



# The effect of particle size on the stability and toxicity of some micro and nano-structured materials

Seminar  
Nanoscience and  
Nanotechnology  
February 3, 2010  
Bucharest,  
Romania

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## OBJECTIVES

### Critical size assessments

Particle Category	Size	
Coarse	Particles with an average diameter of < 10 $\mu\text{m}$ ( $\mu\text{m}$ = micron)	
Fine	Particles with an average diameter of < 2.5 $\mu\text{m}$	
Ultrafine (Nanoparticles)	Particles with an average diameter of < 0.1 $\mu\text{m}$ (< 100nm)	
Ultrafine (Nanoparticles)	UFP - Approx. size	Potential Entry Point <sup>10</sup>
	70 nm	alveolar surface of the lung
	50 nm	cells
	30 nm	central nervous system
	< 20 nm	no comprehensive scientific data as yet

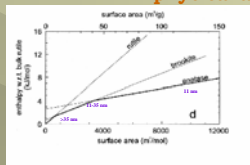
### Particle size versus energetics of nanomaterials

Contribution to answer the following topics are expected:

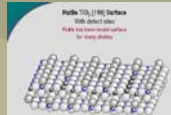
- Which are the general implications for nanophase stability relations?
- Are there compositional or crystal chemical systematics in the energetics of polymorphism and surface energies?
- To what extent can the energetic properties of nanocomposites be predicted from properties of the nanoscale end-members?
- Which is the influence of different compositional variables on the nanophase energetics?
- What environments are likely to harbor nanoscale phenomena, and how would thermodynamic modelling be affected?
- How do environmental effects alter nanoparticle structures and change reactivity?
- Are the existent thermochemical databases enough comprehensible to prevent or for diminution of ecological hazards?
- Are the previously proposed defect structure models suitable to explain the origin of the defects in nanomaterials?

## The size effect on the nanoparticle energetics

### Nanoparticles are often polymorphs of bulk material with different physical and chemical properties



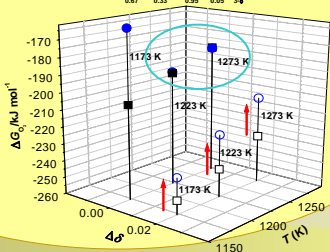
Enthalpy of nanocrystalline samples with respect to bulk rutile (kJ/mol) versus surface area (m²/mol)



Interrelationships among "bulk" structure and defects, surface structures, the environment and reactivity mean the nanoparticle properties depend on **size, environment and history.**

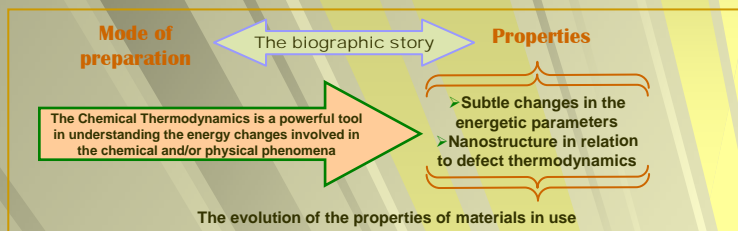
### The variation of $\Delta\bar{G}_0$ , with temperature and oxygen nonstoichiometry change for micro- and nanostructured complex oxides

- $\text{La}_{0.97}\text{Ca}_{0.03}\text{Mn}_{0.99}\text{Al}_{0.01}\text{O}_2$  nanostructure
- $\text{La}_{0.97}\text{Ca}_{0.03}\text{Mn}_{0.99}\text{Al}_{0.01}\text{O}_{1.4}$  nanostructure
- $\text{La}_{0.97}\text{Ca}_{0.03}\text{Mn}_{0.99}\text{Al}_{0.01}\text{O}_2$  microstructure
- $\text{La}_{0.97}\text{Ca}_{0.03}\text{Mn}_{0.99}\text{Al}_{0.01}\text{O}_{1.4}$  microstructure

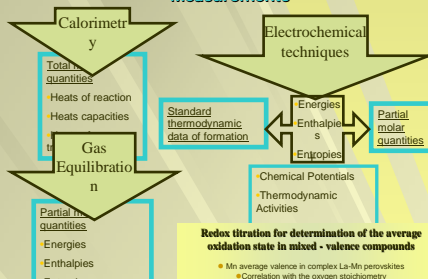


### Nano-Micro + Oxygen Non stoichiometry

## EXPERIMENTAL



### Experimental Techniques for Thermodynamic Measurements

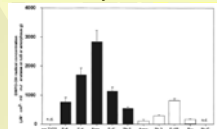


### Correlation between the stability, energetic parameters and the global toxicity of nano-TiO2 nanoparticles

Comparison between the bulk and surface properties of the TiO<sub>2</sub> polymorphs.

TiO <sub>2</sub> polymorphs	Bulk enthalpies (kJ/mol)	Surface enthalpies (kJ/mol)
rutile	0.71 ± 0.38	2.2 ± 0.2 J/m <sup>2</sup>
brookite	0.71 ± 0.38	1.0 ± 0.2 J/m <sup>2</sup>
anatase	2.61 ± 0.41	0.4 ± 0.1 J/m <sup>2</sup>

Oxidative stress hydroxyl radical production (ESR) in different TiO<sub>2</sub> polymorph phases



The nano-TiO<sub>2</sub> particles in the anatase phase, produced the most reactive oxygen species generation and the largest cytotoxic responses following *in vitro* exposures to human dermal fibroblasts or to A549 human lung epithelial cells.

If there is a general correlation between increasing metastability and decreasing surface energy, then **crossovers in thermodynamic stability at the nanoscale may be a key parameter controlling the global reactivity and toxicity.**

## CONCLUSIONS:

The changes of the thermodynamic data can be explained as a consequence of truly grain-size dependent properties. **The nanoparticle properties depend on size, environment and history.**

- Nanostructure:
  - significant changes in the overall defect concentration
  - a reduced energy of oxygen vacancies formation
  - the increase in the binding energy of oxygen and an increase of

The contribution of the oxygen substitution of the complex oxide structure to a particle's toxicity has not been clearly established. However, it does seem, in the light of current knowledge, that the **size effect is considerably more important to UFP toxicity than the actual composition of the material.** The biological behaviour of nanoparticles is determined not only by the **chemical composition**, including coatings on the surface, but also by the corresponding shifts in chemical and physical properties, associated to the increase in surface to volume ratio. One mechanism of toxicity of nanoparticles is likely to be induction of reactive oxygen species and the consequential oxidative stress in cells and organs.

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- Speranta Tanasescu, Cornelia Marinescu, N.D. Totir, Journal Solid State Electrochemistry, in press.
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- S. Tanasescu, D. Berger, A. Orasanu, J. Schoonmann, International Journal of Thermophysics, 26, 2006, p. 543 - 555

### INTERNATIONAL PROJECTS:

- Participant in EU project on "Improving the understanding of the impact of nanoparticles on human health and the environment", ImPart CA, Programme: Priority 3 - NMP, 2005-2008
- SCOPEs Program 2009-2012, Project nr. IZ7320, 128185 F1, 2010-2012: "Mixed Ionic and Electronic Conducting Perovskites"
- Participant 2004-2005 in EU COST Action: Advanced Solder Materials for High Temperature Application (HISOLD), MP06020 COST Action, 2007-2010, project "Design, process and control in a multiscale domain of Cu-Ni-X (X = Sn, Bi, Zn, Ti) alloys based"
- Scientific cooperation with ETH Zurich, Department of Materials - Institute of Nonmetallic Materials, Thermodynamic Group, Switzerland concerning "The thermochemical properties of the compounds in the La-Sr-Mn-O system". Agreement on the scientific collaboration 2001-2005.
- Scientific cooperation with the Institute of Metallurgy and Materials Science "Aleksander Krupkowski" of the Polish Academy of Sciences, Laboratory of Physical Chemistry concerning "The investigation of the influence of phase nonstoichiometry on phase equilibria in Mn-Eu-O system". JRC Project 2003-2005
- Participant 2004-2005 in EU COST Action 525: Advanced Electroceramics: Grain Boundary Engineering, the Project "Structural and dielectric studies of incipient ferroelectrics"
- Participant in EU "Joule II Programme", Sub-Programme "Energy Conservation and Utilisation" (Contract JOU 2-CT 92-0063 "New SOFC Materials and Technology", (Contract JOU 2-CT 92-0063 "New SOFC Materials and Technology", 1993-1995
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