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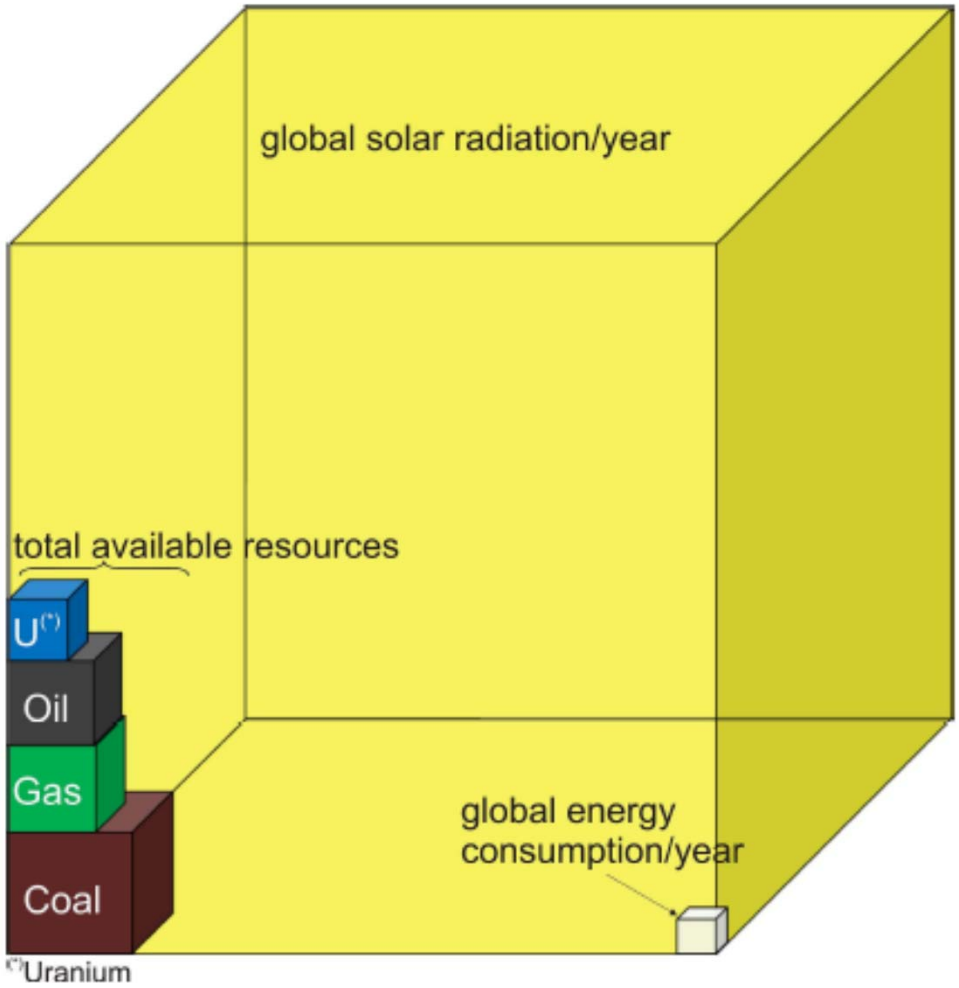
Photovoltaics: Perspective for new materials

Susan Schorr

DPG Frühjahrstagung 2019 / AK Energie
Rostock



"We live in a world bathed in 5,000 times more energy than we consume as a species in the year, in the form of solar energy."

Peter Diamandis,
engineer, physician, entrepreneur, founder and chairman of X Prize Foundation

K. Mertens, Photovoltaik - Lehrbuch zu Grundlagen, Technologie und Praxis, Hanser Verlag, 2013.

Nettostromerzeugung in Deutschland

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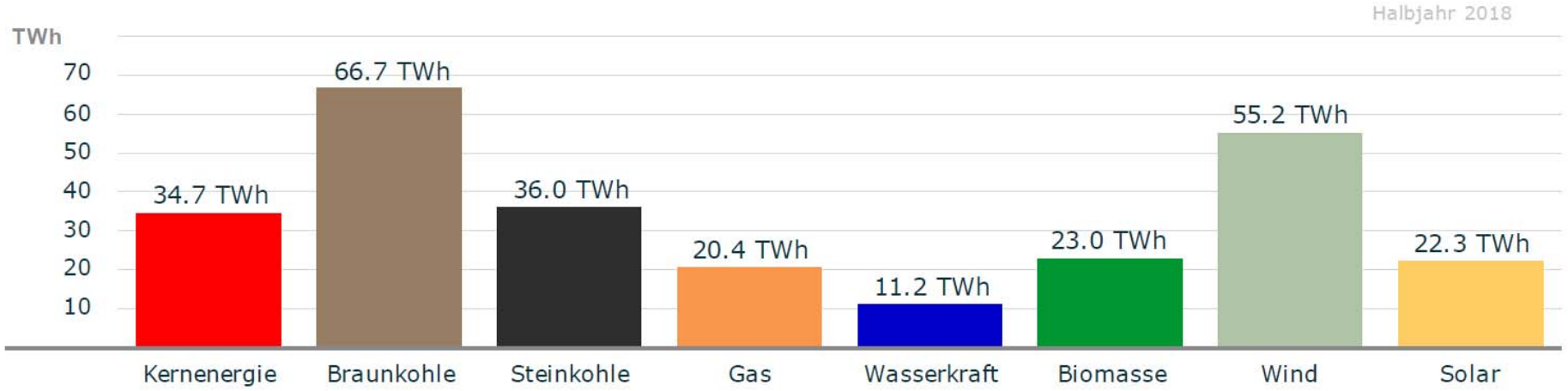
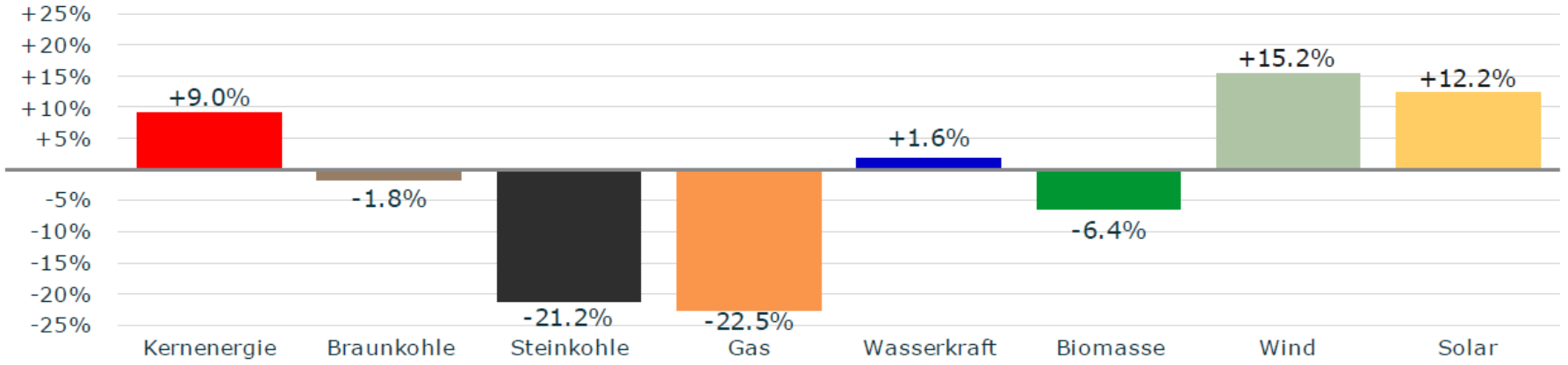
Nettostromerzeugung zur öffentlichen Stromversorgung (1. Halbjahr 2018)



Relative Änderung der Nettostromerzeugung: 1. Halbjahr 2018 vs. 1. Halbjahr 2017



Quelle: www.energy-charts.de

Anteil PV an Bruttostromerzeugung in Dtl.

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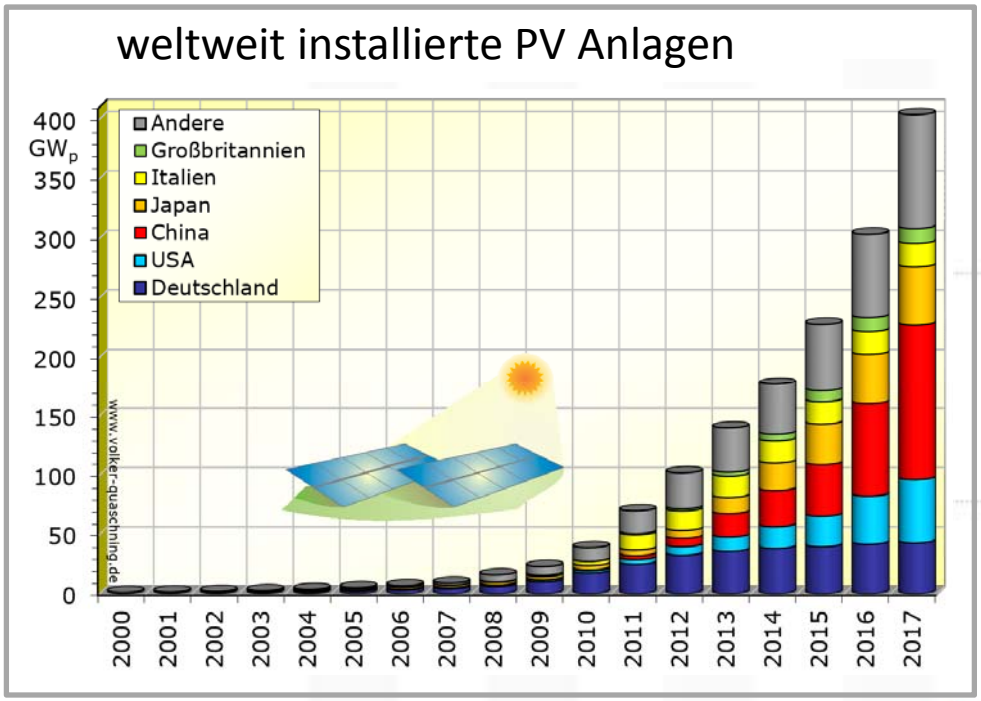
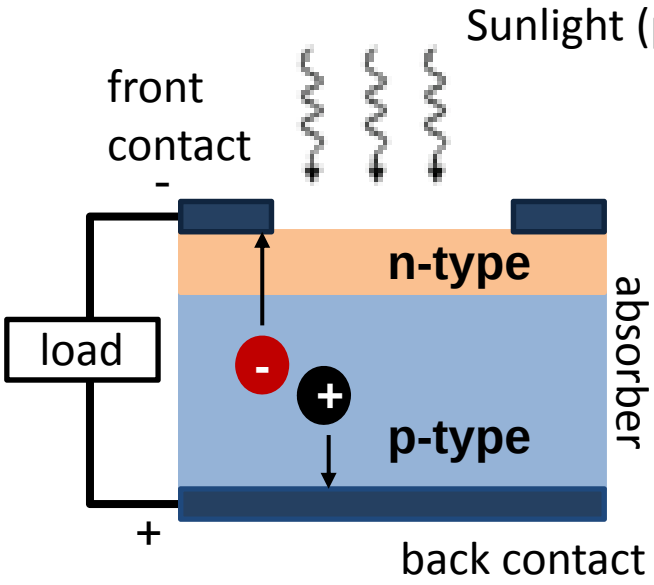
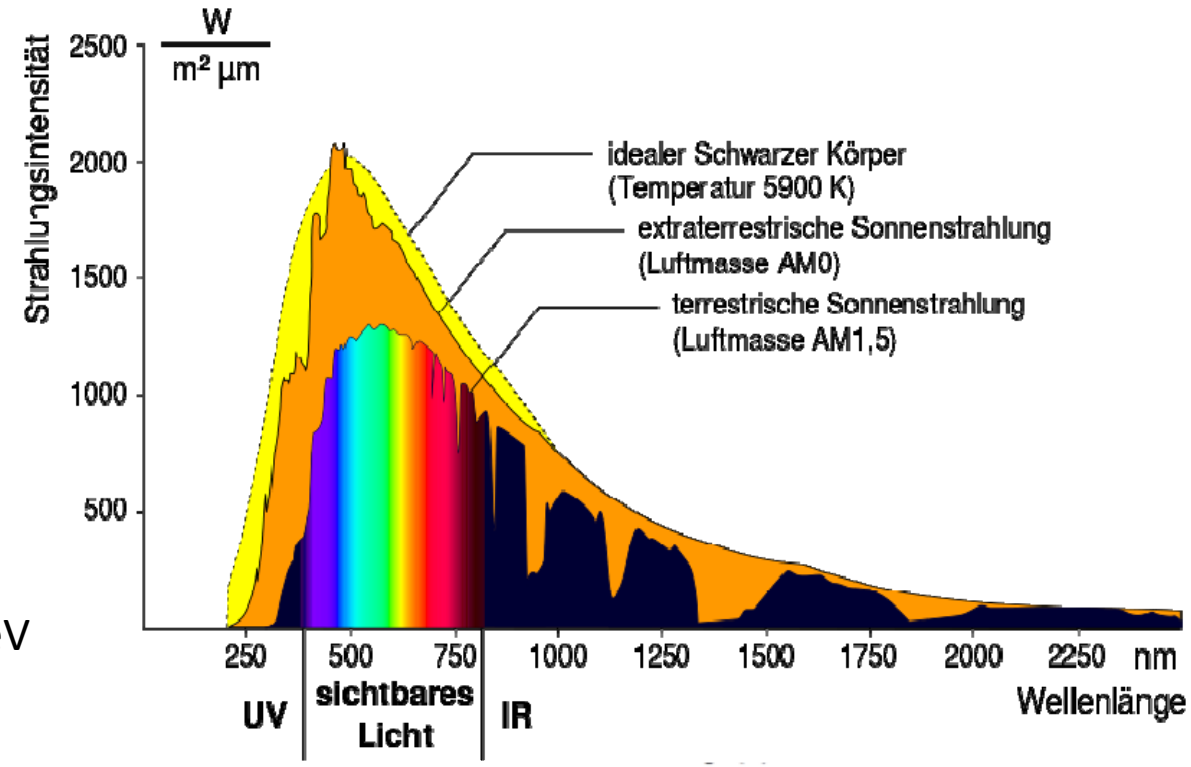
Quellen: BDEW, AGEB, statistisches Bundesamt, PV-Welt



Photovoltaics (PV) is recognized as one of the main **renewable energy technologies** for the achievement of targets defined by the EU Energy Roadmap 2050.

Charge generation & separation in solar cells





Absorber:
semiconductor with
→ optimum E_g between 1 – 1.5 eV
→ high absorption coefficient

Basic functions of a solar cell:
(1) Light absorption: generation of free excess charge carriers → photocurrent, I
(2) Charge separation: separate/extraction of excess electrons and holes → photovoltage, V

main parameters: J_{SC} – short circuit current, V_{OC} – open curcuit voltage, FF – fill factor

PV technologies nowadays

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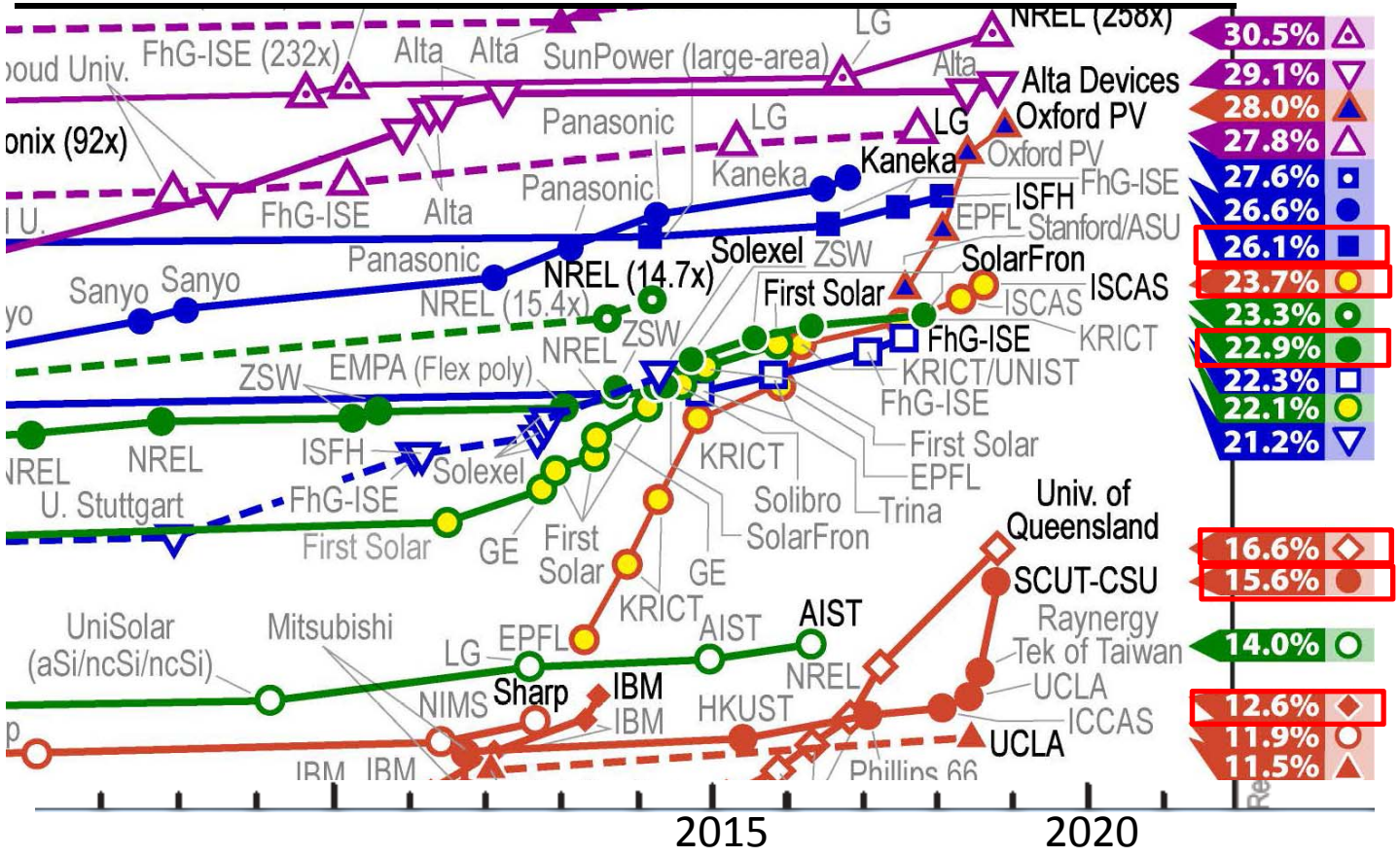
Best Research-Cell Efficiencies

NREL NATIONAL RENEWABLE ENERGY LABORATORY



generation

1st **2st** **emerging**

c-Si

hybrid perovskites

CIGS

quantum dot solar cells

organic PV

CZTSSe

Hanwha Q cells

c-Si
- high efficiency (26.1%)
- indirect semiconductor
- doping nescessary

Manz

CIGS
- high efficiency (22.9%)
- direct & intrinsic semic.
- contains scarce elements

Oxford Solar

hybrid perovskites
- high efficiency (23.7%)
- no long term stability
- contain Pb

CrystalSol

CZTSSe
- contain abundant elements
- lower efficiency (12.6%)

Absorber materials: from mature technologies to newcomers

CHALCOPYRITE TYPE SEMICONDUCTORS

thin film solar cells with the **highest efficiencies** (also flexible solar cells)

$Cu(In,Ga)Se_2$ … CIGS

critical issues:
further increase of power conversion efficiency to be competitive with c-Si

KESTERITE TYPE SEMICONDUCTORS

basis for a **critical raw material** (CRW) free PV technology

$Cu_2ZnSn(S,Se)_4$ … CZTSSe

demonstrated potential and ability as future emerging PV technology

critical issue: power conversion efficiency level

HYBRIDE PEROVSKITES

promising absorber material for **low cost** devices

$CH_3NH_3PbI_3$ … MAPI

critical issues:
lead toxicity
material and device stability

highest power conversion efficiency is reached with **off-stoichiomeric** material → intrinsic point defects (vacancies, anti-sites, interstitials) & structural disorder

Efficiency limit for single junction device

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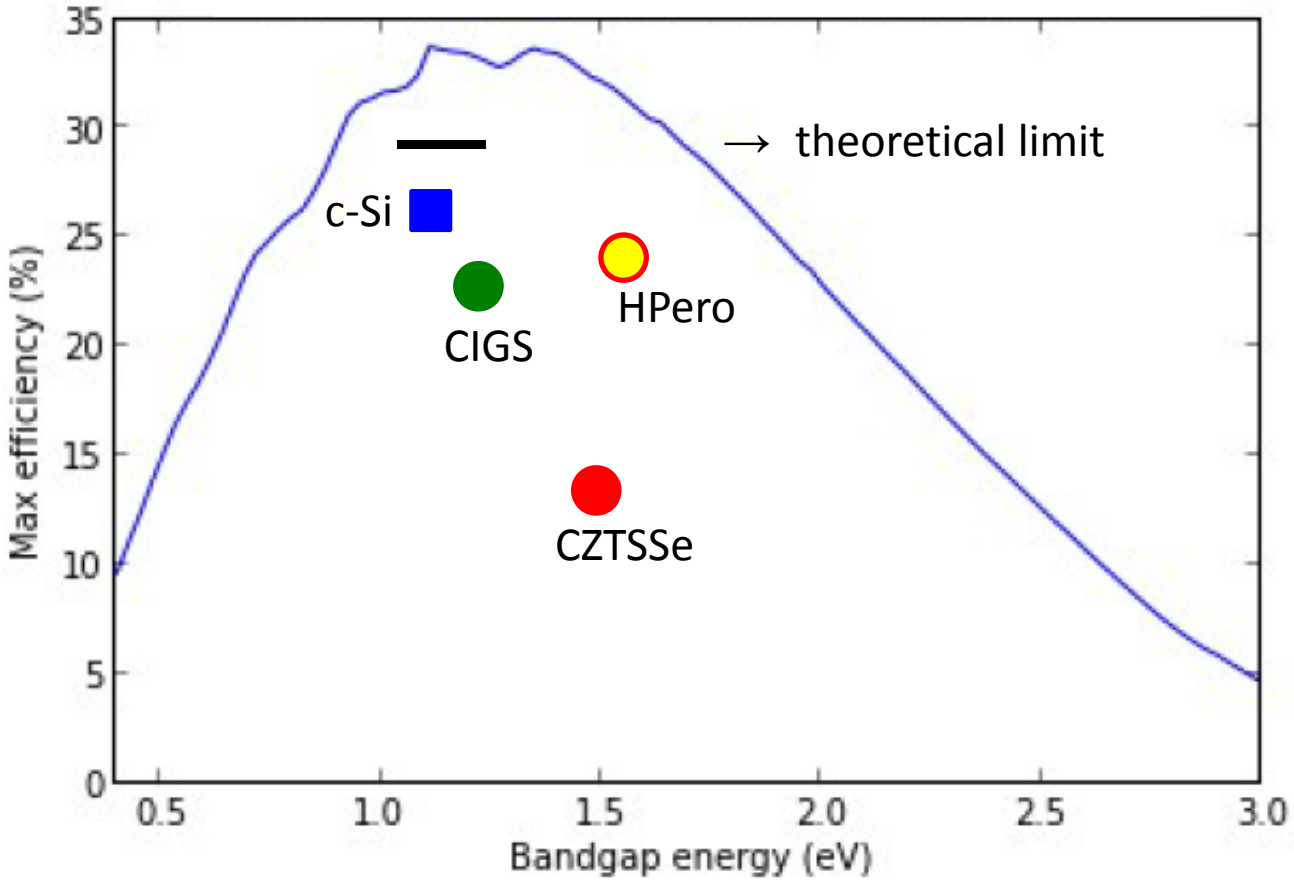
Shockley-Queisser limit for a <u>single p-n junction</u> as function of band gap energy

practical limit → nearly approached for c-Si (~ 29%)



Can the efficiency of a solar cell be improved above the SQ limit?

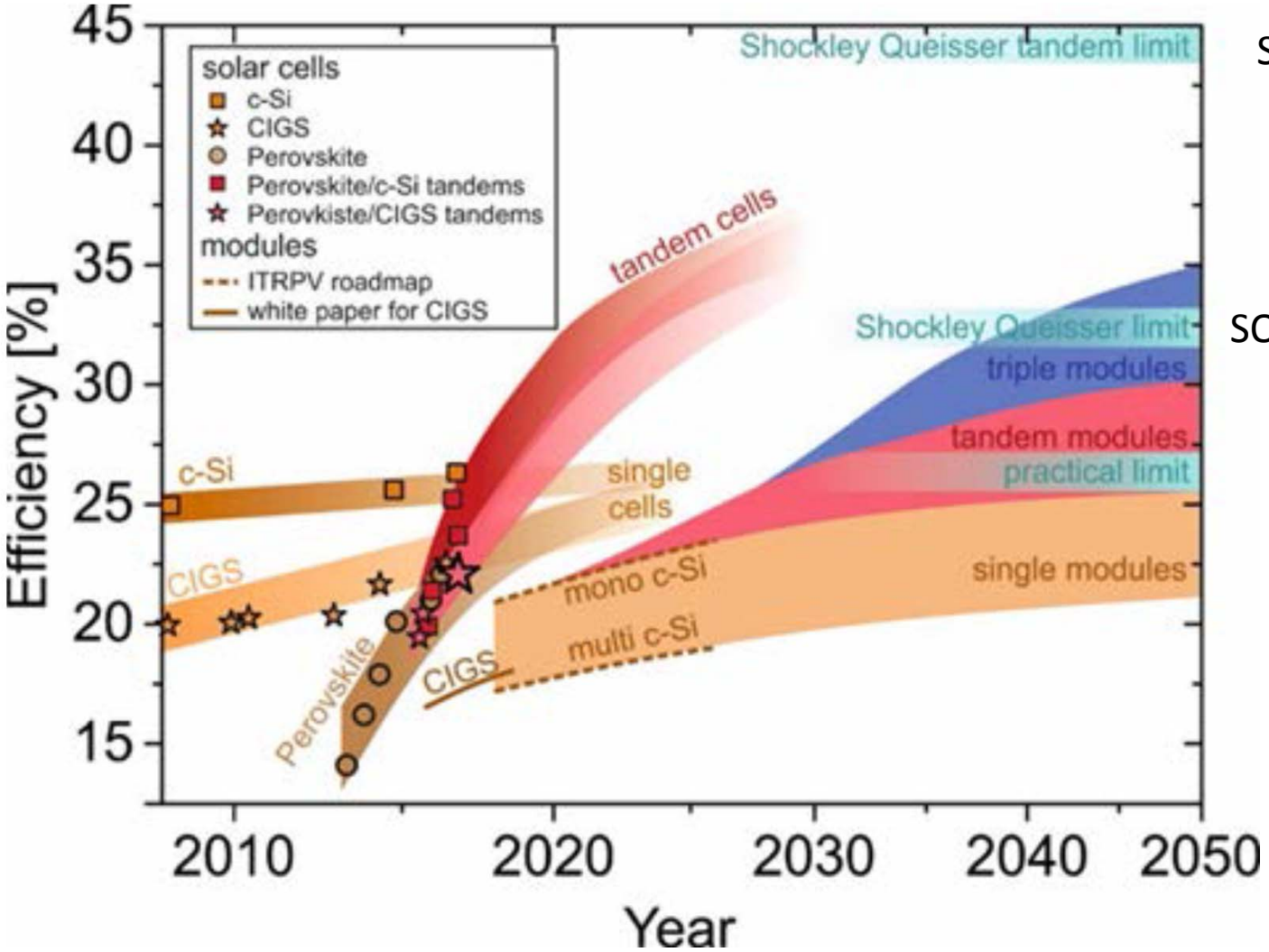
more than one sun
→ concentrator concept

more than one junction
→ multi-junction concept

Shockley & Queisser, *Journal of Applied Physics* 32 (1961) 510

Tandem sola cells: increasing efficiency

multi-junction PV (tandem/triple) can provide efficiencies surpassing todays limits

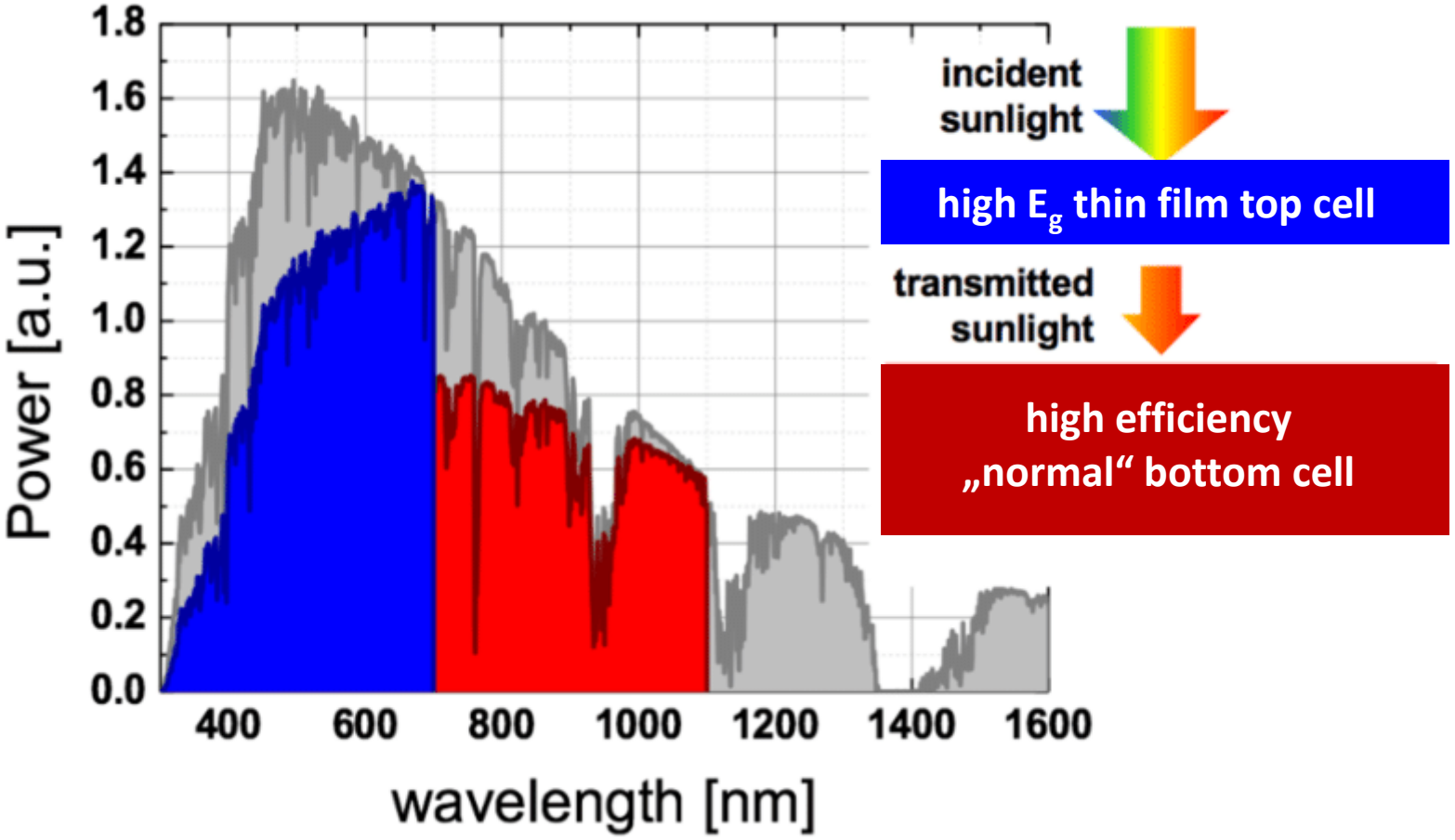


SQ limit: tandem

SQ limit: single junction solar cell

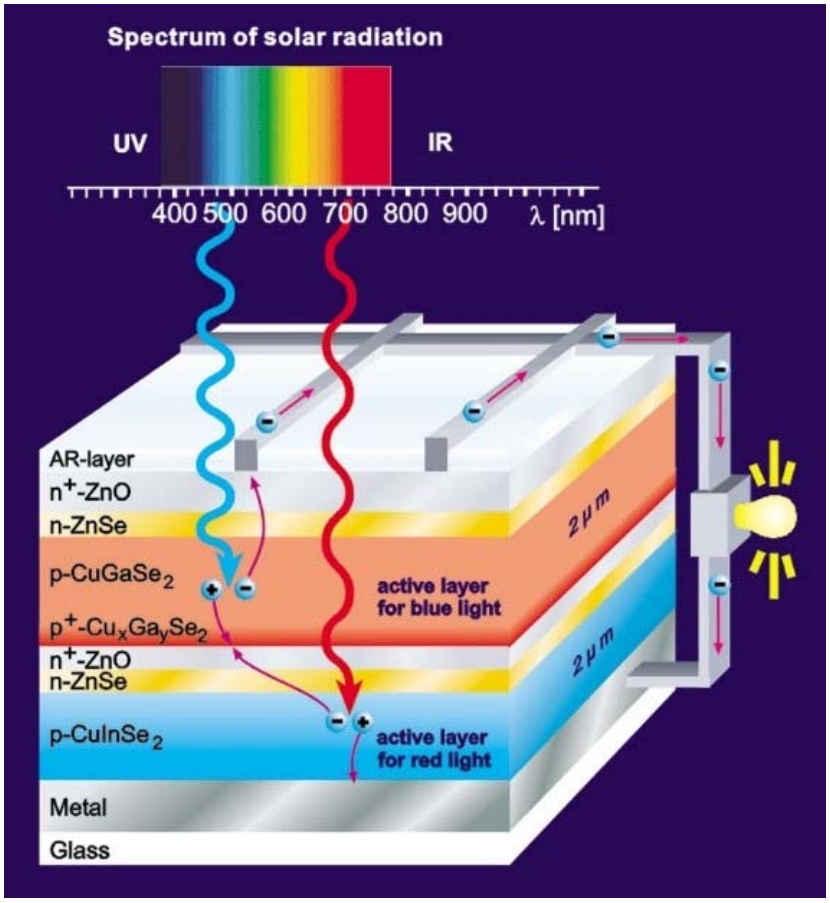
HZB: HySPRINT innovation lab

… more than one junction: tandem solar cells



→ high-E_g material for top cell absorber layer

What means „high“ band gap?



top cell absorber

→ active layer for blue light → E_g ~ 1.7 eV
→ tunable band gap energy

→ high absorption coefficient

→ no critical elements (scarce, toxic,…)

→ material with long term stability

New materials are needed!

Concept of accelerated materials search

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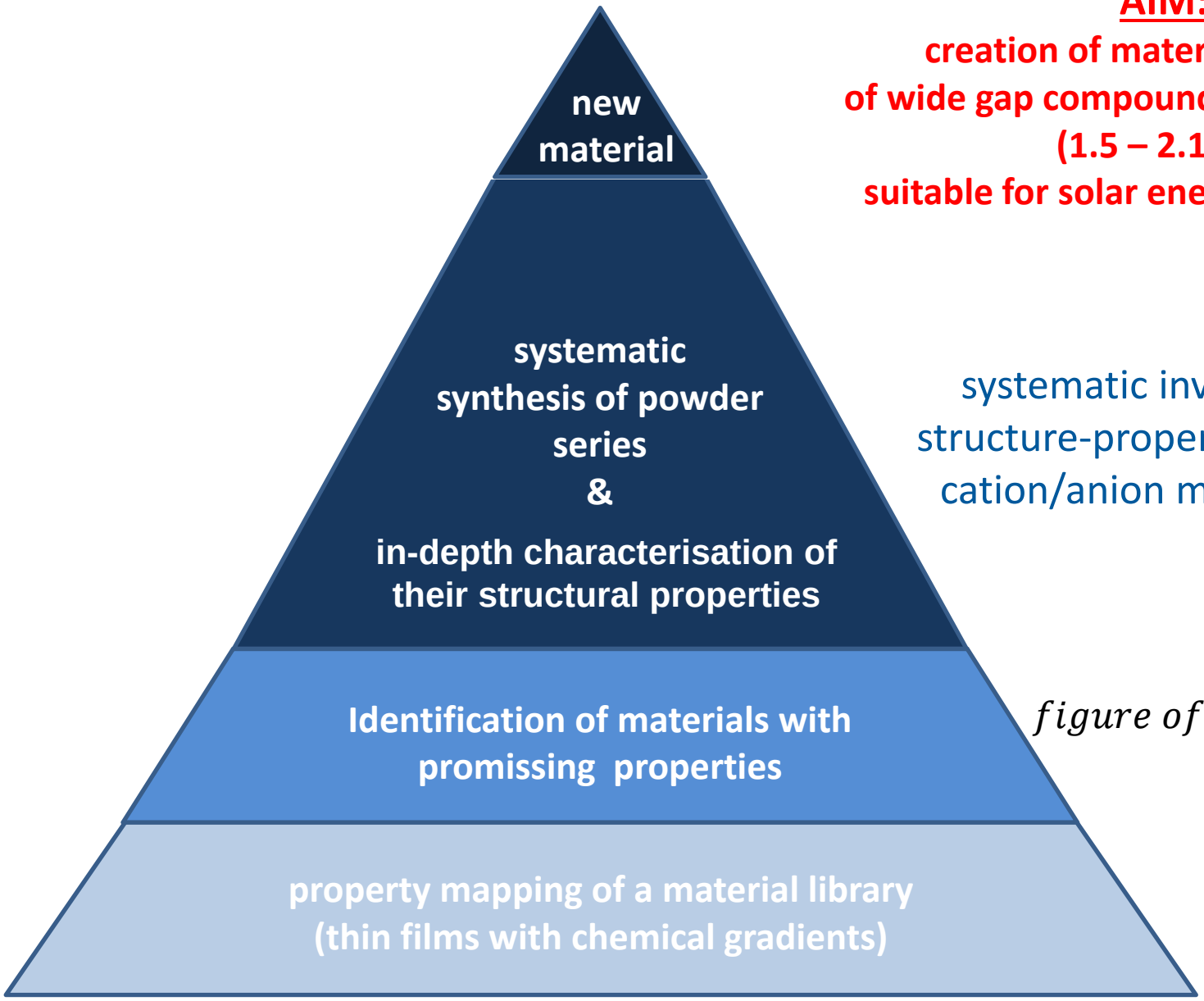

AIM:

creation of materials libraries of wide gap compound semiconductors (1.5 – 2.1 eV) suitable for solar energy applications

systematic investigation of structure-properties relations in cation/anion mutation series

$$figure\ of\ merit = \alpha \cdot \sqrt{D\tau} \gg 1$$

α – absorption
D – diffusivity
τ – life time

New materials for tandem solar cell applications

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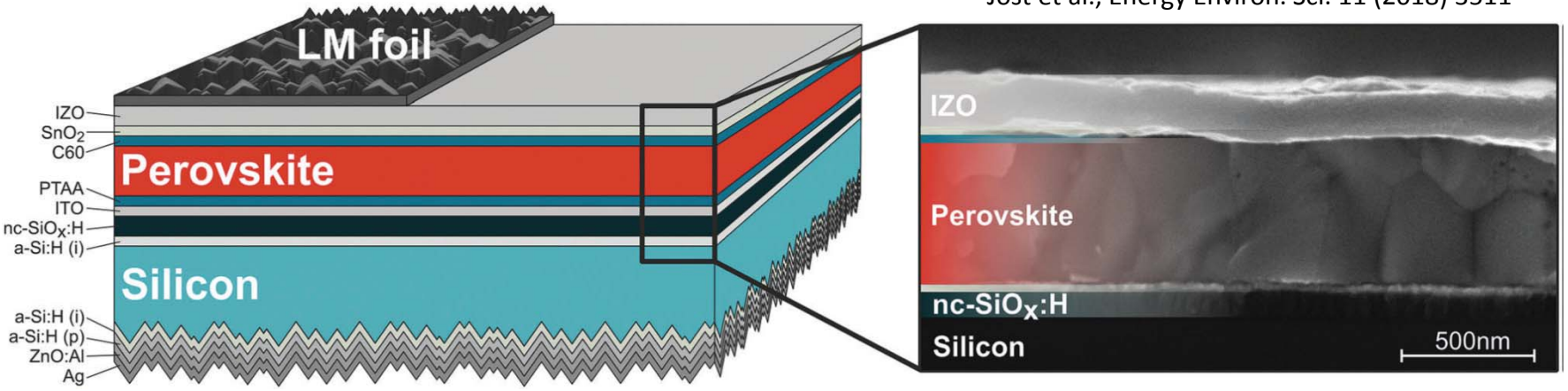
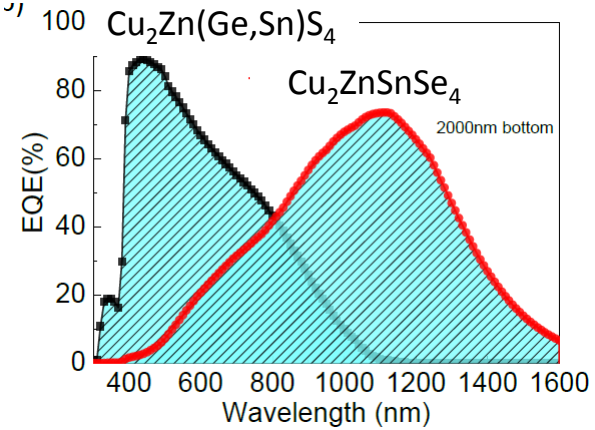
hybrid halide perovskites

Jost et al., Energy Environ. Sci. 11 (2018) 3511



monolithic perovskite/silicon-heterojunction tandem solar cell with η = 25.5%

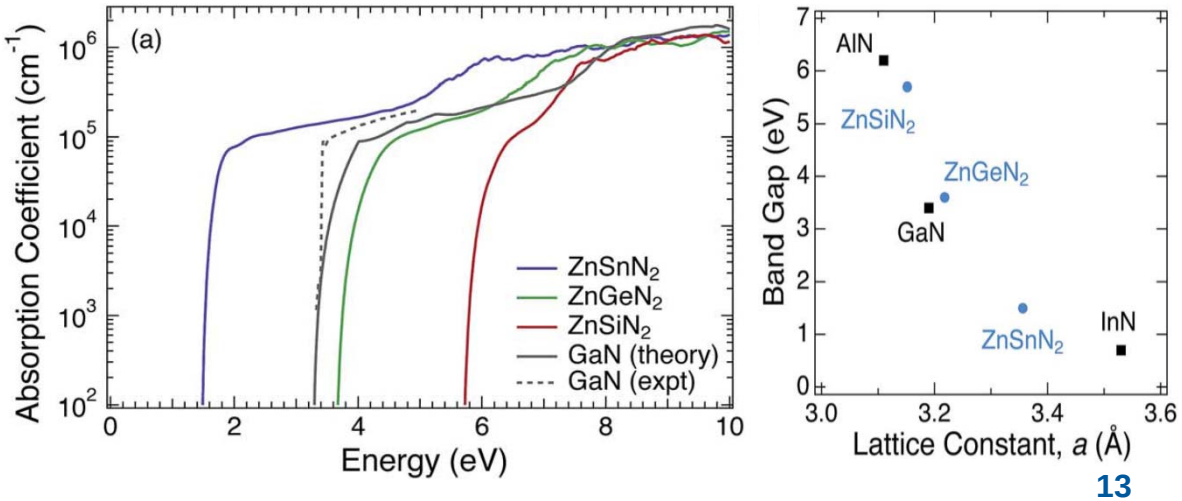
quaternary chalcogenides



simulated EQE

Gupta et al.: arxiv.org/pdf/1801.08498

ternary nitrides



A. Martinez et al., J. Mater. Chem. A 5 (2017) 11418–11435

hybrid lead halide perovskites

lead halide perovskites are mixed electronic–ionic semiconductors that have recently revolutionized the photovoltaics field

COMMUNICATION

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www.rsc.org/ees

Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency†

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Today's best perovskite solar cells use a mixture of formamidinium and methylammonium as the monovalent cations. With the addition of inorganic cesium, the resulting triple cation perovskite compositions are thermally more stable, contain less phase impurities and are less sensitive to processing conditions. This enables more reproducible device performances to reach a stabilized power output of 21.1% and ~18% after 250 hours under operational conditions. These properties are key for the industrialization of perovskite photovoltaics.

Broader context

Due to their enormous potential for use in the future of photovoltaics, perovskite solar cells have attracted much attention recently. However, achieving stable and reproducible high efficiency results is a major concern towards industrialization. To date, the best perovskite solar cells use mixed organic cations (methylammonium (MA) and formamidinium (FA)) and mixed halides. Unfortunately, MA/FA compositions are sensitive to processing conditions because of their intrinsic structural and thermal instability. The films frequently contain detrimental impurities and tend

$Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$ $\eta = 21.1\%$

What defines a perovskite?

Perovskite is a mineral ($CaTiO_3$) and a name of a crystal structure type – **Perovskite type structure**

cubic aristotype of the perovskite type structure

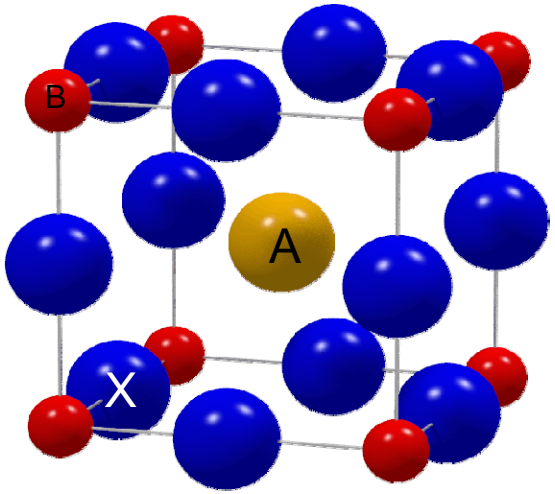
space group: $Pm\bar{3}m$

ABX_3 compounds

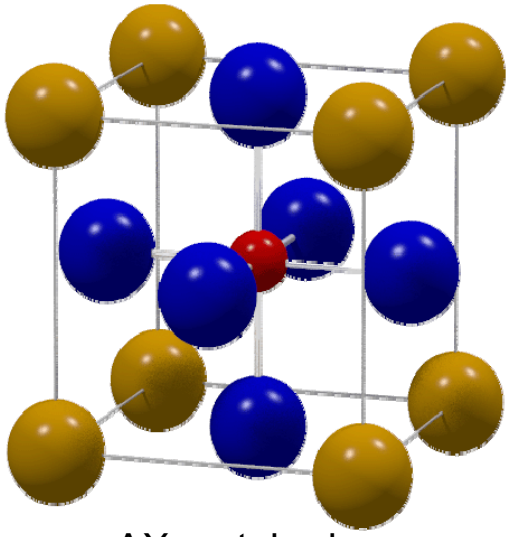
$A^{[12]}B^{[6]}X_3$

A – cubo-octahedral coordination

B – octahedral coordination

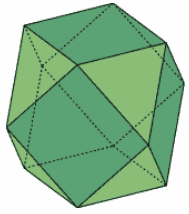


Graphics by A. Franz (2007)



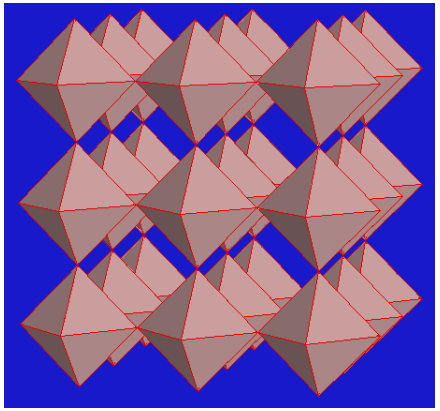
blue – anion

AX_6 octahedra



cuboctahedron

NETWORK of CORNERSHARING PbX_6 octahedra



many lower symmetry variations (hettotypes)

Breternitz, Schorr, Adv. En. Mat (2018) 1802366

Crystal structure of halide perovskites

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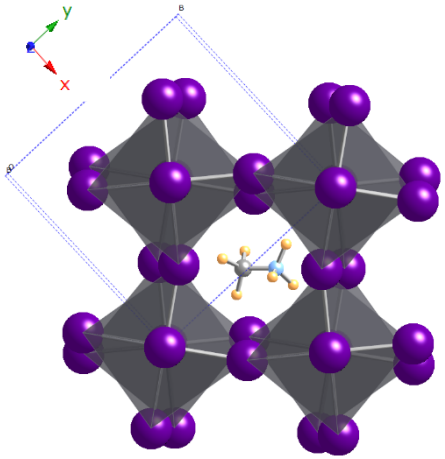
$MAPbI_3$

MA - methylammonium
$[CH_3NH_3]^+$

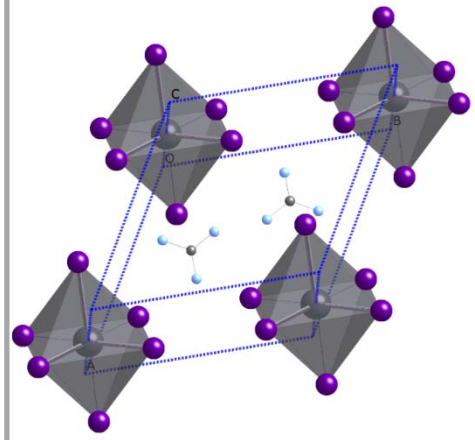


tetragonal perovskite structure
space group $I\frac{4}{m}cm$

Franz et al.,
Cryst.Res.Technol. 51 (2016) 534

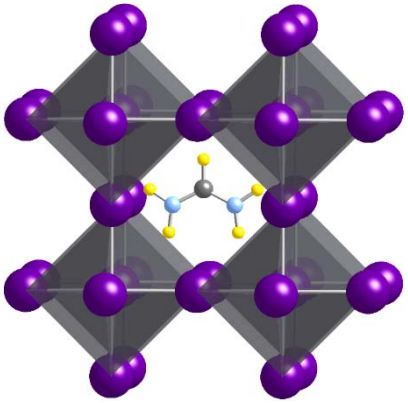
$FAPbI_3$

FA - formamidinium
$[H_2NCH{=}NH_2]^+$



hexagonal non-perovskite structure (δ-phase)
space group $P6_3mc$

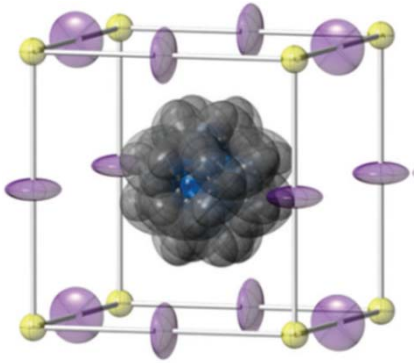
Weller *et al.*,
J. Phys. Chem. Lett. 6 (2015) 3209



cubic perovskite structure
s. g.p $Pm\bar{3}m$
→ not stable!

Stoumpos *et al.*,
Inorg. Chem. 52 (2013) 9019

$MAPbBr_3$



cubic perovskite structure
space group $Pm\bar{3}m$

Baikie et al.,
J. Mater. Chem. 3 (2015) 9298

Figure from: Weller et al.,
Chem. Commun. 51 (2015) 4180

Halide diffusion in perovskite semiconductors

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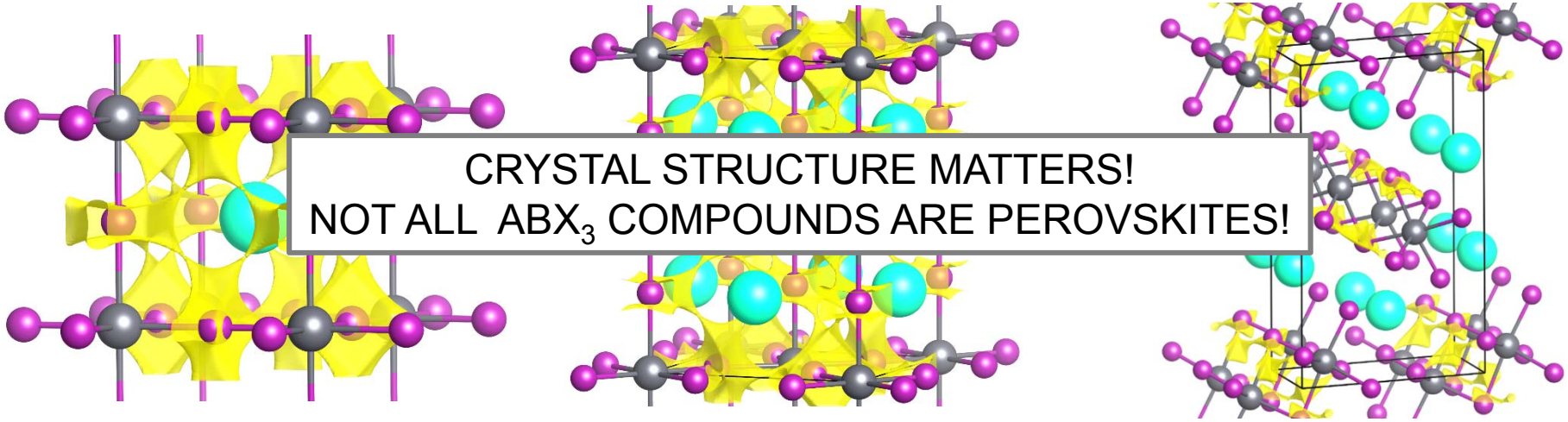
- halide diffusion distinguishes perovskite semiconductors from „classical“ semiconductors
- mixed ionic – electronic semiconductors → high intermixing of ionic and electronic current
- ionic conductivity has been identified as a key player for operational mechanisms in photovoltaic devices (Peng et al., ACS Energy Lett. 3 (2018) 1477)

cubic $CsPbI_3$	**tetragonal $CsPbI_3$**	**orthorhombic $CsPbI_3$**
Perovskite-type structure	**Perovskite-type structure**	**non-Perovskite structure**
(high-T phase)	(not stable)	(stable at RT)

bond-valency-energy-landscape method → calculation of halide diffusion pathways



CRYSTAL STRUCTURE MATTERS!
NOT ALL ABX_3 COMPOUNDS ARE PEROVSKITES!

percolation energies ~ 0.3 eV

percolation energies ~ 0.9-1 eV

Stabilization of the cubic perovskite-type phase

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Anion mutations

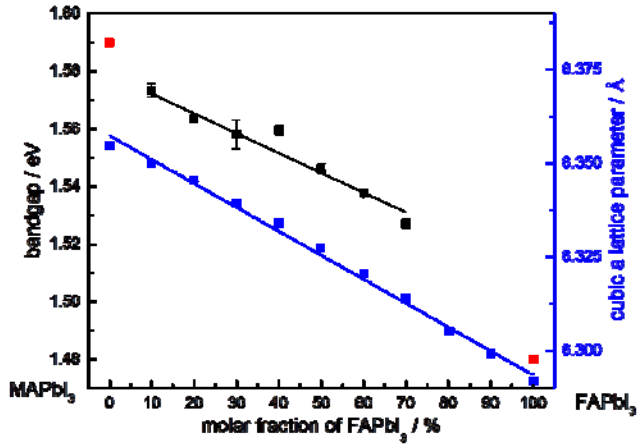
$MAPb(I,Cl)_3$ & $MAPb(I,Br)_3$
large miscibility gaps

$MAPb(I,Cl)_3$
chlorine substitution → leads to a weakening of the hydrogen bonds

Cation mutations

$MA_{1-x}FA_xPbI_3$: phase behaviour
$0 \le x \le 0.1$ → tetragonal perovskite
$0.1 < x < 0.8$ → cubic perovskite
$0.8 \le x \le 1$ → fast degradation to non-perovskite structure (δ-phase)

$MA_{1-x}FA_xPbI_3$: band gap energy



stabilization of the cubic phase by annealing

tetragonal perovskite type phase

Band gap tuning by cation/anion mutation

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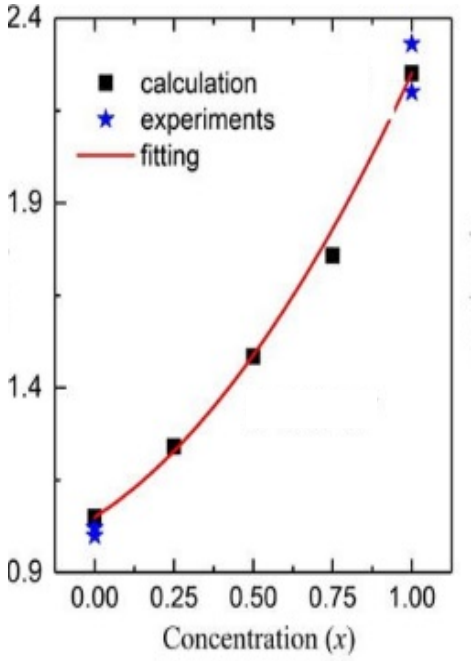
… in quaternary chalcogenides ($A_2^I B^{II} C^{IV} X_4^{VI}$)

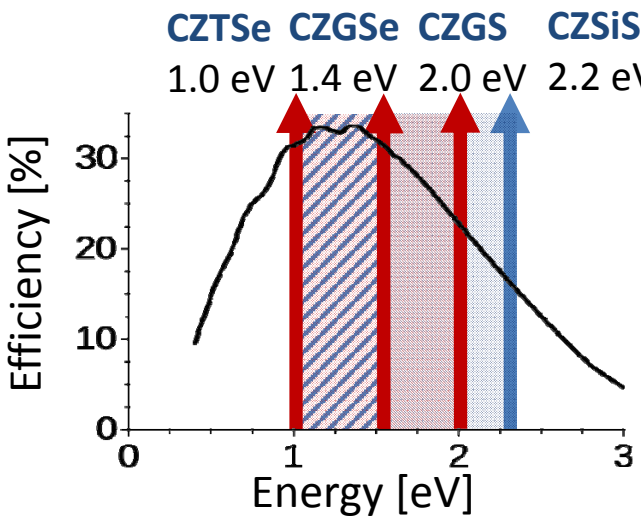
$Cu_2ZnSnSe_4$ – CZTSe
$Cu_2ZnGeSe_4$ – CZGSe
Cu_2ZnGeS_4 – CZGS
$Cu_2ZnSiSe_4$ – CZSiSe

$Cu_2ZnSn_{1-x}Si_xSe_4$

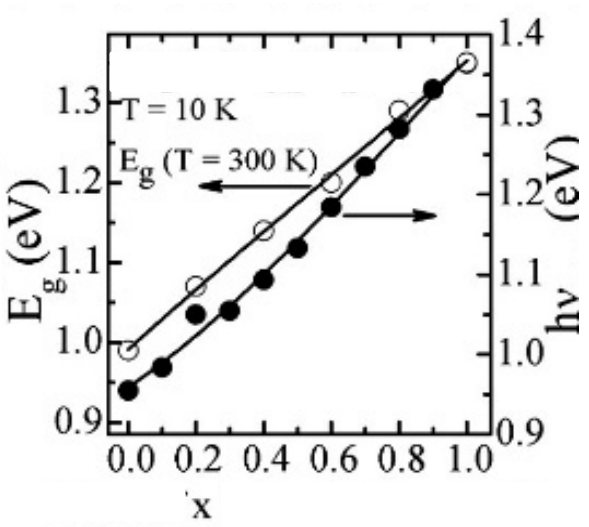


Jibran et al., Chem. Phys. Lett. 705 (2018) 92

Shockley-Queisser limit



$Cu_2ZnSn_{1-x}Ge_xSe_4$



Grossberg et al., Thin Sol. Films 582 (2015) 176

Adamantine compound family

main feature: tetrahedral coordination

elements
Silicon (Si)
Germanium(Ge)

→

binaries
ZnS
GaAs

→

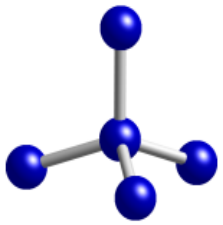
ternaries
$CuInSe_2$
$CuGaSe_2$
$ZnSnN_2$

→

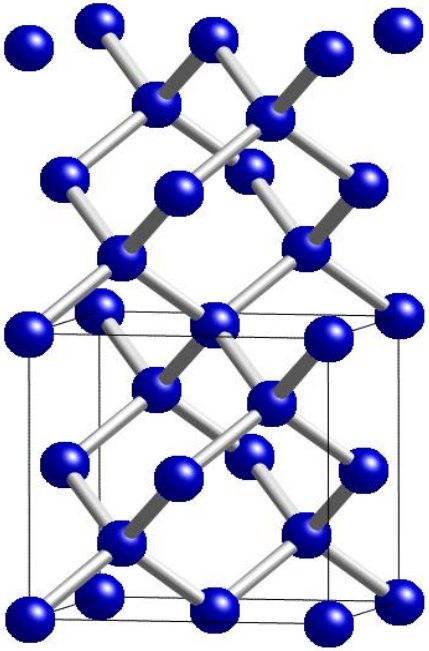
quaternaries
$Cu_2ZnSnSe_4$
$Cu_2ZnGeSe_4$
Cu_2ZnGeS_4
$Cu_2ZnSiSe_4$

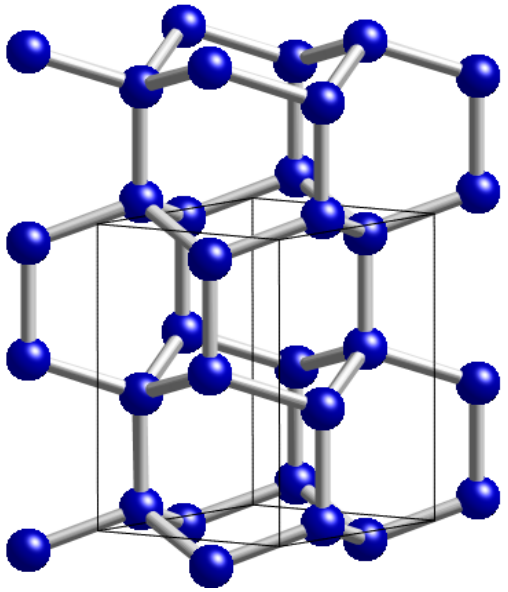
Diamond-type structure - **cubic**

Lonsdaleite-type structure - **hexagonal**



building block





Adamantines: the cubic branch

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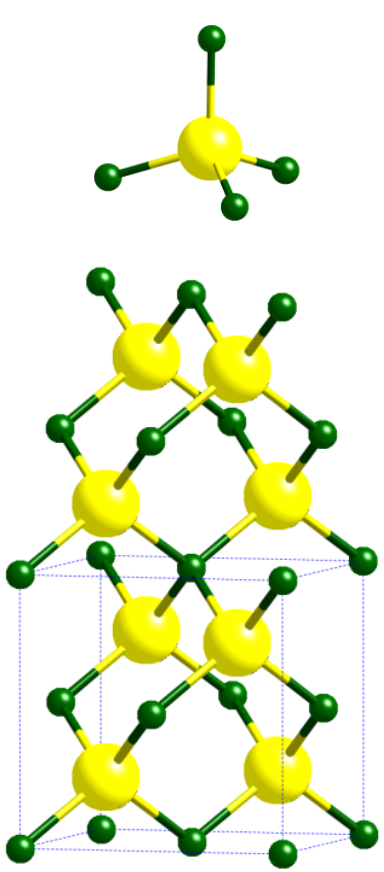
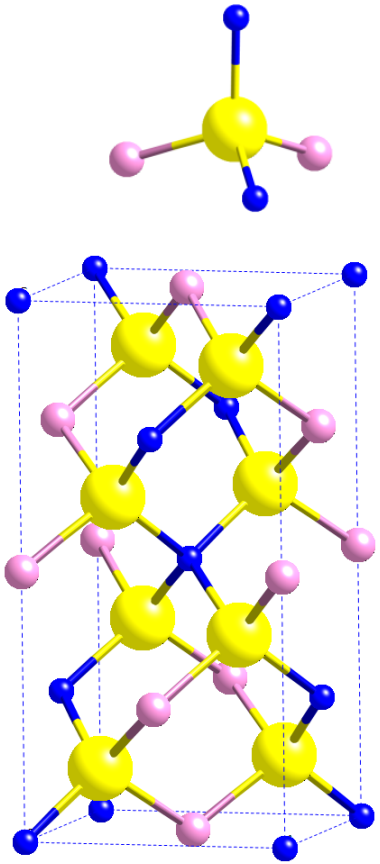
Binaries: ZnS

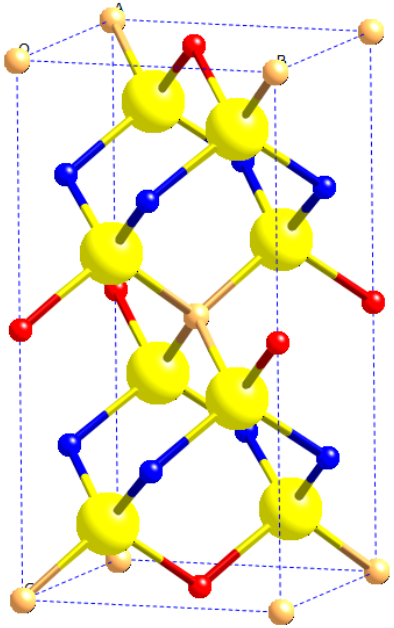
Ternaries: $CuInSe_2$ $CuGaSe_2$

Quaternaries

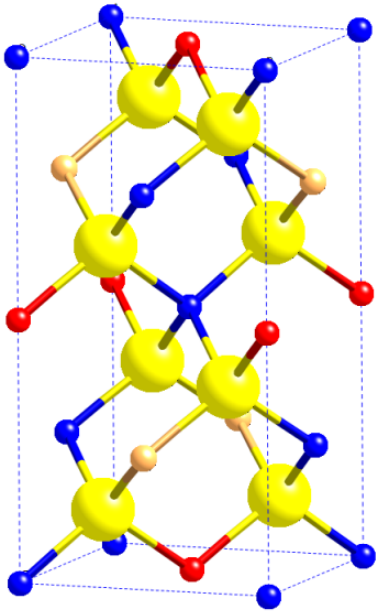




Cu_2FeSnS_4
$Cu_2CdSnSe_4$



$Cu_2ZnSnSe_4$
$Cu_2ZnGeSe_4$



Sphalerite type structure

cubic

Chalcopyrite type structure

tetragonal

Stannite type structure

tetragonal

Kesterite type structure

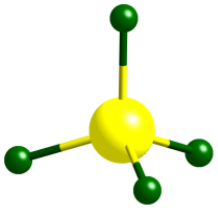
tetragonal

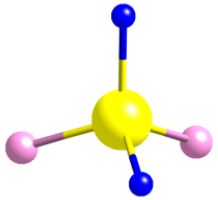
Adamantines: the hexagonal branch

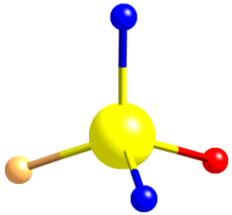
Binaries: GaAs, InP

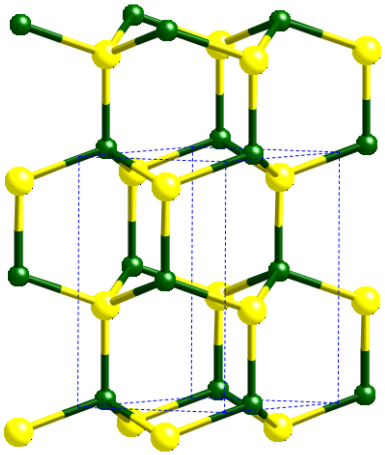
Ternaries: $ZnSnN_2$

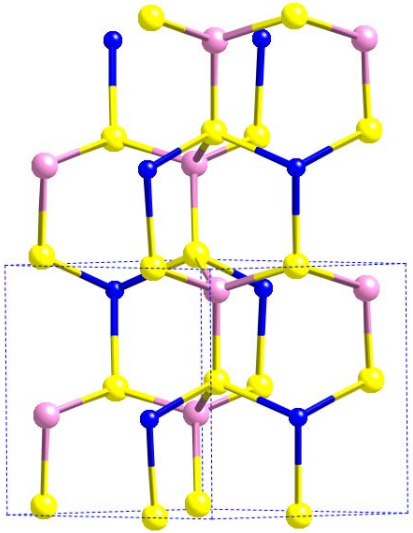
Quaternaries



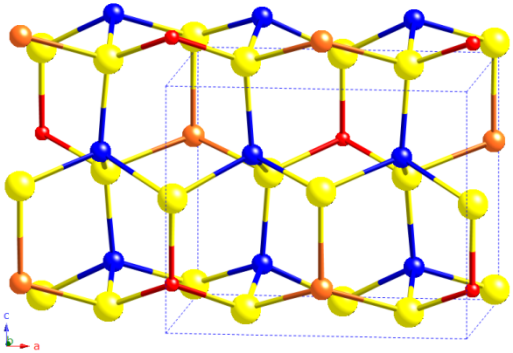


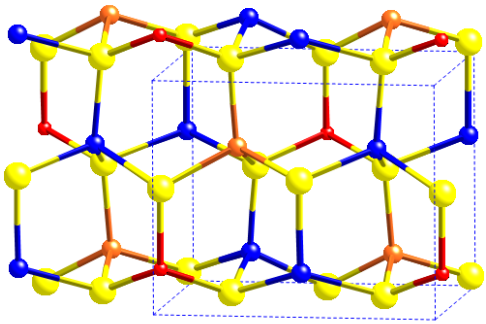






Cu_2ZnGeS_4
$Cu_2ZnSiSe_4$





Wurtzite type structure

hexagonal

β-$NaFeO_2$ type structure

orthorhombic

wurtz-stannite type structure

orthorhombic

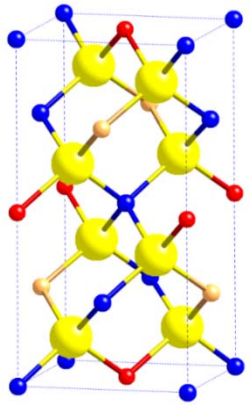
wurtz-kesterite type structure

monoclinic

Quaternary compound semiconductor Cu_2ZnGeS_4

Kesterite-type structure

space group $I\bar{4}$



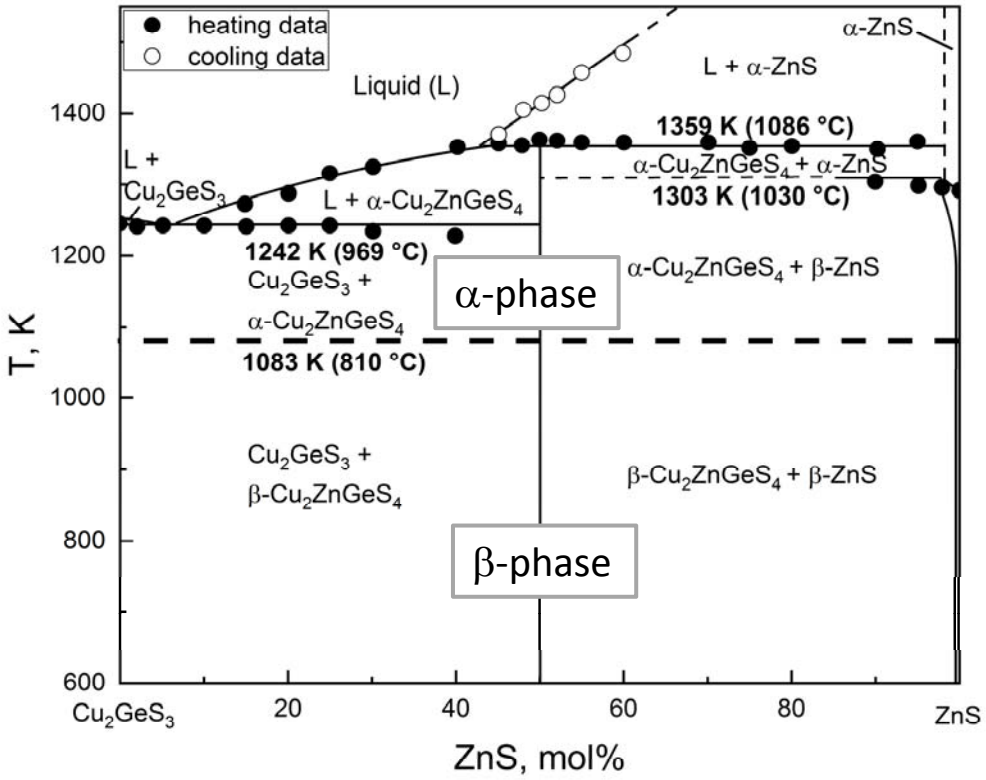
β-Cu_2ZnGeS_4

band gap energy

E_g = 1.7 eV

Cu_2GeS_3 – ZnS phase diagram

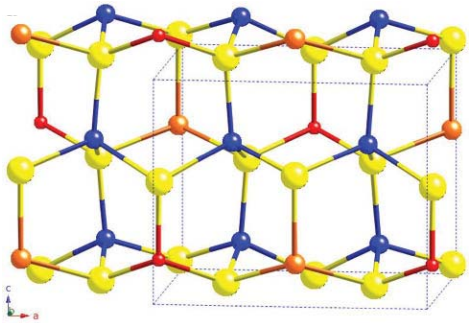
Parasyuk et al. J. Alloys Comp. 397 (2005) 85



CRYSTAL STRUCTURE DETERMINES THE OPTOELECTRONIC PROPERTIES!

Wurtz-Stannite type structure

space group $Pmn2_1$



α- Cu_2ZnGeS_4

band gap energy

E_g = 2.2 eV

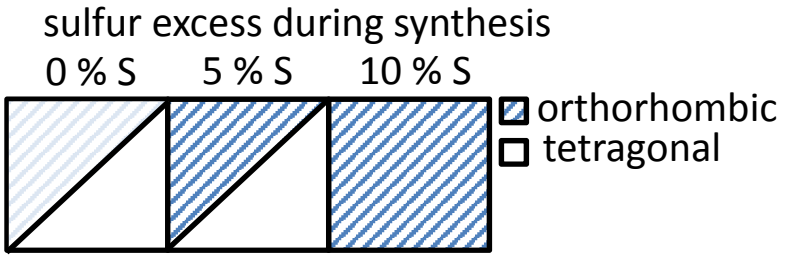
Schnabel et al. Energies (2017) 10, 1813.

Fan et al. Nanoscale (2015) 7, 3247.

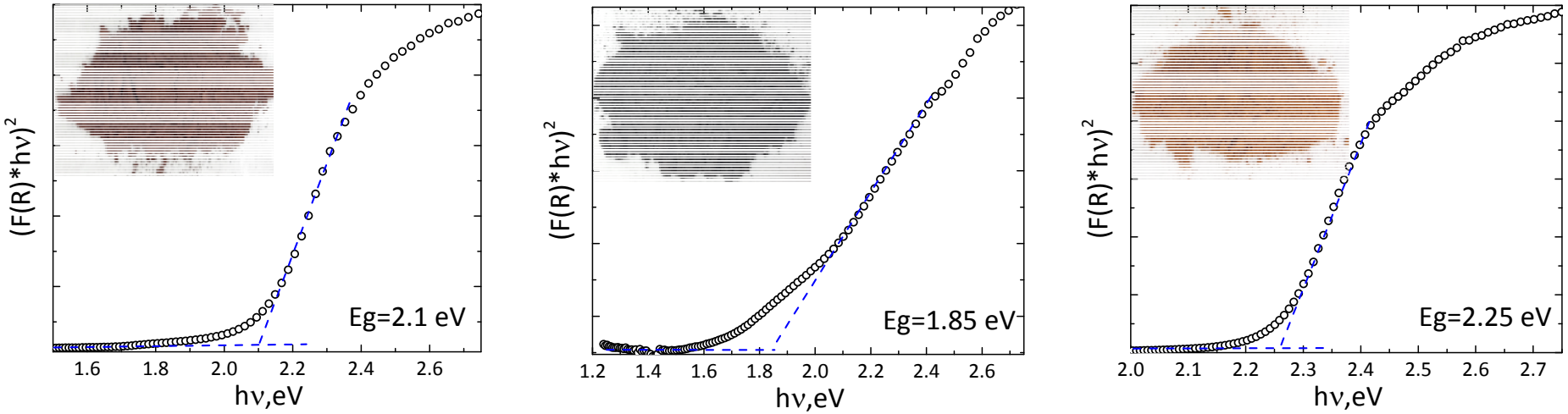
Cu_2ZnGeS_4: influence of synthesis conditions

synthesis by solid state reaction of the elements

sulfur pressure during synthesis influences formation of tetragonal / orthorhombic phase



influences the band gap energy E_g



band gap energies determined by UV-VIS spectroscopy and Kubelka-Munk analysis

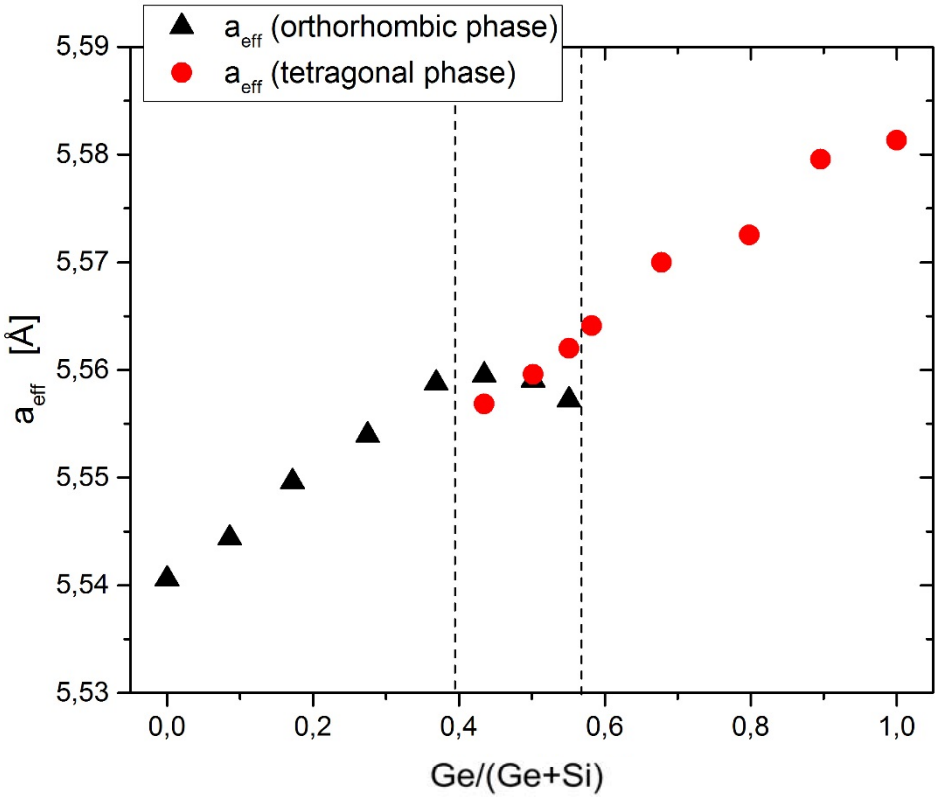
Work in progress: intrinsic point defects & structural disorder → neutron diffraction

Band gap tuning in $Cu_2ZnGe_{1-x}Si_xSe_4$

HZB Helmholtz Zentrum Berlin

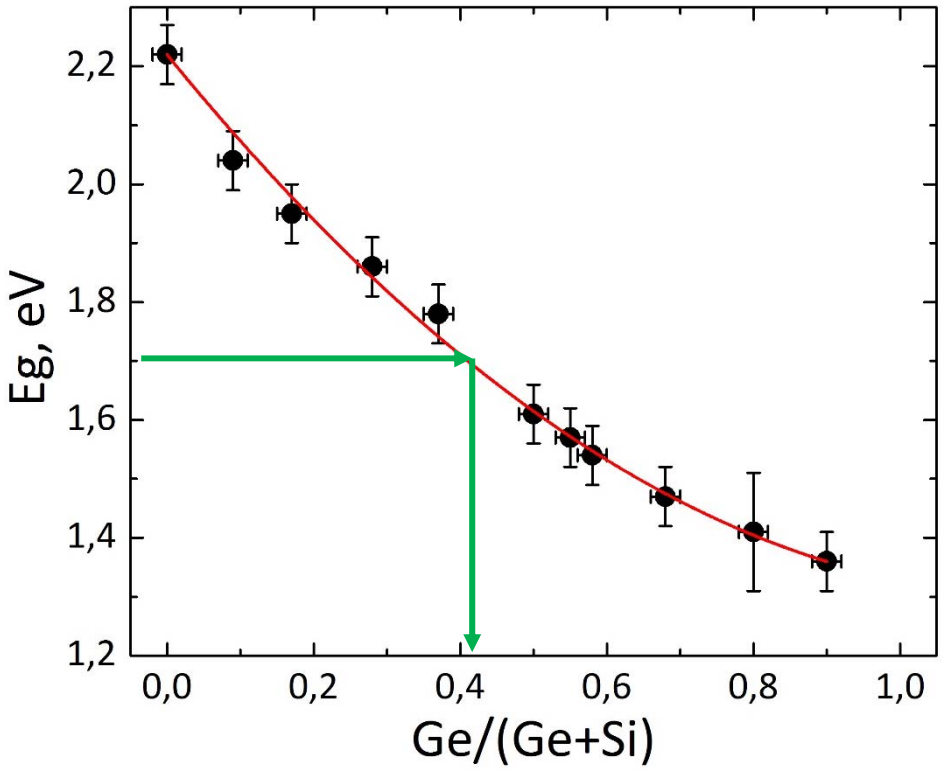
lattice parameter

Rietveld analysis of X-ray diffraction data



band gap energy

Kubelka-Munk analysis of UV-VIS data



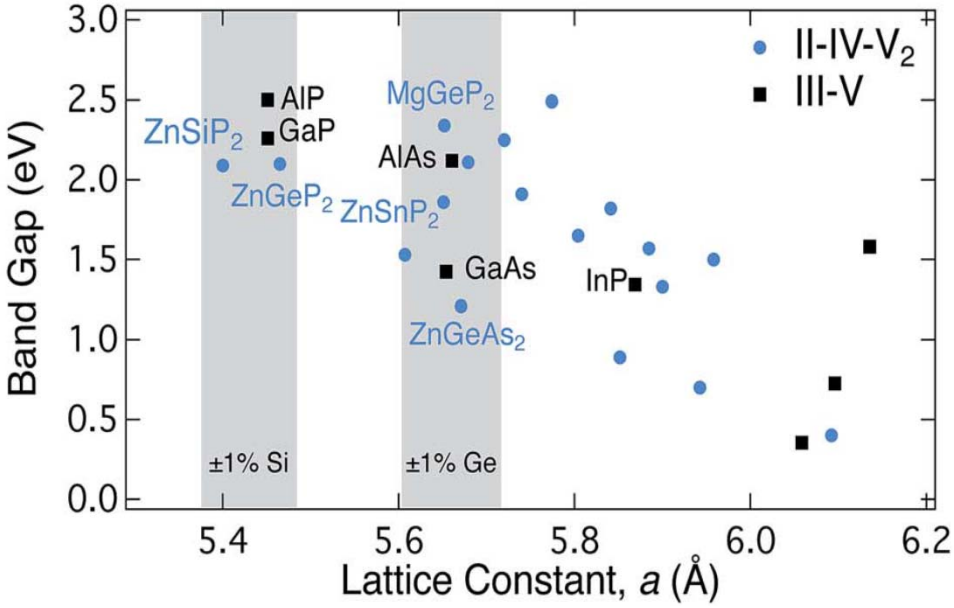
tetragonal phase $a_{eff} = \sqrt[3]{(a_t^2 c_t)/2}$

orthorhombic phase $a_{eff} = \sqrt[3]{(a_o b_o c_o)/2}$

Adachi, Earth-abundant materials for solar cells, Wiley 2015

II – IV – N_2 compound semiconductors

- III-V (e. g. GaAs) solar absorbers are highly efficient
- applications of III-V depend on the use of epitaxial heterostructures
- need for lattice matched alloys to enable low defect densities → limits the parameter space available in device applications

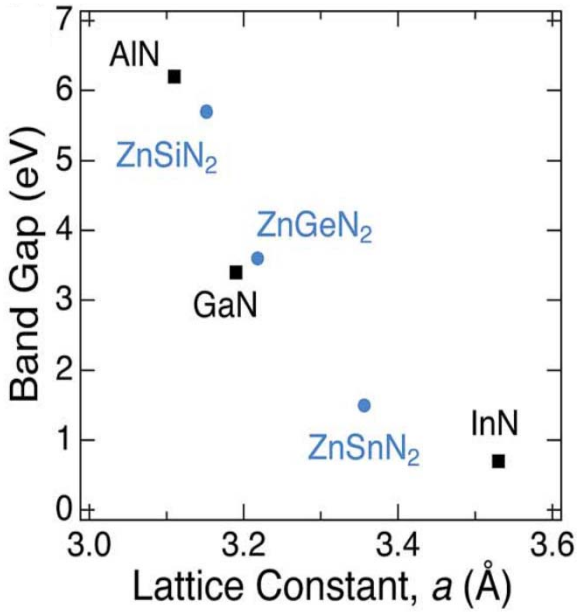


GaN

$ZnGeN_2$

- **II–IV–N_2** materials are very efficient optical absorbers and emitters
- both $ZnSnN_2$ and $ZnGeN_2$ have direct band gaps

Control of cation order in the II–IV–V_2 materials can produce significant **changes in optoelectronic properties at fixed chemical composition**

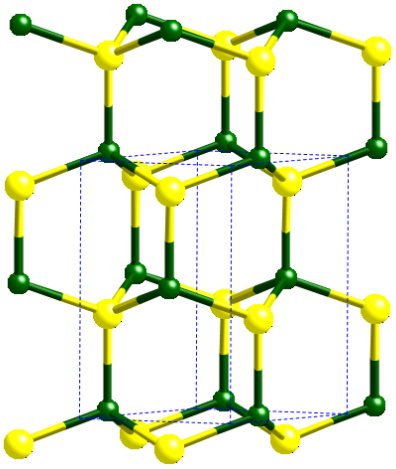


A. Martinez et al., J. Mater. Chem. A 5 (2017) 11418–11435

Ordered and disordered cation distribution

HZB Helmholtz Zentrum Berlin

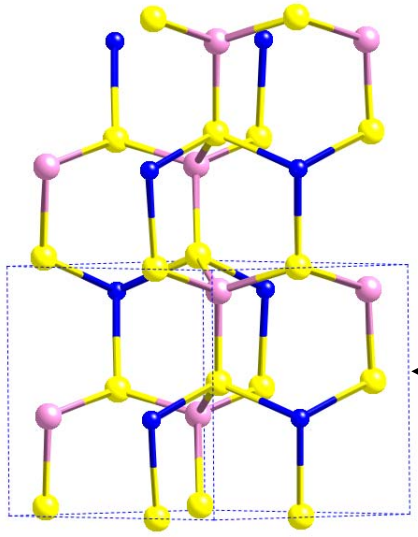
statistic cation distribution



wurtzite-type structure

$ZnGeN_2$
$ZnSnN_2$

ordered cation distribution

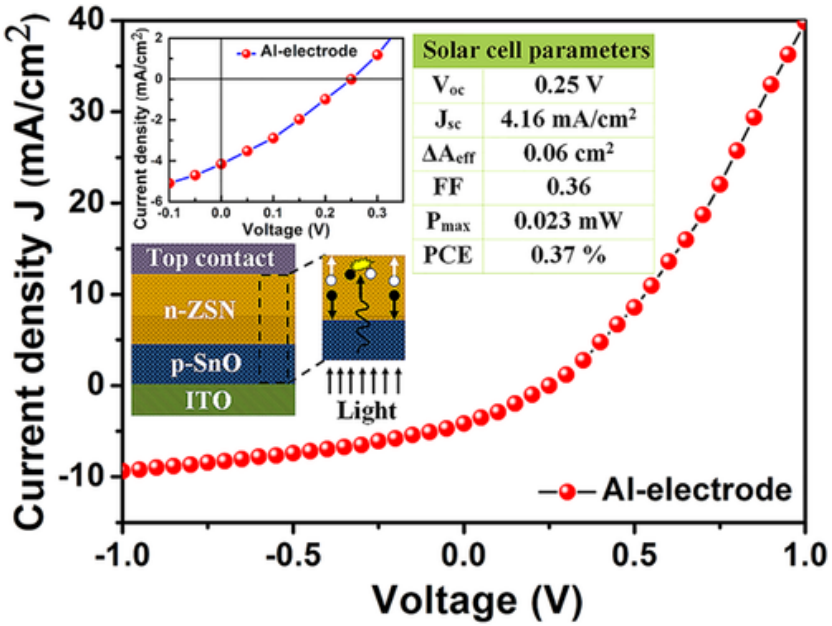


β-$NaFeO_2$-type structure

cation ordering
→ E_g variation

band gap tuning through
✓ cation order/disorder
✓ alloying (Zn-Ge)

first proof-of-concept devices being demonstrated

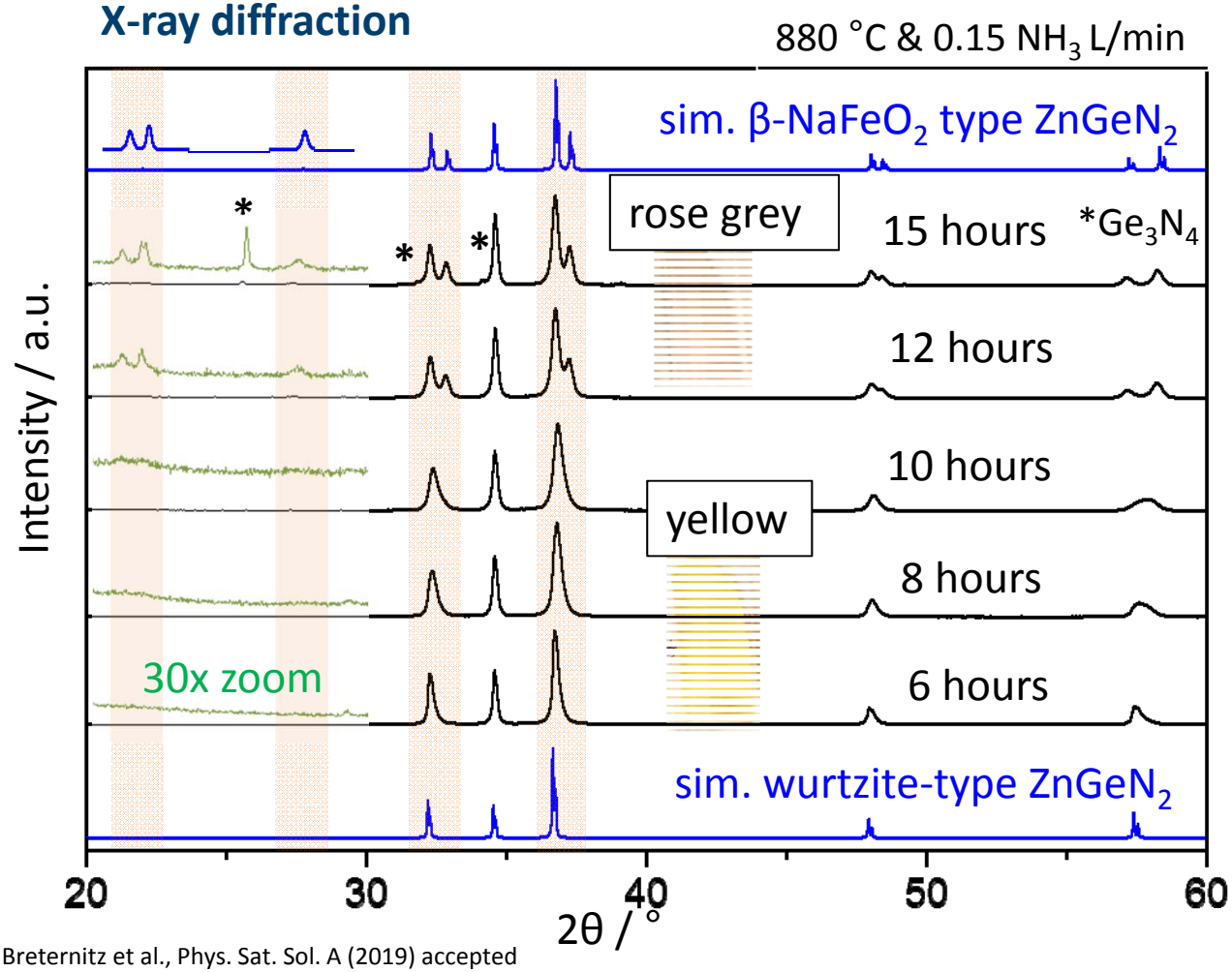


K. Javaid et al., Phys. Status Solidi RRL, 2018, 12, 1700332.

Synthesis of $ZnGeN_2$ by ammonolysis

precursor **Zn_2GeO_4** → intermediate **$Zn_{2-x}GeO_{1-x}N_2$** → final product **$ZnGeN_2$**

X-ray diffraction

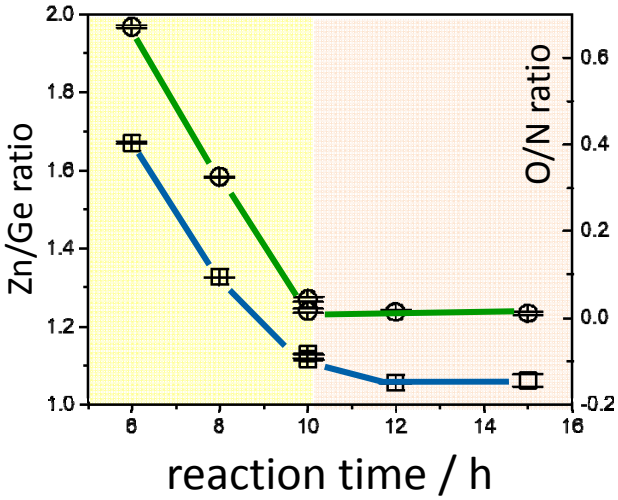


Zn/Ge atomic ratio

- X-ray fluorescence spectroscopy

O/N atomic ratio

- hot-gas extraction



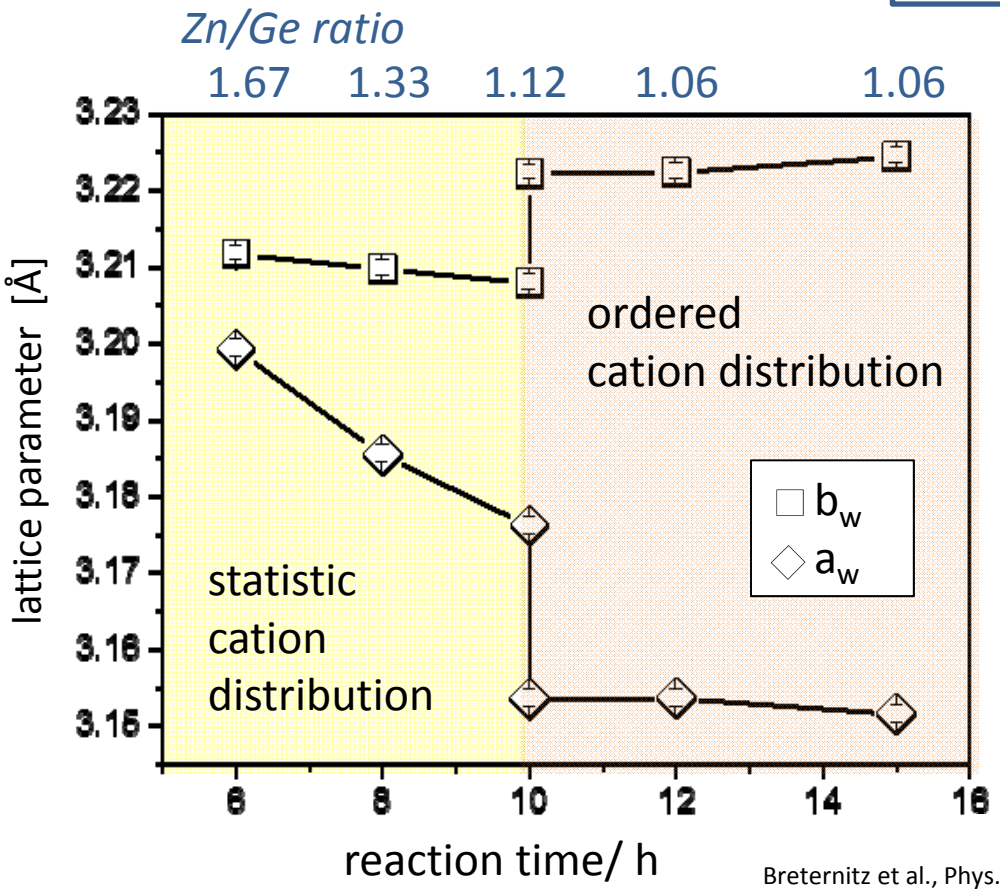
Breternitz et al., Phys. Sat. Sol. A (2019) accepted

Indication for order/disorder transition

orthorhombic lattice parameter Rietveld analysis of X-ray diffraction data (using β-$NaFeO_2$-type structure)

„pseudo wurtzite“ lattice parameter

$$a_w = \frac{a_0}{\sqrt{3}} \qquad b_w = \frac{b_0}{2} \qquad c_w = c_0$$



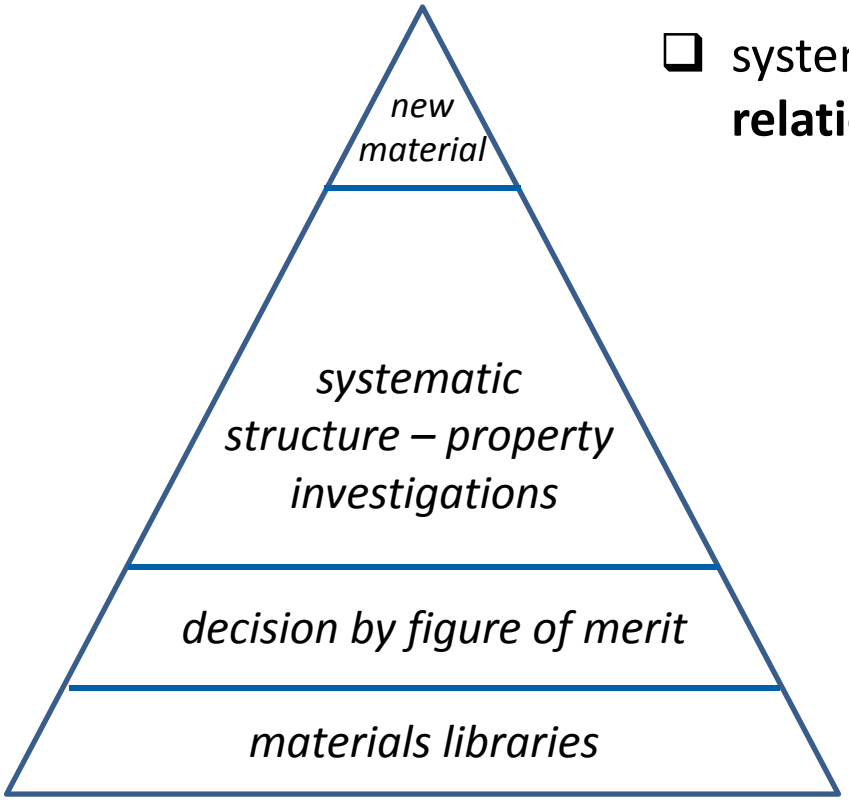
work in progress

- transition from statistic to ordered cation distribution
  → neutron diffraction
- correlation cation distribution - E_g

Breternitz et al., Phys. Sat. Sol. A (2019) accepted

Summary

- **multi-junction PV (tandem/triple)** can provide efficiencies surpassing todays limits
- **new materials** /materials class needed



- systematic investigations of **structure-property relations** in cation/anion mutation series
  - ✓ hybrid halid perovskites
  - ✓ quaternary chalcogenides
  - ✓ ternary group-IV nitrides
- next step: accelerate material discovery by **combinatorial materials research**

Dr. Galina Gurieva
Dr. Alexandra Franz
Dr. Joachim Breternitz

Frederike Lehmann
Sara Niedenzu
Zhenyu Wang

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Thank you for your attention!