Open Challenges in Pnictogen Chalcohalides for Next-Generation Photovoltaics

[1,2]**Cibrán López**
[2,3]Edgardo Saucedo
[1,2]Claudio Cazorla

[1]Departament of Physics, UPC, Barcelona
[2]Department of Electronic Engineering, UPC, Barcelona
[3]Center for Research in Multiscale Science and Engineering, UPC, Barcelona

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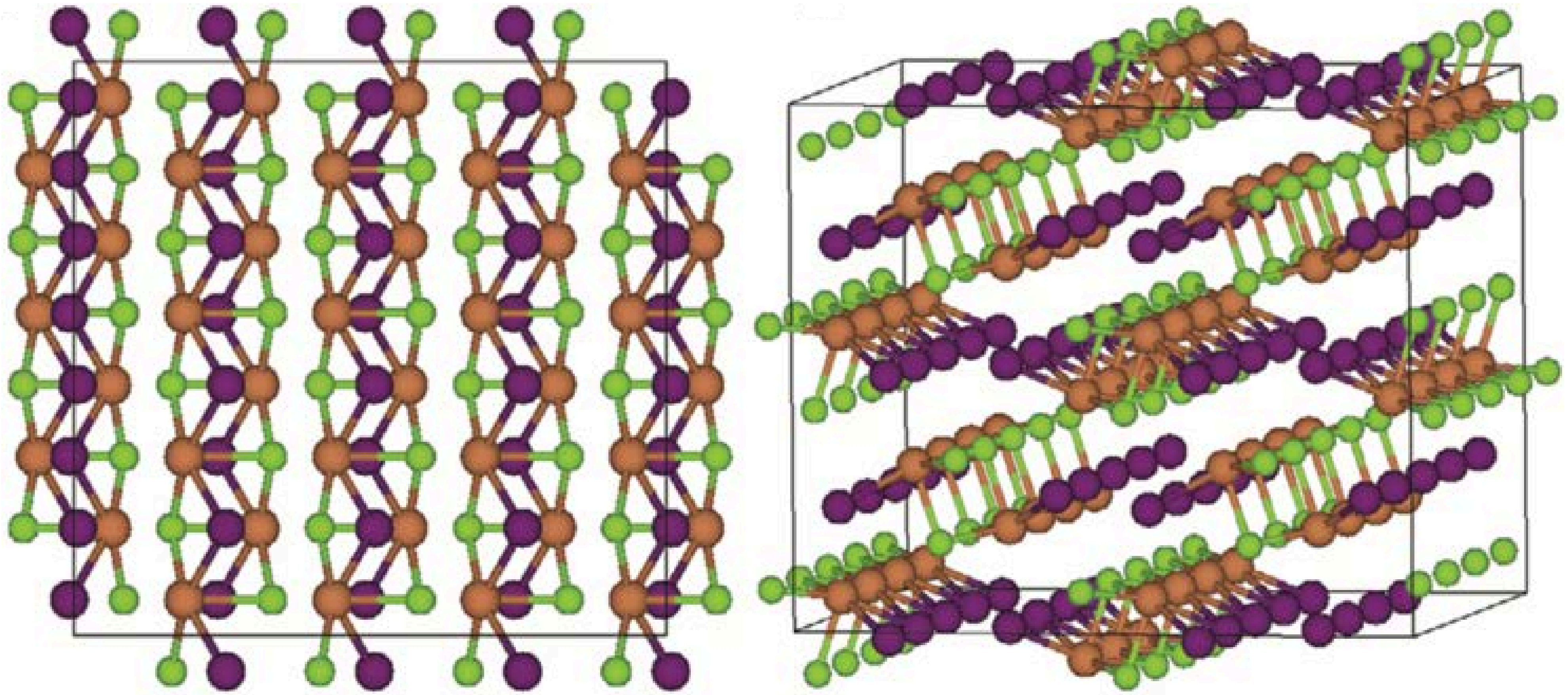
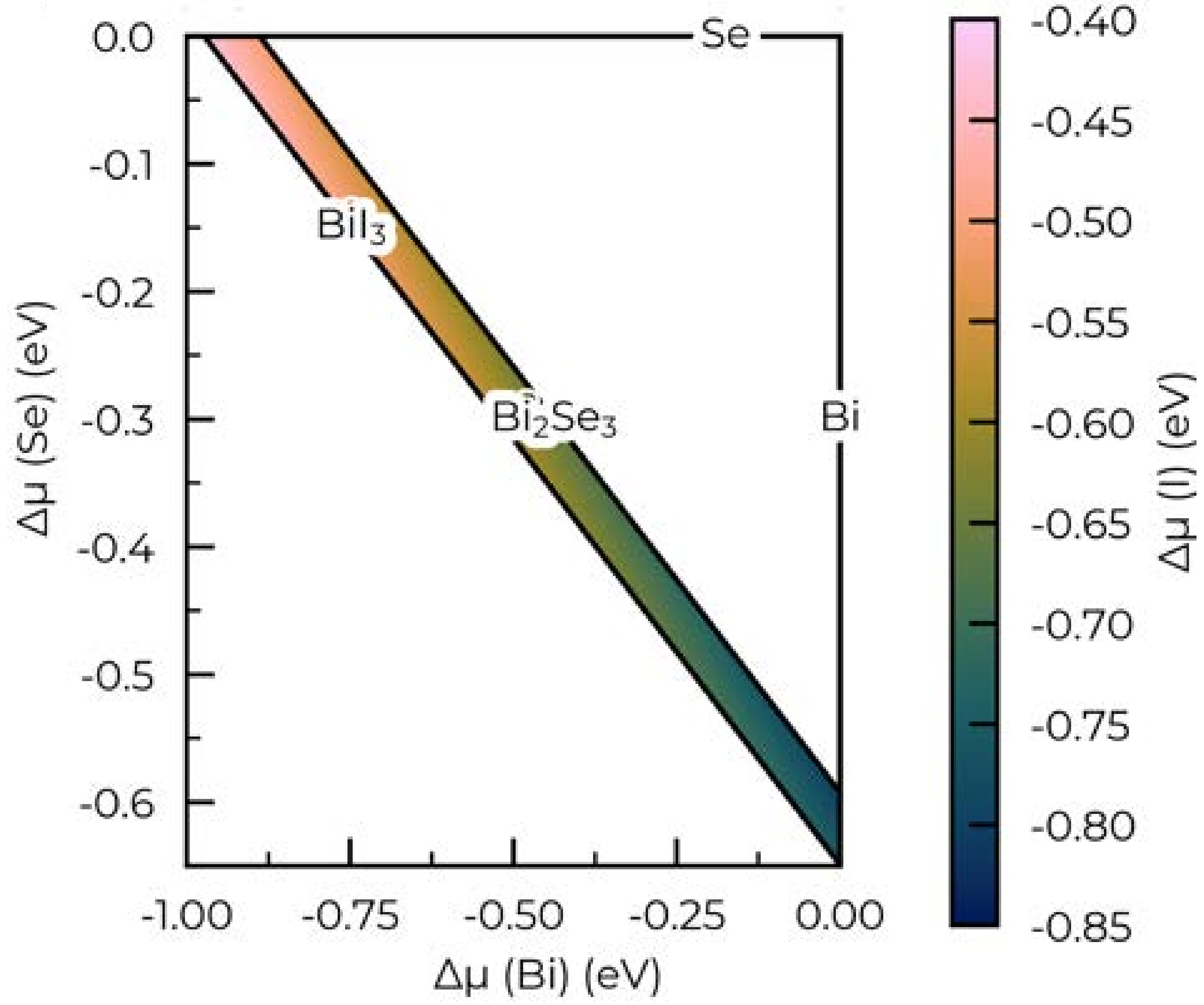
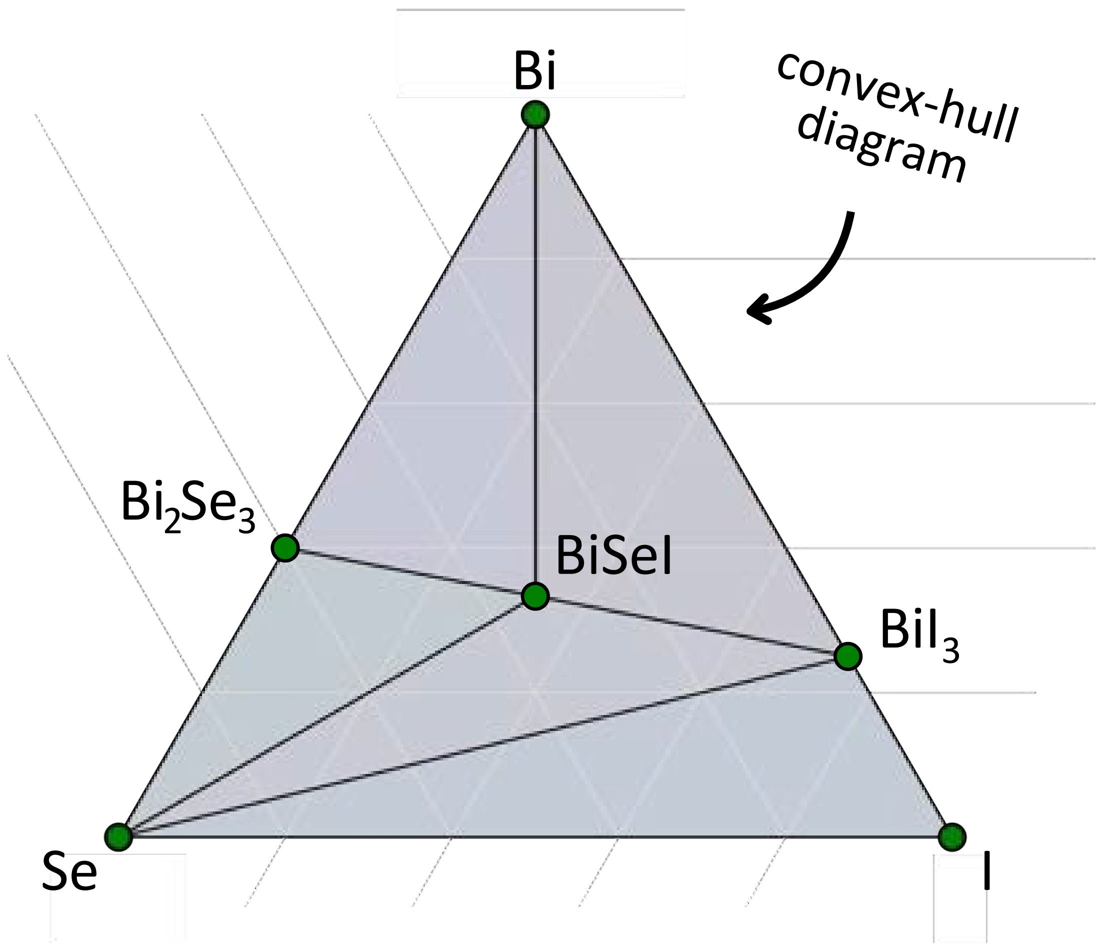
Emerging pnictogen chalcohalides

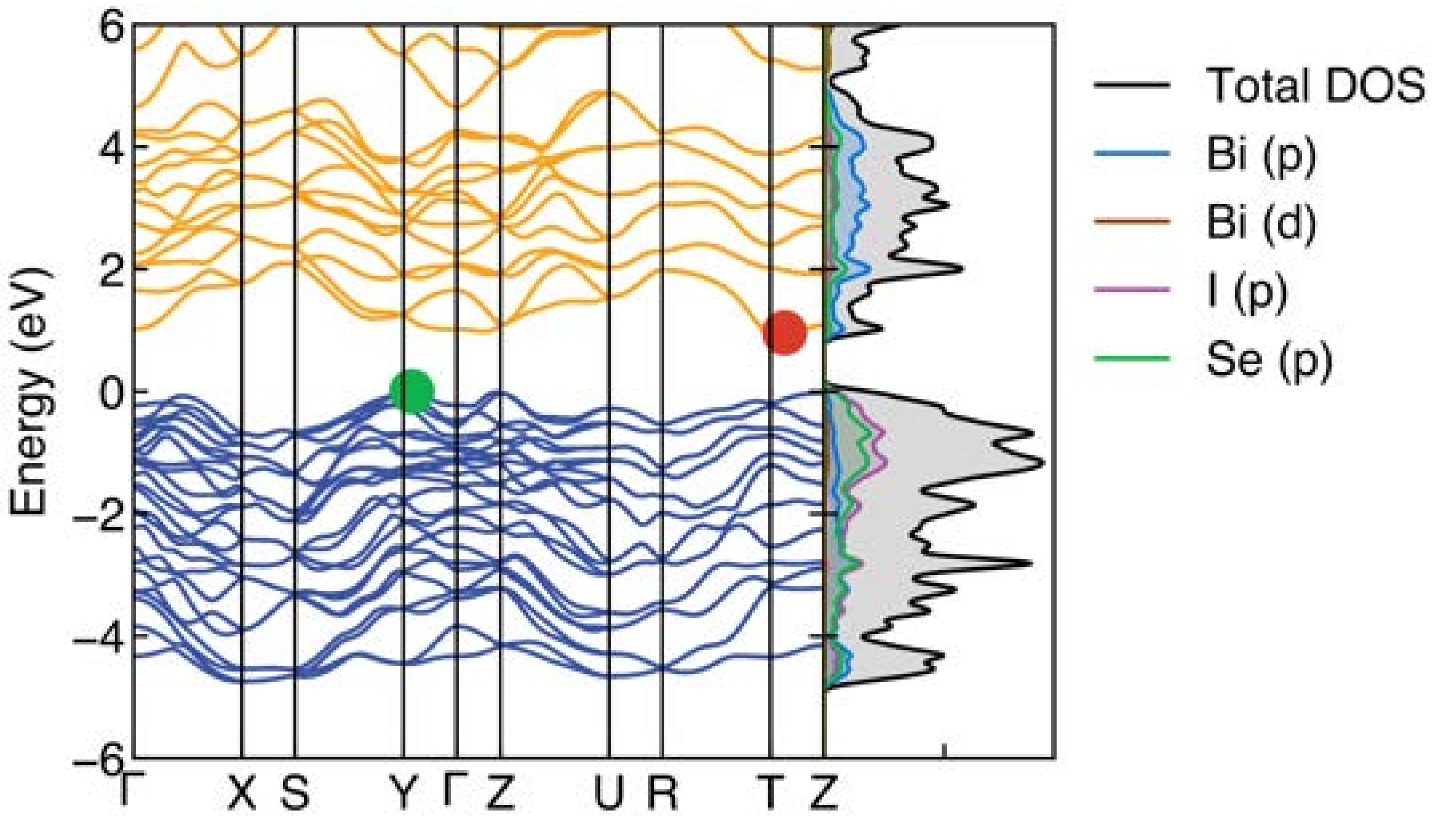
Pnictogen chalcohalides, MChX with M: {Bi, Sb}, Ch: {S, Se} and X: {I, Br}, crystallize into the orthorhombic (Pnma) space group, presenting a quasi-1D strucuture (similar to that found in binary chalcogenides).





Promising optoelectronic properties



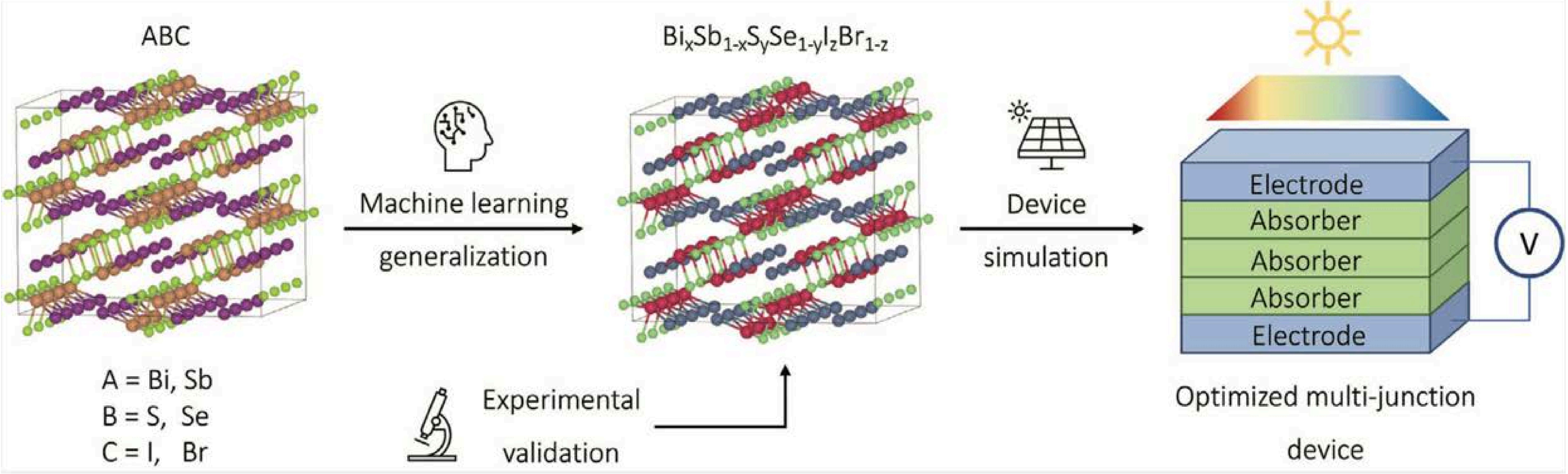


Pnictogen chalcohalides are predicted to be thermodynamically stable against segregation into secondary phases, presenting a negative formation enthalpy relative to the convex-hull surface. This is an approach we use as well for determining the stability of any solid solution.

Meanwhile, they present remarkable optoelectronic properties, including bandgaps ranging from 1.2 to 2.1 eV and elevated absorption coefficients. So far, they are good photoabsorber candidates!

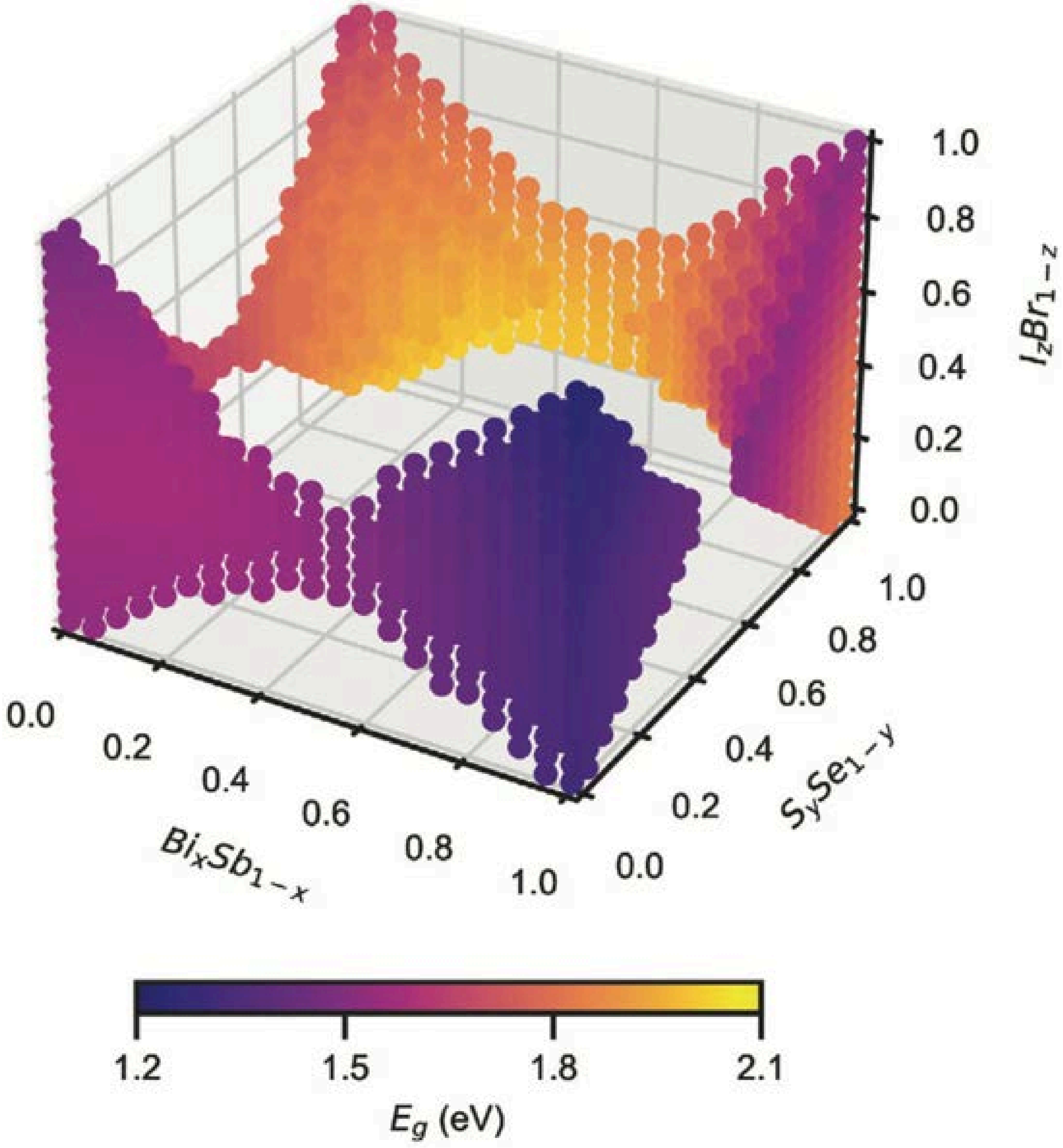
MChX: addressing solid solutions

Efficienct computational approaches, were machine learning is combined with first-principles simulations, yield to optimized devices and materials with enhanced properties. Here, we covered the set of MChX-solid solutions at almost DFT level of accuracy, resulting on an optimized device (although some key aspects can still be improved).

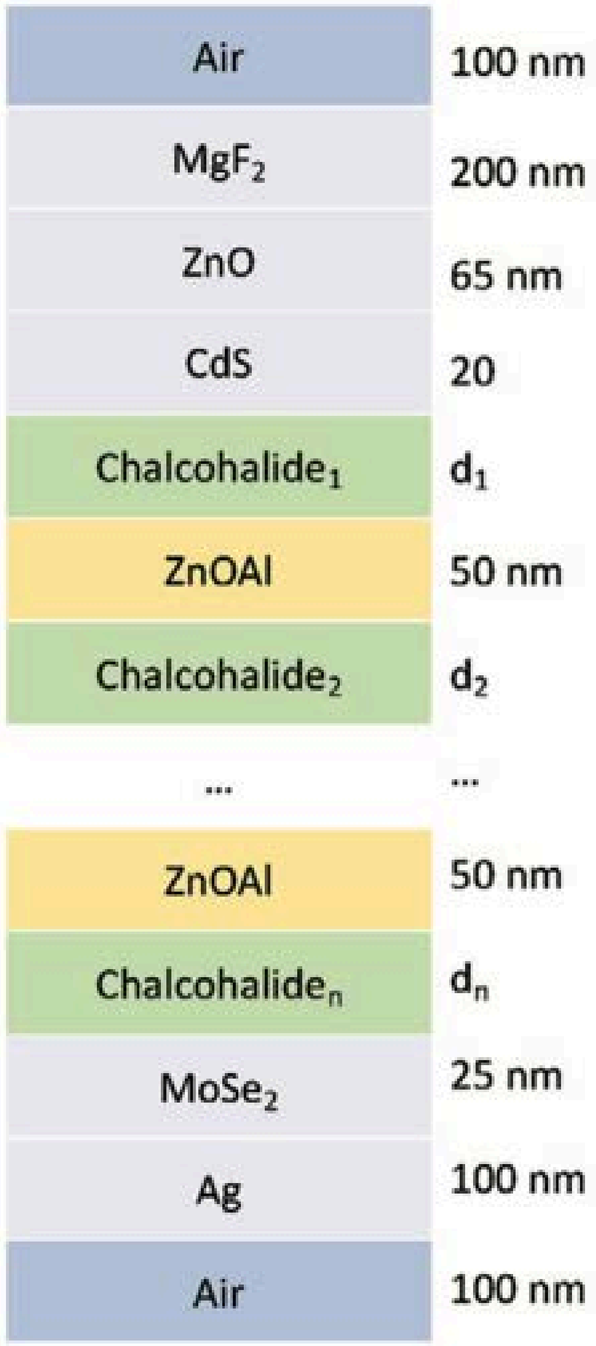


MChX: versatile properties

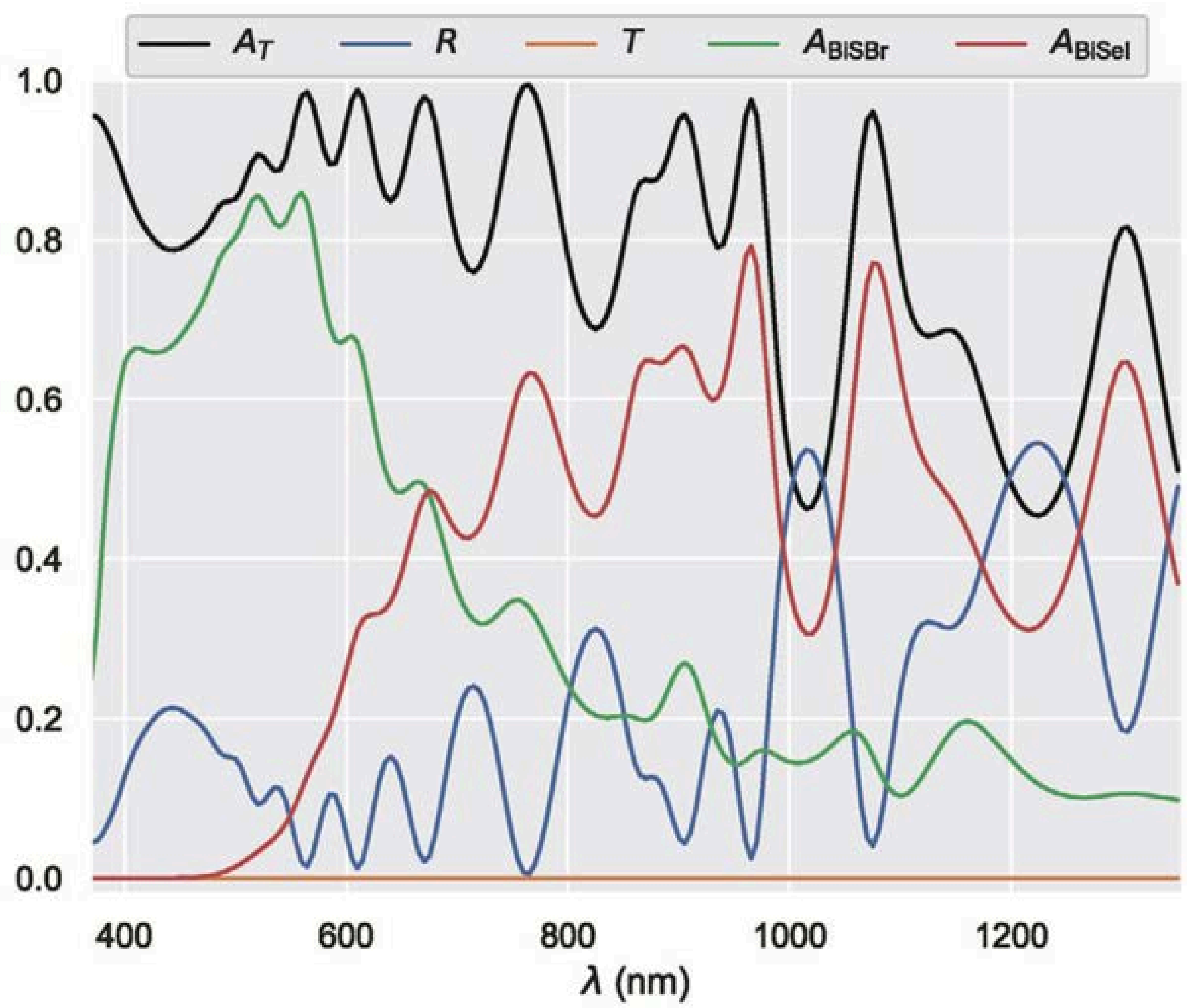
For example, machine learning approaches allow us to extrapolate first-principles results, covering an high dimensional configurational spaces (as the set of MChX-based solid solutions) at low computational cost (or even search for completely new structures with generative AI). Key challenges, however, are still faced on uncertainty estimation: how reliable our predictions are?



MChX: multi-junction devices



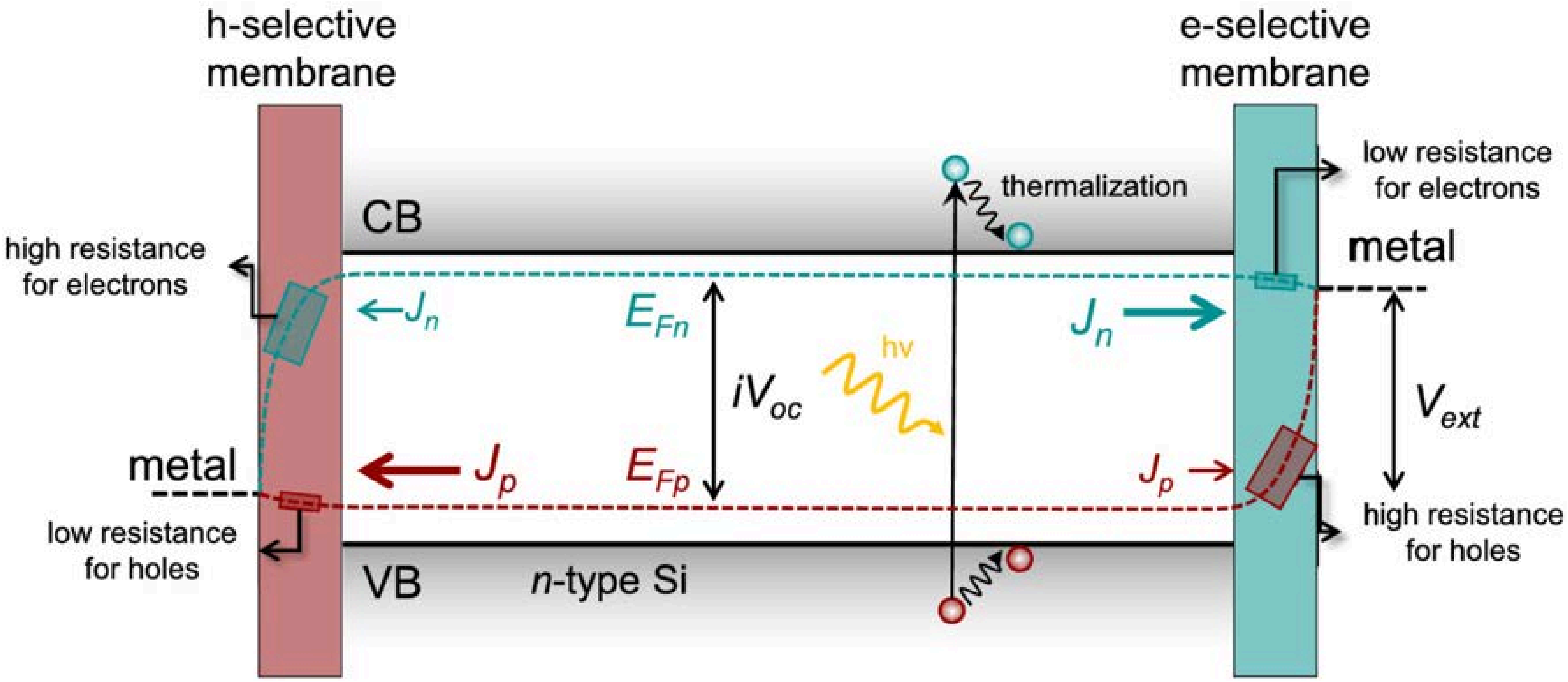
Air	100 nm
MgF_2	200 nm
ZnO	65 nm
CdS	20
$Chalcohalide_1$	d_1
ZnOAl	50 nm
$Chalcohalide_2$	d_2
...	...
ZnOAl	50 nm
$Chalcohalide_n$	d_n
$MoSe_2$	25 nm
Ag	100 nm
Air	100 nm



Multi-junction configurations help overcome typical limitations of single junctions, such as radiative losses. The configurations space is huge, thus we need optimized search strategies, along with data from many systems.

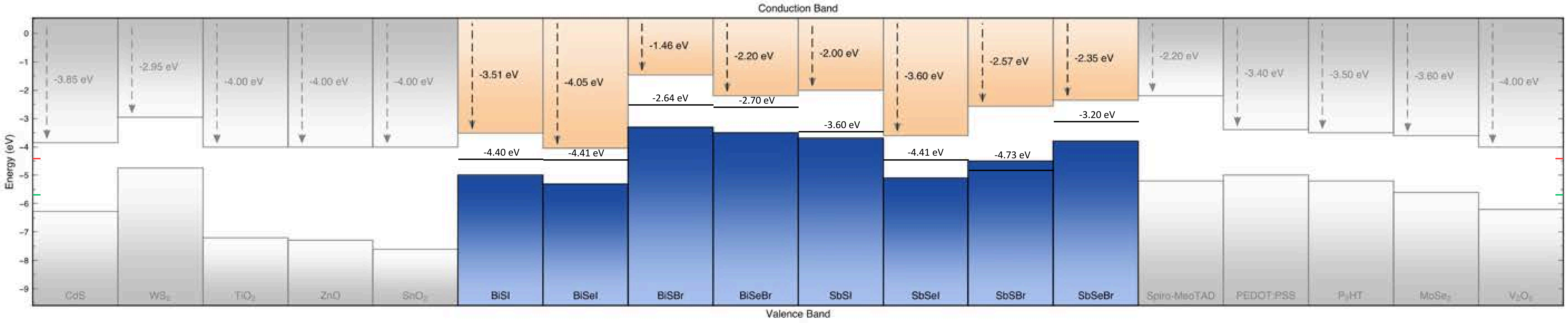
The role of selective contacts

An optimized device requires the efficient extraction of electrons and holes by the selective contacts (ETL/HTL). In order to do so, we should determine the exact positioning of the bands on the device: this is, we need a clear picture of the surface competition of each element in the device.



The pursuit of selective contacts

The positions of the selective contacts should align well with the absorbers, which could be achieved in this case with a correct disposition of the different layers. As well, this information can be found of relevance for (electro)photocatalysis, considering the oxygen (red) and hydrogen (green) reductions potentials.



How do we determine band alignments?

We find many competitive surfaces, with similar energy of formation, although presenting different band alignments. This behaviour matches experiments, but which surface are we going to get in a real device?

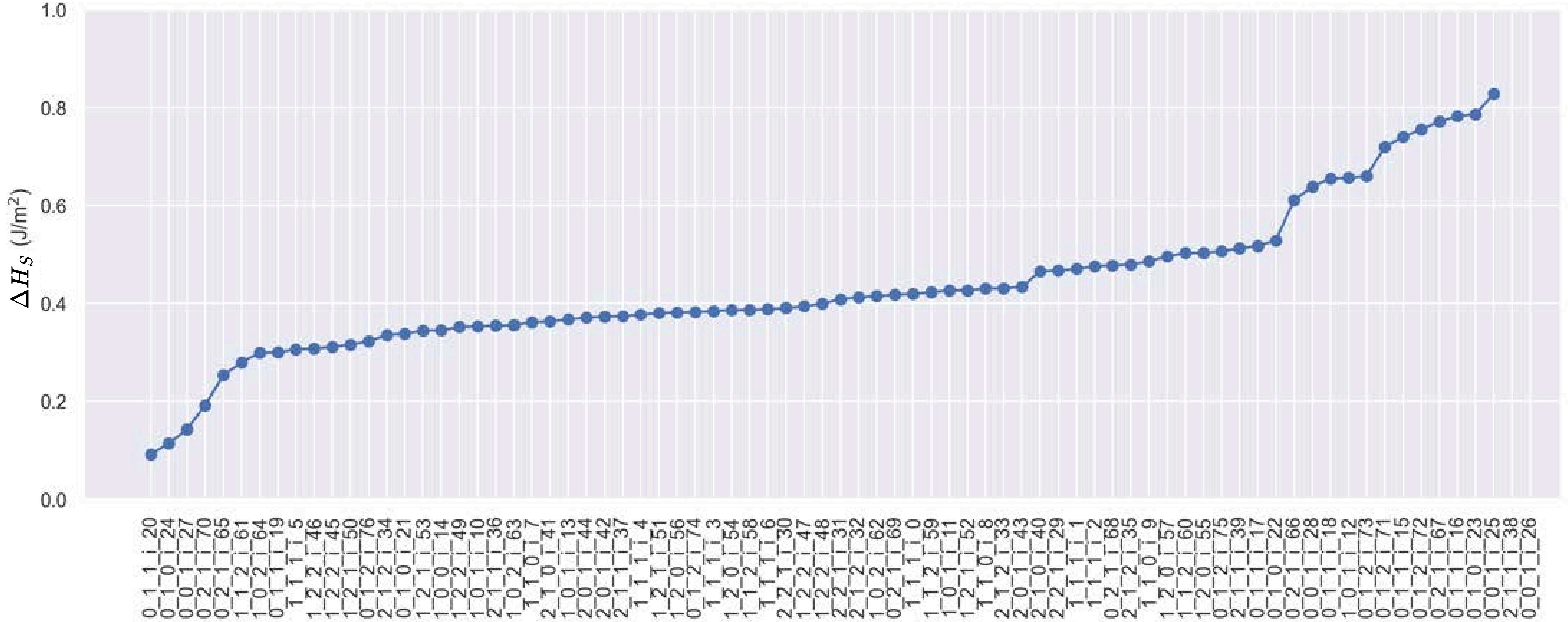
surface energy

bulk energy

$$\Delta H_S = \frac{E_S - E_b}{2S}$$

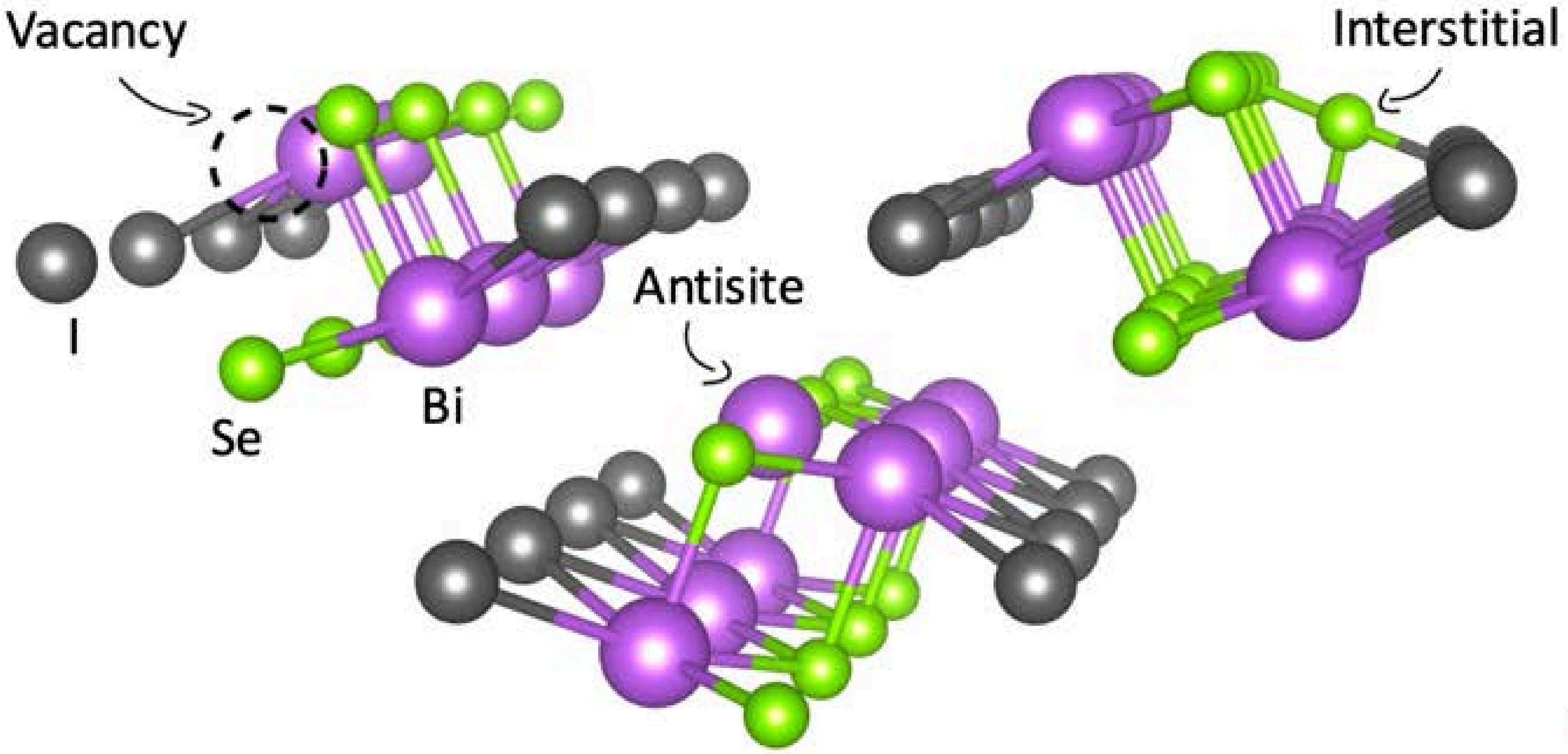
surface energy of formation

surface area



Point defects of MChX

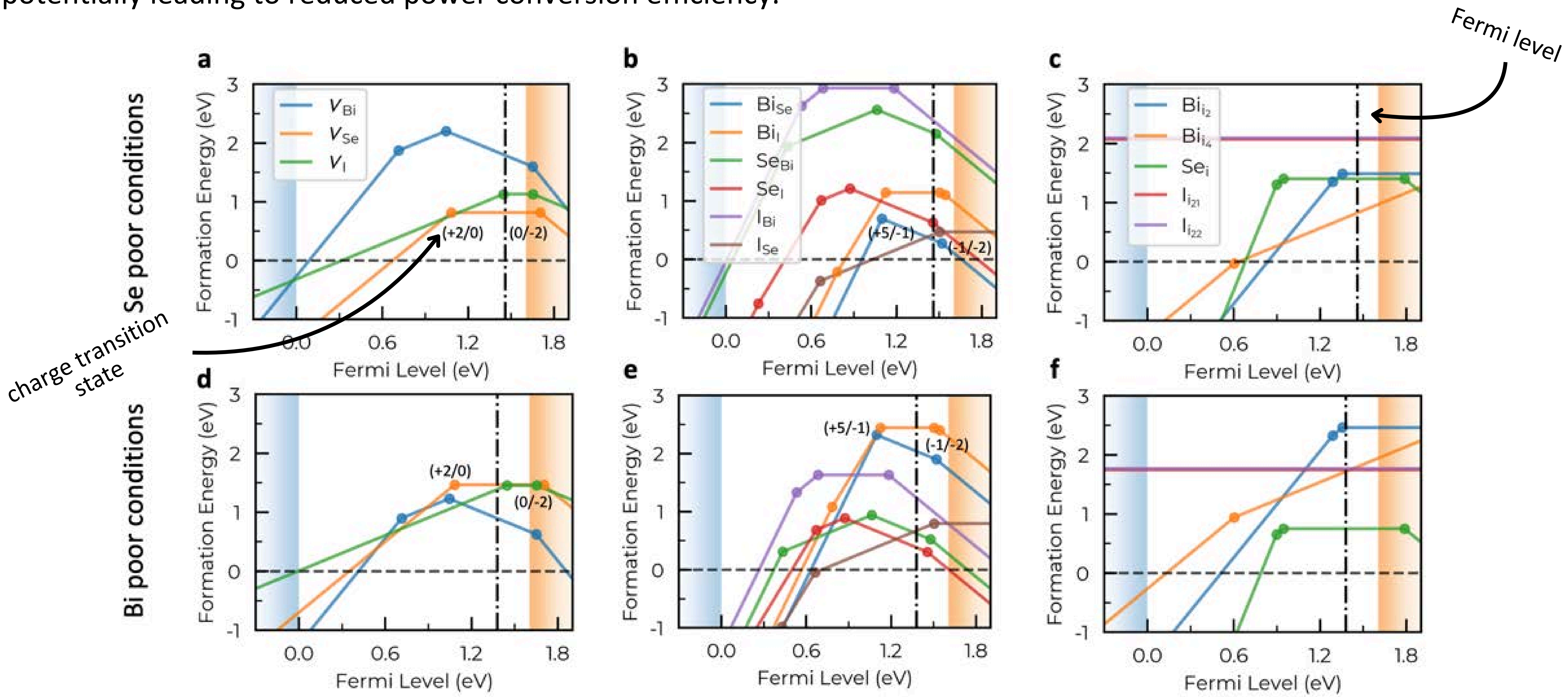
Despite their proposed defect tolerance (stemming from the antibonding nature of their valence and conduction bands), experimental power conversion efficiencies for pnitogen chalcohaldies remain below 10%, far from the Shockley-Queisser limit of 33%: might this gap be explained by the role of point defects?



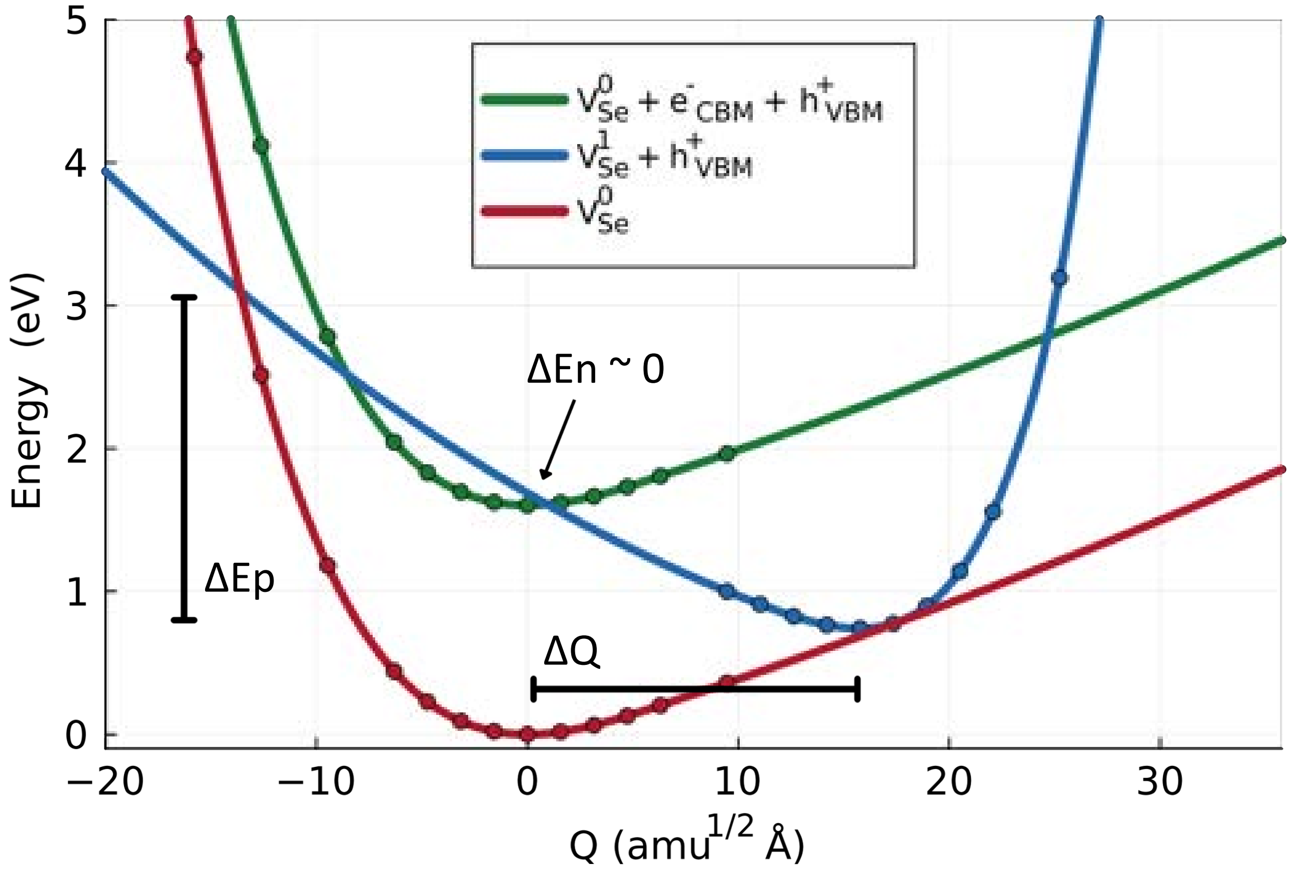
We look into all non equivalent point defect, comprosing vacancies, interstitials and antisites and different charge states, as well as to chemical-guided perturbations of those.

Do point defects limit their efficiency?

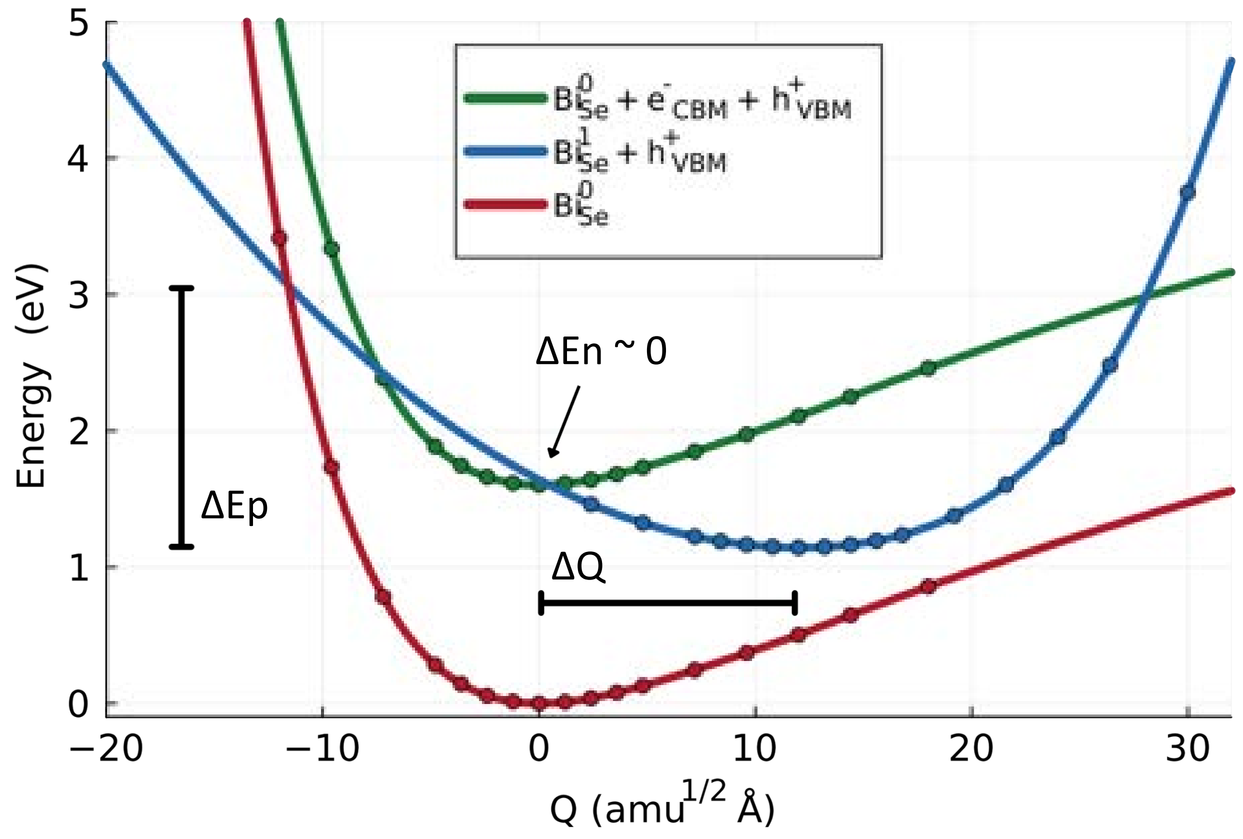
Bi_{Se} antisite and V_{Se} vacancy are identified as potential charge-carrier recombination centers, with small formation energies at the self-consistent Fermi level (this is, high defect concentrations), potentially leading to reduced power conversion efficiency.



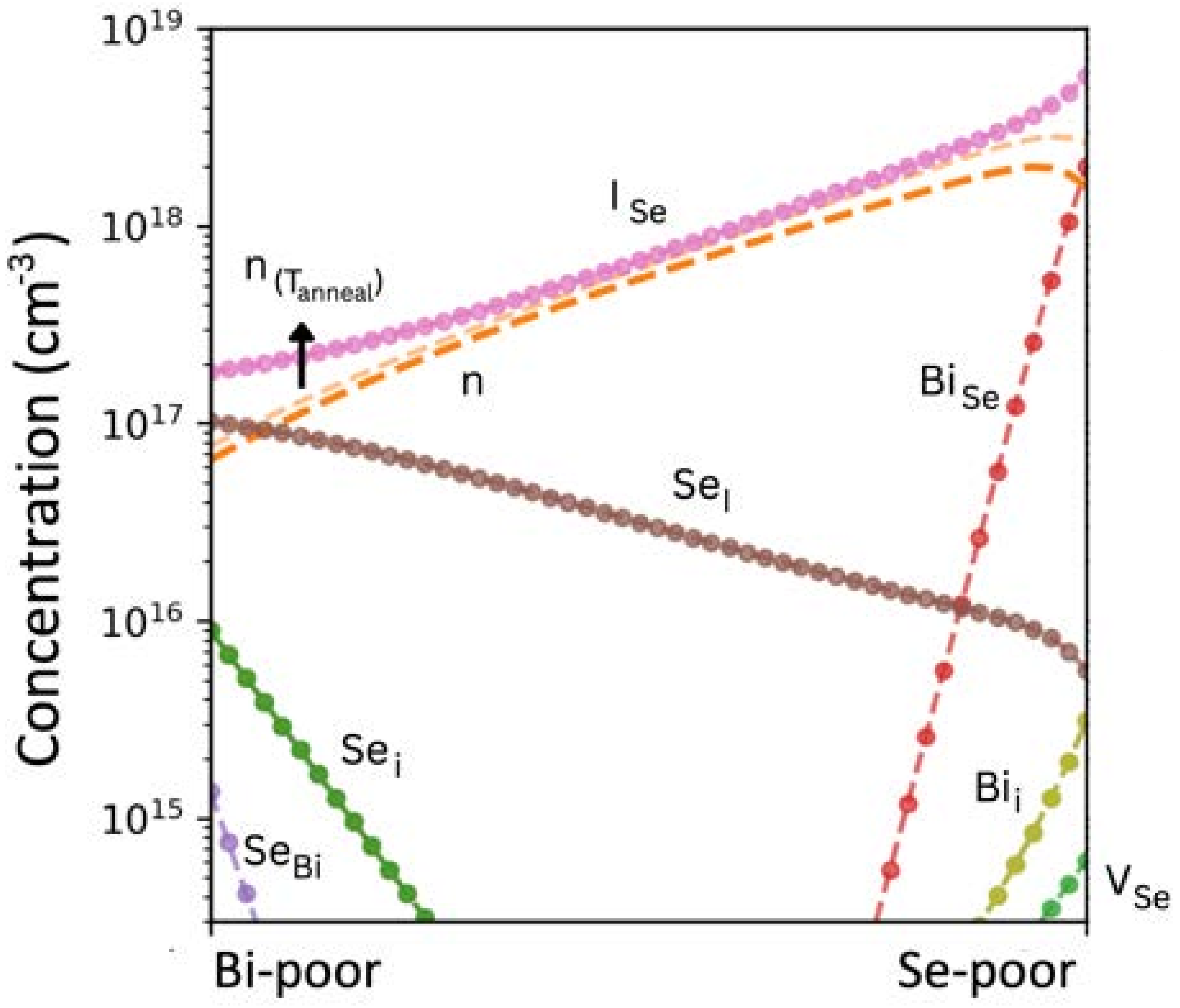
Well… yes, but how much?



Carrier capture dynamics show that, although capture coefficients are not really prominent, the elevated concentration of defects (orders of magnitude above binary chalcogenides) provoke a high, negative impact on efficiency (accounting for losses over 10%, to a maximum PCE of 24% in BiSeI).



However, different strategies to overcome such problems can be proposed, reducing defect concentration significantly (e.g., Bi-poor synthesis conditions or strategic ion substitutions).



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