Thermodynamic stability of nanocrystalline anatase versus rutile

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Thermodynamic data show that microcrystalline anatase is metastable with respect to rutile under all conditions of temperature and pressure[1]. Based on the phenomenological estimation of the surface energies for anatase and rutile phases, Banfield et.al., predicted reversal of phase stability, when the particle size is reduced to nanosize[2] and proposed that below 15 nm, anatase is thermodynamically stable against rutile at ambient conditions. However, there is no direct experimental evidence available to elucidate the phase stability of either micro- or nano-sized anatase and rutile.

We present here our results on the thermodynamic stability of anatase and rutile based on electrochemical e.m.f. measurements made on different particle sizes (1200 nm - 5 nm) in the temperature interval 250 - 450^{o}C. Both electrodes of the cell consist of a composite of $Na_2Ti_6O_{13}$, TiO_2 and Au separated by Na-ß" alumina as electrolyte. The e.m.f. directly reflects the difference of the Gibbs free energies of formation (delta G_f) of the titania crystals on both sides. The e.m.f. values confirm that in microcrystalline state, rutile is more stable compared to anatase, whereas when the particle size is reduced to nanoscale, anatase (5 nm) becomes more stable compared to rutile (rod shaped nanoparticles of size 15 x 40 nm). Gibbs energies for the surfaces of anatase and rutile (relative to microcrystals), as a function of surface area figures out clearly the reversal of the phase stability. On deconvoluting the surface deltaG_f into enthalpy and entropy terms, we present here a direct experimental proof for the stabilization of nanosized anatase and discuss its phase stability in terms of the thermodynamic parameters.

References

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