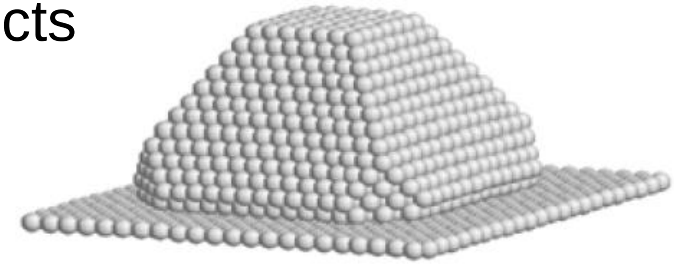
NTNU
Norwegian University of Science and Technology

TMT4320 Nanomaterials
Septemeber 7th, 2016

- Physical properties: size effects
- TNN. Chapter 2.
- NN (Cao). Chapter 8.
- NN (Brechignac). Chapter 2



Last lecture

- Physical properties: size effects
  - Lattice constant
  - Melting point
  - Diffusivity
  - Enhanced solid solubility
  - Magnetic properties

Today

- Physical properties: size effects
  - Magnetic properties
  - Electrical properties
  - Optical properties
  - Thermal properties
  - Mechanical properties
  - Examples

Effect on the magnetic properties

Effect on the magnetic properties

The strength of a magnet is decided by its coercivity (resistance of a material to be demagnetized) and saturation magnetization(effect observed when a materials cannot increase the magnetization applying a magnetic field) values

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Strength of a magnet increase when the grain size decreases and the specific surface area per unit volume of the grains increases

-Soft Magnetic Nanocrystalline Alloys

-Permanent Magnetic Nanocrystalline Materials

-Giant Magnetoresistance

Effect on the magnetic properties

Soft Magnetic Nanocrystalline Alloys

In Microcrystalline soft magnetic alloys, low coercivity has been achieved using coarse-grained materials where magnetic flux pinning at the grain boundaries is avoided.

Effect on the magnetic properties

Soft Magnetic Nanocrystalline Alloys

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In nanocrystalline alloys, when the grain size is much smaller that the domain wall width, the magnetic anisotropy is averaged over many grains and orientations and hence the coercivity is significantly reduced and permeability is enhanced.

Effect on the magnetic properties

Soft Magnetic Nanocrystalline Alloys

Fig. 2.10 Amorphous ribbon of Fe–Si–B–Nb–Cu alloy. (*Courtesy:* Bhaskar Majumdar, DMRL, Hyderabad).

Fe-Si-B-Nb-Cu alloy transform to BCC Fe-Si solid solution with grain size of ~10 nm.

Cu → Increase BCC

Nb → retards grain growth

✓ Low core losses

✓ Good saturation induction but still lower than Fe-metalloid alloys

Effect on the magnetic properties

Soft Magnetic Nanocrystalline Alloys

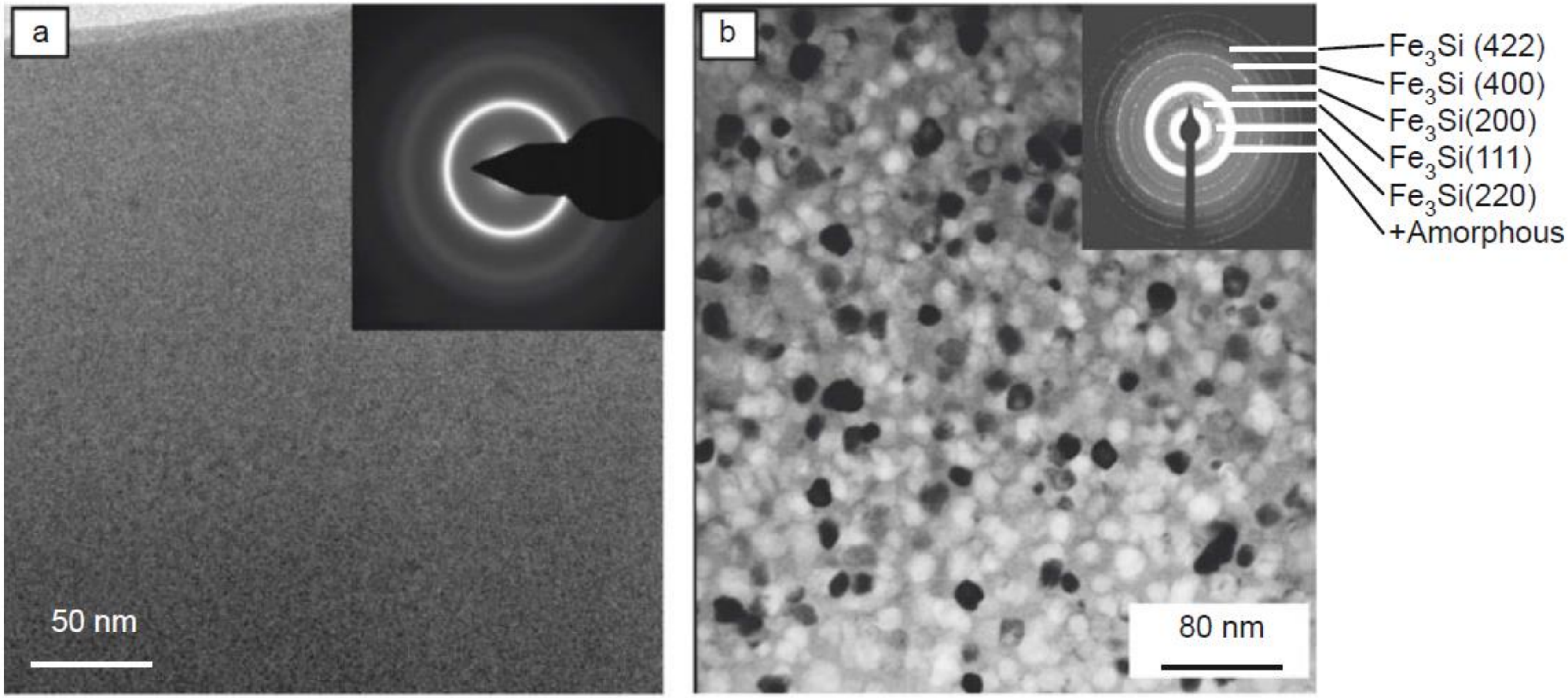

Fig. 2.11 Bright field transmission electron microscopy (TEM) images and corresponding selected area diffraction (SAD) patterns of (a) as melt spun and (b) annealed (525°C for 1 h) ribbons of Fe–Si–B–Nb–Cu alloy. (*Courtesy*: Bhaskar Majumdar, DMRL, Hyderabad).

Effect on the magnetic properties

Soft Magnetic Nanocrystalline Alloys

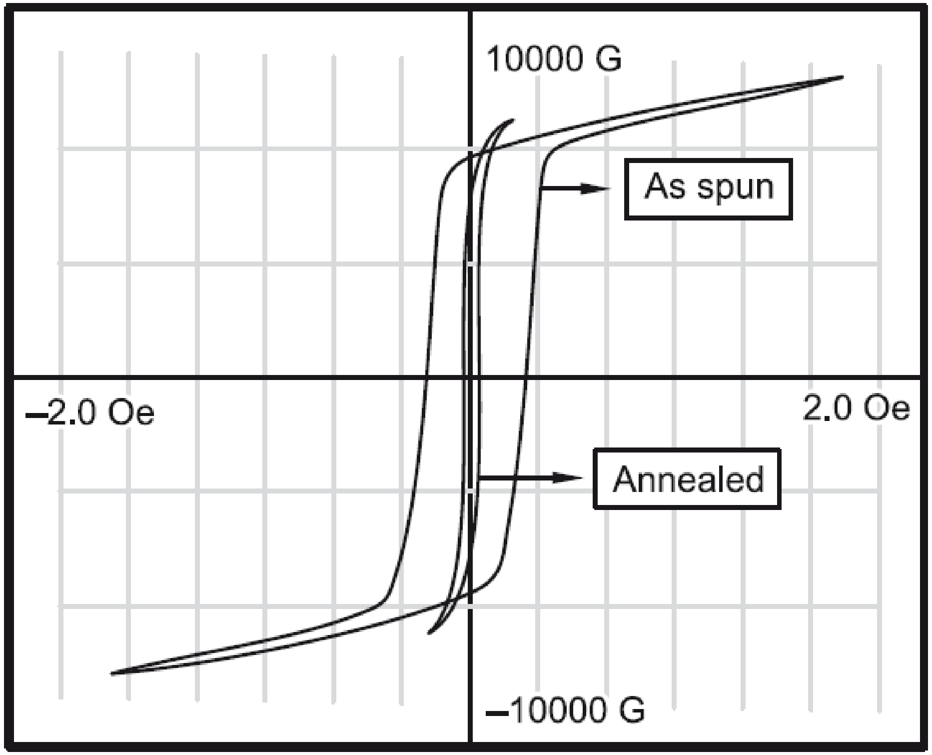

Fig. 2.12 Hysteresis loops of the as-spun and annealed Fe–Si–B–Nb–Cu ribbons. (*Courtesy*: Bhaskar Majumdar, DMRL, Hyderabad).

Effect on the magnetic properties

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Fe-Zr-B better saturation induction → Higher Fe content

Effect on the magnetic properties

Permanent Magnetic Nanocrystalline Materials

Mixture of a hard magnetic phase and a soft magnetic phase can exhibit values of remanent magnetization (M_r) greater than the isotropic calue of 0.5 M_s when the phases are nanosize.

This enhancement is obtained when there is an exchange coupling between the two phases due to the nanocrystalline size and the degree of coherence across interphase boundaries

Effect on the magnetic properties

Permanent Magnetic Nanocrystalline Materials

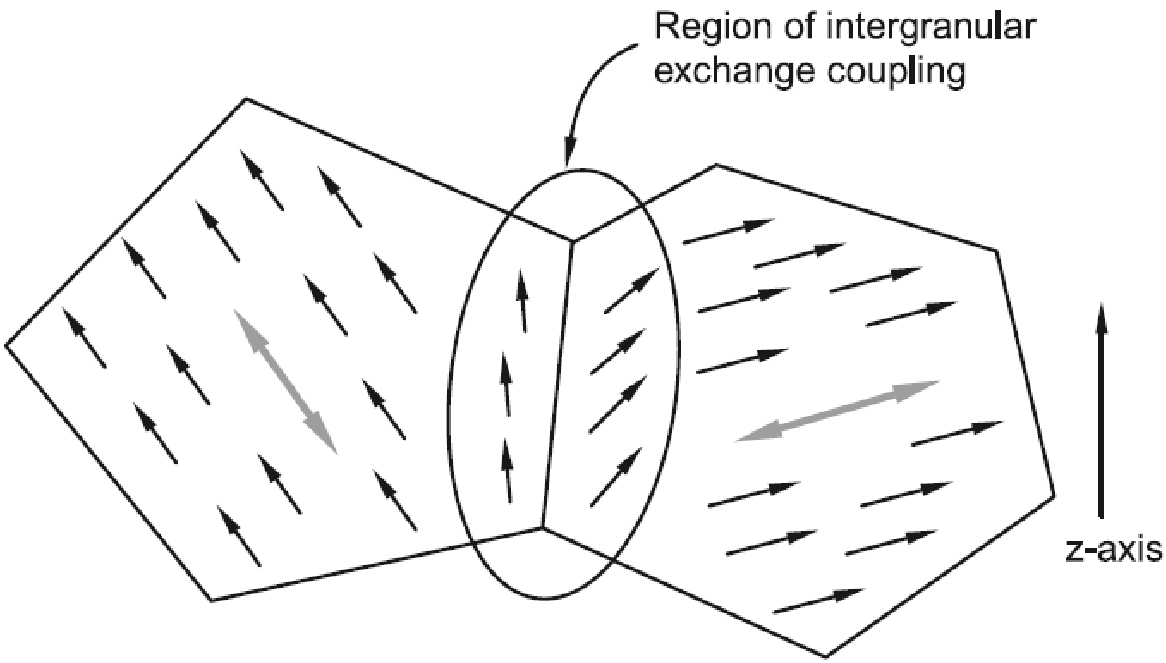
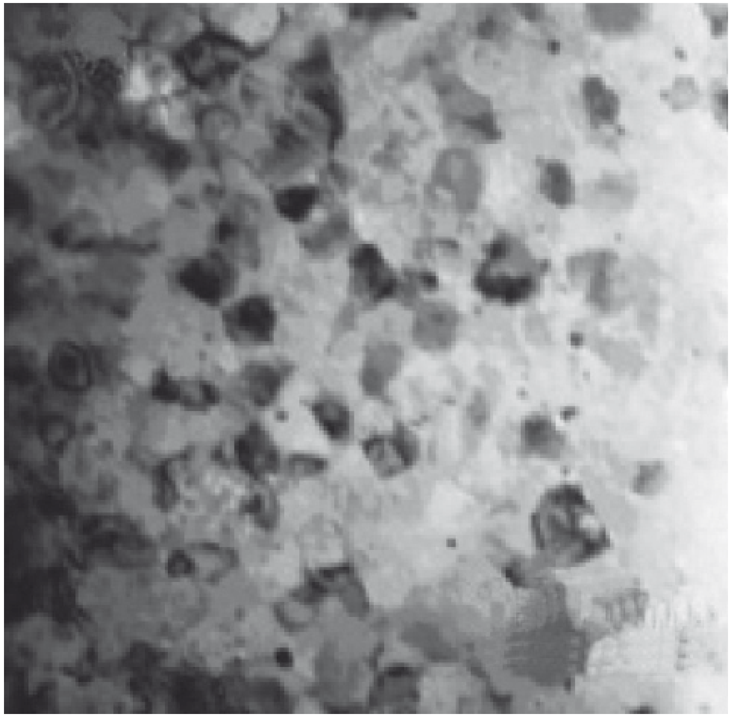


Fig. 2.13 Schematic diagram explaining the principle of exchange coupling in magnetic nanocomposites.

Effect on the magnetic properties

Permanent Magnetic Nanocrystalline Materials



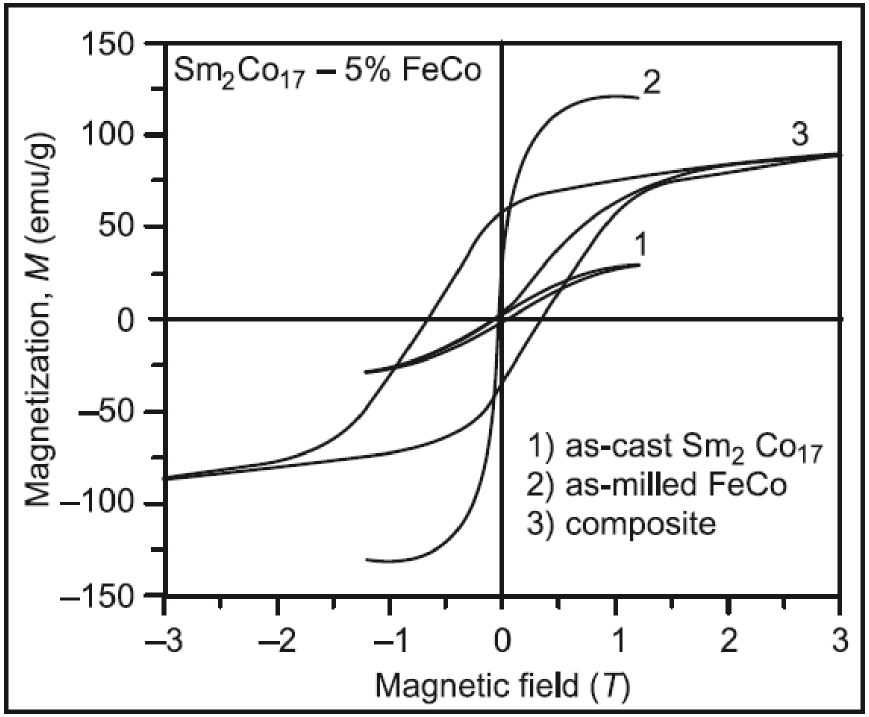


Fig. 2.14 Improvement in magnetic properties in Sm_2Co_{17}–FeCo nanocomposites in relation to bulk microcrystalline composites. The improved magnetic properties can be attributed to exchange coupling between the soft and hard magnetic phases in the nanocomposites. (*Source:* BS Murty, IIT Madras).

Effect on the magnetic properties

Giant Magnetoresistance (GMR)

Significant decrease in electrical resistance when a materials is exposed to a magnetic field

Observe in bulk composites consisting of ferromagnetic and non-magnetic phases or in thin film multilayers of these materials as well as in equiaxed granular nanocrystalline materials

Effect on the magnetic properties

Giant Magnetoresistance (GMR)

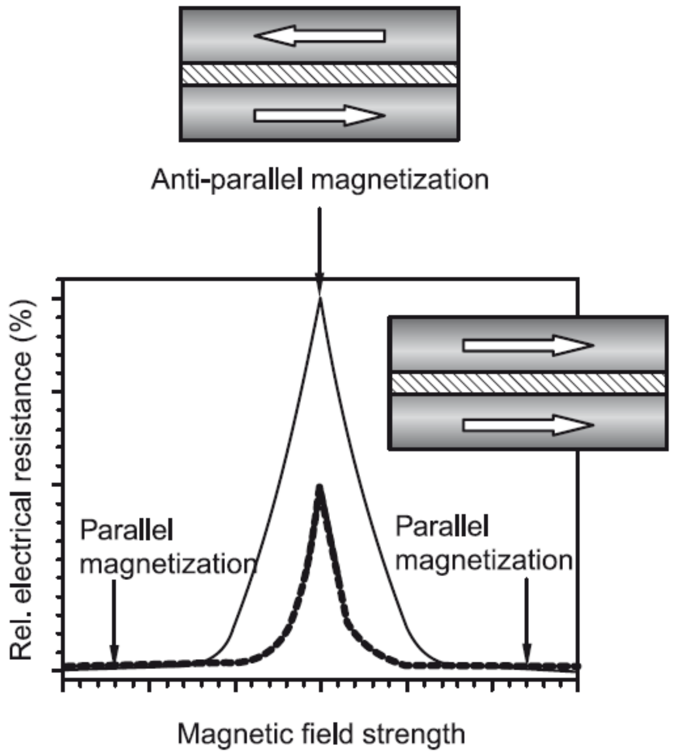


Fig. 2.15 Schematic diagram showing GMR effect in magnetic ultrathin films.

A significant decrease in resistance is evident when the external magnetic fields leads to adjacent ferromagnetic layers, aligning in a parallel fashion due to weak antiferromagnetic coupling between layers.

Effect on the magnetic properties

Giant Magnetoresistance (GMR)

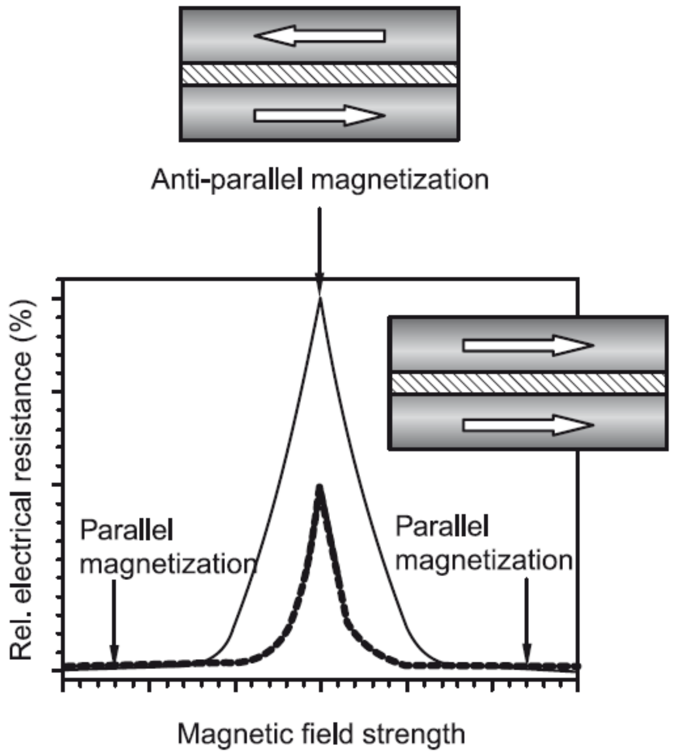


Fig. 2.15 Schematic diagram showing GMR effect in magnetic ultrathin films.

GMR is inversely proportional to the average particle diameters. The effect can be up to 100 % in multiple stacks of ultrathin films.
Fe/Cr multilayer ultrathin films
Cu/Co nanocompoistes
Magnetic reading heads for computer hard discs and position sensors

Effect on the electrical properties

Nanomaterials can hold considerably more energy than conventional coarse-grained materials because of their large surface area.

Optical absorption band can be introduced or an existing band can be altered by the passage of current through these materials or by the application of the electric field.

Batteries and fuel cells are used in many application that need electrical energy. Nanocrystalline materials are good candidates for electrolyte and electrolytes materials for these devices

Examples on batteries and fuell cells will follow.

Effect on the optical properties

Key factors for remarhable optical properties of nanocrystalline materials include quantum confinement of electrical carriers with nanoparticles, efficient energy and charge transfer over nanoscale distance and highly enhance role of interfaces.

Design of optical properties by controlling the crystal dimensions and the chemistry of the surfaces.

Old paintings

Don Quixote example.

A little bit of history…

Are nanomaterials so new?

- beautiful color of XIth century glass paintings due to Au and Ag nanoparticles

Different collors depending of particle sizes.

https://en.wikipedia.org/wiki/File:Muzeum_Su%C5%82kowskich_-_Zabytkowy_Witra%C5%BC.jpg

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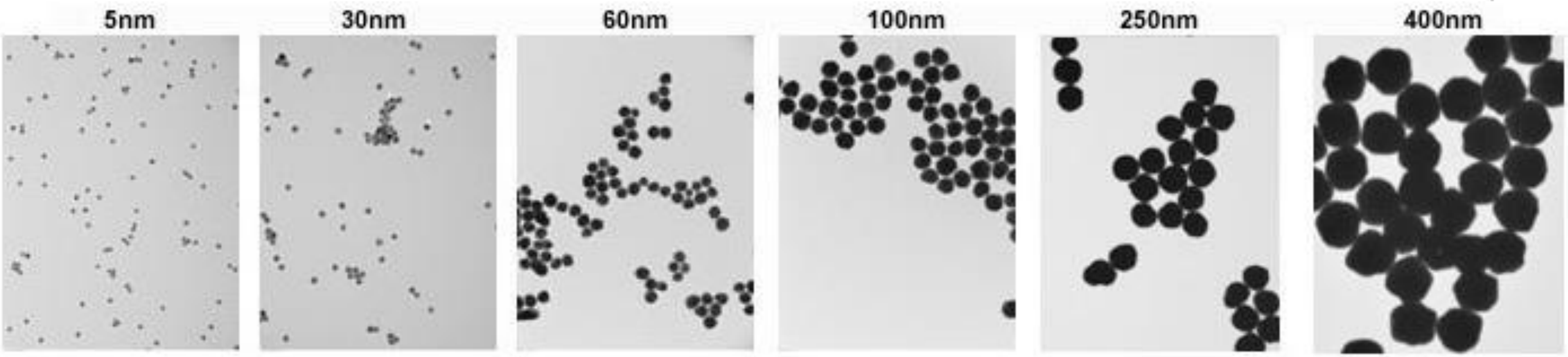


TEM pictures of Au nanoparticles

https://en.wikipedia.org/wiki/File:Muzeum_Su%C5%82kowskich_-_Zabytkowy_Witra%C5%BC.jpg

Effect on the optical properties

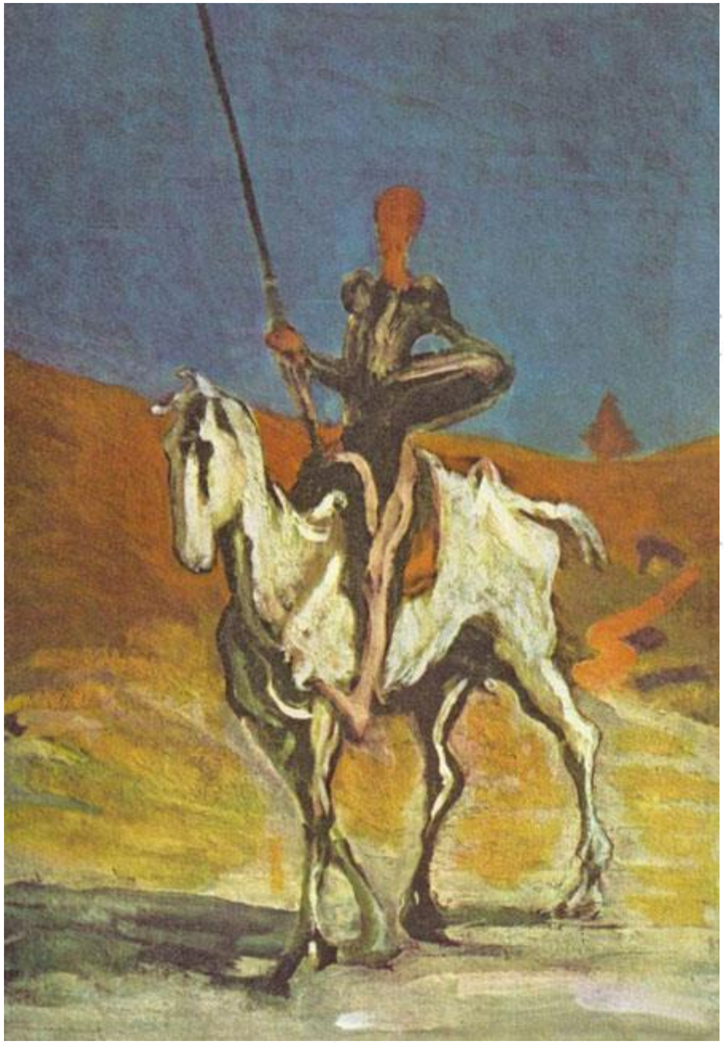
Don Quixote example.

Nanocrystalline VO_2

Below 68 ^{o}C material is transparent.

10 nm particles

Switch to transparent in less than 100 femtoseconds (100×10^{-15} s)
Solids this transitions occur at speed of sound → VO_2 10 times faster



http://www.vanderbilt.edu/exploration/stories/vo2shutter.html

Effect on the thermal properties

Increasing the number of grain boundaries will enhance phonon scattering at the disordered boundaries, resulting in lower thermal conductivity. Thus, nanocrystalline materials would expected to have lower thermal conductivity compared to conventional materials.

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In addition to grain size, shape has also influence in thermal poroperties

Effect on the thermal properties

Examples of thermal conductivity values:

Air	0.03 W/mK
Water	0.6 W/mK
Metals (Ag or Cu)	400 W/mk
Carbon nanotubes	2300 W/mK

Values up to 6600 W/mK along the axial direction → transport direction dependent (shape)

Effect on the mechanical properties

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4. Segregation of solutes at grain boundaries can influence mechanical properties

Examples

$BaTiO_3$:unusual lattice parameters change

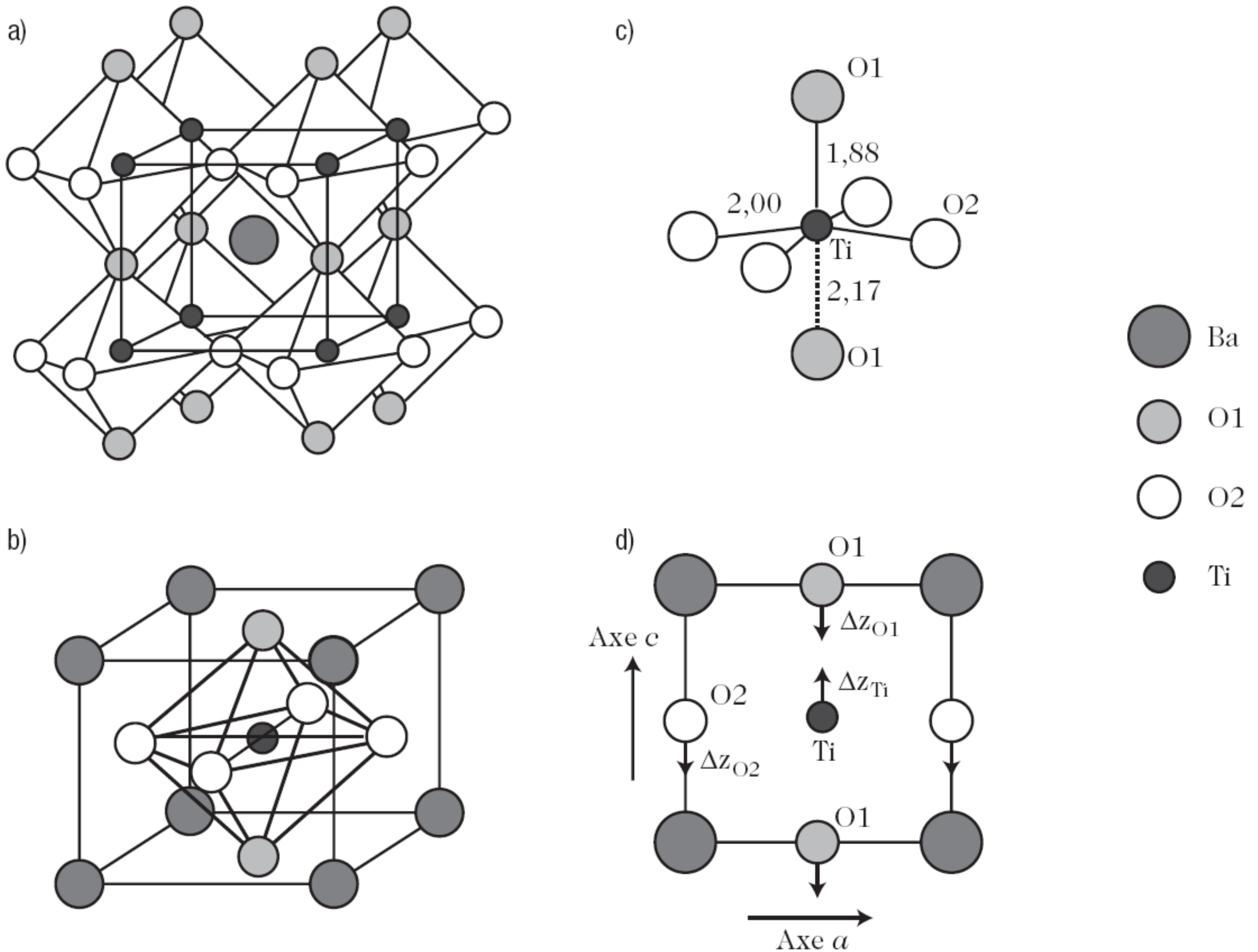
Garnet materials for Li-ion battery electrolytes

Layered double perovskites and Y-doped $BaZrO_3$ as electrode and electrolyte materials for proton conducting fuel cells

$BaTiO_3$

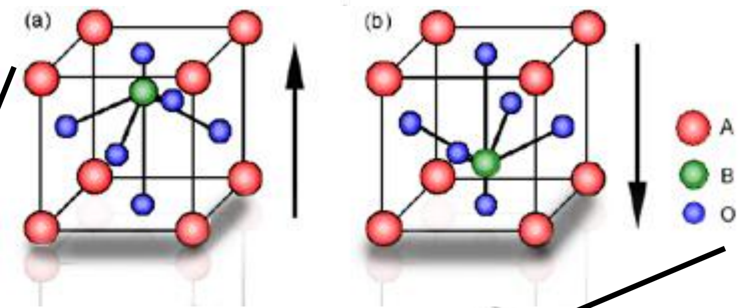
- Ceramic material
  - Inorganic, non-metallic solid prepared by heating and subsequent cooling.
  - May be crystalline, partly crystalline or amorphous (e.g. glass)
  - All oxides are included

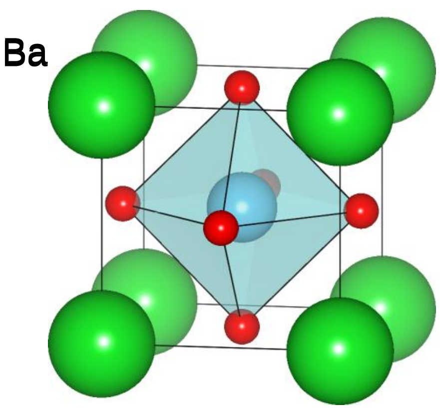
- Perovskite structure
  - ABO_3

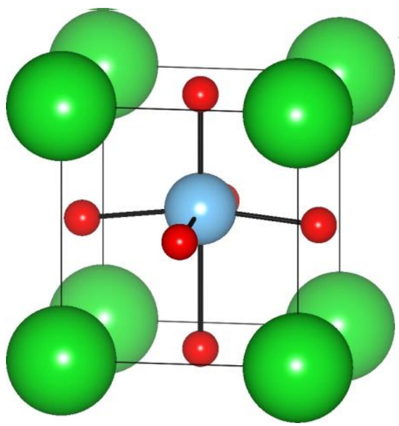

a)
b)
c)
O1
1,88
2,00
O2
Ti
2,17
O1
d)
O1
Axe c
Δz_{O1}
Δz_{Ti}
O2
Ti
Δz_{O2}
O1
Axe a
Ba
O1
O2
Ti

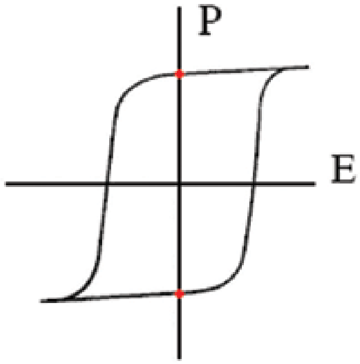
Ferroelectricity

- Definition…









High-temperature
cubic phase

Paraelectric

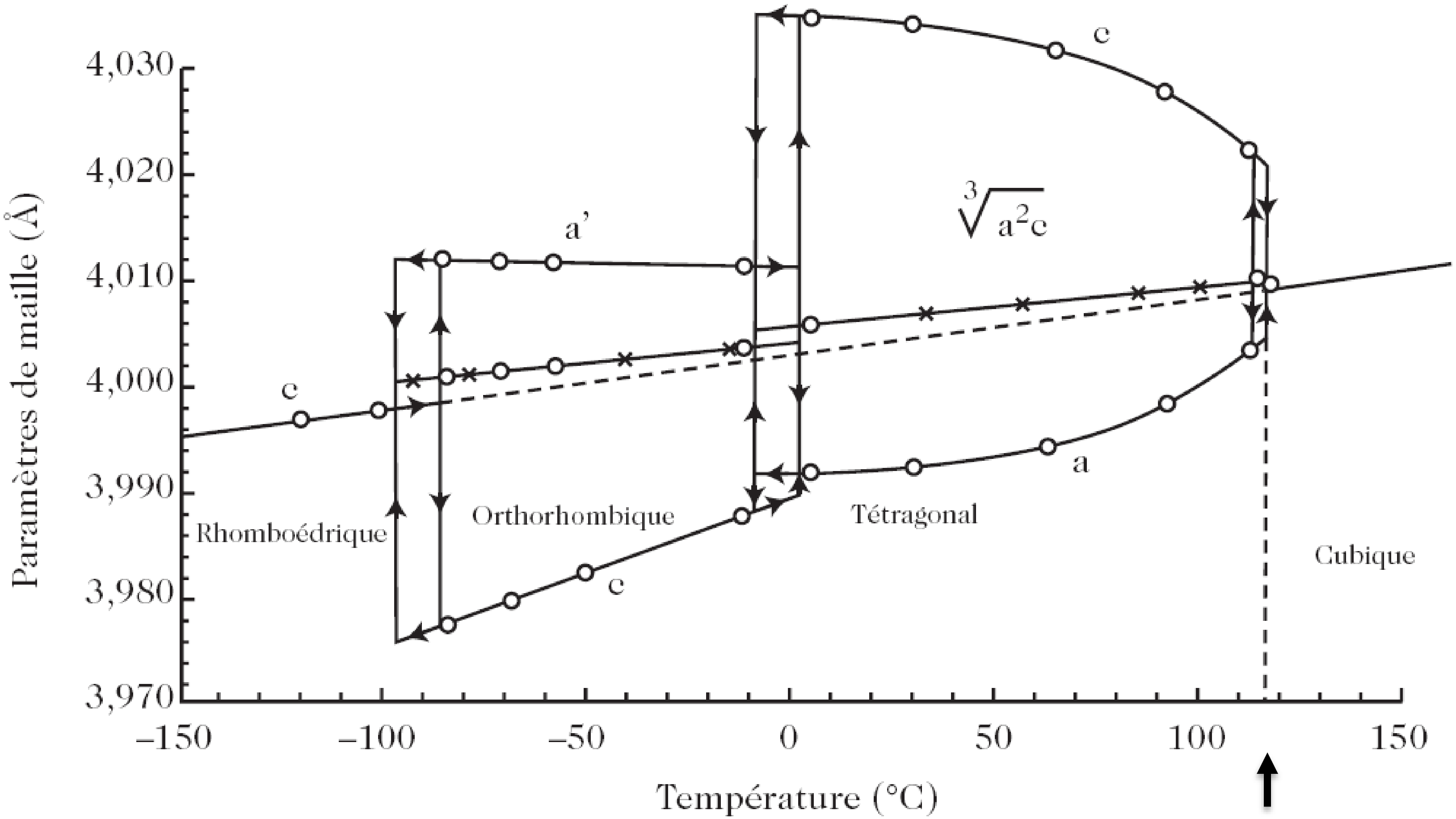
Room-temperature
tetragonal phase

Ferroelectric

Phase transitions at nanoscale

- Crystalline to crystalline
  - Example $BaTiO_3$: tetragonal to cubic
  - The phase transition at small size will generally go towards higher symmetry
- Crystalline to locally ordered
  - Example fcc metal: truncated octahedron to icosahedron
- Crystalline to amorphous
  - Example Si nanoparticle

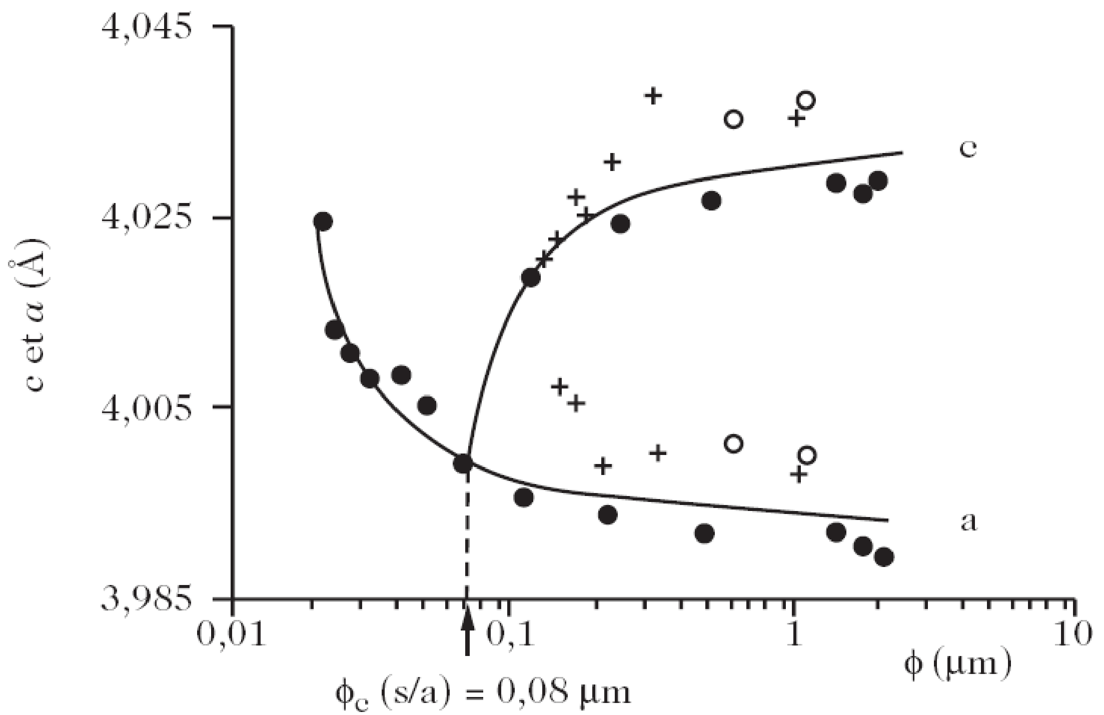
Bulk $BaTiO_3$



T_c

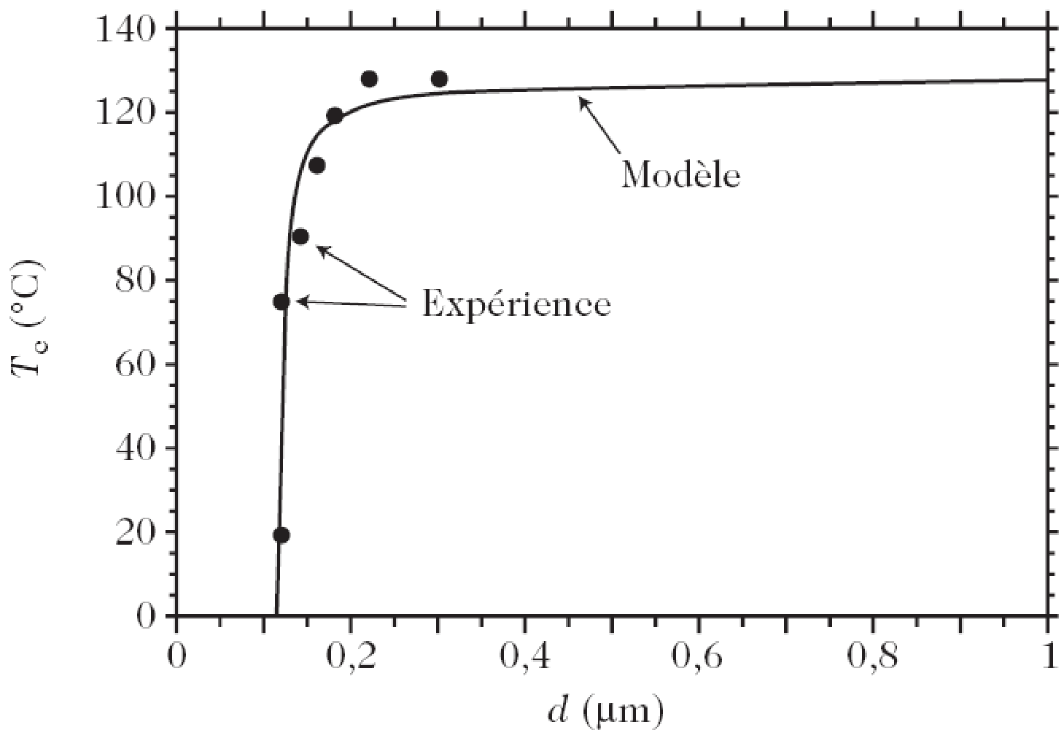
Nanoscale $BaTiO_3$

- $\Phi > \Phi_C$
  - $BaTiO_3$ crystallises with a tetragonal perovskite lattice
- $\Phi < \Phi_C$
  - $BaTiO_3$ crystallises with a cubic perovskite lattice, i.e., *c* = *a*



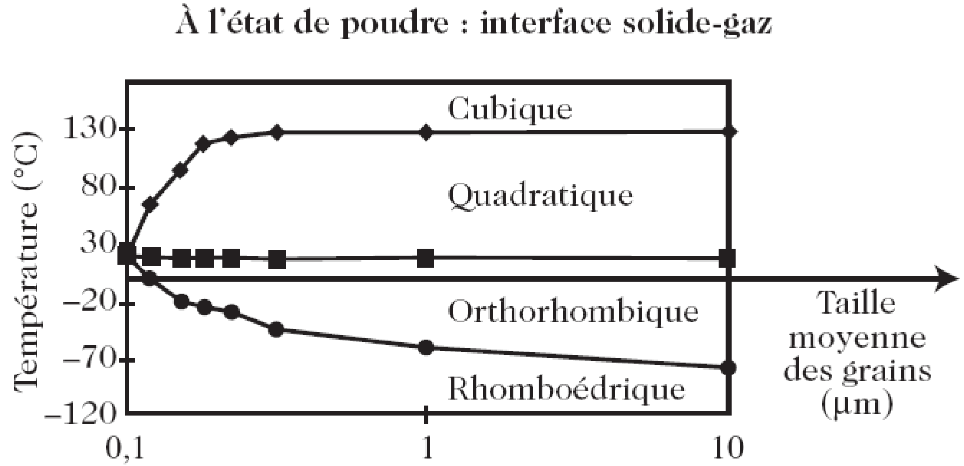
Nanoscale $BaTiO_3$

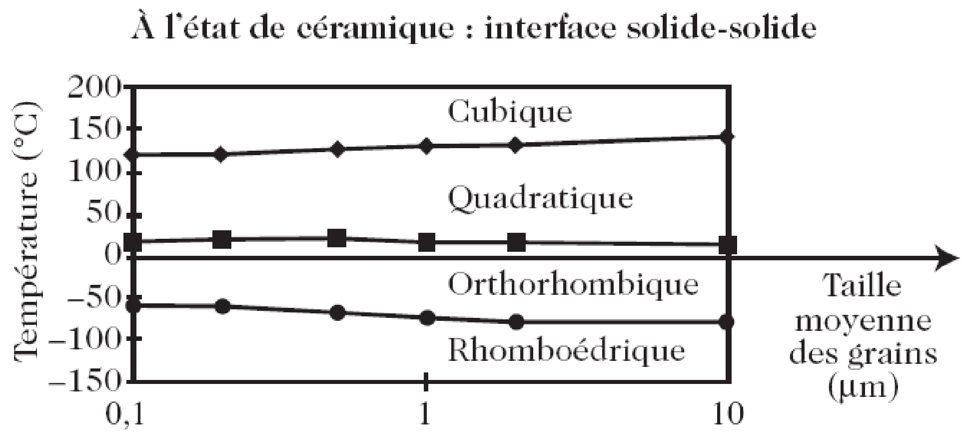
- Curie temperature



Solid-solid interface

- $BaTiO_3$





Transition temperatures for $BaTiO_3$ as a function of grain size. *Upper*: In the powdered state (solid–gas interface). *Lower* : In the ceramic state (solid–solid interface).