# Effects of Particle Size on the Thermodynamic Data of Micro and Nanostructured Transition Metal Oxides

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## OBJECTIVES

### Critical size assessments

| Particle Category | Size | |
|---|---|---|
| Coarse | Particles with an average diameter of < 10 μm (μm = micron) | |
| Fine | Particles with an average diameter of < 2.5 μm | |
| Ultrafine (Nanoparticles) | Particles with an average diameter of < 0.1 μm (< 100nm) | |
| **Ultrafine (Nanoparticles)** | **UFP – Approx. size** | **Potential Entry Point[10]** |
| | 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 generation of the defects in nanomaterials?

## EXPERIMENTAL

**Mode of preparation** ⟷ The biographic story ⟷ **Properties**

The Chemical Thermodynamics is a powerful tool in understanding the energy changes involved in the chemical and/or physical phenomena

- Subtle changes in the energetic parameters
- Nanostructure in relation to defect thermodynamics

The evolution of the properties of materials in use

### Experimental Techniques for Thermodynamic Measurements

**Calorimetry**

Total molar quantities
- Heats of reaction
- Heats capacities
- Heats of transformation

**Gas Equilibration**

Partial molar quantities
- Energies
- Enthalpies
- Entropies

**Electrochemical techniques**

Standard thermodynamic data of formation ⟷
- Energies
- Enthalpies
- Entropies

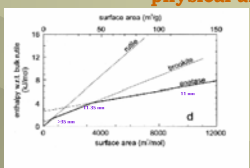
⟷ Partial molar quantities

- Chemical Potentials
- Thermodynamic Activities
- Partial Pressures

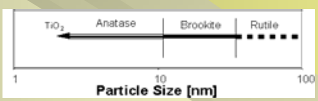
**Redox titration for determination of the average oxidation state in mixed - valence compounds**
- Mn average valence in complex La-Mn perovskites
- Correlation with the oxygen stoichiometry

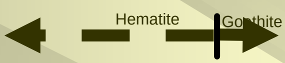
## The size effect on the nanoparticle energetics

### 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**.

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

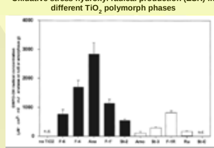
**Surface enthalpy**

**Phase stability**

Comparison between the bulk and surface properties of the $TiO_2$ polymorphs.

| $TiO_2$ polymorphs | Bulk enthalpies | Surface enthalpies |
|---|---|---|
| rutile | 0.71 ± 0.38 kJ/mol | 2.2 ± 0.2 J/m² |
| brookite | 0.71 ± 0.38 kJ/mol | 1.0 ± 0.2 J/m² |
| anatase | 2.61 ± 0.41 kJ/mol | 0.4 ± 0.1 J/m² |

Oxidative stress hydroxyl radical production (ESR) in different $TiO_2$ polymorph phases

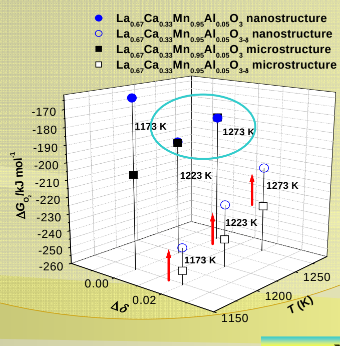


The nano-$TiO_2$ particles in the anatase phase, produced the most reactive oxygen species generation and the largest cytotoxic responses following *in vitro* exposures to human dermal fibroblasts or to A549 human lung epithelial cells.

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.***

**The variation of $\Delta \bar{G}_{O_2}$ with temperature and oxygen nonstoichiometry change for micro- and nanostructured complex oxides**

**Nano-**
**Micro-**
**+**
**Oxygen**
**Non**
**stoichiometry**




## CONCLUSIONS:

The changes of the thermodyamic 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 order in the oxygen sublattice of the complex oxide structure**

**The contribution of size vs. the contribution of material composition to a particle's toxicity** has not been clearly established. However, 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.**

Laboratory of Chemical Thermodynamics

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**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. IZ73ZO_128185 /1, 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-XY (X, Y = Sn, Bi, Zn, Ti) alloys based*"
- Scientific cooperation with ETH Zürich, 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
- The 695/RB(1969-1972) contract with IAEA-Vienna ***"Thermodynamic properties of the uranium oxides"***.