ME4252 Nanomaterials for Energy Engineering

Size Effect on Transport and Thermodynamics

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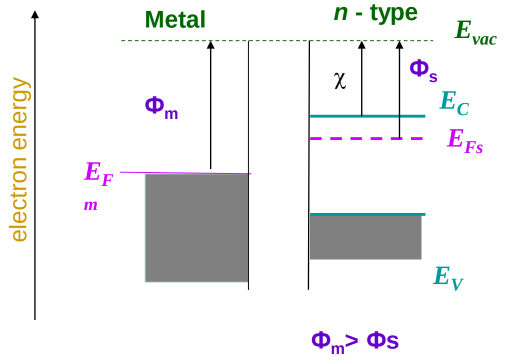
Recall- Schottky barrier

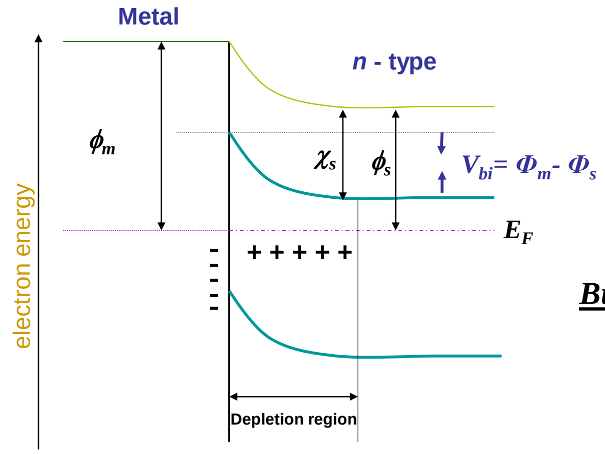
Schottky barrier is formed between a metal and a *n* - or *p* - semiconductor when are brought into contact, such that

$\Phi_m > \Phi_s$



Energy band diagram of the metal and the semiconductor in isolation

Recall - Schottky barrier (in dark)



Built-in voltage

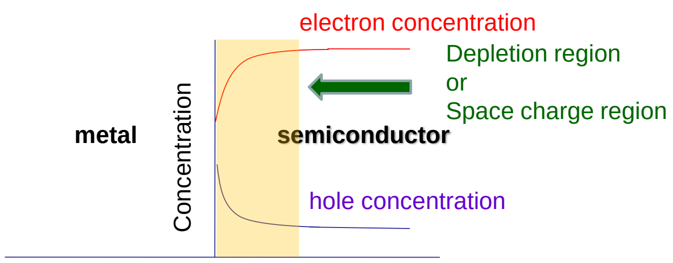
$V_{bi} = \Phi_m - \Phi_s$

Energy band diagram of a metal-semiconductor contact in thermal equilibrium, in the dark

Concentration profile at Schottky barrier

Concentration profile

$$n = N_c e^{-(E_c - E_F)/k_B T}$$
$$p = N_v e^{-(E_F - E_v)/k_B T}$$

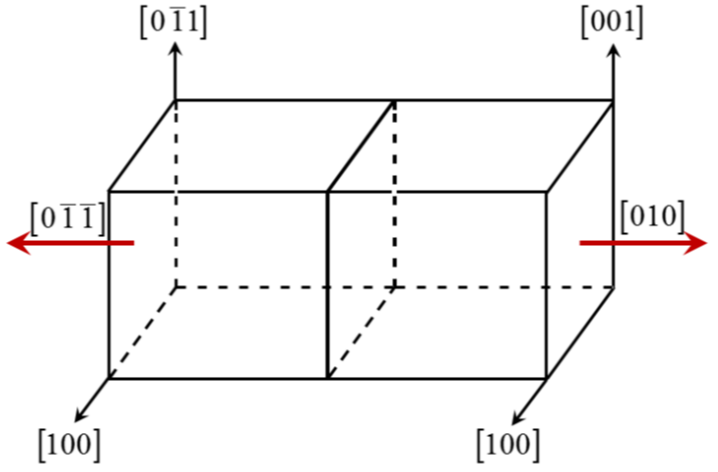


By joining metal and semiconductor we set up an electric field in a layer close to interface

Electric field will drive electrons and holes in opposite direction – separation

Contacts presents a lower resistance path for holes than electrons – from semiconductor to metals – this type of junction is an example for Schottky barrier

Schematic representation of bi-crystal



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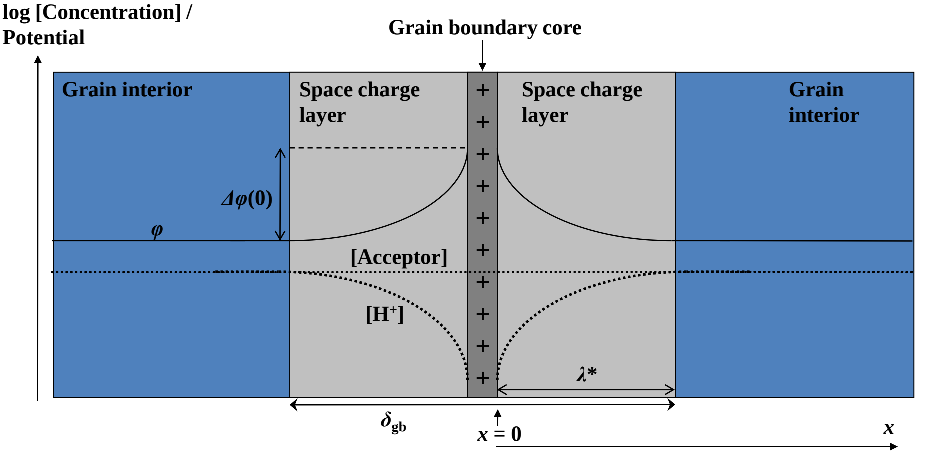
Grain boundary core – space charge model (Mott-Schokky)



$\Delta\varphi(0)$ schottky barrier height δ_{gb} grain boundary width λ^* space charge layer width

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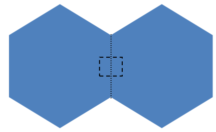
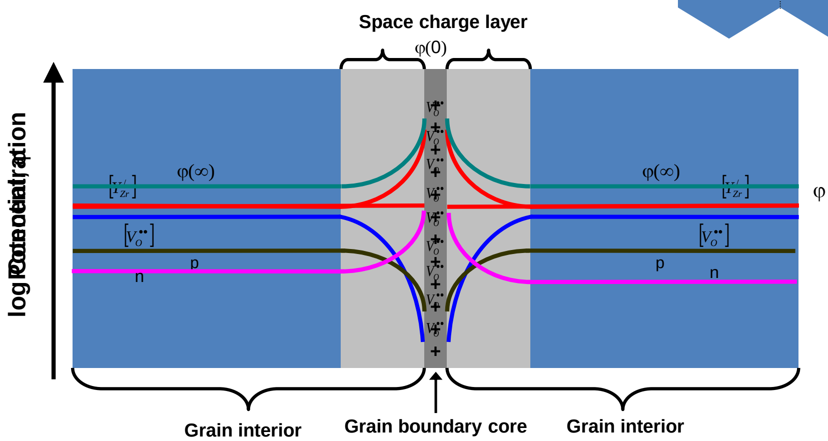
Grain boundary core – space charge model

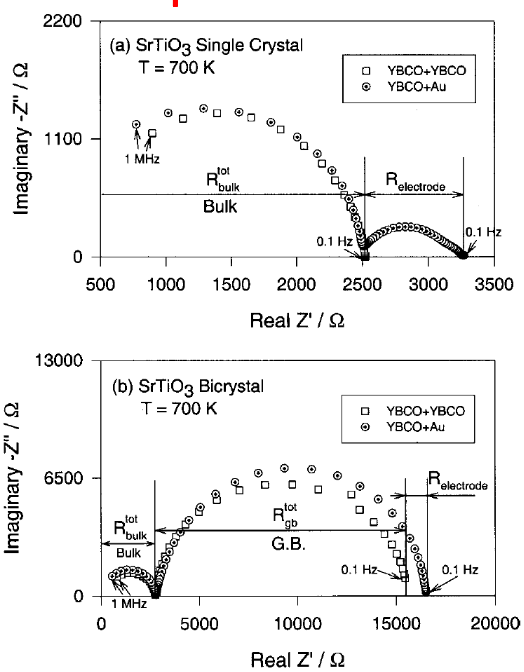
Example: Oxygen ion conductor (Y_2O_3 doped ZrO_2)





Mott-Schottky situation
Gouy–Chapman situation

Impedance measurement on bi-crystal



$(+)\ p_{O_2}$, YBCO/$SrTiO_3$/Au, $p_{O_2}\ (-)$

(+) YBCO/$SrTiO_3$/YBCO (-)

Resistance due to depletion region or space charge region or Schottky battery at the contact of $SrTiO_3$/Au

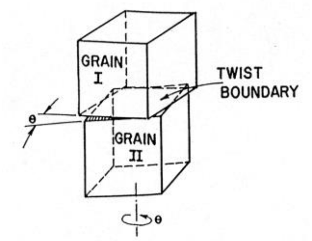
Journal of The Electrochemical Society, **148** (9) J50-J53, 2001

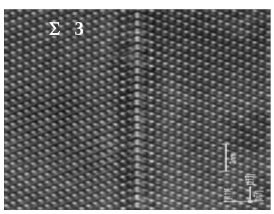
Size Effect on Transport Phenomena

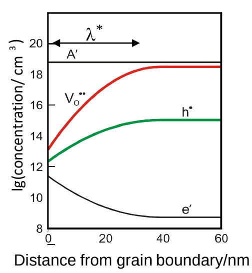
- *Accumulation of space charges (TiO_2)*
- *Depletion of space charges (nanocrystalline $SrTiO_2$)*

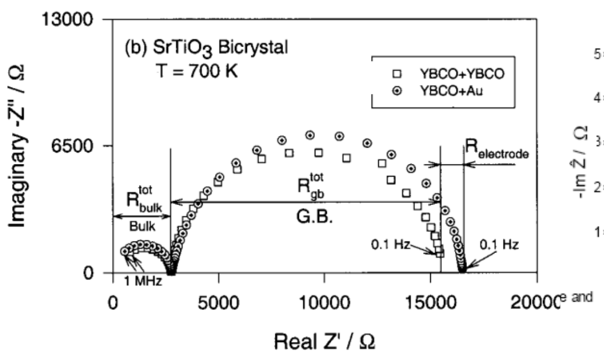
Electrical conduction in bi-crystal with a single interface – role of interfaces and boundaries

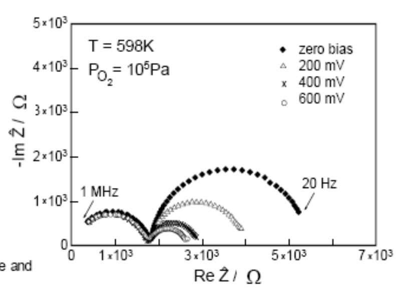
Fe doped $SrTiO_3$ - bicrystal











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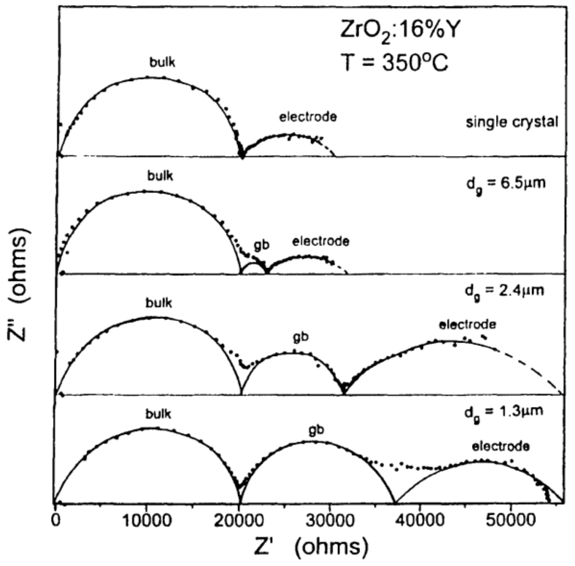
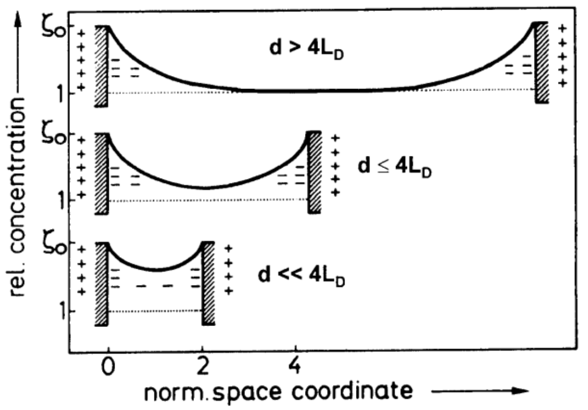
Size effect on grain boundary resistance



Complex impedance spectra obtained for (a) single crystal and microcrystalline YSZ bulk specimens (*H.L. Tuller, Solid State Ionics 131 (2000) 143-157)*. 16

Size effect on conductivity of TiO_2

$$Ti_{Ti}^{x} + 2O_{O}^{x} \leftrightarrow Ti_{i}^{\cdot\cdot\cdot\cdot} + 4e' + O_2(g)$$



Defect profiles in structures with dimension, d. The build defect concentration is not reached when d **<<** 4L, where L, is the Debye length

C D. Terwilliger and Y.-M. Chiang *J, Am. Caam. Sac.*, 78, *2045-55 (1995)*

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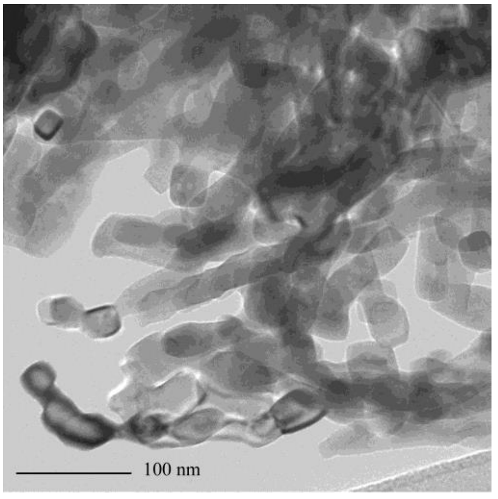
Nanocrystalline $SrTiO_3$



TEM image of $SrTiO_3$ nanopowder

Co-precipitation method

Calcination at 1275 K for 1 hr

Average grain size: (30 ± 5 nm)

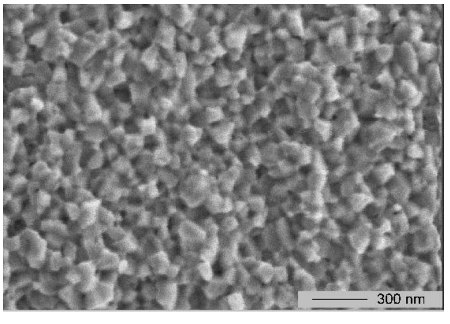
XRD - confirmed single phase formation

Sr/Ti = 1.004

Total amount of electrochemically active impurities present (ICP):

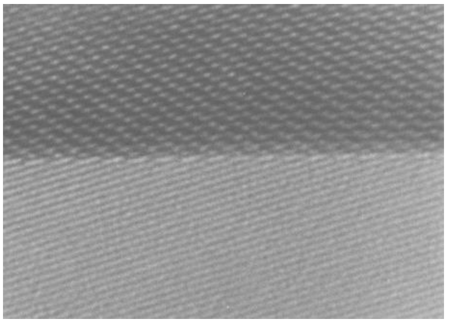
~ 100 ppm (iron)

Nanoceramic $SrTiO_3$



FESEM image - fractured surface,

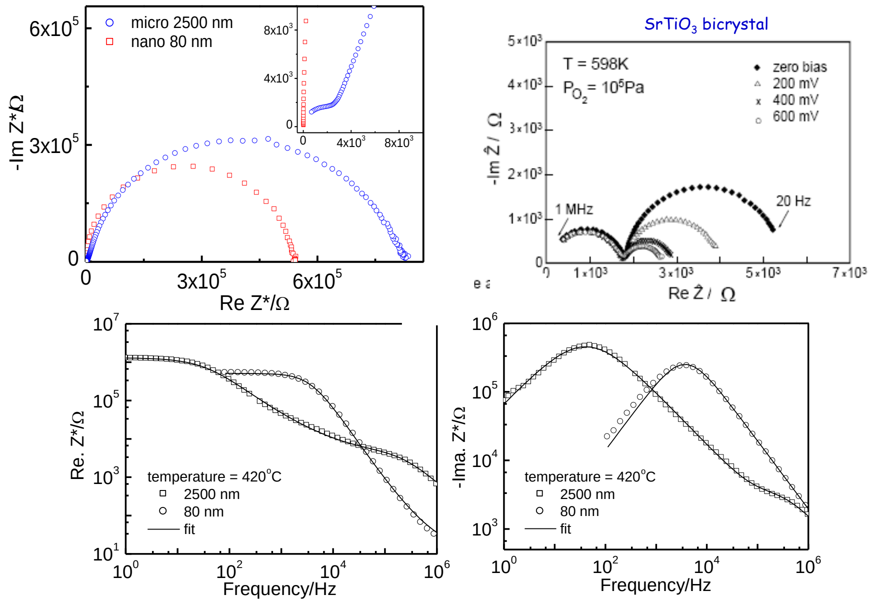
Density : 93 %, Average grain size: 80 nm



Edge-on view of grain boundary - HRTEM

No amorphous phase - during sintering

Impedance spectra of nanocrystalline $SrTiO_3$



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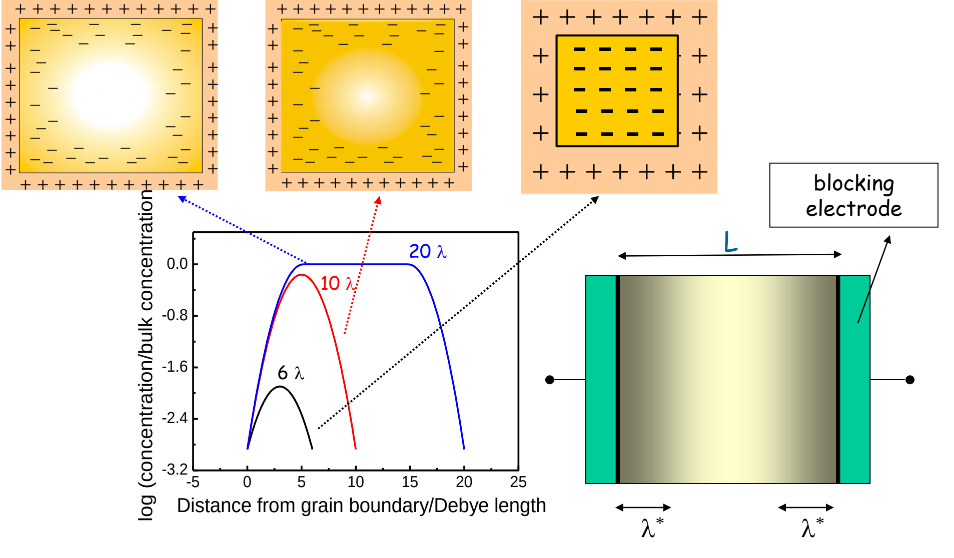
Mesoscopic (depletion) situation



P. Balaya, J. Jamnik, J. Fleig & J. Maier, *Appl. Phys. Lett.*, 86 (2006) 062109;
P. Balaya, J. Jamnik, J. Fleig & J. Maier *J. Electrochem. Soc.* 154 (2007) P69

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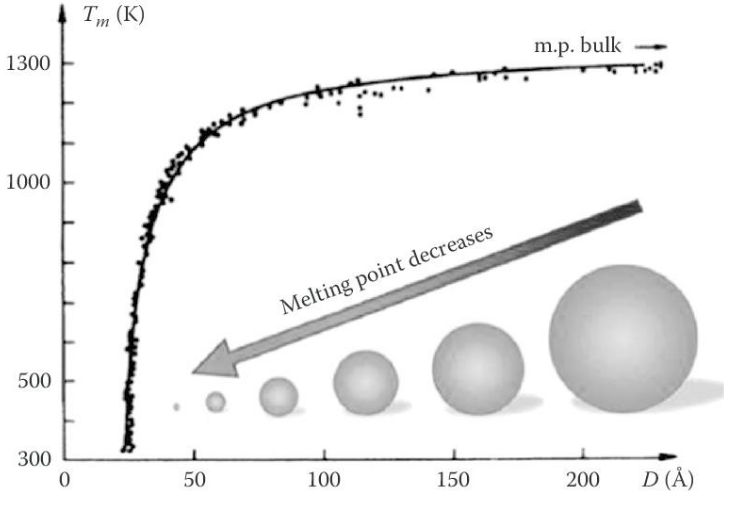
Thermodynamics at Nanosize

Relationship between melting temperature and particle diameter of gold nanoparticles



C. Yang et al., J. Mater. Chem. C, 1 (2013) 4052

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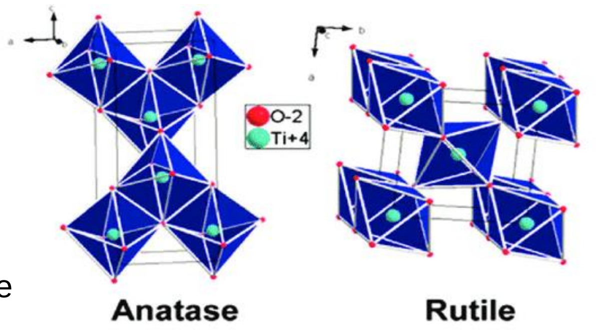
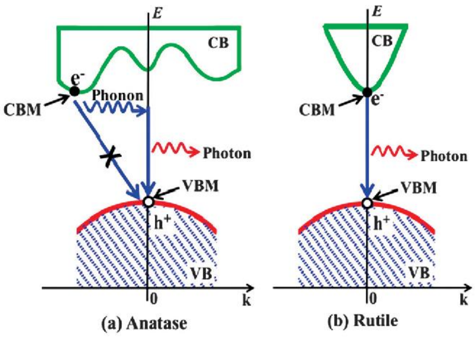
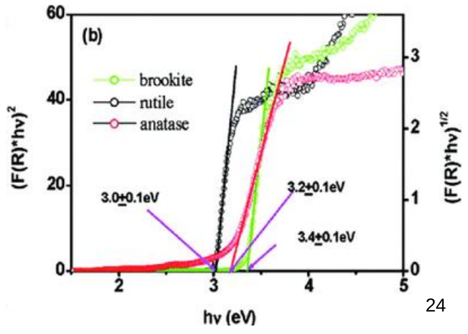
Titanium dioxide (TiO_2)

Anatase (thermodynamically less stable)

Rutile (thermodynamically more stable)







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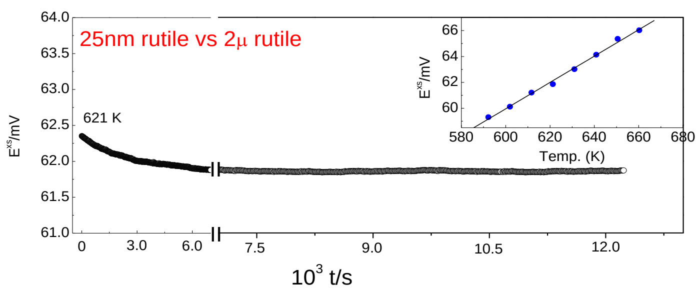
Energetics of nanocrystalline titania

$$\mu_{MX}^{nano} = \mu_{MX}^{\infty} + 2\frac{\bar{\gamma}}{\bar{r}}V_m \qquad \Delta G_{MX}^{nano} = \Delta G_{MX}^{\infty} + 2\frac{\bar{\gamma}}{r}V_m$$

TiO_2 **nano-rutile** , $Na_2Ti_6O_{13}$, Au	β" - Al_2O_3 (Na_2O)	TiO_2 rutile (2 μ), $Na_2Ti_6O_{13}$, Au
Working electrode	Electrolyte	Reference electrode

Electrode reaction: $Na_2Ti_6O_{13} \rightleftharpoons 2Na^+ + 2e^- + 1/2\,O_2 + 6\,TiO_2$

Cell reaction: TiO_2 (nano-rutile) $\longrightarrow$ TiO_2 (micro-rutile)



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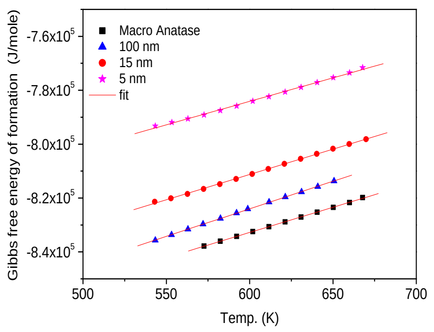
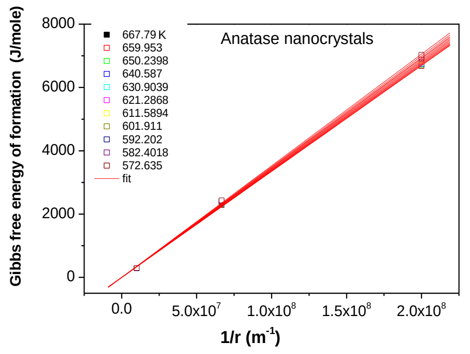
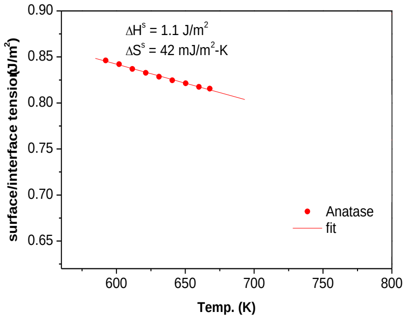
Energetics of nanocrystalline titania







$$\Delta G^{xs} = \frac{2\bar{\gamma}}{\bar{r}} V_M = -nFE^{xs}$$

$$\bar{r} \sim 1nm, \bar{\gamma} \sim 1Jm^{-2}$$

$E^{xs} \sim 100$ mV

P. Balaya and J. Maier, *Phys. Chem. Chem Phys. 12 (2010) 215.*

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