Relevance of Ge incorporation on the physics of deep defects in kesterite materials

T. Ratz[1,2], N-D. Nguyen[1], G. Brammertz[3], B. Vermang[2,3,4], J-Y. Raty[1]

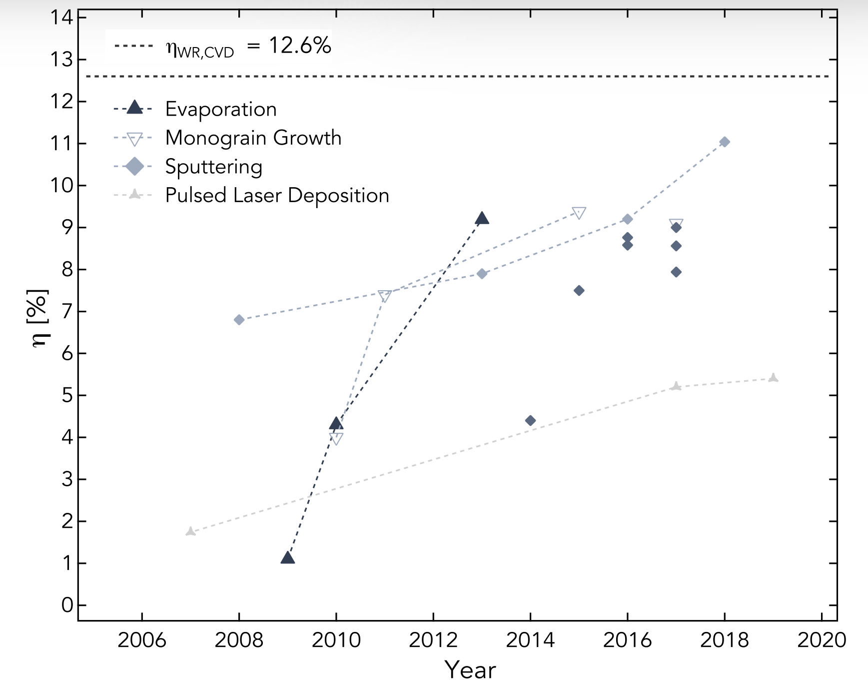
1. *CESAM | Q-MAT | Solid State Physics, Interfaces and Nanostructures, Physics Institute B5a, Allée du Six Août 19, B-4000 Liège, Belgium*
2. *Institute for Material Research (IMO), Hasselt University, Agoralaan gebouw H, B-3590 Diepenbeek, Belgium*
3. *IMEC division IMOMEC | partner in Solliance, Wetenschapspark 1, B-3590 Diepen- beek, Belgium*
4. *Energyville, Thor Park 8320, B-3600 Genk, Belgium*

thomas.ratz@uliege.be
University of Liège [ULiege] - Department of Physics [BAT. B5a]

1. Introduction
2. Kesterite phase diagrams
3. Point defects in Ge-doped and Ge-alloyed kesterites
4. Lattice distortion upon defect incorporation
5. Conclusion

Introduction

- Limitations of the Cu_2ZnSnS_4 kesterite-based solar cell efficiency
- Bulk point defects have been pointed out as efficient recombination centres (Sn_{Zn} and/or [Cu_{Zn} + Sn_{Zn}])
- Cationic substitution as a possible route for efficiency improvement



What is the impact of Ge incorporation on the physics of deep defect in kesterite ?

Journal of Materials Chemistry A

PAPER

View Article Online
View Journal | View Issue

Cite this: J. Mater. Chem. A, 2022, 10, 4355

Relevance of Ge incorporation to control the physical behaviour of point defects in kesterite†

Thomas Ratz,[*ab] Ngoc Duy Nguyen,[a] Guy Brammertz,[c] Bart Vermang[bcd] and Jean-Yves Raty[a]

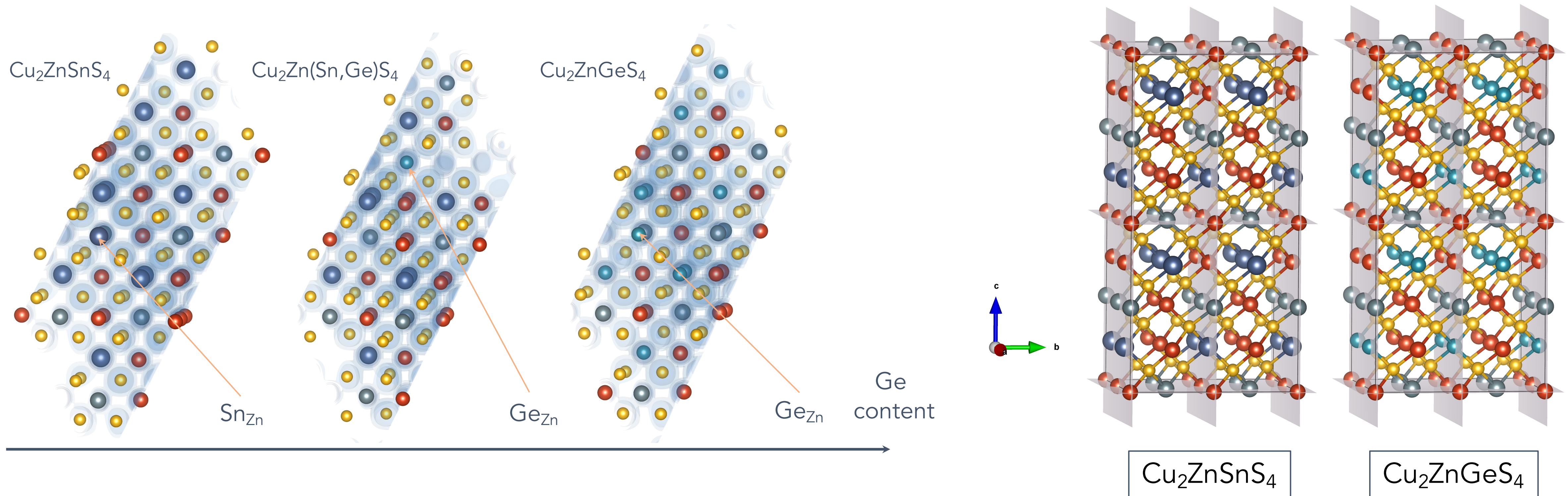
Ratz, Thomas, et al. "Physical routes for the synthesis of kesterite." Journal of Physics: Energy 1.4 (2019): 042003.

Point defect calculations using DFT

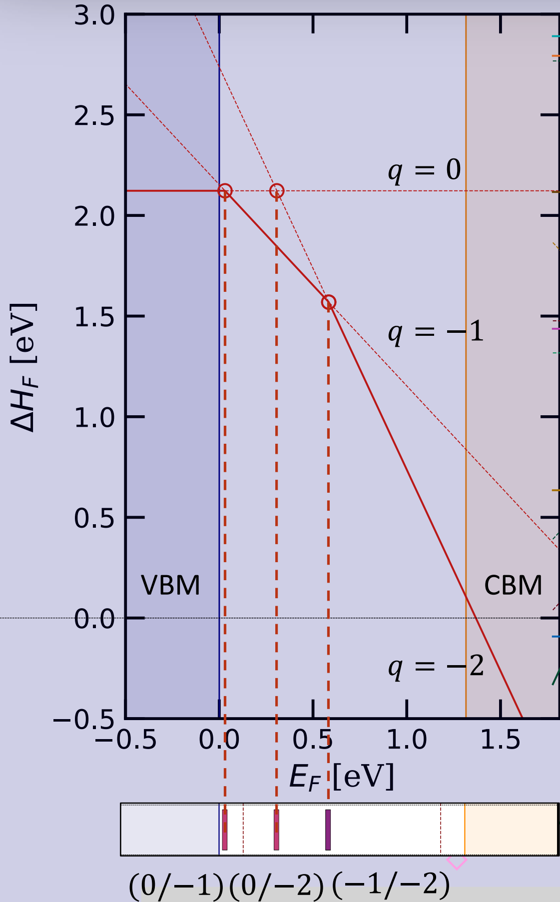
From a perfect kesterite crystal to a defected system – supercell approach (64-atom calculations)

Motivation: reduction of the V_{OC} deficit following Ge incorporation into kesterite materials

Goal: Study of the point defect physical behaviour in Ge doped and alloyed kesterites



Point defect calculations using DFT



Point defect formation energy:

$$\Delta H_F(\alpha, q, \mu_i, E_F) = E(\alpha, q) - E(host) + \sum_i n_i(E_i - \mu_i) + q[\epsilon_{VBM}(host) + E_F]$$

Total energy difference between the defected and pristine supercell

Energy cost for particles (elements) exchange

Energy cost for charges exchange

- Identification of point defects types
  - Acceptor/donor
  - Recombination center

$$\epsilon_{q,q'}(\alpha) = \frac{\Delta H_F(\alpha, q) - \Delta H_F(\alpha, q')}{q' - q}$$

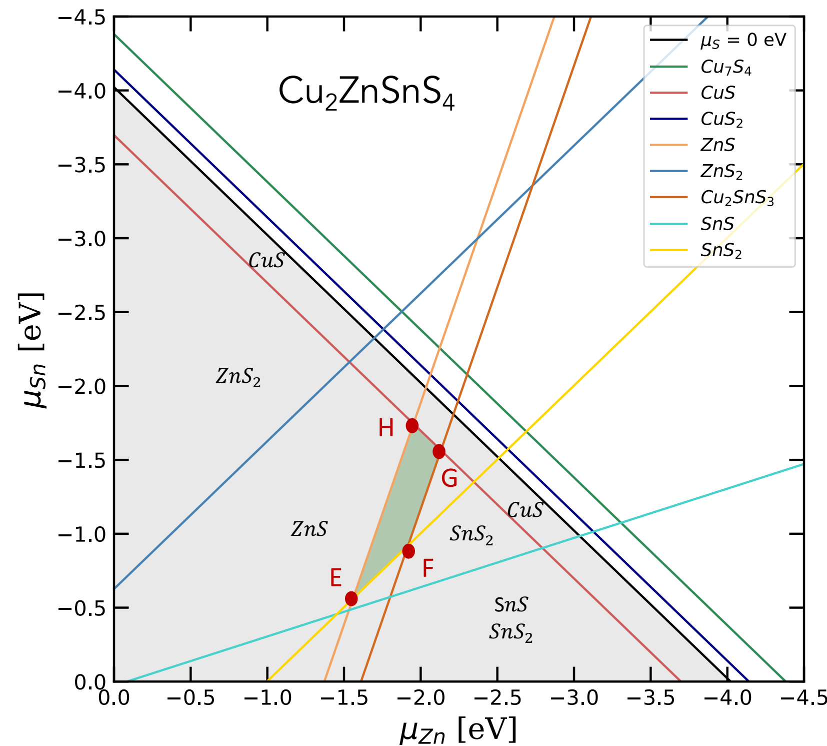
Correction terms:
- Electrostatic interaction between image defects
- Band alignment between charged defects and the host supercell

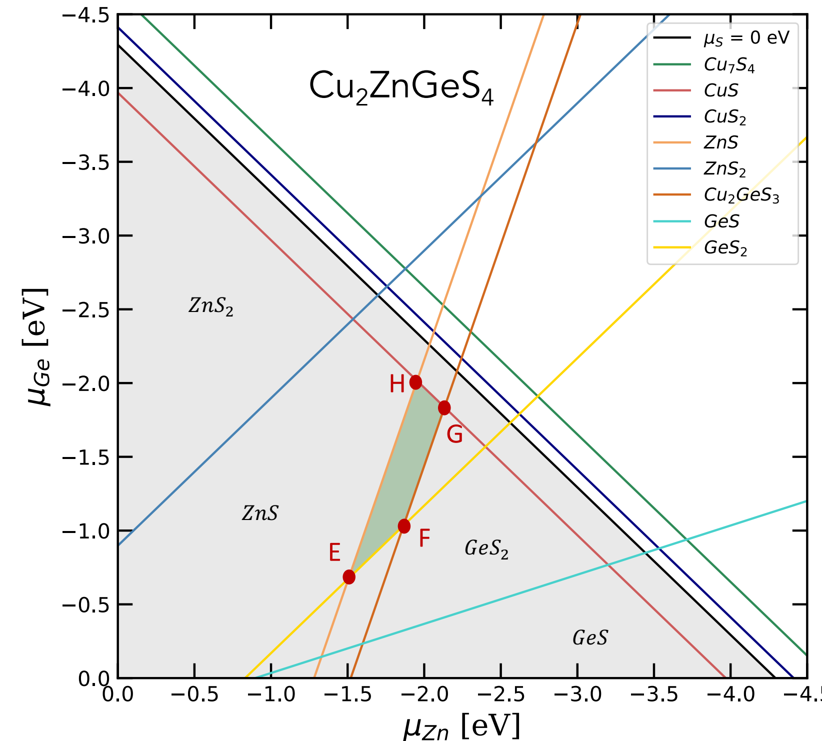
Freysoldt, Christoph, et al. "First-principles calculations for point defects in solids." *Reviews of modern physics* 86.1 (2014): 253.

Phase diagram - Kesterite synthesis

Thermodynamic conditions

- $\mu_{Cu} < 0,\ \mu_{Zn} < 0, \mu_X < 0,\ \mu_S < 0$ — Avoid pure phases
- $2\mu_{Cu} + \mu_{Zn} + \mu_X + 4\mu_S = \Delta H_F(\mathrm{CZXS})$ — Kesterite materials is desired
- $\sum_i n_i\mu_i < \Delta H_F(\mathrm{Secondaries}) = E(\mathrm{A_xB_y}) - xE(\mathrm{A}) - yE(\mathrm{B})$ — No secondary phases





Kesterite phase

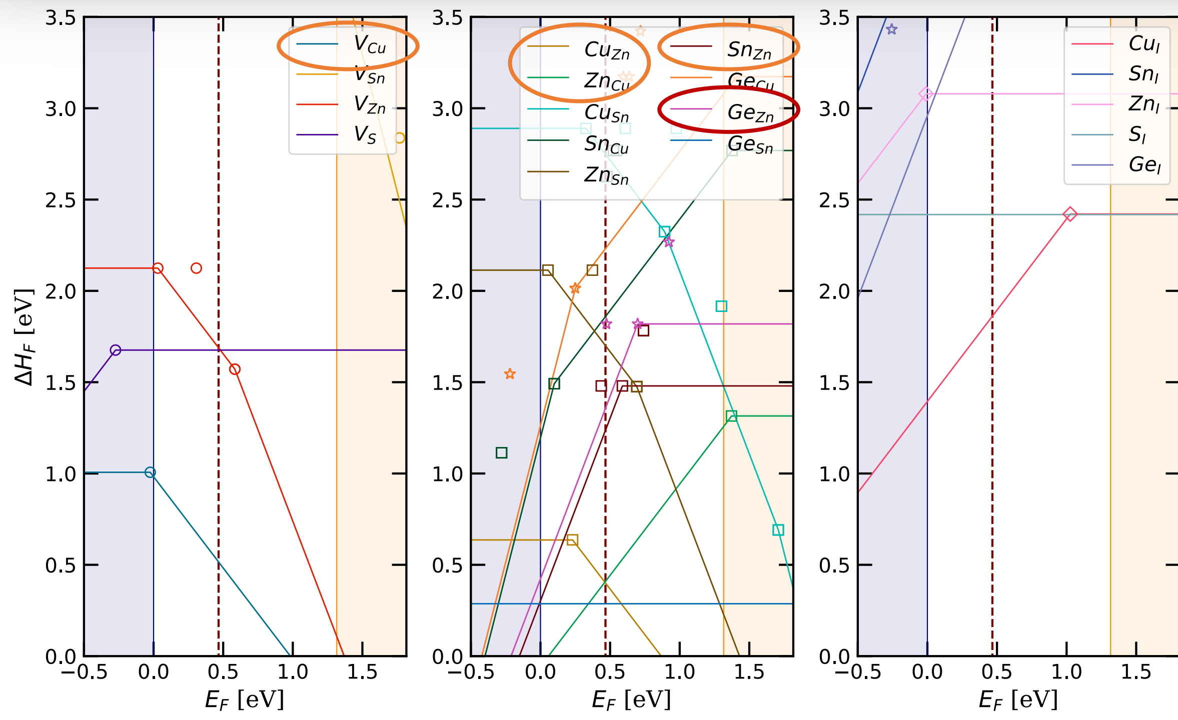
Pure phase

$\mu_i \rightarrow 0$: rich in element i

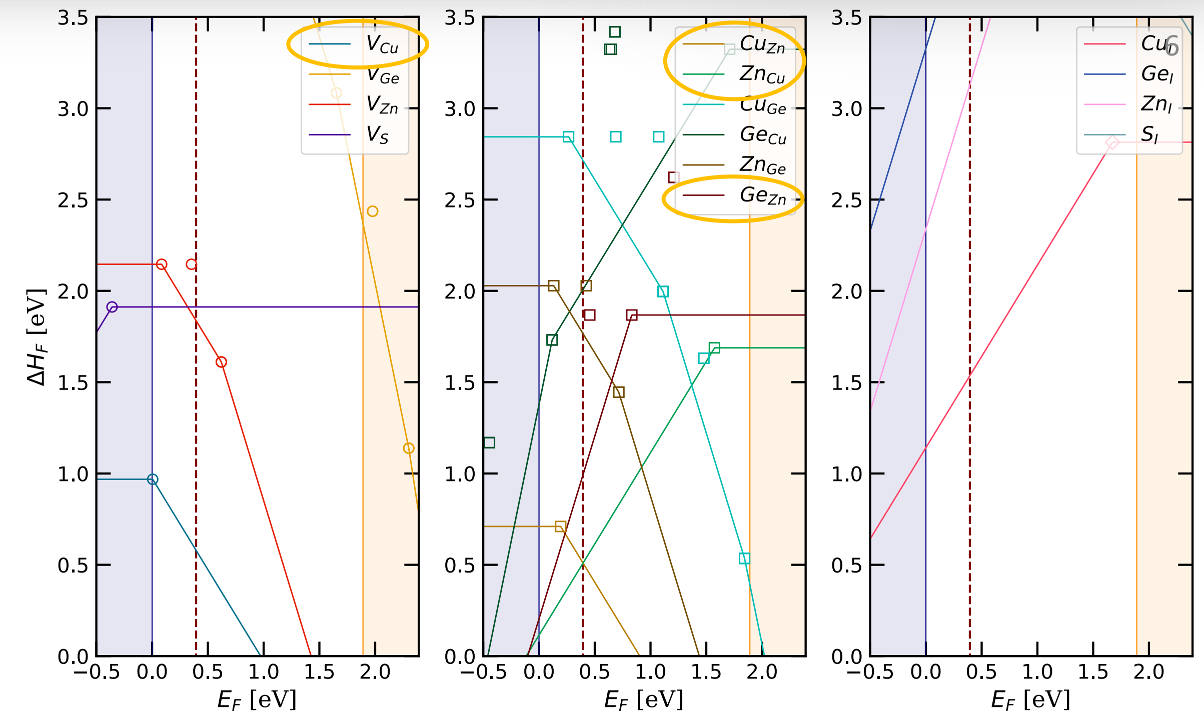
$|\mu_i| \rightarrow \infty$: poor in elment I

$\mu_{Cu} = -0.55$ eV

Point defect formation energies (point E)



Cu_2ZnSnS_4

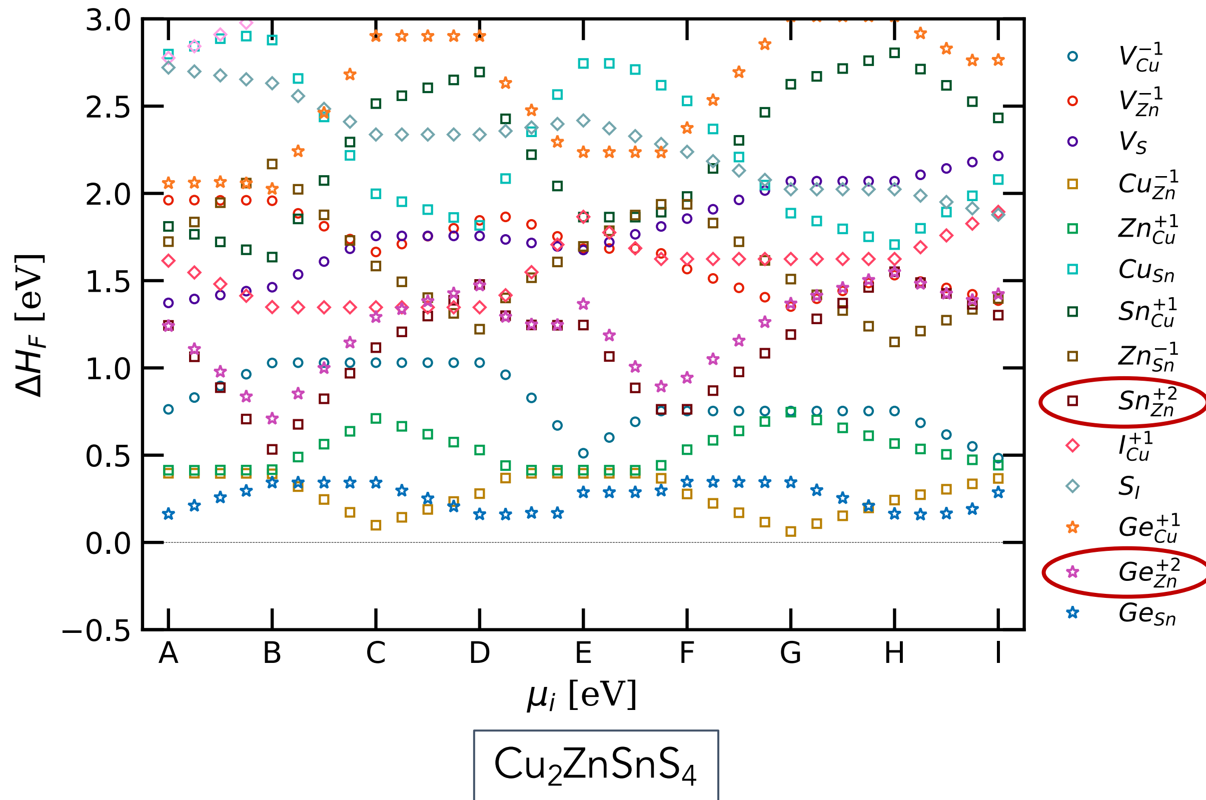


Cu_2ZnGeS_4

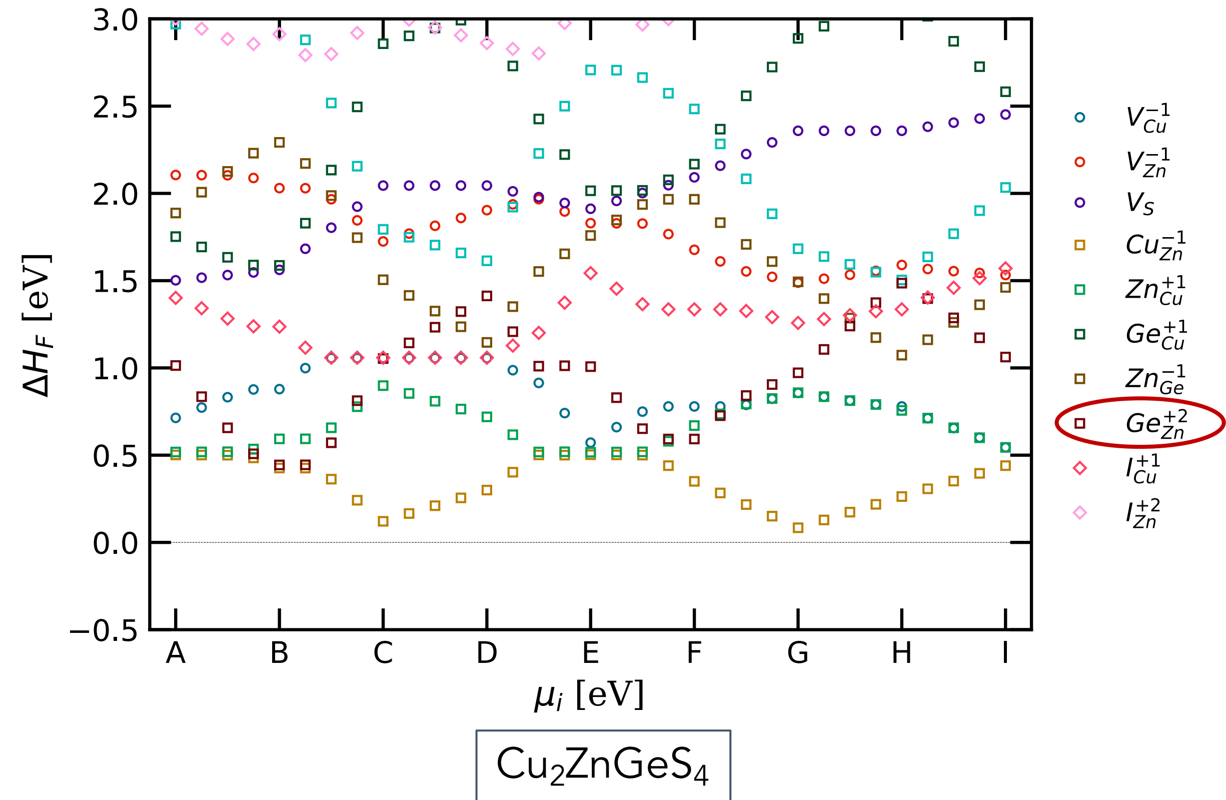
- Fermi energy level under thermodynamic equilibrium condition
- p-type intrinsic conductivity of kesterites
- V_{Cu}, Cu_{Zn}, Zn_{Cu}, X_{Zn} (X=Sn,Ge) low formation energies

Point defect formation energies

Evolution of the point defect formation energies according to the synthesis conditions:



Cu_2ZnSnS_4

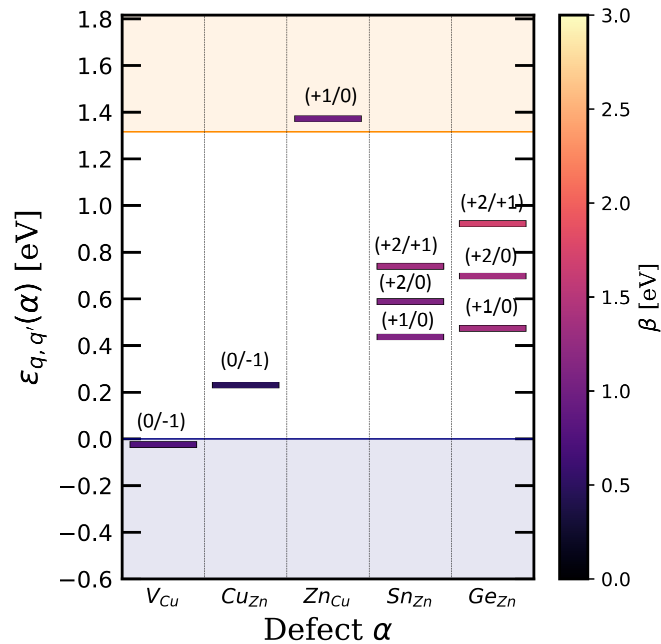


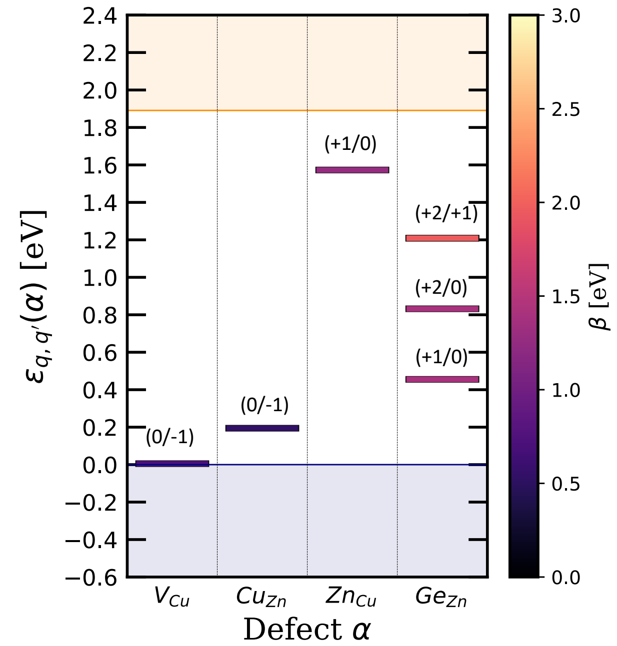
Cu_2ZnGeS_4

- V_{Cu}, Cu_{Zn}, Zn_{Cu}, X_{Zn} (X=Sn,Ge) low formation energies
- Ge_{Sn} most abundant doping defect
- From Sn_{Zn} to the dopant Ge_{Zn} to the Ge_{Zn} substitutional defect in the Ge-based kesterite

Point defect transition levels

Physical behaviour of the defects previously identified as abundant in the materials





- V_{Cu}, Cu_{Zn}, Zn_{Cu} acting respectively as acceptor and donor for the later
- X_{Zn} (X=Sn,Ge) acting as recombination centres
- The formation energy is not the only key ingredient impacting the physical behaviour of a defect

SPIN

What is a deep defect? Combining Shockley-Read-Hall statistics with multiphonon recombination theory

Basita Das,[1] Irene Aguilera,[1] Uwe Rau,[1] and Thomas Kirchartz[1,2]
[1]IEK5-Photovoltaik, Forschungszentrum Jülich, 52425 Jülich, Germany
[2]Faculty of Engineering and CENIDE, University of Duisburg-Essen, Carl-Benz-Str. 199, 47057 Duisburg, Ge

(Received 25 November 2019; revised manuscript received 15 January 2020; accepted 30 January 20
published 26 February 2020)

Transition between two states: Ψ_1 the initial band state and Ψ_2, the final defect state

Transition probability : $W_{1,2} = \frac{2\pi}{\hbar} |\langle\Psi_1|H_{int}|\Psi_2\rangle|^2 V\, N(E_2)$

electron-lattice interaction

cm CHEMISTRY OF MATERIALS
Article
Cite This: Chem. Mater. 2019, 31, 826–833
pubs.acs.org/cm

Effective and Noneffective Recombination Center Defects in Cu_2ZnSnS_4: Significant Difference in Carrier Capture Cross Sections

Jiqiang Li,[†,‡] Zhen-Kun Yuan,[†,‡] Shiyou Chen,[*,§] Xin-Gao Gong,[*,†,‡] and Su-Huai Wei[‖]
[†]Department of Physics, Key Laboratory for Computational Physical Science (Ministry of Education), State Key Laboratory of Surface Physics, Fudan University, Shanghai 200433, China
[‡]Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, Jiangsu, China
[§]Key Laboratory of Polar Materials and Devices (Ministry of Education), East China Normal University, Shanghai 200241, China
[‖]Beijing Computational Science Research Center, Beijing 100193, China

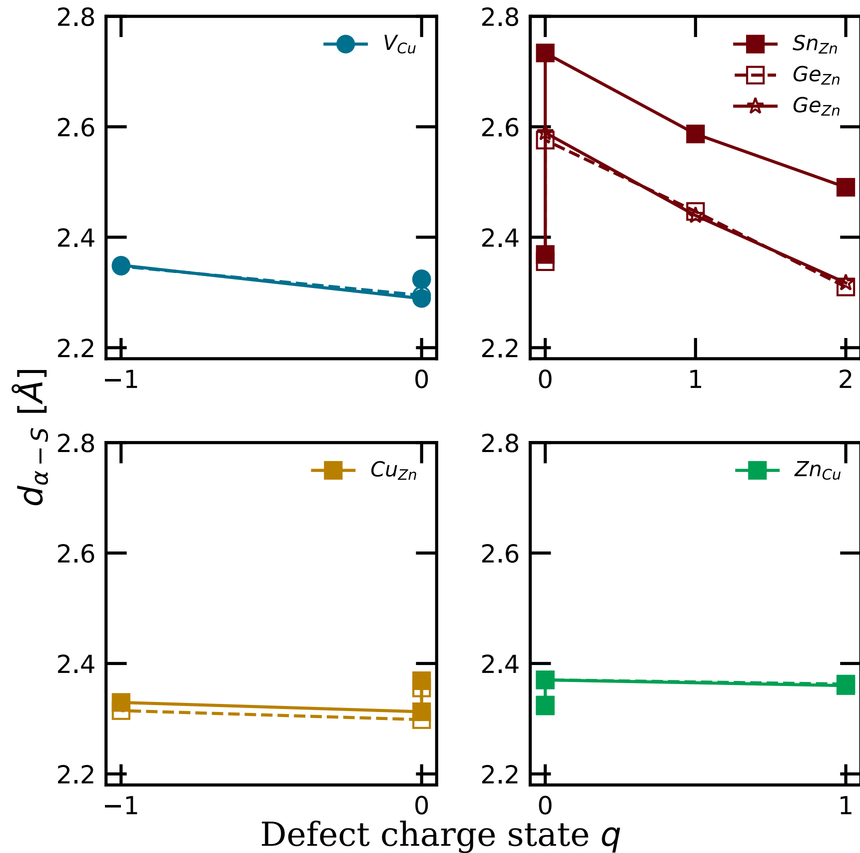
Sn_{Zn}^{+1} (+1/0) and Sn_{Zn}^{+2} (+2/+1) are not equivalent recombination centres as $\sigma_{Sn_{Zn}^{+1}} \ll \sigma_{Sn_{Zn}^{+2}}$

The larger the structural relaxation, the larger the carrier capture cross section σ

What is the impact of the Ge incorporation on the lattice distortion ?

Lattice distortion upon defect incorporation

Relation between the lattice distortion upon defect incorporation and the defect carrier capture cross section



$$e_p = \sigma_p < v_p > N_V \exp\left(-\frac{E_T - E_V}{k_B T}\right)$$

Defect emission rate e_p depends on

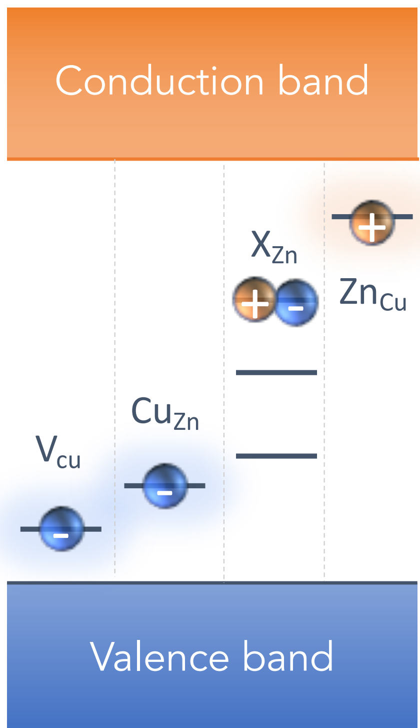
- The energetic position of the defect within the band gap and with respect to the CBM or VBM
- Carrier capture cross section σ_p related to the electron-phonon interaction

→ Reduction of the lattice distortion induced by the formation of the $\mathrm{Ge_{Zn}}$ substitutional defect in comparison to its $\mathrm{Sn_{Zn}}$ parent in the Sn-based kesterite

Conclusion

SPIN

- Similar physical behaviour of intrinsic point defects in Sn-based and Ge-based kesterites
- Via Ge-doping in CZTS, Ge_{Sn} has been identified has the most abundant defect
- Sn_{Zn} and Ge_{Zn} are identified as recombination centres providing energy levels within the materials band gap



- Net reduction of the lattice distortion upon Ge_{Zn} formation both for Ge-doping and alloying in comparison to its Sn counterpart

→ Possible explanation for the V_{OC} improvement reported experimentally

Journal of Materials Chemistry A

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *J. Mater. Chem. A*, 2022, **10**, 4355

Relevance of Ge incorporation to control the physical behaviour of point defects in kesterite†

Thomas Ratz, *[ab] Ngoc Duy Nguyen,[a] Guy Brammertz,[c] Bart Vermang[bcd] and Jean-Yves Raty[a]

Thank you for your attention