Thermal Analysis and Nano-Thermodynamics

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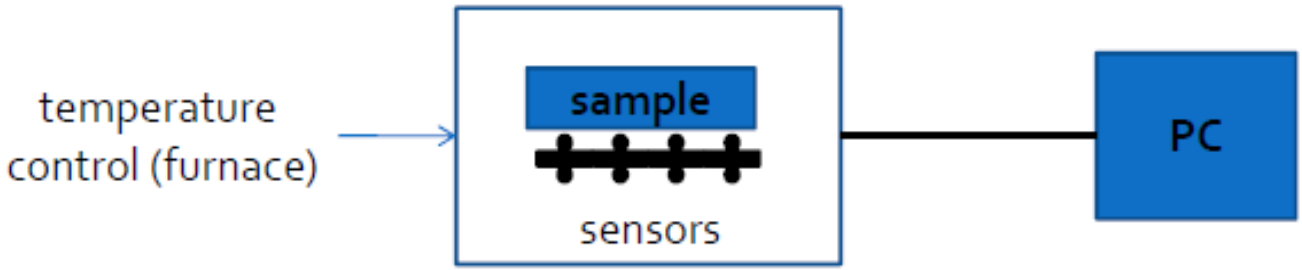
Post-Doc, Ph.D

Thermal analysis

- **Thermal analysis** is a branch of materials science where the properties of materials are studied as they change with temperature. While engaging different techniques to inspect the measurement, both the types of instruments are employed to measure heat flow and this seems to be certified as DSC under the **ICTAC (**International Confederation for Thermal Analysis and Calorimetry**)** defination

Basic Principles of Thermal Analysis

- Modern instrumentation used for thermal analysis usually consists of the following parts:
  - sample holder/compartment for the sample
  - sensors to detect/measure a property of the sample and the temperature
  - an enclosure within which the experimental parameters (temperature, speed, environment) may be controlled
  - a computer to control data collection and processing



Thermal Analysis Techniques

- IUPAC definition - a group of techniques in which a physical property is measured as a function of temperature, while the sample is subjected to a controlled temperature programme (heating, cooling or isothermal).
- A range of techniques e.g.:
  - Differential Thermal Analysis (DTA) – temperature
  - Differential Scanning Calorimetry (DSC) – energy
  - Thermogravimetric Analysis (TGA) – mass
  - Thermomechanical Analysis (TMA) – dimensions

IUPAC: International Union of Pure and Applied Chemistry

Thermal Analysis

- Differential Scanning Calorimetry (DSC)
  - Measure heat absorbed or liberated during heating or cooling
- Differential Thermal Analysis (DTA)
- They are use for thermal investigation where thermal change can be observed and characterised
- Thermal Gravimetric Analysis (TGA)
  - Measure change in weight during heating or cooling
- Thermomechanical Analysis (TMA)
  - Measure change in dimensions during heating or cooling

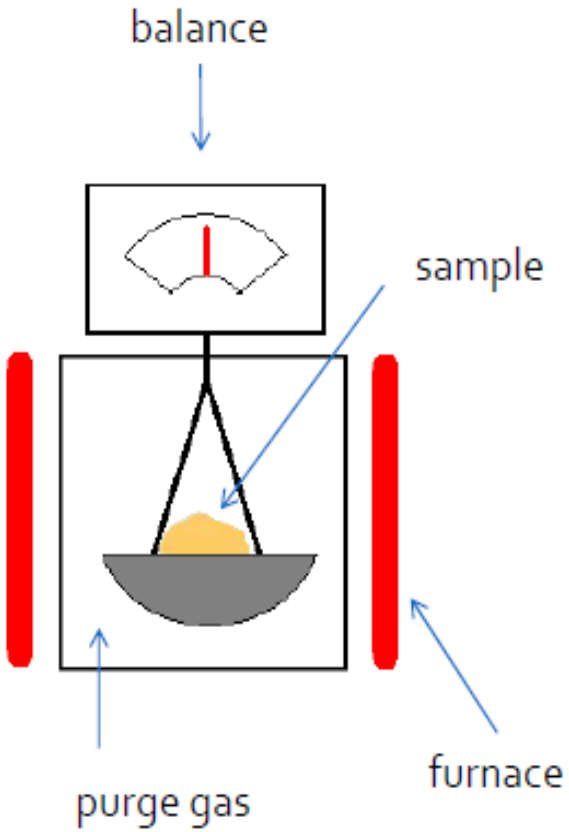
Thermogravimetric Analysis (TGA)- Basic Principle

TGA measures the amount and the rate of weight change of a material with respect to temperature or time in controlled environments. A TGA consists of three major parts a furnace-microgram balance, auto sampler and thermocouple.

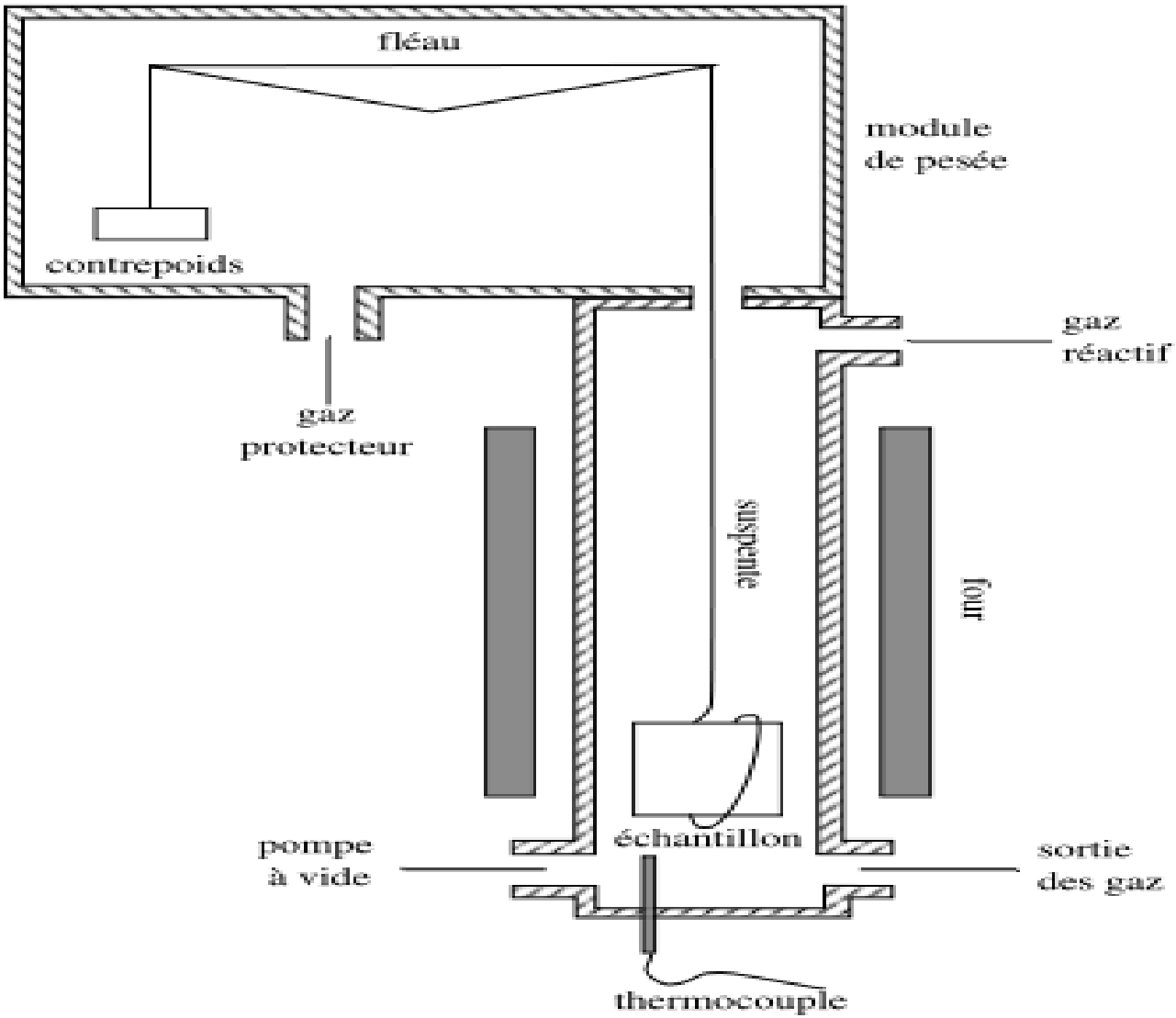
- Nitrogen is the most common gas used to purge samples in TGA due to its inert nature.
- The furnace can raise the temperature as high as 1000°C which is made of quartz.
- The auto sampler helps to load the samples on to the microbalance.
- The thermocouple sits right above the sample.
- Care should be taken at all times that the thermocouple is not in touch with the sample which is in a platinum pan.

Thermogravimetric Analysis (TGA)

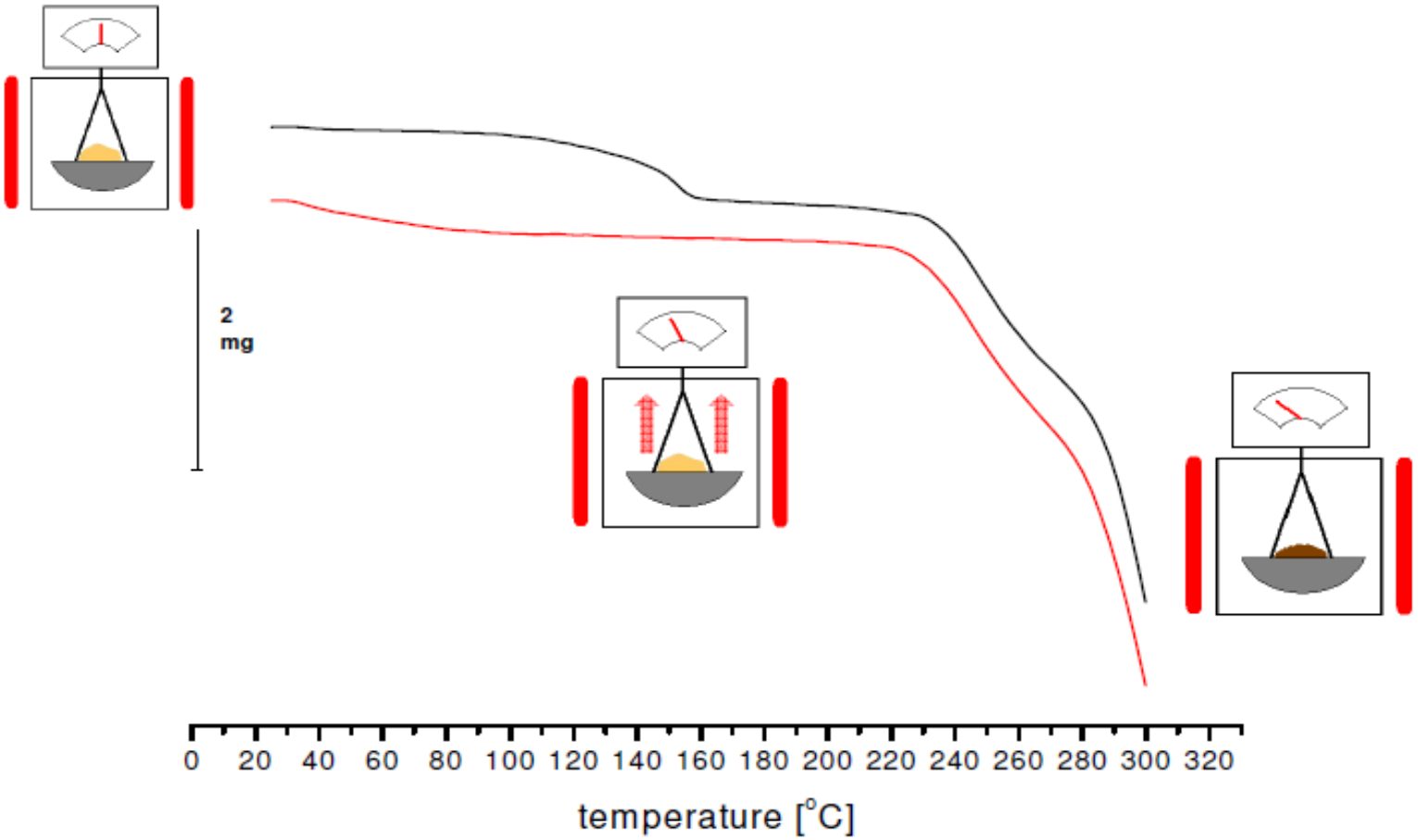
- A technique measuring the variation in mass of a sample undergoing temperature scanning in a controlled atmosphere
- Thermobalance allows for monitoring sample weight as a function of temperature
- The sample hangs from the balance inside the furnace and the balance is thermally isolated from the furnace



Thermogravimetric Analysis (TGA)



Examples of TGA Curves



TGA curves of crystalline and amorphous substance

Applications of TGA

- Thermal stability of materials
- Oxidative stability of materials
- Estimated lifetime of a product
- Decomposition Kinetics of materials
- The effect of reactive or corrosive atmosphere on materials
- Moisture and volatiles contents on materials.
- TGA reveals changes of a sample due to weight, whereas DTA and DSC reveal changes not related to the weight (mainly due to phase transitions)

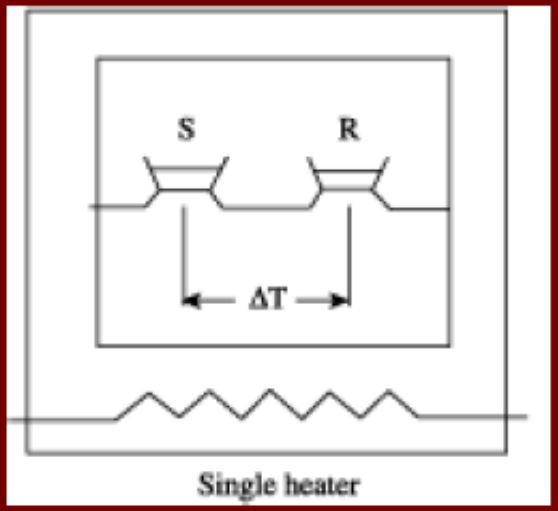
Differential Thermal Analysis(DTA)

Sample holder: Sample and reference cells

Sensors: Thermocouples, one for the sample and one for the reference

Furnace: Block containing sample and reference cells

Temperature controller: Controls temperature program



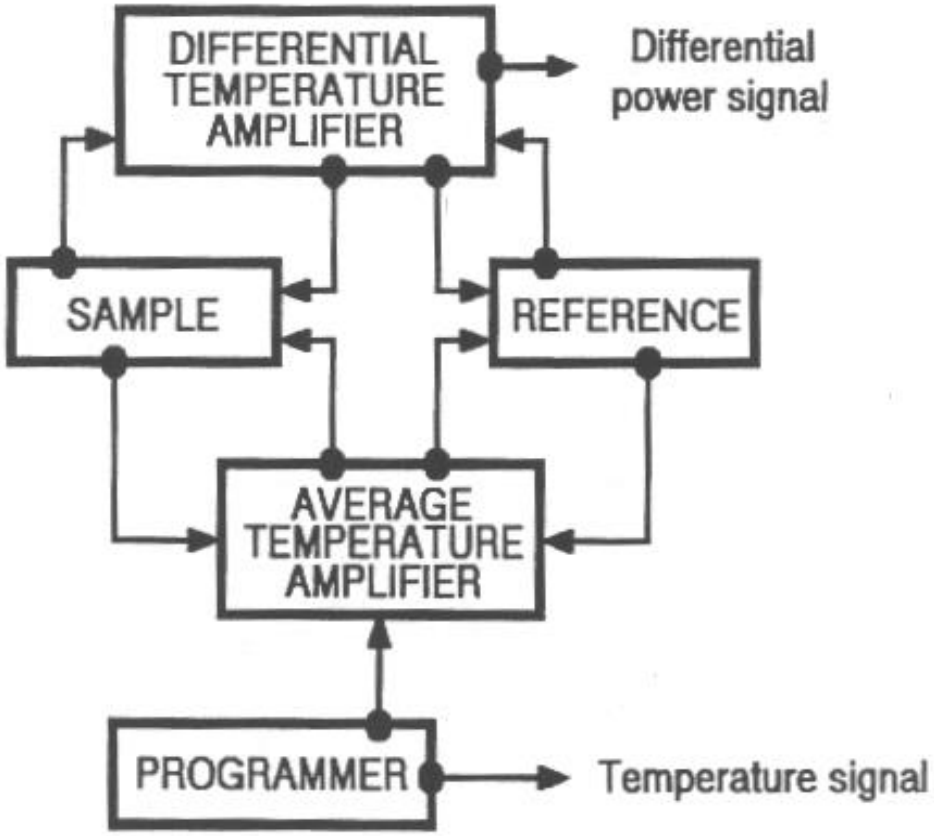
Advantages:

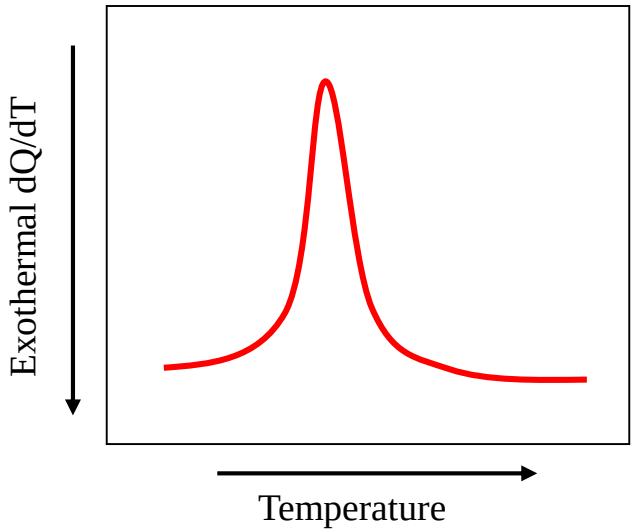
- instruments can be used at very high temperatures
- instruments are highly sensitive
- flexibility in sample volume/form
- characteristic transition or reaction temperatures can be determined

Disadvantages:

- uncertainty of heats of fusion and transition temperatures

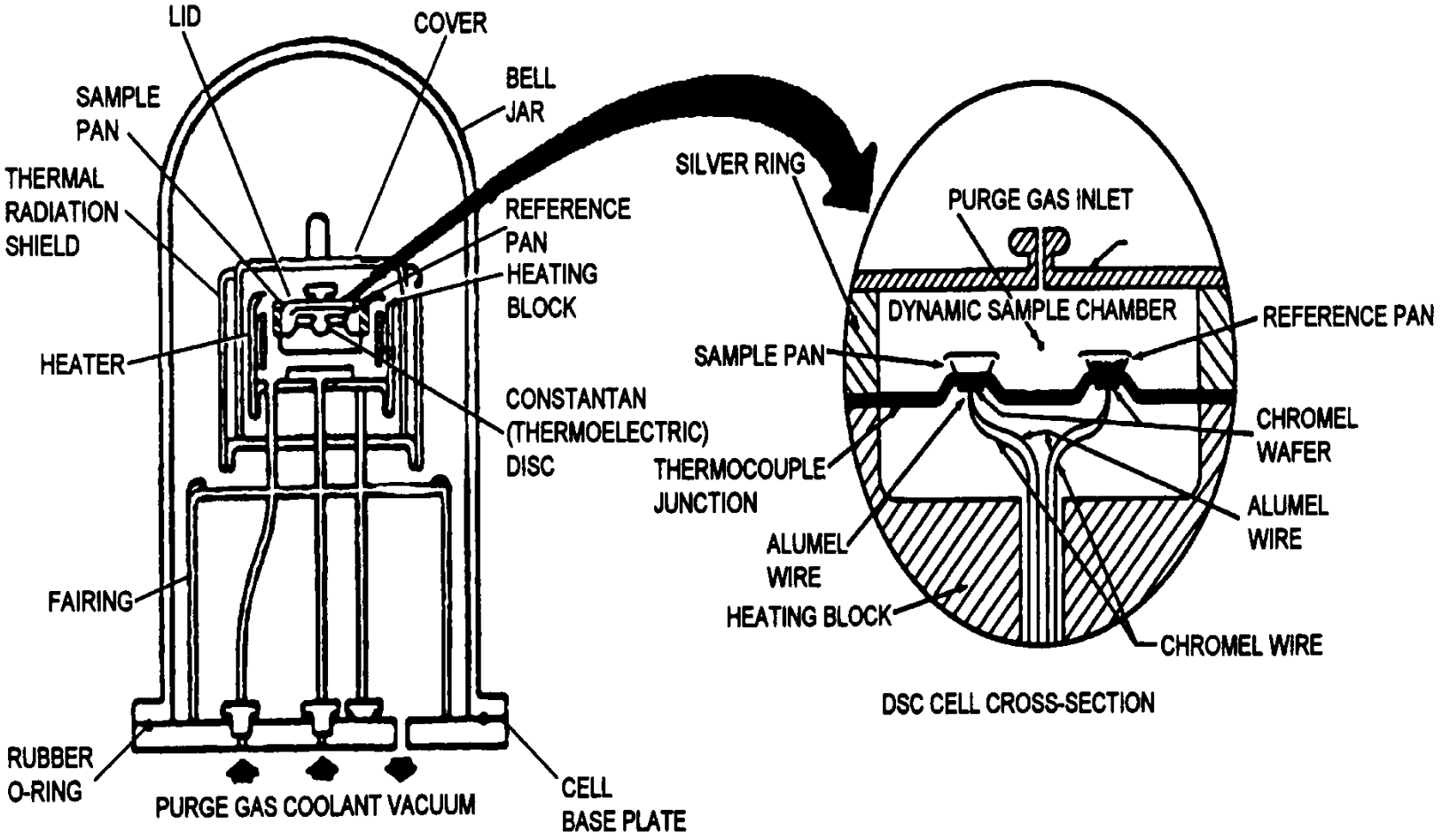
Differential Scanning Calorimetry (DSC)



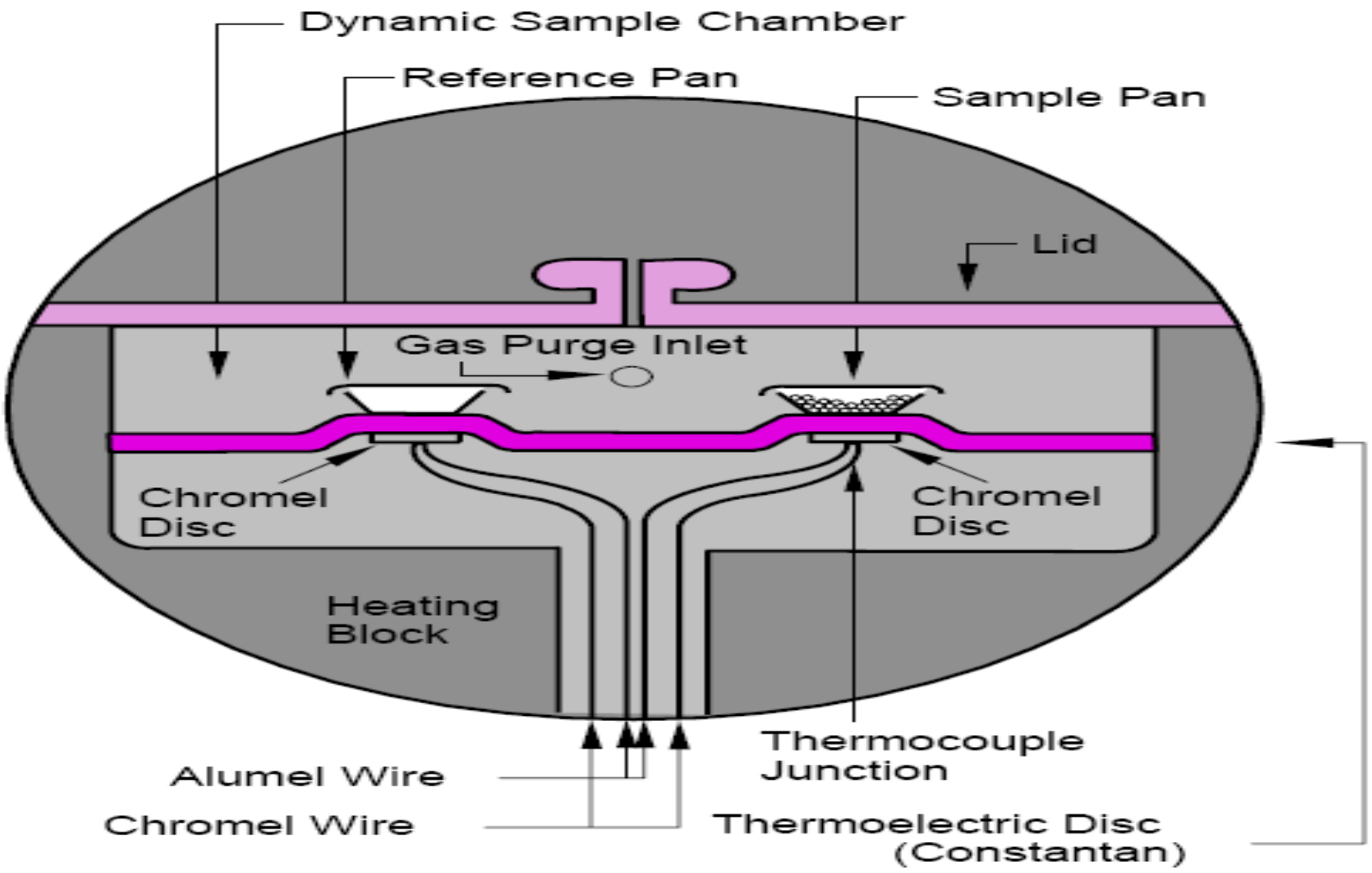


- DSC measures differences in the amount of heat required to increase the temperature of a sample and a reference as a function of temperature

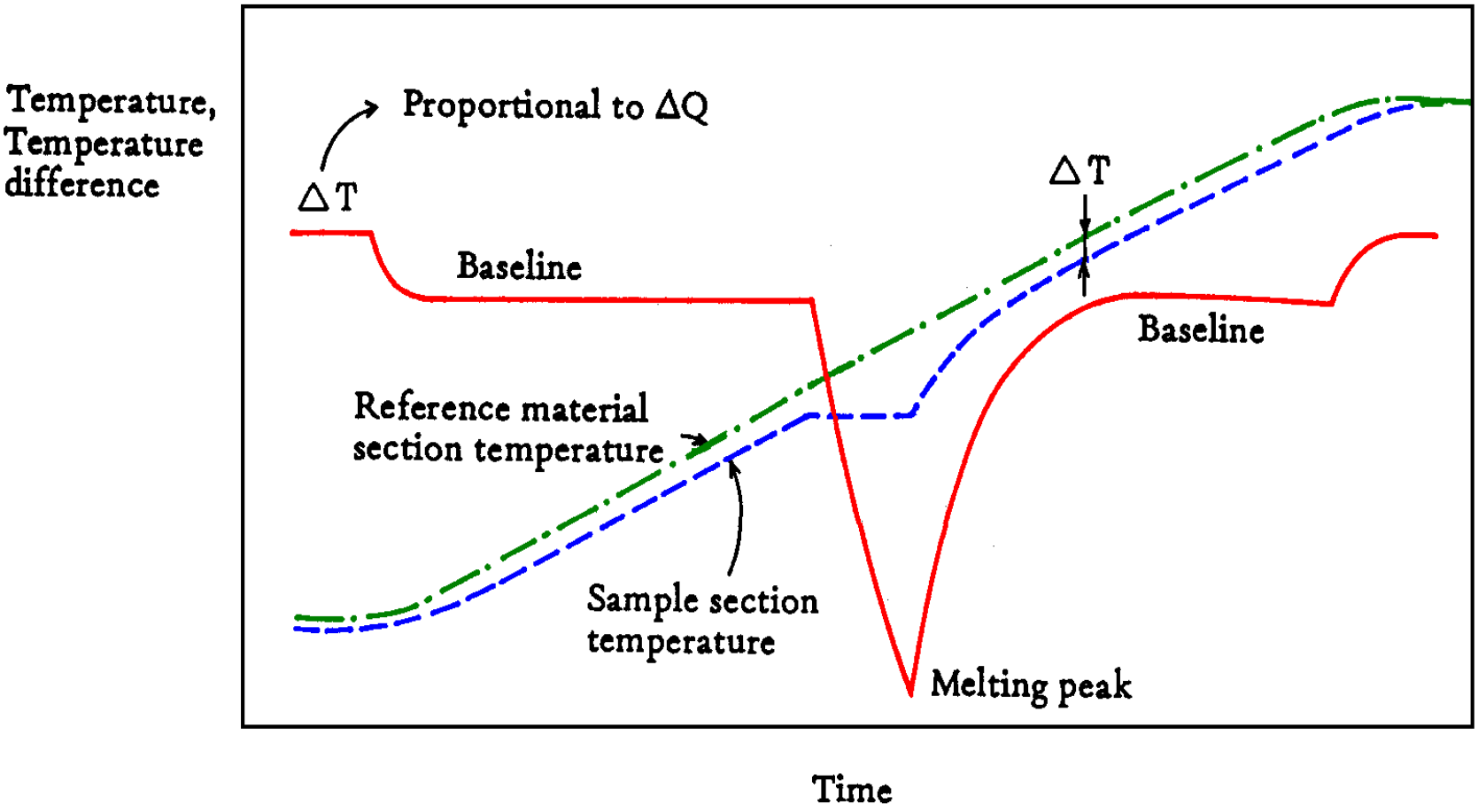
Sample containers and sampling



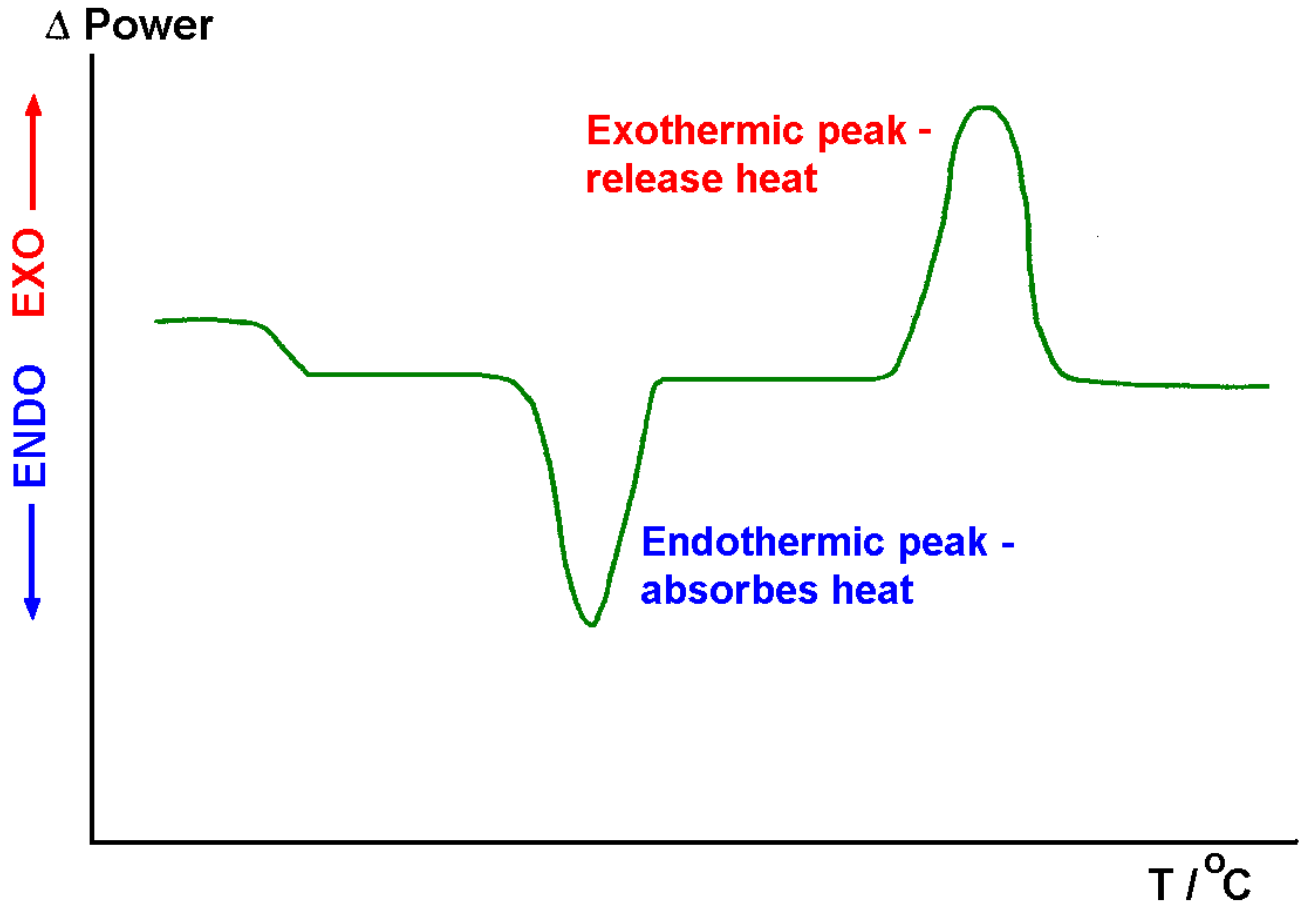
Differential Scanning Calorimeter



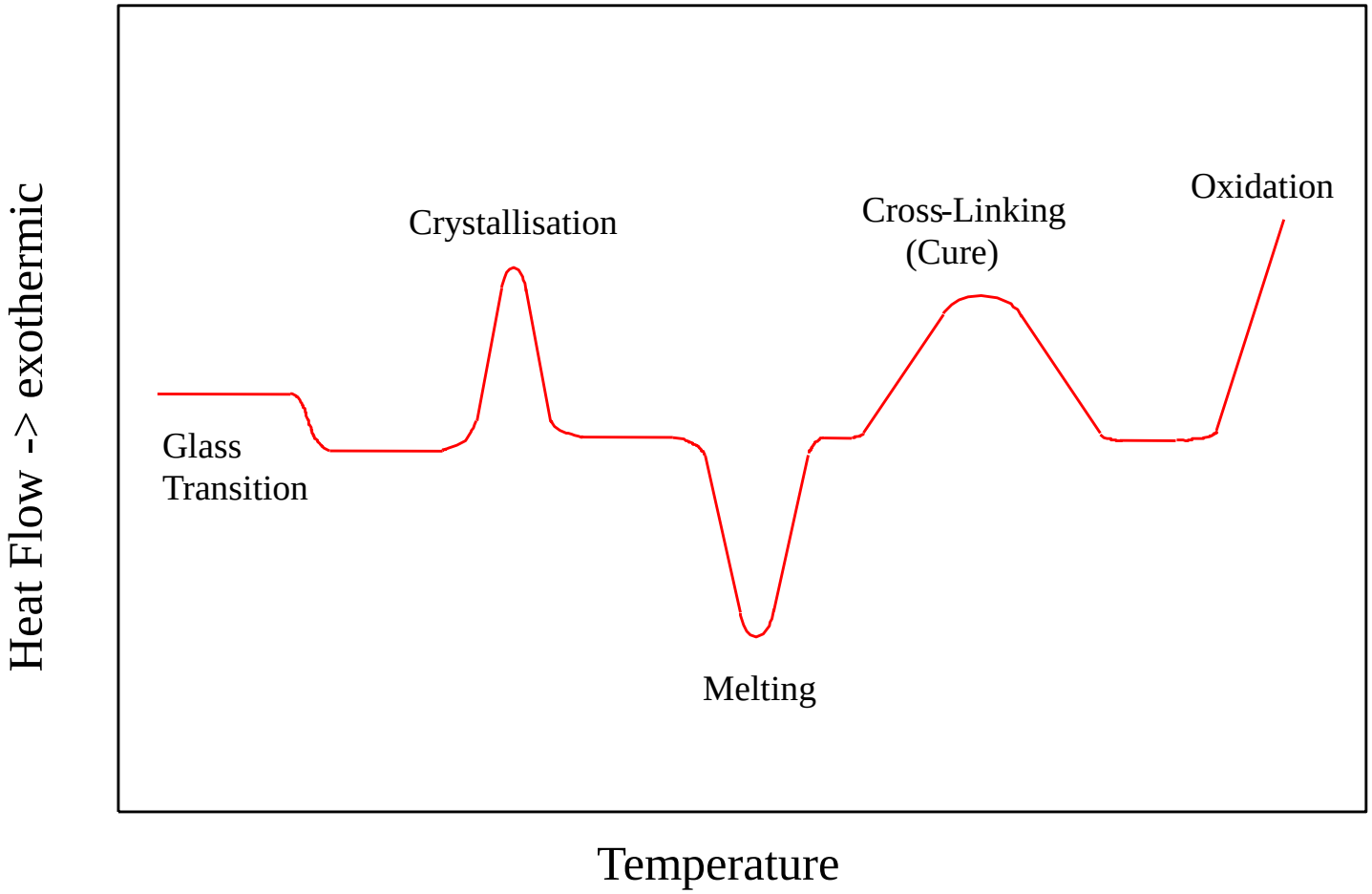
Principle Of DSC



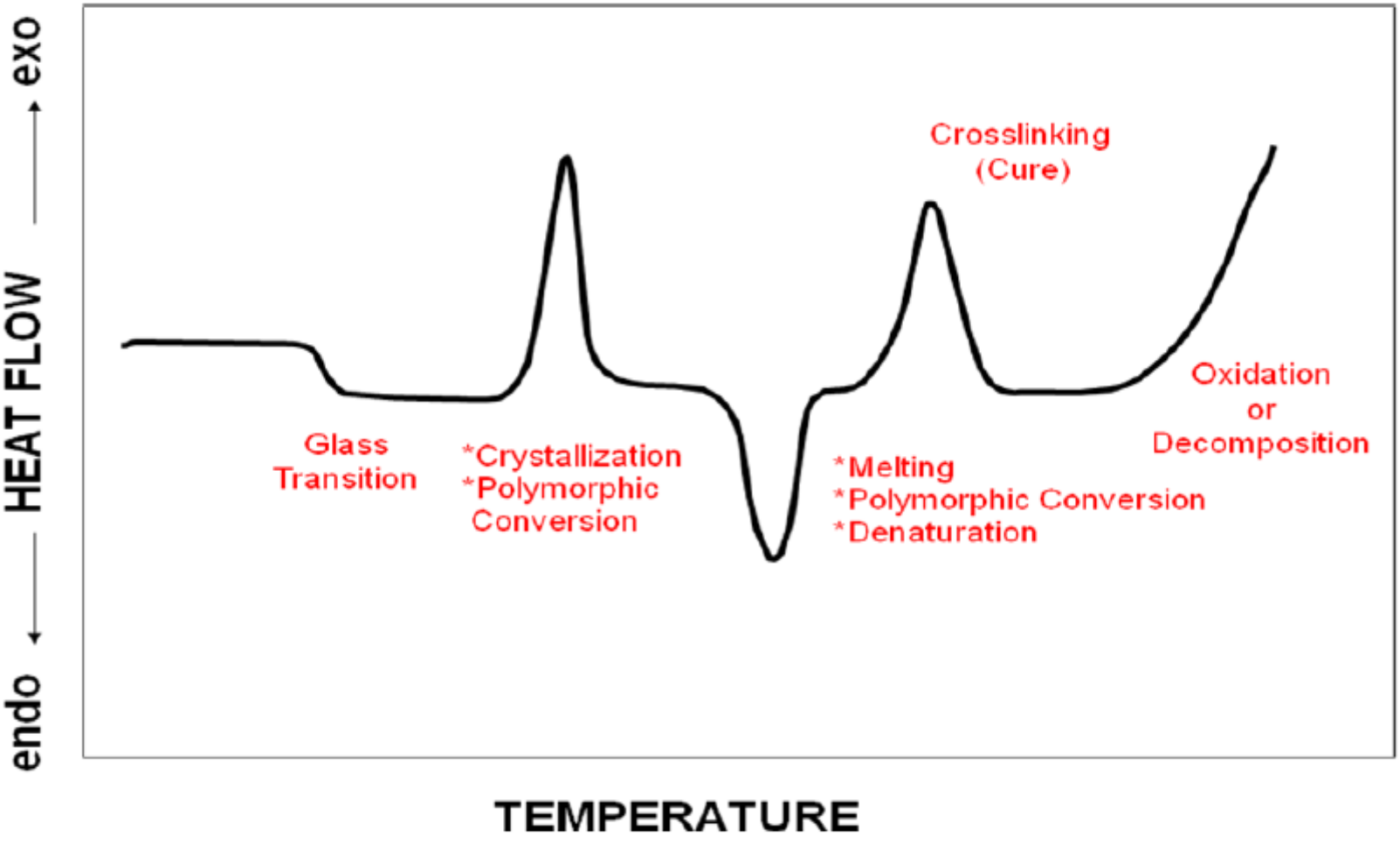
Typical DSC Curve



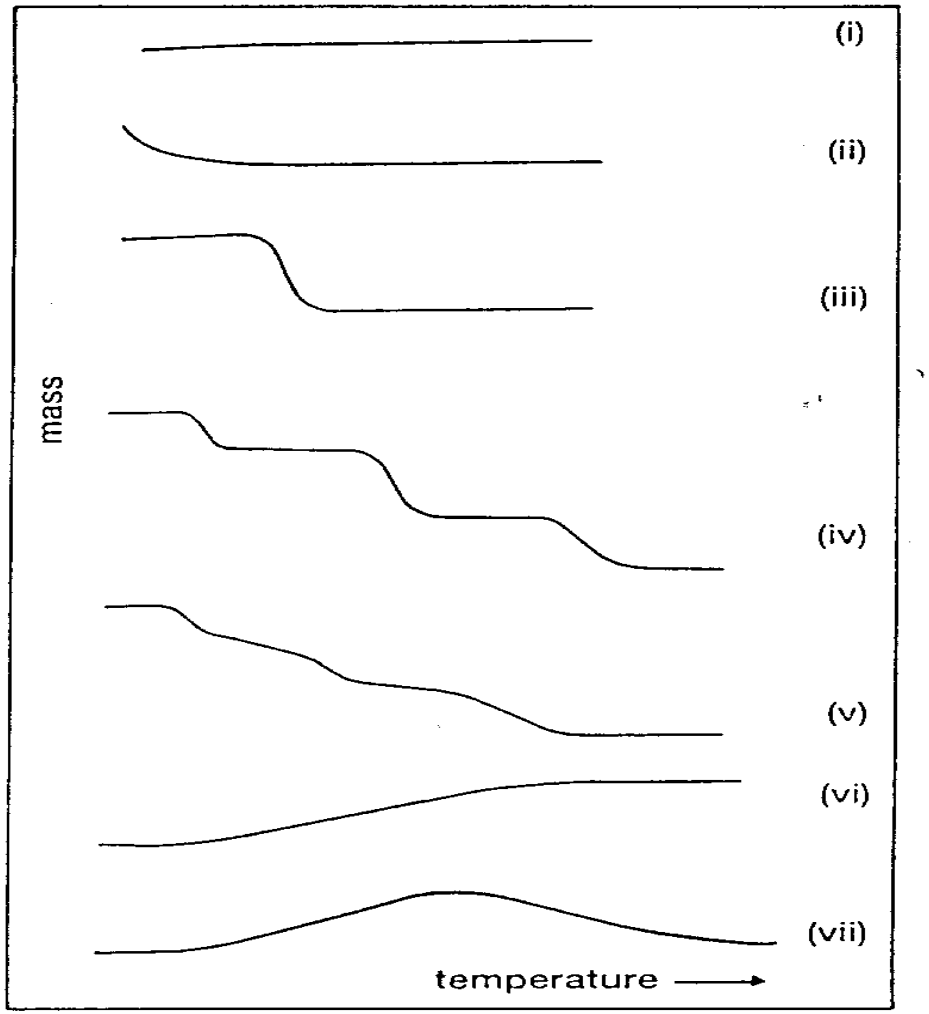
DSC Thermogram



Transitions in a DSC Curve



Interpretation of Thermal curves



i. The sample undergoes no decomposition with loss of volatile products over the temperature range shown but solid phase transformation, melting ,etc can not be detected by TG,

ii. The rapid initial mass loss is characteristic of desorption or drying. If it is true, then re-run the sample should result in type (i) curves,

iii. Single stage decomposition,

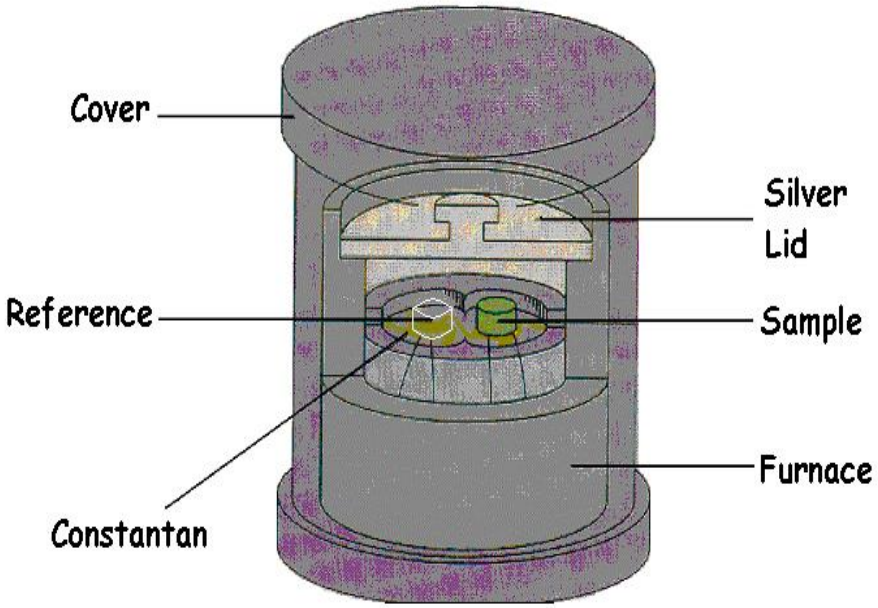
iv. Multi-stage decomposition with relatively stable intermediates : provide information on the temperature limit of stability of reactants and intermediate products and also stoichiometry,

v. Multi-stage decomposition with no stable intermediate product. However heating-rate effect must be considered. At low heating rate, type (v) resemble type (iv). At high heating rate, type (iv) and (v) resemble type (iii) and lose all the details,

vi. Gain in mass due to reaction with atmosphere, e.g. oxidation of metals,

vii. Oxidation product decompose again at higher temperature; this is not often encountered.

DSC and Heating rate Formula



$$dH/dt = Cp * dT/dt + f(T,t)$$

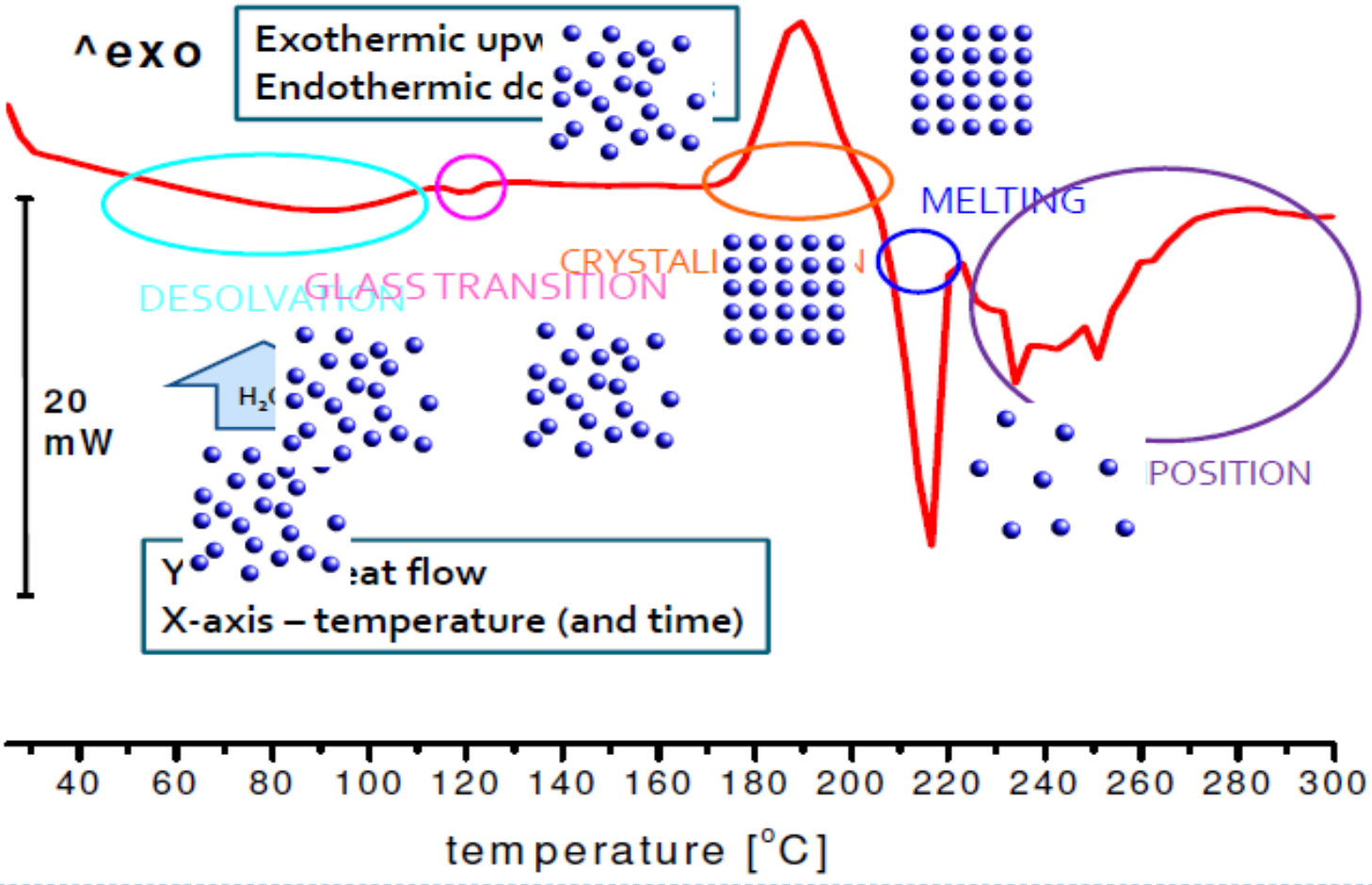
Where dH/dt → heat flow measured by DSC

Cp → heat capacity or weight of the sample

dT/dt → heating rate

$f(T,t)$ → time dependant or kinetic component

Typical Features of a DSC Trace

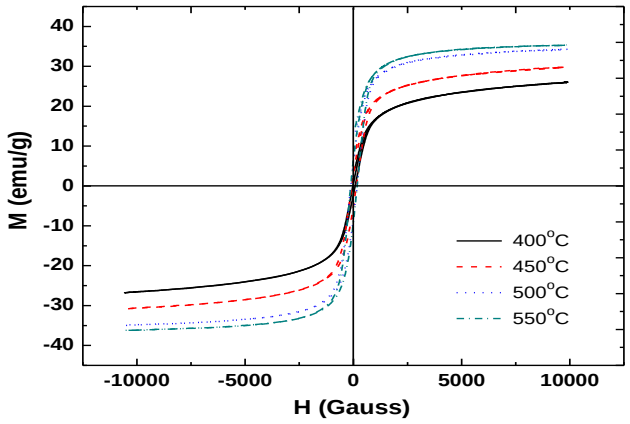


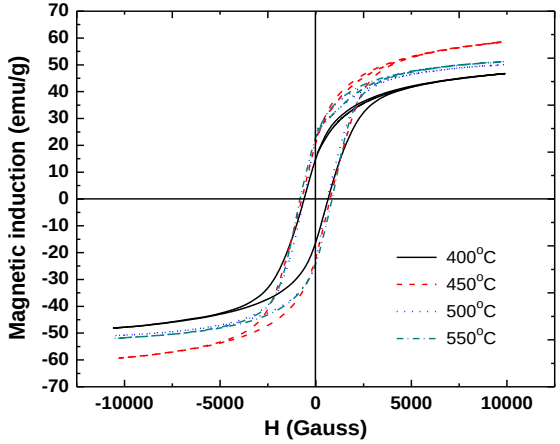
Thermodynamics of Materials at 450C

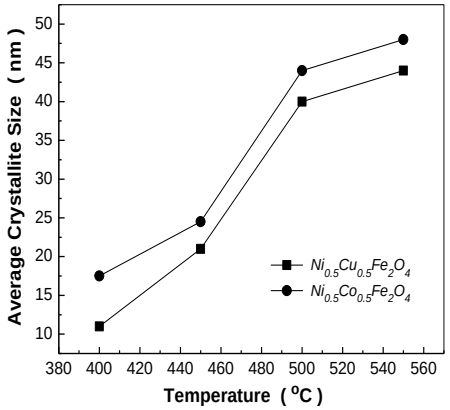
Dependence of magnetic and structural properties of Ni0.5 M0.5 Fe2O4 (M=Co, Cu) nanoparticles and Thermodynamics of prepared materials

Rakesh Kr Singh et al. ***Int.J. of Engineering, Science and Technology, Vol. 2, No. 8, 2010, pp. 73-79***

- The properties of nanosize ferrite Magnetic materials crucially depend on the synthesis temperature. In citrate precursor method, 450C seems to be a critical temperature for growth of Ni-Co and Ni-Cu ferrites in pure phase. The growth of particles becomes much faster beyond this temperature. Crystalline structure changes from cubic spinel to tetragonal spinel as 450C temperature is crossed. The particle size, lattice constant and also magnetization parameters show sharp changes at 450C. This suggests that nucleation/growth/reaction mechanism(Thermodynamic) is different below 450C from that above it(Growth mechanism are shown in figure)



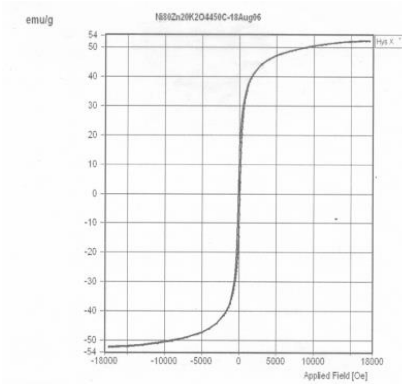


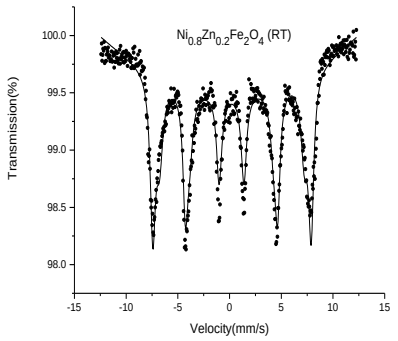


Thermodynamics of Materials at annealing temperature 450C

Rakesh Kr Singh, H.C. Verma et al, Ni-Zn Ferrite Nanoparticles and their Applications, manthan, Int. J.(2011)p

Single annealing temperature 450C for all our samples of nanocrystalline Ni-Zn mixed ferrite. The most interesting case seems to be with Ni0.8Zn0.2Fe2O4 ,where both the coercive field(116.10 Oe) and the saturation magnetization (52.18emu/g) are largest. Values of saturation magnetization is higher than 50 emu/g have so far been achieved by using other methods, only through sintering attemperatures much above 450C. The Mössbauer spectrum shows that Fe occupies both the A and B sites in the sample and superparamegnetic fluctuations are not significant. So, this temperature is assumed as standered tempeature.





Sample	H_c (Oe)	M_r (emu/g)	M_s (emu/g)	Squareness/Particle size(nm)
$Ni_{0.2}Zn_{0.8}Fe_2O_4$.	22.42	0.5744	17.50	0.033/ 16
$Ni_{0.4}Zn_{.6}Fe_2O_4$	1.53	0.1049	43.43	0.002/7
$Ni_{0.5}Zn_{.5}Fe_2O_4$	90.86	5.658	40.54	0.140/16
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	35.77	2.678	43.64	0.059/9
$Ni_{0.75}Zn_{0.25}Fe_2O_4$	93.10	4.610	38.94	0.118/9
$Ni_{0.8}Zn_{0.2}Fe_2O_4$	**116.10**	**11.38**	**52.18**	**0.148/18**

New Findings from R.K. Singh and Co-Authors Describe Advances in Nanotechnology.

According to the authors of **recent research from Bihar, India,** "Two nano aluminate spinel materials ($ZnAl_2O_4$ and $NiAl_2O_4$) were synthesized by the Citrate precursor method. The citrate precursors consisting of co precipitated citrates of Zn^{2+}or Ni^{2+} and aluminum were first subjected to thermal analysis (TG-DSC) for determining the optimum temperature for annealing."

"Two step decomposition was observed incorporating dehydration and formation of the aluminate. The second step gives an endo peak (-2937 J/g) at 356 A degrees C in the DSC curve of the co precipitated nickel (II) citrate-aluminum citrate gel in O_2 atmosphere. Kinetic/mechanistic analysis of the TG data has also been----------.

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Thermal, XRD, and magnetization studies on $ZnAl_2O_4$ and $NiAl_2O_4$ spinels, synthesized by citrate precursor method and annealed at 450 and 650 °C

Rakesh K. Singh · A. Yadav · A. Narayan · Mukesh Chandra · R. K. Verma

29th STAC-ICC Conference Special Chapter

Abstract Two aluminate spinel materials ($ZnAl_2O_4$ and $NiAl_2O_4$) were synthesized by the citrate precursor method. The citrate precursors consisting of coprecipitated citrates of Zn^{2+} or Ni^{2+} and aluminum were first subjected to thermal analysis (TG-DSC) for determining the optimum temperature for annealing. Two step decomposition was observed incorporating dehydration and formation of the aluminate. The second step gives an endo peak (−2937 J/g) at 356 °C in the DSC curve of the coprecipitated nickel(II) citrate–aluminum citrate gel in O_2 atmosphere. Kinetic/mechanistic analysis of the TG data has also been carried out and values of E_a, $\Delta S^{\#}$, $\Delta G^{\#}$, and A were approximated. On the basis of the findings, 450 °C has been chosen for annealing of the gels. Annealing has also been done at 650 °C for 1 h in muffle furnace in an attempt to obtain nanometric particles of aluminates (MAl_2O_4) {M = Ni, Zn} and to find out their magnetic properties which could render them useful for chemical sensing applications, etc. The TG-DSC curves of various powders which were obtained on annealing at the two temperatures did exhibit thermal instability when carried out in N_2 atmosphere. $NiAl_2O_4$ and $ZnAl_2O_4$ spinels (particle size 17 and 34 nm, respectively) are obtained in pure crystalline phase at 650 °C. $ZnAl_2O_4$ prepared this way shows coercivity values of 470 and 58.37 G and $NiAl_2O_4$, 107 and 23.24 G when annealed at 450 and 650 °C, respectively. $ZnAl_2O_4$ prepared by a polymer precursor method and annealed at 1000 °C, has earlier been reported to have coercivity value of 469 G. Thus, the citrate precursor method is good for the synthesis of $ZnAl_2O_4$, producing single phase nanocrystalline powder of high quality and crystallinity. The value of magnetization was found to be small in the present case for the $NiAl_2O_4$ spinel obtained at 450 °C.

Keywords Nickel aluminate · Zinc aluminate · Annealing temperature · XRD pattern · Coercivity · Magnetization · Thermal stability · TG-DSC · Kinetic parameters · Nano particles · Spinel

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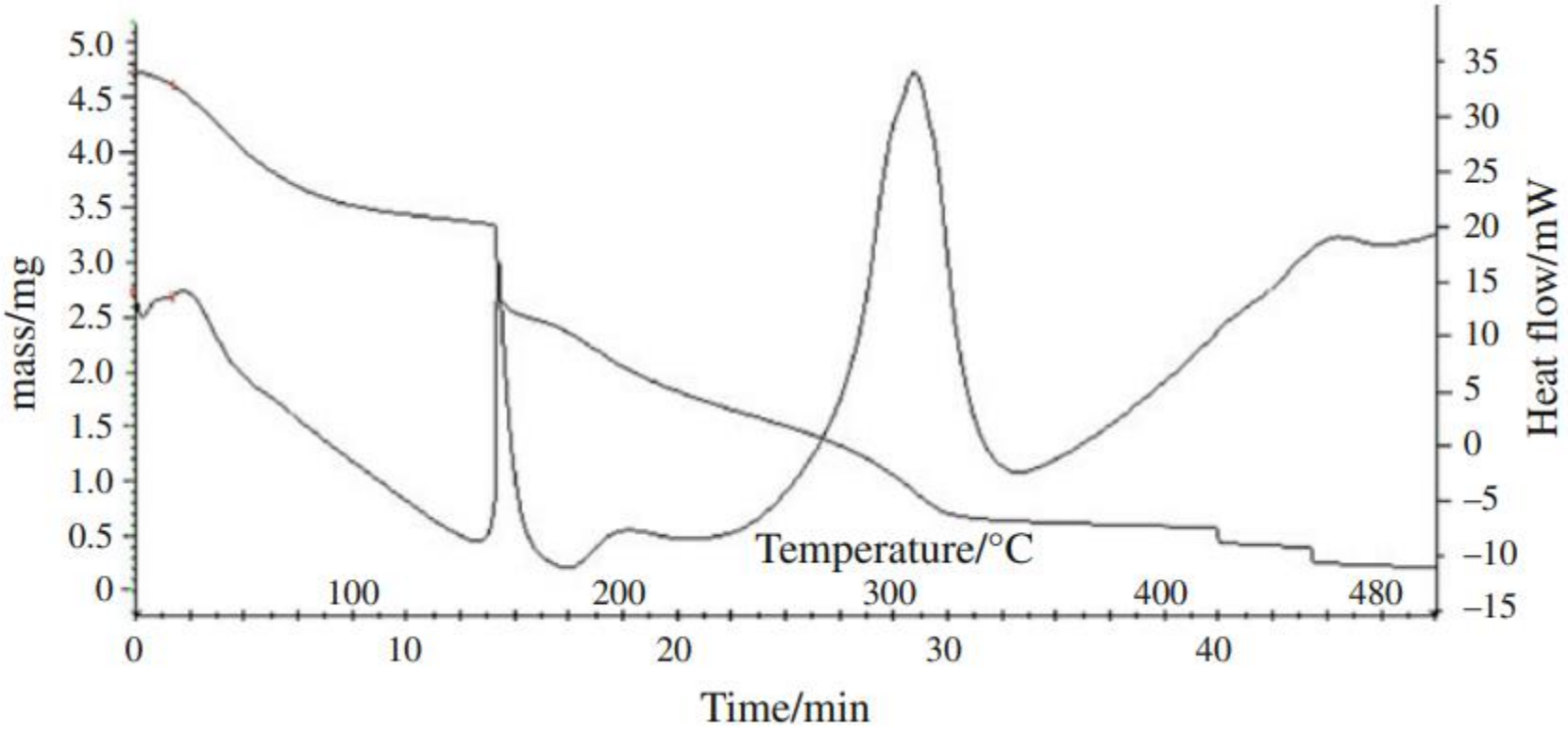
Introduction

Aluminate content brings diverse applications to materials. Ceramic materials (cements, castable ceramics, bioceramics, and electroceramics) are normally formed from cubic crystal systems [1] which include garnets and spinels. Many rare earth aluminate garnets are used as laser host when doped with Nd(III) or Yb(III) and also as scintillators and phosphors. Upon doping, interesting properties have been observed. Eu^{2+}, R^{3+}-doping for example, brings thermoluminiscence properties to calcium aluminate materials [2]. And $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM), is an important blue phosphor of plasma display panel (PDP) [3]. The rare earth aluminate glasses find use as alternatives to sapphire for use in infrared windows. Single crystals of lanthanum aluminate are known to have application as a substrate for deposition of thin films of the high temperature

TG – DSC of the precursor prepared by Citrate method was carried out by NETZSCH STA 449 apparatus. The dehydration and curing was found to be completing in the range of 100-500°C. Thus the sintering temperature was chosen as 400°C for complete crystallization



Thermal Analysis Instrument Manufacturers-References

- Perkin Elmer Thermal Analysis Systems

http://www.perkin-elmer.com/thermal/index.html

- TA Instruments

http://www.tainst.com/

- Mettler Toledo Thermal Analysis Systems

http://www.mt.com/

- Rheometric Scientific

http://www.rheosci.com/

- Haake

http://polysort.com/haake/

- NETZSCH Instruments

http://www.netzsch.com/ta/

- SETARAM Instruments

http://setaram.com/

- Instrument Specialists, Inc.

http://www.instrument-specialists.com/

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