12th Hybrid European Kesterite+ Workshop

# Physics of Ge-related point defects in Sn-based, Ge-doped and Ge-alloyed kesterites


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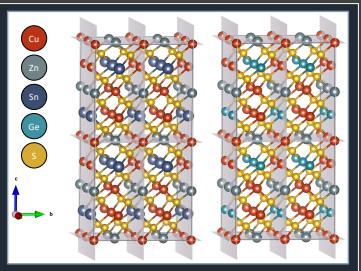
**Ratz, Thomas**, *et al.* "Relevance of Ge incorporation to control the physical behaviour of point defects in kesterite" *Journal of materials chemistry A (2022)*

## Motivations

- ❑ Strengthen our knowledge of CZTS and CZGS [1]
- ❑ Study the behaviour of point defects in Sn-based, Ge-doped and Ge-doped kesterites [2]
- ❑ Understand the physical origin of the $V_{OC}$ improvement reported upon Ge incorporation
- ❑ Link defects and kesterite material properties focusing on PV applications

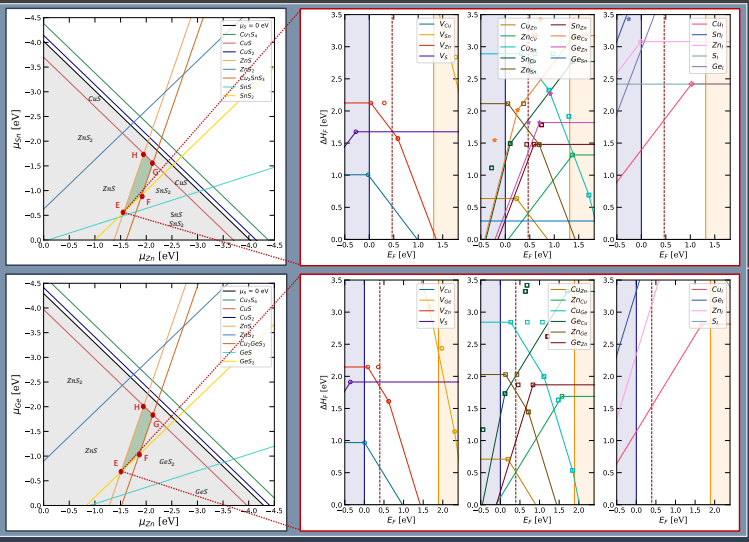



## Identification of dominant point defects

- ❑ Pure phase limitations due to the multiple secondary phases
- ❑ Most abundant defects: $Cu_{Zn}$, $Zn_{Cu}$, $V_{Cu}$ and $X_{Zn}$ (X=Sn,Ge)
- ❑ $Cu_{Zn}$, $Zn_{Cu}$ highlight the Cu/Zn disorder
- ❑ Pinning of the Fermi level led by carrier producing defects: $Cu_{Zn}$, $Zn_{Cu}$ and $V_{Cu}$
- ❑ Upon Ge incorporation:

$$\Delta H_F(X_{Zn}) \text{ (X=Sn,Ge)} \nearrow$$

$$\text{Low } \Delta H_F(Ge_{Sn})$$



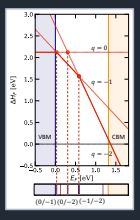

Full details available → https://doi.org/10.1039/D1TA09620F

## Theoretical approach

Thermodynamic conditions

1. $\mu_i < 0$
2. $\Delta H_F(Cu_2ZnXS_4) = 2\mu_{Cu} + \mu_{Zn} + \mu_X + 4\mu_S$
3. $\sum_i n_i\mu_i < \Delta H_F(X_i, n_i)$

Defect formation energy → $\Delta H_F(\alpha, q, E_F, \mu_i) =$




$E(\alpha, q) - E_{host}$

Total energy difference

$-\sum_i n_i(E_i + \mu_i)$

Exchange of atoms

$+q[\epsilon_{VBM} + E_F]$

Exchange of charges

## Methodology

- ✓ SCAN ionic relaxation (1E-3 eV/Å)
- ✓ One-shot HSE06 relaxation (1E-3 eV)
- ✓ 64-atoms supercell approach
- ✓ 520 eV cut-off energy, 2x2x2 **k**-points grid

## Ionisation levels of dominant point defects

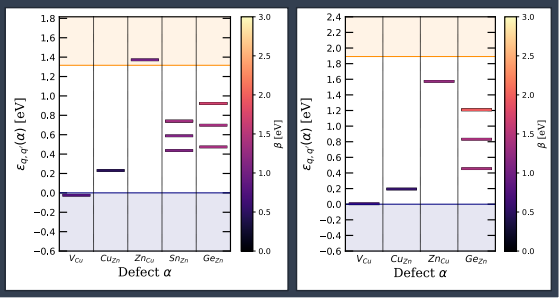
- ❑ $Cu_{Zn}^{-1}$ and $V_{Cu}^{-1}$ providing holes
- ❑ $Zn_{Cu}^{+1}$ providing electrons

} p-type electrical conductivity of CZTS and CZGS

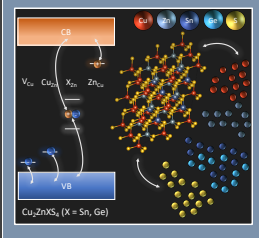
- ❑ $X_{Zn}$ provide 3 transition levels and act as a recombination centre

Transition energy levels

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




## "Bring home" message




- From [1], increase of $V_{OC}$ and decrease of $J_{SC}$ when Sn is substituted by Ge (perfect crystal)
- $\Delta H_F(X_{Zn})$ increases when Sn → Ge
- Net decrease of the $Ge_{Zn}$ lattice distortion with respect to $Sn_{Zn}$ → capture cross-section reduction
- Link to the Sn multivalence and so-called lone-pair effect [2]

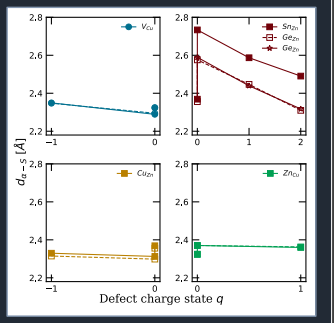
## Lattice distortion associated to dominant point defects

Defect emission rate:

$$e_n = \sigma_n \langle v \rangle N_C \exp\left(-\frac{E_t - E_C}{k_B T}\right)$$ ⇒ capture cross section $\sigma_n$ ⟺ [2] Lattice distortion upon defect incorporation

Lattice distortion

- ❑ Doping type defects lead to small lattice distortion
- ❑ Large lattice distortion reported for $X_{Zn}$ (X=Sn,Ge)
- ❑ Net reduction of the lattice distortion for $Ge_{Zn}$ with respect to $Sn_{Zn}$ defects

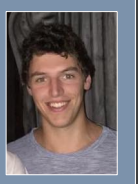



## References


[1] Ratz, Thomas, *et al.* "Opto-electronic properties and solar cell efficiency modelling of $Cu_2ZnXS_4$ (X= Sn, Ge, Si) kesterites." *Journal of Physics: Energy* (2021), **3**, 035005.

[2] Wexler, Robert B., *et al.* "Optimizing kesterite solar cells from $Cu_2ZnSnS_4$ to $Cu_2CdGe(S,Se)_4$." *Journal of Materials Chemistry A* 9.15 (2021): 9882-9897.

[3] Li, Jiqiang, *et al.* "Effective and noneffective recombination center defects in Cu2ZnSnS4: Significant difference in carrier capture cross sections." *Chemistry of Materials* 31.3 (2019): 826-833.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