

II – VI Semiconductors and derivated kesterites structures for photovoltaic conversion

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« Nanophysique et Semiconducteurs » group



the alloys $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$

Motivation: Why these new alloys for photovoltaic conversion

State of the art : The limits of these alloys: potential fluctuations

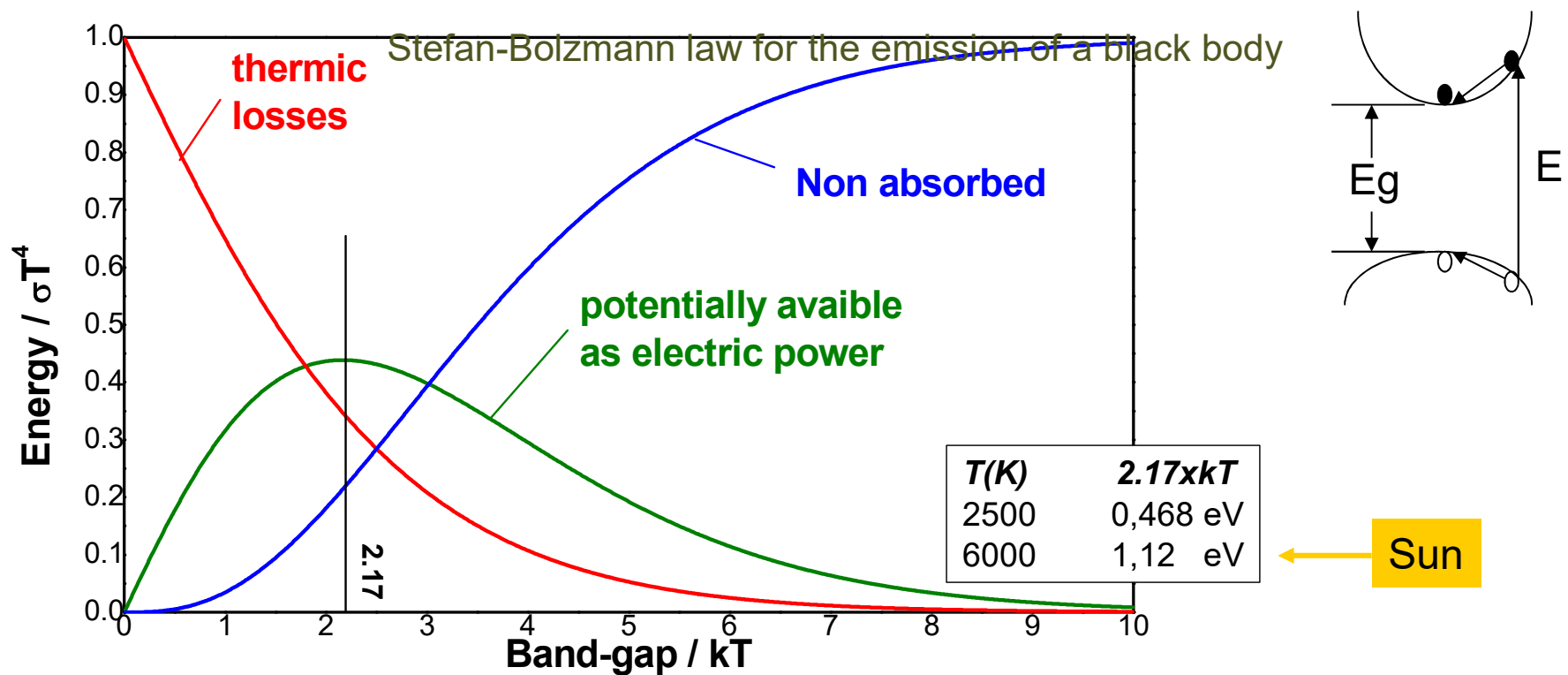
This work : A better understanding to overcome them

- **Optical study: PL, PLE, TRPL spectroscopy**
- Electrical study: admittance spectroscopy

Perspectives: - direct measurements of local disorder

Conversion of energy in solar cells: the issues

$$\int_0^{E_g} E \frac{E^2}{e^{\frac{E}{kT}} - 1} dE + \int_{E_g}^{\infty} (E_g) \frac{E^2}{e^{\frac{E}{kT}} - 1} dE + \int_{E_g}^{\infty} (E - E_g) \frac{E^2}{e^{\frac{E}{kT}} - 1} dE = \sigma T^4$$



Detailed Balance Limit of Efficiency of *p-n* Junction Solar Cells*

WILLIAM SHOCKLEY AND HANS J. QUEISSER

Shockley Transistor, Unit of Clevite Transistor, Palo Alto, California

(Received May 3, 1960; in final form October 31, 1960)

Energy gap from Si to CdTe
CdSe

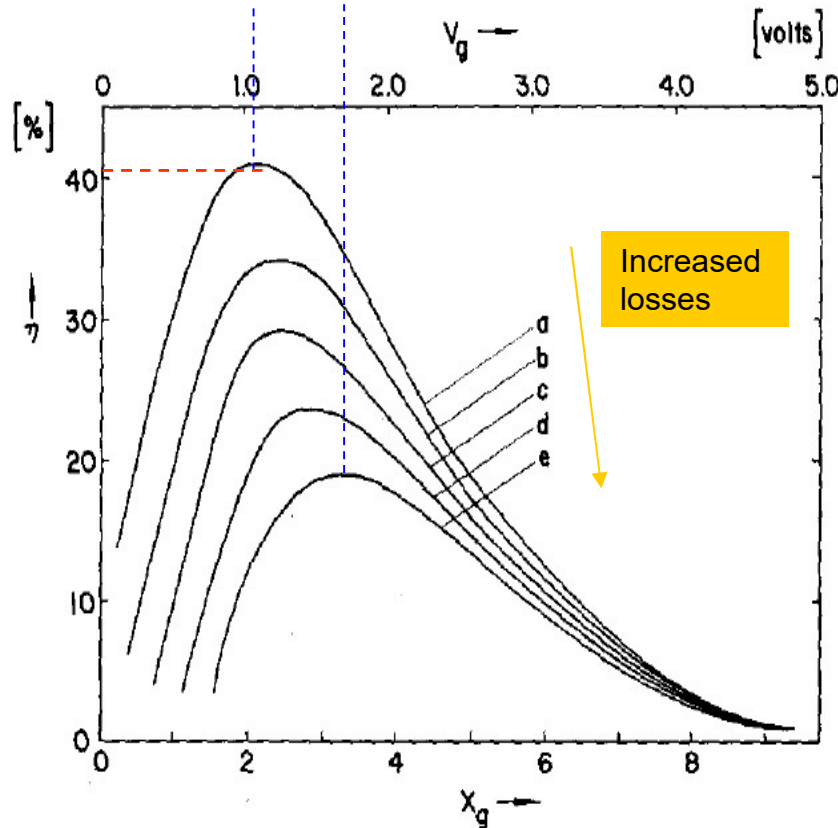


FIG. 5. Efficiency η for a blackbody solar cell at $T_c=300^\circ\text{K}$, with sun at $T_s=6000^\circ\text{C}$, as a function of energy gap for different values of the parameter f : curve (a) $f=1$; (b) $f=10^{-3}$; (c) $f=10^{-6}$; (d) $f=10^{-9}$; (e) $f=10^{-12}$.

Assumptions of the model

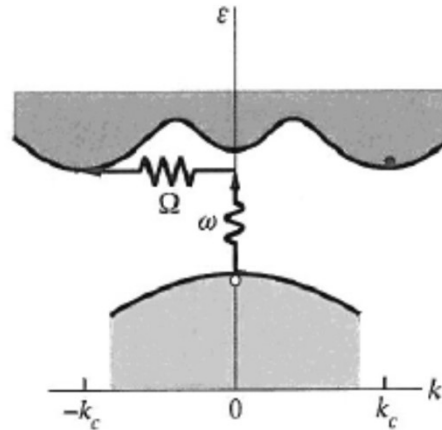
\approx **Goals to reach**

- all the incident photons go into the material
- choice of the semiconductor
Optimal band gap
- good separation/collection of photo-created pairs (no loss by recombination)

Motivation: Why these new alloys for photovoltaic conversion

direct bandgap semiconductors

- Most of the cells made of Si
→ other interesting materials
- the alloys $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$
 - much higher absorption
 - less material needed
 - high recombination rate



$$\alpha \approx 1 \text{ cm}^{-1} \text{ at } E_g$$



$$\alpha \approx 8\,000 \text{ cm}^{-1} \text{ at } E_g$$

State of the art : The limits of these alloys: potential fluctuations

Thin film technologies:

Polycrystalline CdTe module 21 %

- First Solar Compagny
and NREL Golden Colorado
(grain boundary enhanced carrier collection in CdTe
solar cells (PRL, 112, 156103 (2014))

Polycrystalline **CuInGaS₂** (CIGS) module 21 %:

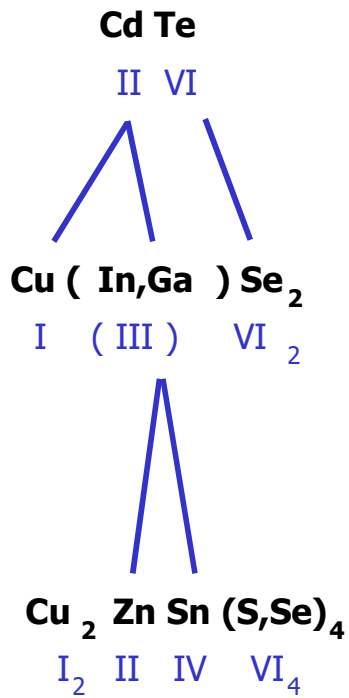
- First Solar Frontier Compagny
and AIST Tsukuba

Monocrystalline **GaAs** 28 %

- Alta Device (Berkeley)

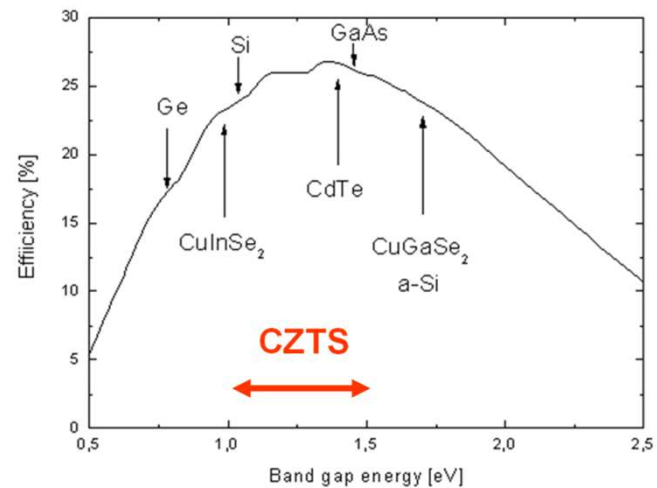
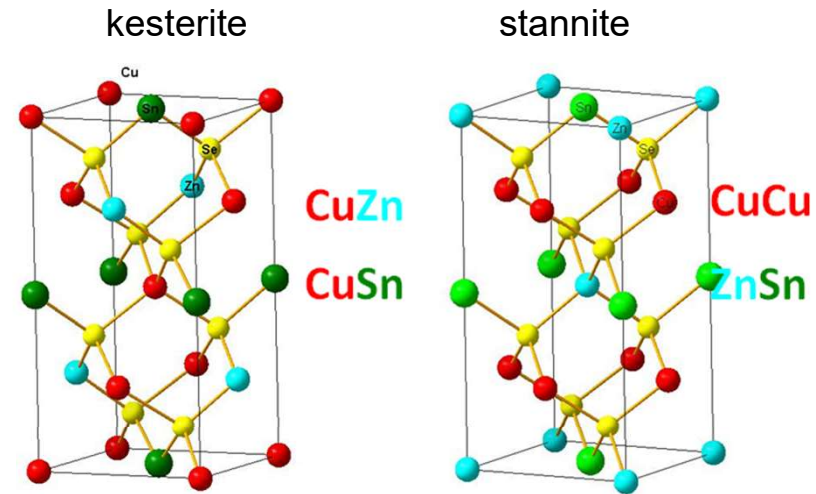
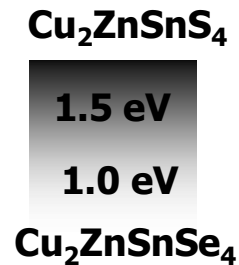
Motivation: Why these new alloys for photovoltaic conversion

the bandgap range of $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$



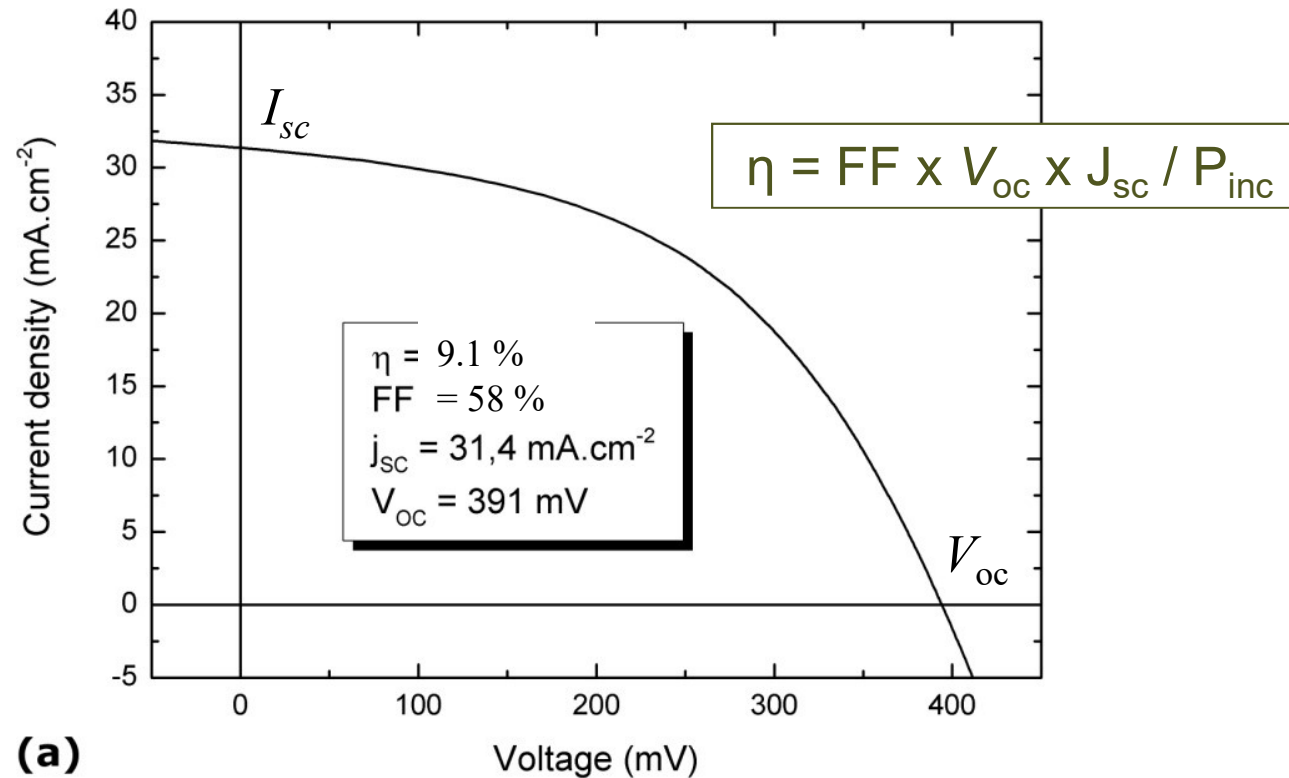
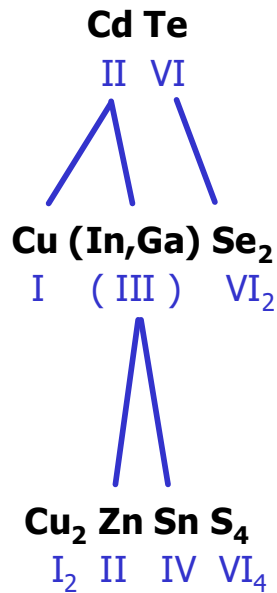
toxic

scarced



Motivation: Why this new compound for photovoltaic conversion

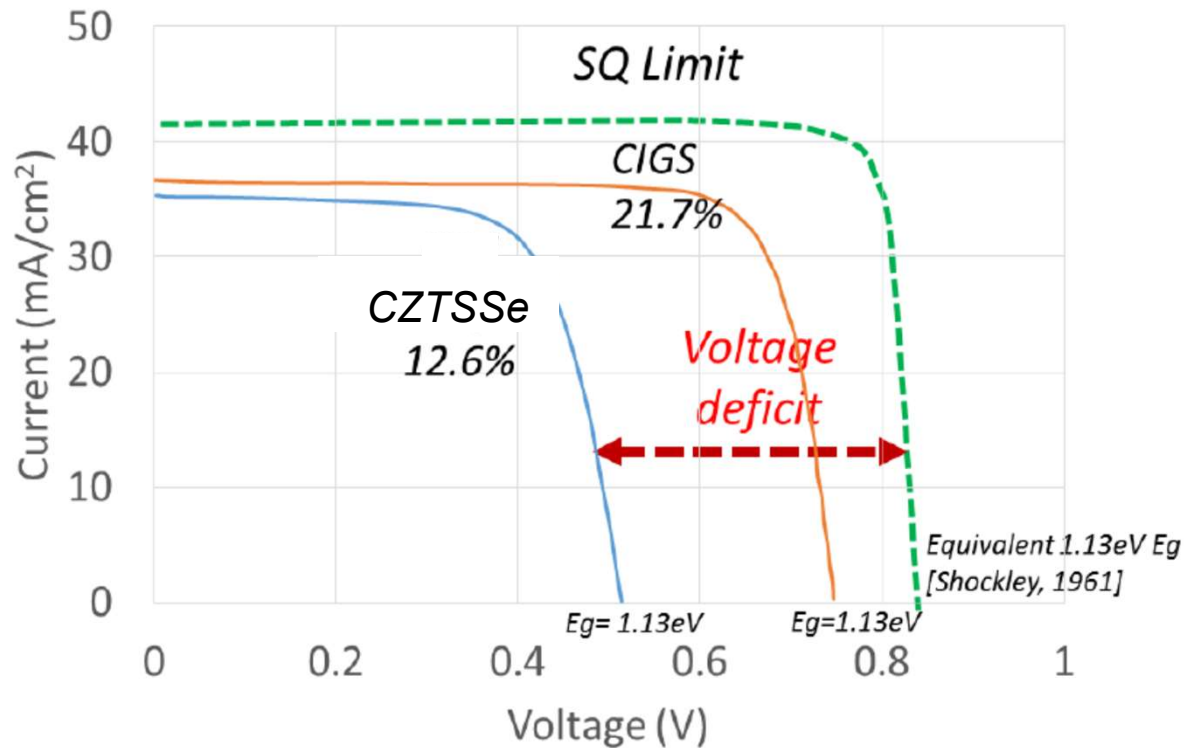
Cu₂ZnSn(S_xSe_{1-x})₄ solar cells



L. Grenet, et al. Solar Energy Material & Solar Cells 101, 11 (2012) Two steps process sputtering
Y. Curé et al. Scripta Material, 130, 200 (2016) Molecular beam epitaxy

State of the art : The limits of these alloys: potential fluctuations

- deficit of V_{OC} in CZTSSe compared to CIGSSe

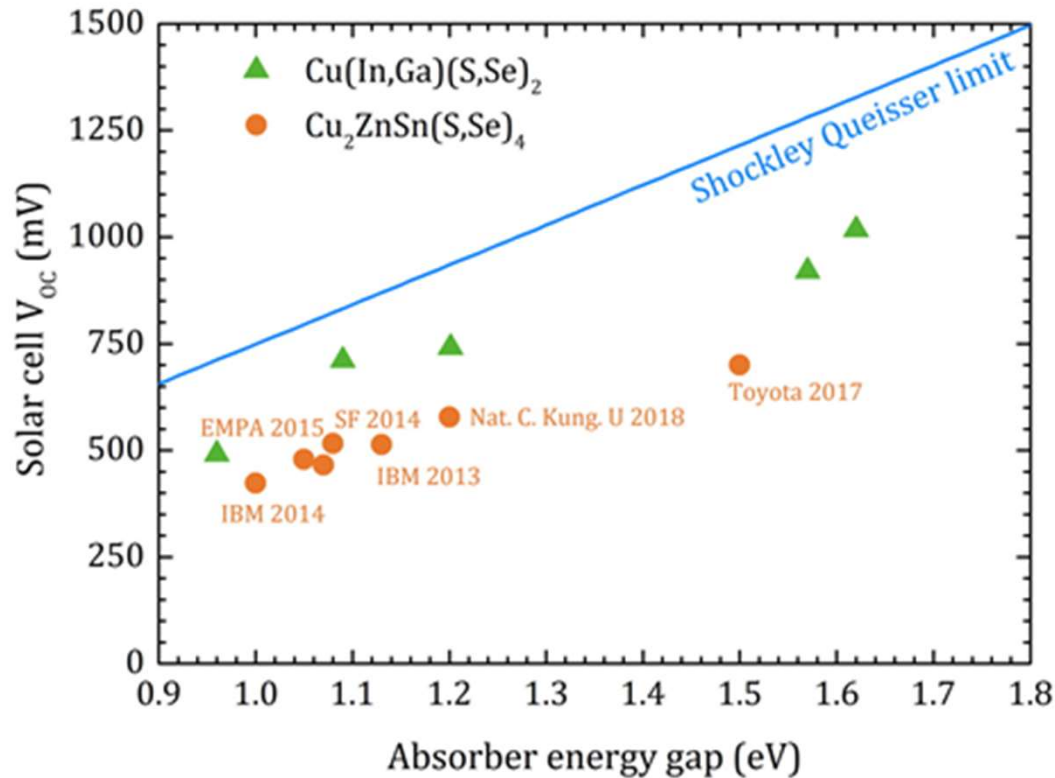


CZTS: W. Wang *et al.* IBM Yorktown-Heights, *Adv. Energy Mater.* 4, 1301465 (2015)

CIGS: P. Jackson *et al.* Zentrum für Sonnenenergie, Stuttgart, *Phys. Stat.Sol. RRL*,10, 583 (2016)

State of the art : The limits of these alloys: potential fluctuations

- deficit of V_{OC} in CZTSSe compared to CIGSSe



- deficit also of the field factor: FF 60% instead of 75%

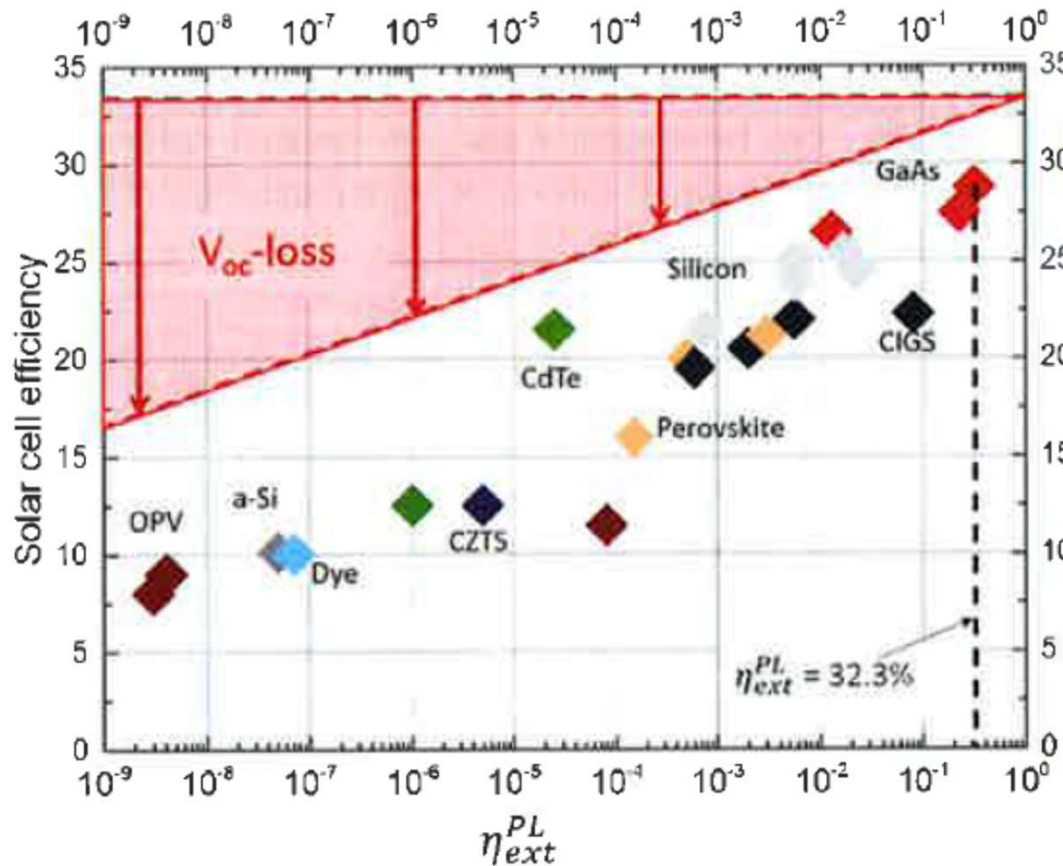
- also strong series resistance at low T => freeze-out effect

- Strong limitation of V_{OC} related to severe band tailing ?

State of the art : The limits of these alloys: potential fluctuations

$$V_{oc} = V_{oc}^{rad} - \left| \frac{kT}{q} \ln(\eta_{ext}^{PL}) \right|$$

$$\eta_{ext}^{PL} = \frac{\tau_{rad}^{-1}}{\tau_{rad}^{-1} + \tau_{nrad}^{-1}} \overline{P_{esc}}$$

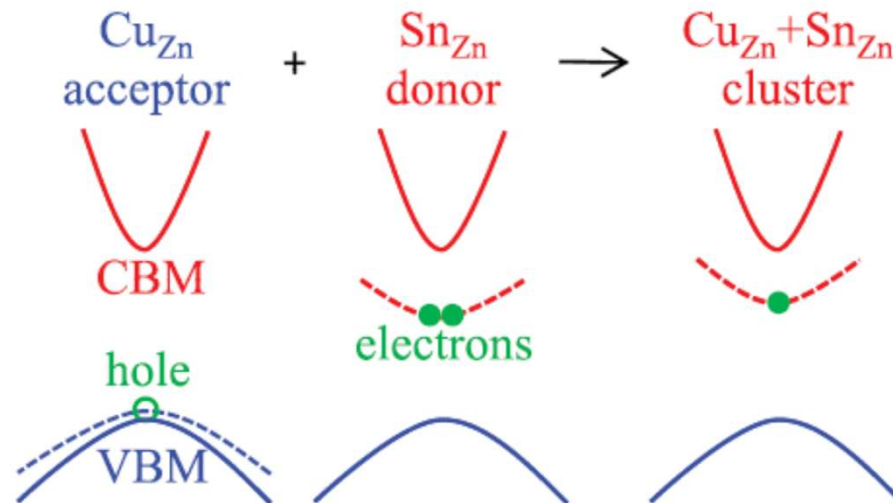


Optimization of V_{oc}

- Optimum bandgap
- 100% internal radiative efficiency
- High Light extraction efficiency

State of the art : The limits of these alloys: potential fluctuations

- Cu_{Zn} antisite has the lowest formation energy
(by contrast with CIGS for which it is V_{Cu} vacancy)
- low formation energy for defect cluster such as the pair
($\text{Cu}_{\text{Zn}} + \text{Sn}_{\text{Zn}}$) and the triplet ($2\text{Cu}_{\text{Zn}} + \text{Sn}_{\text{Zn}}$)

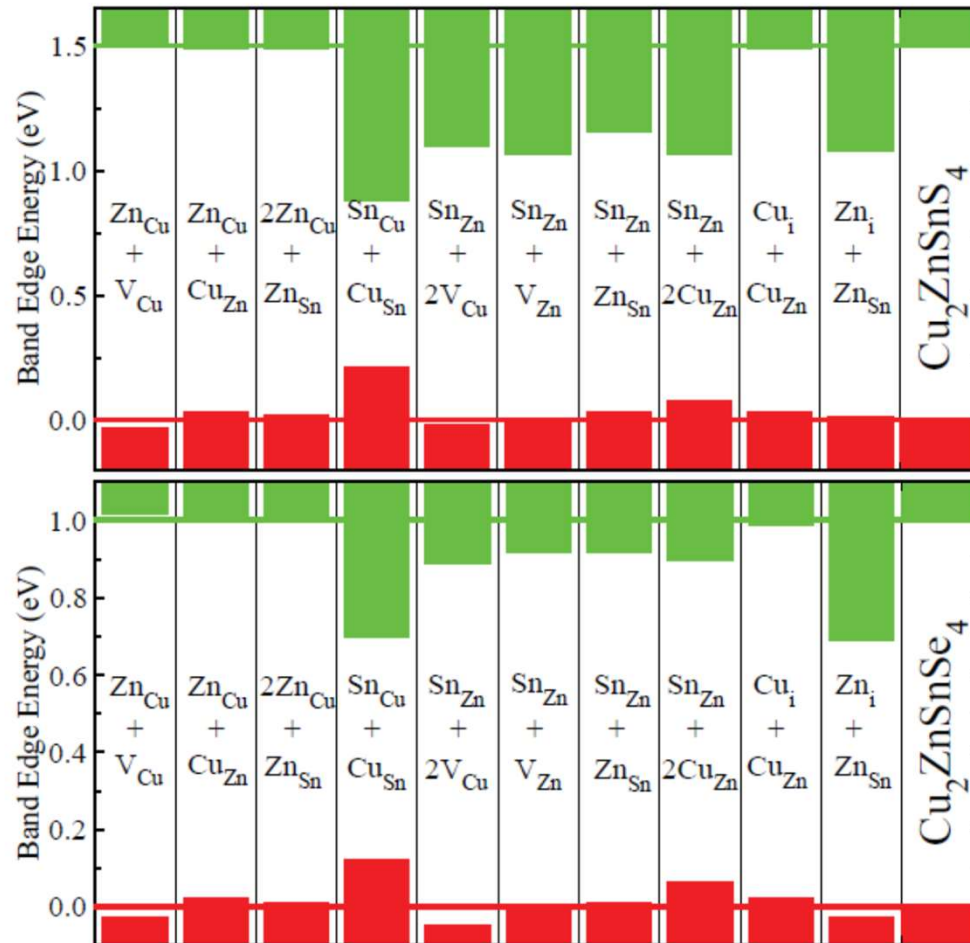


($\text{Cu}_{\text{Zn}} + \text{Sn}_{\text{Zn}}$) => deep donor level in the bandgap

($2\text{Cu}_{\text{Zn}} + \text{Sn}_{\text{Zn}}$) => decrease the gap by about 200 meV

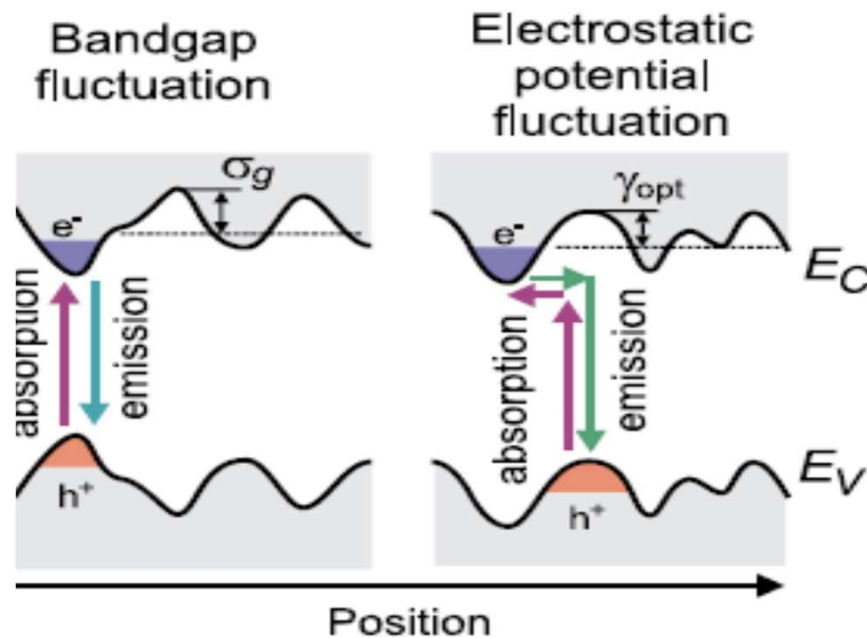
State of the art : The limits of these alloys: potential fluctuations

Calculated energy band shifts caused by different defect clusters induced by cation disorder



State of the art : The limits of these alloys: potential fluctuations

Strong limitation related to severe band tailing ?



in our work, in order to avoid the bandgap fluctuations, study of either $\text{Cu}_2\text{ZnSnS}_4$ or $\text{Cu}_2\text{ZnSnSe}_4$ samples

S. Bourdais, C. Choné, B. Delatouche, A. Jacob, G. Larramona, C. Moisan, A. Lafond, F. Donatini, G. Rey, S. Siebentritt, A. Walsh, G. Dennler, Adv. Energy Mater. 1552276 (2016)

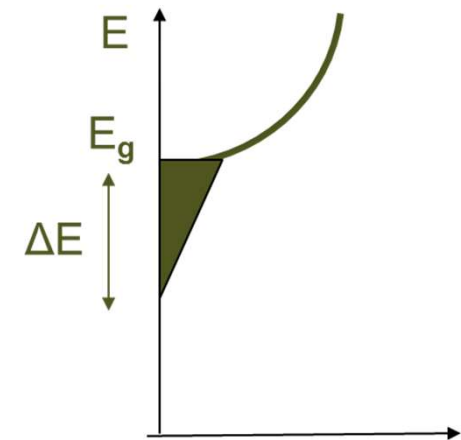
This work: : a better understanding of potential fluctuations

Optical spectroscopy

- Emission properties of CZTS single crystals (population)
photoluminescence (PL)
- absorption properties of CZTS (density of states)
photoluminescence excitation (PLE)
- Time resolved spectroscopy (energy transfer between
localized states, type of recombination).

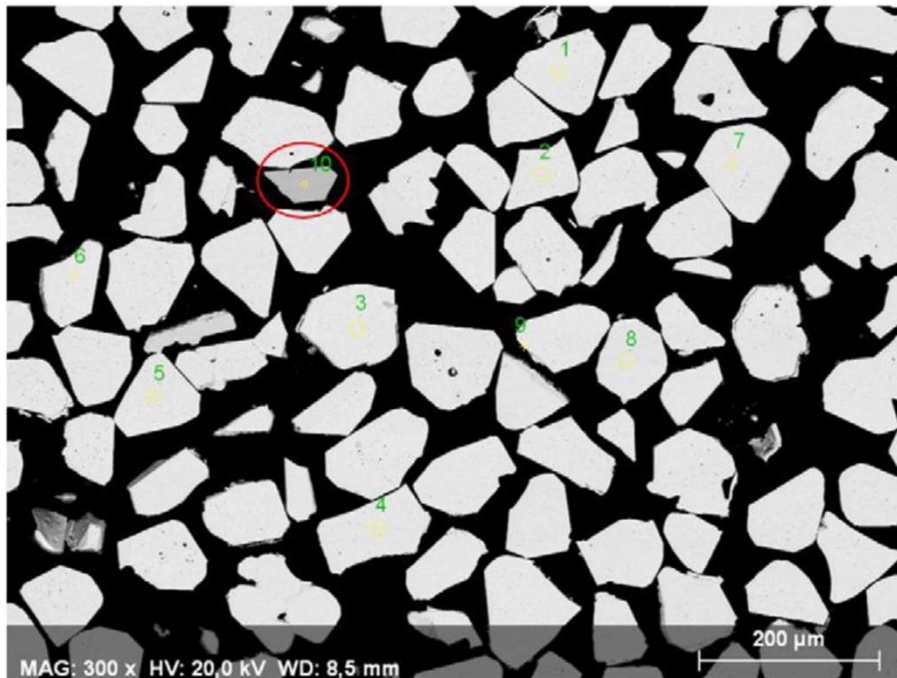
This work: : a better understanding of potential fluctuations

- Evidence of a band-tail of localized states in CZTS
 - Power dependence of the PL emission
 - Energy shift between PL and the PLE (Stokes shift)
 - Time resolved spectroscopy
- Influence of the cation disorder (Cu – Zn) on
 - the band-gap of the alloy
 - the extension of the band tail



The $\text{Cu}_2\text{ZnSnS}_4$ samples

$\text{Cu}_2\text{ZnSnS}_4$ monograin powder synthesized from elemental and binary precursors in a two step process: sputtering followed by sulfurization (annealing during 1 hour at 1013°K under sulfur atmosphere



Cu-poor and Zn-rich conditions

Formation of $\text{Cu}_2\text{ZnSnS}_4$ monograins during the heating process and recrystallization by Oswald ripening.

**Various cooling regimes to RT
=> various Cu – Zn disorder**

single crystals grains of typically 100 μm

The Cu₂ZnSnS₄ samples

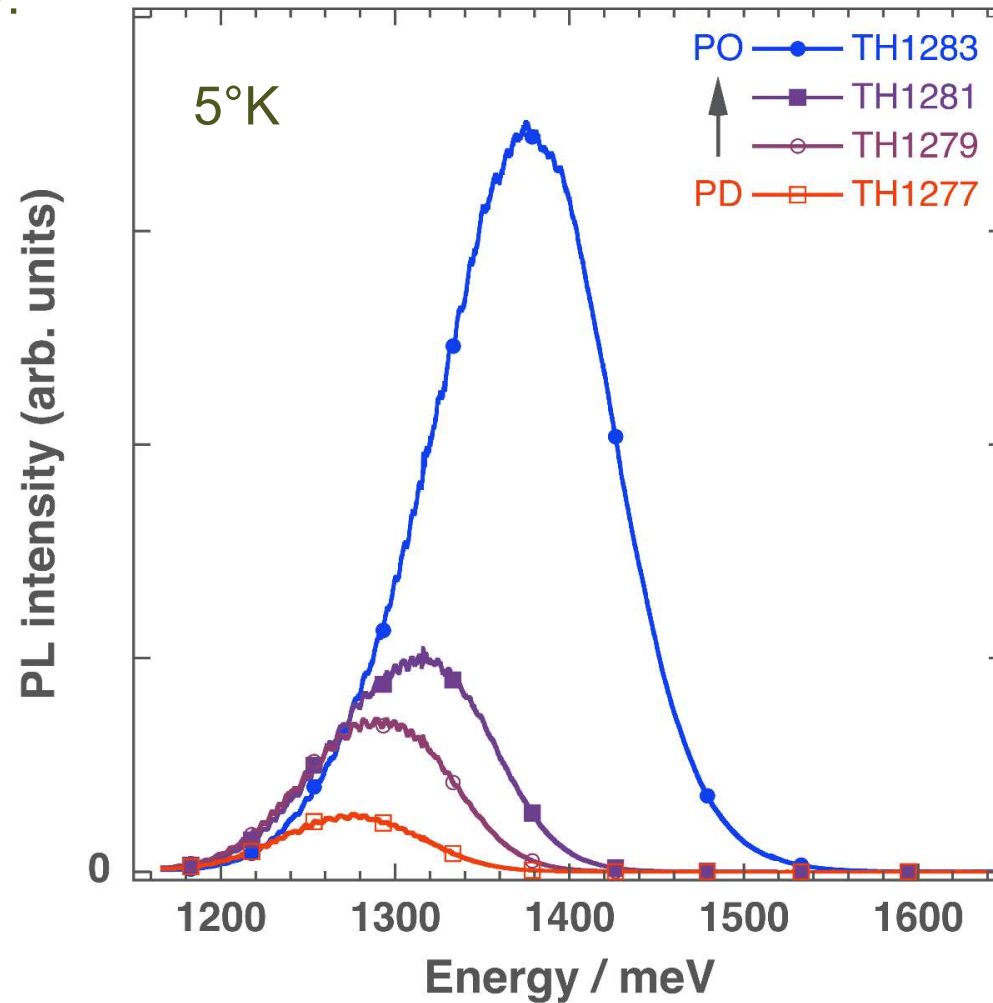
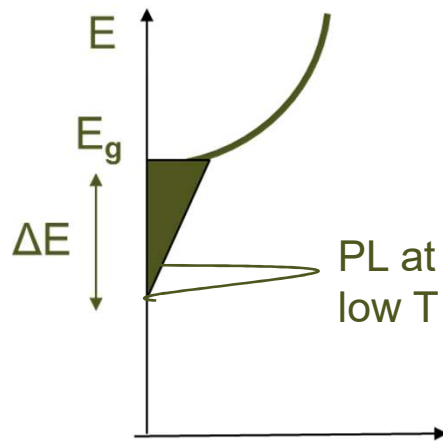
Cu₂ZnSnS₄ single crystals grains

		Concentration ratio of elements				
		Cooling regime	Cu/Zn+Sn	Zn/Sn	S/Met	V _{oc} (mV)
Partially disorder PD	TH-1277	Quenching	0.91	1.05	1.00	582
	TH-1279	5 min to RT	0.92	1.07	1.00	694
	TH-1281	15 min to RT	0.92	1.06	1.00	724
Partially ordered PO	TH-1283	510 min to RT	0.91	1.06	1.00	728
	TH-1215	5 min to RT				672
	TH-1220	5 min to RT+ 24hours 150°C				784

Fastest cooling to freeze the HT thermal equilibrium of lattice defects
=> **maximum Cu-Zn disorder**

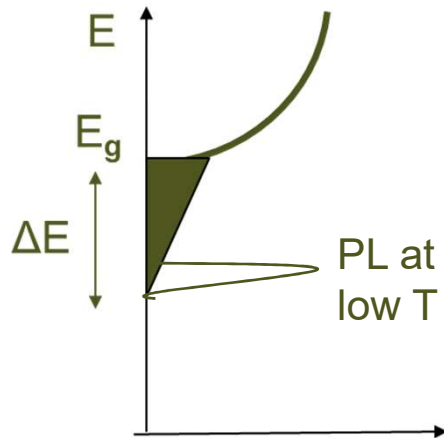
This work: a better understanding of potential fluctuations

Optical spectroscopy:
photoluminescence



This work: a better understanding of potential fluctuations

Optical spectroscopy:
PL excitation



● Bandgap:

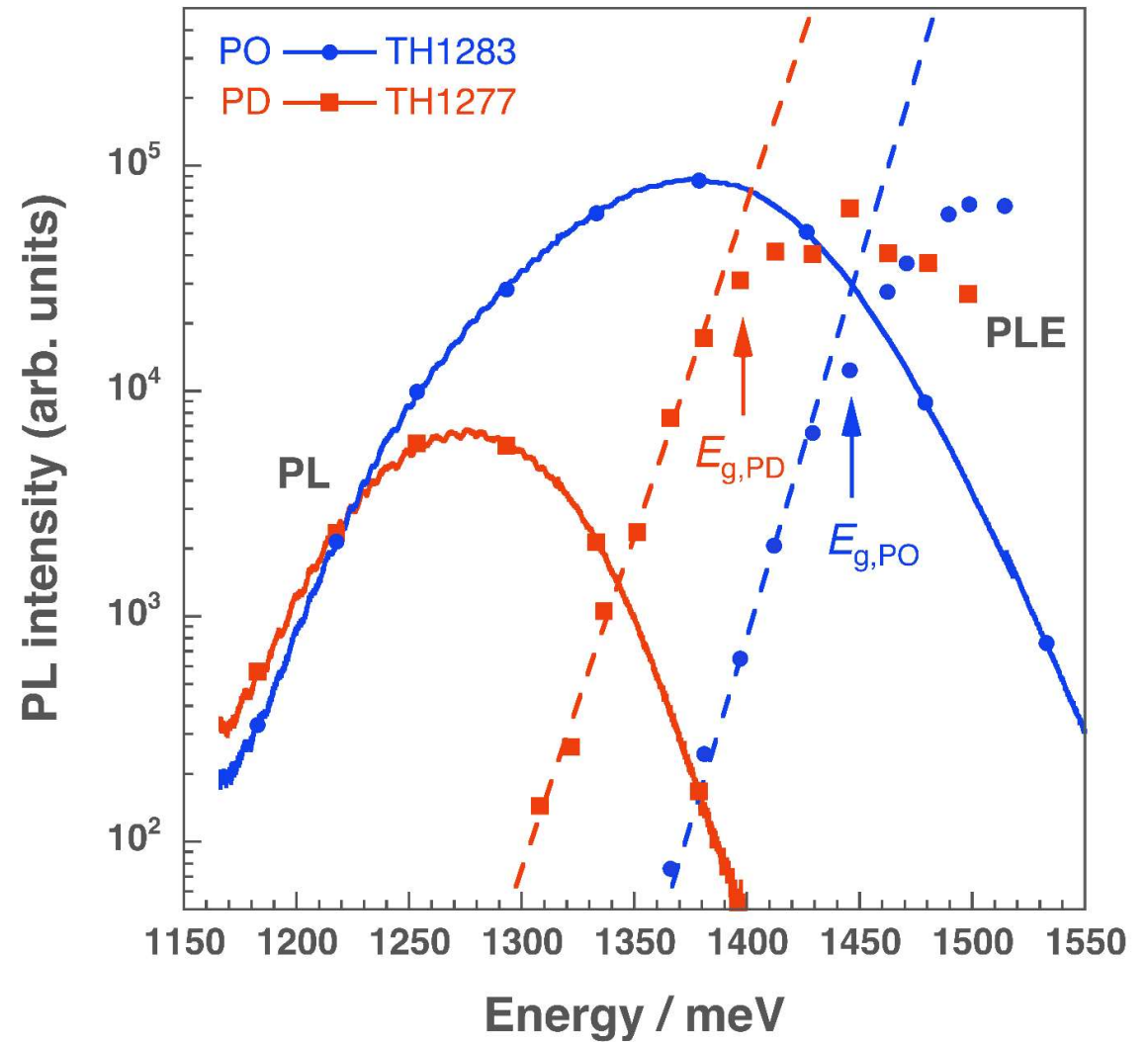
$$E_{g,PO} = 1.446 \text{ eV}$$

$$E_{g,PD} = 1.397 \text{ eV}$$

● Stokes shift:

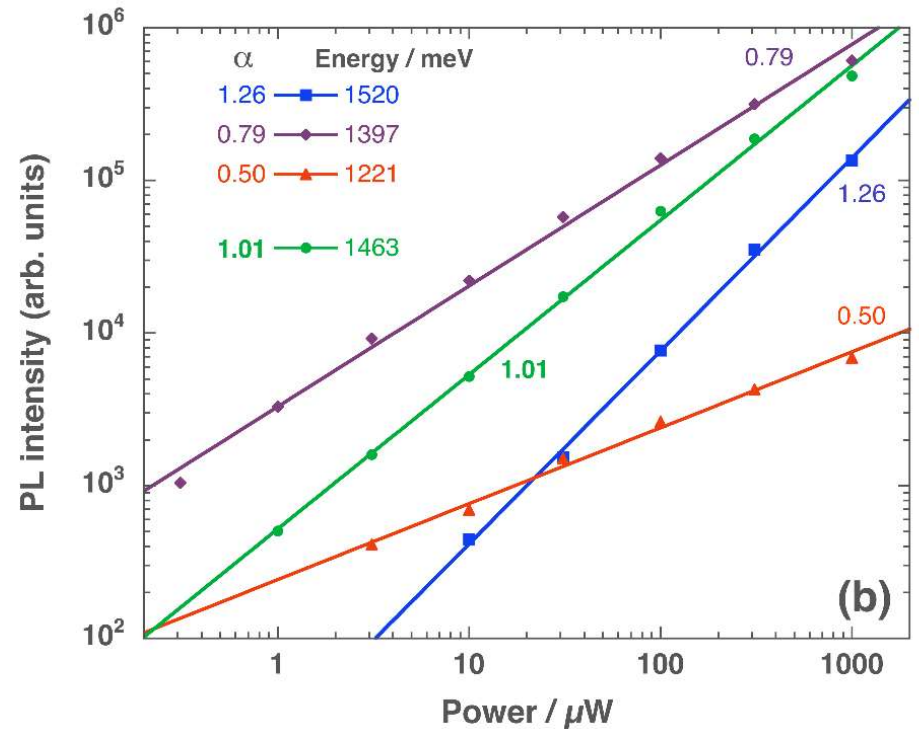
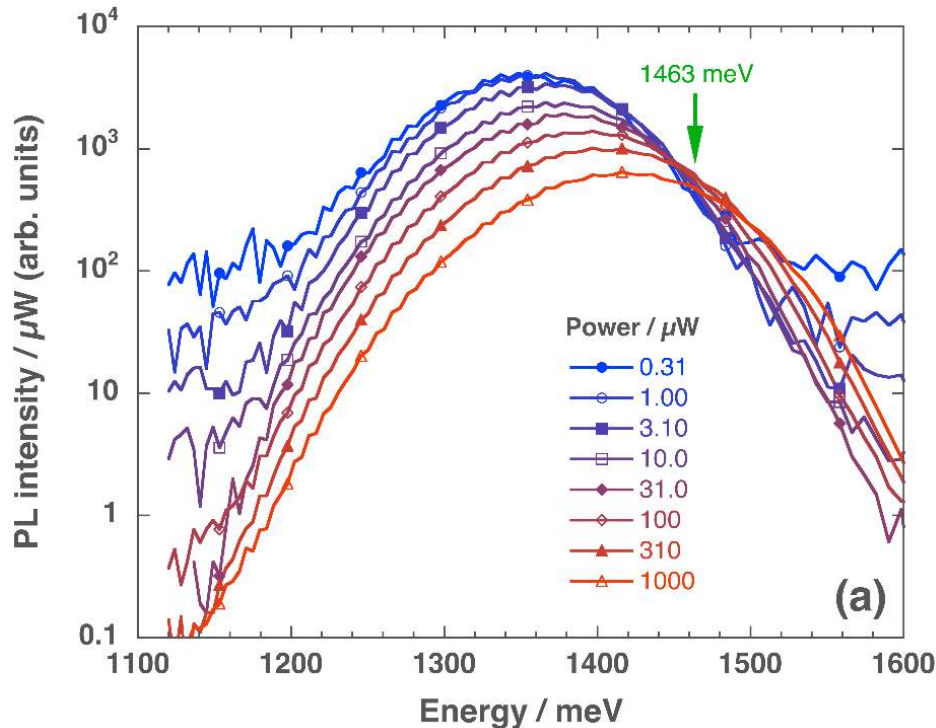
$$\text{PO sample: } \Delta E = 66 \text{ meV}$$

$$\text{PD sample: } \Delta E = 119 \text{ meV}$$



This work: a better understanding of potential fluctuations

Optical spectroscopy: photoluminescence normalized to the power



$$I \equiv P^\alpha$$

if $\alpha > 1$ free e and h

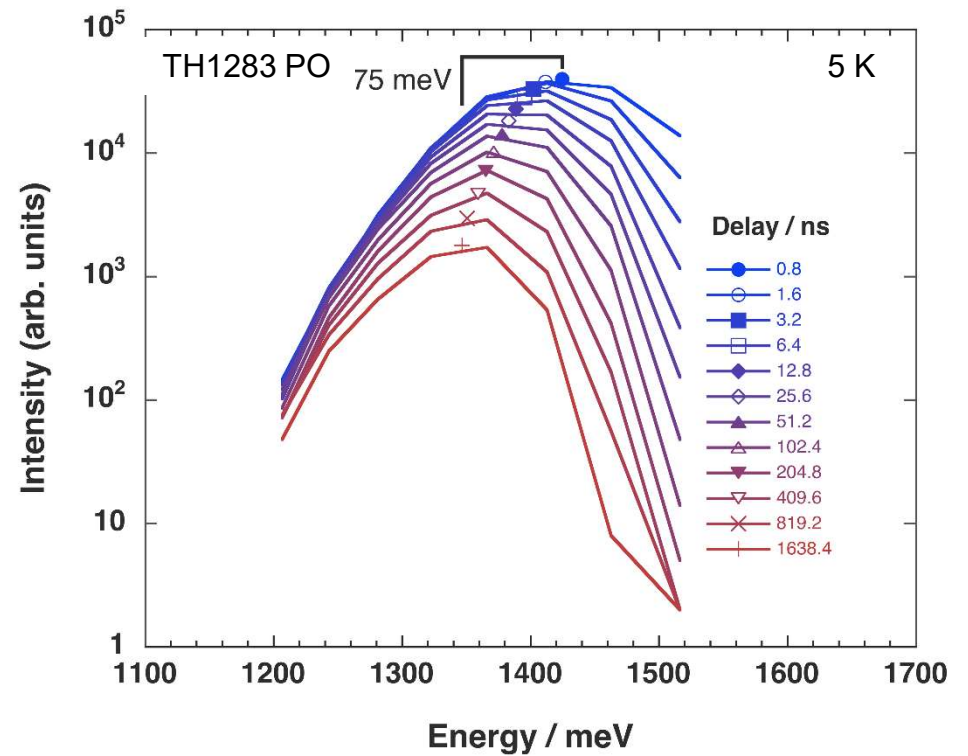
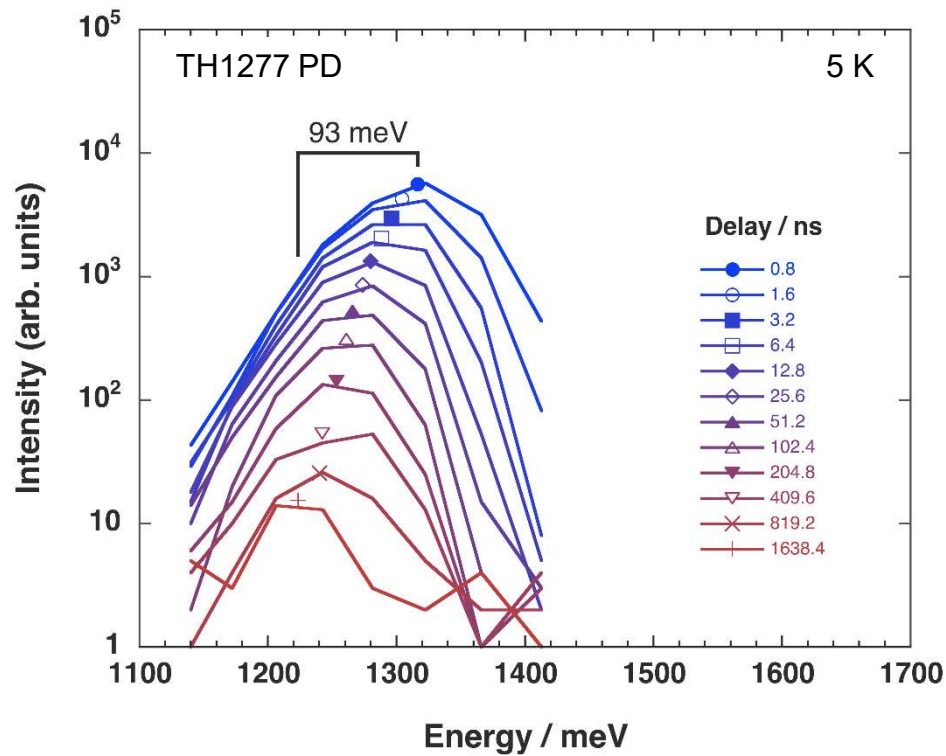
if $\alpha = 1$ excitonic bandgap

if $\alpha < 1$ defect related states

Partially ordered PO

This work: a better understanding to overcome them

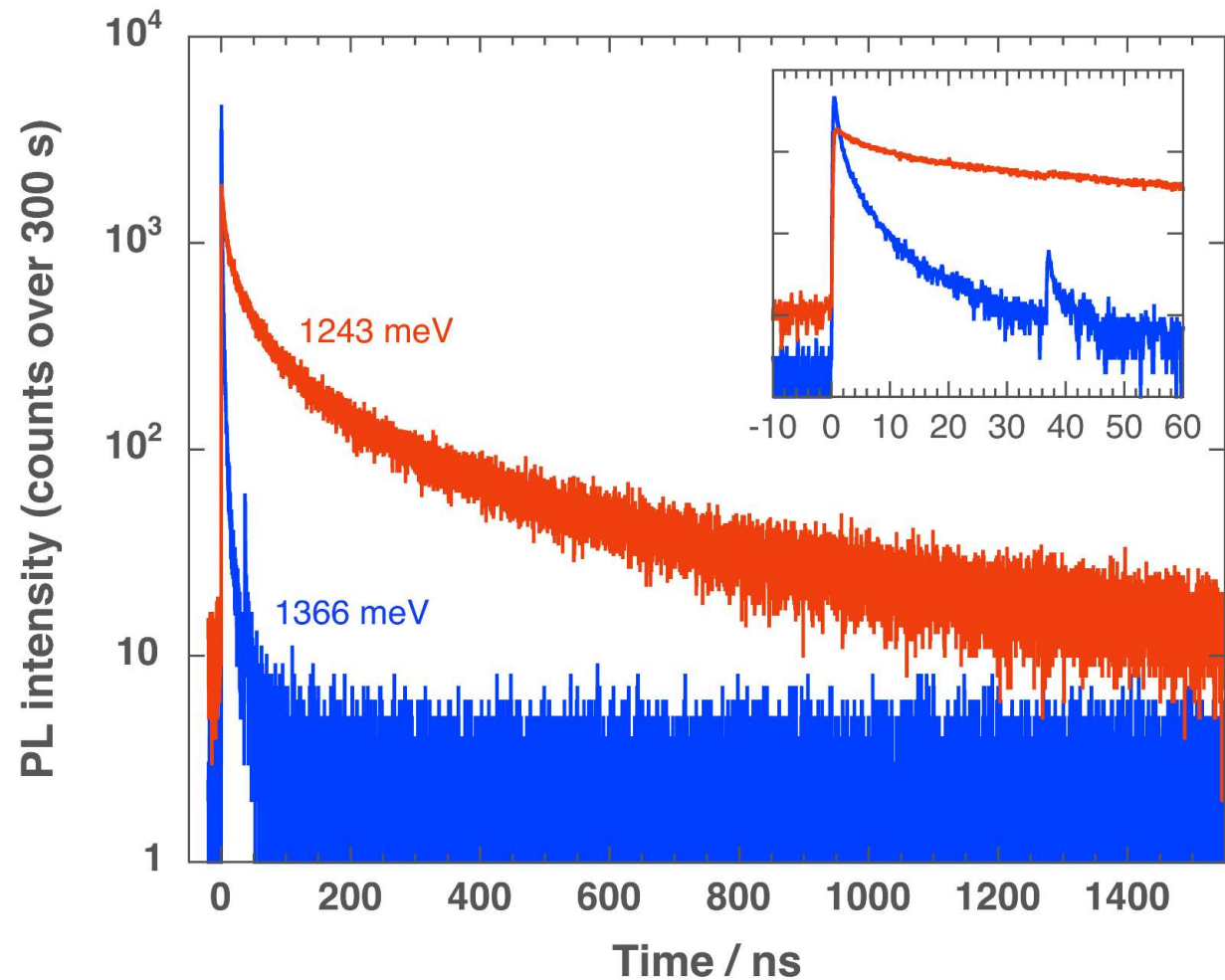
Optical spectroscopy:
Time resolved PL



Efficient carriers transfer between the localized states within the band-tail

This work: a better understanding to overcome them

Optical spectroscopy:
Time resolved PL



transfer between the localized states explains why a decay curve at given energy is useless to account for any recombination time

This work: a better understanding to

Optical spectroscopy:
Time resolved PL

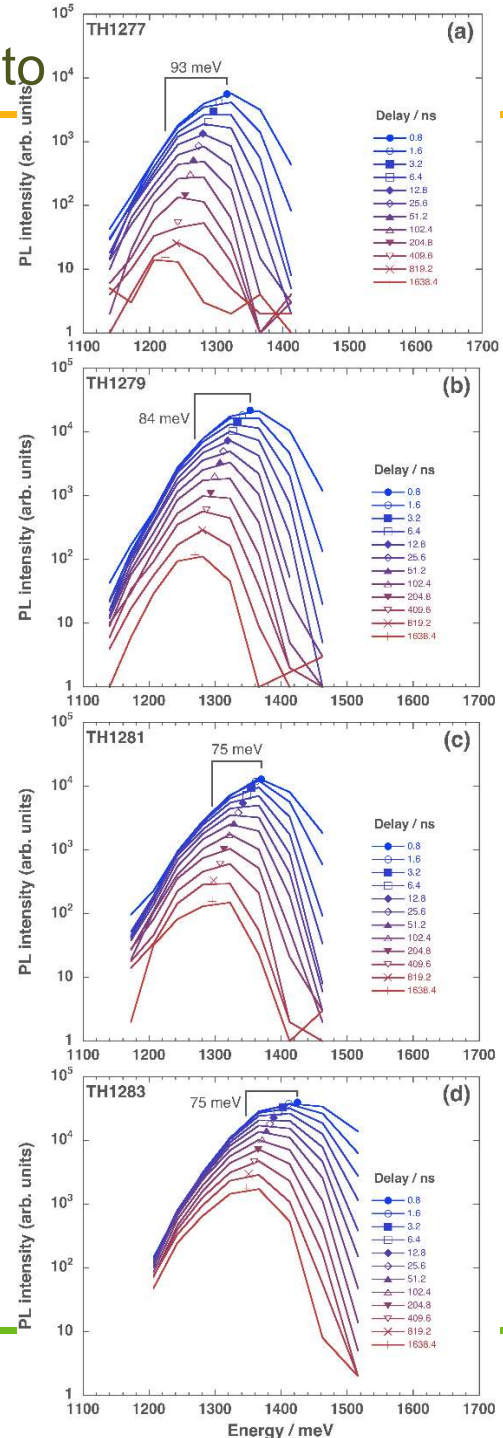
PD sample

From 1.390 eV to 1.297 eV
 $\Delta E = 93 \text{ meV}$

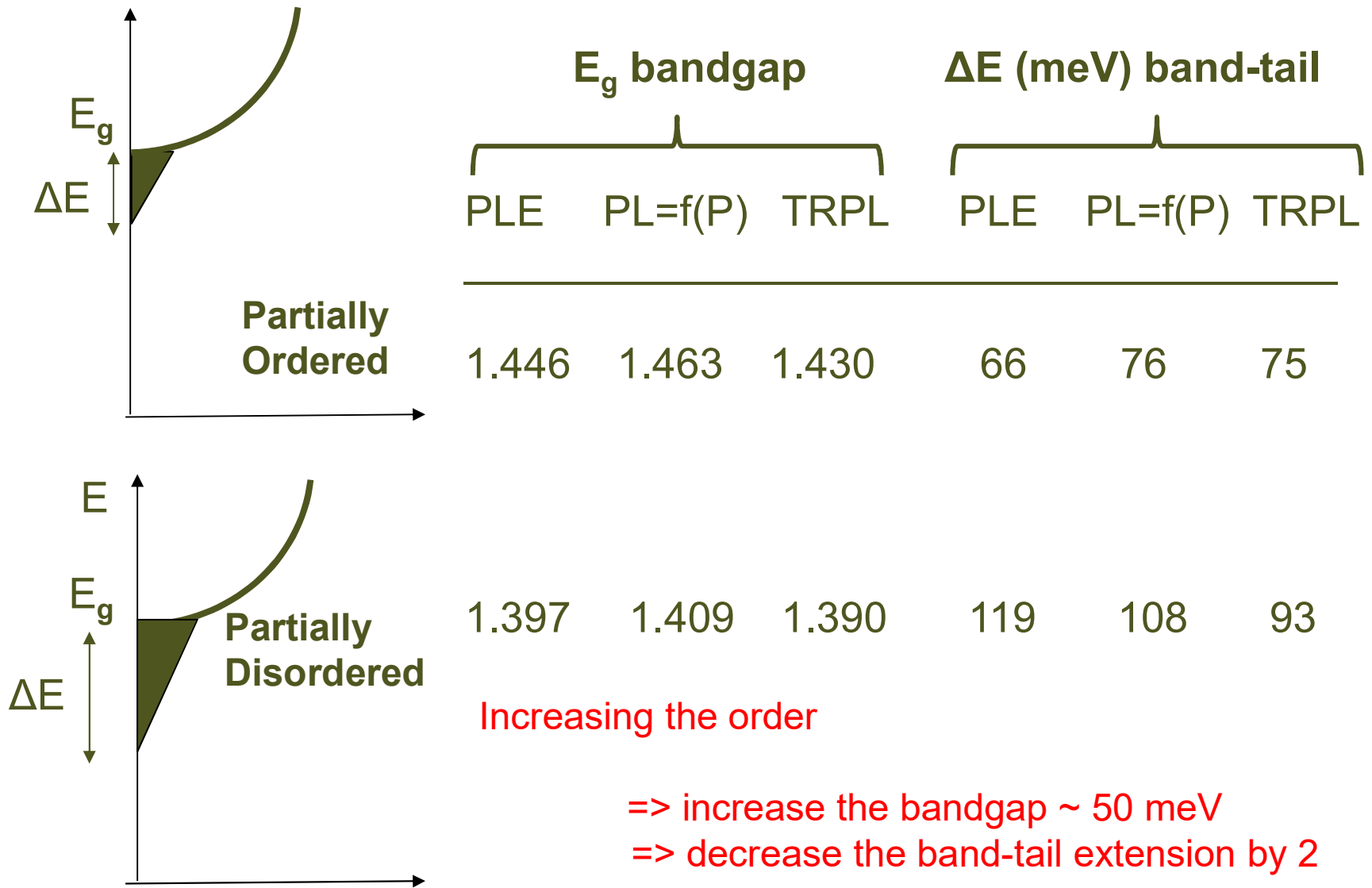
transfer between the localized
states within the band-tail

From 1.430 eV to 1.355 eV
 $\Delta E = 75 \text{ meV}$

PO sample

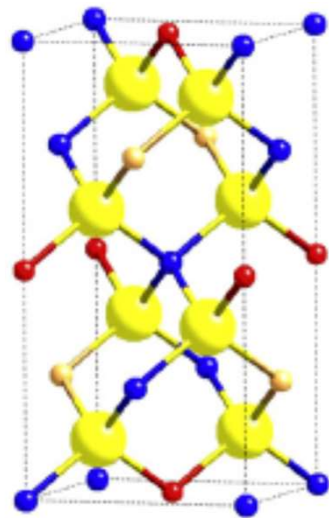


This work: Results deduced from optical spectroscopy



Perspective : direct measurements of structural local disorder

Ordered Kesterite



Cu / Sn

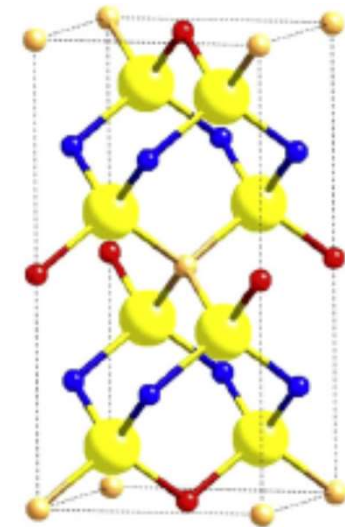
Cu / Zn

Sn / Cu

Zn / Cu



Stannite



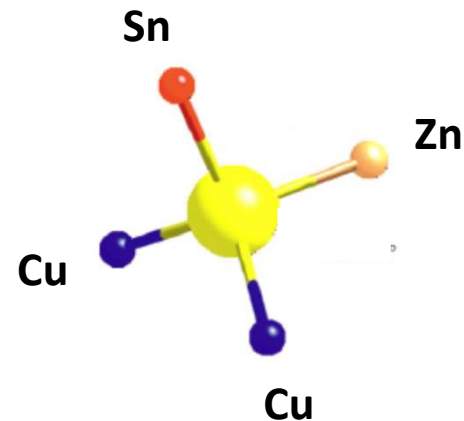
Zn / Sn

Cu / Cu

Sn / Zn

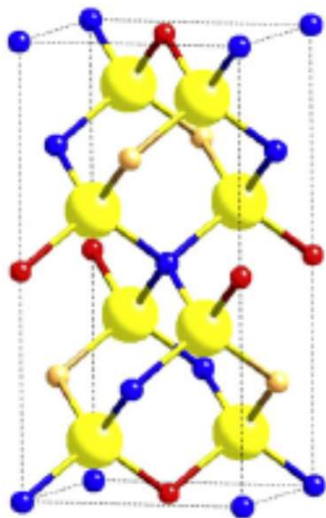
Cu / Cu

always this configuration for the First Nearest Neighbors (FNN)



Ordered Kesterite

Disordered Kesterite



Cu / Sn

Cu / Zn

Sn / Cu

Zn / Cu



S



Sn



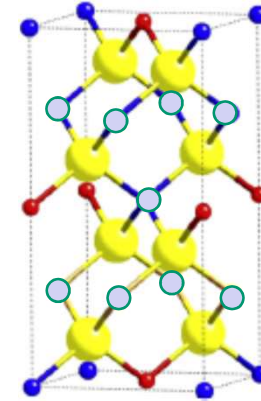
Cu



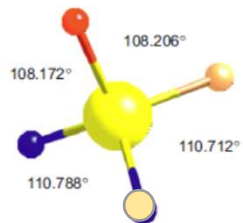
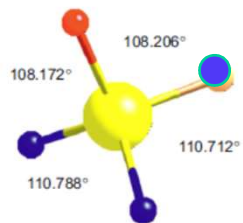
Zn



Mixing
Cu /
Zn
atoms



Example of local fluctuations of atomic configurations

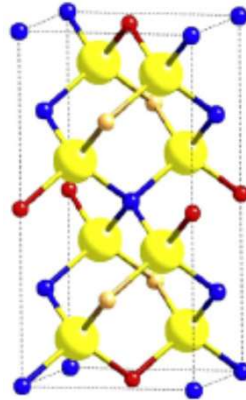


Cu / Sn

Cu / Zn

Sn / Cu

Cu / Zn



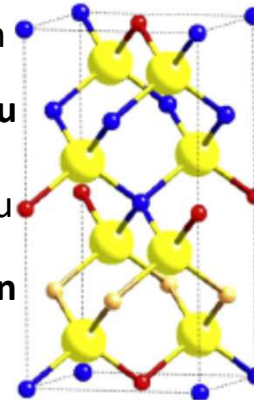
Exchange Cu / Zn
within the same plane

Cu / Sn

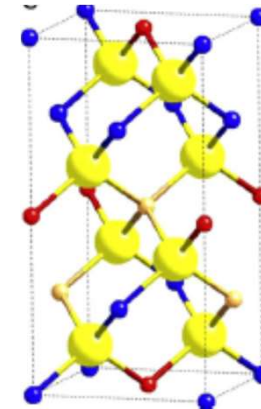
Cu / Cu

Sn / Cu

Zn / Zn



Exchange Cu / Zn
between two planes



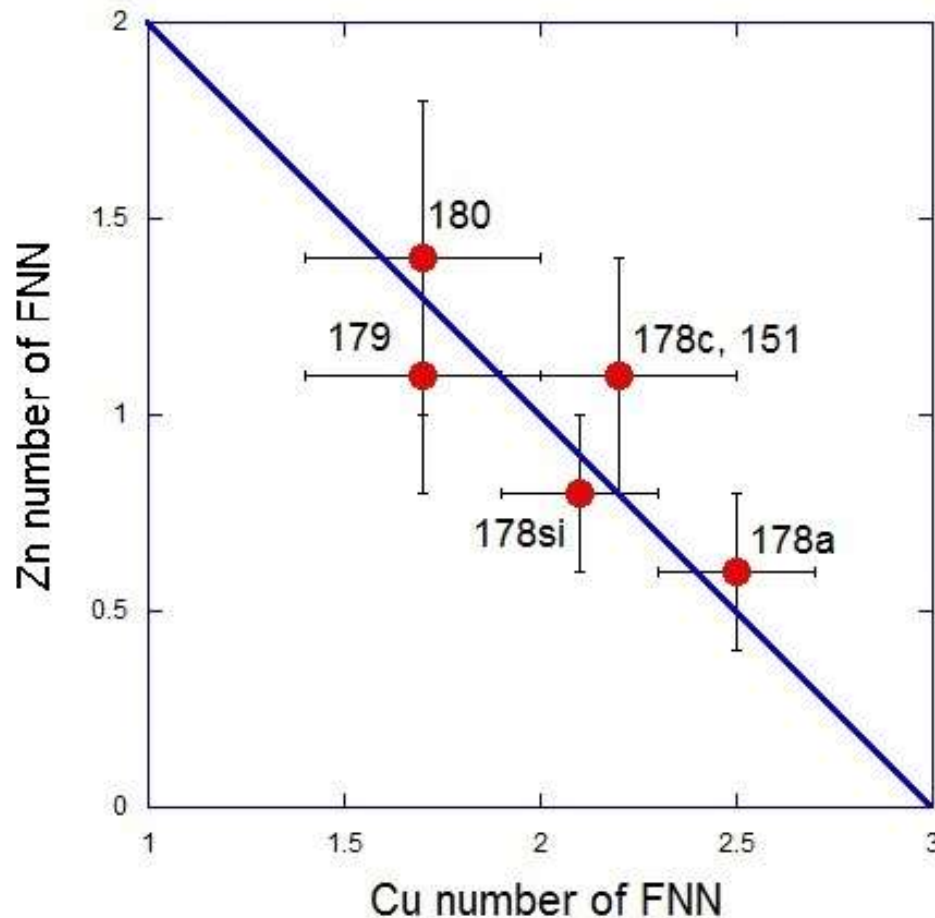
Cu / Cu

Sn / Zn

Exchange Cu / Zn between
two adjacent planes

Perspective : direct measurements of structural local disorder

Extended X-ray Absorption Fine Structure (EXAFS) measurements at the K edges of Se, Cu, Sn and Zn



— Cu+Zn = 3

the local configurations of Cu / Zn as first nearest neighbours around Se atoms vary from the ideal ratio 2:1 in $\text{Cu}_2\text{ZnSnSe}_4$ MBE layers

G.O. Lepore, F. D'Acapito
European Synchrotron Radiation Facilities, Grenoble

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European Synchrotron Radiation Facilities, Grenoble

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