Quantitative Metrics for Defect Tolerance in Semiconductors

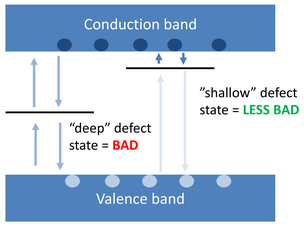
Rachel Kurchin, Prashun Gorai, Tonio Buonassisi, Vladan Stevanović

NREL NATIONAL RENEWABLE ENERGY LABORATORY

Photovoltaic Research Laboratory

What is Defect Tolerance?

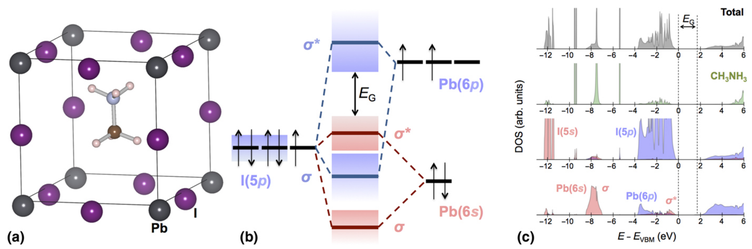
Defect tolerance[1] is the "resilience" of transport properties (**carrier mobility** and **lifetime**) to the presence of crystalline defects. It is a critical characteristic for materials amenable to low-cost manufacturing techniques, as these techniques typically introduce more defects in the nano- and microstructure.



According to **Shockley-Read-Hall statistics,** defects that introduce energy states that are "deep" in the bandgap (close to the middle) cause more recombination and hence are more detrimental to carrier lifetime than those that are "shallow" (near conduction or valence band edges).

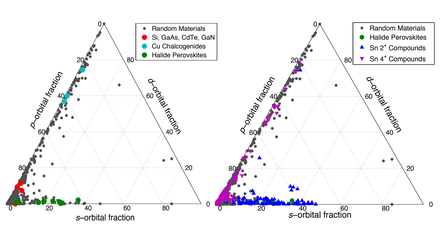
The **hybrid halide perovskites** are a recent example of an extraordinarily defect-tolerant class of materials. We aim to learn from them to design similarly defect-tolerant materials that may be more stable and nontoxic.

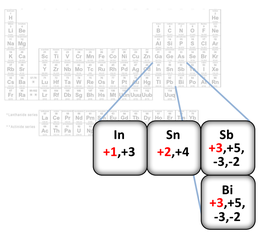
Prior Understanding



Inspired by the perovskites' **electronic structure**, we previously developed[2] screening criteria for defect tolerance focused on proxies that are **computationally accessible** from density functional theory calculations:

Criterion	Outcome	Computational Accessibility
Large dielectric constant	Screen charged defects	Directly calculate
Small effective mass	Large mobility	Good approximation from DOS
Antibonding VBM	Shallow defects	*s*-fraction, presence of partially oxidized cation

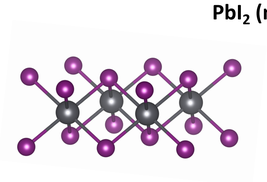


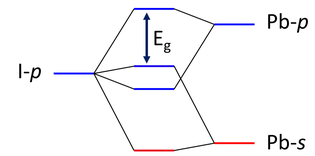


Improved Understanding

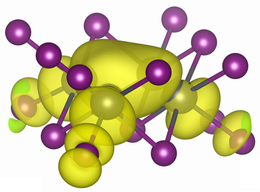
An intrinsic defect (such as a vacancy) introduces **new interactions** between orbitals on neighboring atoms that would otherwise have been bonded to the atom in the vacant site.

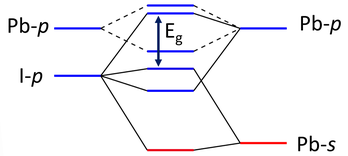
PbI_2 (no vacancy)





PbI_2 with V_I



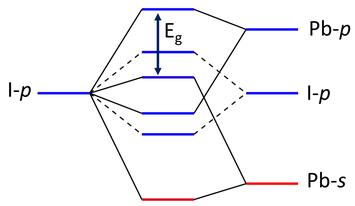


To design a defect-tolerant material, we must **minimize the strength of this new interaction.** We can do this *chemically* and/or *structurally*.

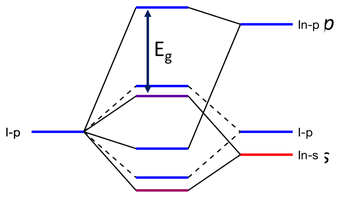
Chemical Criteria

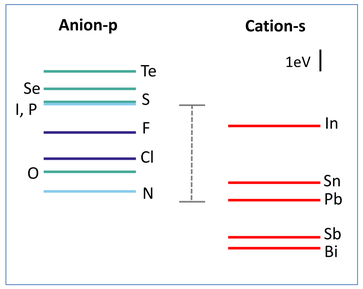
One way to minimize the impact of a new interaction introduced by a defect is to make the host electronic structure robust to this interaction by choosing anion-cation pairs that will have strong (dispersive) interactions forming the VBM so that the majority of the dispersion of the new interaction overlaps with states in the host structure.

PbI_2 (less defect-tolerant)



InI (more defect-tolerant)



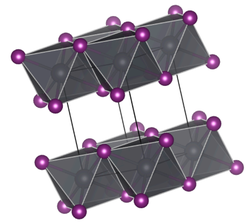


The plot above gives estimated positions of orbital energy levels for selected atoms to enable assessment of favorable cation-anion pairs. Pb-I distance (4.4 eV) shown for reference (grey dotted line).

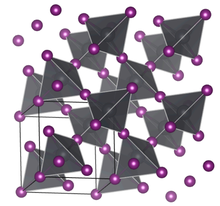
Structural Criteria

Another option is for a compound to have a **crystal structure** that geometrically inhibits the strength of possible defect-induced interactions. In a binary compound, this can be accomplished through **corner-sharing** coordination polyhedra.

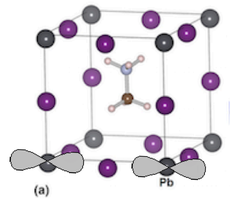
Ground-state PbI_2 structure (edge-sharing, deep defects)



"fake cubic" PbI_2 structure (corner-sharing, shallow defects)



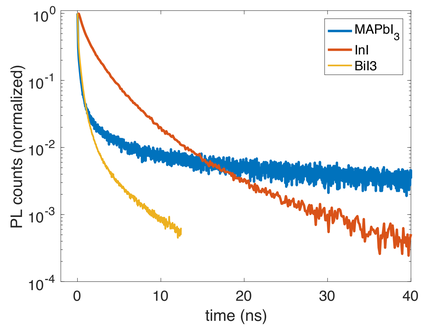
MAPI (corner-sharing, shallow)



This can be assessed (for the case of an anion vacancy in a binary compound) from the following simple ratio:

$$\frac{\text{nearest cation-cation distance}}{\text{nearest cation-anion distance}} \approx 2$$

Preliminary Experimental Validation



We can measure **carrier lifetime** through **time-resolved photoluminescence.** Results for three compounds are shown here, and their adherence to the defect tolerance criteria outlined in the table below. It is clear there is some **compensation** or "tradeoff" between the relative influence of the criteria; the nature and extent of this is the subject of ongoing/future work.

	$MaPbI_3$	InI	BiI_3
Chemical: E_p-E_s	4.4 eV	1.0 eV	6.6 eV
Structural: d_{cc}/d_{ca}	2	1.5	1.4
PL decay	Very long (10-100 ns)	Long (1-10 ns)	Short (<1 ns)

Acknowledgements

The authors acknowledge funding from the Center for Next-Generation Materials by Design, an Energy Frontier Research Center Center funded by the US Department of Energy, as well as SENER (the Mexican Secretariat of Energy) and the Massachusetts Clean Energy Center. They also thank Jeremy Poindexter, Dr. Robert Hoye, and Dr. Lea Nienhaus for TCSPC measurements.

References

1. Zakutayev, A., *et al.* (2014). Defect tolerant semiconductors for solar energy conversion. *Journal of Physical Chemistry Letters*, *5*(7), 1117–1125.
2. Brandt, R. E., Stevanović, V., Ginley, D. S., & Buonassisi, T. (2015). Identifying defect-tolerant semiconductors with high minority-carrier lifetimes: beyond hybrid lead halide perovskites. *MRS Communications*, *5*(2), 265–275.

SENER SECRETARÍA DE ENERGÍA · MASSACHUSETTS CLEAN ENERGY CENTER · CNGMD Incorporating Metastability