

Emerging thin film photovoltaic inorganic materials: kesterite and beyond

S. Giraldo¹, Y. Sánchez¹, M. Placidi¹, Z. Jehl¹, V. Izquierdo-Roca¹,
A. Pérez-Rodríguez^{1,2}, and **E. Saucedo**^{1,3,*}

¹Catalonia Institute for Energy Research (IREC), Sant Adrià del Besòs-Barcelona, Spain

²IN2UB, Departament d'Electrònica, Universitat de Barcelona, Barcelona, Spain

³Electronic Engineering Department, Polytechnic University of Catalonia (UPC), Barcelona, Spain

*e-mail: esaucedo@irec.cat



OUTLINE

Presentation of CUSTOM-ART project

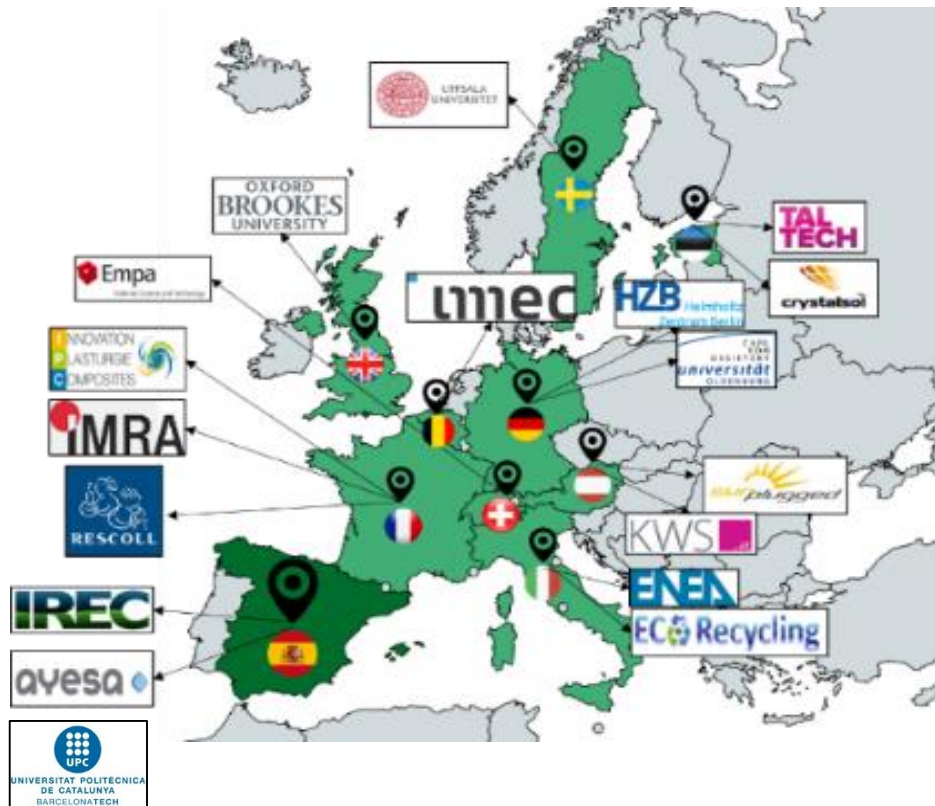
1. Introduction
2. Characteristics and challenges of kesterite
3. Doping and alloying strategies
4. Beyond kesterites
5. Conclusions and perspectives

CUSTOM-ART – H2020-LC-SC3-2020-RES-IA-CSA-952982

Disruptive kesterite-based thin film technologies customized for challenging architectural and active urban furniture applications

Main Objective: CUSTOM-ART will demonstrate that the new generation of CZTS -based solutions developed and tested during the project, will become the most robust and cost-effective thin-film technology in the EU for challenging and demanding architectural and urban furniture applications.

Partners:



Main characteristics:

- ✓ Demonstration at solar cell level of a performance $\eta \geq 20\%$ and at module level of a $\eta \geq 16\%$.
- ✓ Fabrication of large size module prototypes: 1) Monograin module (20x20 cm²; 6.4Wp) and 2) Micro-crystalline module onto steel (5x10 cm²; 0.8Wp).
- ✓ Demonstration in 4 DEMO-Sites (curved façades, curved tiles, bus canopy and urban furniture)



Seville
Spain



Innsbruck
Austria

Coordinator: Prof. Dr. Edgardo Saucedo (UPC and IREC)

Duration: 09/2020 – 02/2024

Total budget: 6.999.745,25 €

www.custom-art-h2020.eu

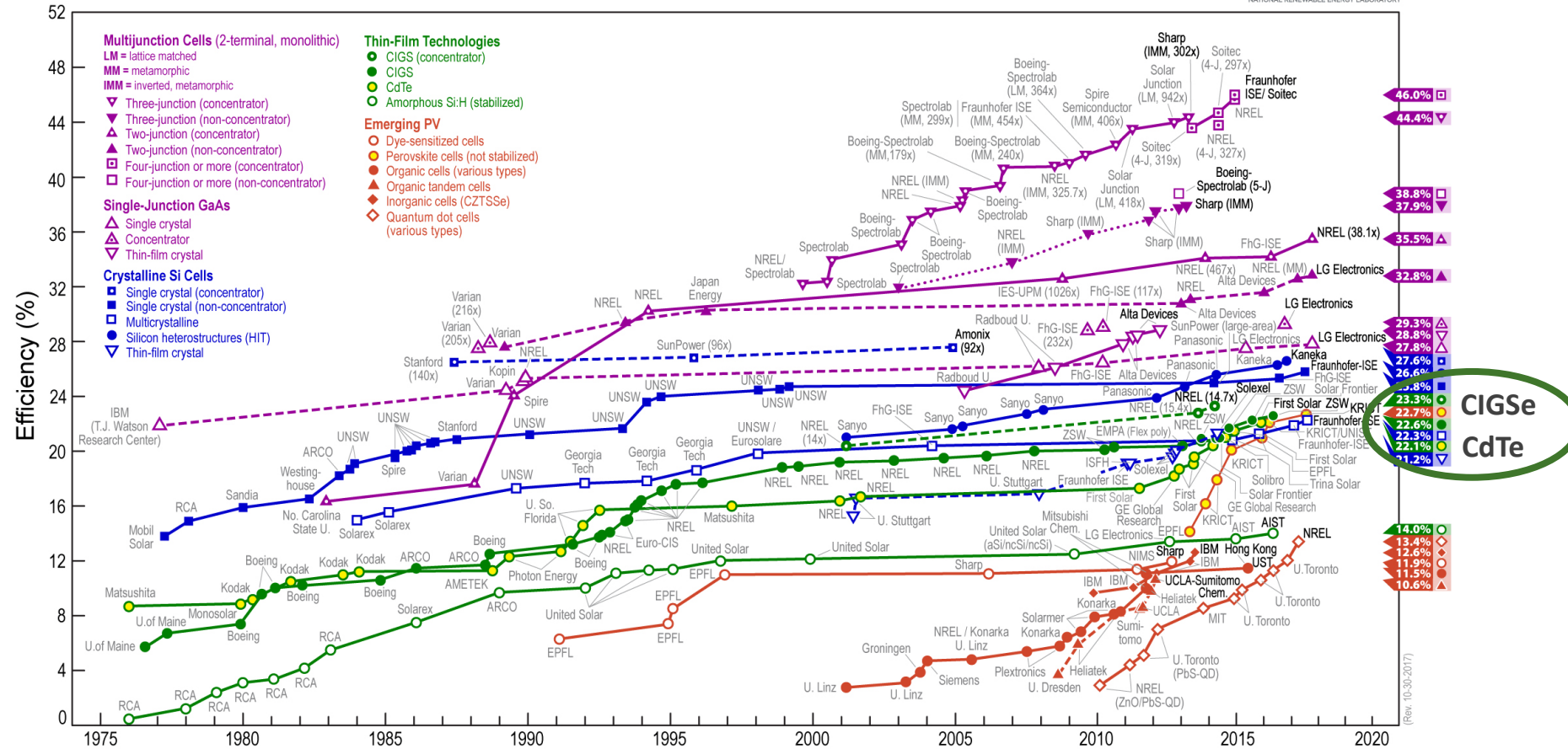


OUTLINE

Presentation of CUSTOM-ART project

- 1. Introduction**
2. Characteristics and challenges of kesterite
3. Doping and alloying strategies
4. Beyond kesterites
5. Conclusions and perspectives

Best Research-Cell Efficiencies



- Main commercially available thin film PV technologies: CdTe and CIGSe
- In, Ga and Te identified by the European Commission as critical raw materials

JPhys Energy

TOPICAL REVIEW • OPEN ACCESS

Emerging inorganic solar cell efficiency tables (Version 1)

Lydia H Wong¹ , Andriy Zakutayev² , Jonathan D Major³ , Xiaojing Hao⁴ , Aron Walsh^{5,6} ,
Teodor K Todorov⁷ and Edgardo Saucedo^{8,9} 

Published 29 July 2019 • © 2019 The Author(s). Published by IOP Publishing Ltd

[Journal of Physics: Energy, Volume 1, Number 3](#)

4961 Total downloads

[Turn on MathJax](#)[Share this article](#)

Material	Eff. (%)	V _{OC} (V)	J _{SC} (mA/cm ²)	F.F. (%)	Area (cm ²)	E _g (eV)	Institutions
Cu ₂ ZnSnS ₄ (CZTS)	11.0±0.2	0.731	21.74	69.3	0.2339	1.5	UNSW. ^[3]
Cu ₂ BaSnS ₄ (substrate)	1.7	0.698	5.3	46.9	0.2	2.01	Central South University, UNSW, Shen Zhen University, Xiamen University. ^[19]
Cu ₂ BaSnS ₄ (superstrate)	2.0	0.933	5.1	42.9	0.2	2.04	The University of Toledo. ^[20]
Cu ₂ FeSnS ₄	3.0	0.610	9.3	52.0	0.1	1.5	Indian Association for the Cultivation of Science. ^[21]
Cu ₂ CdSn(S _{0.xx} Se _{0.yy}) ₄	2.8	0.356	18.8	41.6	0.405	1.55	Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. ^[22]
Cu ₂ BaSn(S _{0.xx} Se _{0.yy}) ₄	5.2	0.611	17.4	48.9	0.425	1.55	Duke University, IBM. ^[23]
Cu ₂ ZnGe(S _{0.xx} Se _{0.yy}) ₄	6.0	0.617	NA	NA	0.25	1.47	ZSW, CNRS. ^[24]
Cu ₂ ZnGeSe ₄	7.6	0.558	22.8	59.0	0.5	1.36	CNRS, IMEC. ^[25]
Ag ₂ ZnSnSe ₄	5.18	0.504	21.0	48.7	0.45	1.35	IBM, UCSD. ^[26]
Cu ₂ (Zn _{0.6} Cd _{0.4})SnS ₄	11.0	0.650	25.5	66.1	0.22	1.38	University of New South Wales, Australia; National Renewable Energy Laboratory, United States; Central South University, China. ^[27]
(Ag _{0.05} Cu _{0.95}) ₂ (Zn _{0.75} Cd _{0.25})Sn ₄	10.1	0.650	23.4	66.2	0.16	1.4	NTU, Singapore; HZB, Germany. ^[29]

Several kesterite type materials at the forefront of the emerging thin film photovoltaic materials

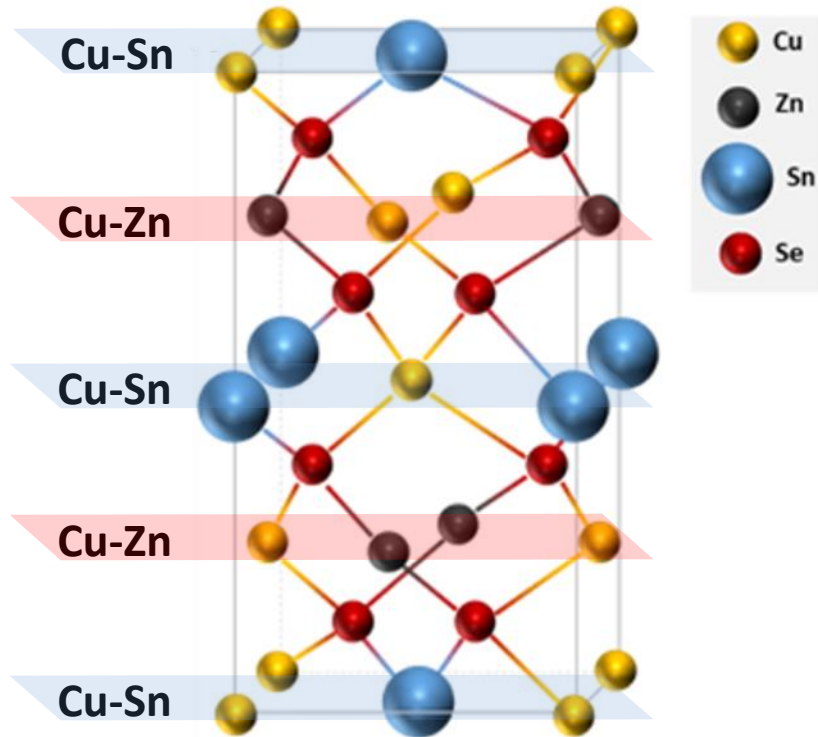
OUTLINE

Presentation of CUSTOM-ART project

1. Introduction
- 2. Characteristics and challenges of kesterite**
3. Doping and alloying strategies
4. Beyond kesterites
5. Conclusions and perspectives

Kesterite: emerging thin film PV materials

Tetragonal structure (I4 space group)

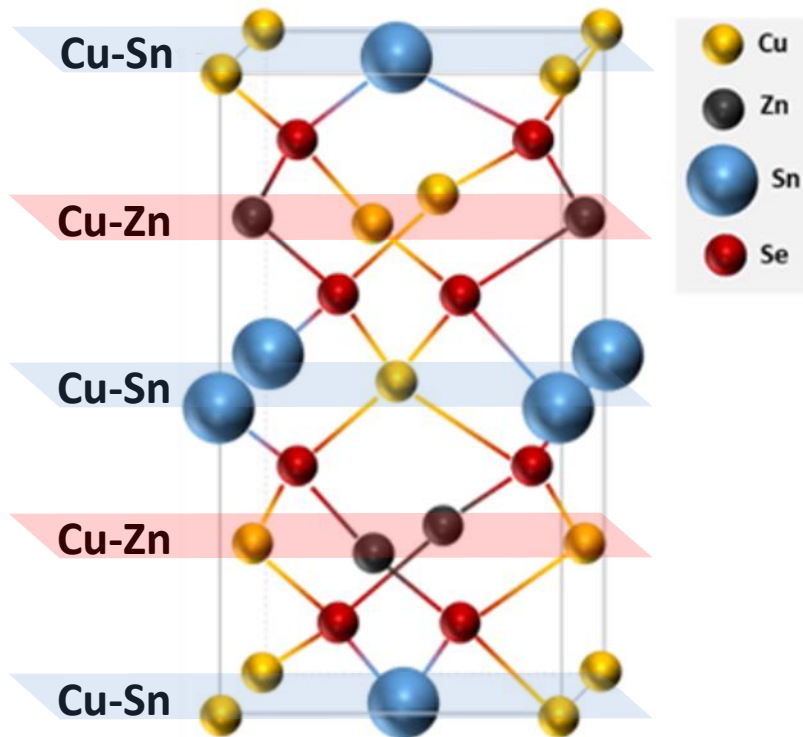


Advantages of kesterites:

- Exclusively formed by **low-toxicity** and earth **abundant elements**.
- **P-type conductivity** naturally due to intrinsic point defects.
- **Direct band-gap** semiconductor with a **high absorption** coefficient ($\sim 10^4 \text{ cm}^{-1}$).
- Easily **tunable band-gap**, either controlling the S/Se ratio or with cation substitution.
- Highly **compatible** with **CIGS** technology.

Kesterite: emerging thin film PV materials

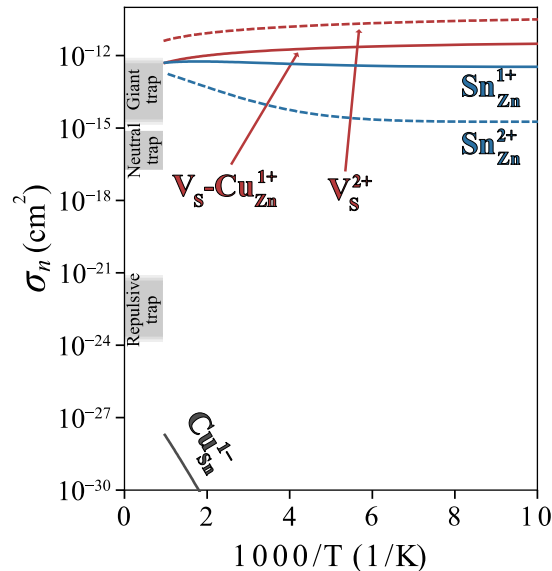
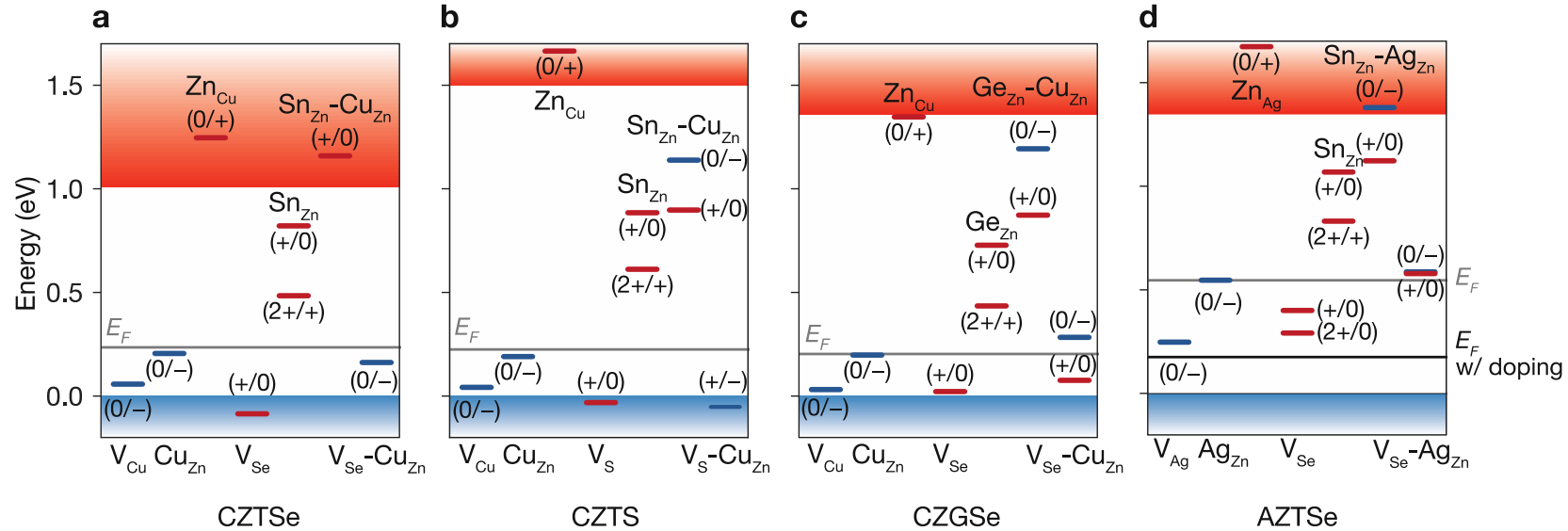
Tetragonal structure (I4 space group)



Challenges of kesterites:

- **Cu and Zn are iso-electronic elements:** easy exchange in the lattice (anti-sites defects formation: Cu_{Zn}, Zn_{Cu}).
- **Sn forms volatile species with Se and S:** Sn exchange with the annealing atmosphere, Sn loss.
- **Sn is a multi-valent element (Sn⁺² and Sn⁺⁴):** formation of defects related to Sn valence.
- **Sn strongly interacts with alkaline elements.**
- **Zn is a relatively volatile element.**

How can we solve this issue?



Recent materials modelling results show that*:

- Sn_{Zn} related anti-sites introduces deep defects
- All of them are giant recombination traps



Most plausible origin of the high non-radiative recombination and low carriers life-time

*Results obtained by Prof. A. Walsh Group (ICL) in STARCELL, Unpublished.

How can we solve this issue?

How to avoid Sn related anti-sites?*



○ Zn-rich

Additional Zn forms ZnS/ZnSe.

○ Sn-poor

The Cu-rich secondary phases are conductive.

○ hole poor (n-type)

The acceptor (Cu_{Zn}) are too many.

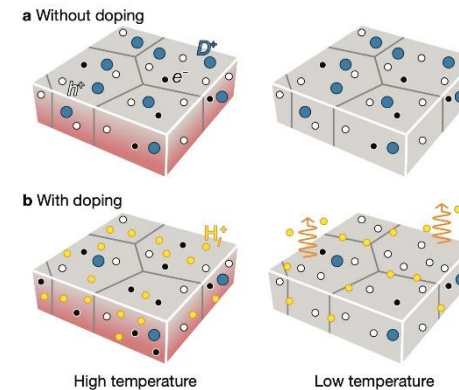


Partial substitution by Ge:

- Ge related defects are less detrimental
- Higher efficiencies theoretically predicted

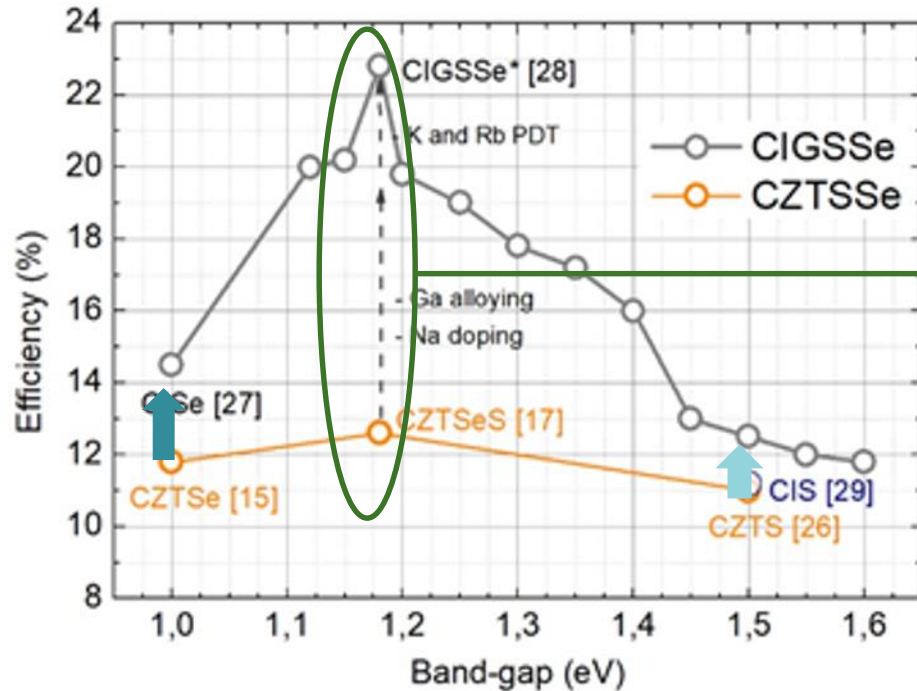
Doping with H_i^+ :

- Removes free e-
- Reduce recombination



*Results obtained by Prof. A. Walsh Group (ICL) in STARCELL, Unpublished.

We can learn several things from CIGS...



“Progress and Perspectives of Thin Film Kesterite Photovoltaic Technology: A Critical Review”, Sergio Giraldo, Zacharie Jehl, Marcel Placidi, Victor Izquierdo-Roca, Alejandro Pérez-Rodríguez, Edgardo Saucedo, Advanced Materials, Volume 31, Issue 16, 201806692, 2019.

Doping

Alloying

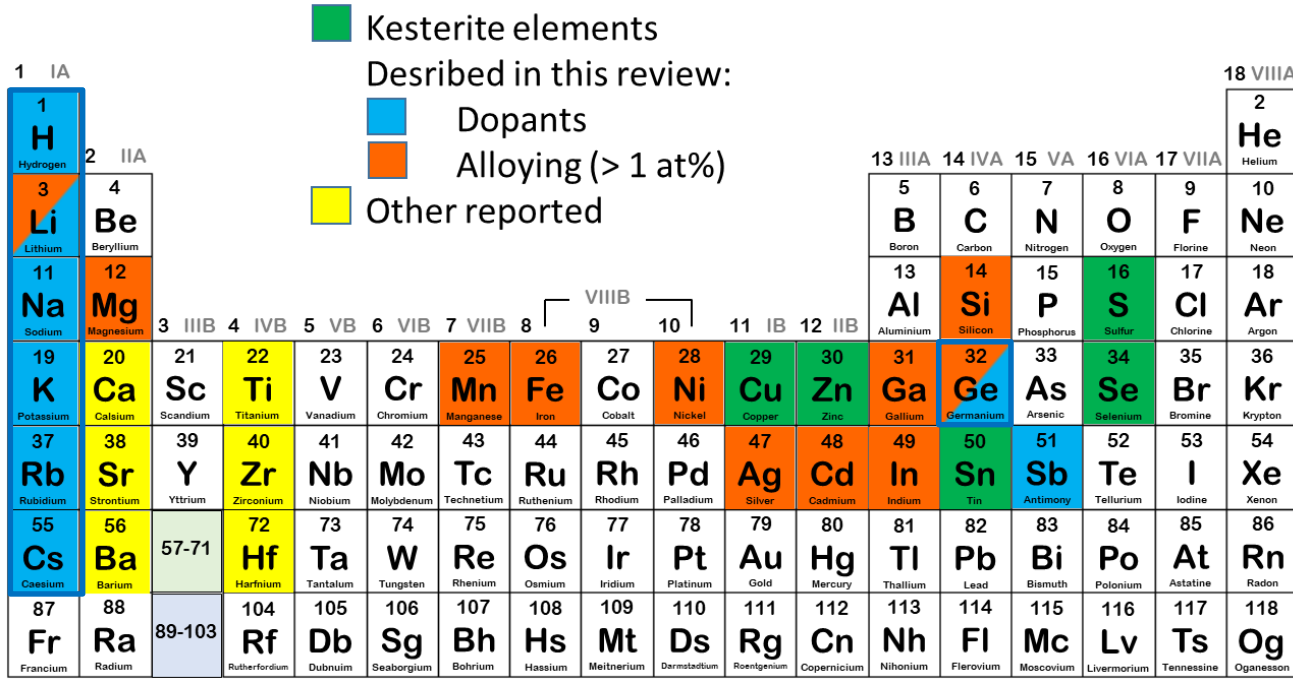
- CuInSe_2 and $\text{Cu}_2\text{ZnSnSe}_4$ – About 2% efficiency difference
- CuInS_2 and $\text{Cu}_2\text{ZnSnS}_4(\text{Cd})$ – About 1% efficiency difference
- **$\text{Cu}(\text{In,Ga})\text{Se}_2$ and $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ – About 10% efficiency difference**

OUTLINE

Presentation of CUSTOM-ART project

1. Introduction
2. Characteristics and challenges of kesterite
- 3. Doping and alloying strategies**
4. Beyond kesterites
5. Conclusions and perspectives

Extrinsic Doping



“Doping and alloying of kesterites”, Yaroslav Romanyuk, Stefan Haass, Sergio Giraldo, Marcel Placidi, Devendra Tiwari, David Fermin, Xiaojing Hao, Hao Xin, Thomas Schnabel, Marit Kauk-Kuusik, Paul Pistor, Stener Lie and Lydia Helena Wong, J. Physics Energy 2019 (DOI: 10.1088/2515-7655)

Most relevant

Doping: alkali elements and Ge

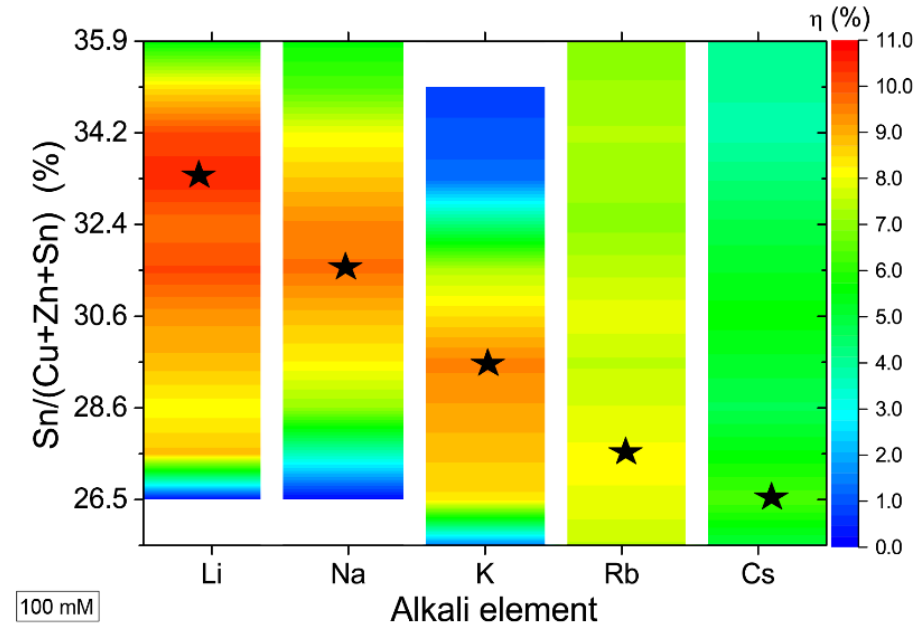
57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

What is the best alkaline dopant?

Author	Order of performance improvement
Mule et al. Thin Solid Films 2016	Na > Cs > K > Rb > Li
Hsieh et al. Adv. Energy Mater. 2016	K > Rb > Na > Li > Cs
Altamura et al. Scientific Reports 2016	Li > Na > Rb
López-Marino et al. J. Mater. Chem. A 2016	K > Na
S. Haass et al. Adv. Energy Mater. 2017	Li > Na > K > Rb > Cs

- ✓ Some discrepancy in the literature about the most efficient alkaline
- ✓ Effect on morphology quite well documented
- ✓ Role of each of them is still matter of intensive research
- ✓ PAT (or doping before/during the annealing) more effective than PDT for the moment
- ✓ Lighter elements more effective than heavier elements for the moment

Brief review on alkaline doping...

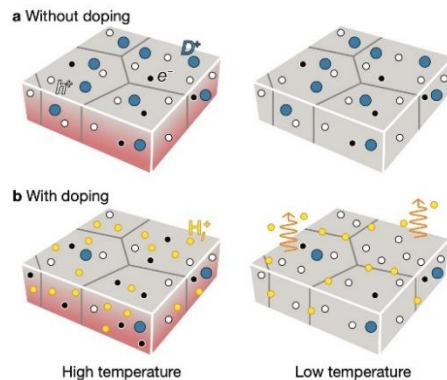


- ✓ For each alkali metal adjustment of Sn content and alkali concentration is mandatory!*
- ✓ Strong interaction with Sn
- ✓ This is something very particular of kesterites, and no yet understood
- ✓ $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$

*Stefan G. Haass et al., Adv. Energy Mater. 2018, 8, 1701760.

1	
H	2
Hydrogen	
3	
Li	Be
Lithium	
11	

- ✓ Li has been demonstrated as a relevant doping and alloying element to improve kesterite efficiency
- ✓ Li^+ is the most similar cation to H^+



Is this related to the technological solution proposed by ICL in STARCELL????

I have no idea!!!! But at least is very promising!!!

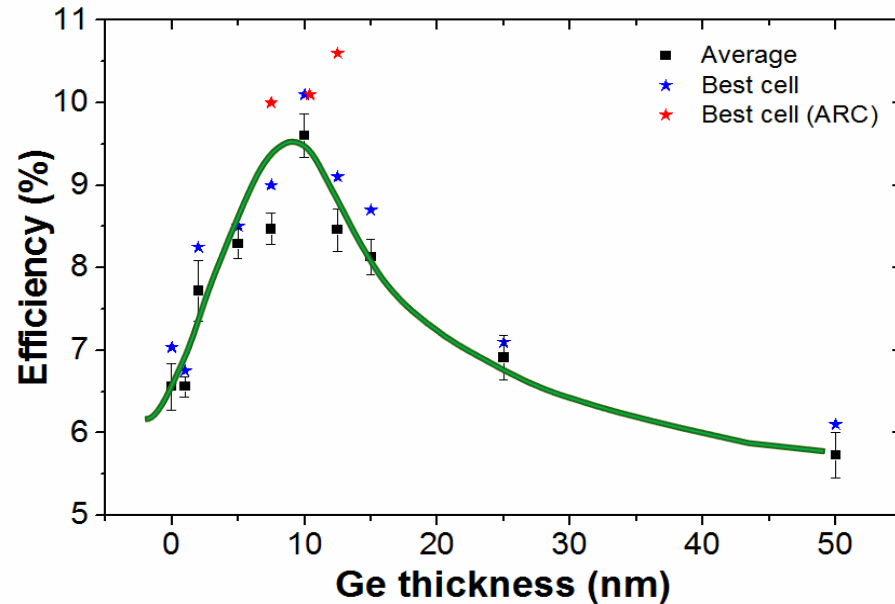
Materials Views
www.MaterialsViews.com

ADVANCED ENERGY MATERIALS
www.advenergymat.de

Large Efficiency Improvement in $\text{Cu}_2\text{ZnSnSe}_4$ Solar Cells by Introducing a Superficial Ge Nanolayer

Sergio Giraldo, Markus Neuschitzer, Thomas Thersleff, Simón López-Marino, Yudania Sánchez, Haibing Xie, Mónica Colina, Marcel Placidi, Paul Pistor, Victor Izquierdo-Roca, Klaus Leifer, Alejandro Pérez-Rodríguez, and Edgardo Saucedo*

COMMUNICATION



S. Giraldo et al., Adv. Ener. Mater. 5, 2015, 1501070.

Energy & Environmental Science
ROYAL SOCIETY OF CHEMISTRY

PAPER

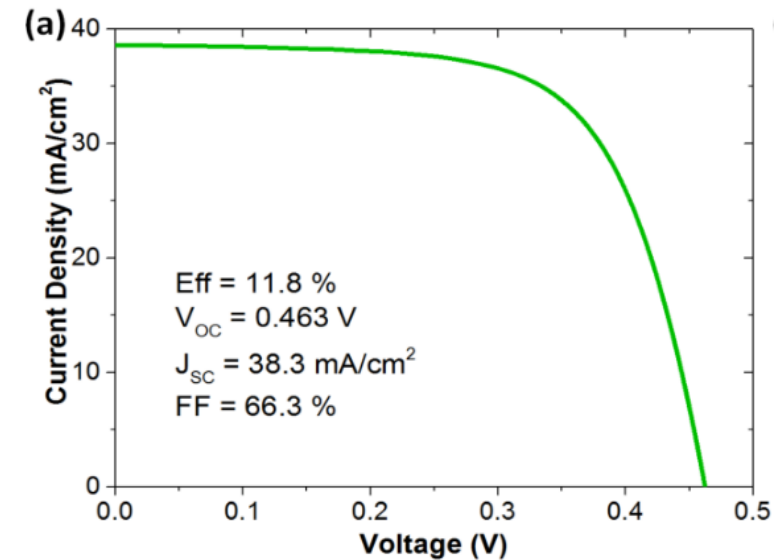
View Article Online
View Journal | View Issue

Check for updates

How small amounts of Ge modify the formation pathways and crystallization of kesterites

Cite this: Energy Environ. Sci., 2018, 11, 582

S. Giraldo,^a E. Saucedo,^{a*} M. Neuschitzer,^{b*} F. Oliva,^{c*} M. Placidi,^{c*} X. Alcobé,^d V. Izquierdo-Roca,^e S. Kim,^f H. Tampo,^g H. Shibata,^g A. Pérez-Rodríguez^{g,h} and P. Pistor^g



S. Giraldo et al., Energy Env. Sci. 11, 2018, 582.



- ✓ Ge has been demonstrated as a relevant doping and alloying element to improve kesterite efficiency
- ✓ Ge^{+4} substitutes Sn^{+4} in the kesterite structure

Extrinsic Doping

■ Kesterite elements
■ Dopants
■ Alloying (> 1 at%)
■ Other reported

1 IA																	18 VIIIA
1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII B	9	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Caesium	56 Ba Barium	57-71	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89-103	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson

- ✓ Ge and Li are the only elements proved as efficient doping/alloying solutions
- ✓ Both of them demonstrates a strong interaction with Sn



- ✓ **Something wrong happens with Sn.**
- ✓ **To understand and solve it can be one of the breakthrough for increasing the conversion efficiency**

57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

Alloying

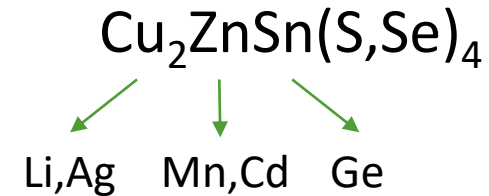
■ Kesterite elements
 Described in this review:
■ Dopants
■ Alloying (> 1 at%)
■ Other reported

1 IA 1 H Hydrogen	2 IIA 4 Be Beryllium																	18 VIIIA 2 He Helium																			
3 3 Li Lithium	4	13 IIIA 5 B Boron	14 IVA 6 C Carbon	15 VA 7 N Nitrogen	16 VIA 8 O Oxygen	17 VIIA 9 F Fluorine	18	13 IIIA 13 Al Aluminium	14 IVA 14 Si Silicon	15 VA 15 P Phosphorus	16 VIA 16 S Sulfur	17 VIIA 17 Cl Chlorine	18	11 IB 11 Na Sodium	12 IIB 12 Mg Magnesium	3 IIIB 21 Sc Scandium	4 IVB 22 Ti Titanium	5 VB 23 V Vanadium	6 VIB 24 Cr Chromium	7 VIIB 25 Mn Manganese	8 26 Fe Iron	9 27 Co Cobalt	10 28 Ni Nickel	11 IB 29 Cu Copper	12 IIB 30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton						
19 K Potassium	20 Ca Calcium	37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon	55 Cs Caesium	56 Ba Barium	57-71	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89-103	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson																				

“Doping and alloying of kesterites”, Yaroslav Romanyuk, Stefan Haass, Sergio Giraldo, Marcel Placidi, Devendra Tiwari, David Fermin, Xiaojing Hao, Hao Xin, Thomas Schnabel, Marit Kauk-Kuusik, Paul Pistor, Stener Lie and Lydia Helena Wong, J. Physics Energy 2019 (DOI: 10.1088/2515-7655)

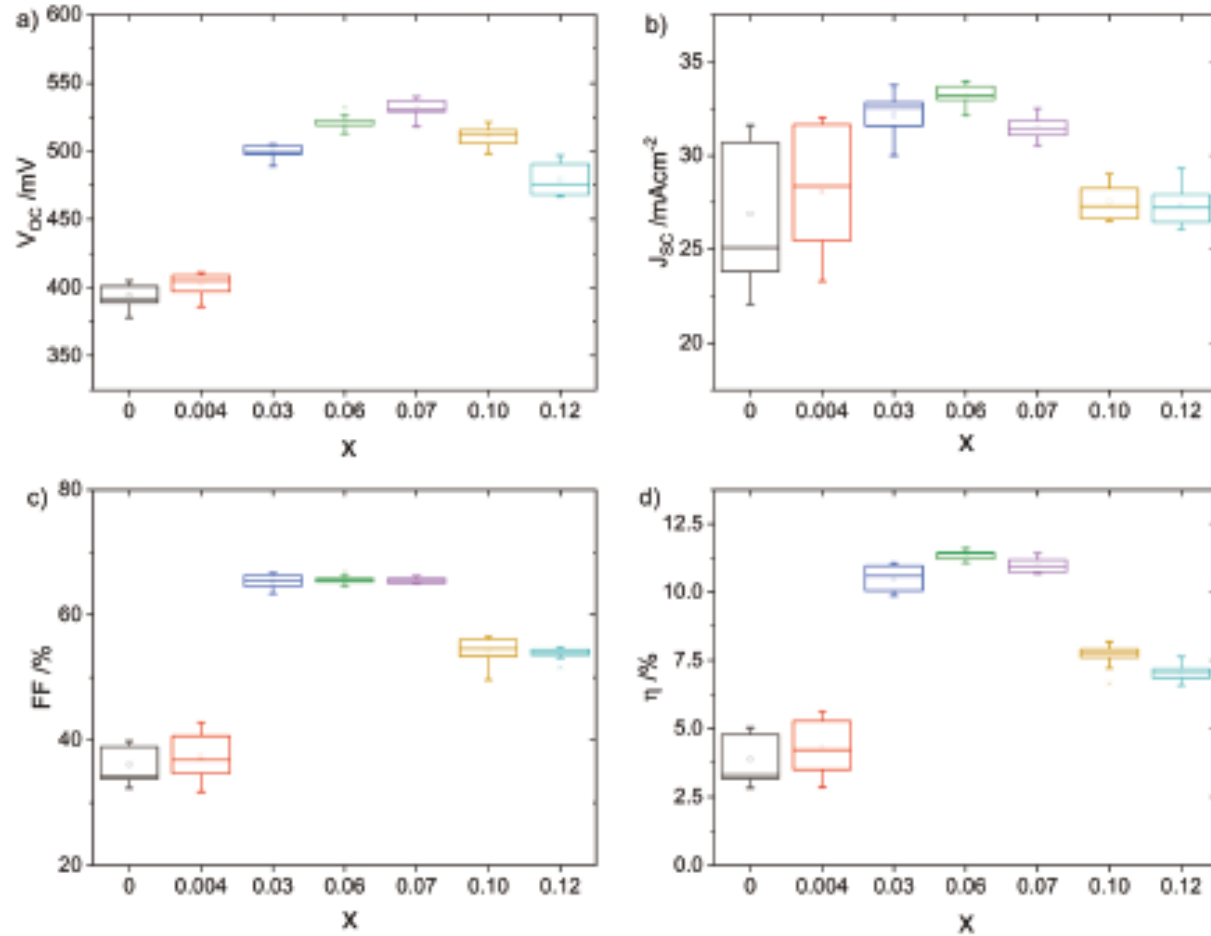
Most relevant

Alloying: Li, Mn, Ag, Cd and Ge



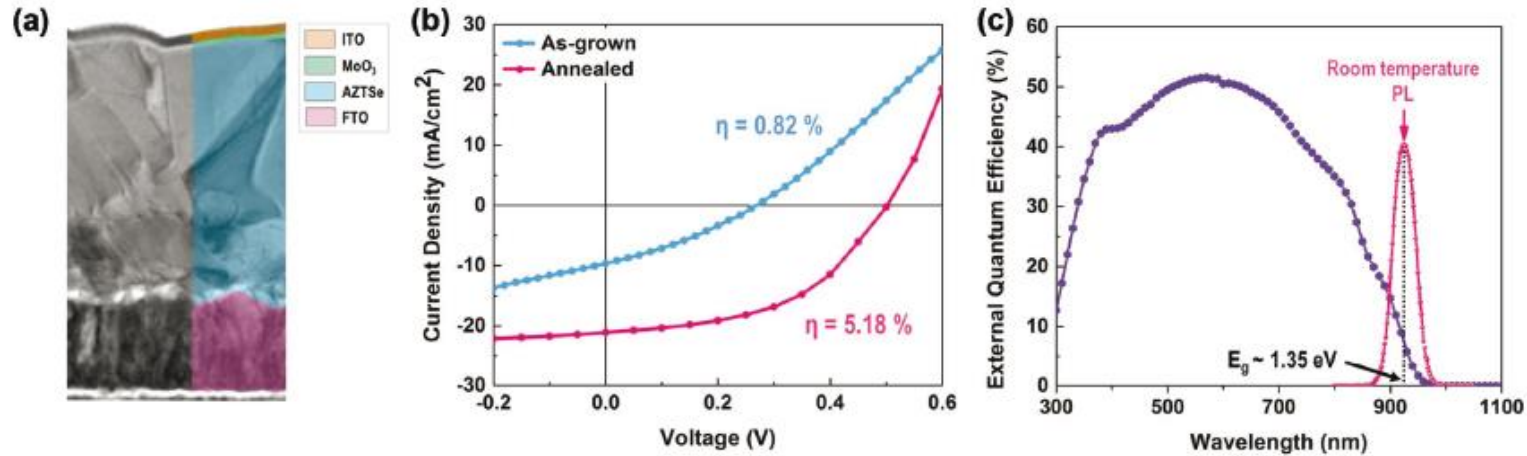
57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

Lithium*: substitutes Cu



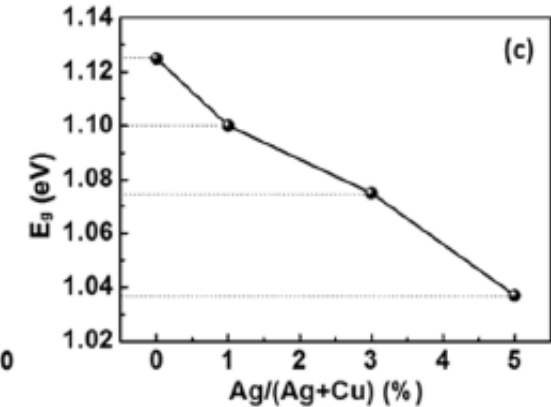
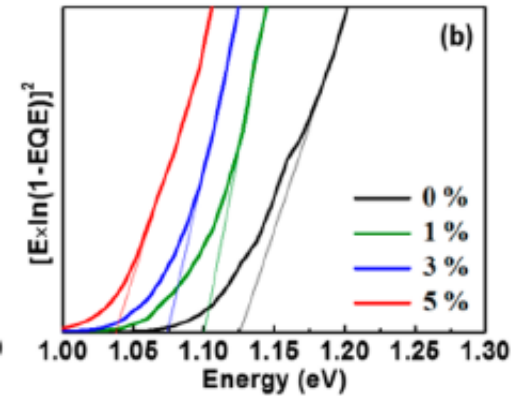
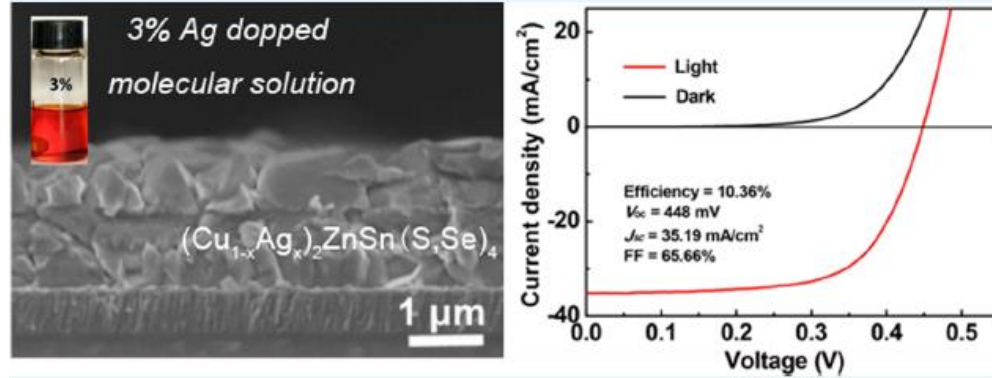
- ❖ Up to 12% Li alloying
- ❖ Large efficiency improvement with 3-7% Li (mainly Voc and FF improved)
- ❖ **Increase in the apparent carrier concentration with Li**
- ❖ **Increase of the quantum yield**
- ❖ No improvement in the minority carrier life-time
- ❖ Efficiency up to 12.2% is obtained

Silver*: substitutes Cu



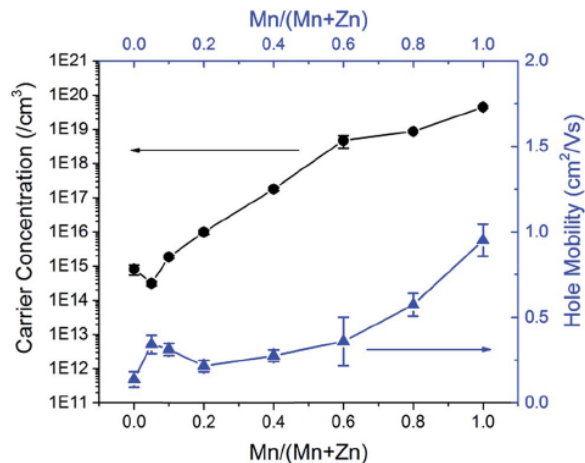
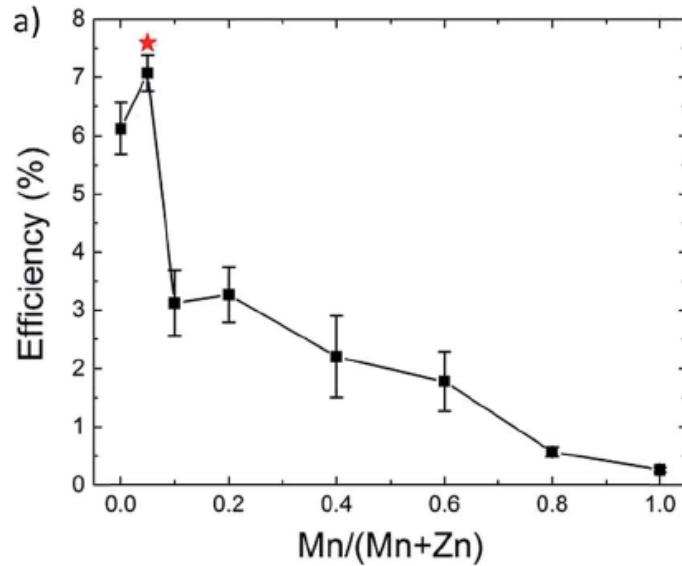
- ❖ Decent efficiencies have been reported using Ag in substitution of Cu^[1]
- ❖ Band-gap suitable for graded E_g concepts
- ❖ Has shown to probably solve one of the main issues of kesterites: **Cu-Zn disorder**, most probably related to a change of the structure from kesterite to stannite
- ❖ Problems:
 - change of conductivity for high Ag concentrations
 - Ag is expensive

Silver*: substitutes Cu



- ❖ Possibility to **tune the band-gap** has been demonstrated*
- ❖ Ag seems to help **to improve the efficiency** of the devices
- ❖ Nevertheless, possibility of band-gap grading is not demonstrated
- ❖ The feasibility is in doubt, cause the high mobility of Cu ions, and the large quantity of Cu vacancies in kesterite

Manganese*: substitutes Zn



- ❖ Substitution of Zn with Mn in CZTSSe thin films is shown to induce **structural transformation at $x = 0.2$** which is largely attributed to the difference in the atomic radius
- ❖ The variation of the Mn content is also found to **change the charge density, mobility and carrier lifetime** in CMZTSSe
- ❖ Improvement in the conversion efficiency of solar cell devices is observed for low Mn contents
- ❖ The improved open circuit voltage (V_{oc}) and fill factor (FF) are attributed to the **improved shunt resistance and carrier transport** due to lower defect density especially at the CdS/CMZTSSe interface
- ❖ If **Mn** content is more than 5% ($x > 0.05$), the efficiency was reduced due to the significant **increase of carrier density**

Cadmium*: substitutes Zn

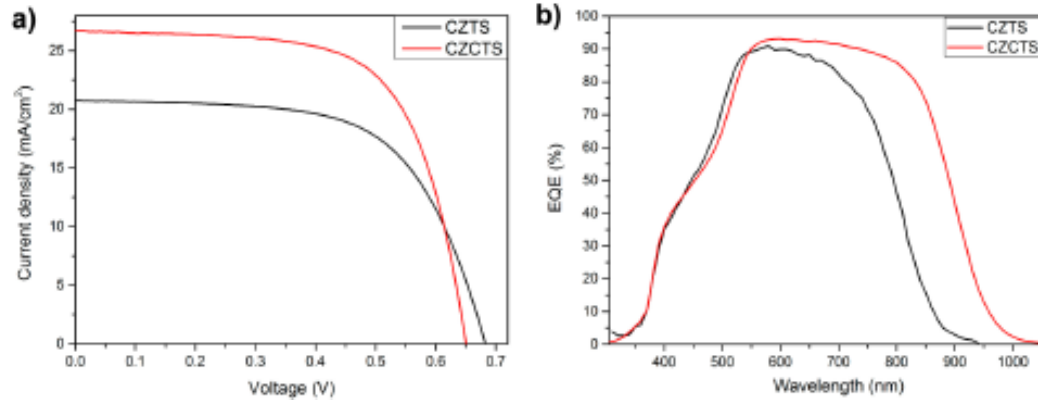
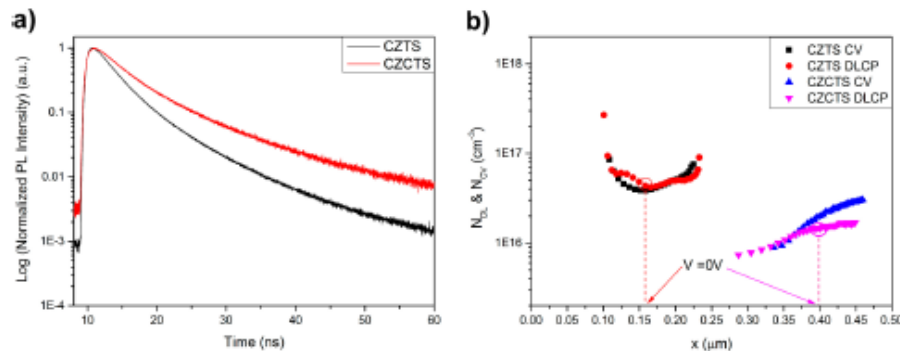


Figure 5. (a) J - V curves and (b) EQE curves of CZTS and champion CZCTS devices.

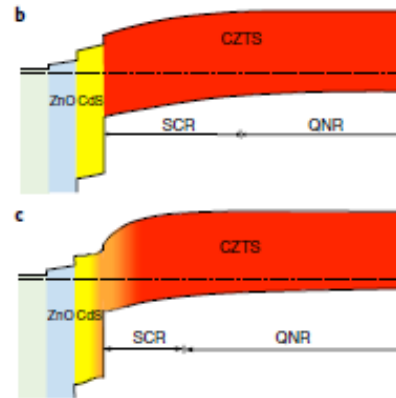
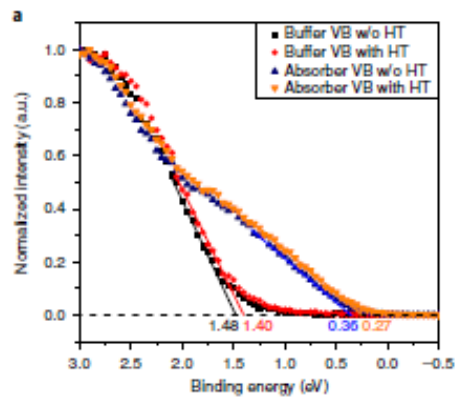
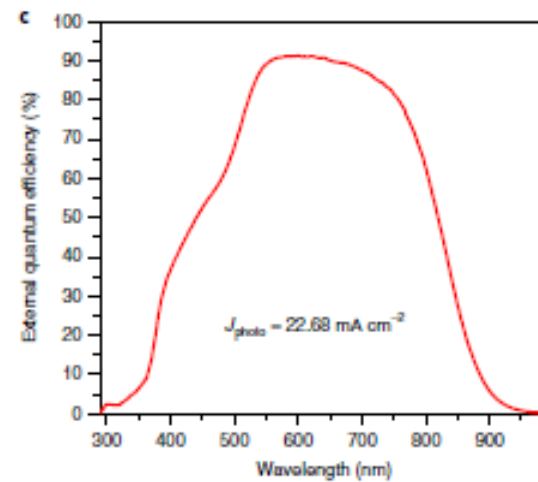
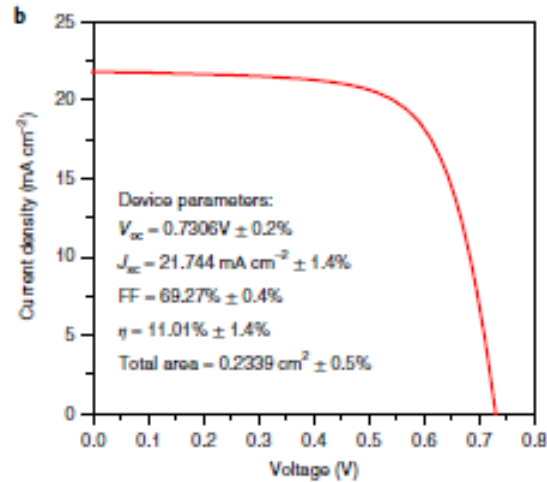
Table 2. Device Characteristics of the CZTS and CZCTS Solar Cells

absorber	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	Eff (%)	E_g/qV_{oc} (mV)	R_{scL} (Ω cm ²)	G_{sL} (mS cm ⁻²)	A	J_0 (A/cm ²)
CZTS	683	20.7	62.5	8.8	847	0.96	0.67	3.3	8.1×10^{-6}
CZCTS	650	26.7	66.1	11.5	730	0.45	1.0	2.5	1.2×10^{-6}



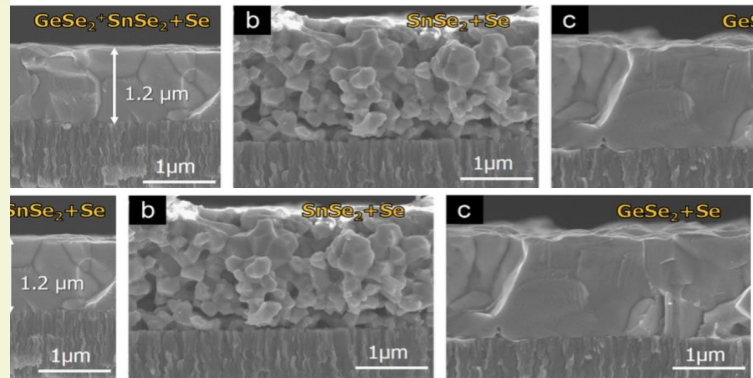
- ❖ Suitable for the S or S/Se compound
- ❖ Cd alloying into CZTS can **improve the microstructure** by facilitating the growth of larger grains and change the nature of the secondary phases of the absorber
- ❖ Alloying of Cd in CZTS can reduce the V_{oc} deficit and recombination by **reducing the band tailing problem**
- ❖ Alloying of Cd can **increase minority carrier lifetime** and lowers the doping density (free carrier)
- ❖ Cd incorporation elevates the VBM position of CZTS rather than lower the CBM position of CZTS, suggesting an undesirable cliff-like heterojunction interface
- ❖ Efficiencies over 11% are achieved

Cadmium*: substitutes Zn



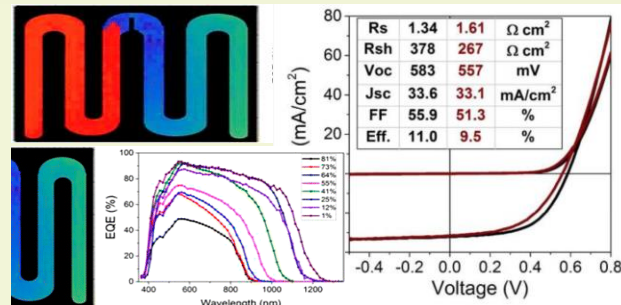
- ❖ Recent reported **10% certified efficiency** solar cell in large area ($>1\text{cm}^2$) (11% in standard size)
- ❖ **Inter-diffusion of CZTS/CdS** (selective surface alloying/doping)
- ❖ Elemental inter-diffusion: Zn into CdS and Cd into CZTS
- ❖ Na accumulation and local Cu depletion at the heterojunction
- ❖ **New phases formation:** $\text{Cu}_2\text{Cd}_x\text{Zn}_{1-x}\text{SnS}_4$, $\text{Zn}_x\text{Cd}_{1-x}\text{S}$, and $\text{Cu}_{2-x}\text{Na}_x\text{ZnSnS}_4$.
- ❖ **More favorable band-alignment** is demonstrated and **recombination** at the hetero-junction is **reduced**

Germanium: substitutes Sn



First group reporting Ge alloyed CZTSe with Eff > 10%: [1]

- **Improved morphological properties:** flat surfaces, dense morphologies, and large grains.
- Highest **efficiency of 10.03%**, with an **open-circuit voltage (V_{OC}) of 0.54 V**, as well as an **improved V_{OC} deficit of 0.647 V**

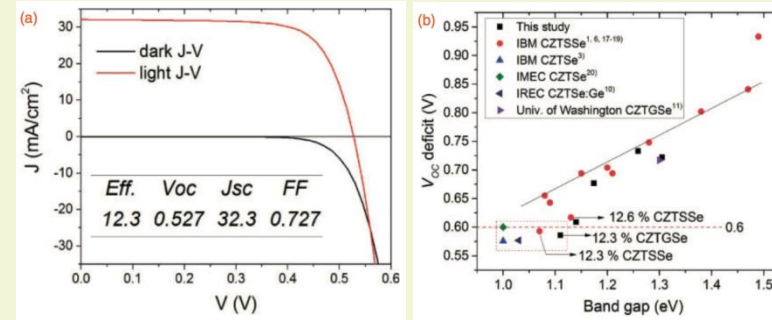


Study of CZTGeSe devices as function of Ge/(Ge+Sn) rel. content using spray coated absorbers with molecular inks: [3]

- **Highest efficiency: 11.0% with 25%Ge relative content** (band gap of about **1.2 eV**) with reduction of V_{OC} deficit

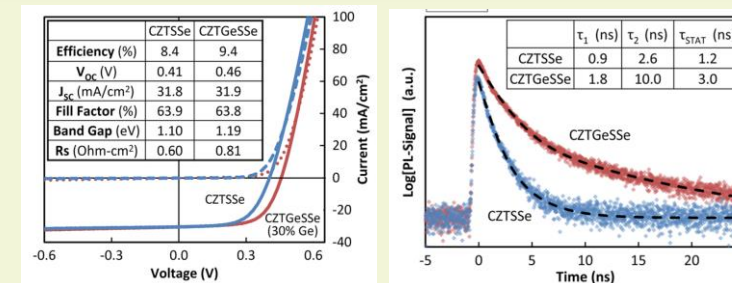
[1] S. Kim et al, Sol. Energy Mater. Sol. Cells. 2016, 144, 488-492

[2] S. Kim et al. Appl. Phys. Express 2016, 9, 102301



Best efficiency reported for Ge alloyed CZTSe: [2]

- **Conversion efficiency of 12.3%**
- **Improved V_{OC} deficit of 0.583 V and FF of 72.7%**
- Reduced band tailing and carrier recombination.



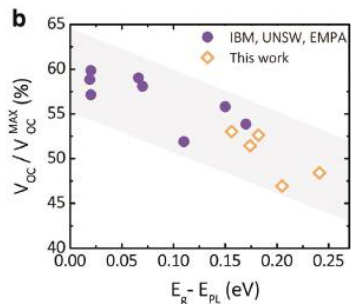
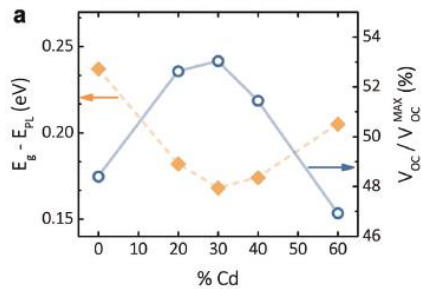
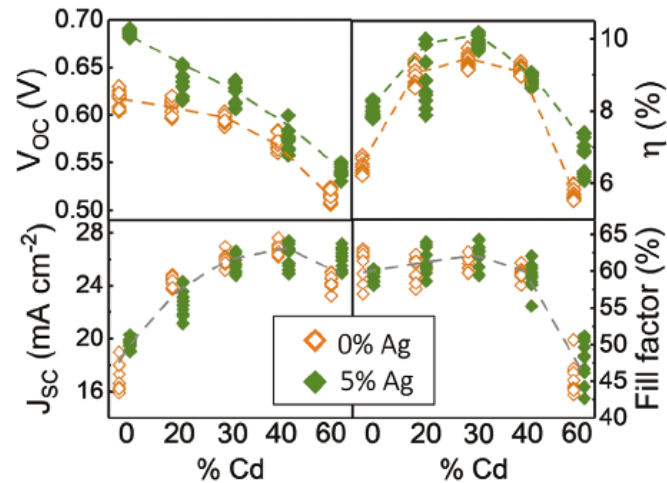
Nanocrystal-based CZTGeSe absorbers with tunable band gap: [4]

- Maximum conversion **efficiencies of up to 9.4%** are achieved with a Ge content of 30 at.%
- Enhanced performance due to **increased minority charge carrier lifetimes** as well as **reduced voltage-dependent charge carrier collection**.

[3] A.D. Collord, H.W. Hillhouse. Chem. Mater. 2016, 7, 2067–2073

[4] C.J. Hages et al, Prog. Photovoltaics Res. Appl. 2015, 23, 376–384

Bonus!: double cation substitution (Cd, Ag)



- ❖ Double cation substitution can be used to **improve** upon the device **performance** achievable via single cation substitution, if the **two cations affect different limiting factors** of CZTS.
- ❖ **Cd alters the position of acceptor defects near the valence band**, and the maximum device performance is obtained at the Cd content corresponding to the shallowest acceptor defects.
- ❖ **Ag decreases the charge carrier density, improves the photoluminescence decay time and efficiency**, as well as the open-circuit voltage, indicating a **reduction** of the **nonradiative recombination** via defects.
- ❖ Double cation substitution can be used as a tool to fine-tune the properties of the absorber material.
- ❖ Efficiencies over 10% are reported (5% Ag and 25% of Cd)

Summary*

Material	Doping element	E _g (eV)	V _{oc} (mV)	Eff (% total area)	Ref
CZTSSe	nominally undoped*	1.13	513	12.6	[3]
CZTSSe	Li	1.04	449	11.5	[26]
CZTSe	Na*	1.0	423	11.6	[39]
CZTSe	K	1.02	432	9.7	[45]
CZTSSe	Rb	0.96	419	8.8	[26]
CZTSSe	Cs	0.97	439	9.1	[26]
CZTSe	In	1.02	423	7.8	[82]
CZTSe	Ge	1.04	463	11.8	[106]

Material	Alloying element	E _g (eV)	V _{oc} (mV)	Eff. (% total area)	Ref.
ACZTSSe	Ag/(Ag+Cu)=3%	1.07	448	10.4	[57]
CMZTSSe	Mg/(Mg+Zn)=4%	1.01	419	7.2	[72]
CZCTS	Cd/(Cd+Zn)=40%	1.38	650	11.5	[75]
CZTGSe	Ge/(Ge+Sn)=22%	1.11	527	12.3	[113]
CMZTS	Mn/(Mn+Zn)=5%	1.055	418	8.9	[142]
ACZCTSSe	Ag: 5%, Cd:25%	1.4	650	11.1	

❖ Most promising doping elements: Li, Na and Ge

❖ Most promising alloying elements: Cd and Ge, maybe double cation substitution?

*"Doping and alloying of kesterites", Yaroslav Romanyuk, Stefan Haass, Sergio Giraldo, Marcel Placidi, Devendra Tiwari, David Fermin, Xiaojing Hao, Hao Xin, Thomas Schnabel, Marit Kauk-Kuusik, Paul Pistor, Stener Lie and Lydia Helena Wong, J. Physics Energy 2019 (DOI: 10.1088/2515-7655)

OUTLINE

Presentation of CUSTOM-ART project

1. Introduction
2. Characteristics and challenges of kesterite
3. Doping and alloying strategies
- 4. Beyond kesterites**
5. Conclusions and perspectives

You are very lucky!!!..

IOP Publishing

J. Phys.: Energy 1 (2019) 032001

<https://doi.org/10.1088/2515-7655/ab2338>

JPhys Energy



TOPICAL REVIEW

Emerging inorganic solar cell efficiency tables (Version 1)

OPEN ACCESS

RECEIVED
29 March 2019

REVISED
17 May 2019

ACCEPTED FOR PUBLICATION
21 May 2019

PUBLISHED
29 July 2019

Original content from this work may be used under the terms of the [Creative Commons Attribution 3.0 licence](#).

Any further distribution of this work must maintain attribution to the

Lydia H Wong¹ , Andriy Zakutayev² , Jonathan D Major³ , Xiaojing Hao⁴ , Aron Walsh^{5,6} , Teodor K Todorov⁷ and Edgardo Saucedo^{8,9}

¹ Nanyang Technological University, 637553 Singapore, Singapore

² National Renewable Energy Laboratory, Golden, Colorado 80401, United States of America

³ University of Liverpool, Liverpool, L69 7ZF, United Kingdom

⁴ University of New South Wales, Sydney, NSW 2052, Australia

⁵ Imperial College London, London SW7 2AZ, United Kingdom

⁶ Yonsei University, Seoul 03722, Republic of Korea

⁷ IBM Thomas J. Watson Research Center, New York 10598, United States of America

⁸ Catalonia Institute for Energy Research (IREC), E-08930 Sant Adrià del Besòs- Barcelona, Spain

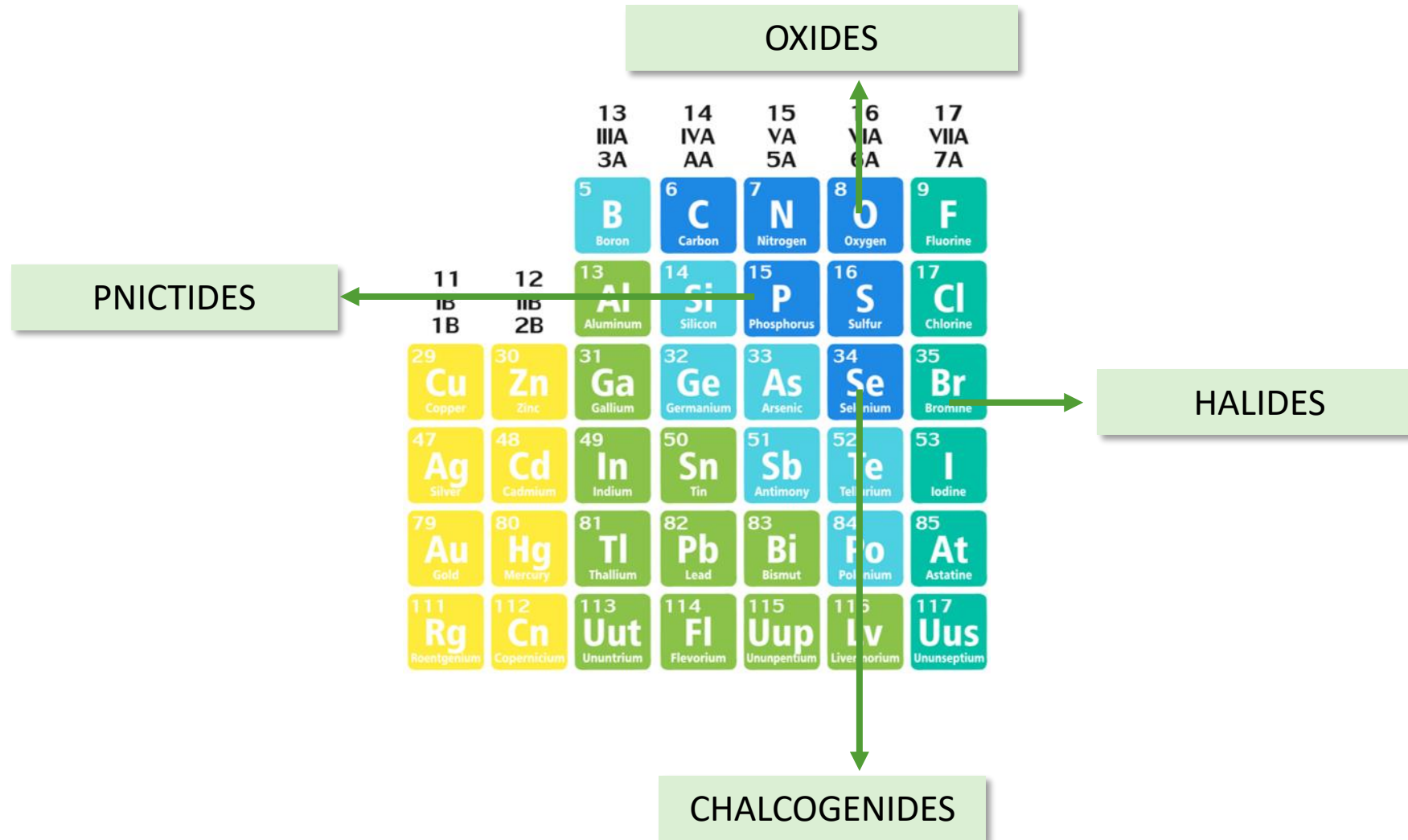
⁹ Author to whom any correspondence should be addressed.

E-mail: lydiawong@ntu.edu.sg, andriy.zakutayev@nrel.gov, jon.major@liverpool.ac.uk, xj.hao@unsw.edu.au, a.walsh@imperial.ac.uk, tktdoro@us.ibm.com and esaucedo@irec.cat

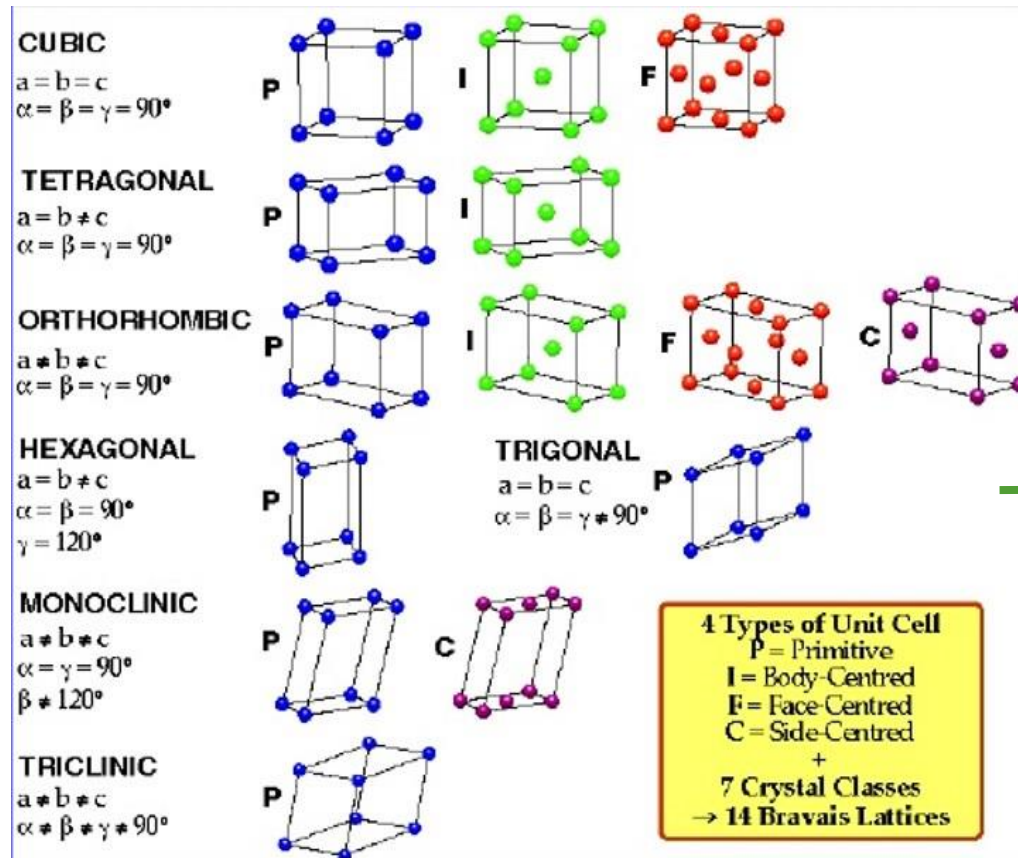
Keywords: thin film inorganic photovoltaics, emerging photovoltaic technologies, solar energy, photovoltaic conversion efficiency tables

- Since last year a group of international scientists we are compiling the Efficiency Tables of Emerging PV Inorganic Materials in collaboration with Institute of Physics of UK (IOP)

What options do we have?



Example: selection through the structure



Most of the good performing PV materials belong from Cubic or Tetragonal crystal system with tetrahedrally bonded elements

Recently, more disordered systems (orthorhombic, hexagonal, monoclinic), with non-tetrahedrally bonded elements: anisotropic materials, low dimensional materials...

J. Phys.: Energy 1 (2019) 032001

<https://doi.org/10.1088/2515-7655/ab23>

JPhys Energy

TOPICAL REVIEW

Emerging inorganic solar cell efficiency tables (Version 1)

Lydia H Wong¹, Andriy Zakutayev², Jonathan D Major³, Xiaojing Hao⁴, Aron Walsh^{5,6}, Teodor K Todorov⁷ and Edgardo Saucedo^{8,9}

CHALCOGENIDES

- Se
- GeSe
- PbS
- Sb₂Se₃
- Sb₂S₃
- Bi₂S₃
- SnS
- AgBiS₂
- Cu₂SnS₃
- CuSbS₂
- CuSbSe₂
- Cu₂FeSnS₄
- Cu₂ZnGeSe₄
- Ag₂ZnSnSe₄
- (Li,Cu)₂ZnSn(S,Se)₄
- Cu₂(Zn,Mn)Sn(S,Se)₄
- Cu₂BaSnSe₄
- Cu₂BaSnS₄
- Cu₂ZnSnSe₄
- Cu₂ZnSnS₄
- Cu₂CdSnS₄

OXIDES

- Cu₂O
- Bi₂FeCrO₆

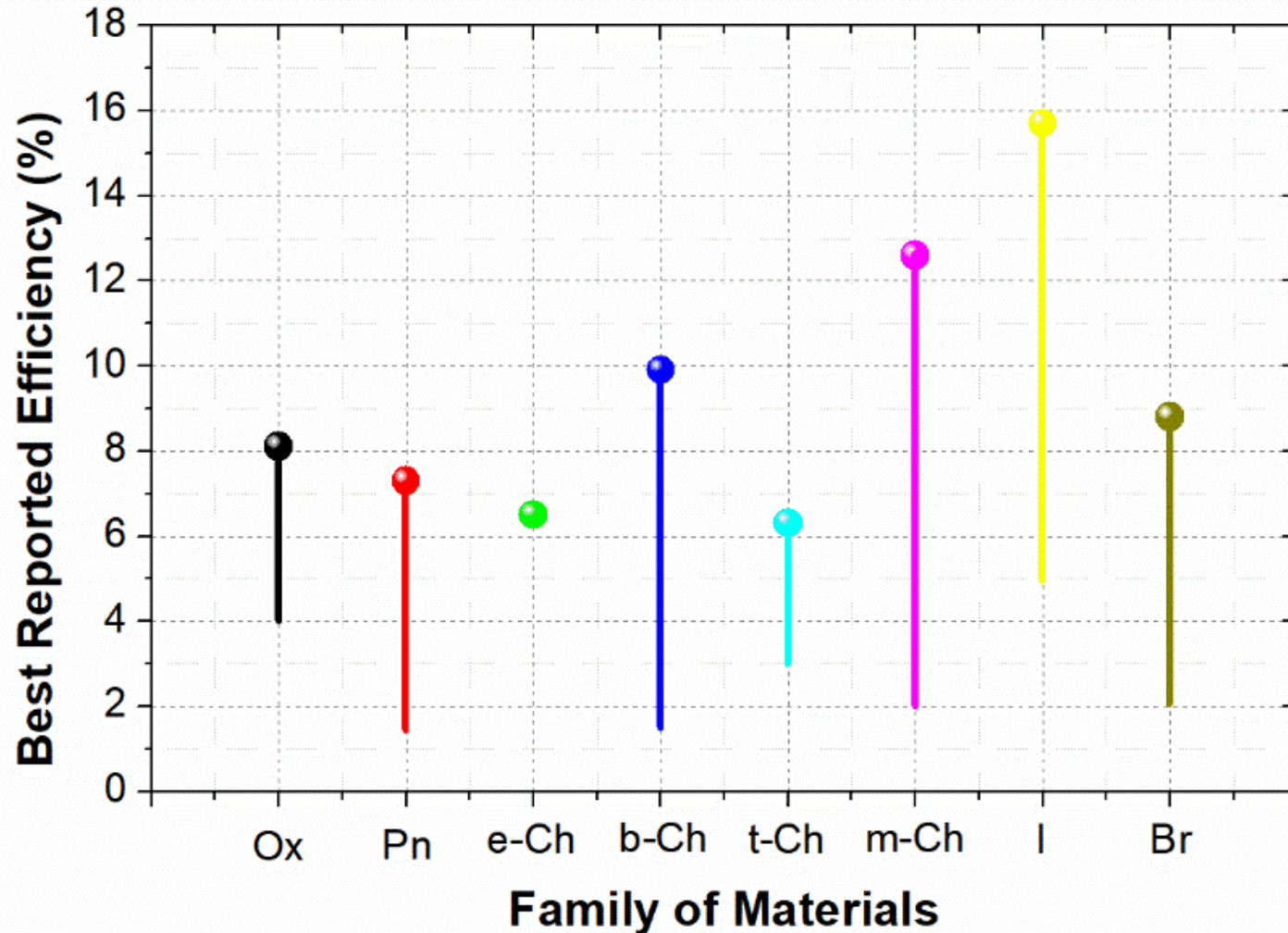
PNICTIDES

- InP
- (In,Ga)N
- (Zn,Sn)N₂

HALIDES

- BiI₃
- CsPbBr₃
- CsPbI₃
- CsSnBr₃
- CsSnI₃
- Cs(Sn,Ge)I₃

- Few oxides and pnictides
- Some halides but increasing interest
- Several chalcogenides, from simple to multinary compounds

**MOST PROMISING:**

- Multinary chalcogenides not only with kesterite structure
- Perovskites mainly iodides or mixed iodides/bromides
- Binary chalcogenides, mainly anisotropic materials

NON CUBIC OR TETRAGONAL
INORGANIC MATERIALS BECOMES FOR
THE FIRST TIME VERY RELEVANT



LOW DIMENSIONAL SEMICONDUCTORS FOR OPTICALLY TUNEABLE SOLAR HARVERSTERS

H2020-ERC-CoG-2019-866018

Project Coordinator: Prof. Dr. Edgardo Saucedo (Polytechnic University of Catalonia)

Starting date: 1st June 2020 (5 years)



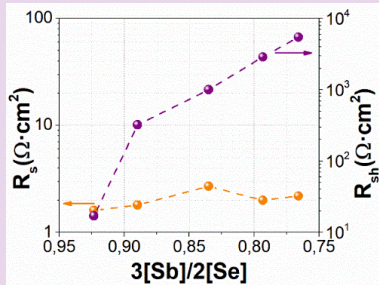
Q-1D PV Absorbers

High throughput screening of (Ge,Sn,Sb,Bi):

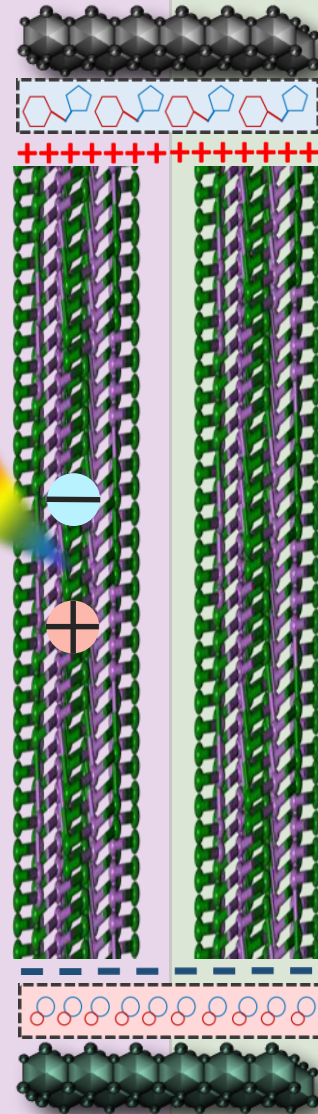
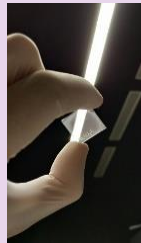
- Chalcogenides
- Halides
- Mixed chalco-halides



Best suited anisotropic **Q-1D** materials with
"A la carte" **tuneable optical/electrical** properties



Eff. = 5.9%



Selective contacts with dipoles

Bi-layer nano-scale asymmetric contact structure:

- p- and n-type transition metal oxides already developed at IREC
- Dipolar organic and inorganic molecules



Very efficient charges extraction creating
highly asymmetric polarized interfaces

OUTLINE

Presentation of CUSTOM-ART project

1. Introduction
2. Characteristics and challenges of kesterite
3. Doping and alloying strategies
4. Beyond kesterites
5. **Conclusions and perspectives**

CONCLUSIONS AND PERSPECTIVES

- KESTERITE**
- ❖ Unambiguously demonstrated **alkaline doping as a key issue** for kesterite technology. Other dopants like **Ge** becomes very relevant.
 - ❖ **Ge, Li and Cd** are identified as the most **versatile** alloying elements.
 - ❖ Something happens with Sn! Maybe there one of the solutions to increase the efficiency is waiting for us.

- BEYOND KESTERITE**
- ❖ **Oxides, Pnictides, Chalcogenides, Halides**...examples in the literature abound
 - ❖ Among them, **perovskite halides** and **anisotropic chalcogenides** are at the forefront for the moment in terms of efficiency
 - ❖ **We are facing the revolution of the non-cubic/non-tetragonal materials!!!???**

ACKNOWLEDGMENTS



H2020-LC-SC3-2020-RES-IA-CSA-952982



H2020-ERC-CoG-2019-866018

To the organizing Committee:
Alex Redinger, Amit Munshi, Jiro Nishinaga,
Negar Naghavi, Romain Carron,
Rutger Schlatmann, and Sophie Spangenberg



Virtual Chalcogenide PV Conference 2020.

Thanks for your attention!