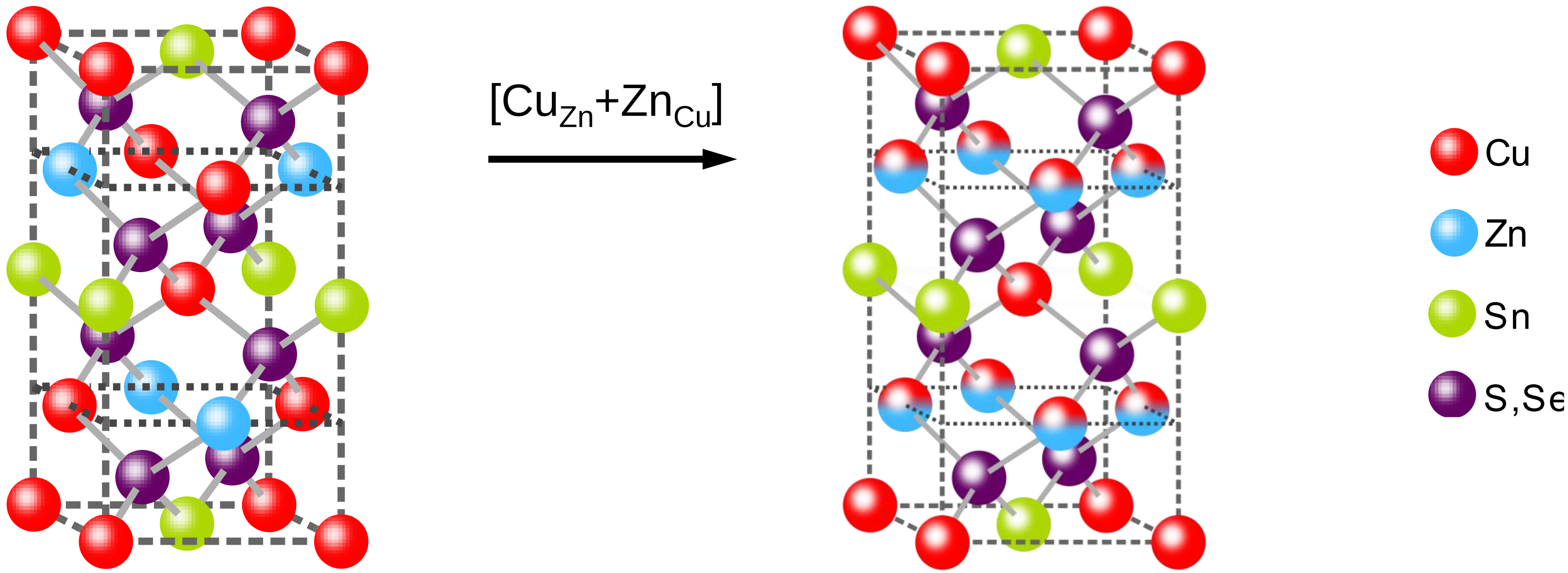


[1] S. De Wolf *et al.* J. Phys. Chem. Lett., **5** (2014) 1035

[2] S. Siebentritt *et al.* Sol. Ener. Mat. & Sol. Cells, **158** (2016) 126

Introduction

- Ordered Kesterite
- Disordered Kesterite

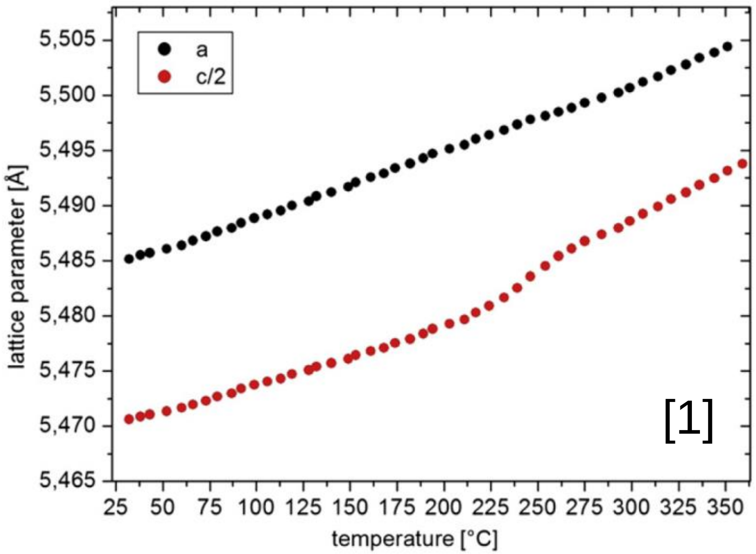


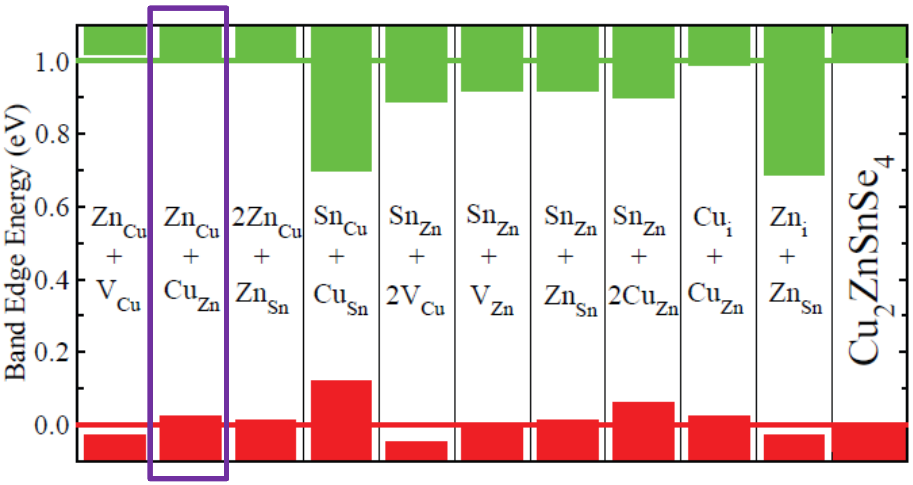
- Structural observation of disorder in Cu/Zn planes:
  - Neutron diffraction [1], NMR [2], anomalous XRD [3]
- Theoretical prediction:
  - Low formation energy of [Cu_{Zn}+Zn_{Cu}] [4]

[1] S. Schorr SEM&SC **95** (2011) 1482
[2] L. Choubrac *et al.* PCCP **15** (2013) 10722
[3] A. Lafond *et al.* Acta Cryst. B **70** (2014) 390
[4] S. Chen *et al.* Adv. Mater. **25** (2013) 1522

Introduction

- Cu-Zn Disorder:
  - Increase in unit cell volume
  - Rise Valence band



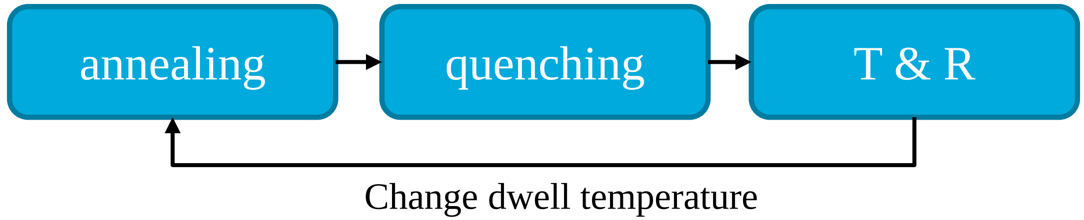


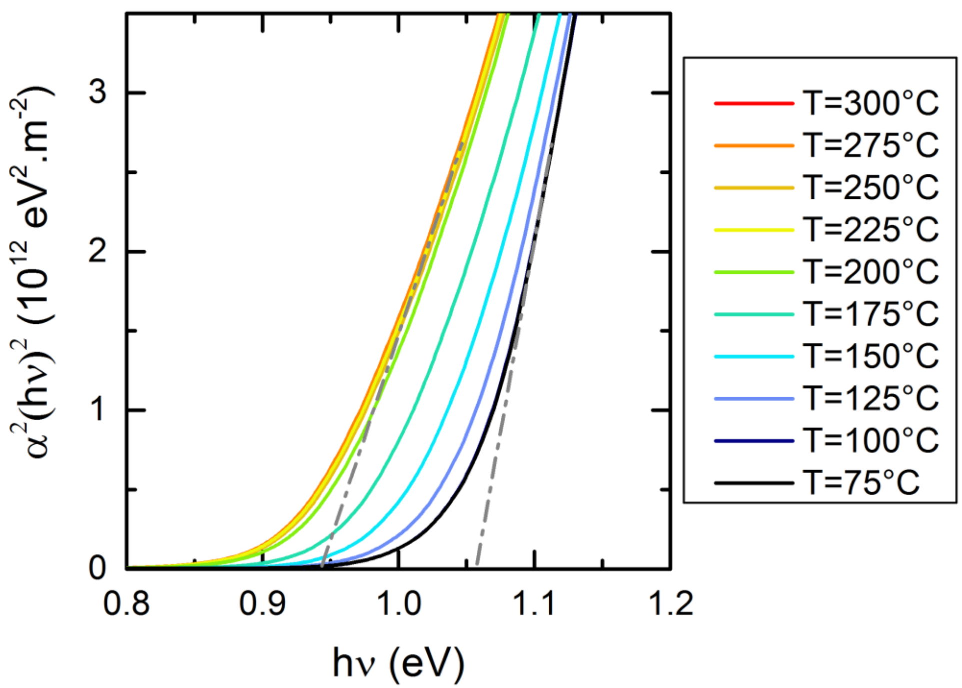
[1] S. Schorr SEM&SC **95** (2011) 1482

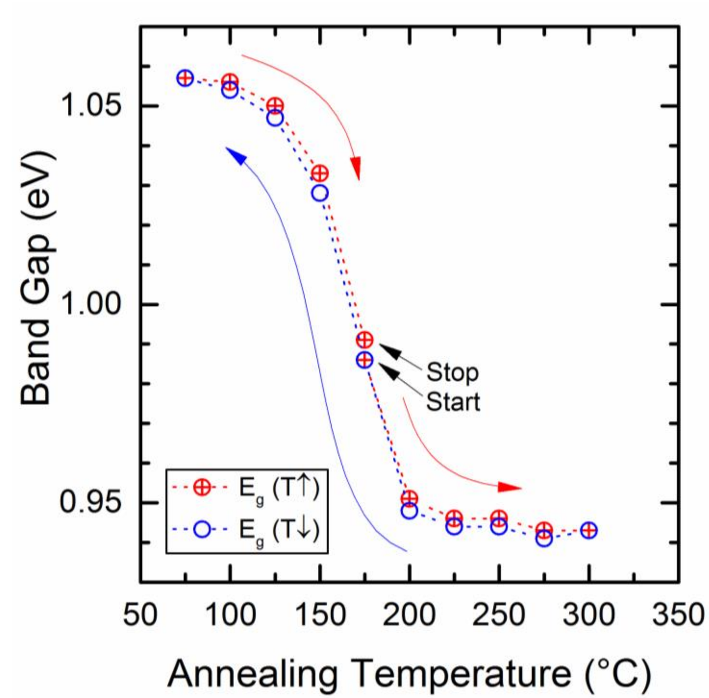
[2] S. Chen *et al.* Adv. Mater. **25** (2013) 1522

g.rey@unsw.edu.au

CZTSe Band gap and Cu-Zn (dis)order







ΔEg = 110 meV

Reversibility and continuity => order-disorder transition

G. Rey *et al*. Applied Physics Letters, **105** (2014) 112106

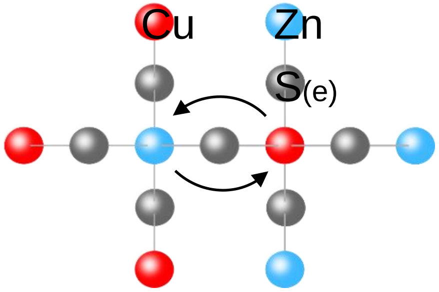
Theoretical description: Vineyard's model[1]

- Long range order parameter: $S = \frac{P_{Cu}^{Cu} - F_{Cu}}{1 - F_{Cu}}$
  - Perfect order S=1
  - Complete disorder S=0

- Theoretical description: Vineyard's model [1]
  - Motion equation for direct exchange:

$$\frac{dS}{dt} = \frac{1}{2}\left[K_O(1-S)^2 - K_D(1+S)^2\right]$$

$$\text{with } K_{O/D} = 4f \exp\left(\frac{-U}{k_B T}\right) \exp\left(\frac{\pm 3VS}{k_B T}\right)$$

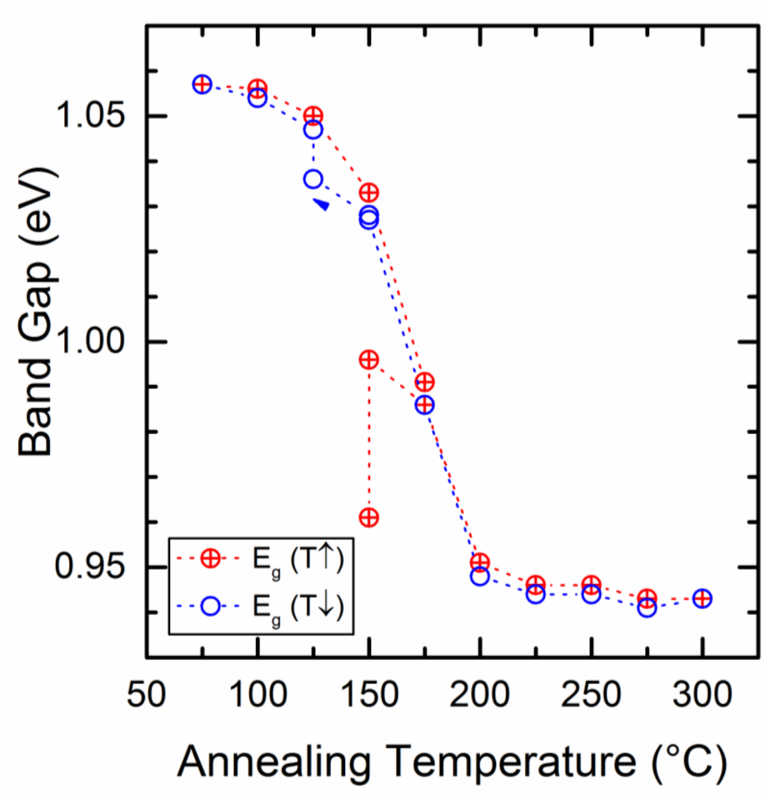


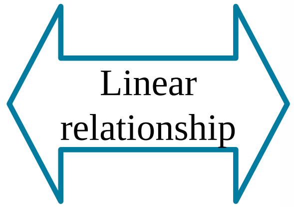
[1] G. Vineyard Phys. Rev. **102** (1956) 981

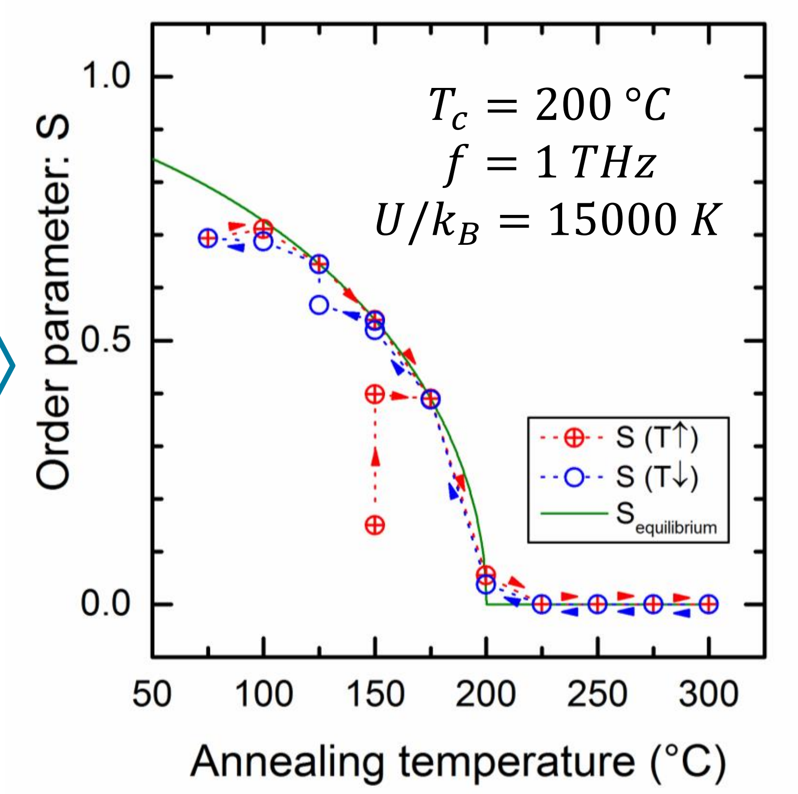
G. Rey *et al.* Applied Physics Letters, **105** (2014) 112106

CZTSe Band gap and Cu-Zn (dis)order

- Comparison band gap and order parameter



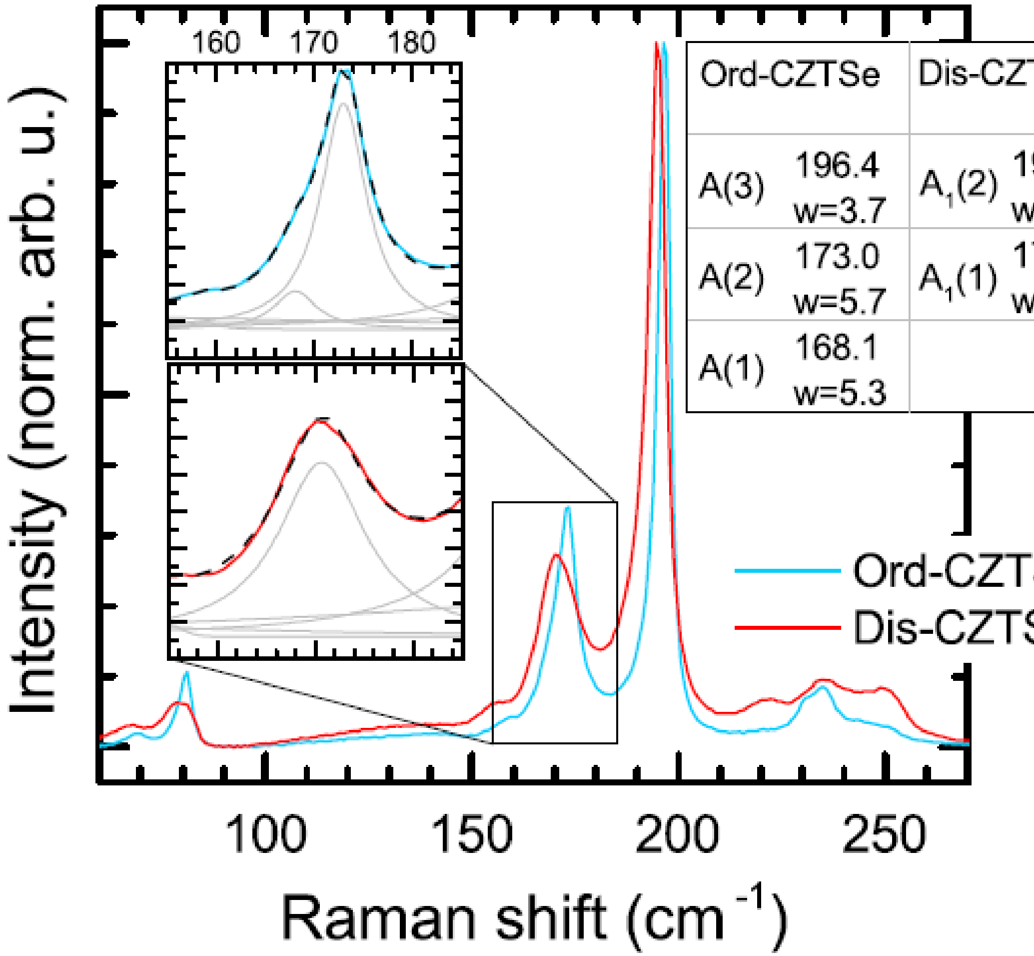




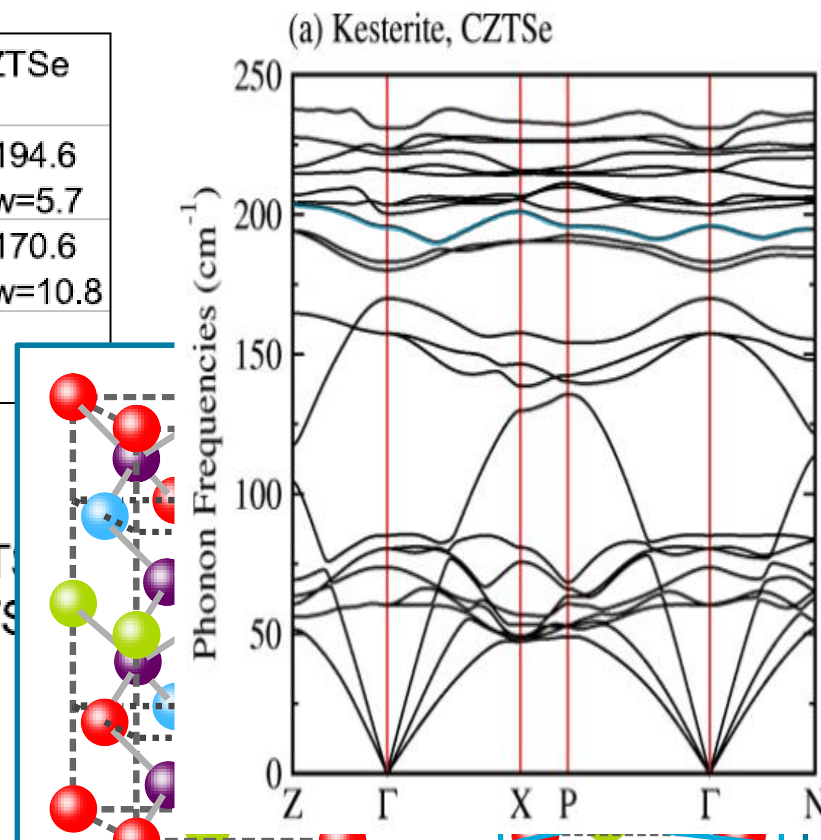
Critical temperature = 200°C for CZTSe
Eg can be used as an order parameter

G. Rey *et al*. Applied Physics Letters, **105** (2014) 112106

Cu-Zn (dis)order probed by Raman



Ord-CZTSe		Dis-CZTSe	
A(3)	196.4 w=3.7	A_1(2)	194.6 w=5.7
A(2)	173.0 w=5.7	A_1(1)	170.6 w=10.8
A(1)	168.1 w=5.3		



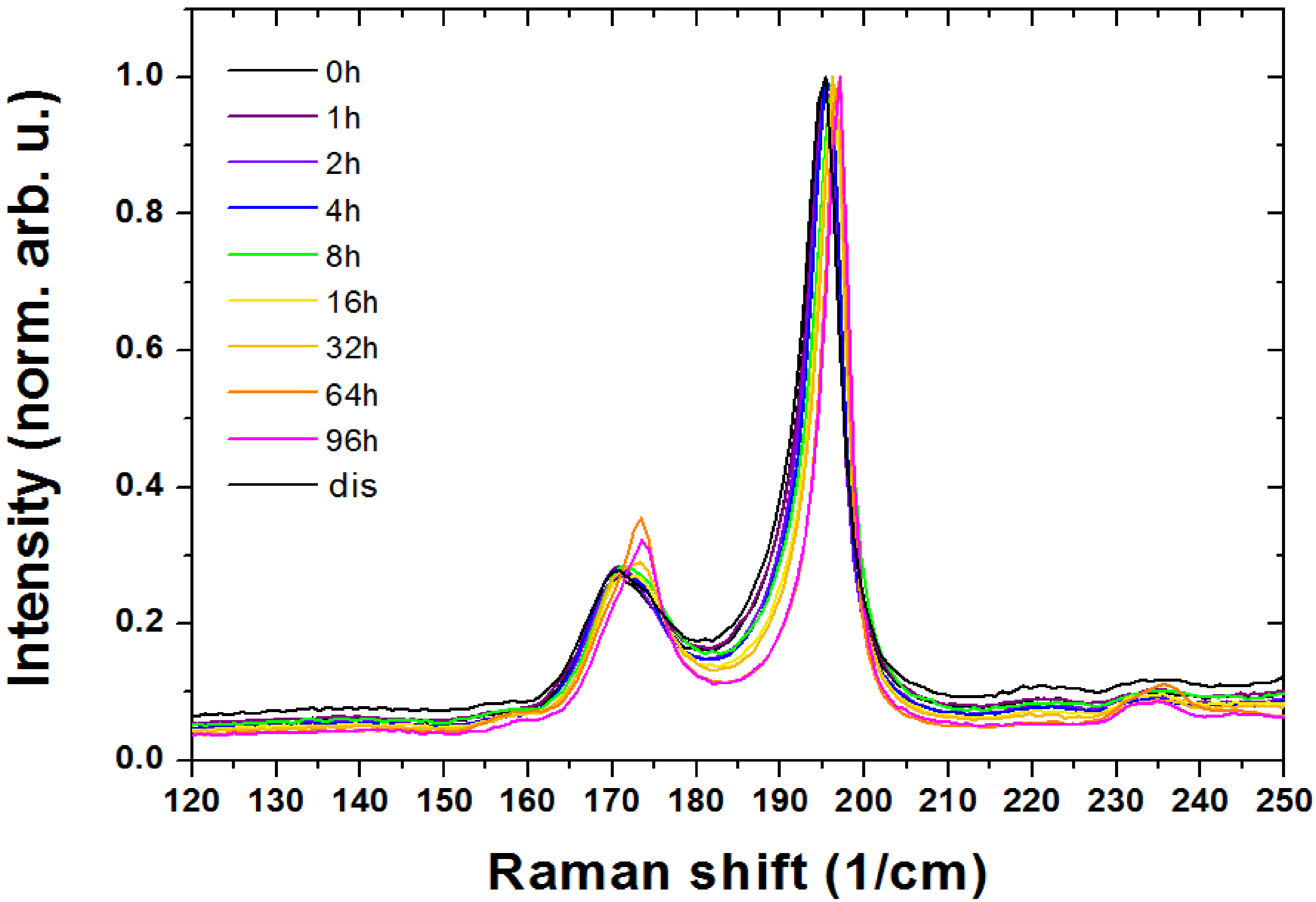
[1] T. Gurel *et al.* Phys. Rev. B **84** (2011) 205201

Modification of Raman spectrum : phonon confinement
+ change in symmetry (Ord K: I$\bar{4}$, Dis K: I$\bar{4}$2m)

G. Rey *et al.* Applied Physics Letters, **105** (2014) 112106

Cu-Zn (dis)order probed by Raman

- Evolution of Raman spectrum during ordering at 100°C



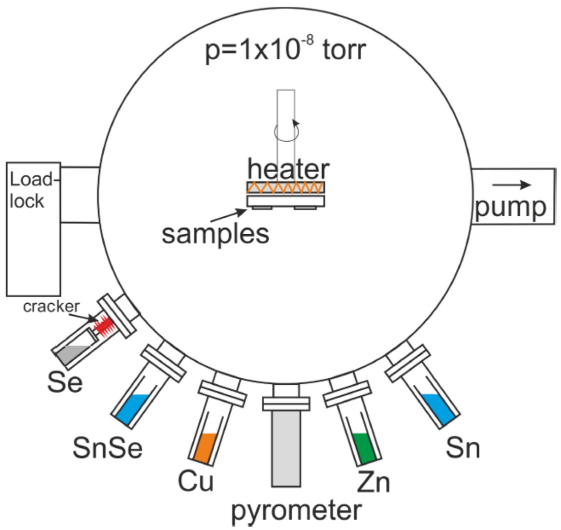
Reversibility and continuity => order-disorder transition

CZTSe thin film and Cu-Zn (dis)order

- Ordering increases the band gap by ~ 10%
- Tc for the order-disorder transition in CTZSe 200°C
- The band gap can be used as a secondary order parameter
- Raman spectrum reflects the changes induced by the order-disorder transition :
  - symmetry
  - coherence length

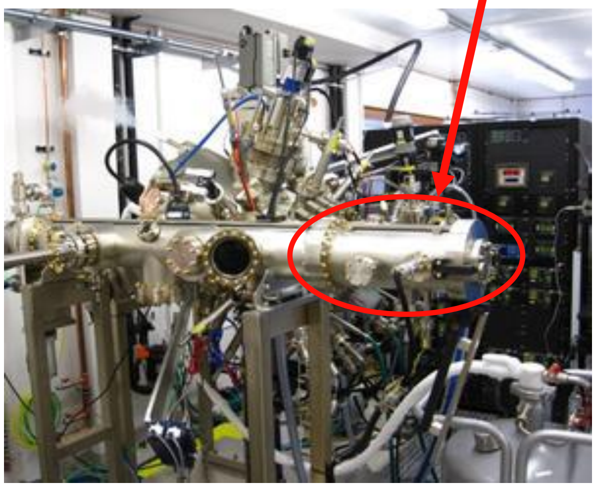
Cu-Zn (dis)order effect on device

- Sample preparation:
  - Coevaporation at 470°C

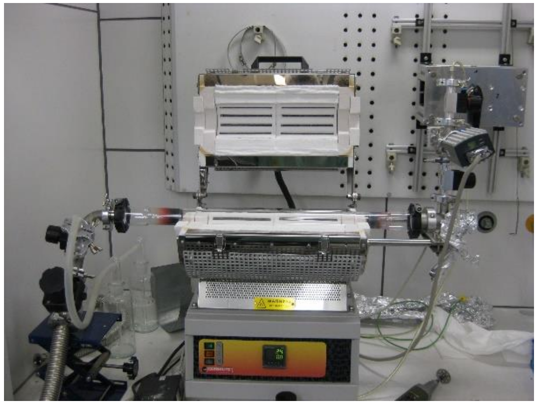


- ORD DIS post-treatment

In-situ

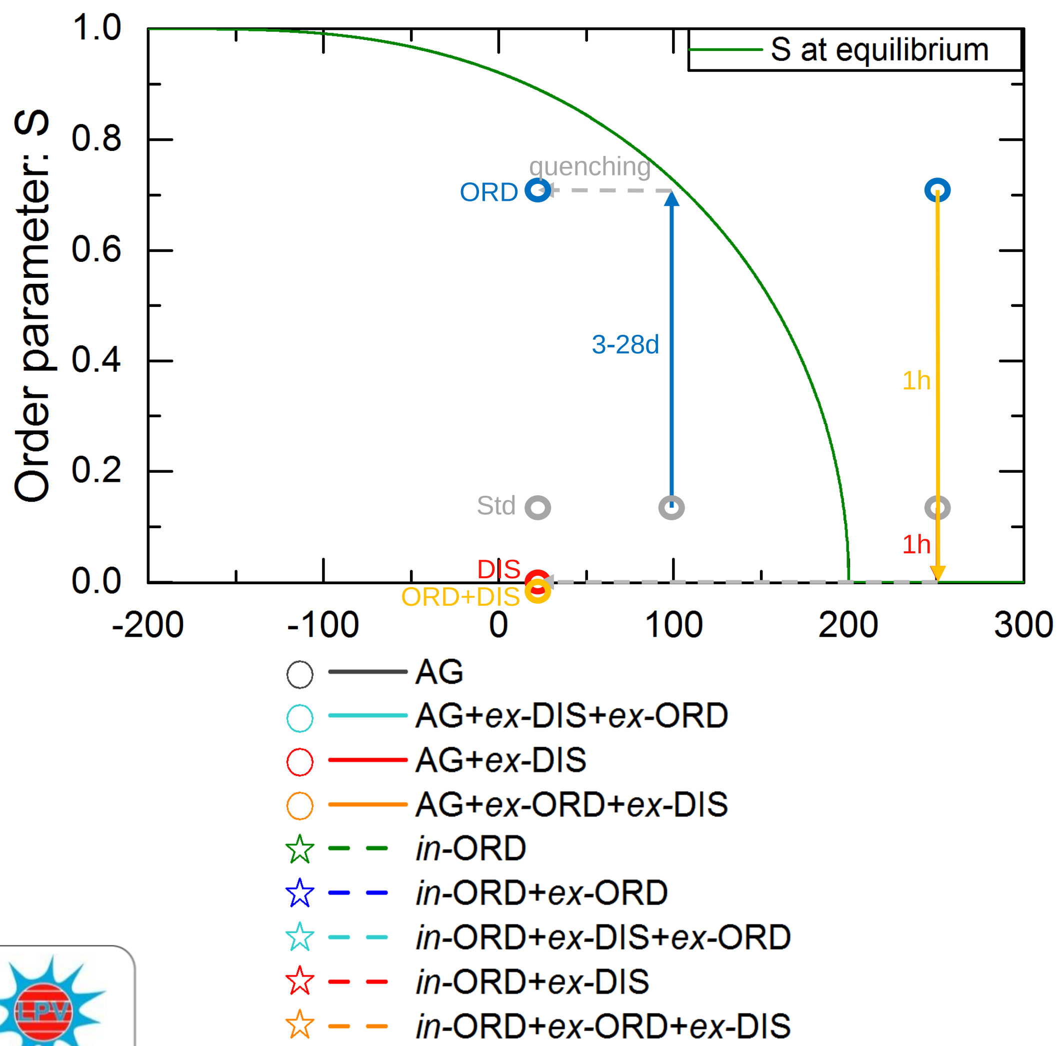


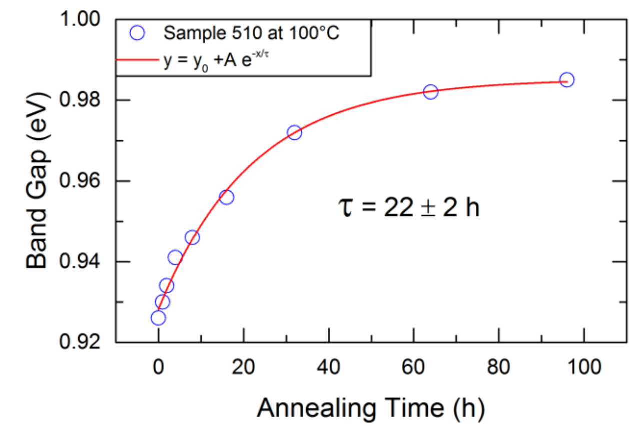
Ex-situ

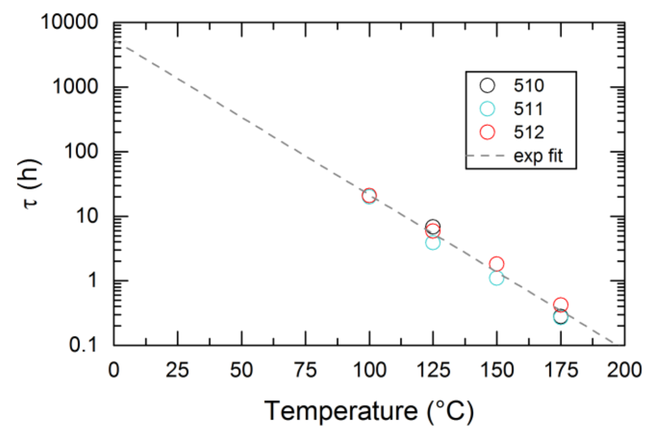


Cu-Zn (dis)order effect on device

- ORD and DIS postdeposition treatment



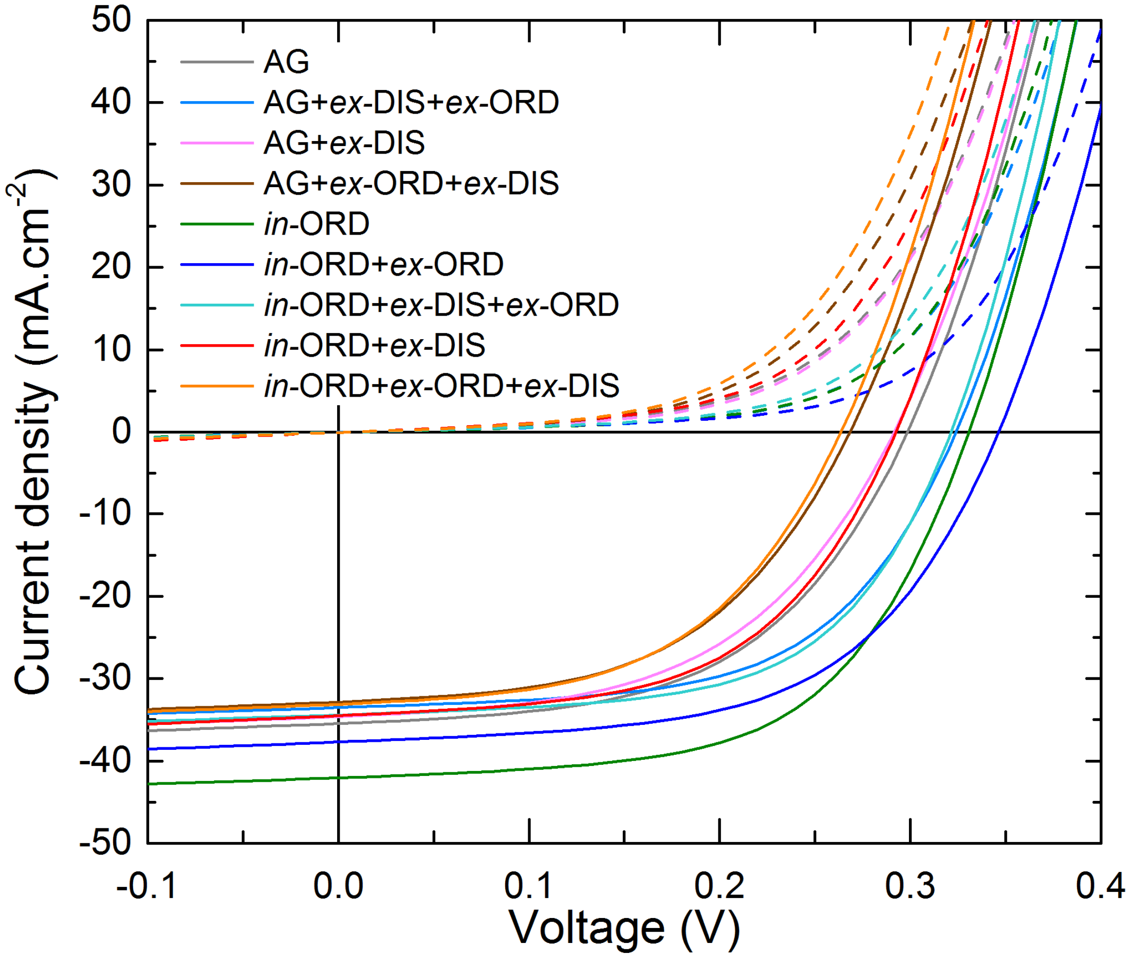




g.rey@unsw.edu.au

Cu-Zn (dis)order effect on device

- ORD and DIS postdeposition treatment

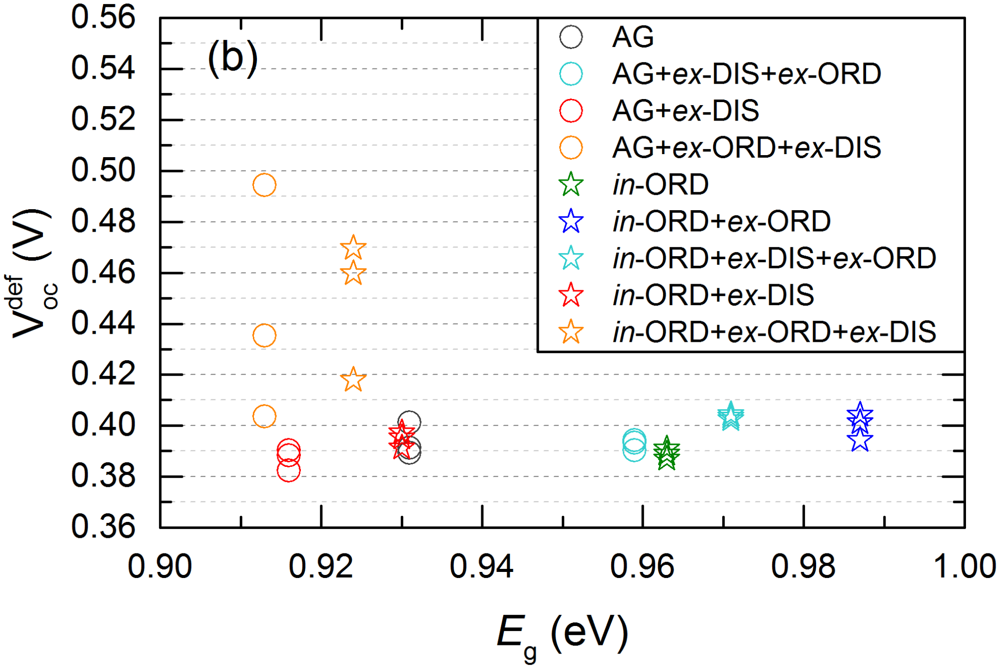


G. Rey *et al.* Sol. Ener. Mat. & Sol. Cells, **151** (2016) 131

Cu-Zn (dis)order effect on device

- Voc deficit

$$V_{oc}^{def} = V_{oc}^{SQ} - V_{oc}$$



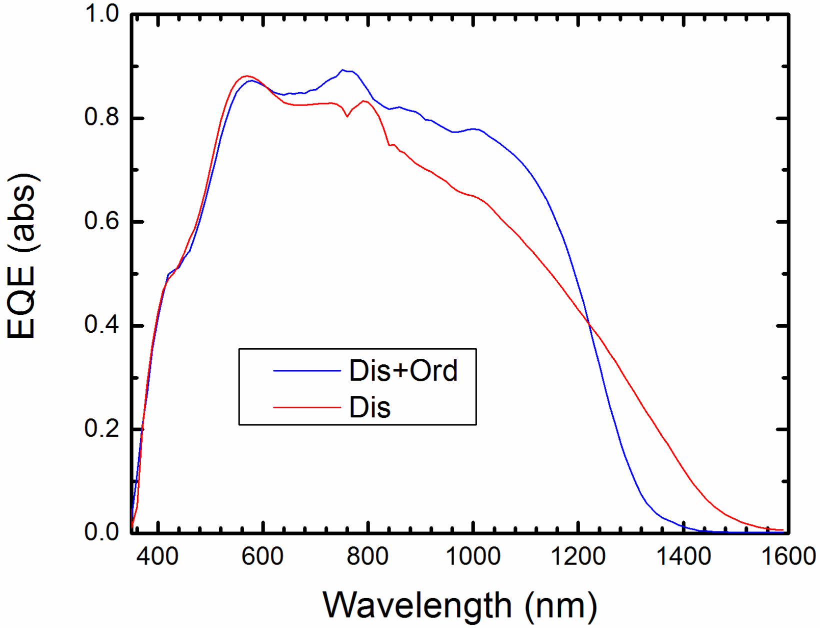
Constant Voc deficit with order:

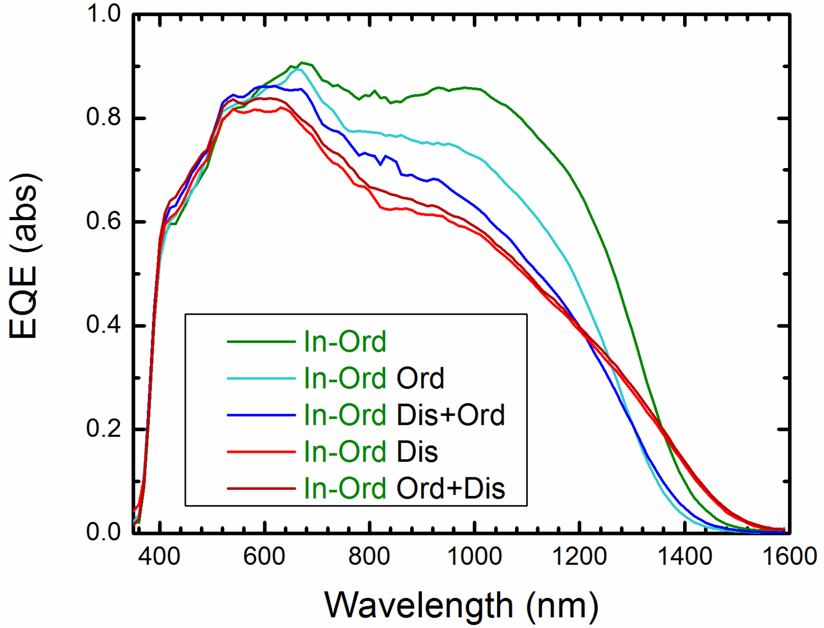
↑ Order ↑ Eg ↑ Voc : ↑ Voc/Eg

G. Rey *et al*. Sol. Ener. Mat. & Sol. Cells, **151** (2016) 131

Cu-Zn (dis)order effect on device

- Effect on QE and Jsc





	n_d (cm^{-3}) by CVp
Dis+Ord	10^{15}
Dis	10^{16}

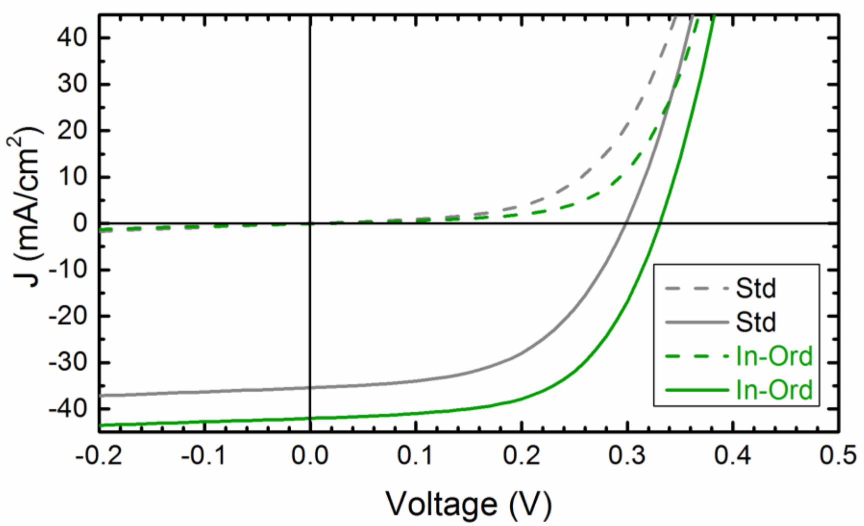
	n_d (cm^{-3}) by CVp
In-Ord	3×10^{16}

Ex-situ Ord or Dis -> no or limited effect on Jsc (change in doping)
In-situ Ord -> ↑ Jsc (7 mA/cm2) due to ↑ collection at long λ

G. Rey *et al.* Sol. Ener. Mat. & Sol. Cells, **151** (2016) 131

Cu-Zn (dis)order effect on device

- Carrier collection length is increased by the ordering treatment
- Ordering increases the band gap and Voc
- Ordering does not affect Voc deficit



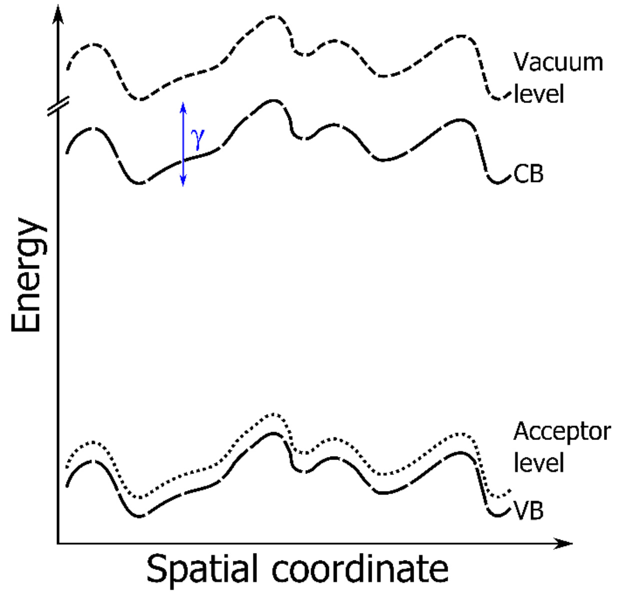
	Voc (mV)	Jsc (mA/cm^2)	Eff (%)
Std	299	35.5*	5.6*
In-Ord	331	42.1*	8.1*
	+32	+6.6*	+2.5*

* measured with an halogen lamp

G. Rey *et al.* Sol. Ener. Mat. & Sol. Cells, **151** (2016) 131

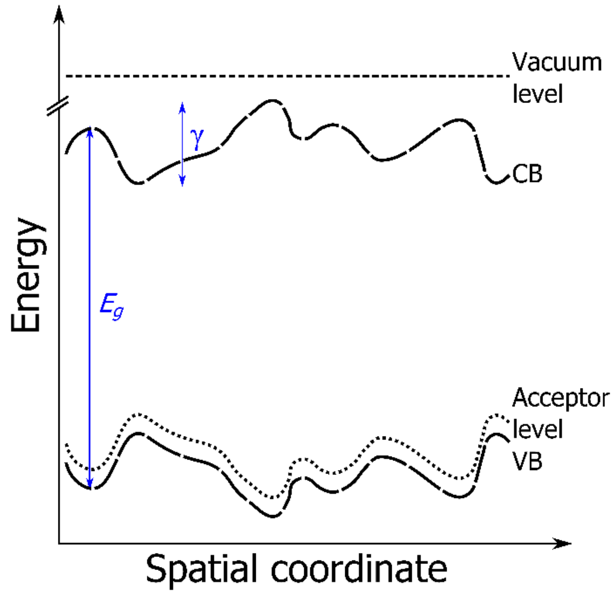
Nature of kesterite tails

- Fluctuating electrostatic potential



$$\gamma_{el} \propto \left(\frac{N_I^2}{p + \Delta p + \Delta n}\right)^{1/3} \quad [1]$$

- Fluctuating band-gap energy

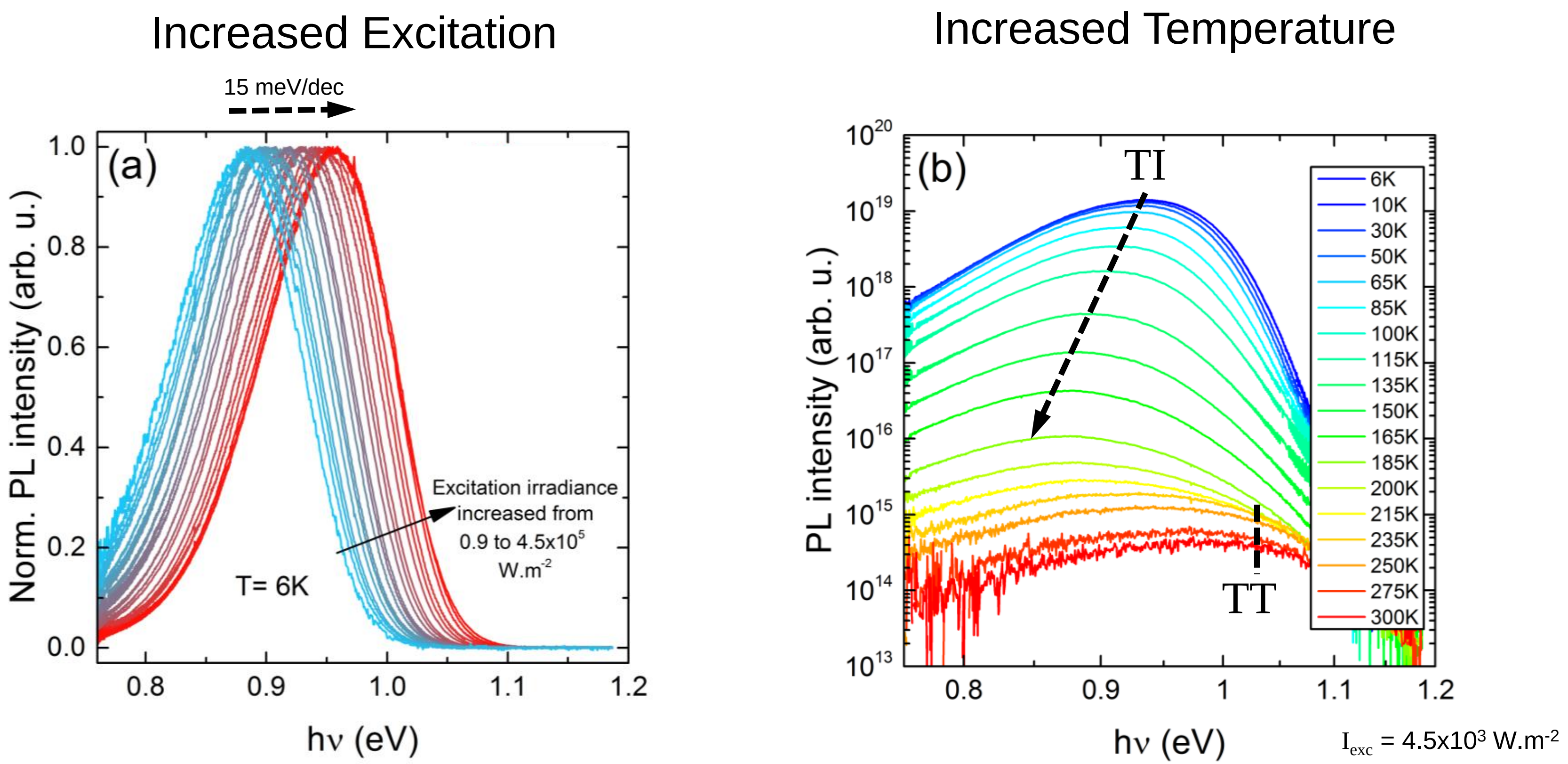


Electrostatic potential fluctuation can be screened

[1] B. Shklovskij & A. Efros, Electronic Properties of Doped Semiconductors (1984) Springer-V.

Nature of kesterite tails

- Temperature and excitation dependent PL of CZTSSe (~9% eff.)

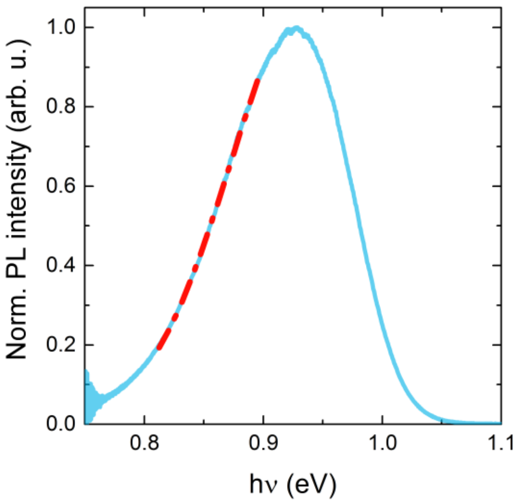


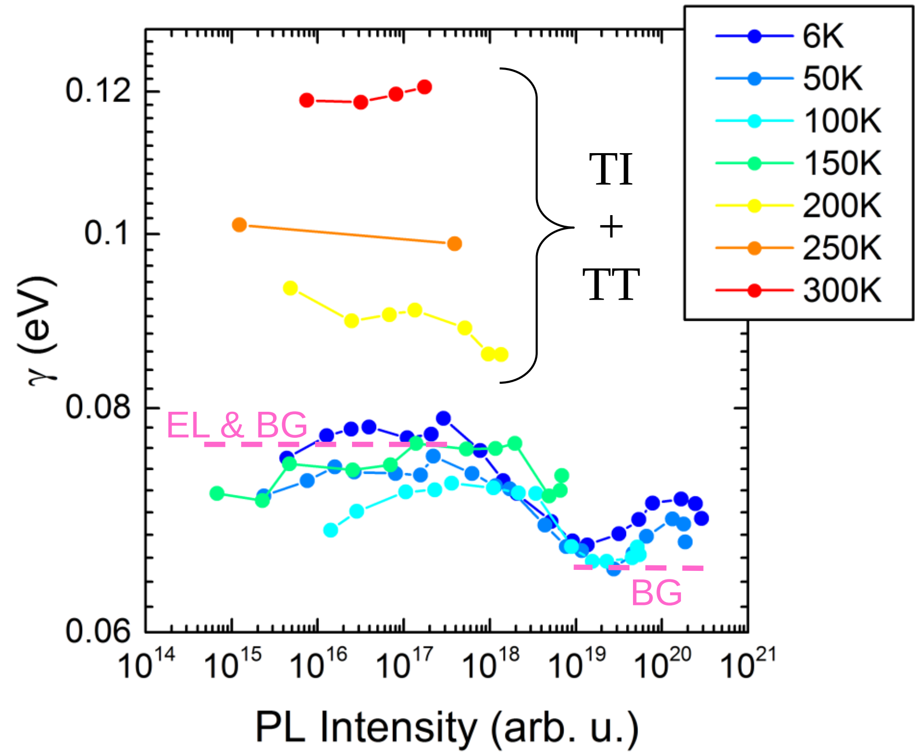
Strong blue shift w. excitation & red shift w. temperature
=> fluctuating band-edges

G. Rey *et al.* Solar Energy Material and Solar Cells **179** (2018) 142

Nature of kesterite tails

- Behaviour of fluctuation depth with excitation





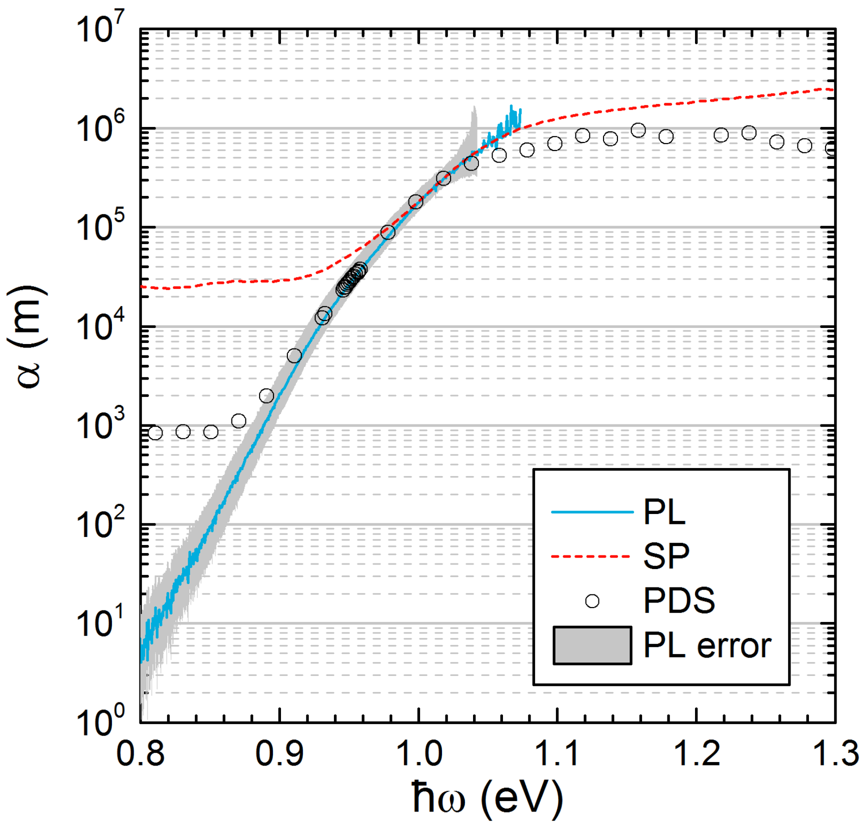
Limited decrease in γ => Band-gap fluctuation is the main mechanism of band-tail formation:

2/3 Band-gap fluctuations + 1/3 Electrostatic fluctuations

G. Rey *et al.* Solar Energy Material and Solar Cells **179** (2018) 142

Cu-Zn (dis)order effect on band-tail

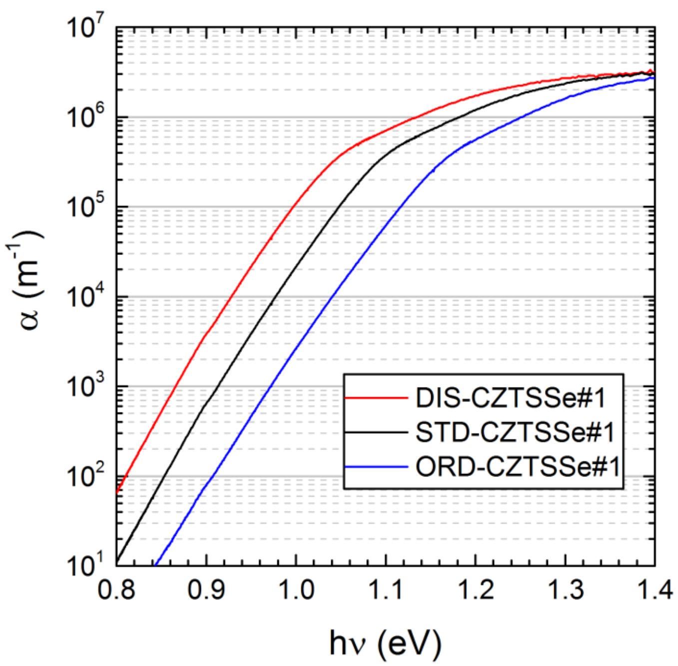
- Measurement of tail absorption using PL [1] +TMM [2]

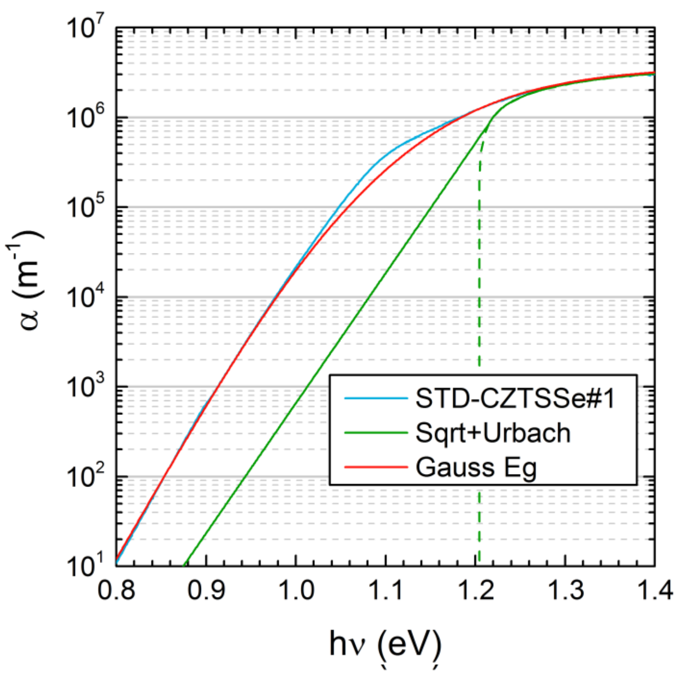


[1] E. Daub & P. Würfel Phys. Rev. Lett. **74** (1995) 1020
[2] G. Rey *et al.* Phys. Rev. Appl. **9** (2018) 064008

Cu-Zn (dis)order effect on band-tail

- CZTSSe Absorption vs Cu-Zn (dis)order

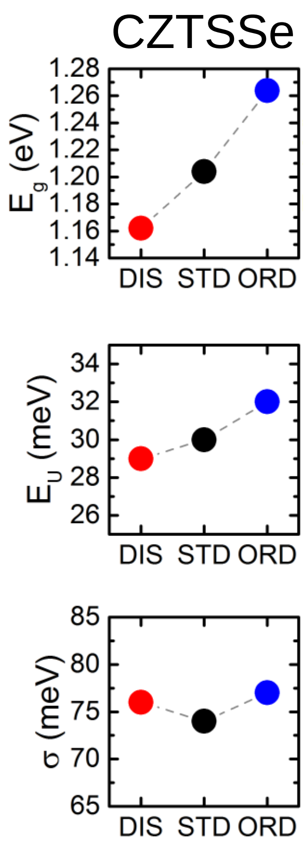


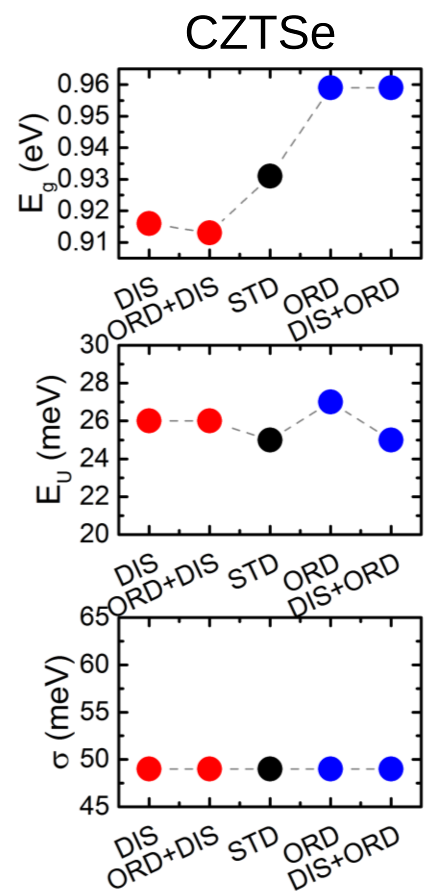


Cu-Zn (dis)order parameter: Eg
Band-tail parameters: Eu and σ

G. Rey *et al.* Solar Energy Material and Solar Cells **179** (2018) 142

Cu-Zn (dis)order effect on band-tail





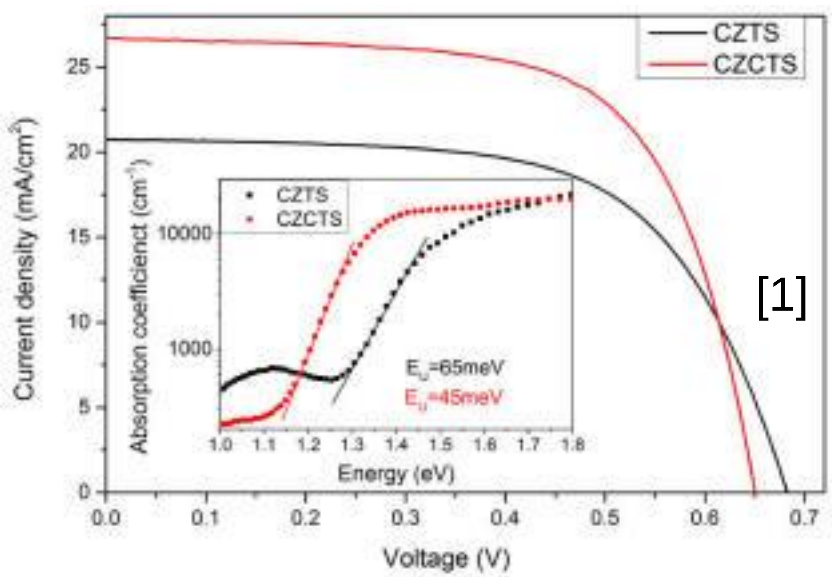
Cu/Zn ordering by thermal postdeposition treatment does not reduce Eu and σ
=> No reduction of the PL red-shift vs. Eg [1]
=> No improvement of Voc deficit [1][2]

[1] G. Rey *et al.* Solar Energy Material and Solar Cells **151** (2016) 131 - 138
[2] S. Bourdais *et al.* Advanced Energy Materials **6** (2016)

Cu-Zn (dis)order effect on band-tail

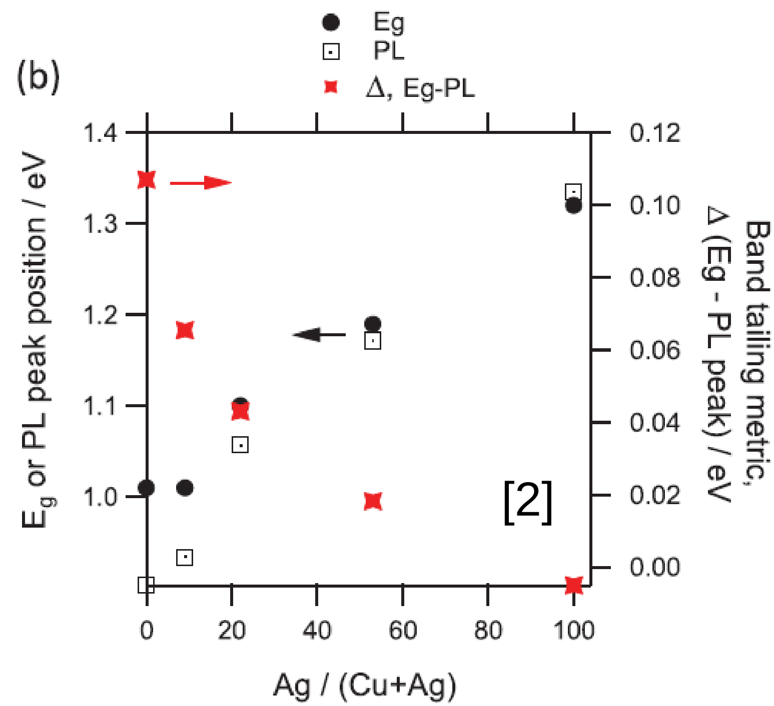
- Avoiding disorder by alloying, example from literature:

Cu(Zn,Cd)SnS_4



absorber	optical E_g (eV)	PL Peak (eV)	$\Delta(E_g$–PL peak) (mV)	E_{Urbach} (meV)
CZTS	1.54	1.37	~170	65
CZCTS	1.38	1.31	~70	45

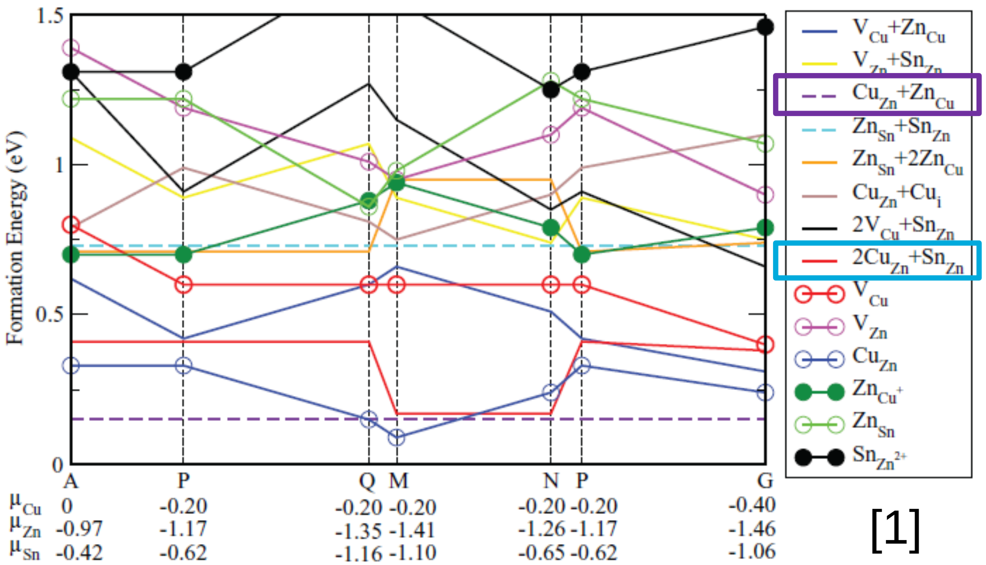
(Cu,Ag)ZnSnSe_4



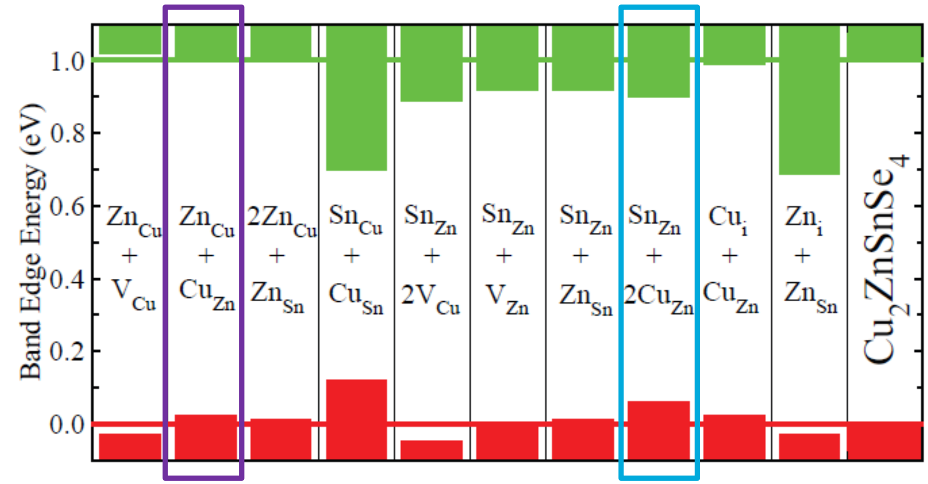
[1] C. Yan *et al.* Energy Letter **2** (2017) 930
[2] T. Gershon *et al.* Advanced Energy Materials **6** (2016)

Cu-Zn (dis)order effect on band-tail

- Potential candidate:



[1]



[1]

[$2Cu_{Zn}$ + Sn_{Zn}] would be a good candidate to explain the large band-tailing in kesterite

[1] S. Chen *et al.* Advanced Materials **25** (2013) 1522-1539

UNIVERSITÉ DU LUXEMBOURG

Cu-Zn (dis)order effect on band-tail

- Nature of the kesterite band-tail:
  - 2/3 band-gap fluctuations
  - 1/3 electrostatic fluctuations
- Cu-Zn ordering by post-deposition annealing has no effect on Eu or σ.
- [Cu_{Zn}+Zn_{Cu}] is not the direct main cause of band-tailing, instead we propose [$2Cu_{Zn}$+Sn_{Zn}] as potential candidate.

Thank you for your attention

- Acknowledgments:
  - Susanne Siebentritt and Laboratory for PV team
  - G. Dennler, G. Larramona & S. Bourdais
  - M. Guennou
  - R. Carius & M. Nuys

UNIVERSITÉ DU LUXEMBOURG

LUXEMBOURG INSTITUTE OF SCIENCE AND TECHNOLOGY LIST

IMRA EUROPE S.A.

JÜLICH FORSCHUNGSZENTRUM

- Funding:

Fonds National de la Recherche Luxembourg

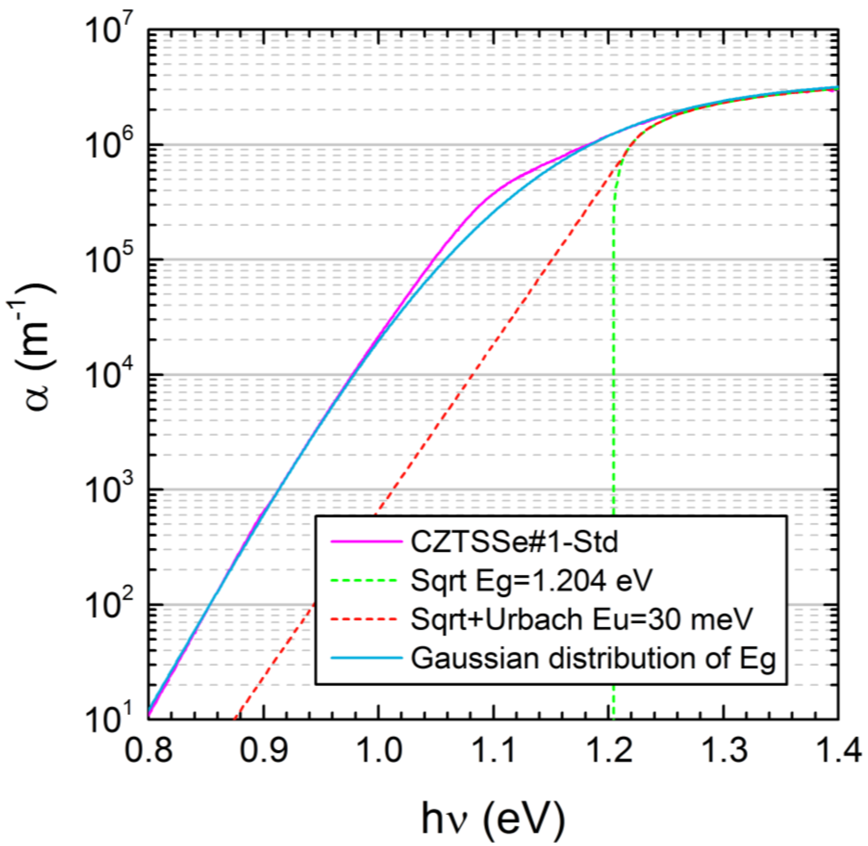
SEVENTH FRAMEWORK PROGRAMME

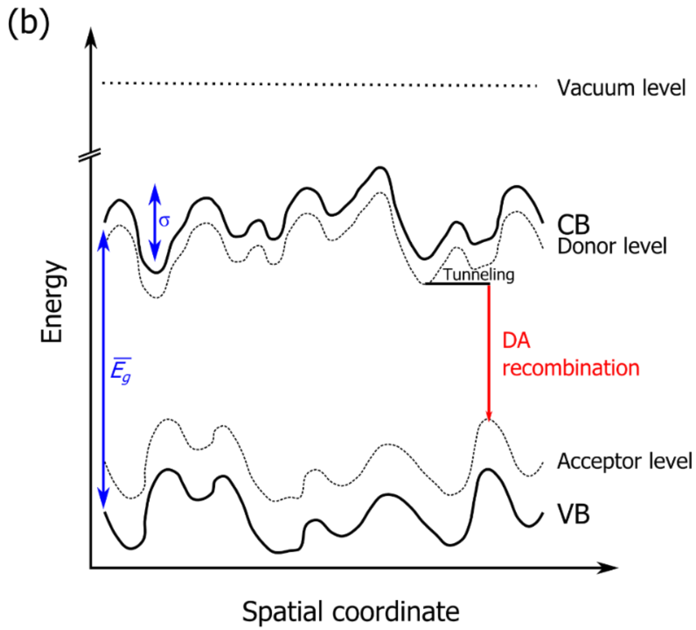
MARIE CURIE ACTIONS

KESTCELLS

Disorder and Band-Tail

- Absorption spectrum of kesterite:





$\overline{E_g}$ =1.184 eV and Eu = 25 meV and σ = 74 meV

$$\alpha = \int_0^\infty \frac{A}{\sqrt{2\pi\sigma}} e^{\frac{-(E_g-\overline{E_g})^2}{2\sigma^2}} \left[\mathcal{H}(aE_g)\,\frac{\sqrt{h\upsilon-E_g}}{E_g} + \mathcal{H}(-aE_g)\,\frac{\sqrt{a-1}\,e^{\frac{-aE_g}{Eu}}}{a\sqrt{E_g}}\,e^{\frac{h\upsilon}{Eu}}\right] dE_g$$

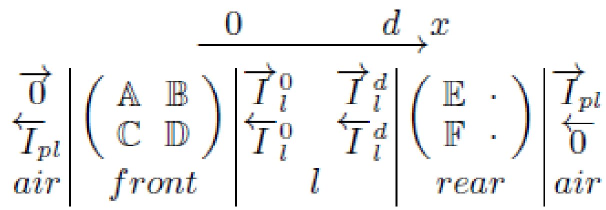
Disorder and Band-Tail

- Measuring α from PL:

$$r_J = \frac{n^2\,\Omega}{4\pi^3\hbar^3c^2}\,\alpha\,\frac{(\hbar\omega)^2}{\exp\left(\frac{\hbar\omega-\Delta\mu}{k_BT}\right)-1} = \alpha Y,$$

$$\frac{\partial \overrightarrow{I}_l^{\,x}}{\partial x} = \alpha\hbar\omega Y - \alpha\overrightarrow{I}_l^{\,x}$$

$$\frac{\partial \overleftarrow{I}_l^{\,x}}{\partial x} = \alpha\overleftarrow{I}_l^{\,x} - \alpha\hbar\omega Y.$$



$$\overleftarrow{J}_{pl} = Y\,\frac{\left(\mathbb{D}-\frac{\mathbb{B}}{\mathbb{A}}\mathbb{C}\right)\left(1-e^{-\alpha d}\right)\left(1+\frac{\mathbb{F}}{\mathbb{E}}e^{-\alpha d}\right)}{1+\frac{\mathbb{F}}{\mathbb{E}}\frac{\mathbb{B}}{\mathbb{A}}e^{-2\alpha d}} = Y\Phi.$$

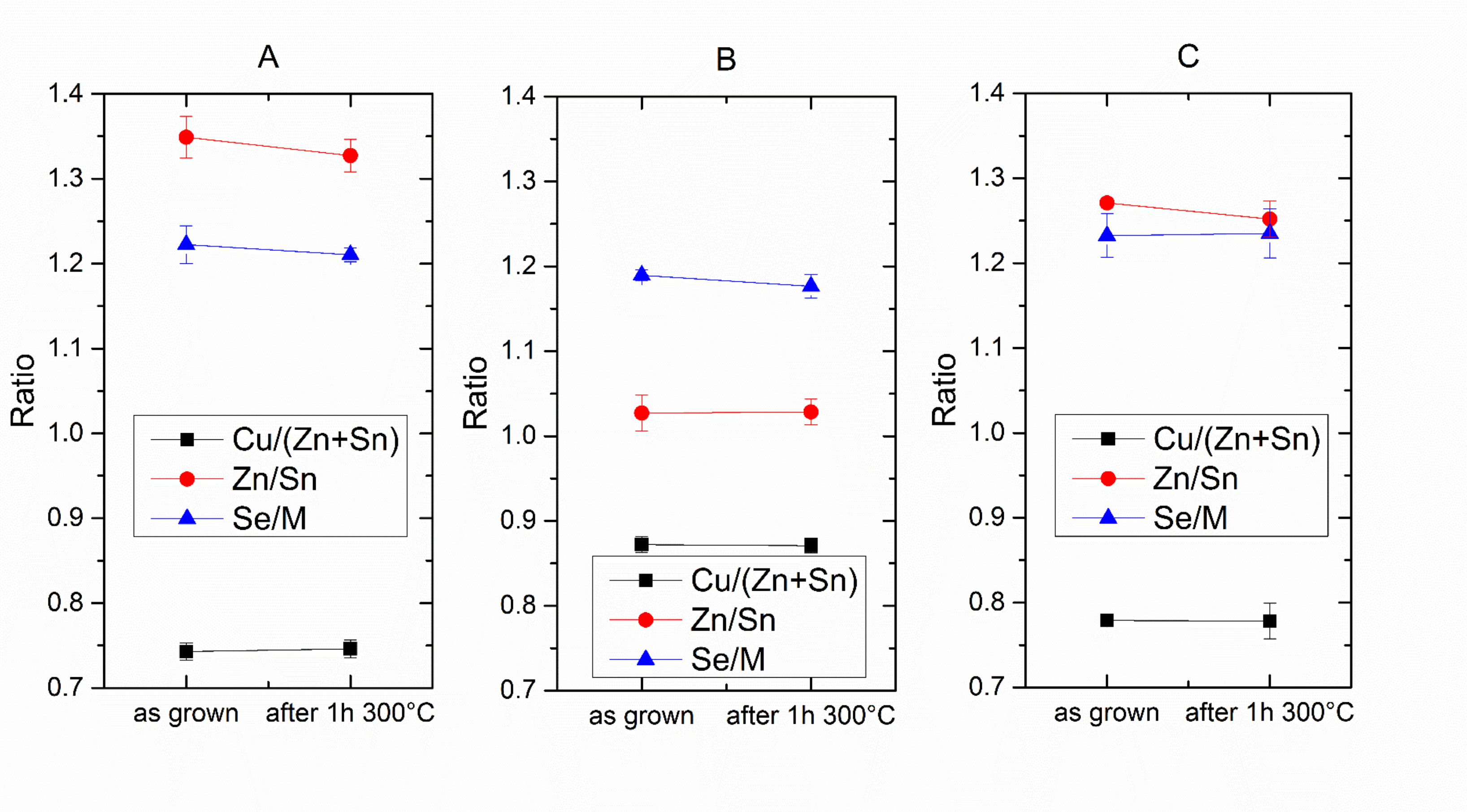
$$\frac{\hbar\omega-\Delta\mu}{k_BT} = \ln\left[\frac{n^2\,\Omega}{4\pi^3\hbar^3c^2}\,\frac{\Phi(\hbar\omega)^2}{\overleftarrow{J}_{pl}} + 1\right]$$

$$\begin{pmatrix}I_0\\ I_r\end{pmatrix} = \begin{pmatrix}A & B\\ C & D\end{pmatrix}\begin{pmatrix}e^{+4\pi kd/\lambda} & 0\\ 0 & e^{4\pi kd/\lambda}\end{pmatrix}\begin{pmatrix}E & G\\ F & H\end{pmatrix}\begin{pmatrix}I_t\\ 0\end{pmatrix},$$

$$\alpha = -\frac{1}{d}\ln\left(\frac{\left(\frac{F}{E}-1\right)+\sqrt{\left(\frac{F}{E}-1\right)^2+4\frac{F}{E}\left(1+\frac{I_{pl}}{\left(\frac{A}{B}D-C\right)\frac{1}{4\pi^2\hbar^3c^2}\frac{(\hbar\omega)^2}{\exp\left(\frac{\hbar\omega-\mu}{k_BT}\right)-1}}\right)\left(1-\frac{I_{pl}}{\left(D-\frac{A}{B}C\right)\frac{1}{4\pi^2\hbar^3c^2}\frac{(\hbar\omega)^2}{\exp\left(\frac{\hbar\omega-\mu}{k_BT}\right)-1}}\right)}}{2\frac{F}{E}\left(1+\frac{I_{pl}}{\left(\frac{A}{B}D-C\right)\frac{1}{4\pi^2\hbar^3c^2}\frac{(\hbar\omega)^2}{\exp\left(\frac{\hbar\omega-\mu}{k_BT}\right)-1}}\right)}\right),$$

Band gap and (dis)order

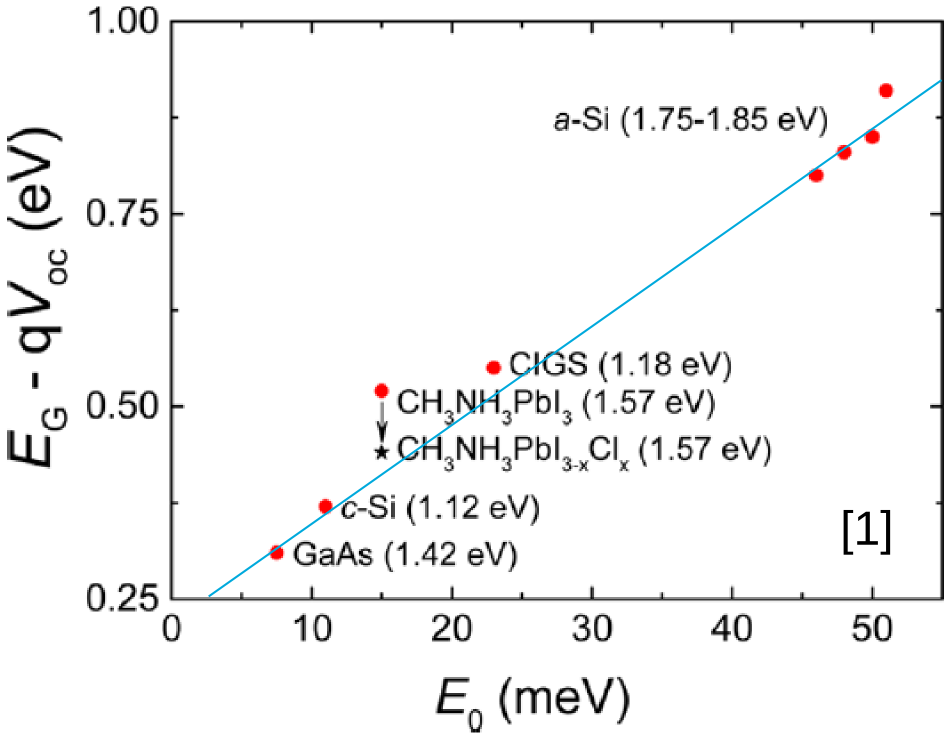
- Composition EDX 20kV



No significant change in composition after annealing

Cu-Zn (dis)order effect on band-tail

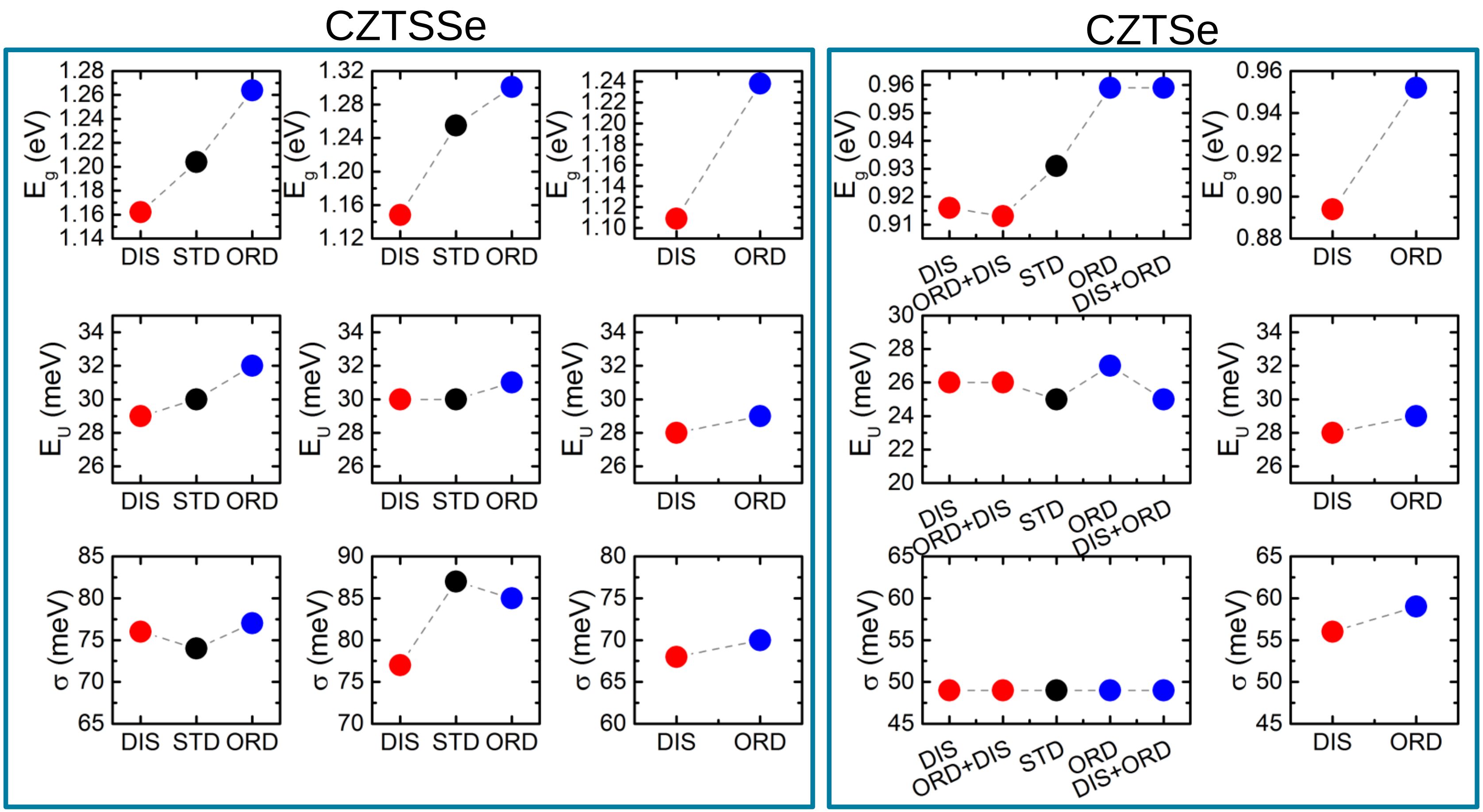
- Voc and Band-tail



[1] S. De Wolf *et al.* J. Phys. Chem. Lett., **5** (2014) 1035

Band-tailing & Cu-Zn (dis)order

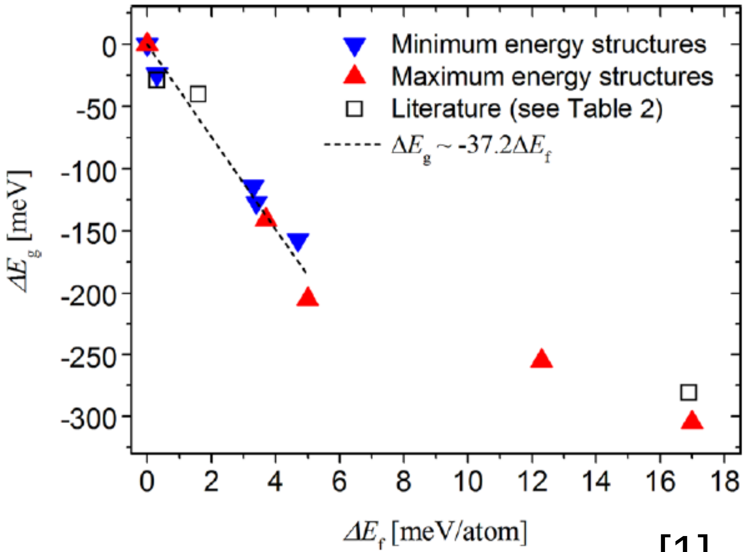
- CZTSSe & CZTSe Band-tail vs Cu-Zn (dis)order



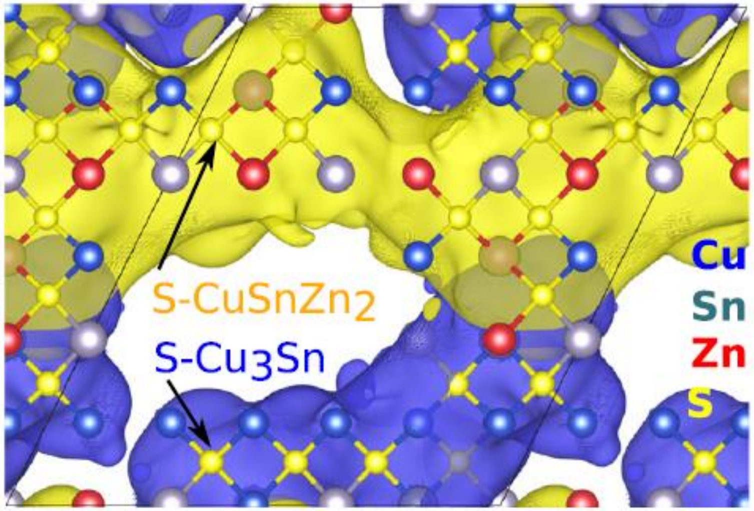
Cu/Zn ordering by thermal treatment does not reduce Eu and σ

Band-tailing & Cu-Zn (dis)order

- CZTSSe & CZTSe Band-tail vs Cu-Zn (dis)order



[1]

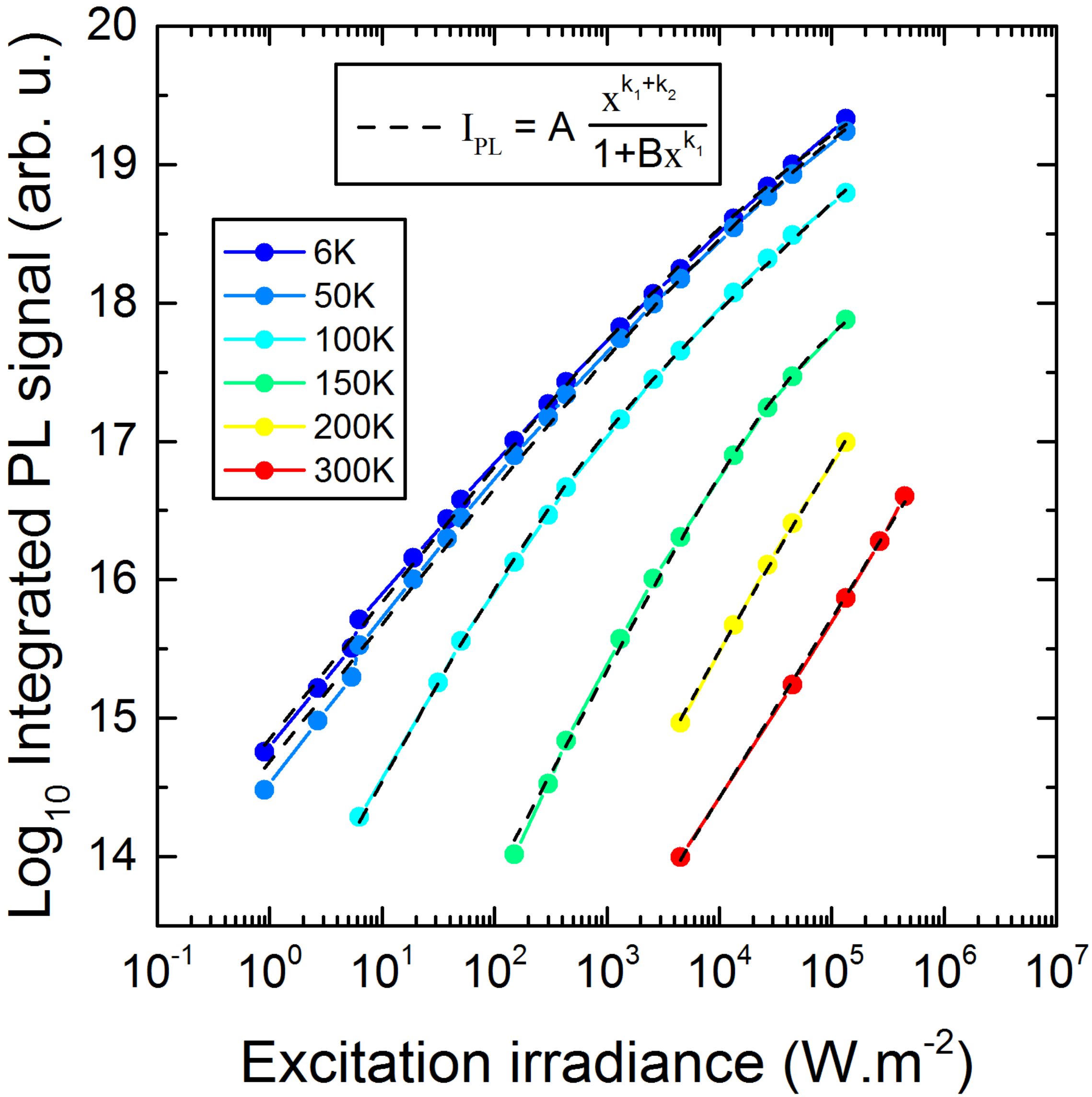


[2]

Cu-Zn (dis)order is not the main cause of potential fluctuation

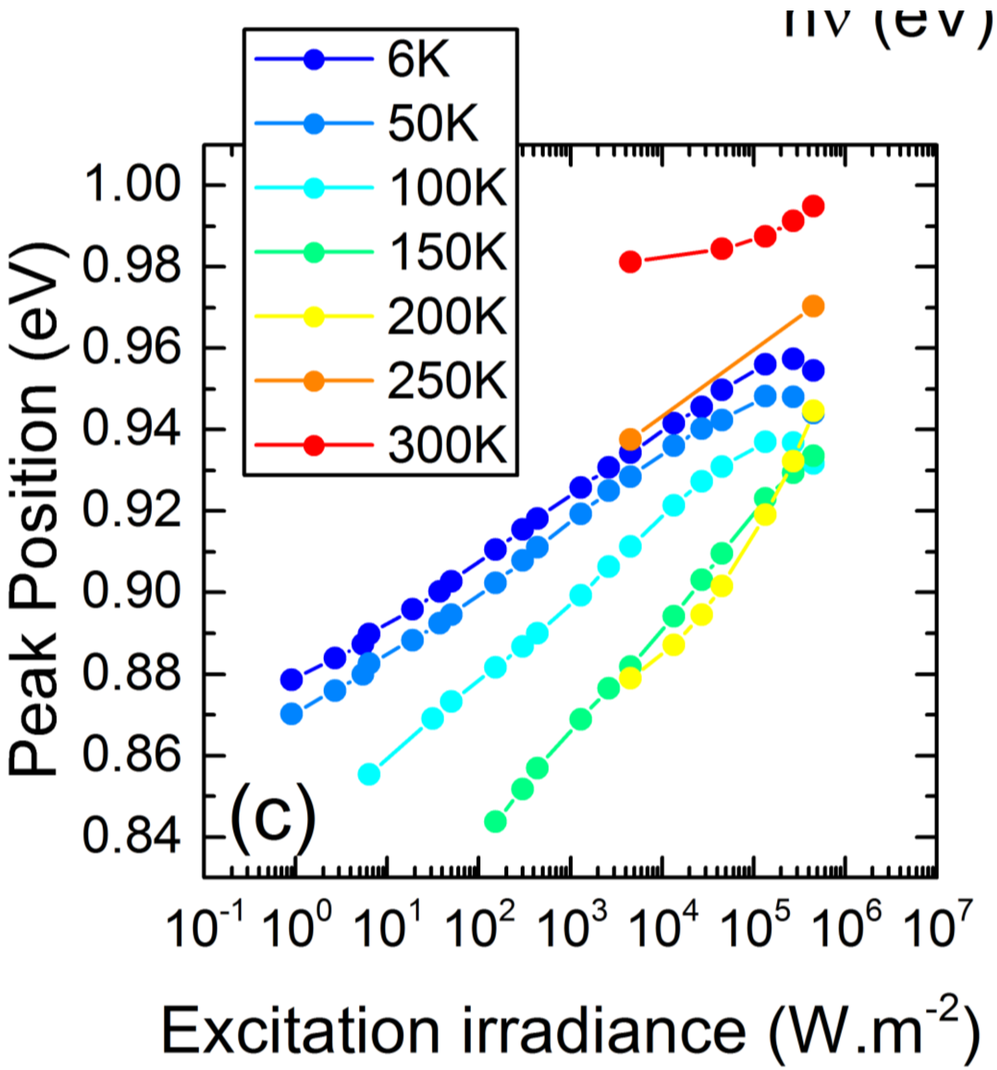
[1] J. J. S. Scragg *et al.* Physica Status Solidi (b) **253** (2015) 247–254
[2] P. Zawadzki *et al.* Physical Review Applied **3** (2015) 034007

K value

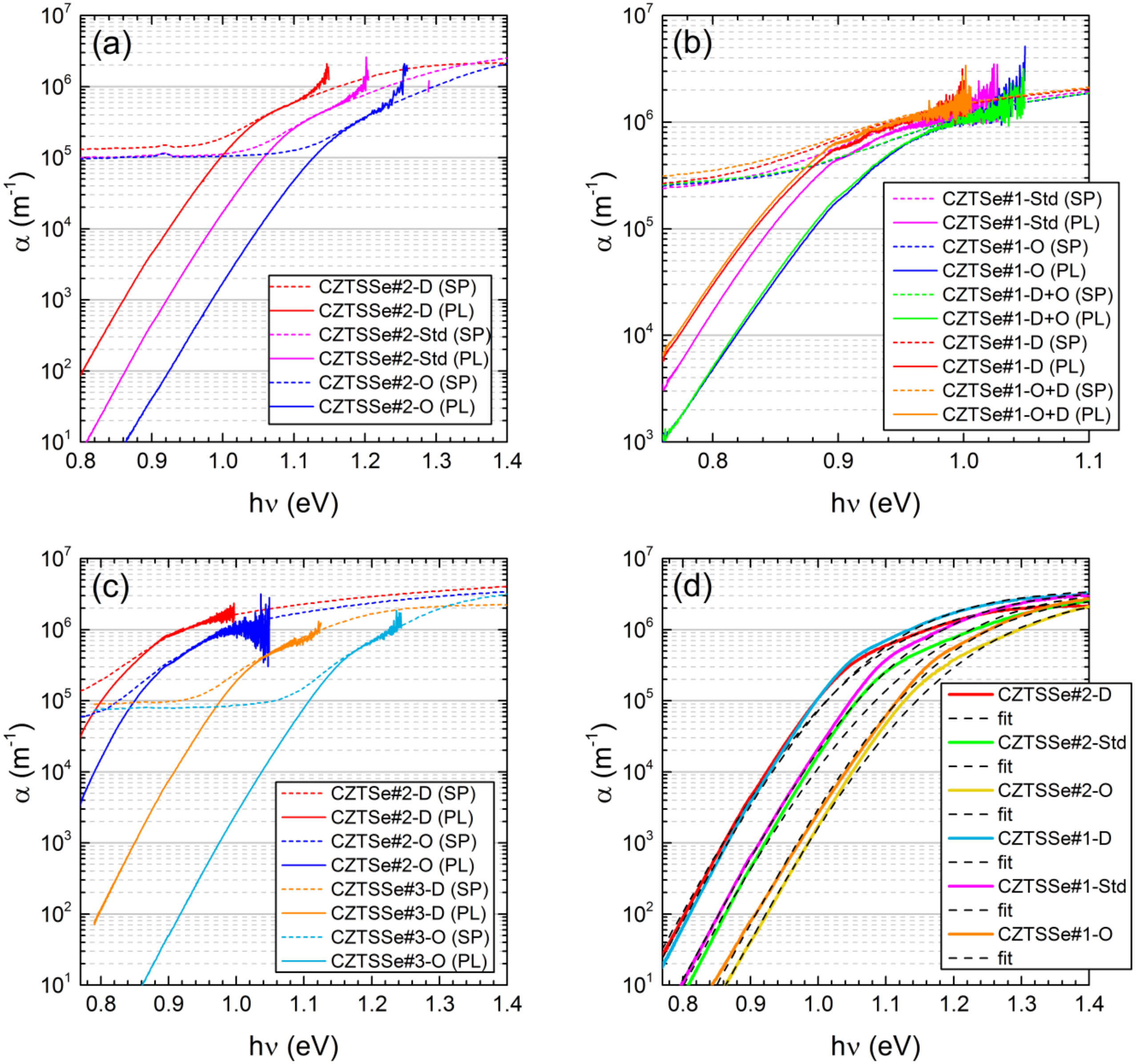


20
19
18
17
16
15
14
Log_{10} Integrated PL signal (arb. u.)
$I_{PL} = A \frac{x^{k_1+k_2}}{1+Bx^{k_1}}$
6K
50K
100K
150K
200K
300K
10^{-1} 10^{0} 10^{1} 10^{2} 10^{3} 10^{4} 10^{5} 10^{6} 10^{7}
Excitation irradiance ($W.m^{-2}$)

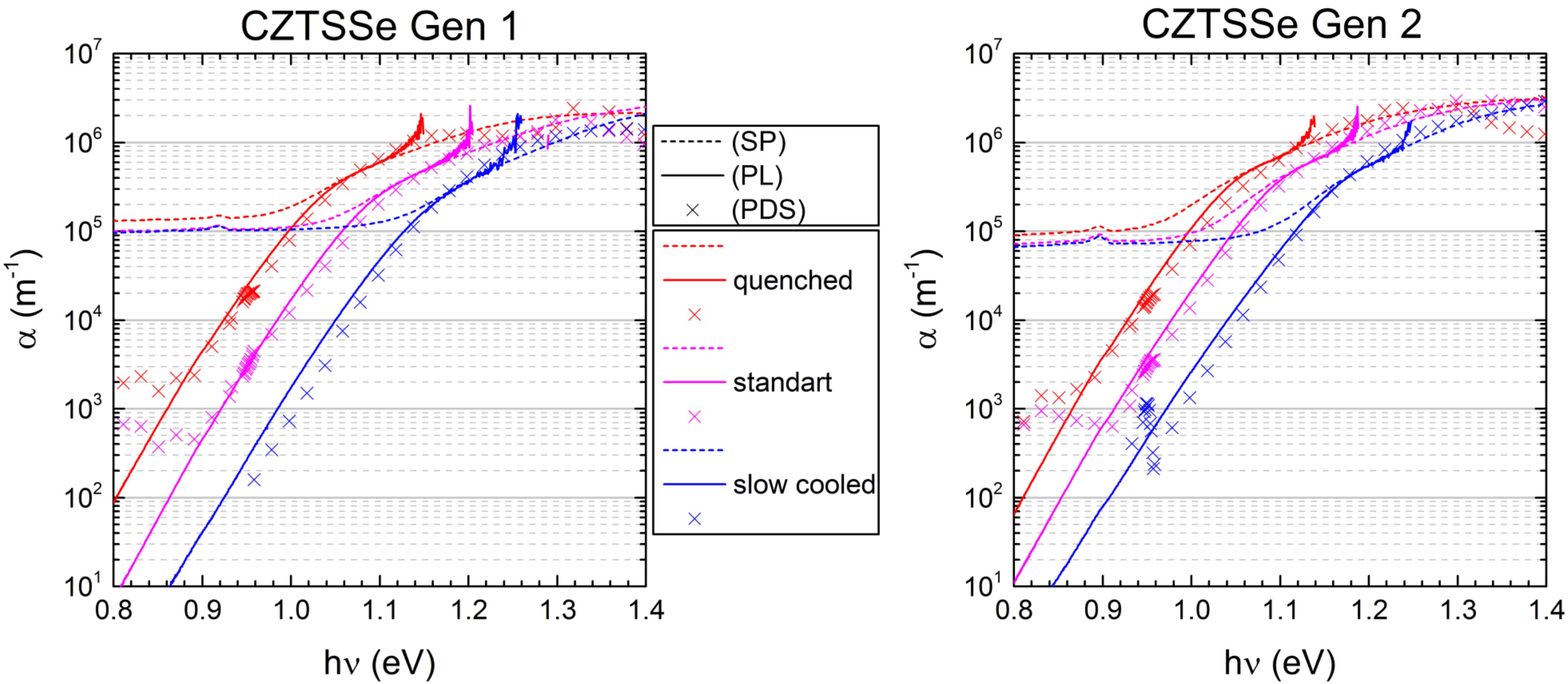
Shift



hv (eV)
6K
50K
100K
150K
200K
250K
300K
1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
Peak Position (eV)
(c)
10^{-1} 10^{0} 10^{1} 10^{2} 10^{3} 10^{4} 10^{5} 10^{6} 10^{7}
Excitation irradiance ($W.m^{-2}$)


(a)
CZTSSe#2-D (SP)
CZTSSe#2-D (PL)
CZTSSe#2-Std (SP)
CZTSSe#2-Std (PL)
CZTSSe#2-O (SP)
CZTSSe#2-O (PL)
(b)
CZTSe#1-Std (SP)
CZTSe#1-Std (PL)
CZTSe#1-O (SP)
CZTSe#1-O (PL)
CZTSe#1-D+O (SP)
CZTSe#1-D+O (PL)
CZTSe#1-D (SP)
CZTSe#1-D (PL)
CZTSe#1-O+D (SP)
CZTSe#1-O+D (PL)
(c)
CZTSe#2-D (SP)
CZTSe#2-D (PL)
CZTSe#2-O (SP)
CZTSe#2-O (PL)
CZTSSe#3-D (SP)
CZTSSe#3-D (PL)
CZTSSe#3-O (SP)
CZTSSe#3-O (PL)
(d)
CZTSSe#2-D
fit
CZTSSe#2-Std
fit
CZTSSe#2-O
fit
CZTSSe#1-D
fit
CZTSSe#1-Std
fit
CZTSSe#1-O
fit
α (m⁻¹)
hν (eV)

PDS



Acknowledgment: R. Carius and M. Nuys from Forschungszentrum Jülich GmbH Institut für Energie und Klimaforschung, 52425 Jülich, Germany.

Disorder and Band-Tail

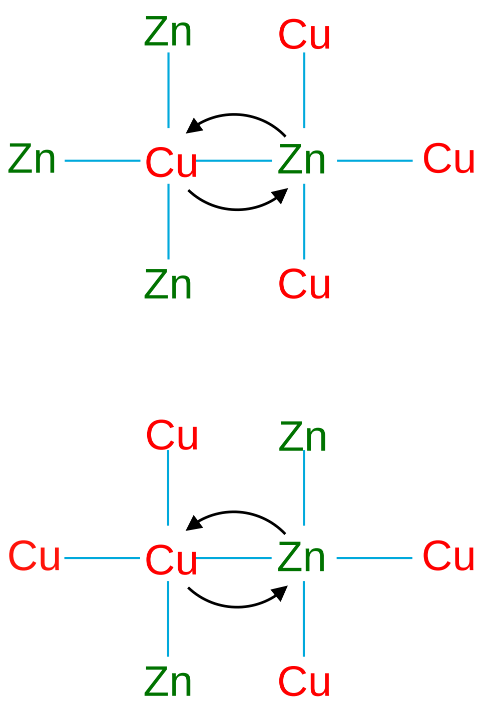
- Cu-Zn disorder and tail in kesterite:

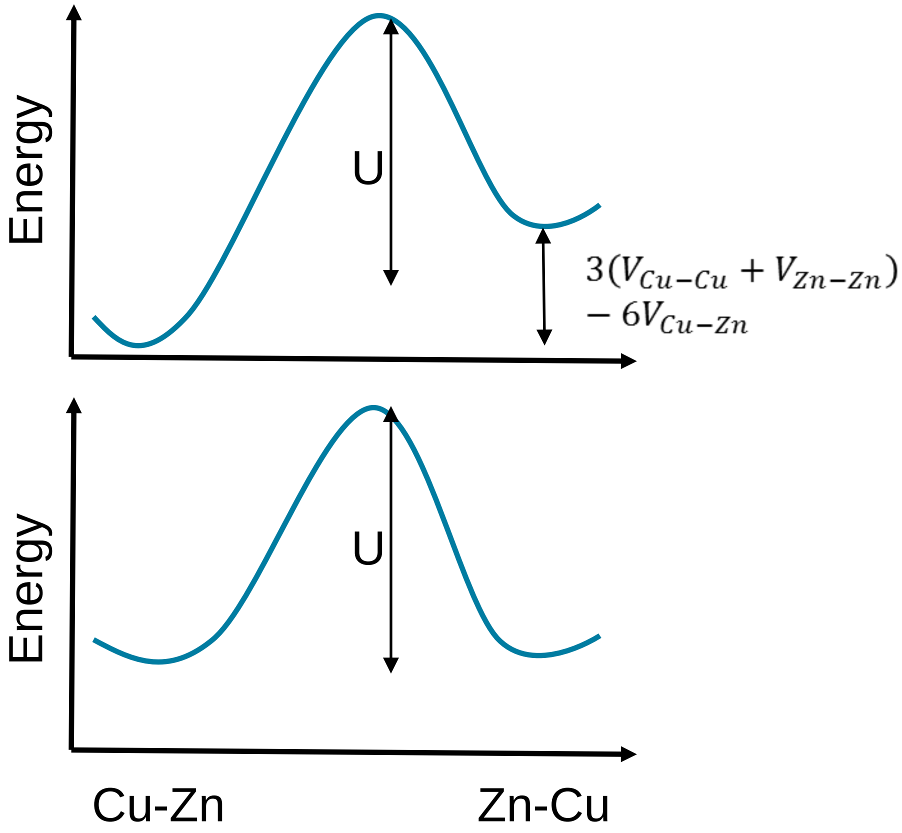
Material	Sample	Post synthesis thermal treatment	E_g (eV)	E_u (meV)	σ (meV)
CZTSSe	#1-D	1 h at 300°C + quench to RT	1.162	29	76
CZTSSe	#1-Std	none	1.204	30	74
CZTSSe	#1-O	1h at 180°C + 180→80°C in 10 h	1.264	32	77
CZTSSe	#2-D	1 h at 300°C + quench to RT	1.148	30	77
CZTSSe	#2-Std	none	1.255	30	87
CZTSSe	#2-O	1h at 180°C + 180→80°C in 10 h	1.301	31	85
CZTSSe	#3-D	1 h at 300°C + quench to RT	1.109	28	68
CZTSSe	#3-O	3 h at 170°C + 170→100°C in 3 d + 28 d at 100°C	1.238	29	70
CZTSe	#1-D	1 h at 250°C + quench to RT	0.916	26	49
CZTSe	#1-O+D	3 d at 100°C + 1 h at 250°C + quench to RT	0.913	26	49
CZTSe	#1-Std	none	0.931	25	49
CZTSe	#1-O	3 d at 100°C	0.959	27	49
CZTSe	#1-D+O	1 h at 250°C + quench to RT + 3 d at 100°C	0.959	25	49
CZTSe	#2-D	1 h at 300°C + quench to RT	0.894	28	56
CZTSe	#2-O	3 h at 170°C + 170→100°C in 3 d + 28 d at 100°C	0.952	29	59

No change of tail parameters with
Cu-Zn disorder

Theoretical description

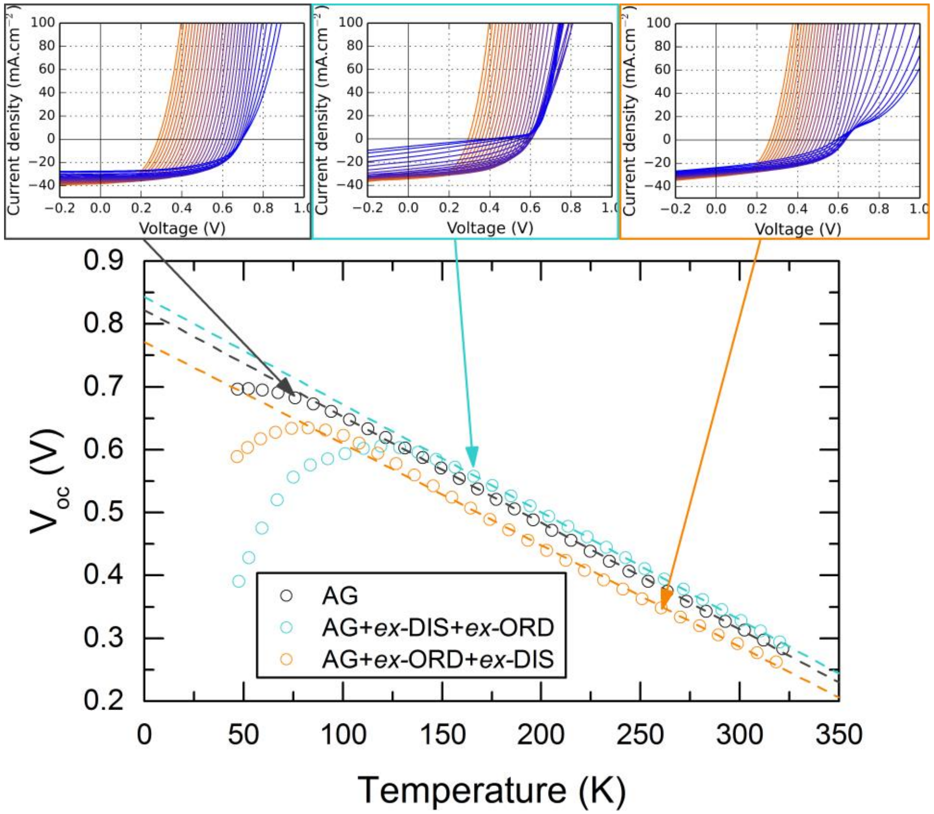
- Vineyard model





$$exchange\ rate = f\ exp[-(U + (k - j)V)/kT]$$

Voc deficit



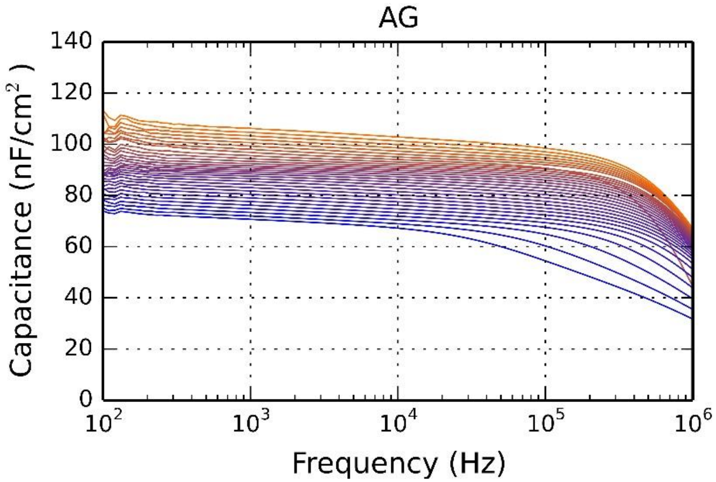
$$V_{oc} = \frac{E_a}{q} + \frac{AkT}{q}\ln\left(\frac{-J_{sc}\eta}{J_{00}}\right) \qquad [1]$$

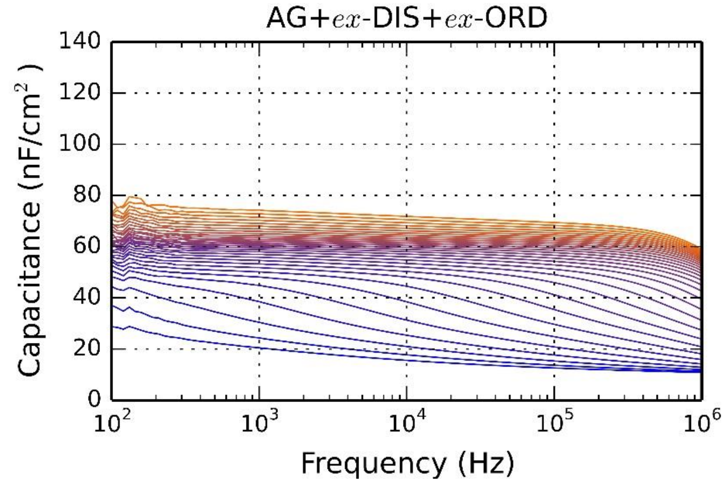
Sample	PL_m meV	E_a^{mrp} meV
AG	836	822
AG+*ex*-DIS+*ex*-ORD	866	843
AG+*ex*-DIS	817	810
AG+*ex*-ORD+*ex*-DIS	816	771
in-ORD	865	860
in-ORD+*ex*-ORD	898	870
in-ORD+*ex*-DIS+*ex*-ORD	867	855
in-ORD+*ex*-DIS	817	807
in-ORD+*ex*-ORD+*ex*-DIS	821	766

Ea matches PLmax except for ORD+DIS
Recombination occur mainly in the bulk

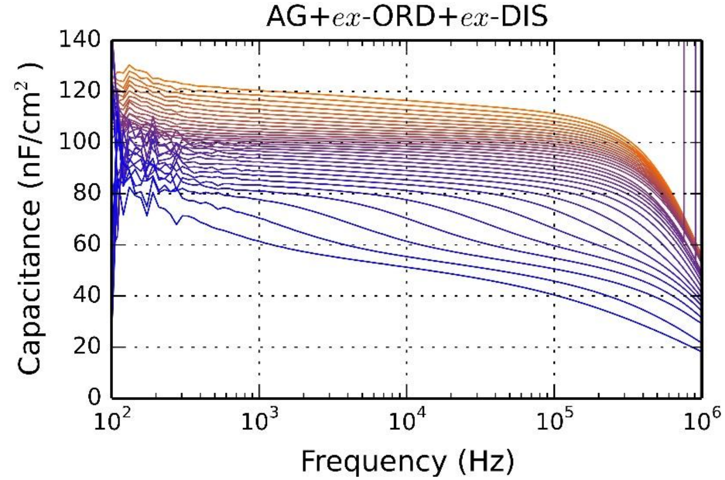
[1] R. Scheer & H.-W. Schock, Chalcogenide Photovoltaics Wiley-VCH

Admittance spectroscopy and CV





Sample	p $10^{16}\mathrm{cm}^{-3}$
AG	8
AG+*ex*-DIS+*ex*-ORD	2
AG+*ex*-DIS	18
AG+*ex*-ORD+*ex*-DIS	11
in-ORD	3
in-ORD+*ex*-ORD	2
in-ORD+*ex*-DIS+*ex*-ORD	4
in-ORD+*ex*-DIS	20
in-ORD+*ex*-ORD+*ex*-DIS	12

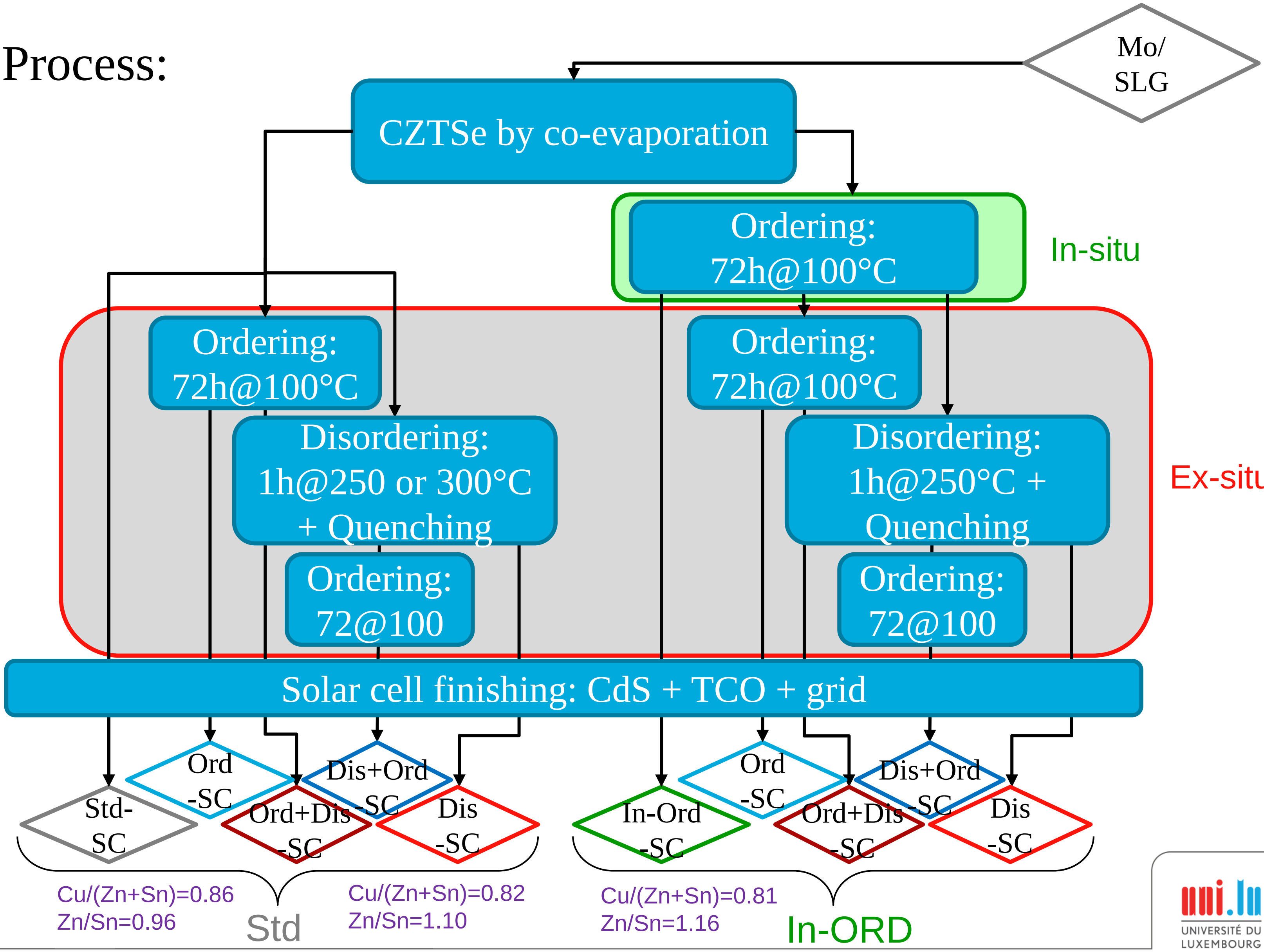


↑order ↓p

Order changes the carrier freeze out

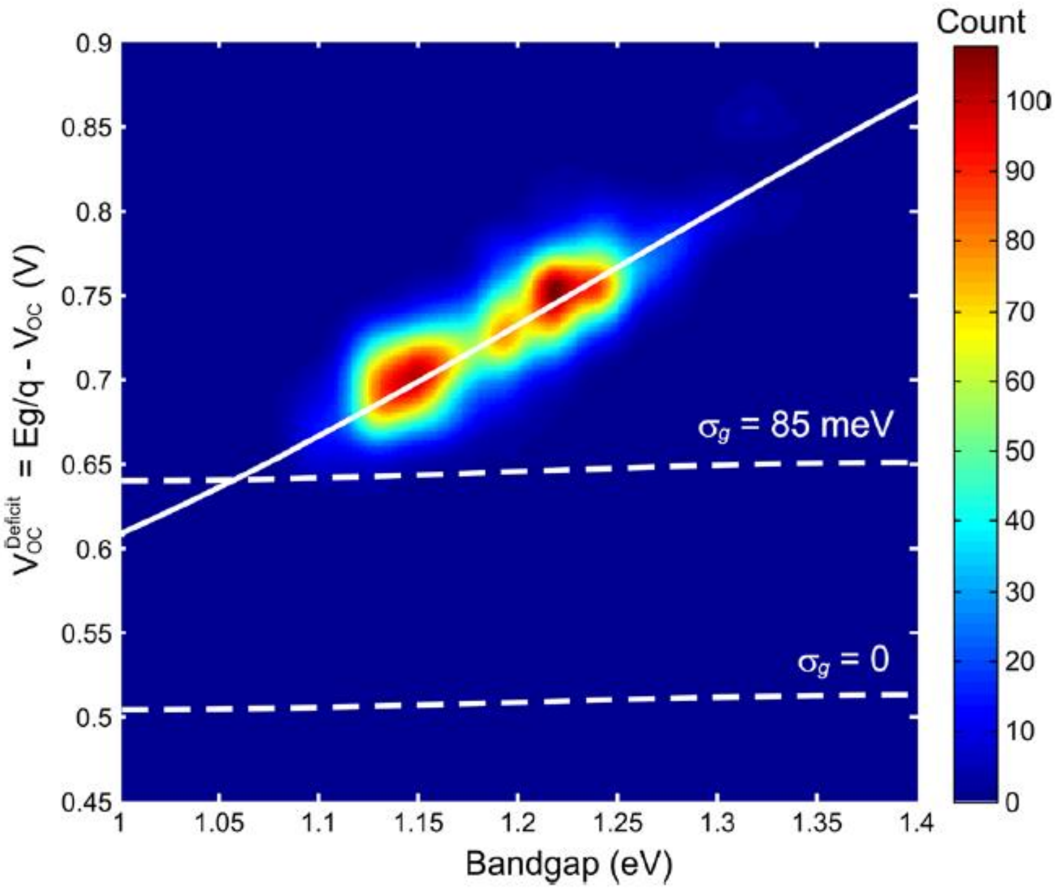
(Dis)order effect on device

- Process:



Introduction

- Voc: the kesterite chalenge

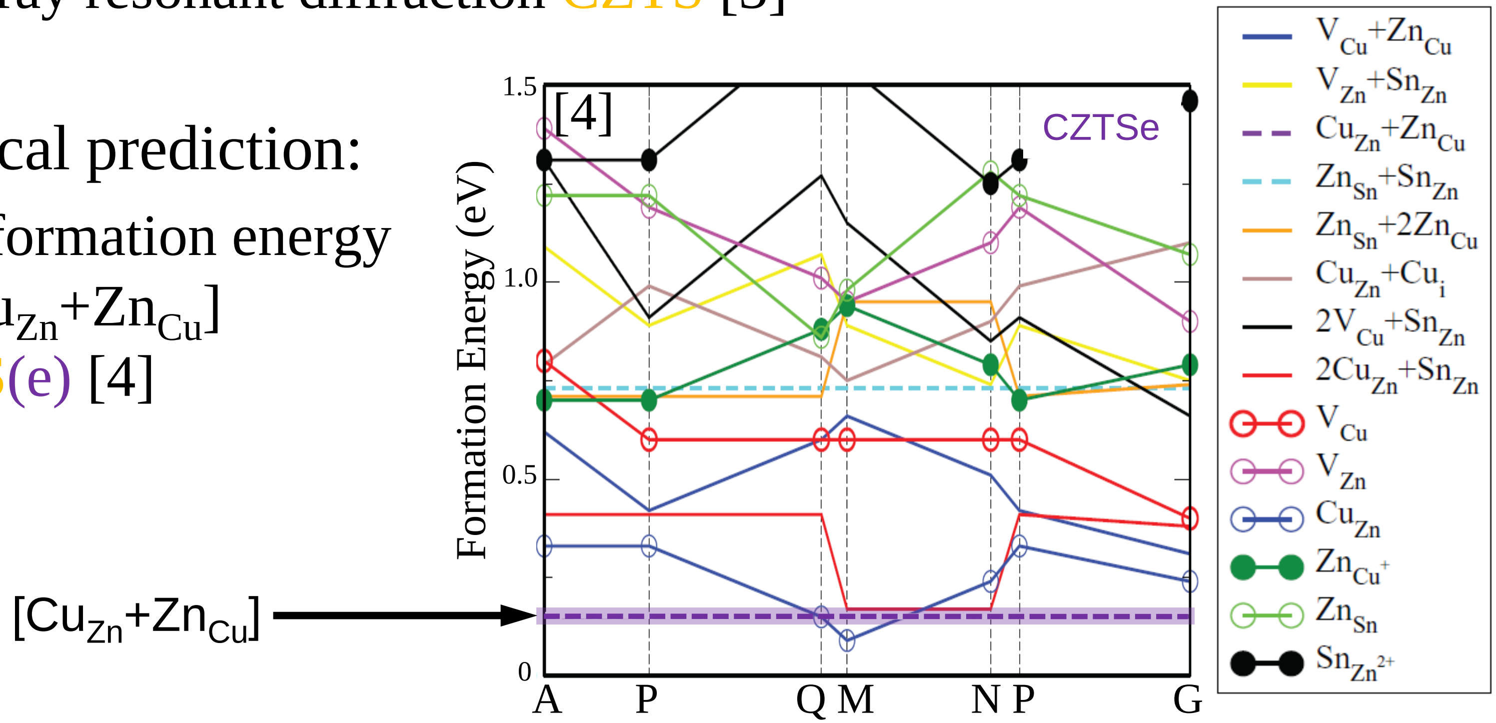


Gokmen *et al.* Appl. Phys. Lett. **103**, 103506 (2013)

Introduction and review

- Structural observation of disorder in Cu/Zn planes:
  – By neutron diffraction CZTS(e) [1]
  – By NMR CZTS [2]
  – By x-ray resonant diffraction CZTS [3]

- Theoretical prediction:
  – Low formation energy of [Cu_{Zn}+Zn_{Cu}] CZTS(e) [4]

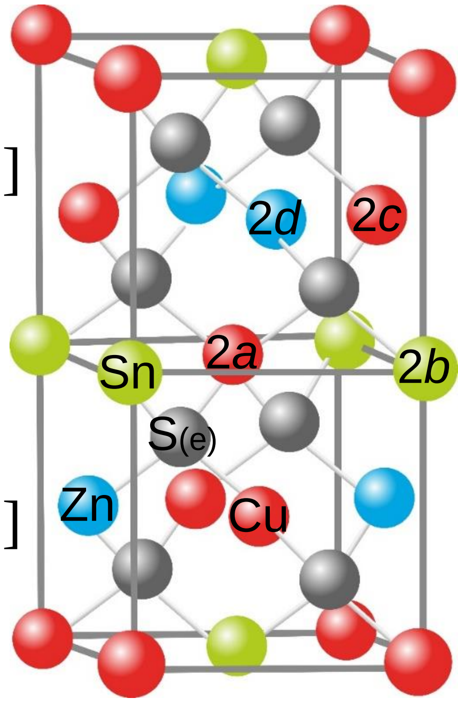


[1] S. Schorr SEM&SC **95** (2011) 1482
[2] L. Choubrac *et al.* PCCP **15** (2013) 10722
[3] A. Lafond *et al.* Acta Cryst. B **70** (2014) 390
[4] S. Chen *et al.* Adv. Mater. **25** (2013) 1522

Introduction and review

- No Cu(2*a*)/Zn(2*d*) exchange :
  - Position 2*a* occupied by Cu only (ND) CZTS(e) [1]
  - No Zn on 2*a* (NMR) CZTS [2]

- No disorder in the Cu/Sn planes:
  - Position 2*a* occupied by Cu only (ND) CZTS(e) [1]
  - Plane randomisation energy (*ab initio*) CZTS[3]:
    - Cu/Sn plane = 78 meV/at
    - Cu/Zn plane = 9 meV/at

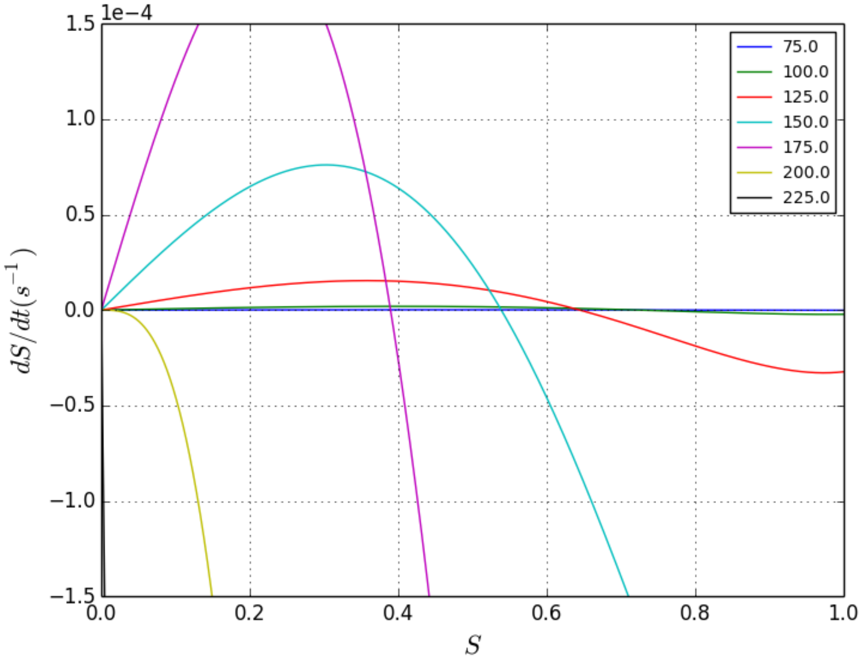


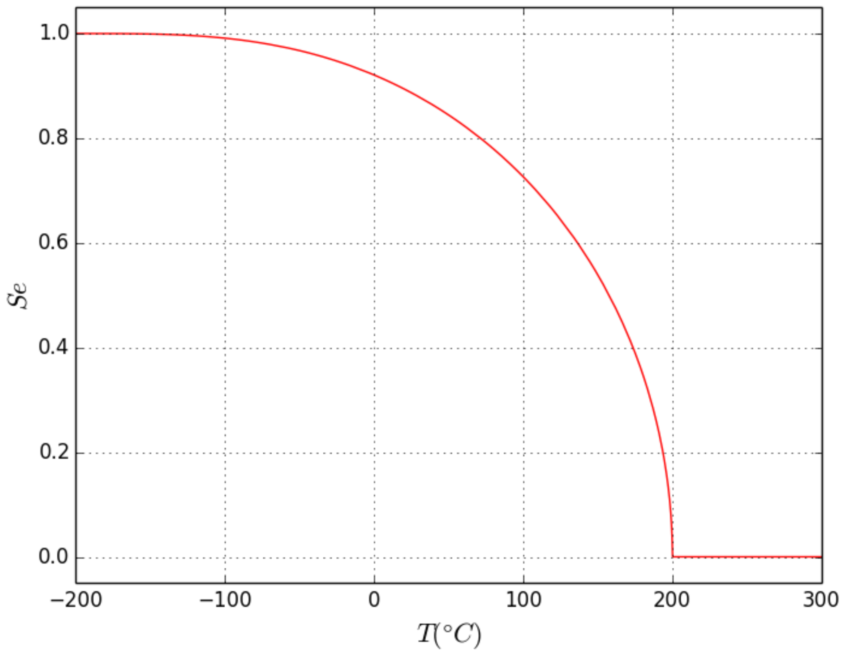
[1] S. Schorr SEM&SC **95** (2011) 1482
[2] L. Choubrac *et al.* PCCP **15** (2013) 10722
[3] S. Chen *et al.* APL **94** (2009) 041903

Theoretical description

- Motion equation for direct exchange

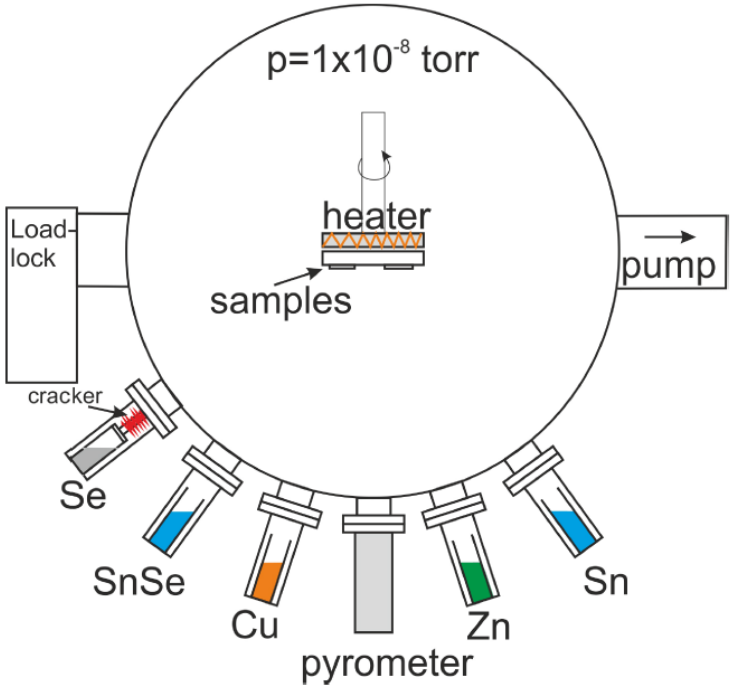
$$\frac{dS}{dt} = \frac{1}{2}\left[K_O(1-S)^2 - K_D(1+S)^2\right] \qquad \frac{K_O}{K_D} = 4f\ \exp\left(\frac{-U}{k_B T}\right)\exp\left(\frac{\pm 3vS}{k_B T}\right)$$

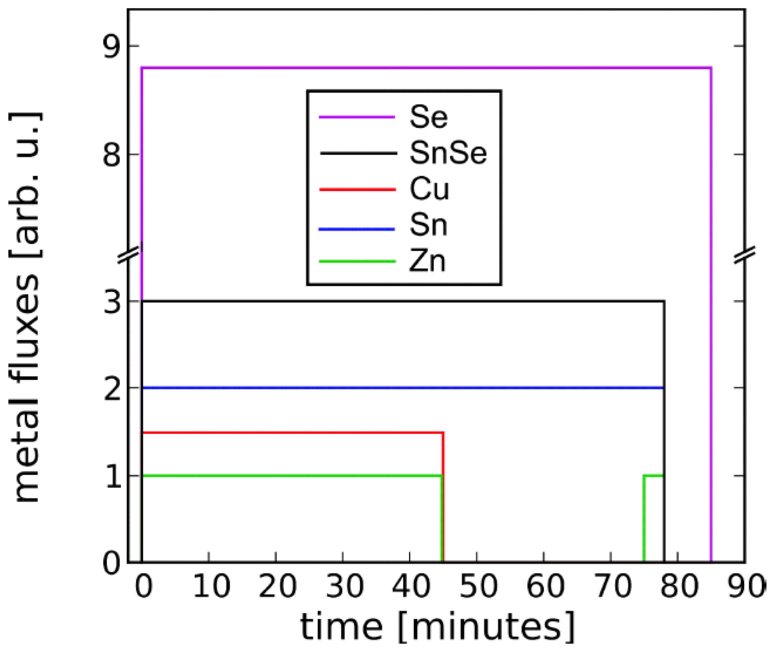




Band gap and (dis)order

- Sample preparation:
  – Coevaporation at 490°C



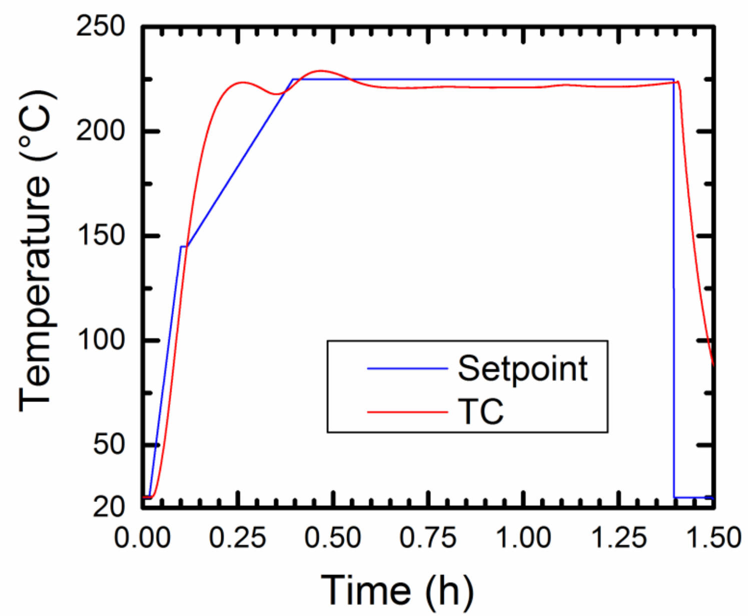


Composition: Cu/(Zn+Sn) = 0.86

Zn/Sn = 0.96

Band gap and (dis)order

- Annealing:
  - Two zones tubular oven
  - Vacuum (2.10^{-3} mbar)



- Quenching:
  - Transfert to cold zone
  - N_2 gaz flow

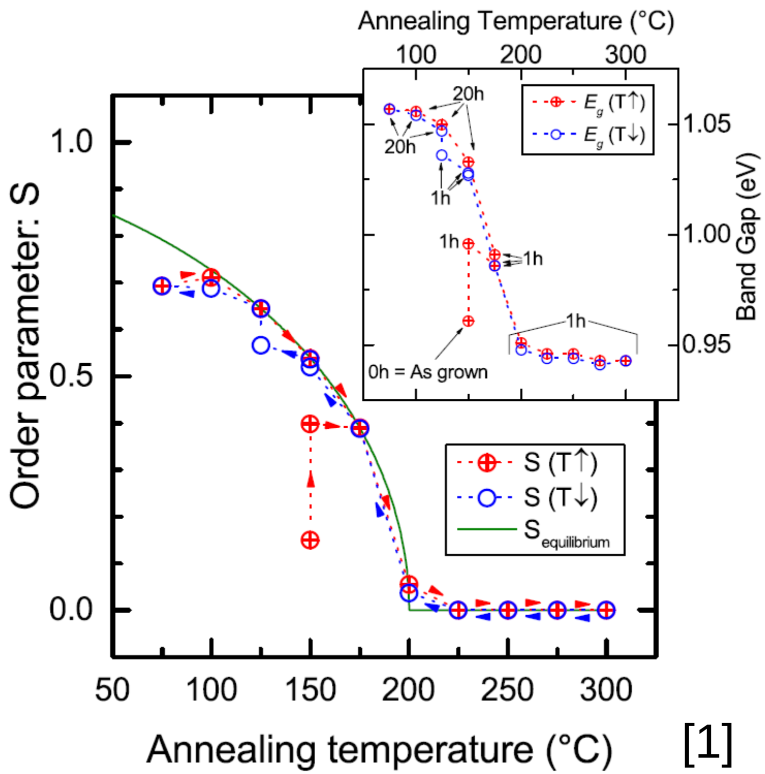
- Band gap measurement by spectrophotometry:
  - Non coherent free standing film

$$\alpha = \frac{1}{d} ln\left(\frac{R_s - \chi}{\chi T_s}\right)$$

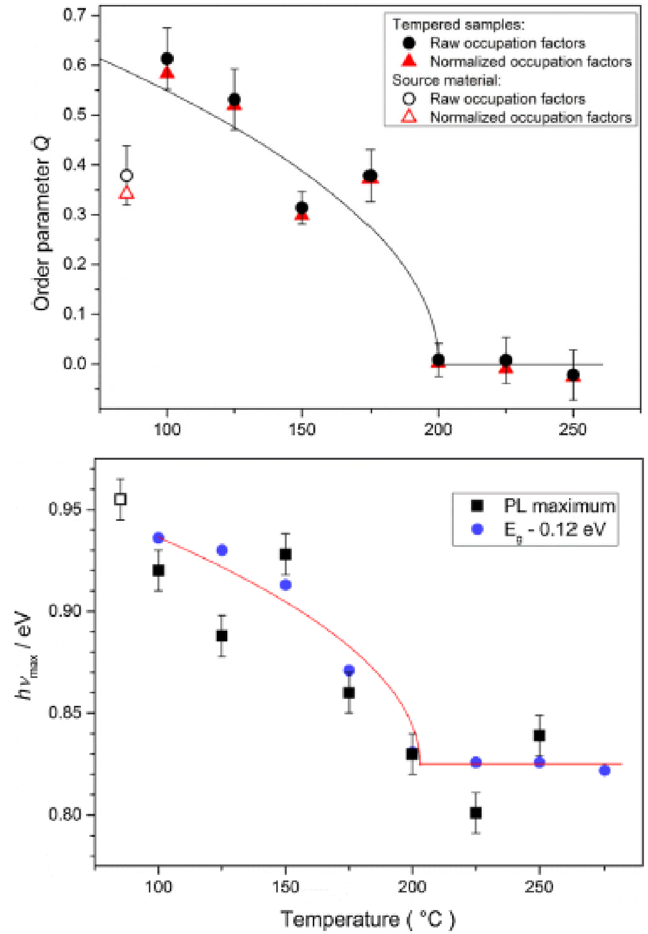
$$\chi = \frac{(\mathcal{T}_s^2 + 2) - (\mathcal{R}_s - 1)^2}{2\,(2 - \mathcal{R}_s)} - \sqrt{\left\{\frac{(\mathcal{T}_s^2 + 2) - (\mathcal{R}_s - 1)^2}{2\,(2 - \mathcal{R}_s)}\right\}^2 - \frac{\mathcal{R}_s}{2 - \mathcal{R}_s}}$$

Band-tailing & Cu-Zn (dis)order

- Cu-Zn (dis)order and band-gap



[1]



[2]

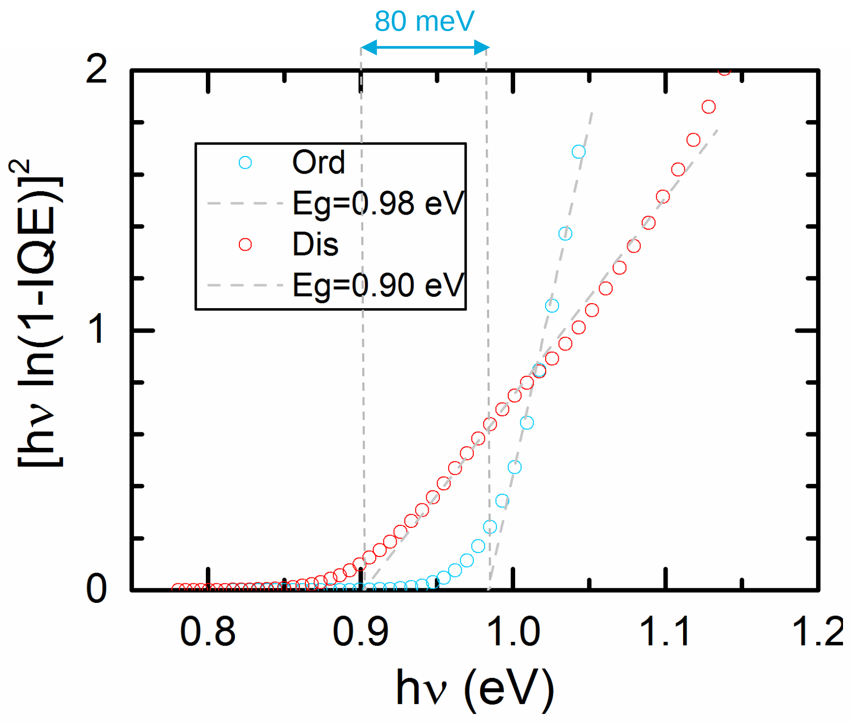
Cu-Zn (dis)order could be a potential source of band-gap fluctuations

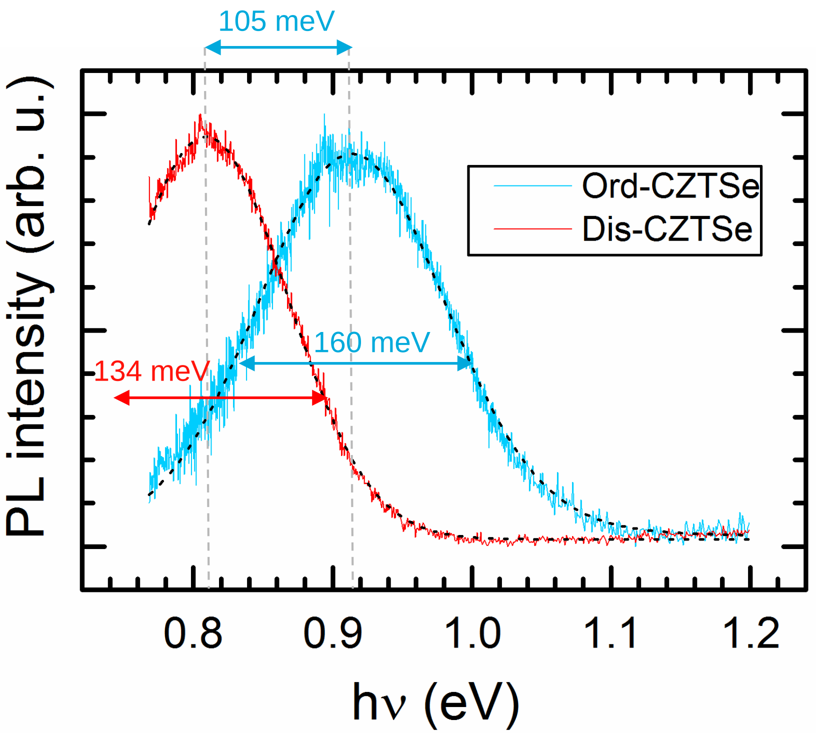
[1] G. Rey *et al.* Applied Physics Letters **105** (2014) 112106

[2] D. Többens *et al.* Physica Status Solidi (b) **253** (2016) 1890-1897

(dis)order effect on device

- EQE and PL for CZTSe on Mo/SLG

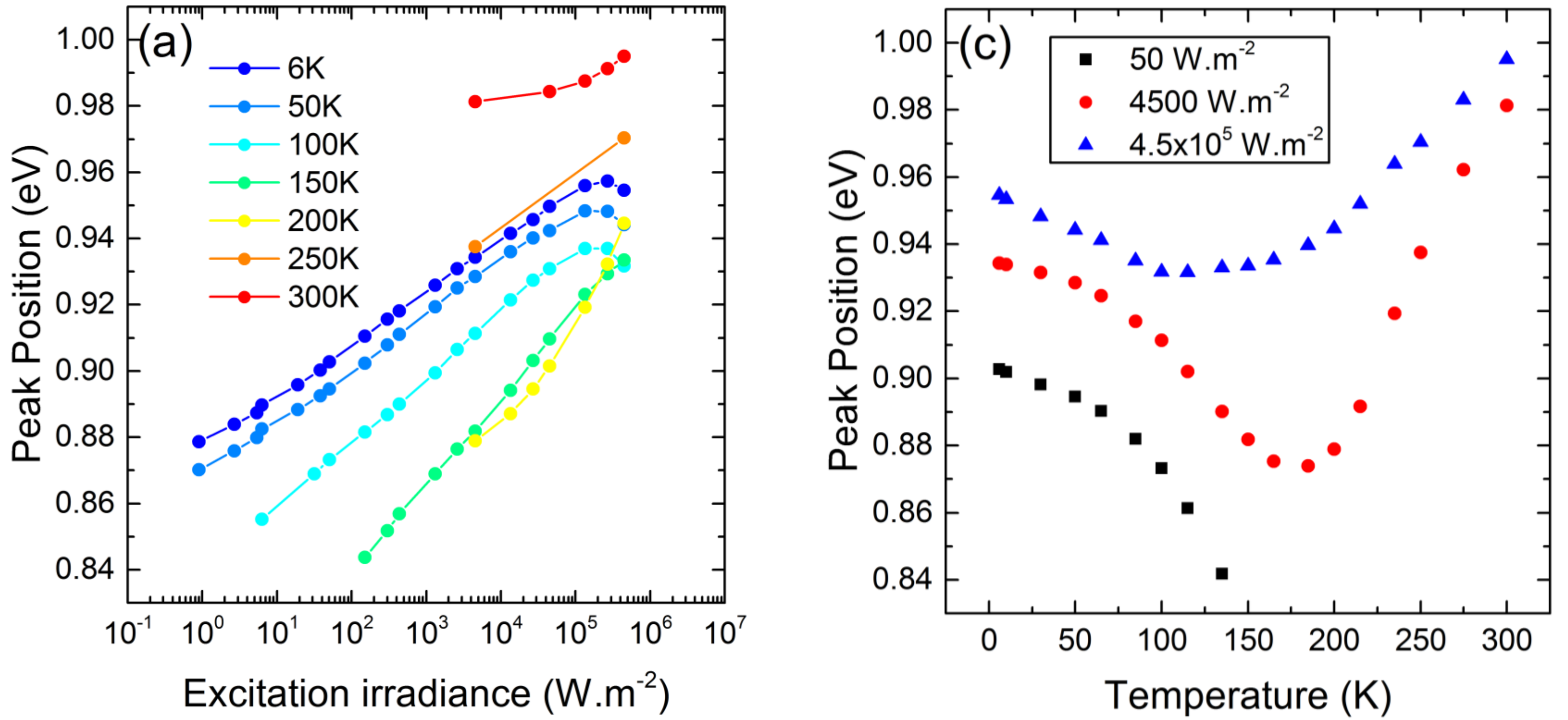




Decrease in band gap with decrease in order

Temperature and excitation dependent PL

- Peak position evolution:

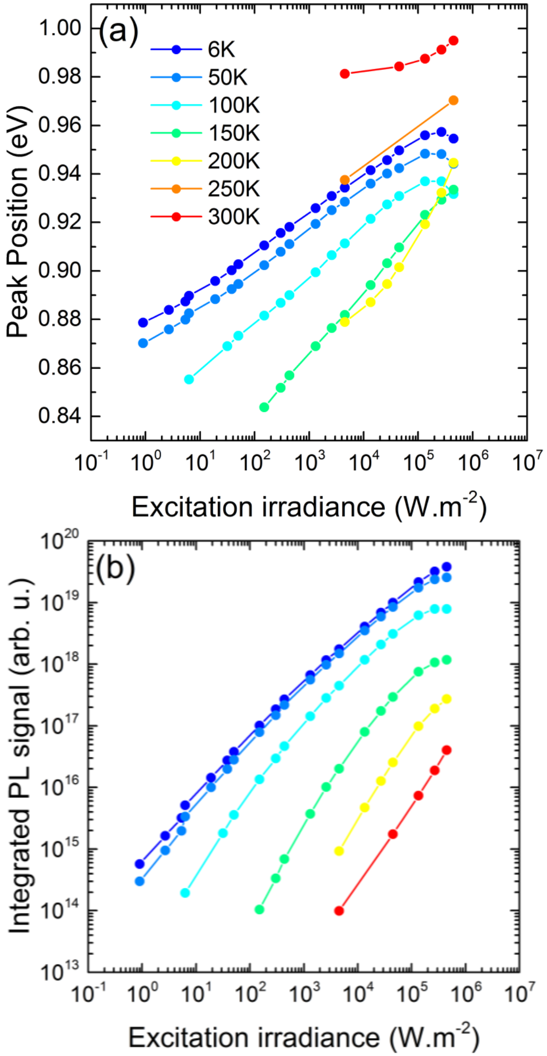


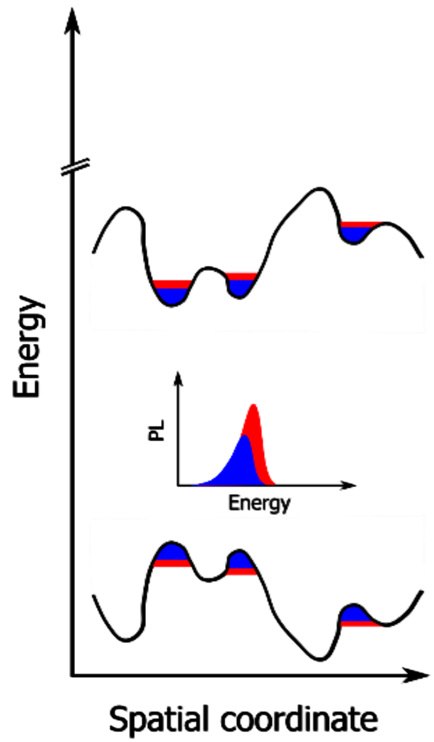
Blue-shift w. excitation, red-shift w. temperature (low T)
Heavily doped & heavily compensated SC

-Yu, P. W.
Excitation dependent emission in Mg , Be , Cd , and Zn implanted GaAs
Journal of Applied Physics, **1977**, *48*, 5043-5051

Temperature and excitation dependent PL

- Peak position evolution w. excitation:

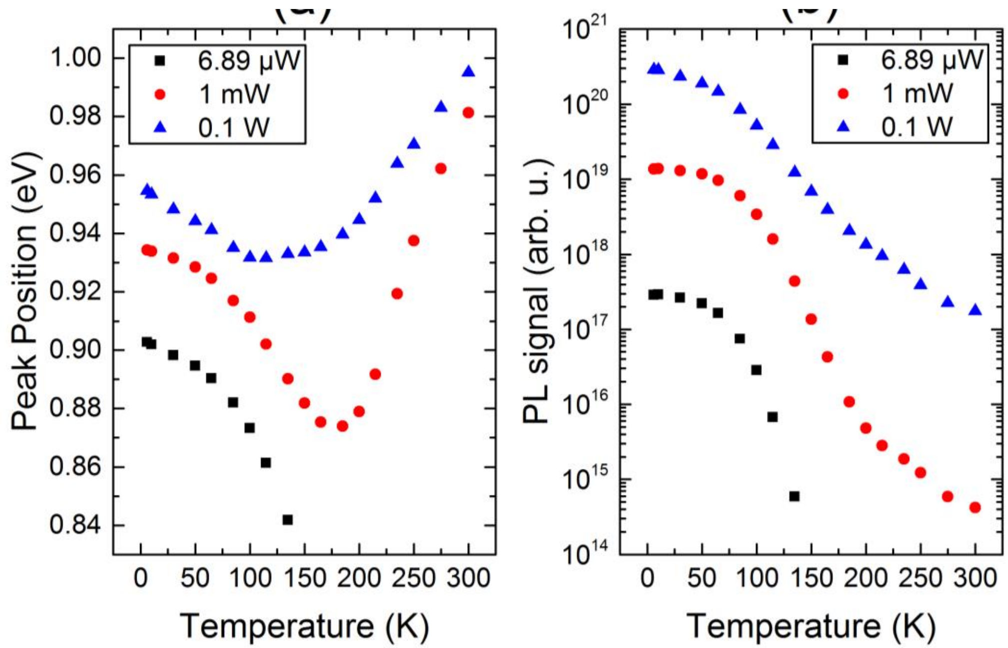


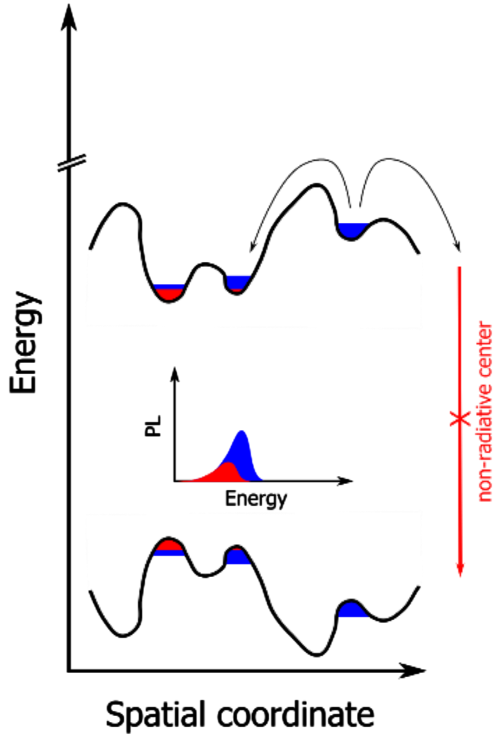


Non-mobile carrier at low T

Temperature and excitation dependent PL

- Peak position evolution w. temperature (low T):



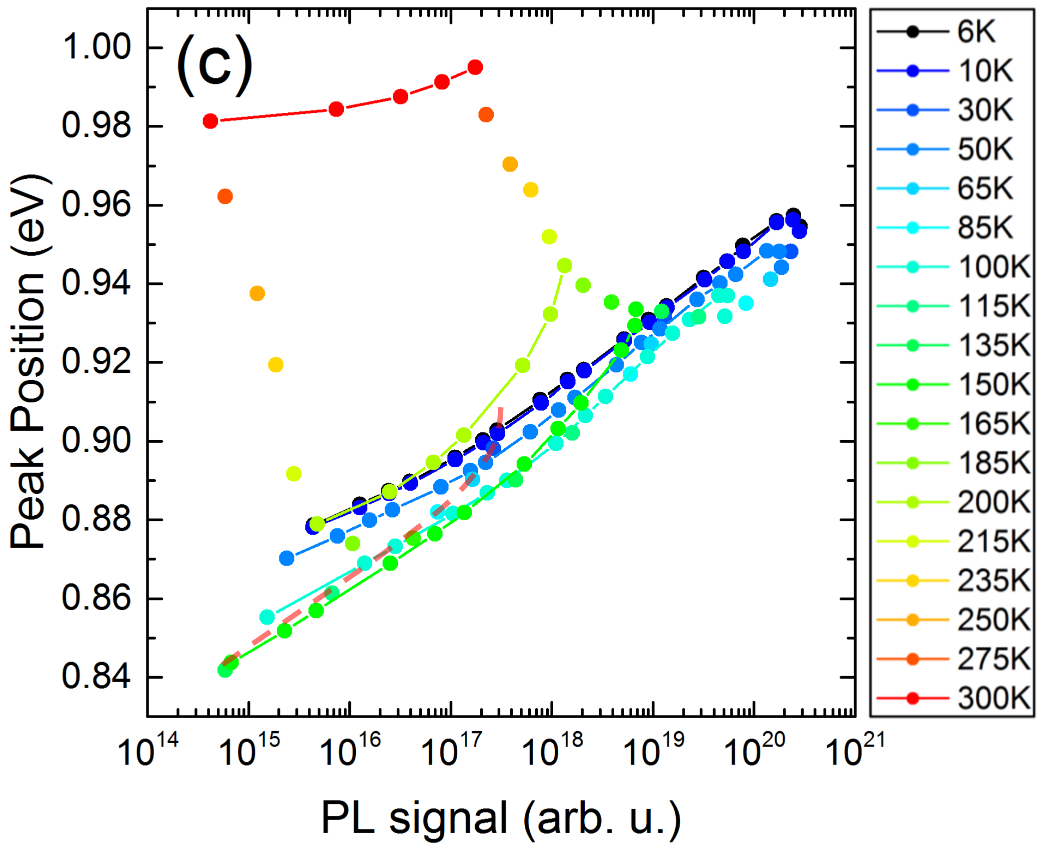


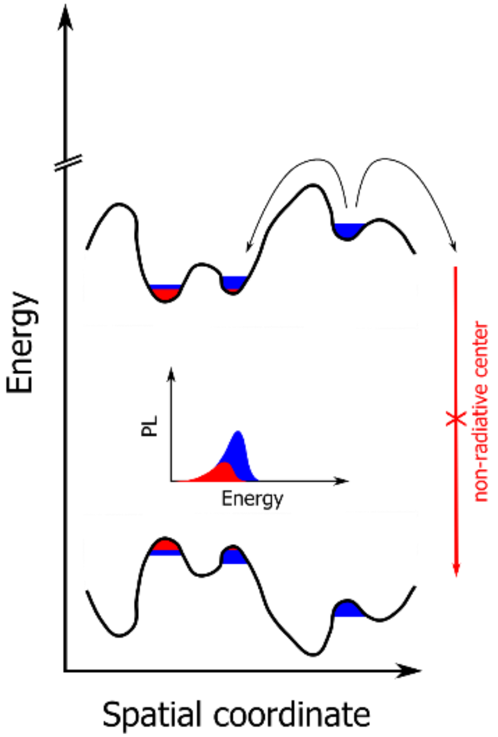
Mobility ↑ with T

-Gokmen, T.; Gunawan, O.; Todorov, T. K. & Mitzi, D. B.
Band tailing and efficiency limitation in kesterite solar cells
Applied Physics Letters, **2013**, *103*, 103506

Temperature and excitation dependent PL

- Peak position evolution w. temperature (low T):

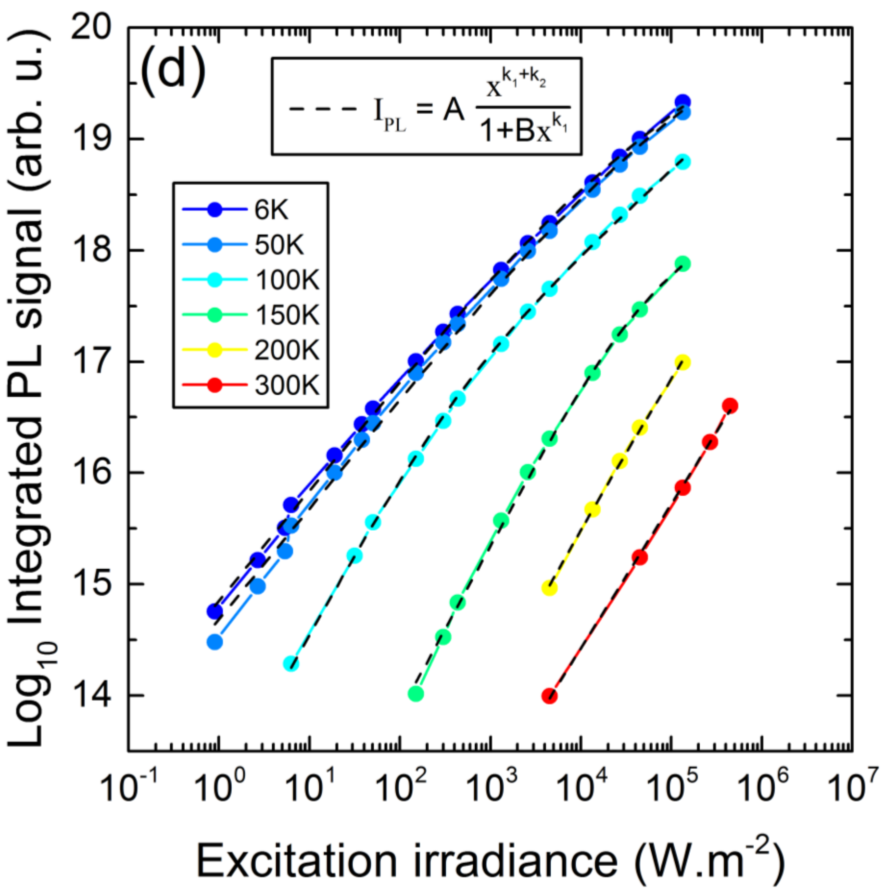




Effect of non-radiative recombination ↑ with T

Temperature and excitation dependent PL

- Radiative transition vs. temperature:



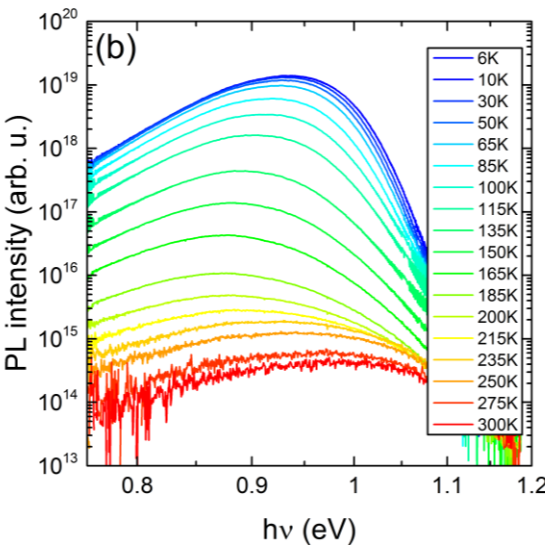
Temperature (K)	A	B	k_1	k_2
6	14.9	$1.1x10^{-2}$	0.5	0.5
50	14.7	$7.1x10^{-3}$	0.5	0.5
100	13.1	$1.2x10^{-2}$	0.75	0.75
150	10.9	$2.9x10^{-5}$	1	0.5
200	9.6	$2.1x10^{-3}$	0.5	1
300	9.2	0	0	1.30

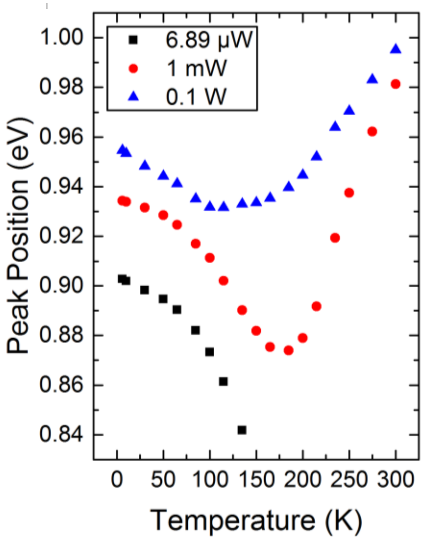
-Spindler, C.; Regesch, D. & Siebentritt, S. Revisiting radiative deep-level transitions in CuGaSe2 by photoluminescence *Applied Physics Letters*, **2016**, *109*, 032105

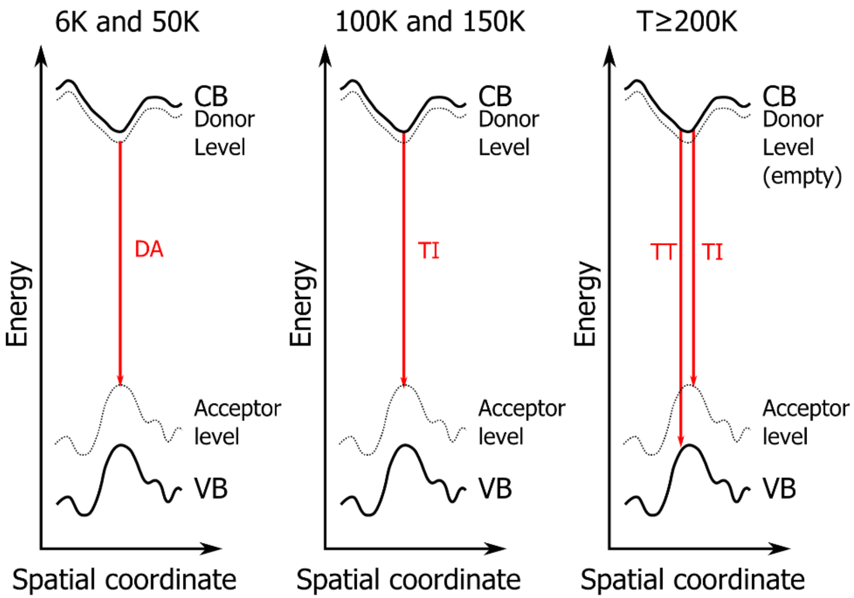
Temperature and excitation dependent PL

- Radiative transition vs. temperature:

Temperature (K)	A	B	k_1	k_2
6	14.9	$1.1x10^{-2}$	0.5	0.5
50	14.7	$7.1x10^{-3}$	0.5	0.5
100	13.1	$1.2x10^{-2}$	0.75	0.75
150	10.9	$2.9x10^{-5}$	1	0.5
200	9.6	$2.1x10^{-3}$	0.5	1
300	9.2	0	0	1.30



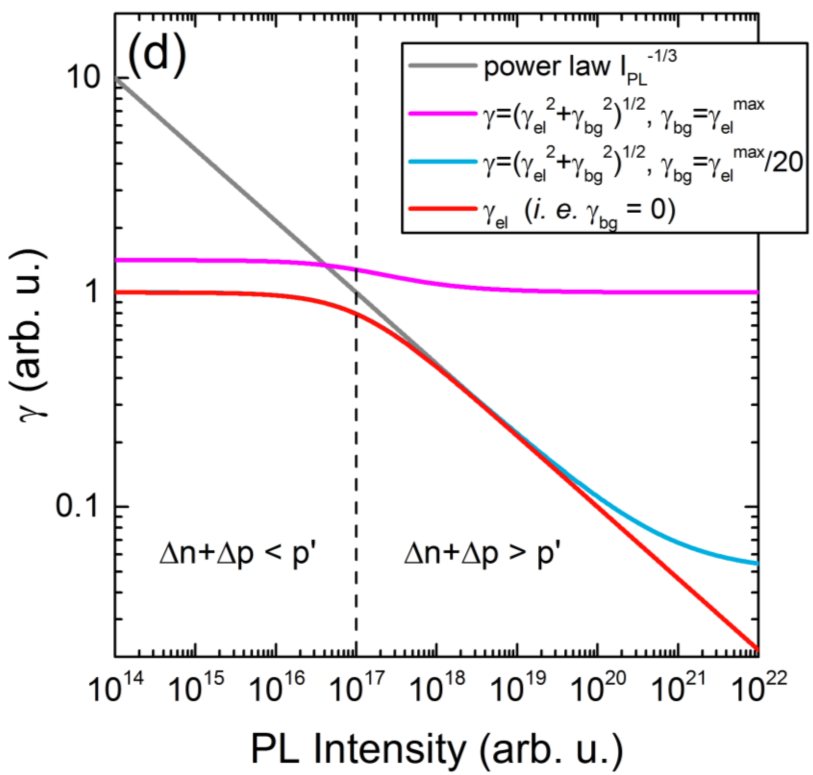


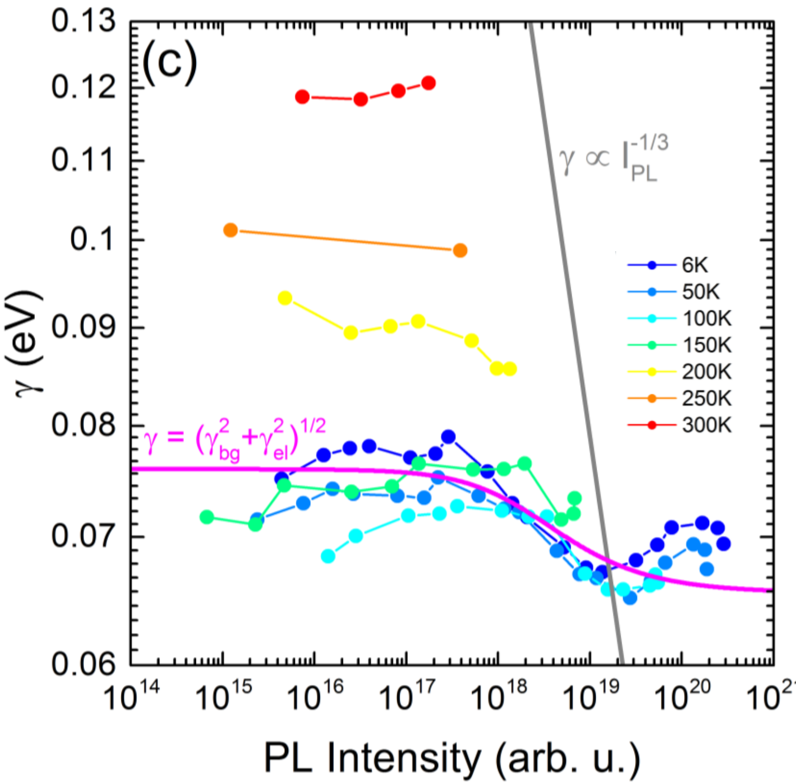


-Levcenko, S.; Just, J.; Redinger, A.; Larramona, G.; Bourdais, S.; Dennler, G.; Jacob, A. & Unold, T. Deep Defects in Cu$_2$Sn(S, Se)$_4$ Solar Cells with Varying Se Content *Phys. Rev. Applied*, **2016**, *5*, 024004

Temperature and excitation dependent PL

- Nature of the fluctuation:





$$\gamma_{el} = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0}\frac{N_I{}^{2/3}}{p^{1/3}}$$