Phase Transitions in Nano-Structured Materials

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Outline

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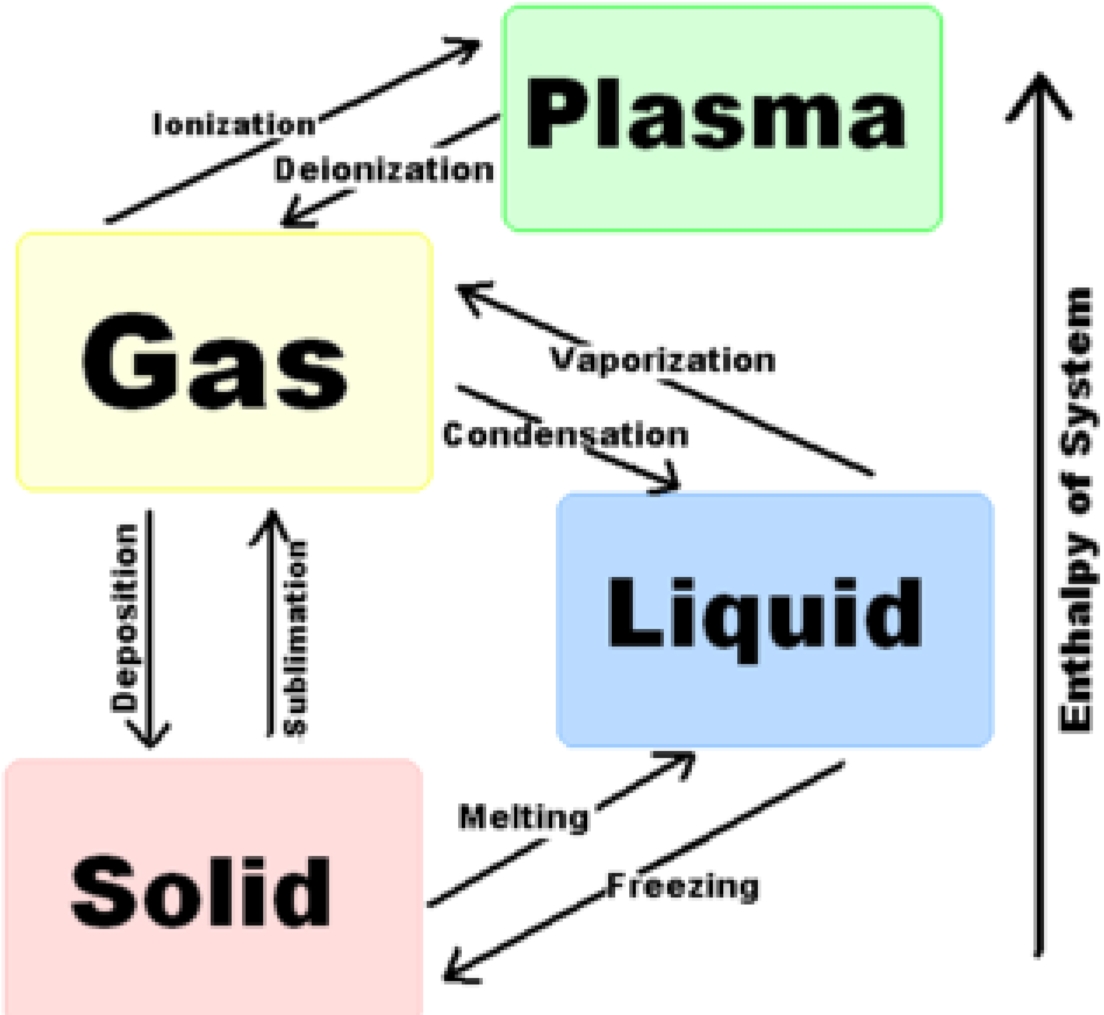
Introduction

- Phase: It is a region of material that is chemically uniform, physically distinct, and (often) mechanically separable.

- In thermodynamics, **phase transition** or **phase change** is the transformation of a thermodynamic system from one phase to another.
- Crystallisation is a condensation process involving the creation of a crystalline daughter phase from a parent phase.
- The ***formation of any new phase*** from a bulk parent phase requires the ***creation of an interface*** between the two phases.
- The creation of this interface requires an ***amount of work***, dependant upon the ***surface/interfacial tension*** of the interface.

Phase Transformation

The nomenclature for the different phase transitions.



The distinguishing characteristic of a phase transition is an abrupt sudden change in one or more physical properties, in particular the heat capacity, with a small change in a thermodynamic variable such as the temperature.

Phase Diagram of a Simple System

- The crystal phase is stable at high P and low T.
- The liquid phase is stable at high P and high T.
- The vapour phase is stable at low P and low/high T.

Other Forms of Phase Transitions

- **The transition between the ferromagnetic (Anti-ferromagnetic) and paramagnetic phases of magnetic materials at the Curie point (Neel's Temperature).**

- **The emergence of superconductivity in certain metals when cooled below a critical temperature.**

- **Changes in the crystallographic structure such as between ferrite (bcc) and austenite (fcc) of iron.**
- **Order-disorder transitions such as in alpha-titanium aluminides.**

- Quantum condensation of bosonic fluids, such as Bose-Einstein condensation and the superfluid transition in liquid helium.

- The martensitic transformation which occurs as one of the many phase transformations in carbon steel and stands as a model for displacive phase transformations.

How to Classify Phase Transitions

- ***First Order and Second Order Phase Transitions***

- ***First-order phase transitions* exhibit a discontinuity in the first derivative of the free energy with a thermodynamic variable.**

i.e.

(dG/dX (where X is any thermodynamic variable)

- ***Second-order phase transitions* have a discontinuity in a second derivative of the free energy.**

- ***Modern Classification* is basd upon latent heat**
  - ***first order involes latent heat while 2nd order does not).***

Some Tools to detect Phase Transitions

- XRD (For Structure)
- Resistivity (ρ)
- Susceptibility (Χ)
- Specific Heat (Cp)
- Pressure
- Volume

(Should be a function of Temperature)

Phase Transition in Nanostructures

- The same thermodynamic and kinetic principles that control phase transitions in bulk materials can be applied to nanostructured materials.
- However, oftentimes common simplifications that are used in these two fields are not appropriate for use with nanophase materials. Therefore, there are a number of noteworthy phase transition phenomena that occur in nanomaterials. Say ‘Melting Point’.

- The melting point of a solid is size dependent. In the nano regime, this dependence becomes significant.
- Why?

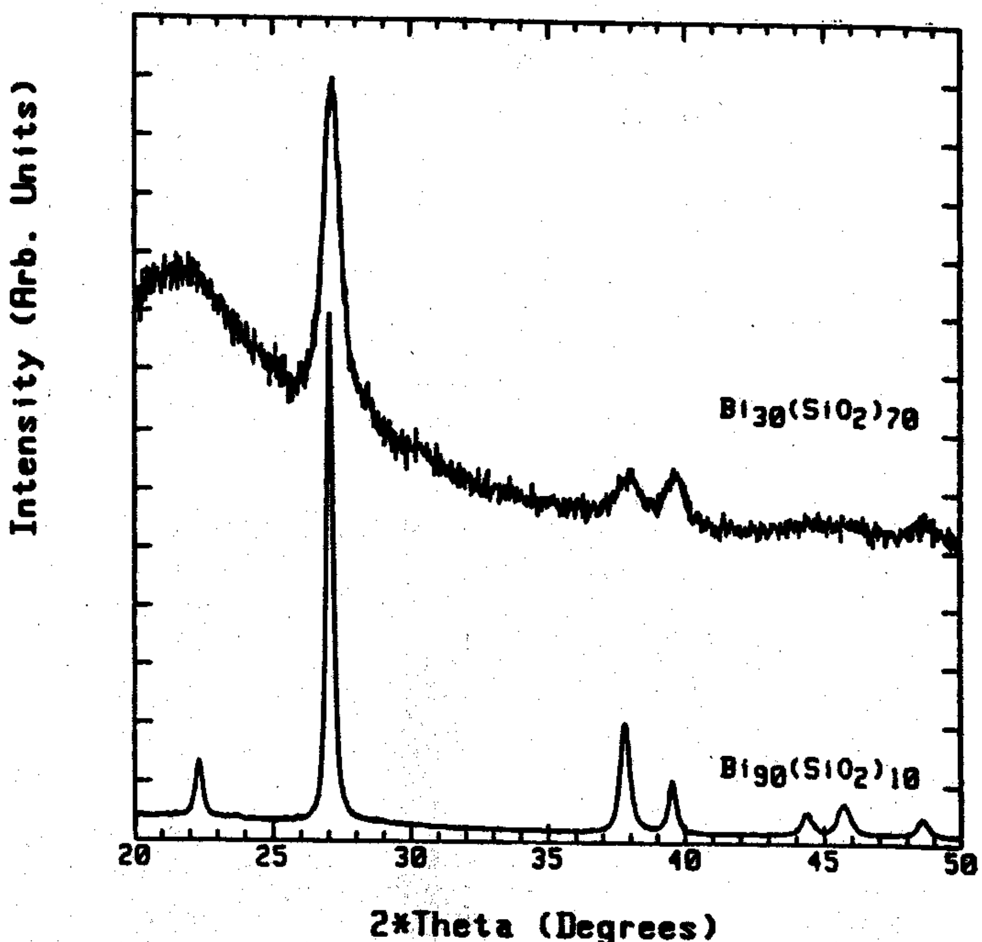
Melting Temperature

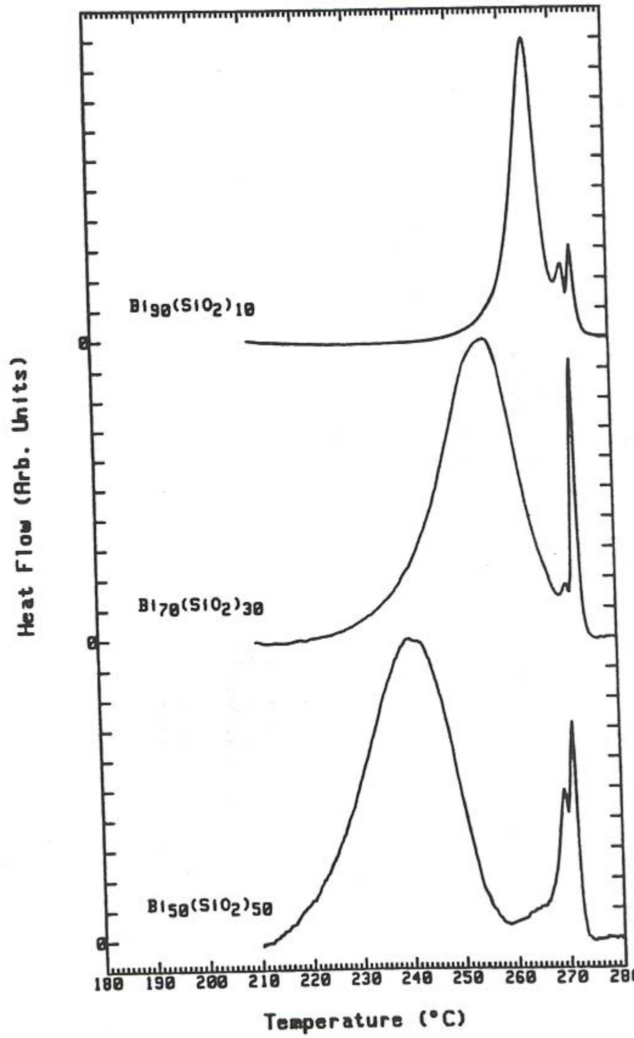
- Environmental effects
  - Pressure of the system
  - Contaminants or Impurities
- Structural effects
  - Grain size
  - Phases present

Unruh, Patterson, and Shah

- Studied the effects of particle size on the melting behavior of $Bi_x(SiO_2)_{100-x}$ films
- Amorphous SiO_2 substrate created by vapor deposition

X-ray Diffraction and DSC (Unruh et. al.)





Thermodynamics

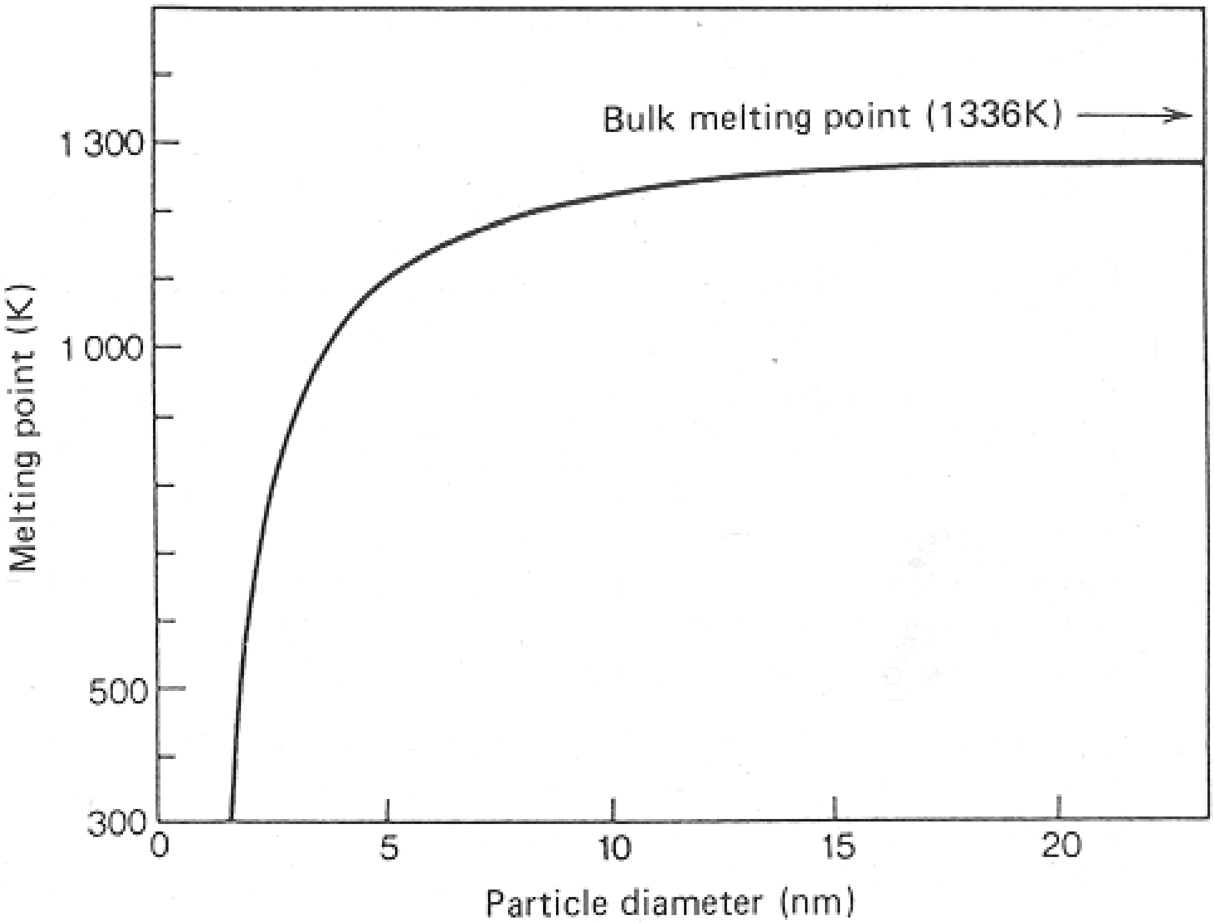
- Pressure in the solid does not equal the pressure in the liquid: $P_s = P_l + 2\gamma/r$
- $d\mu = -SdT + VdP$
- $\Delta S_m dT = 2V\gamma \, dr/r^2$
- Bulk melting temperature: $T_m = \Delta H_m/\Delta S_m$
- Simplifying and combining all the above Eqs. Thefinal result is:

$$\Delta T = (2V\gamma T_m) / (r\Delta H_m)$$

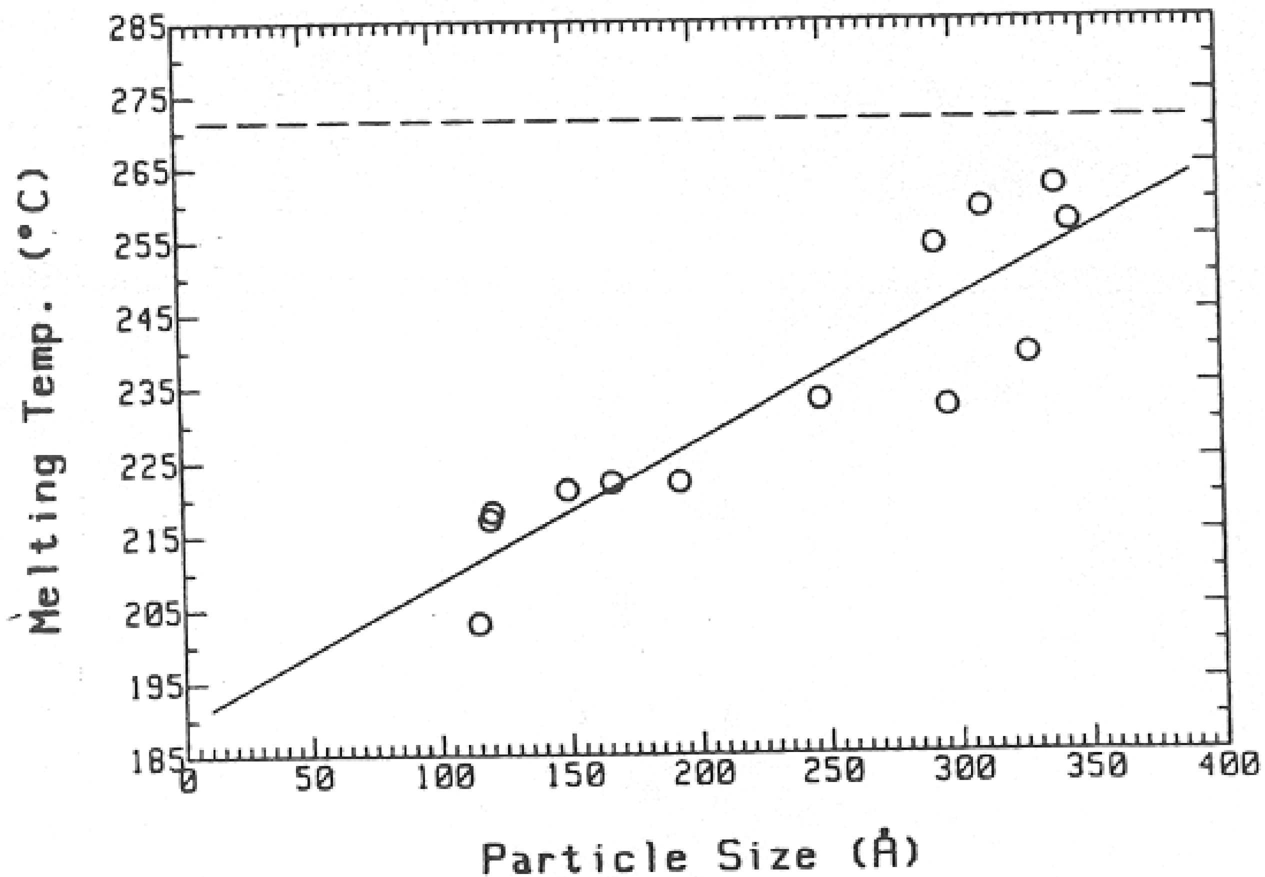
(which means that change in M.P. is inversely proportional to the radius of the sphere).

Calculated Melting Point of Gold

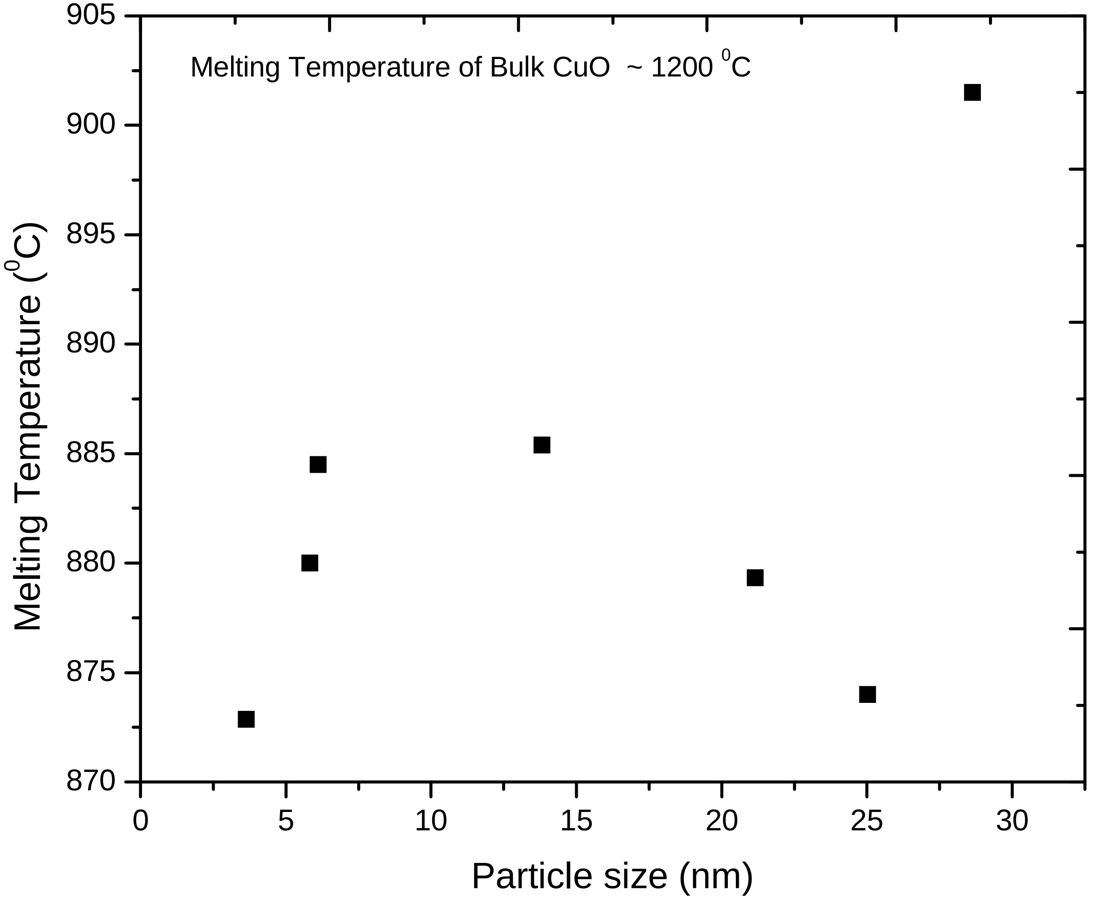
(Ichimose et al.)



Observed Melting point of Bi (Unruh et. al)



Observed Melting Temperature of CuO Nano-Particles



The Crystallization of Metallic Glasses

Mainly two factors are important:

- Nucleation
  - Critical radius requirement causes a nucleation energy barrier ΔG^*
- Crystal (Grain) Growth

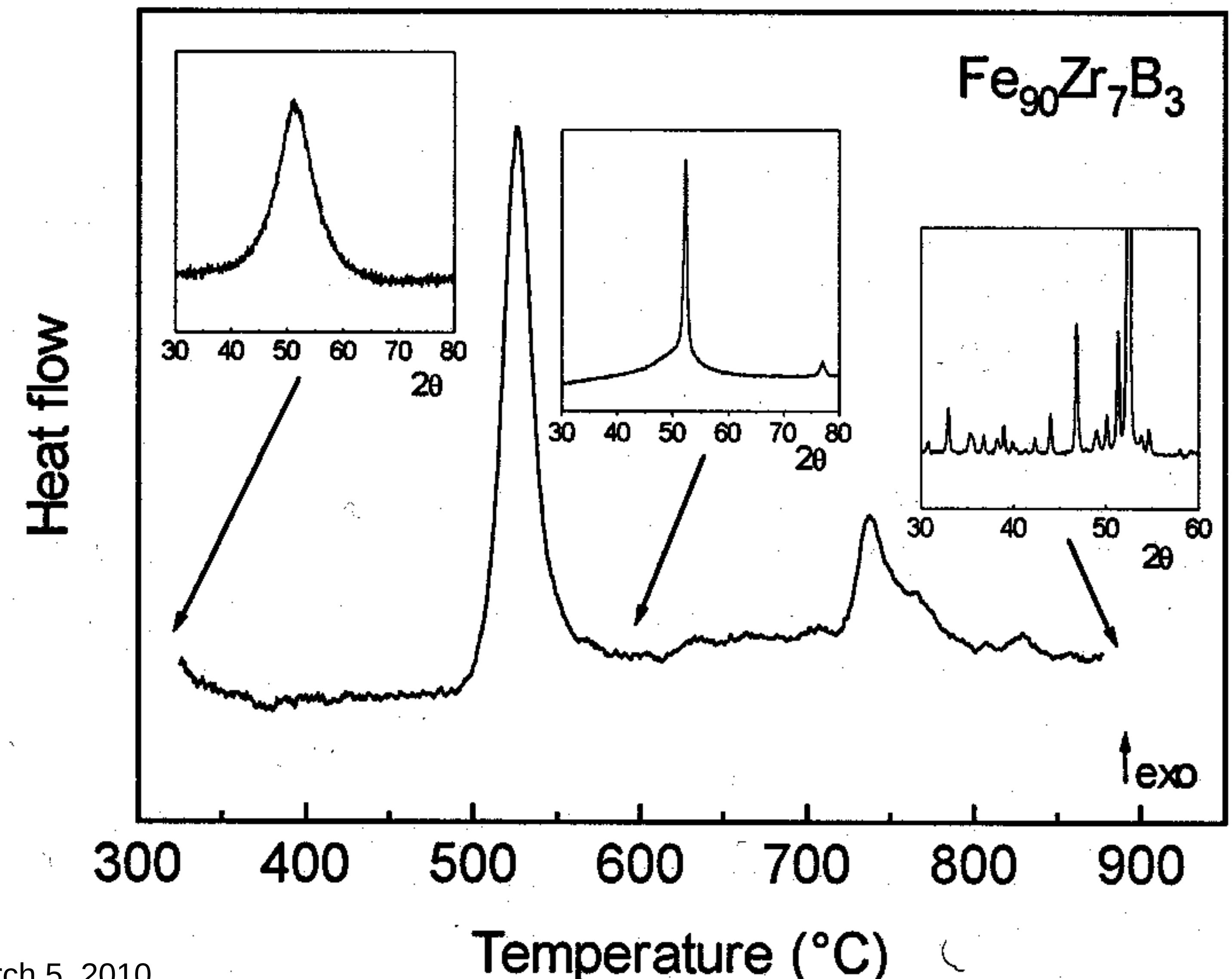
Grain Growth

- $\Delta G = \Delta H - T\Delta S$
- Initially reduced the free energy of the system due to the reduction in surface to volume ratio
- Ultimately slows due to entropy requirements

Grain Growth Kinetics

- Driving force for grain growth:
    - $v \approx 2M\gamma/D \approx dD / dt$
  - Where:
    - v = the driving force for grain growth
    - M = Mobility
    - γ = surface energy
    - D = Mean grain diameter
    - t = time of reaction
- Mean grain diameter:
    - $D = K't^n$
    - (K is proportionality constant that increases with temperature, 'n' is the fractional constant)
- Composition and temperature dependent

DSC and X-ray Diffraction (Baricco et.al.)



Crystallization of Ceramic Glasses

- Spassov and Meinhardt studied $Co_{33}Zr_{67}$
- Unable to experimentally conclude whether nanophase was due to polymorphic transformation or primary crystallization
- Kinetic analysis showed it to be a time dependent primary crystallization

High Pressure Phase Stabilization

- Unexpected metastable phases are present in some nano-structured ceramics
- Trend seems to be that these phases are typically seen under high-pressure conditions
- Some are observed in doped materials of the same chemical composition

Solid-state Diffusion

- Solid-state diffusion does not control nano-materials in the same manner as it does in bulk materials
- Mathematically the same, but occurs relatively quickly due to the finite size of the particle
- Temperature, but not pressure, dependent

SnO_2

- Used in oxygen sensors
- Normal annealing results in a tetragonal phase
- Under high pressure conditions, orthorhombic crystal structure can form
- Not stable under ambient conditions (cannot generally be forced through doping)

Nanophase SnO_2

- Shows evidence of a post-anneal orthorhombic phase when heat treated in O_2 deficient environment
- Evidence suggests the material is not stoichiometric SnO_2
- Overall stress of the system is reduced by the formation of orthorhombic structure

ZrO_2

- Used in oxygen sensors, and the fabrication of fuel cells
- Microcrystalline material is tetragonal
- High temperature or high pressures can cause a reversible martensitic transformation to monoclinic
- Dopants can be used to stabilize monoclinic at ambient conditions

Nanocrystalline ZrO_2

- Monoclinic phase is stable at ambient conditions
- Produced by sol-gel method
    - Appears to be the result of preparation pH
    - Transformation is neither martensitic or reversible
- OH^- ions coupled with Zr vacancies provide the required stress on the system

Grain size Stability

- Grain size stability in nanocrystalline materials has been found to be closely related to the:
- structural characteristics of the material, such as grain size and its distribution,
- grain morphologies,
- triple junctions,
- porosity in the sample,
- and so on.

Conclusions

- Thermodynamics and kinetics both play an important role in phase transformations.
- The phase transformations and stabilizations are particle size dependent.
- This dependence is critical in the nano regime.

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Our Group

Material Science/Nano-Technology Research Laboratory
Department of Physics
GCU, Lahore

The Group stepped into the field of Nano-science in 2005

Running Projects

Colossal Magneto-resistant (CMR) Nanomaterials
Metal Oxide Nanomaterials
Doped Metal Oxide Nanomaterials
Doped Sulfide Nanomaterials
Transparent Conducting Oxides for Solar cells
Carbon Nano-tubes
Nanotechnology for Cancer Treatment

Facilities Available:

Fabrication of Nano-Materials:

Include Two State of the Art Furnaces

1). RT to 1400 ^{0}C (Muffle)
2). Tube Furnace (RT to 1800 ^{0}C) with controlled environment
3). PVD Set-up (under construction)

Characterization Techniques

Structural and Phase Analysis using XRD
Thermal Properties by DSC/TGA (RT to 1500 ^{0}C) and a DSC for low temperature down to 90 K
Magnetic Properties by AC Susceptibility Measurement (77-300K)
Electrical Properties using Resistivity Measurement (77- 300K)

Open to Collaborate