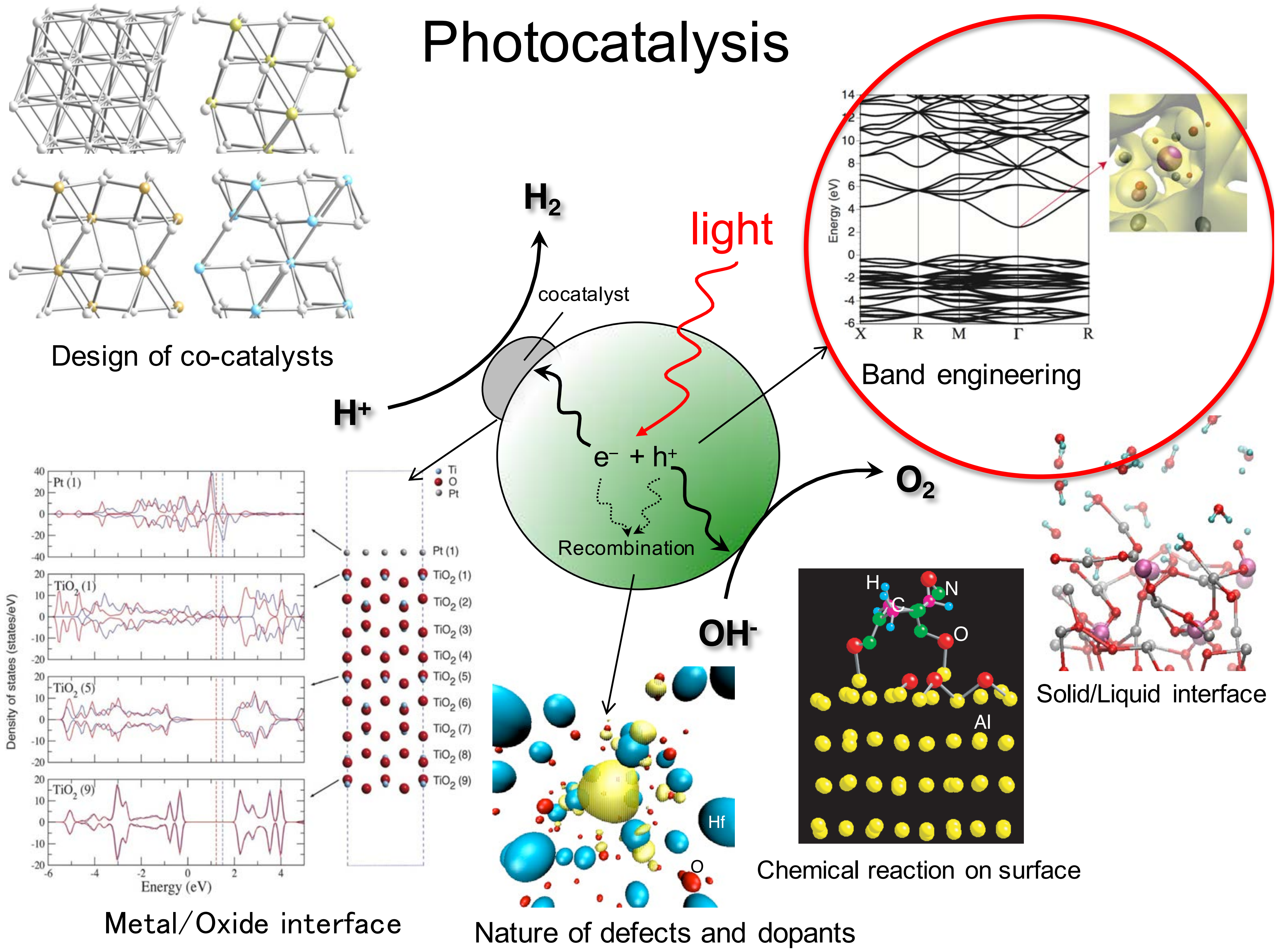
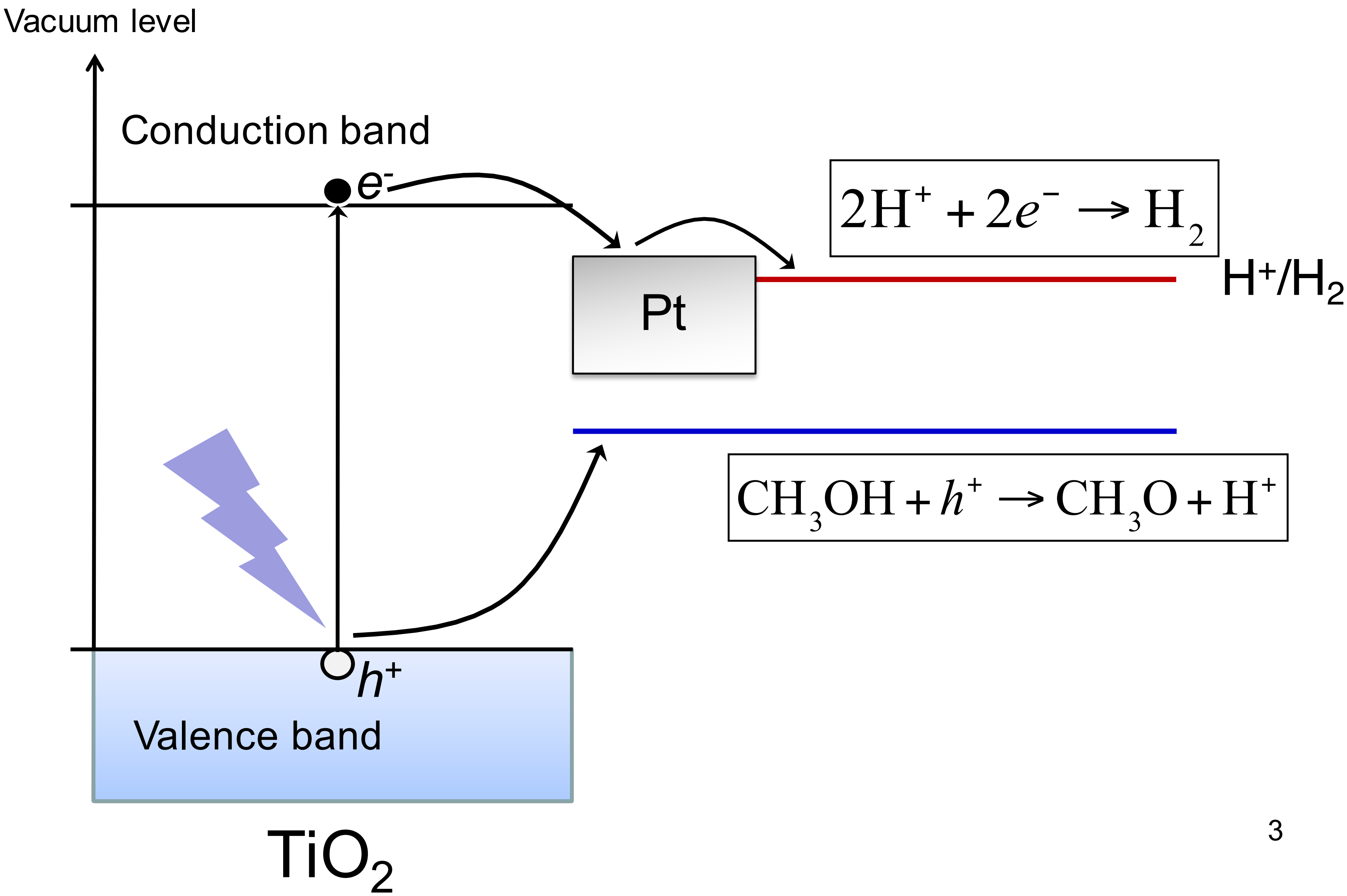
混合価数スズ酸化物の結晶構造予測と光機能材料としての可能性

梅澤直人

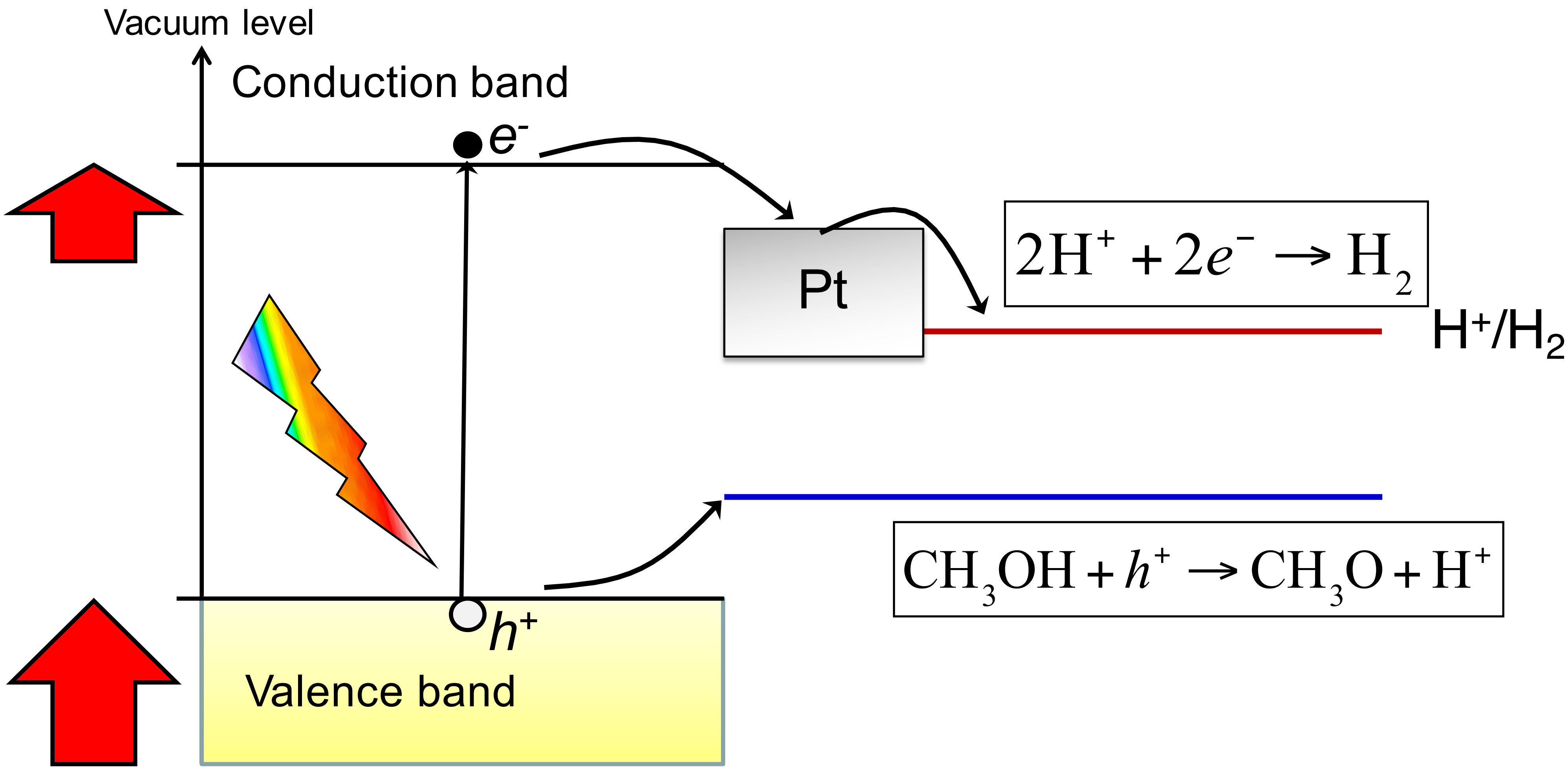
物質・材料研究機構
環境再生材料ユニット


Photocatalysis
Design of co-catalysts
H2
H+
cocatalyst
light
e⁻ + h⁺
Recombination
O2
OH-
Band engineering
Energy (eV)
X R M Γ R
Solid/Liquid interface
Chemical reaction on surface
H C N O Al
Nature of defects and dopants
Hf
O
Metal/Oxide interface
Pt (1)
TiO2 (1)
TiO2 (5)
TiO2 (9)
Density of states (states/eV)
Energy (eV)
Ti O Pt
Pt (1)
TiO2 (1)
TiO2 (2)
TiO2 (3)
TiO2 (4)
TiO2 (5)
TiO2 (6)
TiO2 (7)
TiO2 (8)
TiO2 (9)

H_2 evolution from methanol solution on semiconductor photocatalysts



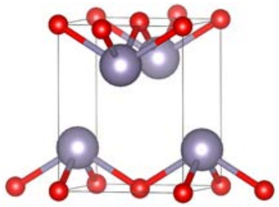
H_2 evolution from methanol solution on semiconductor photocatalysts



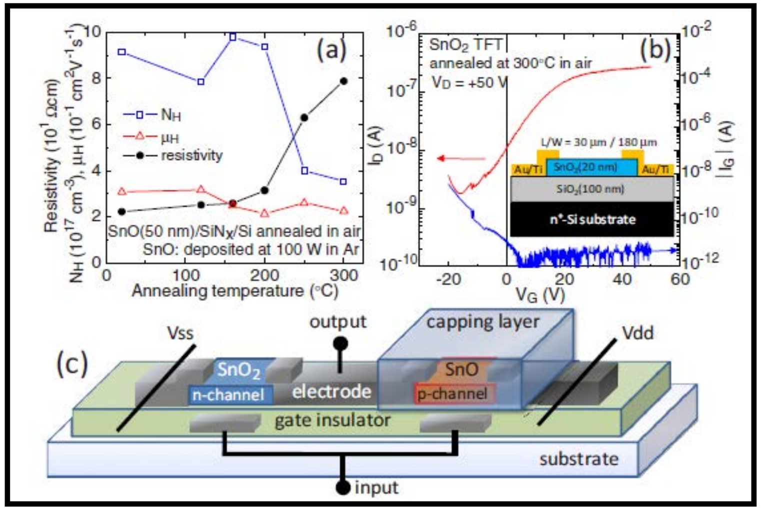
Ideal semiconductor

Tin oxides

SnO



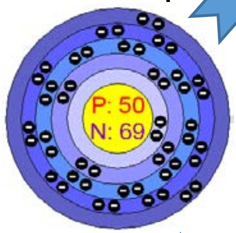
- ***p*-type semiconductor**
- **Thin film transistor**



Hisato Yabuta *et al., Appl. Phys. Lett.* 97, 072111 (2010)

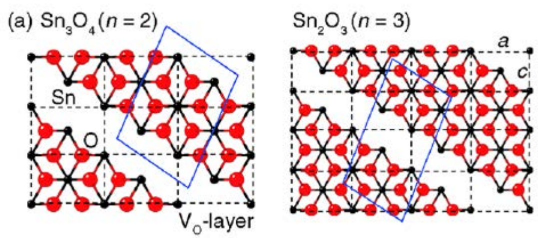
Tin (Sn)

$4d^{10}5s^25p^2$



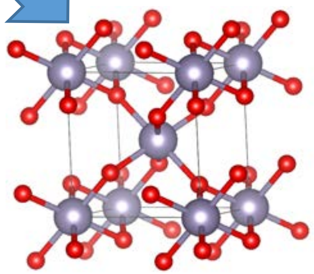
…Sn_xO_y…
?

Sn_2O_3 $Sn^{2+}Sn^{4+}O_3$	**Sn_3O_4** $(Sn^{2+})_2Sn^{4+}O_4$	**Sn_4O_5** $(Sn^{2+})_3Sn^{4+}O_5$
Sn_5O_6 $(Sn^{2+})_4Sn^{4+}O_6$	**Sn_6O_7** $(Sn^{2+})_5Sn^{4+}O_7$	**Sn_7O_8** $(Sn^{2+})_6Sn^{4+}O8$

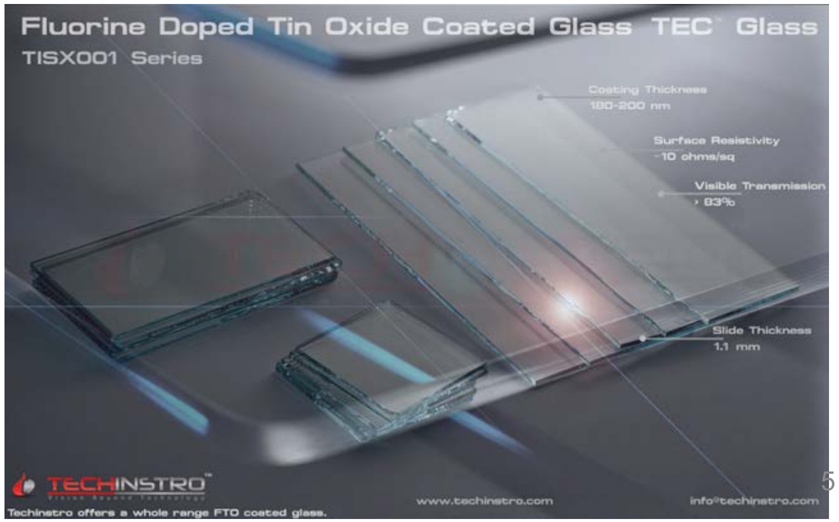


Seko, *et. al. Phys. Rev. Lett.* 100, 045702 (**2008**)

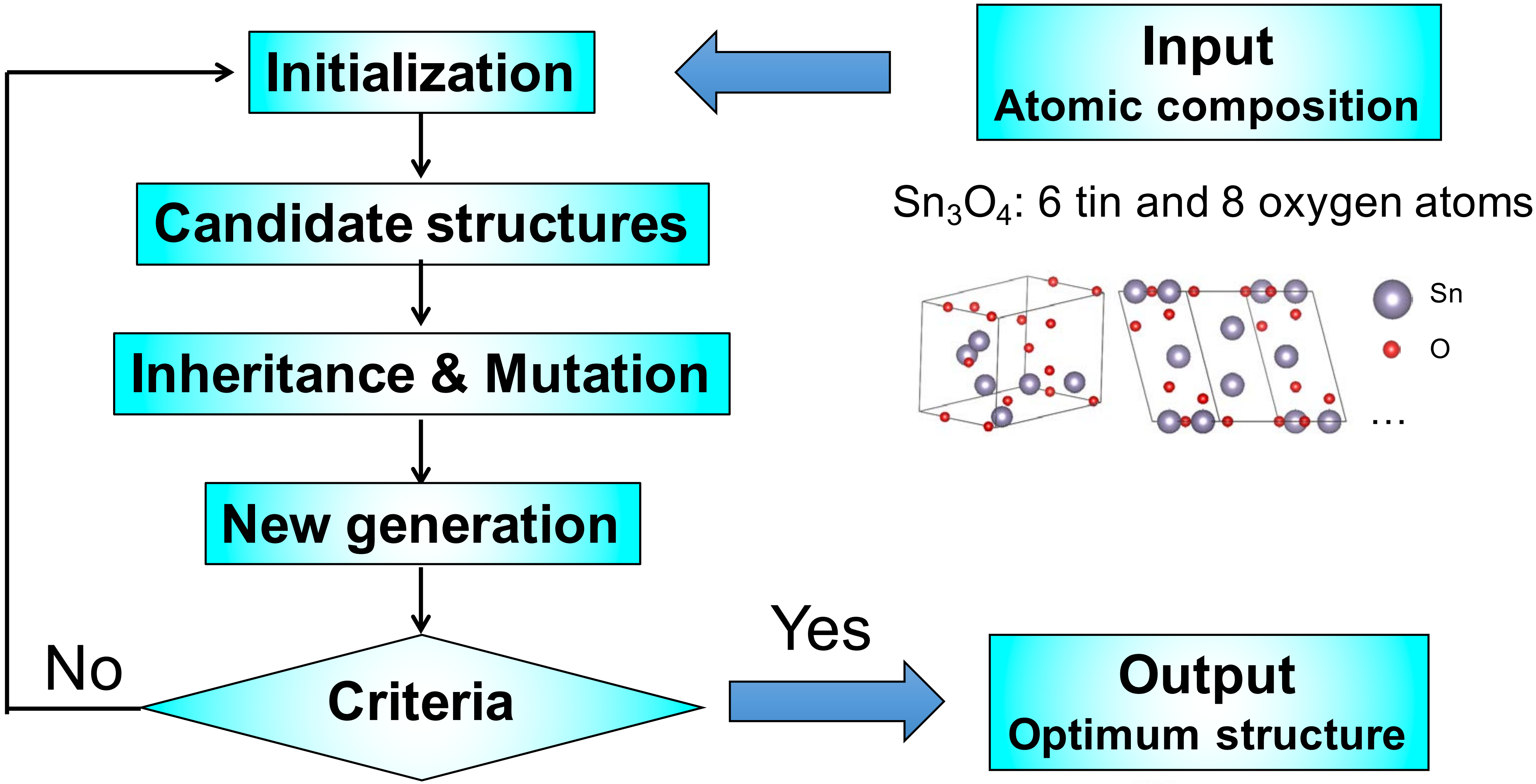
SnO_2

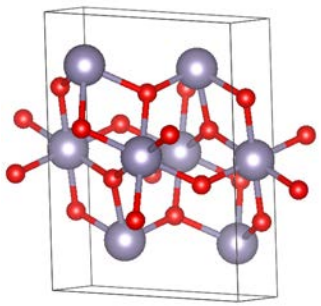


- **Sensor materials**
- **Oxidation catalysts**
- ***n*-type transparent conductors**



Crystal structure prediction from evolutionary algorithm





USPEX

Lyakhov A.O., Oganov A.R., Valle M. (2010). How to predict very large and complex crystal structures. *Comp. Phys. Comm.* **181**, 1623-1632.
Oganov A.R., Lyakhov A.O., Valle M. (2011). How evolutionary crystal structure prediction works - and why. *Acc. Chem. Res.* **44**, 227-237.

Computational details

❑Structure Prediction

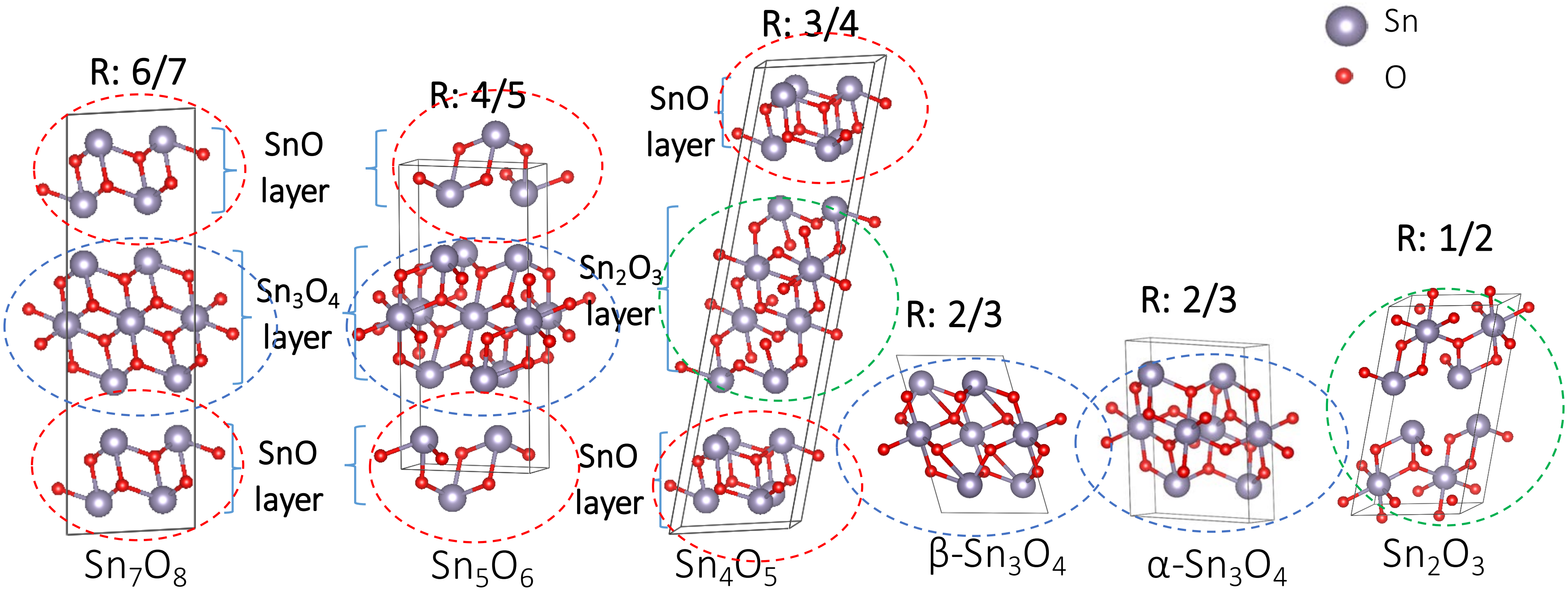
- Global optimization: Evolutionary Algorithm (USPEX)
- Local optimization: First Principles Calculation (VASP)
- Functional: optB86b vdW-DF (van der Waals correction)
- Cutoff Energy: 400 eV

❑Post Processing

- Structure Refinement: First Principles Calculation (VASP)
- Functional: optB86b vdW-DF (van der Waals correction)
- Cutoff Energy: 800 eV
- Electronic Structure: First Principles Calculation (VASP)
- Functional: HSE06 (hybrid functional)+optB86b (van der Waals correction)
- Cutoff Energy: 600 eV

Novel crystal structures of Sn_xO_y

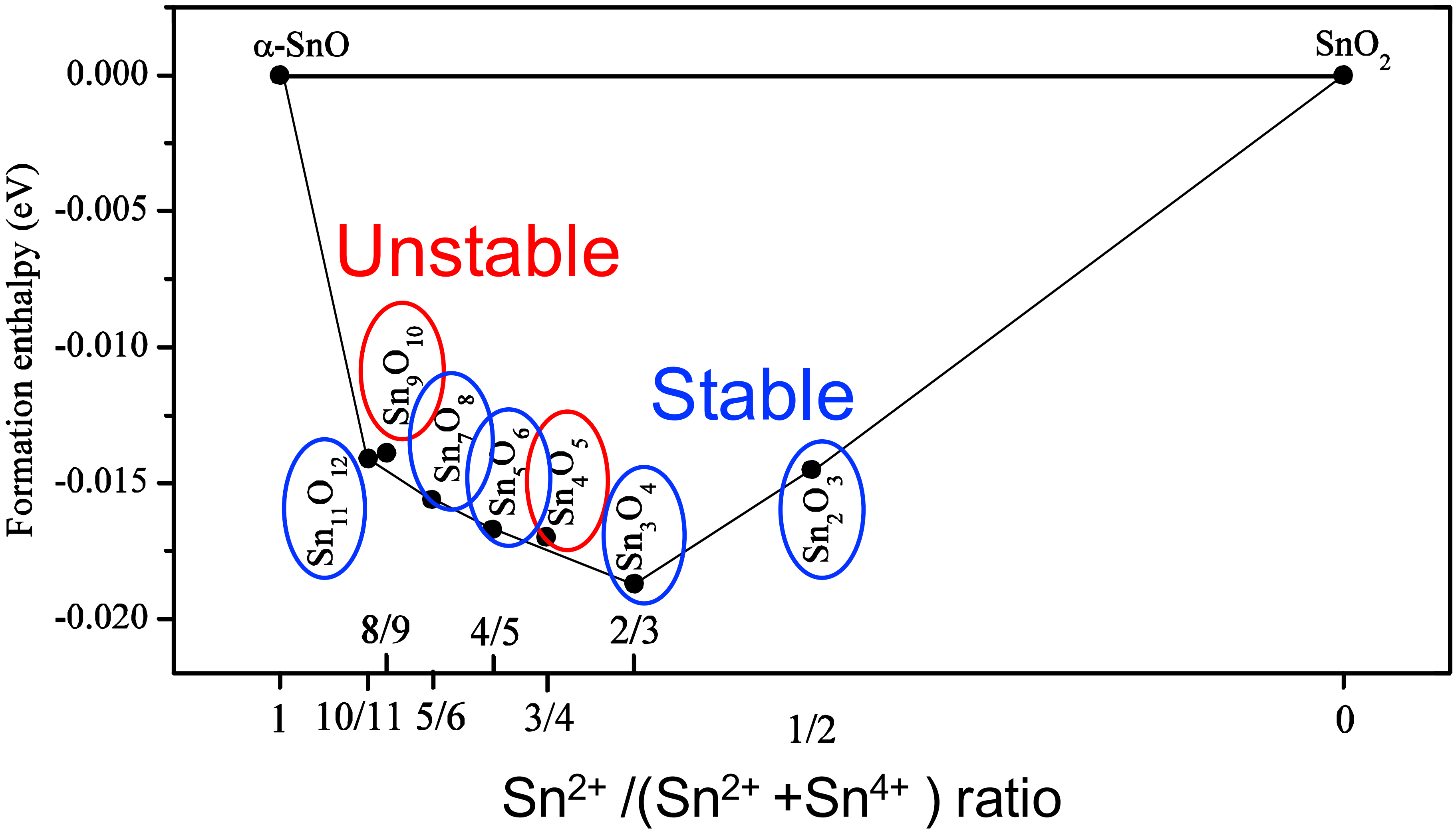
Searching conditions: Atmosphere Pressure and 0 K.



R is the ratio of $[Sn^{2+}]/([Sn^{2+}]+[Sn^{4+}])$

J. Wang, N. Umezawa*, and H. Hosono, *Adv. Energy Mater.* 2015, DOI: 10.1002/aenm.201501190.

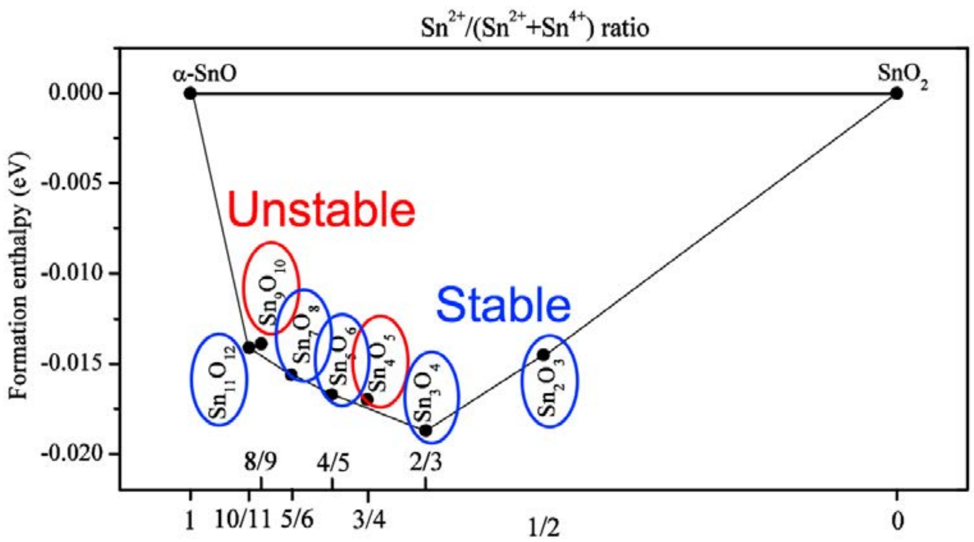
Stability of Sn_xO_y structures



J. Wang, N. Umezawa*, and H. Hosono, *Adv. Energy Mater.* 2015, DOI: 10.1002/aenm.201501190.

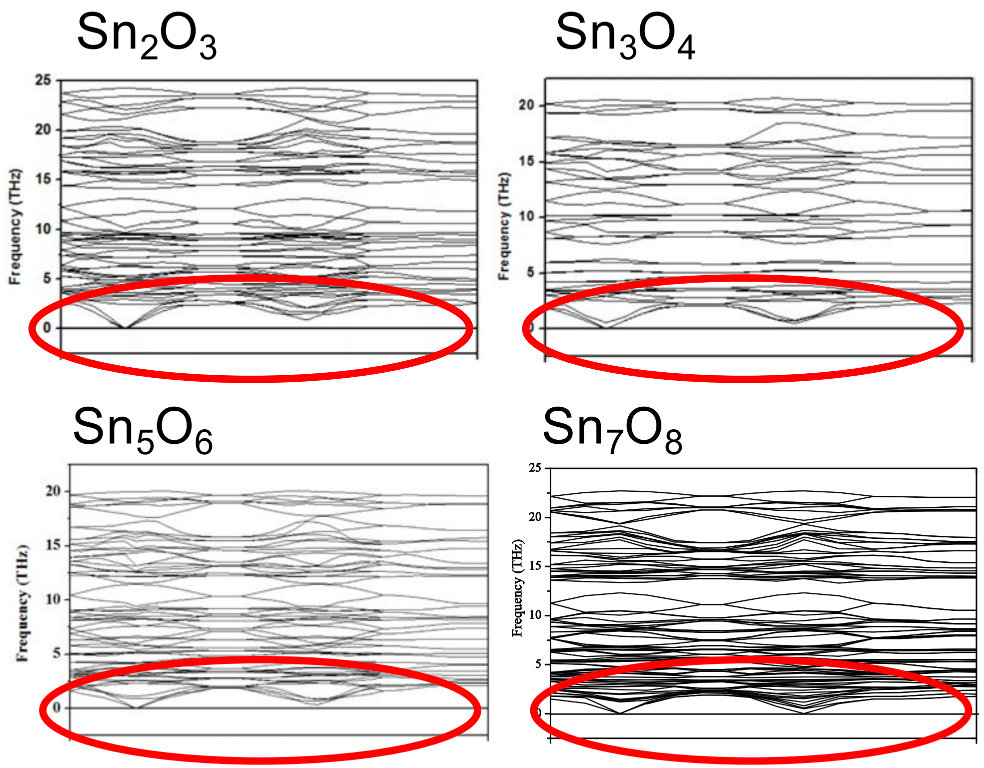
Stability of Sn_xO_y structures

Thermodynamic stability



Convex hull diagram for Sn_xO_y system

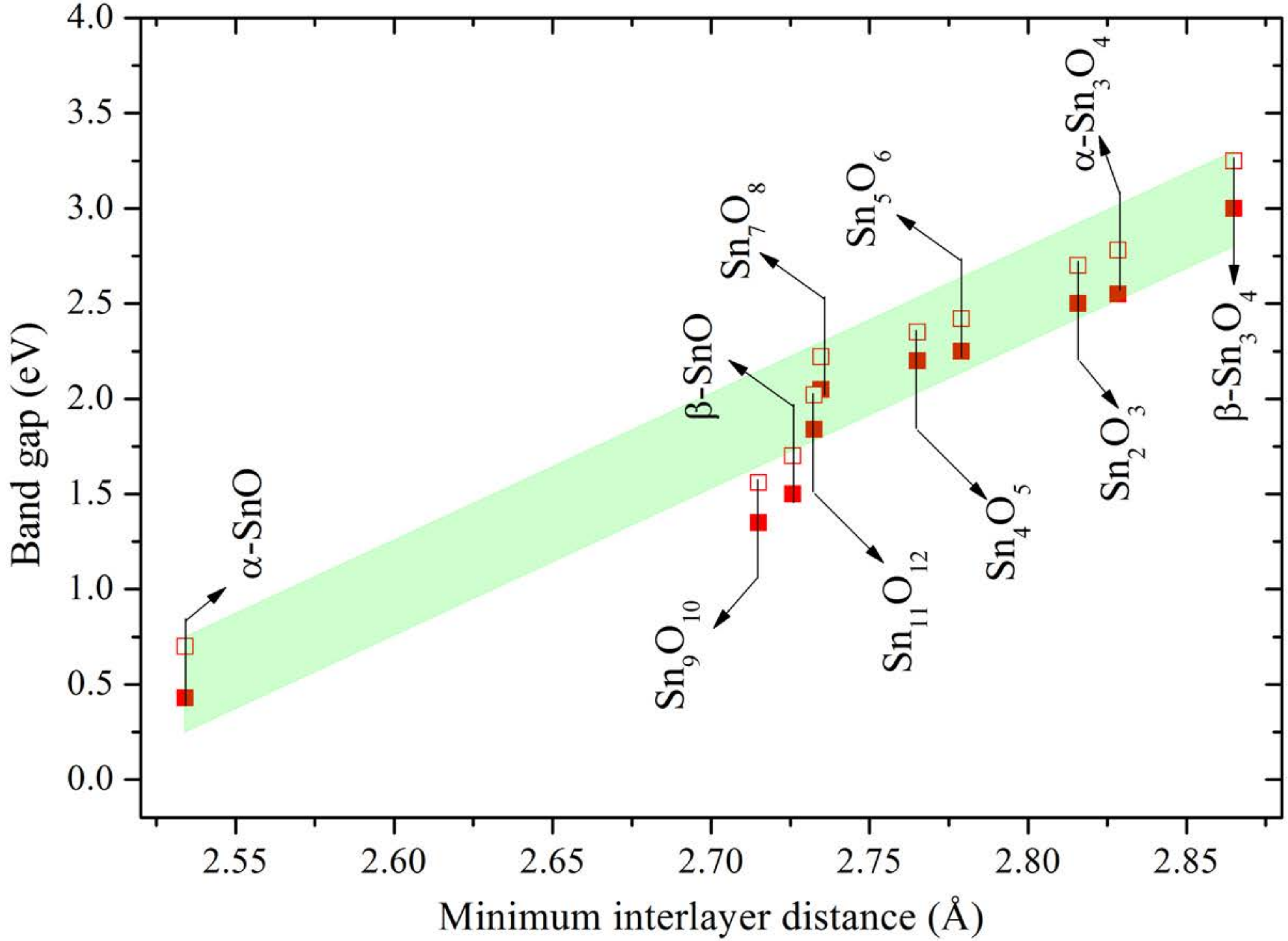
Dynamic stability



Phonon bands for Sn_xO_y system

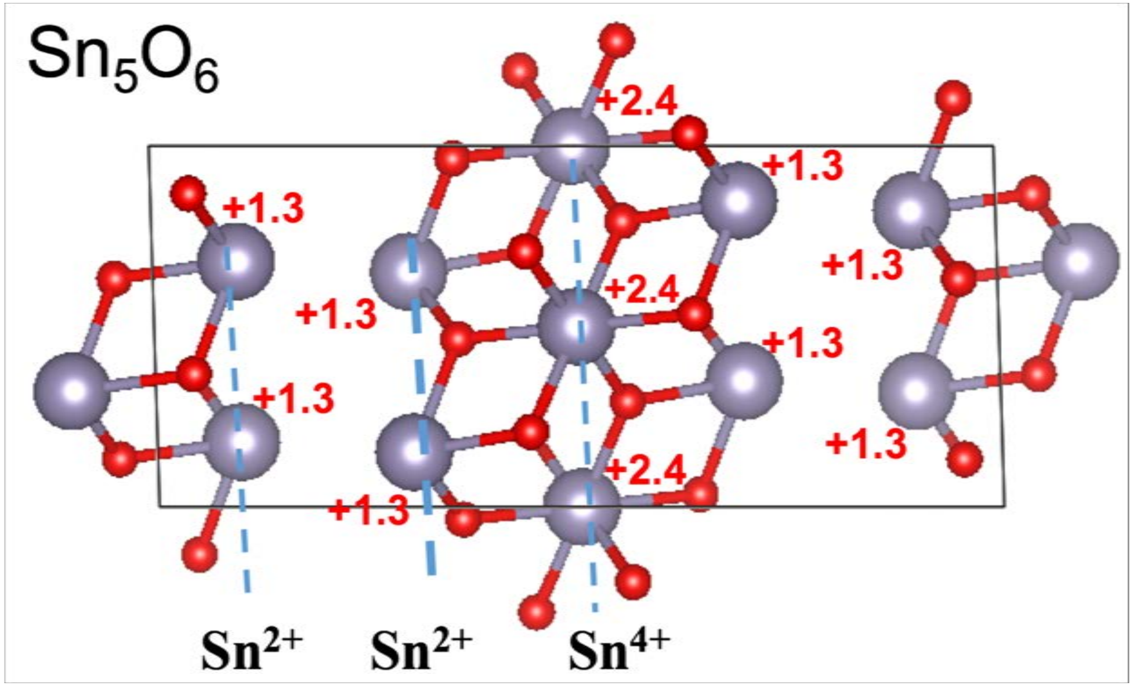
No negative frequency

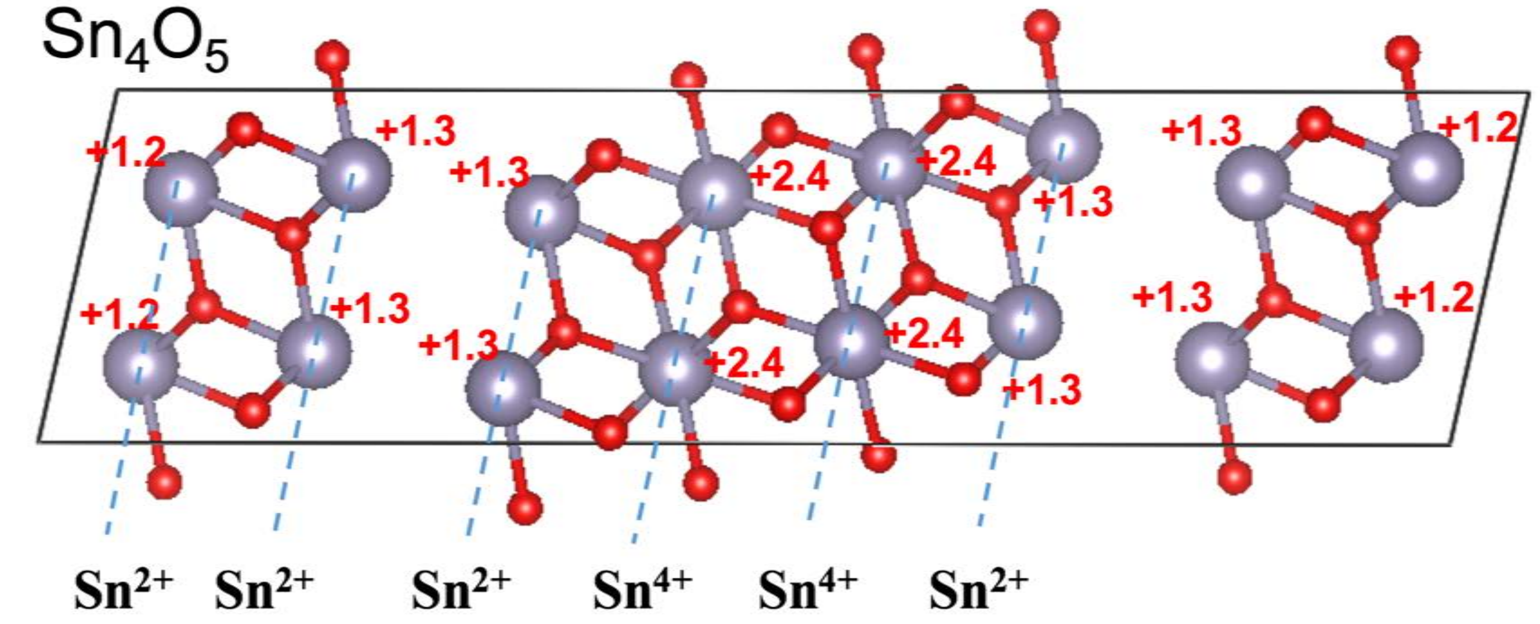
Linear dependence of the band gap on the interlayer distance



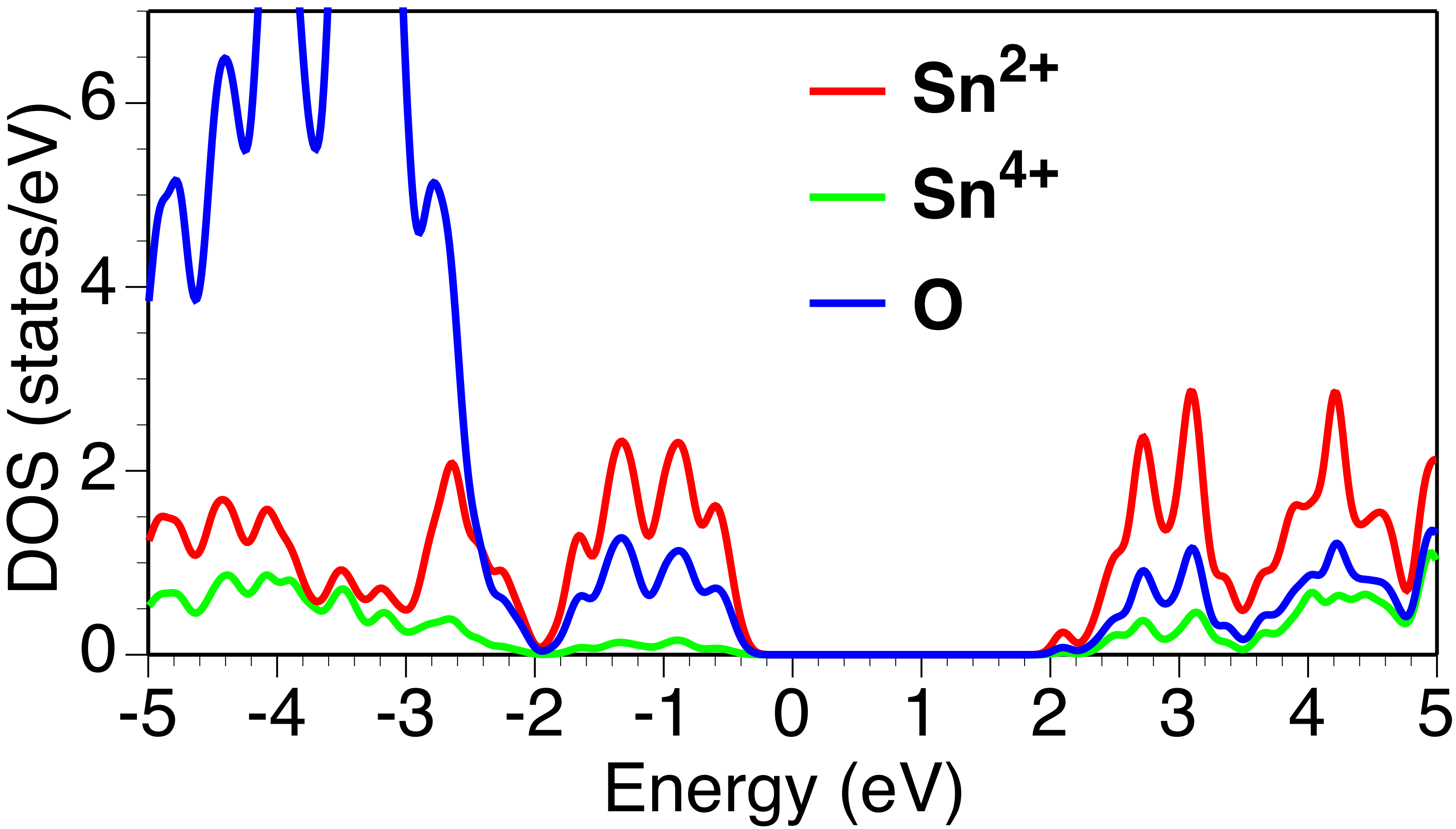
J. Wang, N. Umezawa*, and H. Hosono, *Adv. Energy Mater.* 2015, DOI: 10.1002/aenm.201501190.

Bader charge analysis to identify Sn^{2+} and Sn^{4+}



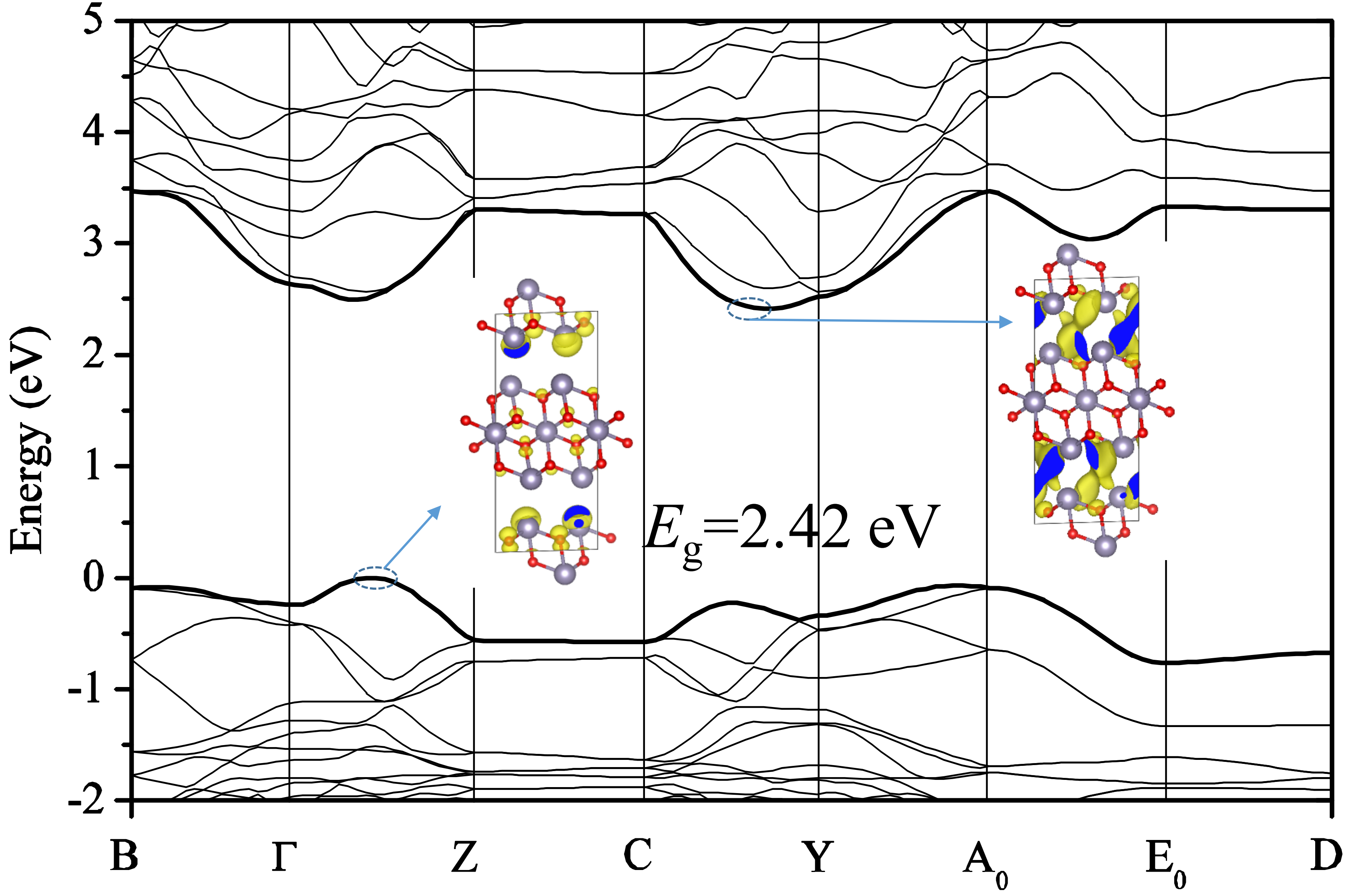


Density of states of Sn_3O_4



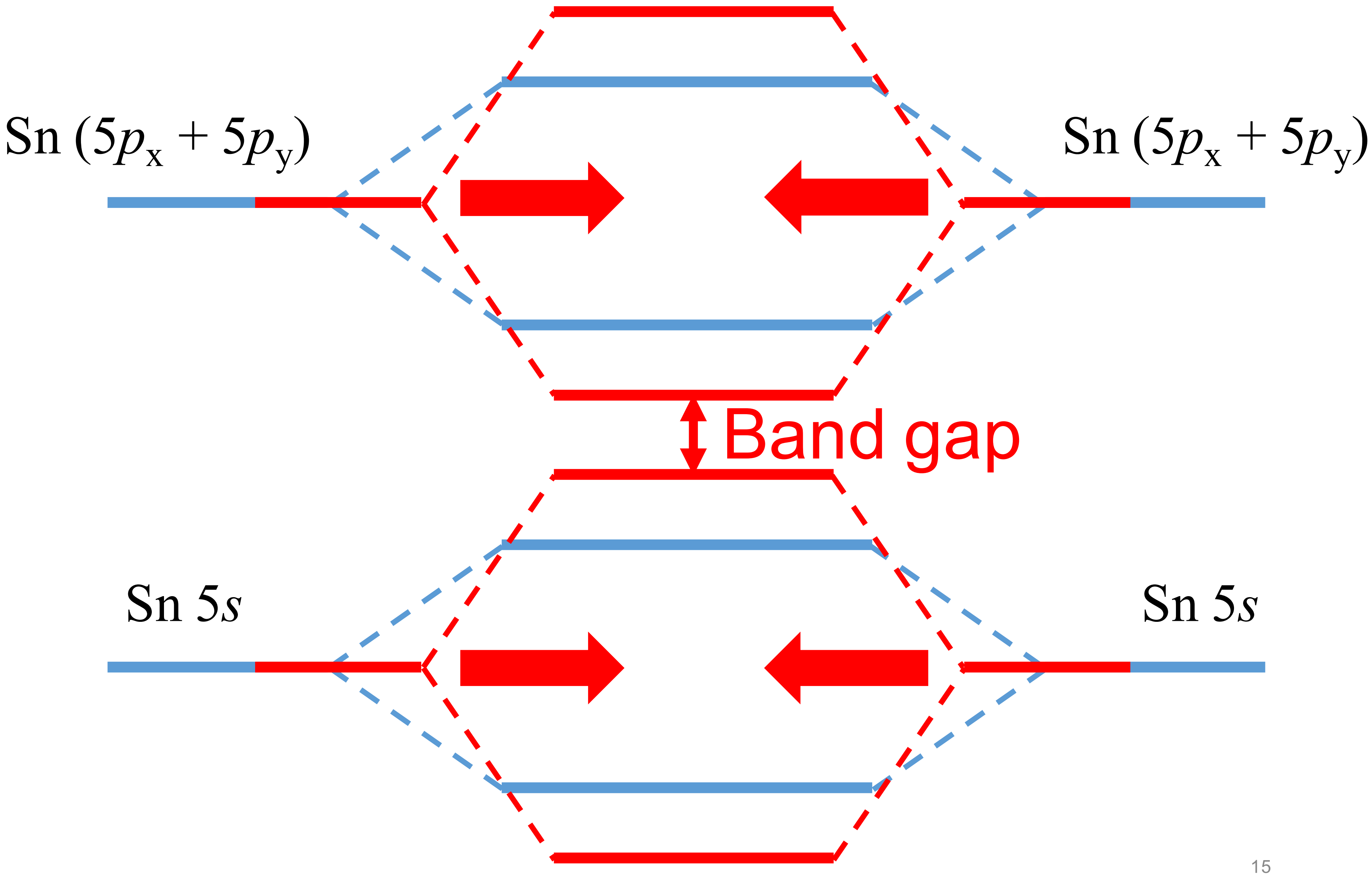
Sn^{2+} is responsible for the band edges !

Band structure of Sn_5O_6

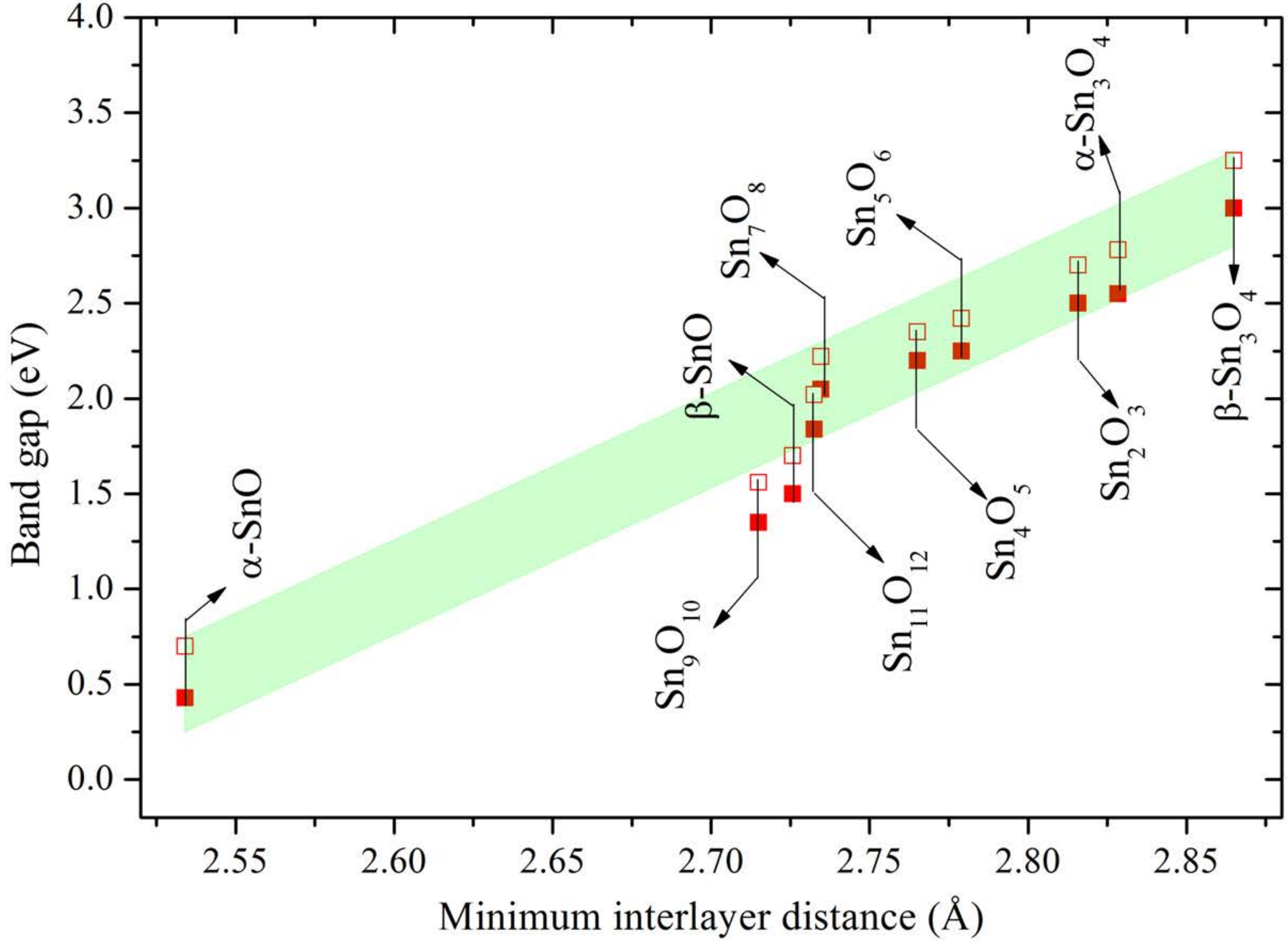


J. Wang, N. Umezawa*, and H. Hosono, *Adv. Energy Mater.* 2015, DOI: 10.1002/aenm.201501190.

Interlayer Sn^{2+} - Sn^{2+} interactions

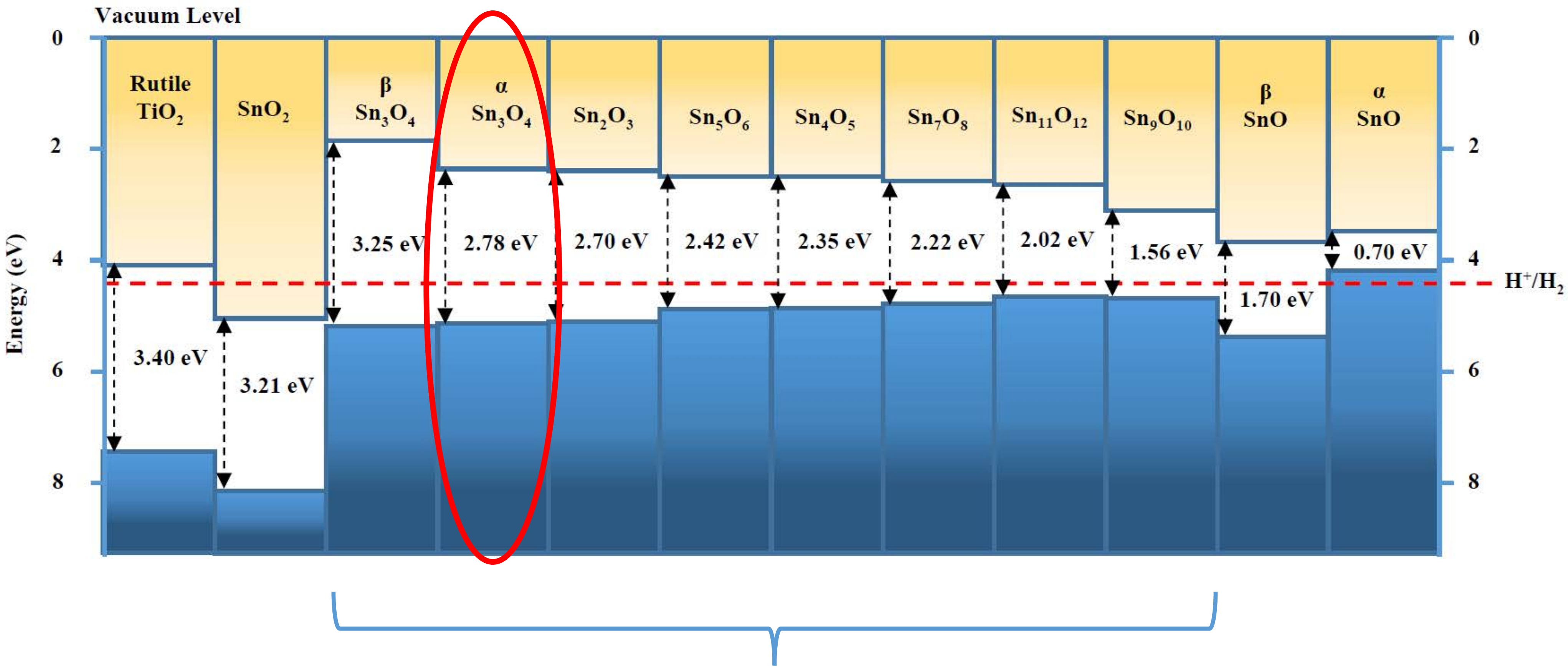


Linear dependence of the band gap on the interlayer distance



J. Wang, N. Umezawa*, and H. Hosono, *Adv. Energy Mater.* 2015, DOI: 10.1002/aenm.201501190.

Band alignment of Sn_xO_y with respect to the reduction potential of water

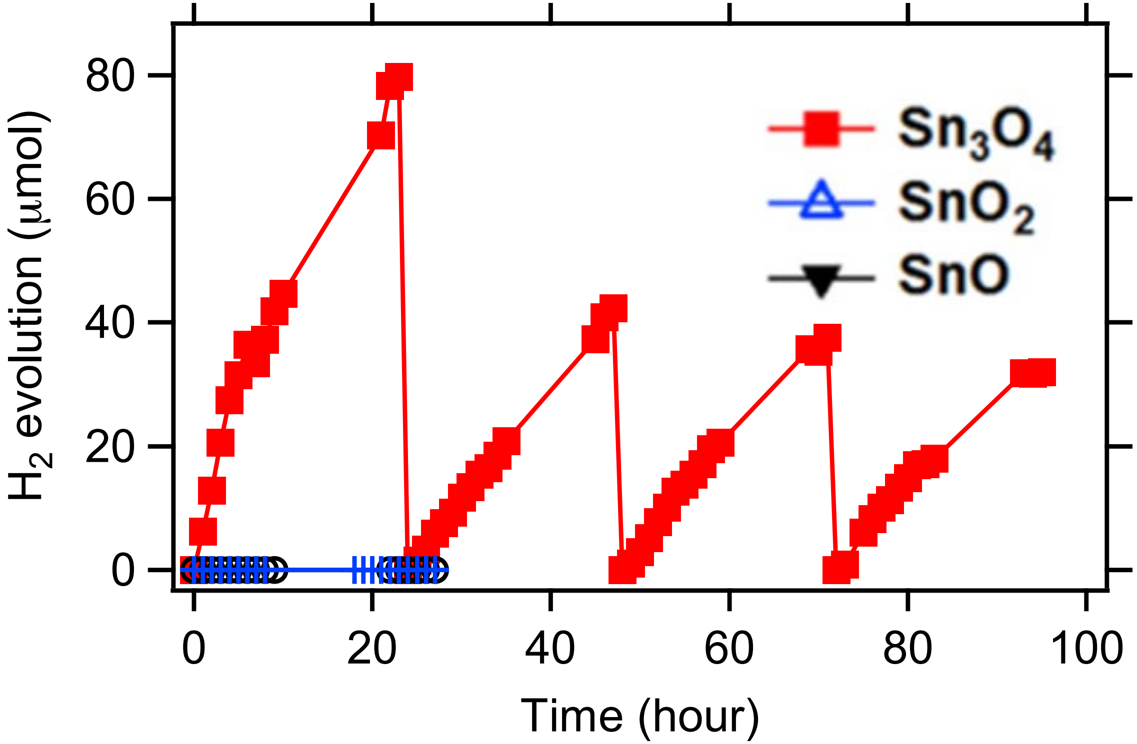


Sn_xO_y show promise as visible-light responsive photocatalysts for H_2 evolution reaction

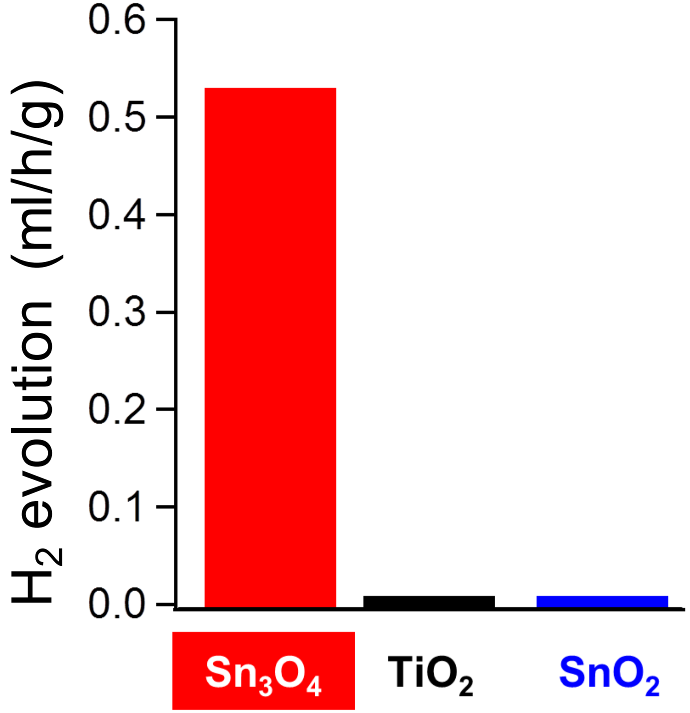
J. Wang, N. Umezawa*, and H. Hosono, *Adv. Energy Mater.* 2015, DOI: 10.1002/aenm.201501190.

H_2 evolution from methanol solution under visible light irradiation

ACS Applied Materials & Interfaces, **6**, 3790-3793, 2014.



H_2 evolution rate under the standard condition



Firstly identified material for H_2 evolution !

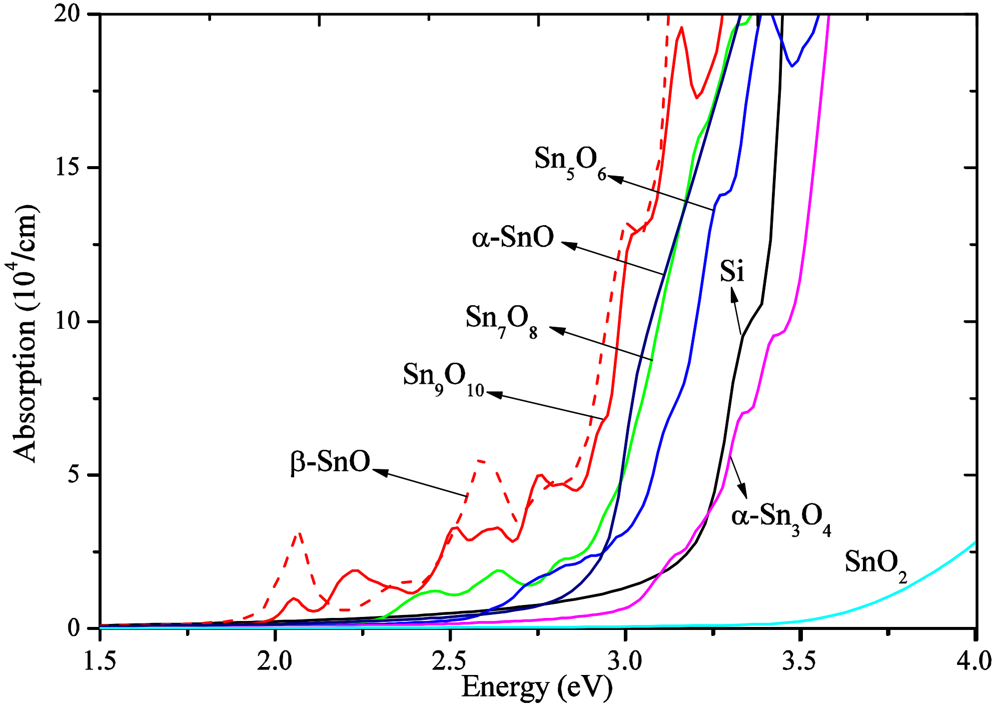
Visible-light responsive photocatalysts

Photocatalysts	**Activity (μmol/h)**	**A.Q.E. / % (around 420nm)**	**Research Group**
$CaFe_2O_4/MgFe_2O_4$	25 (0.3g cat.)	10.1	Lee J.
$WO_3/W/PbBi_2Nb_{1.9}Ti_{0.1}O_9$	15 (0.3g cat.)	6.06	Lee J.
Rh doped $SrTiO_3$	90 (0.3g cat.)	5.2	Kudo A.
Cr doped $SrTiO_3$	21 (0.2g cat.)	0.86	Our Group
Cu doped $BiTaO_4$	88 (0.1g cat.)	----	Zhang H., et. al.
Sb, Cr codoped $SrTiO_3$	78 (0.5g cat.)	----	Kudo A.
Sn^{2+} doped $KTiNbO_5$	54 (0.2g cat.)	----	Kudo A.
La,Cr codoped $SrTiO_3$	78 (0.3g cat)	4.8	Our Group
Sn_3O_4	**6.93 (0.3g cat)**		Our Group

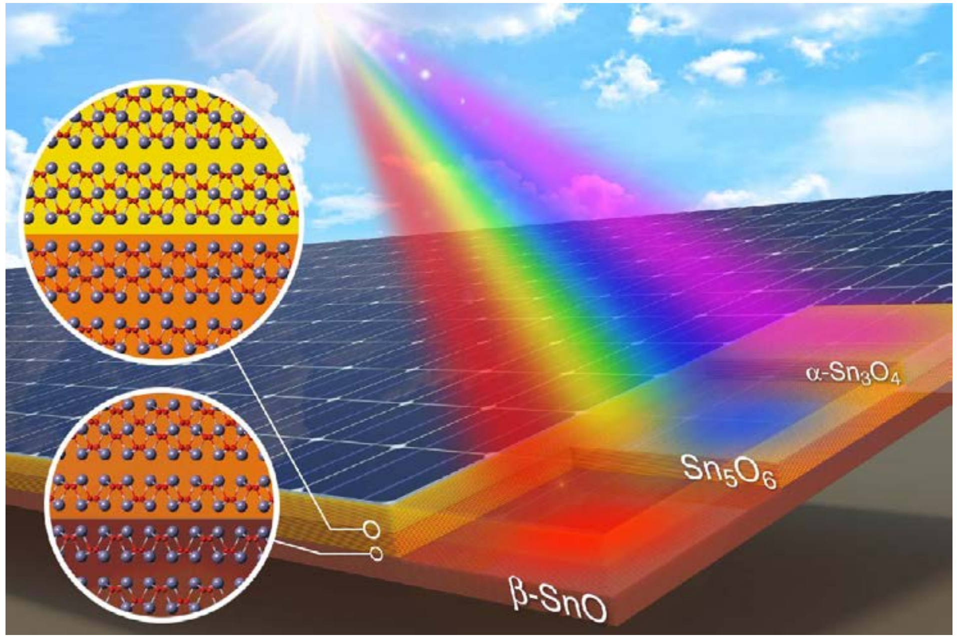
Ref.: X. Chen, et. al, *Chem. Rev*, **2010**, *110*, 6503.

Highly active earth abundant non-toxic photocatalyst !

Potential application to photoabsorber materials for solar cells



Calculated absorption coefficients of α-Sn_3O_4, Sn_5O_6, Sn_7O_8, Sn_9O_{10} and β-SnO, plotted in comparison with those of silicon, α-SnO and SnO_2 over the visible spectrum.



A proposed multilayer photoabsorber using predicted structures from the present study.

J. Wang, N. Umezawa*, and H. Hosono, *Adv. Energy Mater.* 2015, DOI: 10.1002/aenm.201501190.

Conclusion

- **Novel crystal structures** for mixed-valence Sn_xO_y have been discovered by evolutional algorithm combined with density functional calculation.
- **The band gap of Sn_xO_y linearly depends on the interlayer distance** as a result of he interactions of Sn^{2+}-Sn^{2+} at the layer surfaces.
- Our study suggests a possibility that materials properties of the newly found **van der Waals Sn_xO_y can be controlled by adjusting their layer compositions**.

Acknowledgements

Maidhily Manikandan, Toyokazu Tanabe, Peng Li, Shigenori Ueda, Gubbala V. Ramesh, Rajesh Kodiyath, Toru Hara, Arivuoli Dakshanamoorthy, Shinsuke Ishihara, Katsuhiko Ariga, Jinhua Ye, and Hideki Abe,

Artem R. Oganov and Qiang Zhu, The State University of New York at Stony Brook, USA.

Qingfeng Zeng, Northwestern Polytechnical University, China.

JW is supported by the Japan Society for the Promotion of Science (JSPS). This work is also partly supported by the Japan Science and Technology Agency (JST) Precursory Research for Embryonic Science and Technology (PRESTO) program and by the World Premier International Research Center Initiative on Materials Nanoarchitectonics (MANA), MEXT. HH acknowledges the support by the MEXT Element Strategy Initiative to form core research centers.