Morphology control of TaC nanoparticles via surface doping

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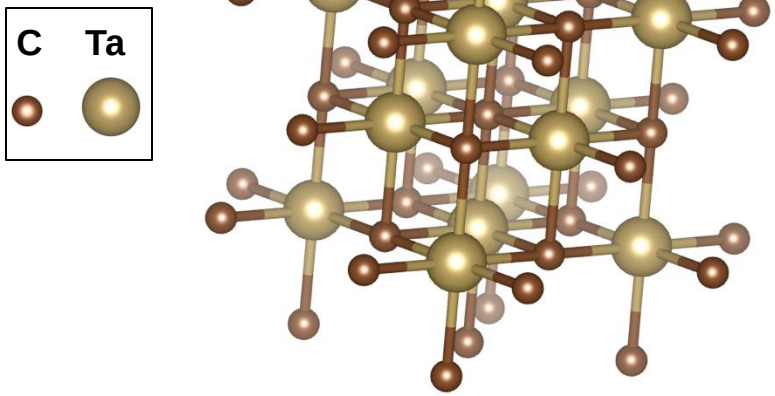
Kelly, J. P., Kanakala, R., & Graeve, O. A. (2010). A solvothermal approach for the preparation of nanostructured carbide and boride ultra-high-temperature ceramics. *Journal of the American Ceramic Society*, *93*(10), 3035–3038. https://doi.org/10.1111/j.1551-2916.2010.04007.x

UHTC nanoparticles

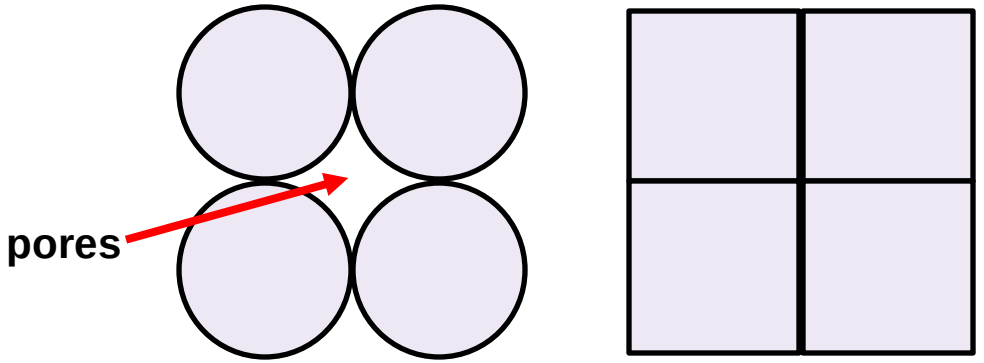
TaC:

- **Rock-salt ($Fm\bar{3}m$)**
- **Ultrahigh temperature ceramic**
- **T_m=4100 K**
- **Covalent+metallic bonds**

TaC coated graphite

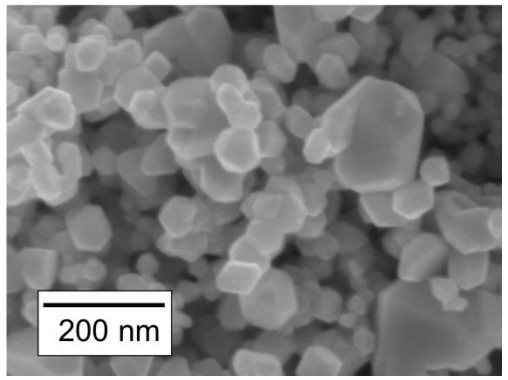


Sintering

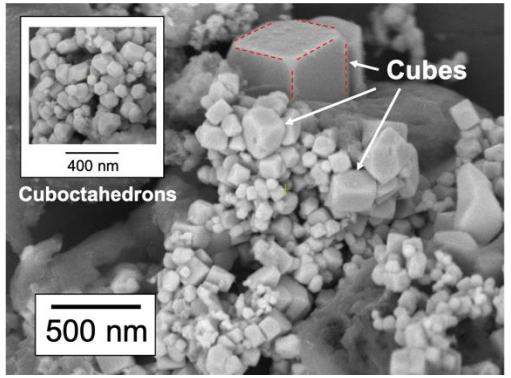


Doping induced morphology

No dopants

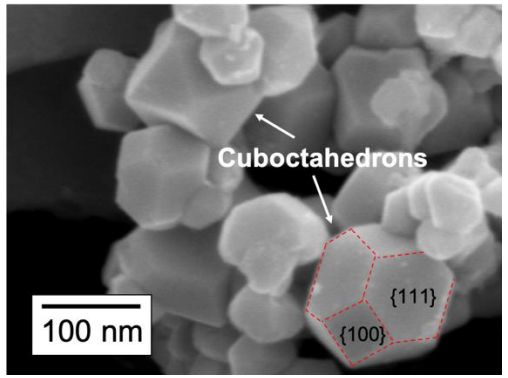


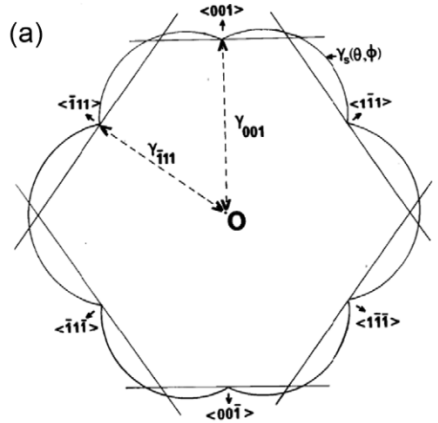
X = Fe



- **Adsorption?**
- **Segregation?**
- ***p-d* hybridization?**
- **Others?**

X = Ni

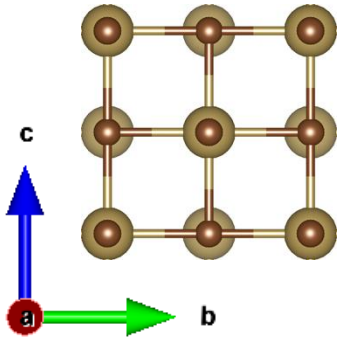




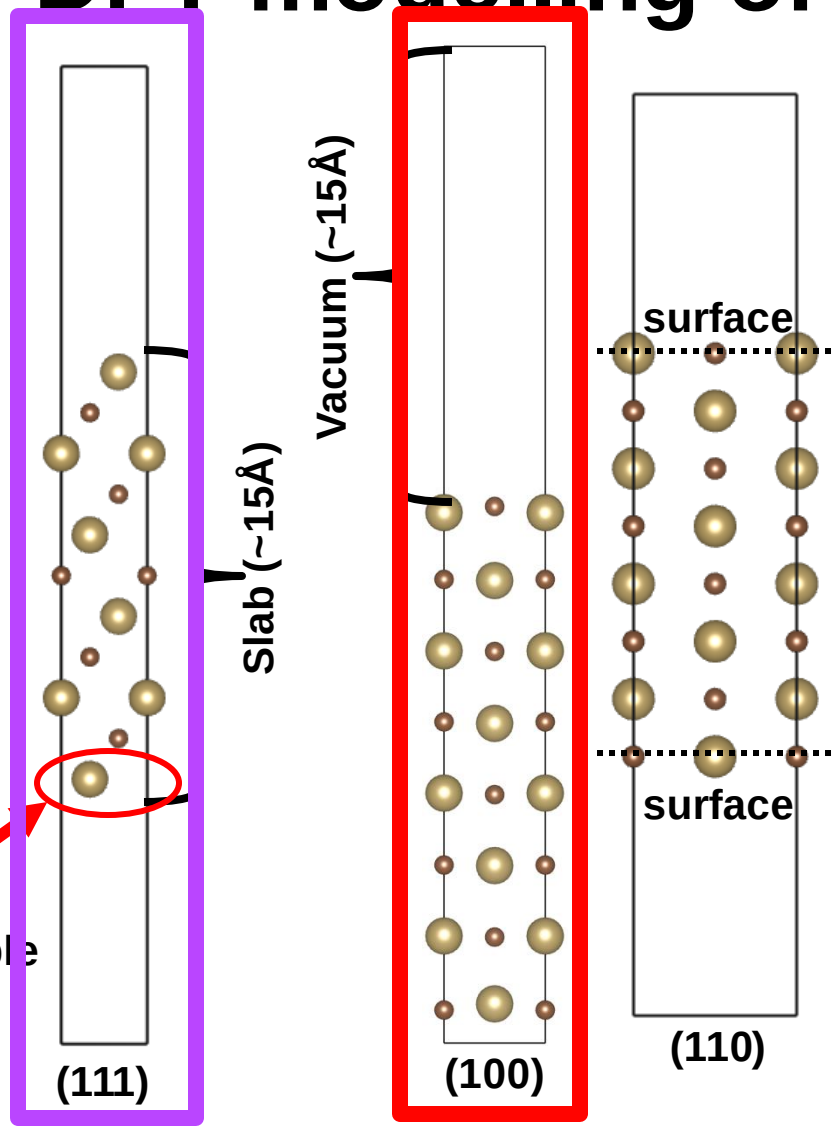
G. Wulff (1901). Zeitschrift für Krystallographie und Mineralogie. 34 (5/6): 449–530.

DFT modelling of TaC surfaces

DFT parameters:
- VASP
- GGA(PBE)

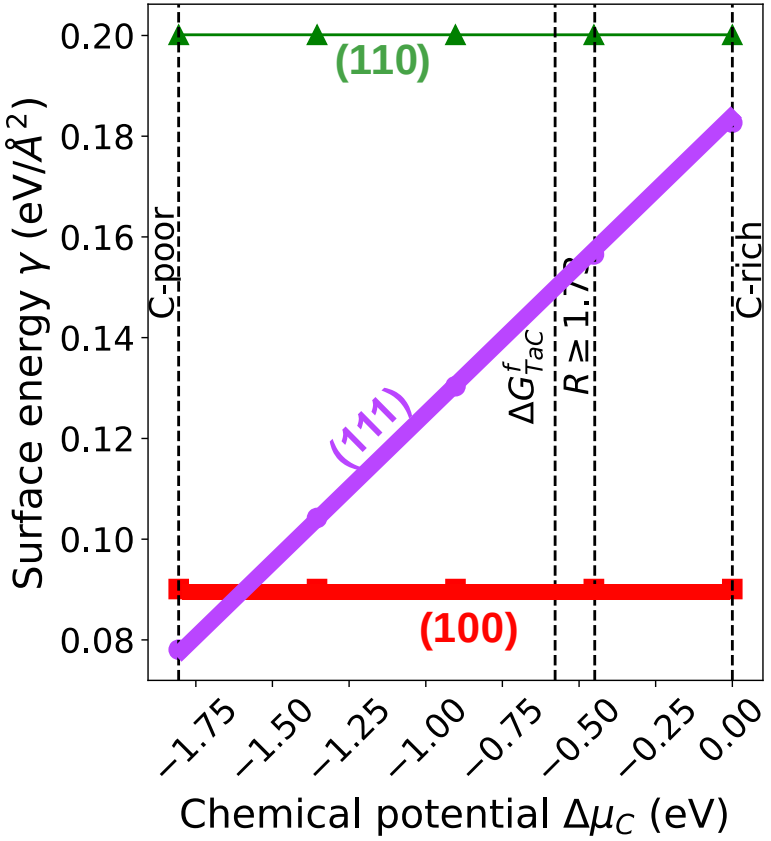


TaC conventional unit cell

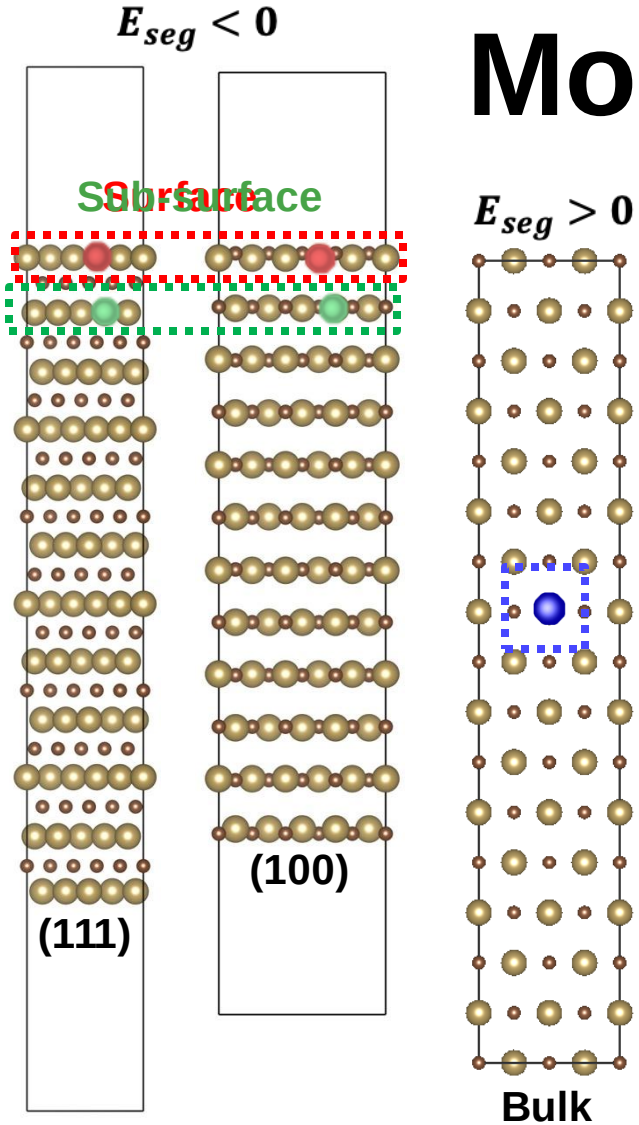


Several possible terminations

$$\gamma = \frac{E^{slab} - \sum_i N_i \mu_i}{2A}$$



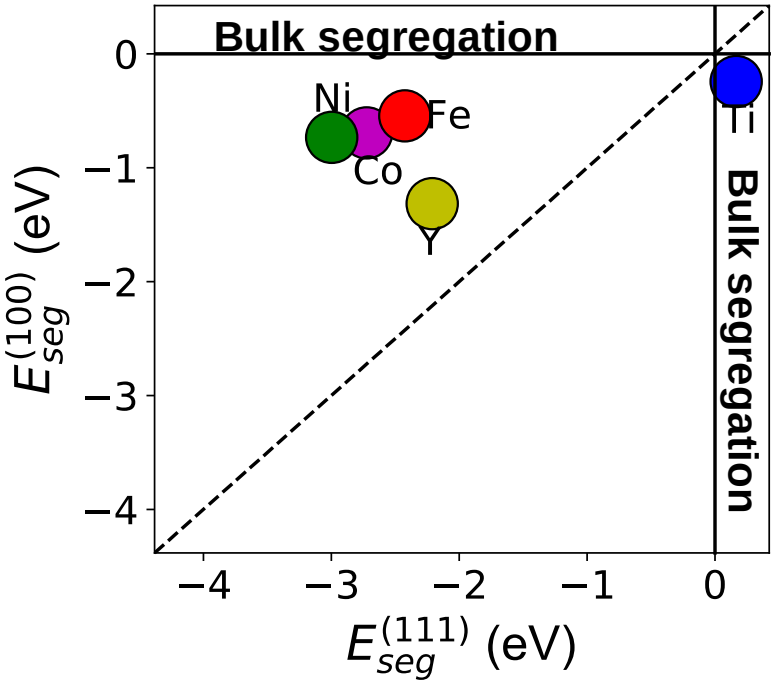
Modelling surface doping

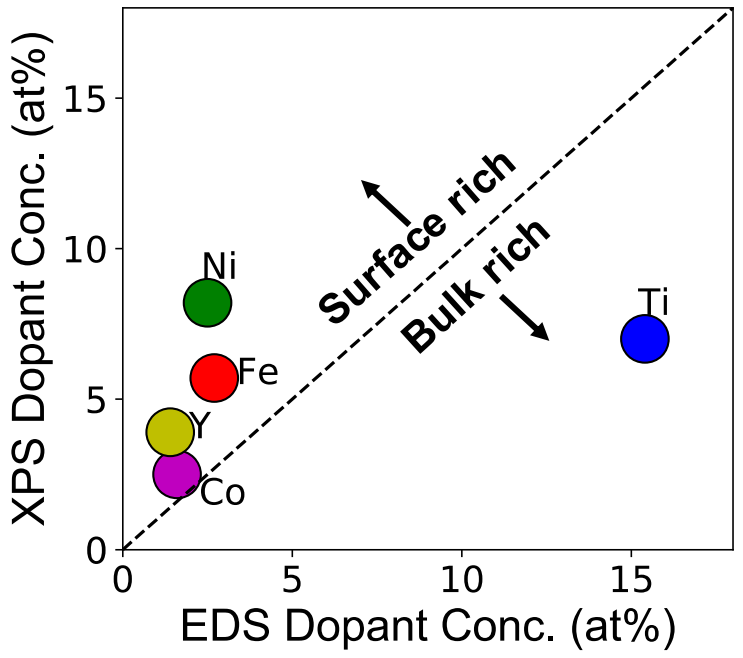


Segregation energy:

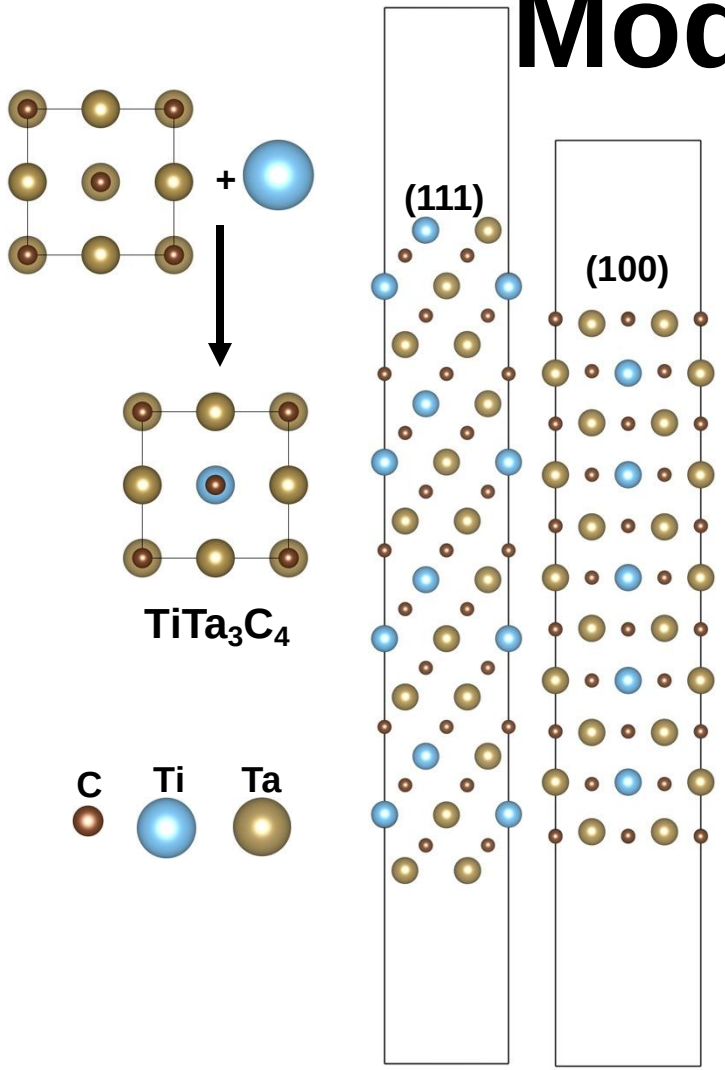
$$E_{seg} = \left(E^{X}_{slab} - E_{slab}\right) - \left(E^{X}_{bulk} - E_{bulk}\right)$$

Dopants: Ti, Y, Ni, Co, Fe





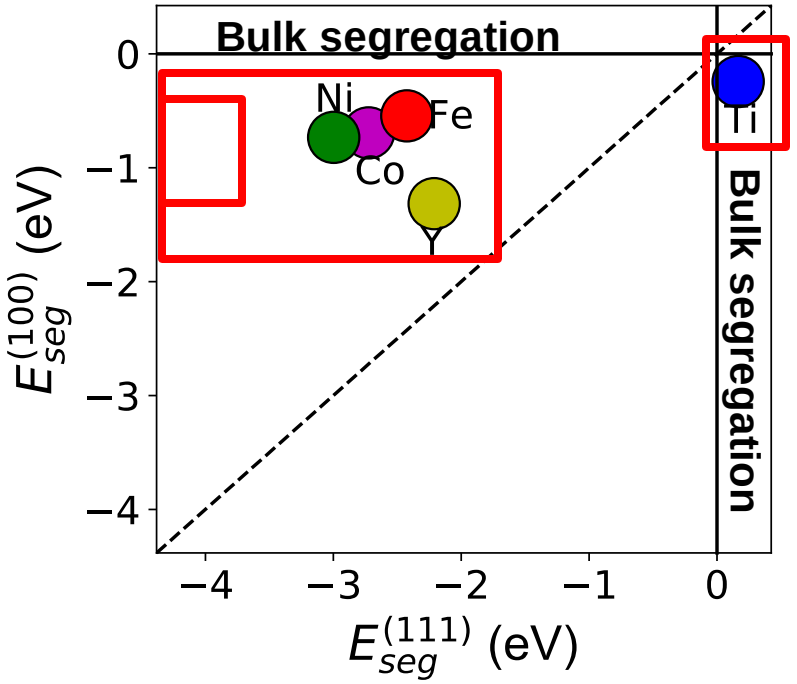
Modelling surface doping

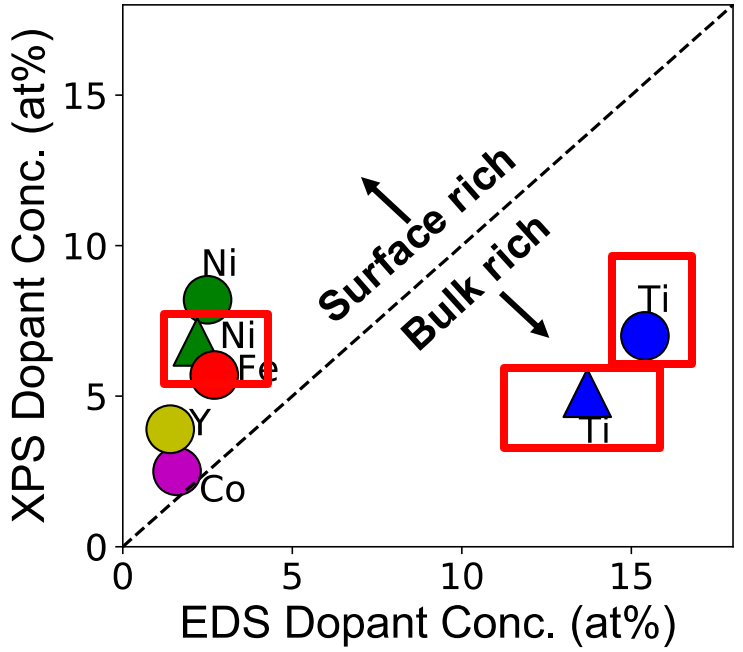


Segregation energy:

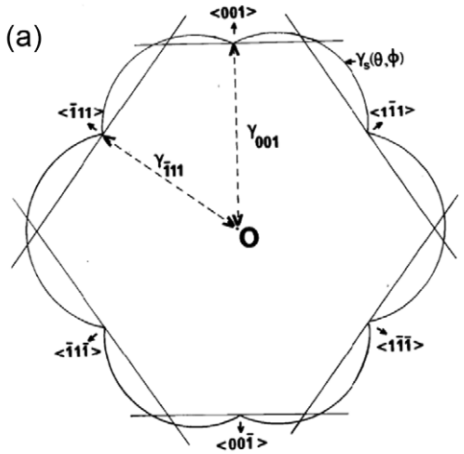
$$E_{seg} = \left(E^{X}_{slab} - E_{slab}\right) - \left(E^{X}_{bulk} - E_{bulk}\right)$$

Dopants: Ti, Y, Ni, Co, Fe, Ni-Ti co-doping





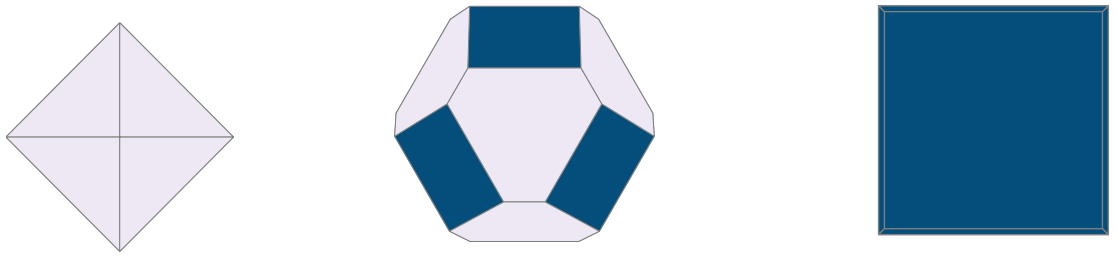
Surface energy and Wulff shape



G. Wulff (1901). Zeitschrift für Krystallographie und Mineralogie. 34 (5/6): 449–530.

(100) (111)

R=0.58 **R=1** **R=1.73**

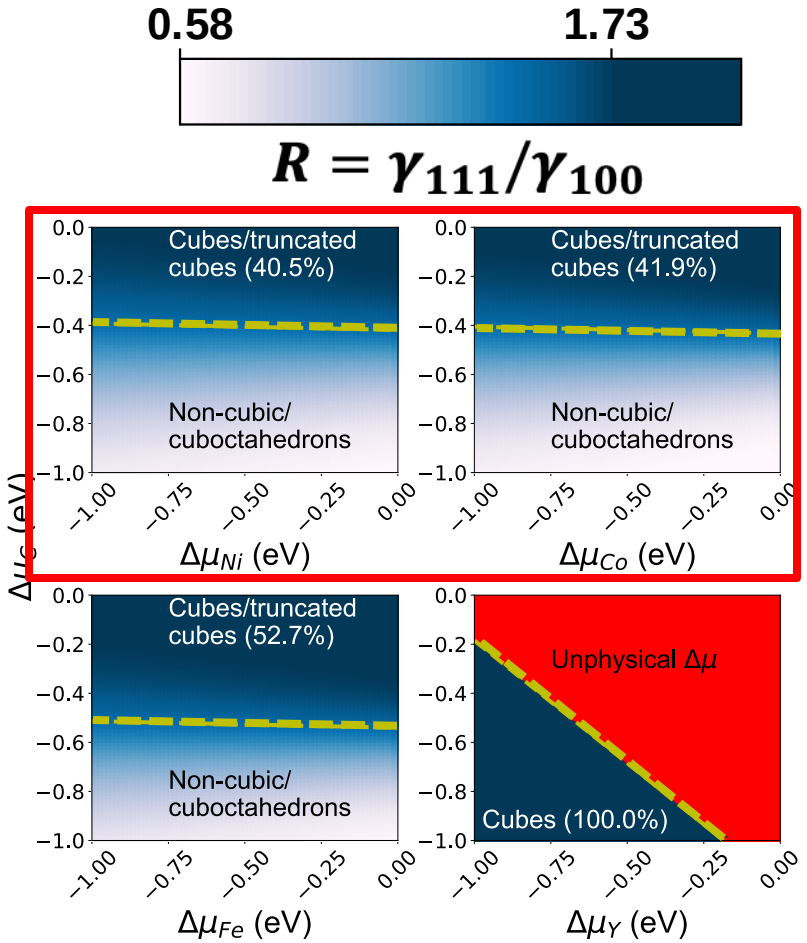


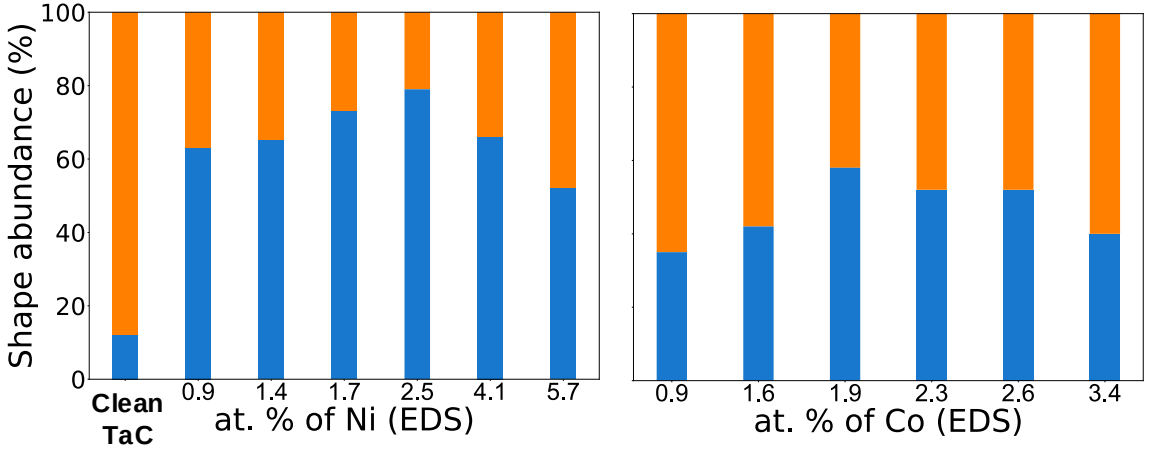
- **Surface energy:**

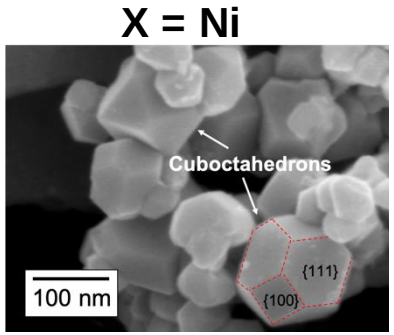
$$\gamma = \gamma(\mu_C, \mu_X) = \frac{E_{slab} - \sum_i N_i \mu_i}{2A}$$

- **NP morphology is a function of γ_{111} and γ_{100}**
- **We define a shape by a geometric ration: $R = \frac{\gamma_{111}}{\gamma_{100}}$**
- **As such: R is a function of $R = R(\mu_C, \mu_X)$**

Morphology enthalpy map



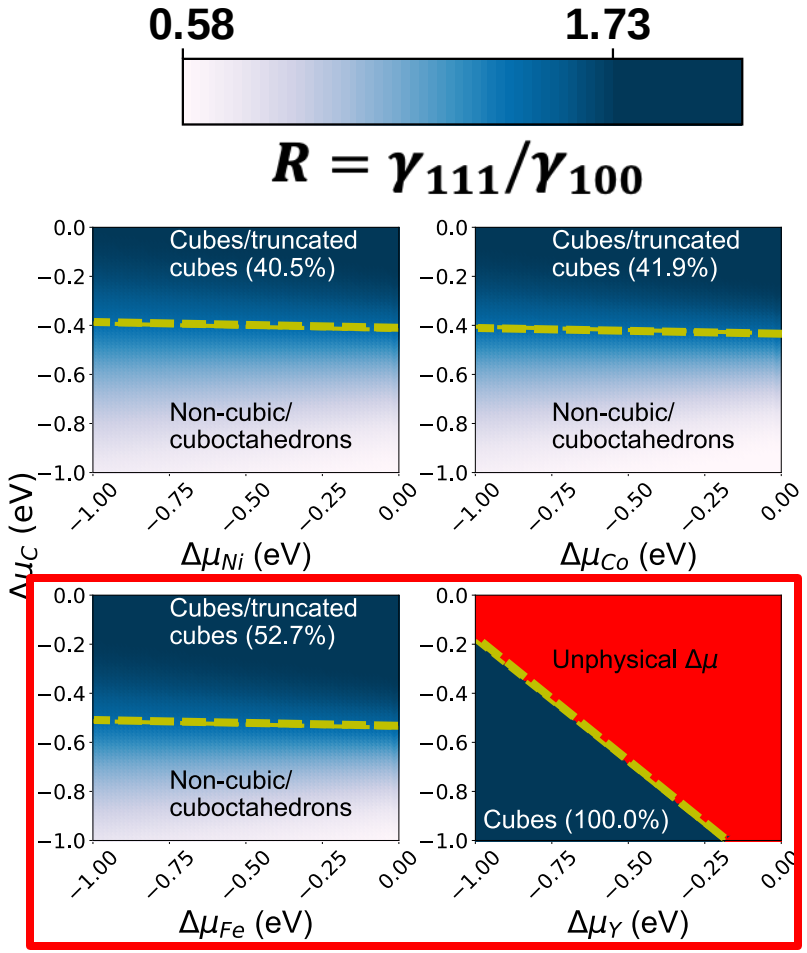


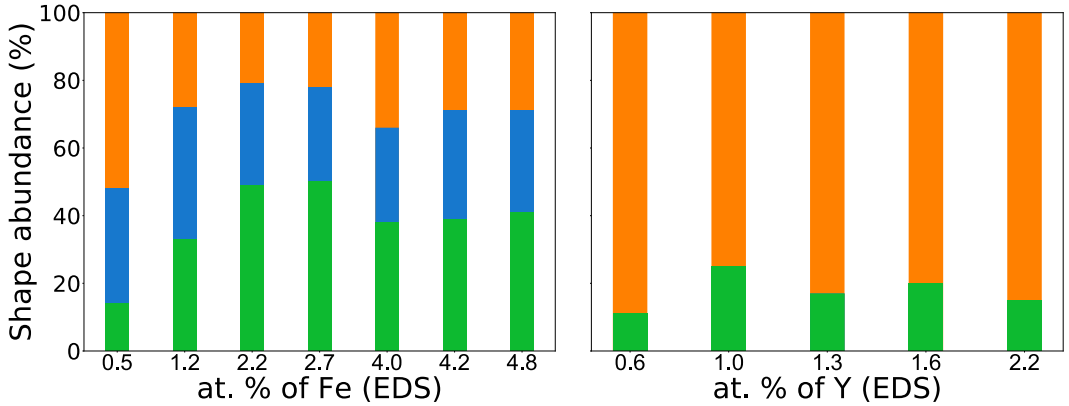


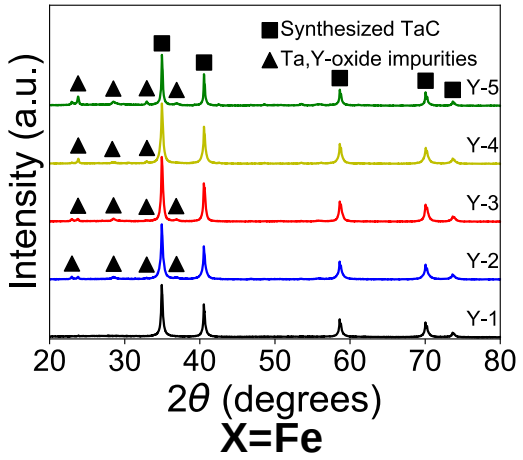
No-faceting

Non-cubic / Cuboctahedrons

Morphology enthalpy map





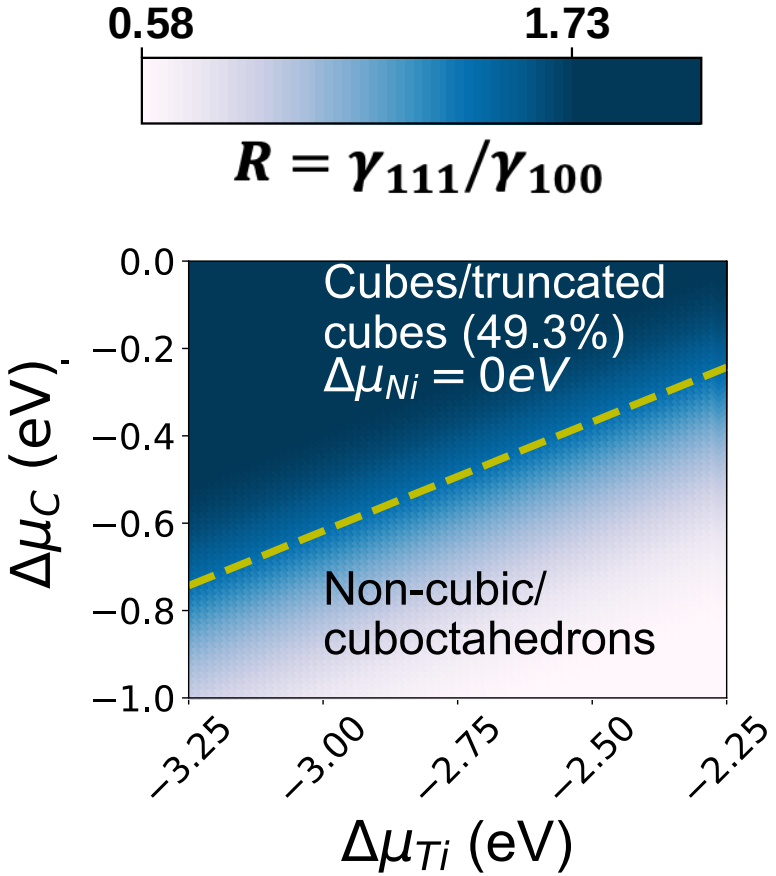


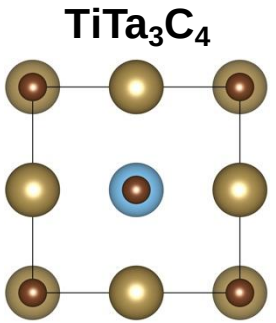
No-faceting

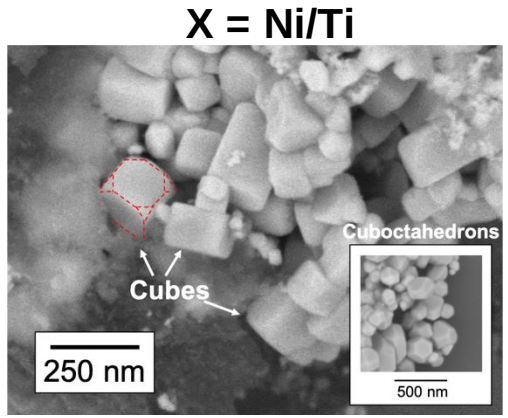
Non-cubic / Cuboctahedrons

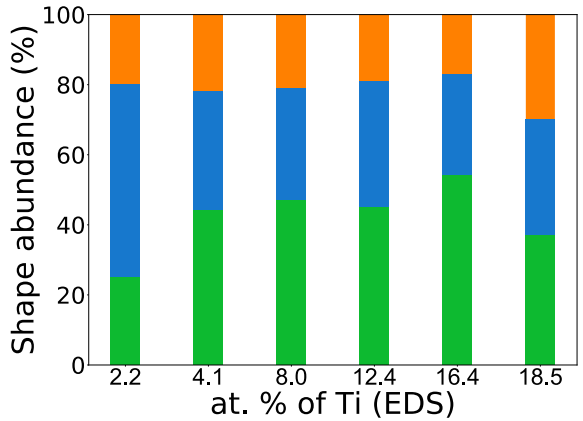
Cubes

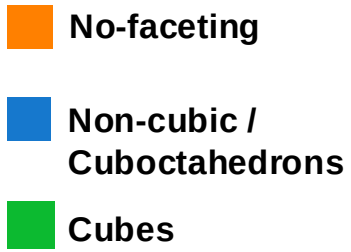
Morphology enthalpy map



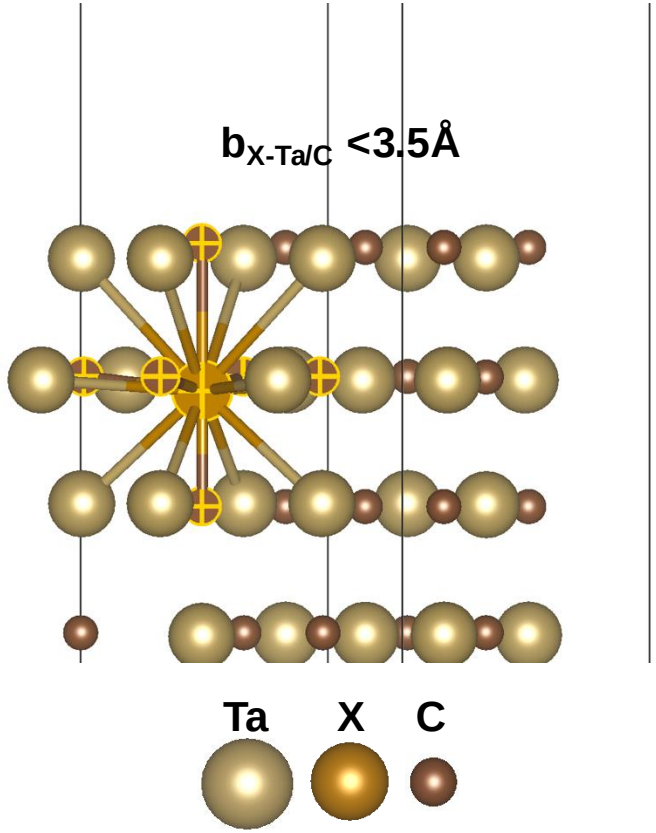


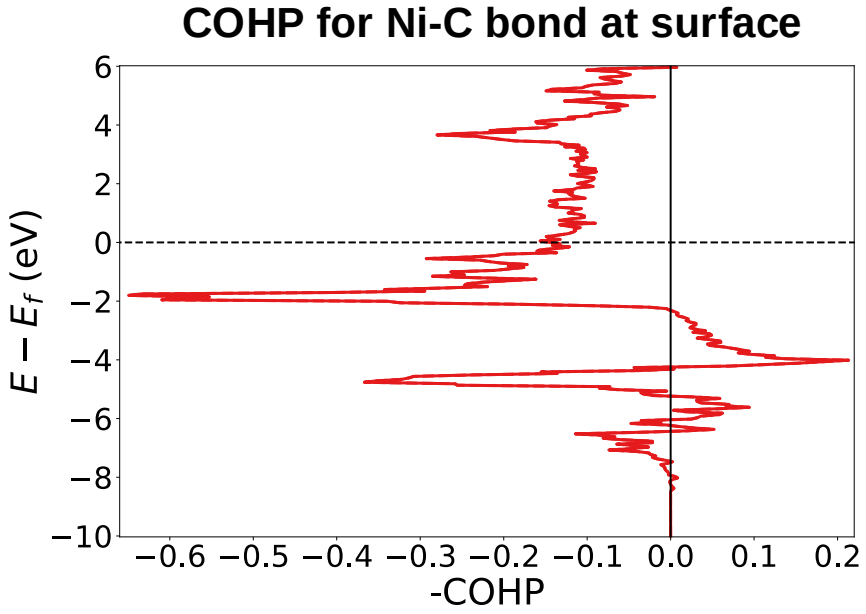






Integrated Crystal Orbital Hamilton Populations





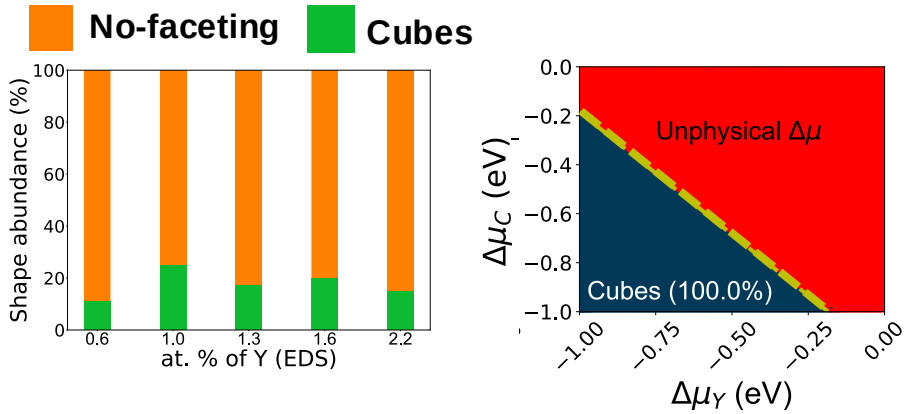
$$\%Covalency = \frac{ICOHP_{X-C}}{ICOHP_{X-Ta} + ICOHP_{X-C}}$$

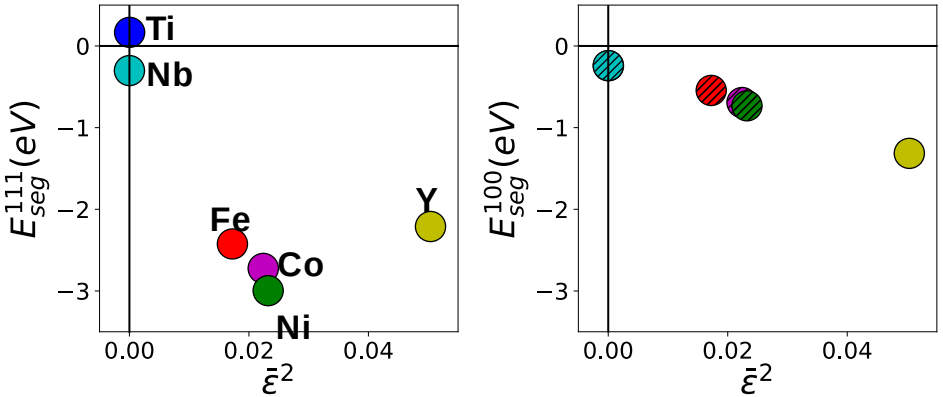
$$\%Metallicity = \frac{ICOHP_{X-Ta}}{ICOHP_{X-C} + ICOHP_{X-Ta}}$$

Dopant	(hkl)	% covalency
Co	(111)	50.30
	(100)	54.54
Fe	(111)	49.67
	(100)	54.55
Ni	(111)	45.90
	(100)	41.39
Ni*	(111)	46.18
	(100)	53.27
Y	(111)	46.12
	(100)	42.73

*Ni in $TiTa_3C_4$

Atomic Strain effect



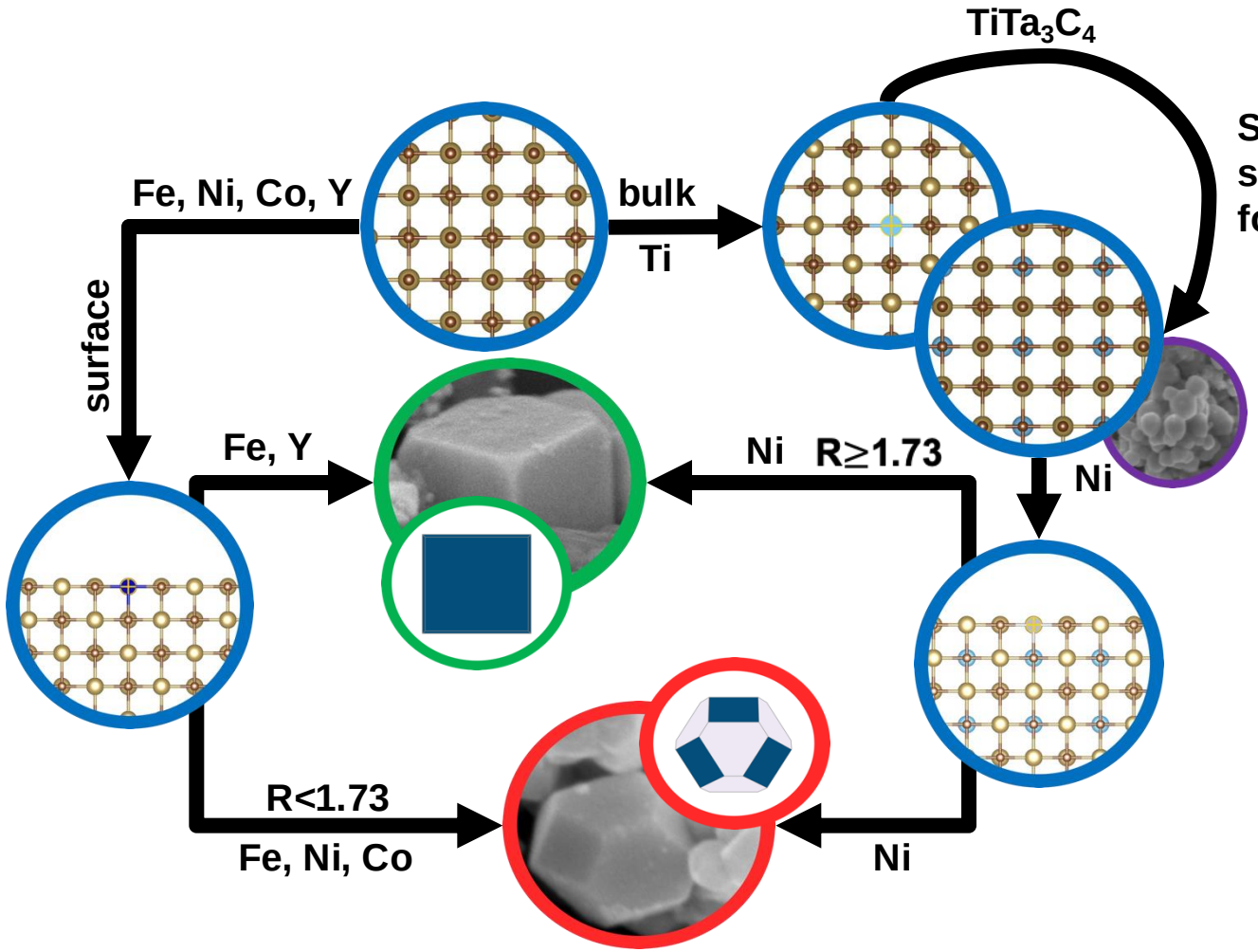


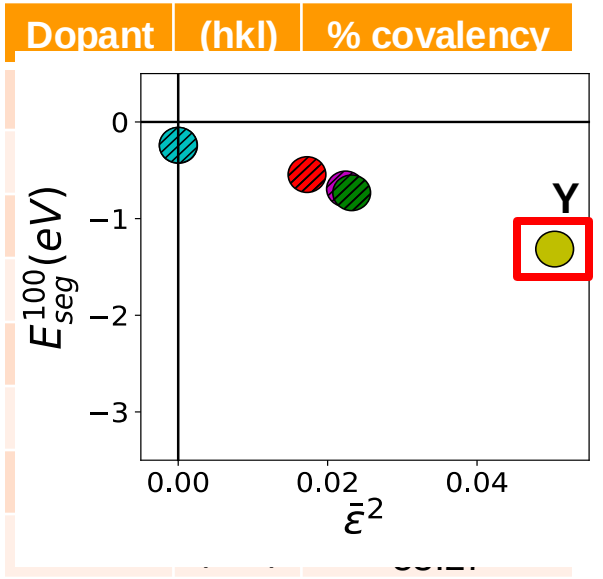
Sub surface
Surface

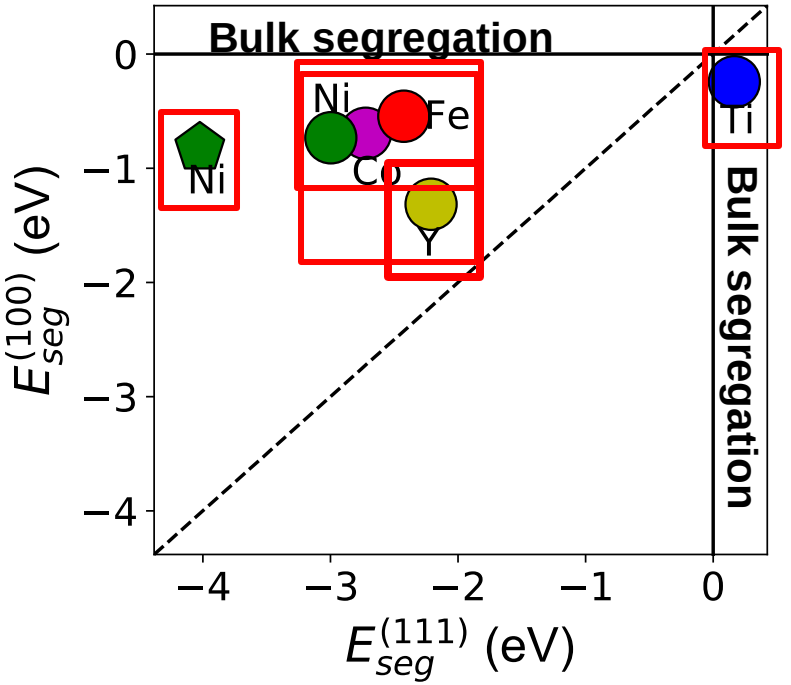
Dopant	(hkl)	% covalency
Co	(111)	50.30
	(100)	54.54
Fe	(111)	49.67
	(100)	54.55
Ni	(111)	45.90
	(100)	41.39
Ni*	(111)	46.18
	(100)	53.27
Y	(111)	46.12
	(100)	42.73

Atomic strain: $\bar{\epsilon}^2 = \left(\frac{\epsilon_{Ta} - \epsilon_X}{\epsilon_{Ta}}\right)^2$

Summary


$TiTa_3C_4$
Solid solution formation
Fe, Ni, Co, Y
bulk
Ti
surface
Fe, Y
Ni R≥1.73
Ni
R<1.73
Fe, Ni, Co
Ni


Dopant
(hkl)
% covalency
$E_{seg}^{100}(eV)$
$\bar{\varepsilon}^2$
Y


Bulk segregation
$E_{seg}^{(100)}$ (eV)
$E_{seg}^{(111)}$ (eV)
Ni
Fe
Co
Y
Ti
Bulk segregation

Acknowledgements

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materials virtual·lab

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ARL

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- **Mr. Sebastian Lee**

National Autonomous University of Mexico: Nanostructures Laboratory. Dep. Of Physics

Prof. Manuel Herrera

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