Materials Chemistry

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Module - 3
Lecture - 4
Applications of Thermal Analysis Techniques

In this module, we have been looking at several characterization techniques, which are useful for materials characterization.

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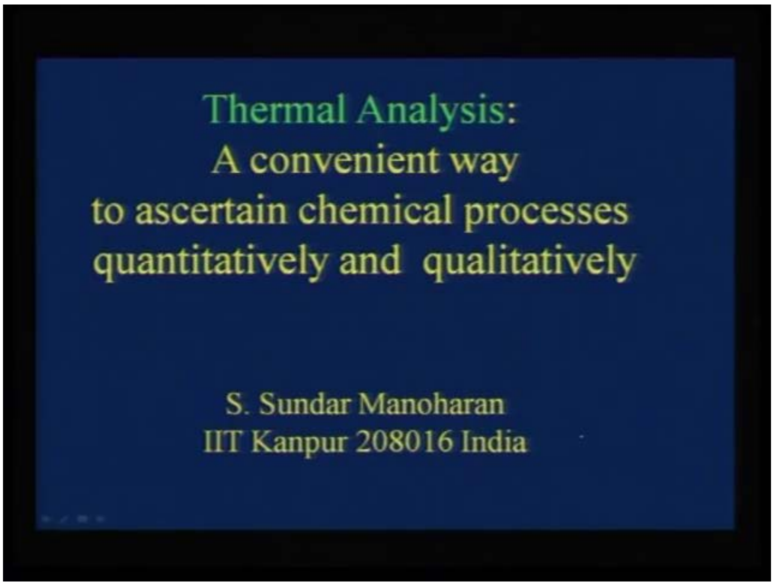

Thermal Analysis:
A convenient way
to ascertain chemical processes
quantitatively and qualitatively

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One of the most prolific characterization methods, which has found useful application in a variety of areas mainly focusing on material chemistry is thermal analysis, it is also called as thermo analytical methods. Brightly because it is now become a family of convenient techniques merged together, it is not a single technique, but it has included many related techniques to itself and spreading to a briefly. Why I want to single out and give a separate lecture on thermal analysis is that, there are more than 3 journals international journals, which are floated on just thermal analysis and those are nearly 3 decades old and still several fascinating studies are coming up.

So, this is a very useful technique, which has proved to very useful both to chemist physicist and material scientist, I will call this as a very convenient technique, because it is affordable and most of the labs can have this instrument. And the chemical processes that happens during, heating of the sample can be actually map both qualitatively and quantitatively, therefore you this is both qualitative measurement as well as, it is a quantitative measurement.

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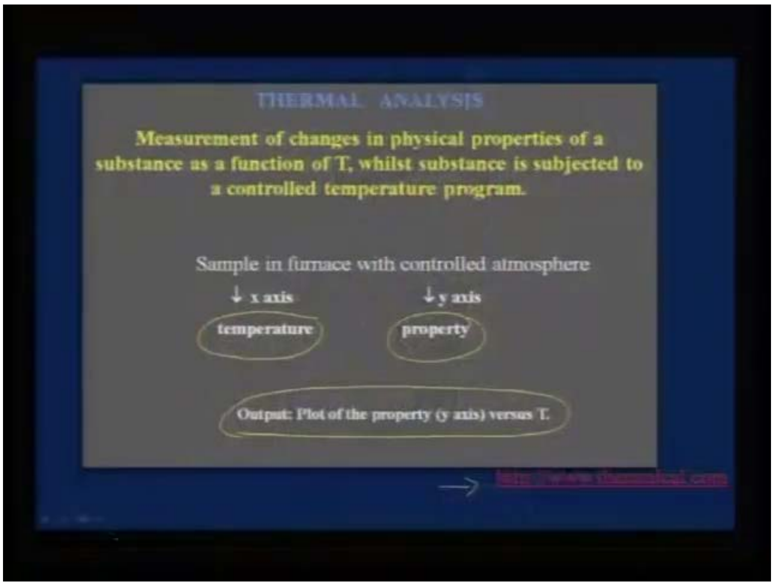

THERMAL ANALYSIS

Measurement of changes in physical properties of a substance as a function of T, whilst substance is subjected to a controlled temperature program.

Sample in furnace with controlled atmosphere

↓ x axis ↓ y axis

temperature property

Output: Plot of the property (y axis) versus T.

So, what does thermal analysis means, it is a measurement of changes in physical properties of the substance as a function of temperature, when the sample is undergoing a controlled temperature program. So, you can actually do this variety of evens, that are happening, you can try to trace using a isothermal heating also, suppose I do not have a thermal analysis instrument, the first thing that, I can do is freeze out on a particular temperature and then try to map the changes that are happen.

But, we can also do a controlled temperature program, which can take the sample from room temperature to a known temperature and whatever that happens is nothing but the property, which you can map it in the y axis. So, in the x axis it is always temperature and in y axis, it can be anything that is coming out of such a process and output can these days be mapped very conveniently using a computer, therefore you can analyze the data in a very sophisticated way. So, it is a fairly simple technique, but the amount of information that one can get is it can transcend their imagination, lot of references or particulars about this technique has been taken from this website.

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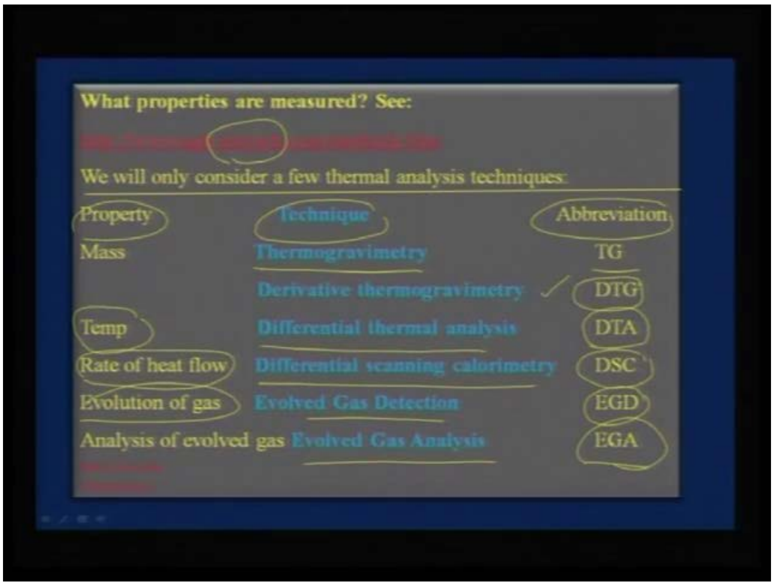

What properties are measured? See:

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We will only consider a few thermal analysis techniques:

Property	Technique	Abbreviation
Mass	Thermogravimetry	TG
	Derivative thermogravimetry ✓	DTG
Temp	Differential thermal analysis	DTA
Rate of heat flow	Differential scanning calorimetry	DSC
Evolution of gas	Evolved Gas Detection	EGD
Analysis of evolved gas	Evolved Gas Analysis	EGA

Therefore, I request you to note this, there are also groups working in U K and specially spiral dot com, which gives you useful information about it, mesh is the another company, which has brought out commercial thermogravimetric instruments, therefore it is good to new outrage. So, what properties are measured, we can see here, first regarding the property and the correspondence technique and the abbreviation that is used.

So, it is useful to get use to it if there is only a change in the mass then you call this as thermogravimetry usually called as T G or it is also called as T G A thermogravimetric analysis. If it is to do with temperature, then you call this is as differential thermal analysis and this is nothing but D T A you look at that thermal changes, in a differential pattern. And when we say differential pattern, you always have standard sample and with respect to that, what are all the thermal effects, that are happening you try to study in a differential way.

The same thing do to do with the thermogravimetric material also, you can try to map this as a differential plot, so even if there are minute variations, you can pinpoint that very clearly by differential edging. Suppose, there is a heat flow or heat exchange, that is happening, then you call this as a D S C, its calorimetry as you know, calorimetry means measurement of heat. And therefore, you can also conveniently determine the heat of crystallization, heat of fusion, heat of transition or a any enthalpy change, that is associated with different chemical process, you can try to do that, it is a very popular method called D S C used by material scientist.

And sometimes, we miss out on very, very important mechanistic issues, if you let go some of the gases, which are coming out of the processes. So, in such cases, it is also useful, if you have a T G instrument and trap the gases, that are coming out and those gases can be in a sealed tube. So, that it is only the gases, which can be mounted into infrared spectrophotometer and that would give you exactly the details of what the gases, that are coming out.

So, your predictions are not just quantitative, but you can also have a mapping of what a fractions that are coming up. So, it is called a evolved gas detection or evolved gas analysis, so you can analyze that using spectro photometry. So, as you see here, there are multiple events that are happening, in just heating a sample and you can try to map several issues out of it.

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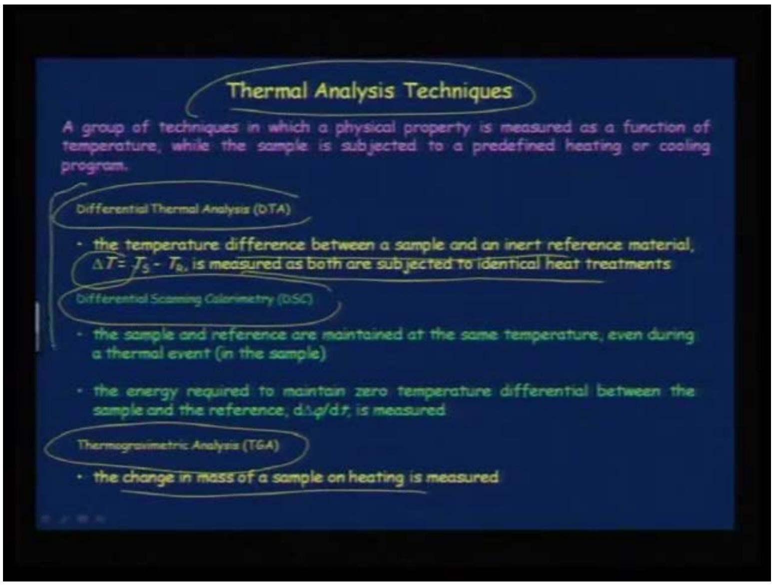

Thermal Analysis Techniques

A group of techniques in which a physical property is measured as a function of temperature, while the sample is subjected to a predefined heating or cooling program.

Differential Thermal Analysis (DTA)

- the temperature difference between a sample and an inert reference material, $\Delta T = T_S - T_R$, is measured as both are subjected to identical heat treatments

Differential Scanning Calorimetry (DSC)

- the sample and reference are maintained at the same temperature, even during a thermal event (in the sample)
- the energy required to maintain zero temperature differential between the sample and the reference, $d\Delta q/dt$, is measured

Thermogravimetric Analysis (TGA)

- the change in mass of a sample on heating is measured

There are 3, which I want to pickup and well little bit more and instrumentation and principle, so this of all the thermal analysis measurements, that are listed thermal analysis a group of techniques, in which a physical property is measured as a function of temperature, while the sample is subjected to a predefined heating or cooling program. So, as I pointed out, I am going to single out, these 3 methods, differential thermal analysis is nothing but your measuring the difference between the sample and a inert reference material, usually you are measuring delta T. And this measured as both are subjected to identical heat treatments, both the references as well as the sample are heated under same thermal conditions or a same temperature and the difference between these 2 is noted therefore, your reference material has to be inert to this temperature program.

In other words, it should be stable with the no physical or chemical changes happening to that particular solid therefore, whatever that is happening the difference between the reference and sample will solely be the manifestation of that example. Differential scanning calorimetry here, we are not measuring the difference in temperature between sample and the reference, but we are actually going to maintain same temperature for the sample and the reference irrespective of whatever changes that is happening to the sample.

Therefore, if the sample is undergoing a particular change, whether it is a heat releasing or a heat absorbing reaction, then the temperature will all the time be maintained, such a way the processes will map how much of heat is absorbed or how much of heat is evolved during the reaction. So, this is a not the reaction, the temperature difference between sample and the reference, it is the heat flow, whether it is taken by the system or given out by the system because you are maintaining both the reference and the sample temperature at the same time.

And in thermogravimetric analysis, it is nearly a change in the mass of the sample on heat, so these are the primary differences, but if you look at the complementary nature. The first 2 are complementary, because they almost give the same information, but D S E is more a quantifying picture, D T is more a qualitative picture and T G is a very different analysis altogether.

So, basic principles of thermal analysis, mainly revolves around the instrumentation, so modern instrumentations, used for thermal analysis consists of four parts. So, if you think of a T G instrument, you should know that, there is a sample and that specific sample holder. You do not just dump it into any container, a specific sample holder is there and relevance of that, I will emphasize shortly now. And then you have very sensitive sensors, which you mostly we call it as thermocouples, then an enclosure, in which the experimental parameters can be controlled.

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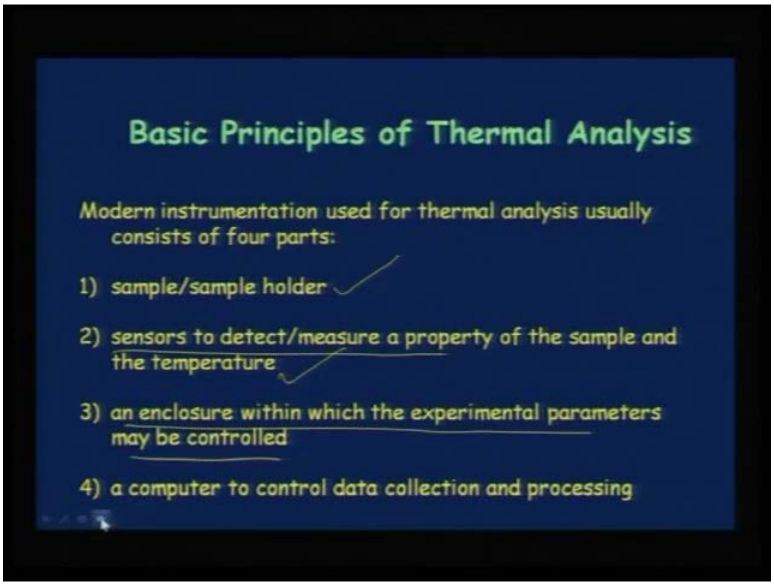

Basic Principles of Thermal Analysis

Modern instrumentation used for thermal analysis usually consists of four parts:

1) sample/sample holder
2) sensors to detect/measure a property of the sample and the temperature
3) an enclosure within which the experimental parameters may be controlled
4) a computer to control data collection and processing

For example, we can do the heating of the sample using a heating element or a furnace, sophisticated thermal analysis measurements are using I R based heating, you do not have a heating furnace, but you just use the I R heating. So, that you can concentrate on the sample or the center of the sample, so several sophistications are there with respect to the nature by which, we can heat and then approach the computer to map and analyze the whole thing.

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Types of thermal event

phase transition
adsorption, desorption
melting (fusion)
sublimation
thermal decomposition
radiolytic decomposition
glass transition
oxidation/ combustion
heterogeneous catalysis
double decomposition
addition
desolvation

When you consider a thermal event, that can happen in a particular sample, there are several issues that are undergoing in a sample decomposition, I would like to list it out, so that. When we look at specific examples, you will see how much of information, that we can get out of a simple heating protocol. Now, one is phase transition a liquid to solid or solid to gas, you can map the phase transition, absorption or desorption that can happen in heterogeneous catalysis can also be evaluated with the sensitive thermal analytical probe.

Melting that is fusion or sublimation, both can be mapped very clearly using D T and D S C and thermal decomposition a solid a going to solid b plus c, c may not be a solid, it can be a gaseous product. So, thermal analysis can play a vital role radiolytic decomposition or simple glass transition, where you can think about the solid going to a liquid phase or a amorphous going to crystalline phase. All this can be mapped oxidation and combustion reactions can be mapped very clearly heterogeneous catalysis, as you said double decomposition adhesion and the dehydration or desolvation reaction. So, many chemical effects are there, when we heat a sample and all this can be usefully map, lets come little bit to understand.

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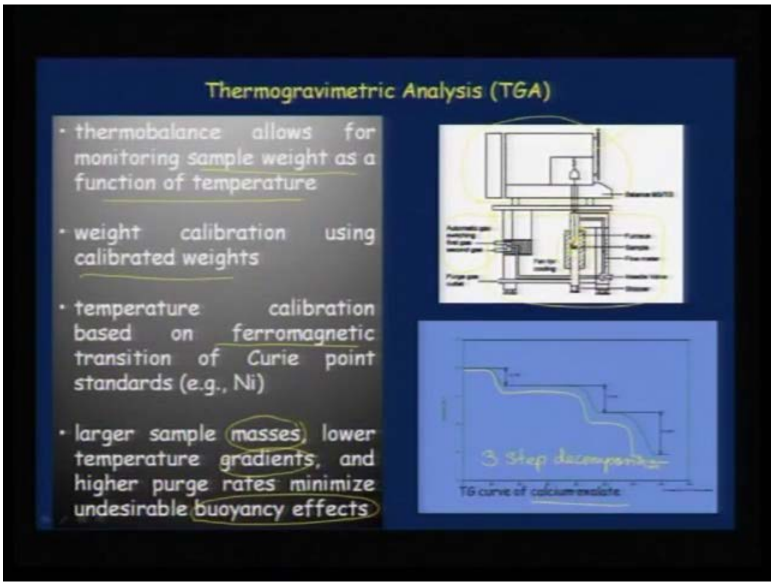

Thermogravimetric Analysis (TGA)

- thermobalance allows for monitoring sample weight as a function of temperature
- weight calibration using calibrated weights
- temperature calibration based on ferromagnetic transition of Curie point standards (e.g., Ni)
- larger sample masses, lower temperature gradients, and higher purge rates minimize undesirable buoyancy effects

What a simple thermal gravimetric analysis, we all know in the postgraduate or under graduate level, we have done nickel D N G complex, biometric glyoxime, which is a red precipitate. And this is a very useful, but a time consuming and a very laborious gravimetric exercise, but the same material can be very usefully and easily determined using thermogravimetric analysis with a modern instrumentation.

I will tell you basically, what this instrument is all about, in the top part of this picture, you can see it is a balance, it is a micro balance, which is sensitive with the 5 digit sensitivity. So, any change in milligram quantity can be usefully mapped, usually the sample are in milligram quantity therefore, you need to have 5 digit precision. So, a typically, it is a material balance, which we use and this in this balance, you actually suspend the sample here and the sample is kept in between furnace wall.

So, you can actually do the heating here and depending on the weight intake or weight loss, the information can be fed from the microbalance, as a result you can see, what is the weight loss against the particular decomposition processes, that is going on. And it is not that simple as we see here, in this case the lower chamber, you can apply vacuum and then, there are facilities by which you can actually purge the sample with flow of either argon or air atmosphere. So, that whatever reaction, that is happening, suppose there is gas evolution, it is not exactly concentrated here and it will be flushed out periodically.

So, a inert gas is usually flushed or we can even have air, if the sample needs air, we can flush sample and we can try to map it, this is a typical T G analysis curve, which is used. And the most referred and example is calcium oxalate and as you would see typical T G curve looks like, this where you see a bend here and another bend, we call this as thermogravimetric steps. And each step has something to convey, therefore if there is one step and then there is another step, we call this as a 3 step decomposition.

And each step might relate to a different physical change and a chemical reaction, I will show you some of the example of this in the upcoming slides, in thermobalance allows monitoring of a sample weight as a function of temperature. Now, before we run any sample, 2 things we need to do, one you need to do a weight calibration, another one you need to do a temperature calibration. Weight calculation you can do with calibrated weights, if you want to temperature calibration, usually you try to take a ferromagnetic sample and take it beyond the ferromagnetic transition for example, nickel.

And then you can calibrate your temperature, whether the reaction the transition is exactly happening at the end, then you can do the correction terms, usually buoyancy effects are very, very crucial, when we do T G. Therefore, this buoyancy effects are largely manifested with the simple quantity or with the temperature gradients or the purging rate, you cannot just flush the sample with whatever atmosphere you want, you cannot try to bubbled vigorous flow of these gasses, all this will cause buoyancy effects as a result, it will largely affect your results.

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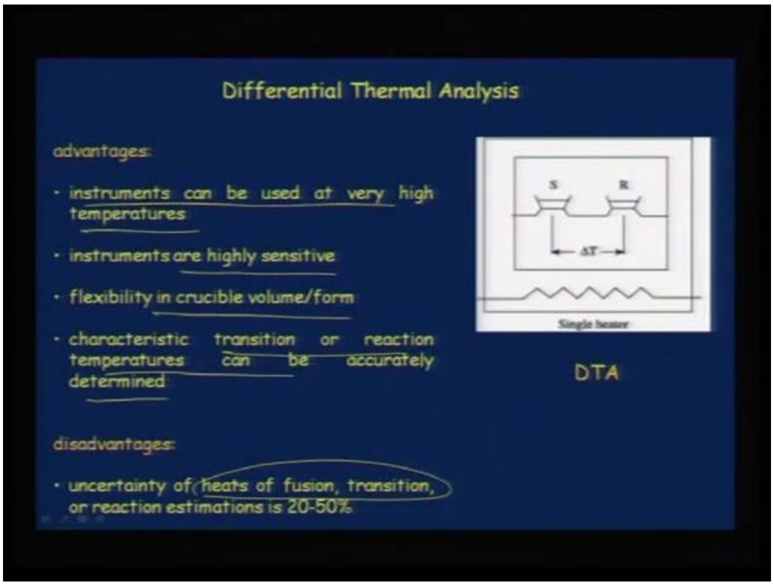

Differential Thermal Analysis

advantages:

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

disadvantages:

- uncertainty of heats of fusion, transition, or reaction estimations is 20-50%

Differential thermal analysis on the other hand is a true cup cavity, in the next slide I will show you that, advantages instruments can be used at very high temperature for differential thermal analysis, you can go up to 1000 degree 1000 Kelvin comfortably. And it is very sensitive to measure and there is also flexibility in using the sample size and whichever form you want, characteristic transition or reaction temperatures can be accurately determined. And one of the disadvantage in D T A could be the uncertainty of heats of fusion heats of transition and heats of reaction and it can involve a error of 20 to 50 percent. Therefore while determining the enthalpy of reaction transition usually, we resort to differential scanning calorimetry, rather than D T A, but D T A also gives essentially same inputs.

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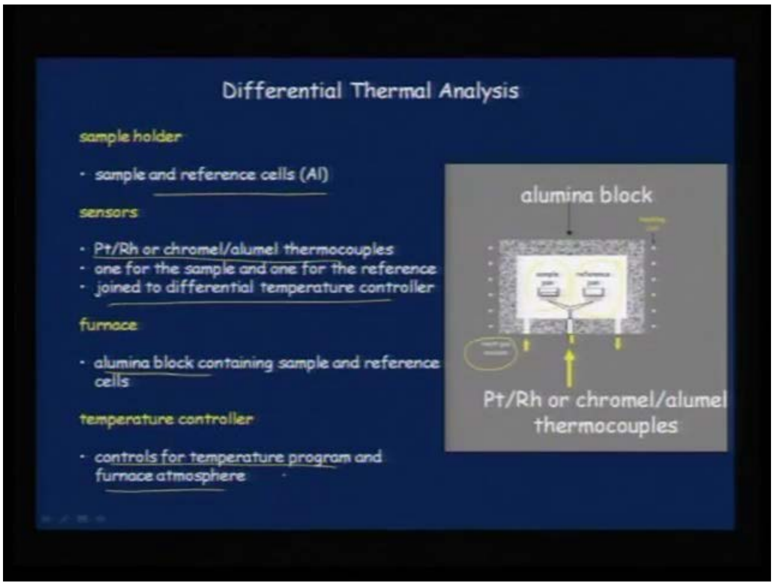

Differential Thermal Analysis

sample holder

- sample and reference cells (Al)

sensors

- Pt/Rh or chromel/alumel thermocouples
- one for the sample and one for the reference
- joined to differential temperature controller

furnace

- alumina block containing sample and reference cells

temperature controller

- controls for temperature program and furnace atmosphere

Differential thermal analysis that way, you have a alumina block here and in the alumina block, you actually have a sample pan and you also have a reference pan and both are connected to the same thermocouple platinum rhodium or chromel alumel thermocouple. And you purge it with the either vacuum or inert gas, now the difference in the temperature between the sample and the reference will determine, your delta key.

So, that will be plotted against the temperature, sample holders are usually aluminum, because it is very easy to handle less expensive and you wouldn’t like to use the aluminum cups again, you would rather discard, so that it is free from contamination. Sensitive sensors are needed for measuring the difference, because you are using milligram quantities, platinum rhodium is a very useful one, because it shows a linear curve, at in the high temperature regime, from room temperature upto 1000 Kelvin, there is linearity, therefore you can use this. So, calibration becomes useful, these are joined together with the differential temperature controller, therefore whatever you get is a differential plot. In a furnace is usually aluminium block, as I mentioned earlier and temperature controller, controls the furnace temperature.

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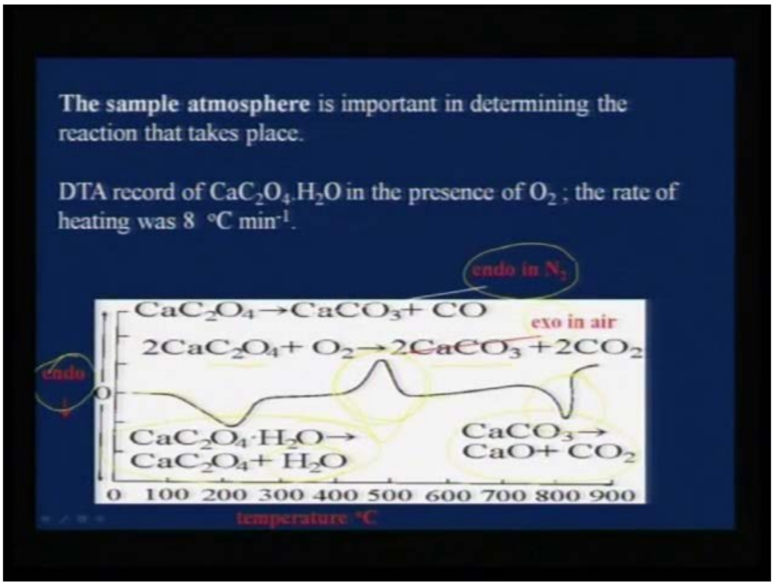

The sample atmosphere is important in determining the reaction that takes place.

DTA record of $CaC_2O_4.H_2O$ in the presence of O_2 ; the rate of heating was 8 °C min^{-1}.

The sample atmosphere is important in determining the reaction, that that takes place D T A can record, either in the presence of oxygen or in inert condition for example, this is a typical D T A plot, that is coming out of instrument. And you would see, there is a small hump here, which is actually recorded as a endo peak, endothermic peak and there is another one, which is actually called a exothermic peak. But, what you would see here, this is a endothermic peak relating, to the physically change, that is happening where calcium oxalate losses the water molecule.

And therefore, dehydration inside endothermic peak, but this is not crucial as much as the second peak is mentioned, in the second peak it is a exo peak, which involves a unhydrated calcium oxalate going to calcium carbonate. But, this exo peak can miss out, if I am going to heat the sample in nitrogen, because in nitrogen it does not get the required amount of oxygen to decompose into calcium carbonate therefore, it goes as a end of week, in other words it will come out like this.

So, these 2 peaks are not important for atmosphere, but this middle peak becomes important, because it will determine, whether it is endo or exo. So, in D T A it is very very important to know, in which atmosphere you did it. So, purging air purging gas is not just for mere purging, but it also effects the chemical processes, that is happening therefore, we need to know for sure again, the last step is a endothermic reaction where calcium carbonate goes to calcium oxide, whether you do it in air or in nitrogen, it will give the same.

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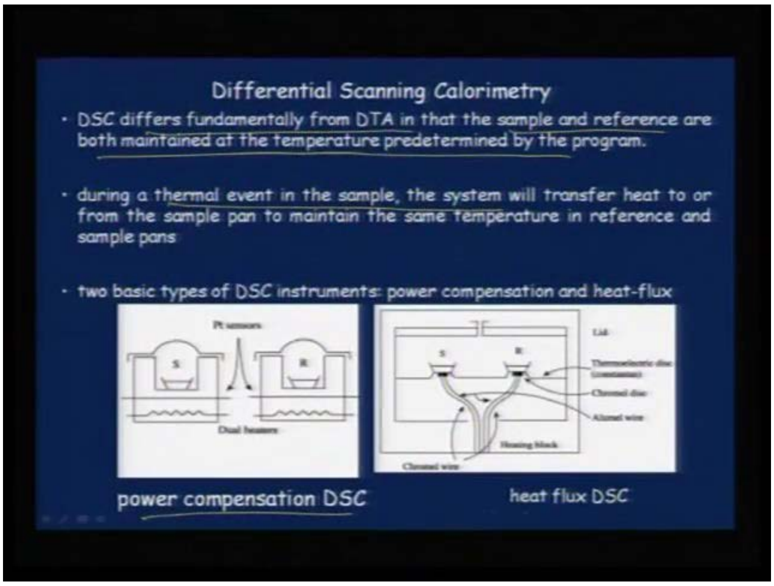

Differential Scanning Calorimetry

- DSC differs fundamentally from DTA in that the sample and reference are both maintained at the temperature predetermined by the program.
- during a thermal event in the sample, the system will transfer heat to or from the sample pan to maintain the same temperature in reference and sample pans
- two basic types of DSC instruments: power compensation and heat-flux

power compensation DSC

heat flux DSC

So, the middle peak is determine by the nature of the purging gas, in differential scanning calorimetry the main of difference from D T A is that, the sample and reference are both maintained at temperature predetermined by the program. So, at every temperature, during the temperature programmed reaction, suppose the sample is at 100, then both the sample and the reference will be maintained at 100, but during the processes of the sample change whatever that is happening, that will be recorded either as a end or a exo peak.

This is the main difference between D T and D S C, during a thermal event in the sample the system below transform, it transfer heat to or from the sample pan to maintain the same temperature. So, transfer of heat will be happening, in order to keep the sample and reference at the same temperature, there are 2 ways, that you can achieve this either using a power compensation method or using a heat flux method.

I will show that, in the next 2 slides power compensation method, you actually have 2 different alumina blocks to heat the pans. So, you have a sample pan in a different heating block, you have the reference in a different heating block and the they both are connected to the thermocouple, where your delta t is actually maintained as 0, delta t is equal to 0.

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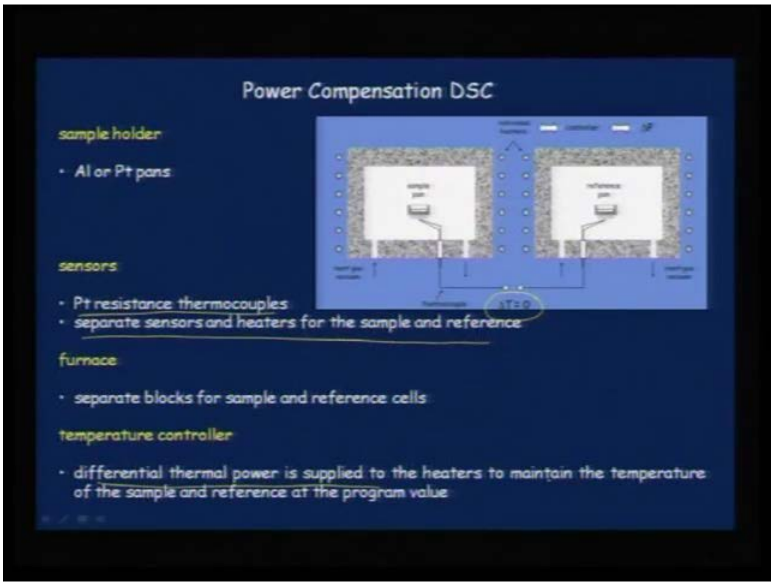

Power Compensation DSC

sample holder

- Al or Pt pans

sensors

- Pt resistance thermocouples
- separate sensors and heaters for the sample and reference

furnace

- separate blocks for sample and reference cells

temperature controller

- differential thermal power is supplied to the heaters to maintain the temperature of the sample and reference at the program value

So, in this case your platinum resistance thermocouple is what we use, separate sensors and heaters for the sample and the reference, then the differential thermal power is supplied to the heaters to maintain the temperature of the sample and the reference as the program value. So, these are the main issues when we talk about power compensation D S C when you think of a heat flux D S C, you actually have the same block to heat both your sample and reference.

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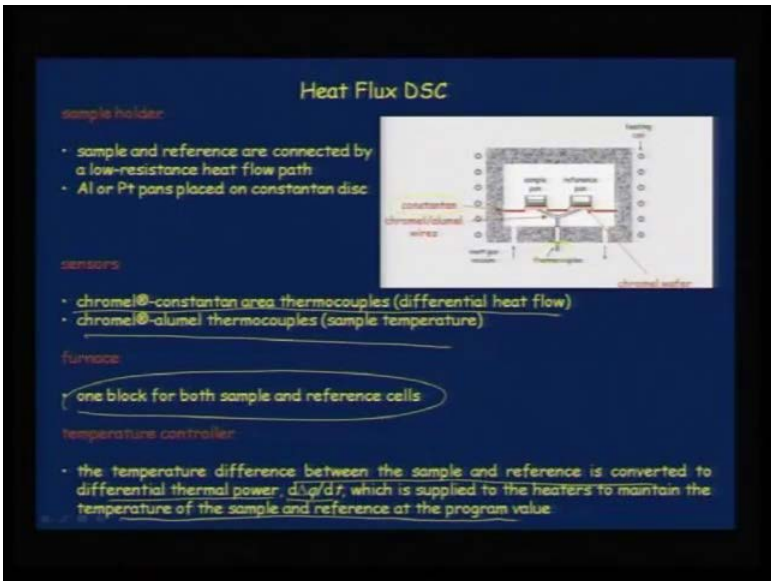

Heat Flux DSC

sample holder

- sample and reference are connected by a low-resistance heat flow path
- Al or Pt pans placed on constantan disc

sensors

- chromel®-constantan area thermocouples (differential heat flow)
- chromel®-alumel thermocouples (sample temperature)

furnace

- one block for both sample and reference cells

temperature controller

- the temperature difference between the sample and reference is converted to differential thermal power, d∆q/dt, which is supplied to the heaters to maintain the temperature of the sample and reference at the program value

And this is actually mounted onto a constant and that is a very sensitive, heating block and you actually have 2 type of sensors there, one is chromel constantan thermocouple, this is for maintaining the differential heat flow whereas, chromel alumel thermocouples is there. So, you have both the thermocouples coming together, the chromel constantan for differential flow and chromel alumel thermocouple for measuring the individual sample temperatures.

So, 2 different sensors are there in a heat flux D S C, unlike the other case, so and you the primary difference here is you have one block for heating both the samples, temperature difference between the sample and reference is converted to differential thermal power, which is nothing but d delta q by d t. So, this is what is measured, which is supplied to the heaters to maintain the temperature of the sample and the reference at the same value. So, this is the primary difference.

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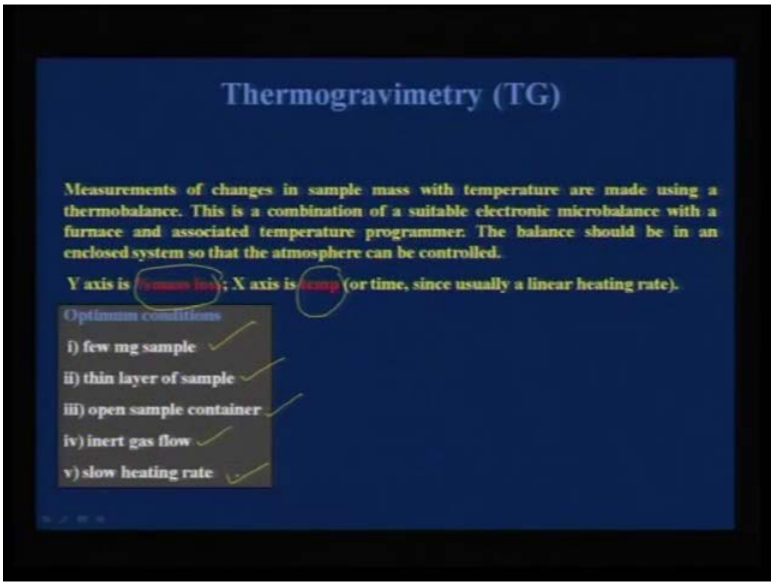

Thermogravimetry (TG)

Measurements of changes in sample mass with temperature are made using a thermobalance. This is a combination of a suitable electronic microbalance with a furnace and associated temperature programmer. The balance should be in an enclosed system so that the atmosphere can be controlled.

Y axis is %mass loss; X axis is temp (or time, since usually a linear heating rate).

Optimum conditions

i) few mg sample ✓
ii) thin layer of sample ✓
iii) open sample container ✓
iv) inert gas flow ✓
v) slow heating rate ✓

Now, I will take specific example for thermogravimetry and tell, how T G can be used and what are all the protocol, that we need to follow, as I told you, it is heating with the thermobalance, therefore you are essentially measuring the percentage weight loss as a function of temperature. The optimum conditions in measuring T G comes from taking only few milligrams and these few milligrams of samples should essentially have a good support on the pan.

In other words, it does effective contact area between the pan and the sample has to be maximum, because you are playing with very few milligram and thin layer of sample can be should be uniformly spread, throughout the sample. And then it should be a open sample container, you cannot close the container where, as in the case of D S C, you need to actually close it, it cannot be operated without. The open sample container mainly, because if there is any evolving gas, it does not really create any bust inert gas flow is recommended and then slow heating rate, these are important principals for T G.

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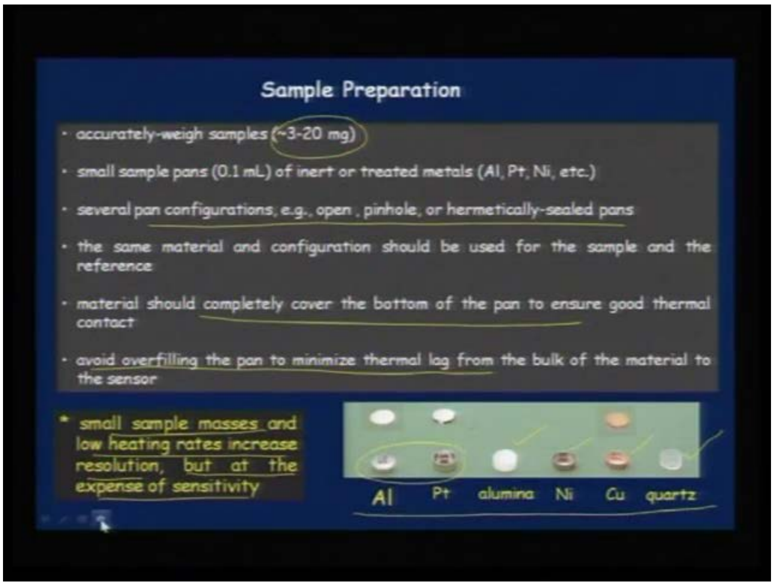

Sample Preparation

- accurately-weigh samples (~3-20 mg)
- small sample pans (0.1 mL) of inert or treated metals (Al, Pt, Ni, etc.)
- several pan configurations, e.g., open , pinhole, or hermetically-sealed pans
- the same material and configuration should be used for the sample and the reference
- material should completely cover the bottom of the pan to ensure good thermal contact
- avoid overfilling the pan to minimize thermal lag from the bulk of the material to the sensor

- small sample masses and low heating rates increase resolution, but at the expense of sensitivity

So, there are several sample cups, which can be used quartz, you can use because you heat you can go comfortably upto 1000 K, copper and nickel they are very sensitive therefore, only for reactions where you anticipate the sample to, undergo chemical reactions below 200 degrees or so. You can use the samples convinency is it is a much more cheaper compare to other one, so you can actually do a onetime reaction and discard it.

So, copper samples can also be used alumina samples are available, but more expensive for sensitivity aspects, you use aluminium and platinum bolts, small sampled masses and low heating rates increase the resolution, but at the expense of sensitivity. Suppose you use very fast heating rate and large amount of sample, you increase the sensitivity, but the resolution may be missing, I will show one of the example how you need to make a compromise.

So, depending on the nature of the sample, you need to optimize on the sample weight, typically 3 to 20 milligram is taken and there are several pan configurations that are there, you can have a sealed one also, but with lot of holes, so that gases can escape. Same material in configuration should be used for both the sample and the reference you cannot use 2 different sample holders. Material should be completely covered to the bottom of the pan, so that good thermal contact is there and to avoid overfilling the pan to minimize thermal lag, we need to make sure that less amount of sample is there, so that sample does not jump out and create any temperature like that.

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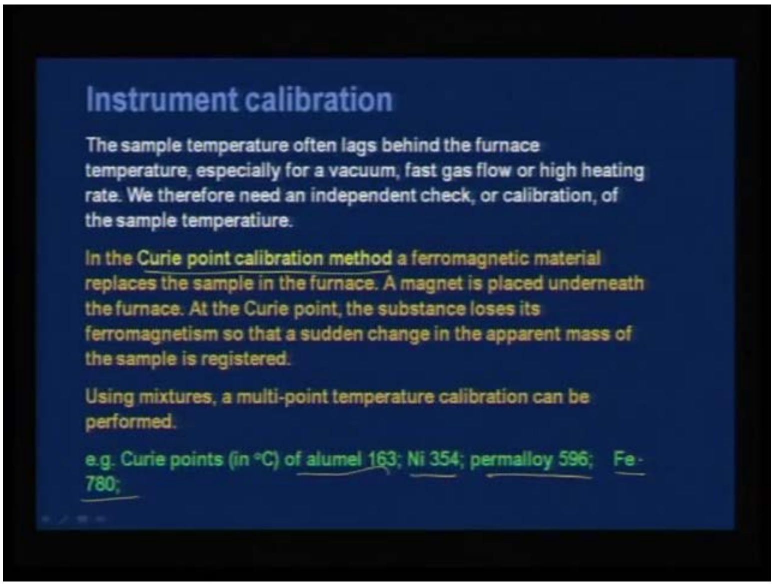

Instrument calibration

The sample temperature often lags behind the furnace temperature, especially for a vacuum, fast gas flow or high heating rate. We therefore need an independent check, or calibration, of the sample temperatiure.

In the Curie point calibration method a ferromagnetic material replaces the sample in the furnace. A magnet is placed underneath the furnace. At the Curie point, the substance loses its ferromagnetism so that a sudden change in the apparent mass of the sample is registered.

Using mixtures, a multi-point temperature calibration can be performed.

e.g. Curie points (in °C) of alumel 163; Ni 354; permalloy 596; Fe - 780;

As I told you earlier T G involves instrument calibration and weight calibration is needed as well as the curie temperature calibration is needed. Today, there are many instruments where curie temperature calibration is not needed, because you can 0 it and adjust the error for temperature. So, but there are several standards, which are available like alumel nickel permalloy and iron all this are having the curie points at the specific temperatures. So, you can use them for internal calibrations, so it is important to have these calibrations made before, you start typical T G closer like this.

Where you can have a flat one, the line is flat what do you mean then there is no change, there is no problem, but if there is a small change in the baseline, then that can amount to a glass transition or it could be a desorption and drying a small amount of adsorbed gases or water can be escaping. So, that can be easily mapped to a small change in the slope then suppose there is a clear step like this.

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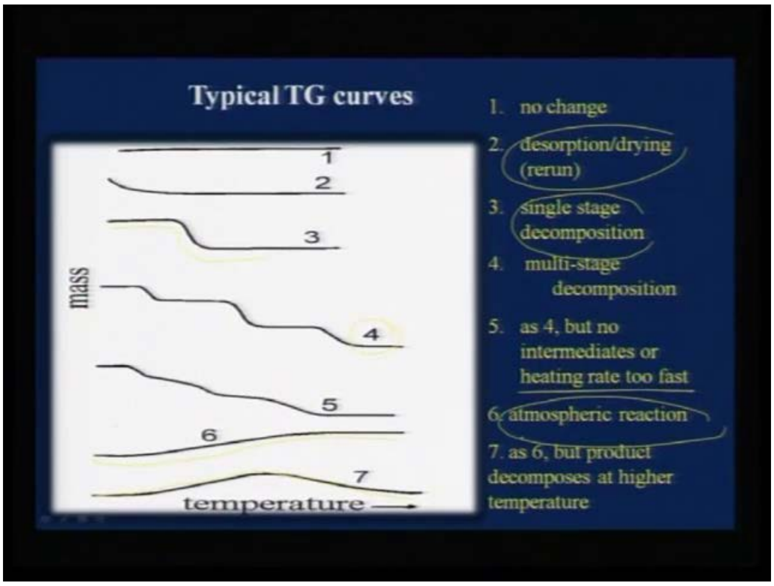

Typical TG curves

1. no change
2. desorption/drying (rerun)
3. single stage decomposition
4. multi-stage decomposition
5. as 4, but no intermediates or heating rate too fast
6. atmospheric reaction
7. as 6, but product decomposes at higher temperature

Then you can think about a single stage or single step decomposition, if it is a multi step decomposition, then you will see curve 4 and you have some steps there, but which is not resolved. Then you may have multistep decomposition, because of the heating rate, you do not see the more pronounced, there is another way, you suddenly see the curve increasing and reaches the plateau. Then it is a atmospheric reaction, which means the there is a uptake of air or oxygen to the sample or it could be increasing and then it is going down, which could be like your 6 interacting with atmosphere, but decomposes at higher temperature all this possible in a T G curve.

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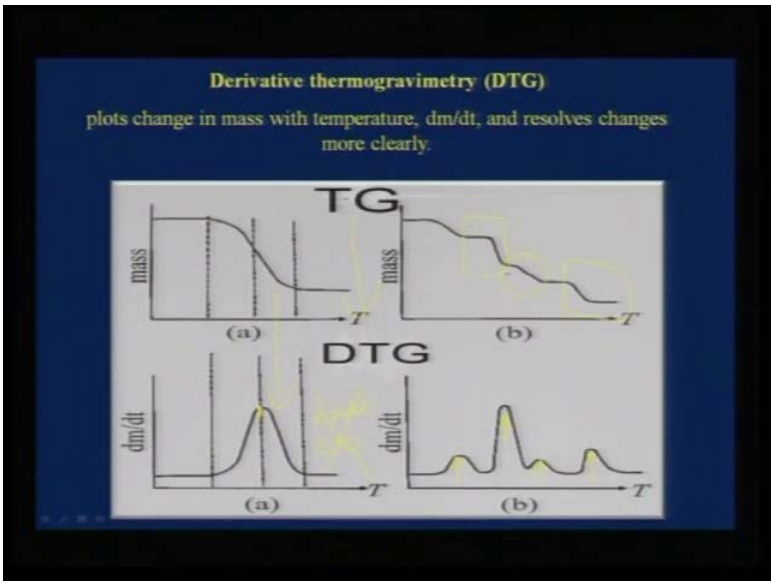

Derivative thermogravimetry (DTG)

plots change in mass with temperature, dm/dt, and resolves changes more clearly.

As I told, you if it is just one step, one stage decomposition, then it is very easy for us to map, but if there is a curve like this, you really do not know, because it is not very well resolved at sometimes. So, you do not know what is this, but you can easily map, this slope and this slope, because there is a clear plateau. So, in such case, you actually transfer the data T G data and you make a differential plot.

So, differential T G will tell you how many crucial steps are there, for example, this single set decomposition means in T D T G will give you only one maxima and this is not exo or endo, we should not confuse this with D T A, this is not endo exo peak, this is just a differential plot. So, you can know for sure, that this is the midpoint of such a transition, suppose this is a multistage decomposition, then you have essentially 4 maxima. So, 4 different things are happening, so this D T G is more useful, if you have a multistep reaction or many processes are going through such a reaction.

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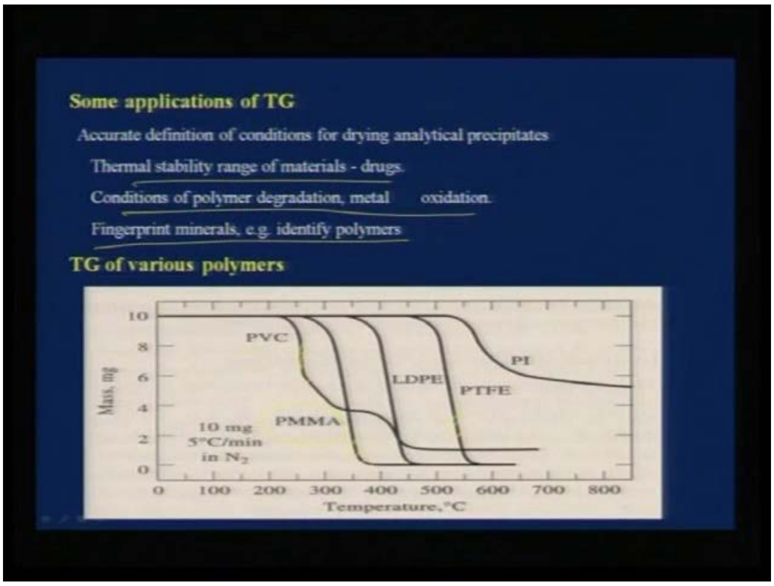

Some applications of TG

Accurate definition of conditions for drying analytical precipitates

Thermal stability range of materials - drugs.

Conditions of polymer degradation, metal oxidation.

Fingerprint minerals, e.g. identify polymers

TG of various polymers

Some more applications of T G accurate, definition of conditions for drying analytical precipitates can be notable. Thermal stability of different materials for example, drugs conditions of polymer degradation metal oxidation, metal combustion can be noted fingerprint minerals or you can identify polymers, for example, this is a D T H sorry, T G curve of various polymers.

As you would see this is polymethyl methacrylate showing this trace polyvinylchloride shows like this, low density polyethylene or teflon P T F E, they all show a different weight loss, which means you can understand the thermal stability of such polymers, using a simple thermogravimetric protocol. And if you are actually doing this processes for a particular sample, it is good to involved all the exercise where, you have a combined measurement that is T G D T G and D T A.

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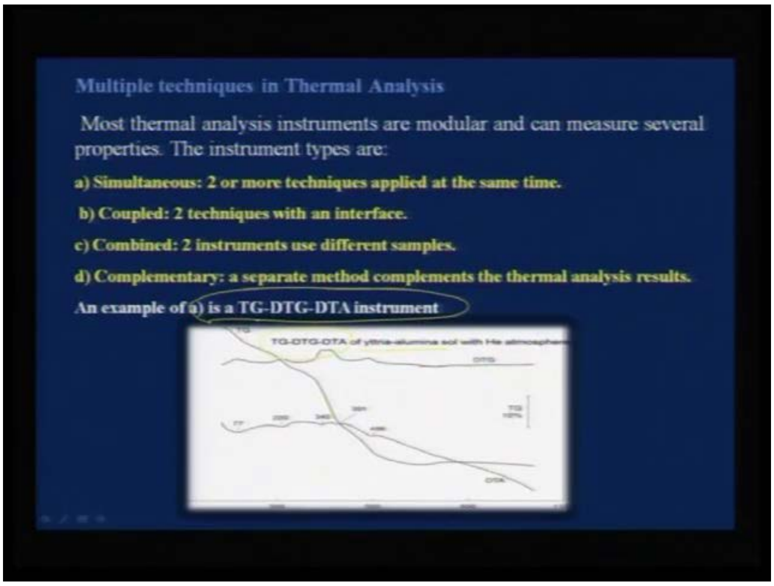

Multiple techniques in Thermal Analysis

Most thermal analysis instruments are modular and can measure several properties. The instrument types are:

a) Simultaneous: 2 or more techniques applied at the same time.

b) Coupled: 2 techniques with an interface.

c) Combined: 2 instruments use different samples.

d) Complementary: a separate method complements the thermal analysis results.

An example of a) is a TG-DTG-DTA instrument

So, that all the parameters can be evaluated not just the weight loss, but also find out what is the nature of such chemical reactions. So, typically this is your D T A plot, which shows several valleys with each one amounts to a particular phenomena, that is happening in yttria alumina salt. So, that may be many useful informations coming, if you have a combined technique, will show some more examples of that in the next few slides. So, what are the first ever multiple technique or combined approach, that was in the form of a instrument was T G D T G D T A. Now, we also have a combined technique will be easy, which is coming in the modern instruments.

I am going to give you some examples, from our own work where, T G has proved useful in some of the lectures, in the in this present course, I have touched on the same example, but I just highlight this in a with respect to T G as the this lecture is mainly on thermogravimetric. First I will try to show you how alloys can be mapped, then hydrogen bonding can be evaluated using thermal technique and how in old application, this can be used and also in magnetic materials.

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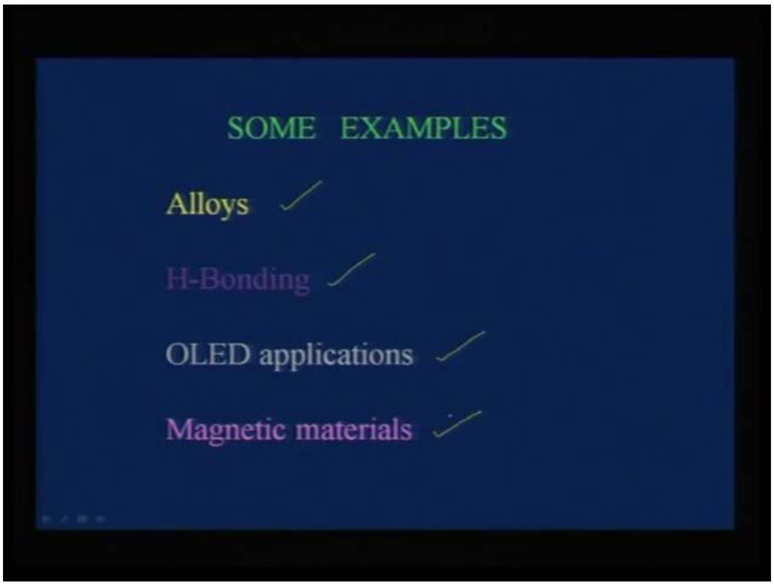

SOME EXAMPLES

Alloys ✓

H-Bonding ✓

OLED applications ✓

Magnetic materials ✓

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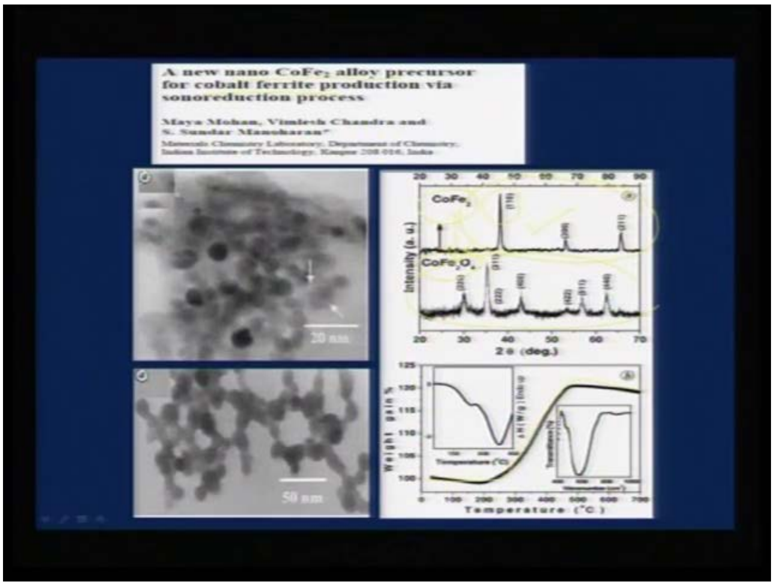

A new nano $CoFe_2$ alloy precursor for cobalt ferrite production via sonoreduction process

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Materials Chemistry Laboratory, Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

This is one of the useful work where, a new cobalt iron alloy precursor was made and this was converted into cobalt ferrite and it is very difficult to prepare this C o F e 2 alloy. So, how do we know, that we have made this alloy, if you actually do a x r d, you can clearly see that, this is the x-ray pattern of the alloy precursor, it is a very reactive alloy precursor, but if you actually heat this sample, then it gets converted to cobalt ferrite.

Now, one should know whether, it is truly the alloy which is getting converted to the iron oxide or how much of this cobalt ferrite is getting converted to iron oxide. This is the place where, T G comes into picture, this is the thermogravimetric curve, which clearly shows that, there is nearly a 20 percent 21 percent of a gain in the weight. So, instead of losing weight here, you see a uptake, which means C o F e 2 is getting converted to C o F e 2 O 4 by taking atmospheric air, as a result you see nearly a 20 percent weight loss, but if you really quantify this result, you will find out, that around 1 to 2 percent or 1 to 5 percent. So, to say of cobalt ferrite is already present in the sample, which cannot be detected by the x-ray and nearly 95 percent of the alloy is in actual C o F e 2 alpha, this is a very important information to know whether any ferrite precipitates are already, there in this sample, even before conversion from alloy to oxide. So, such fine details you can try to get it and this is another important work where, we found.

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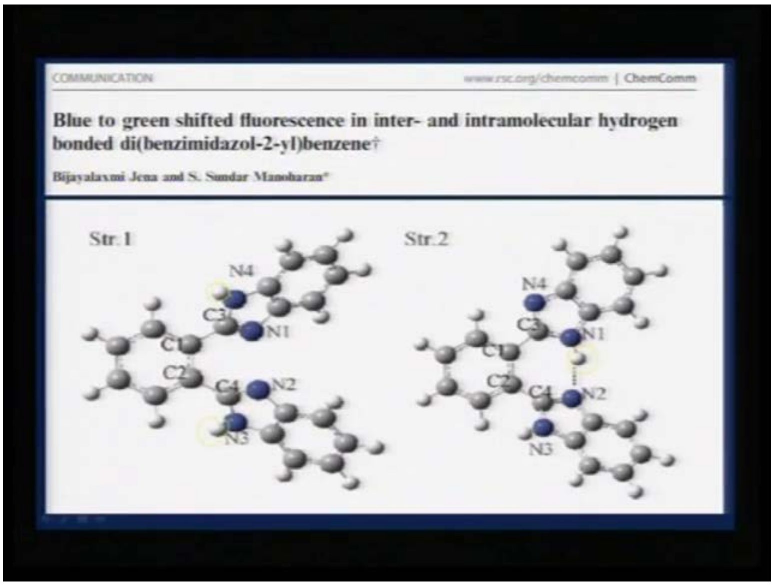

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Blue to green shifted fluorescence in inter- and intramolecular hydrogen bonded di(benzimidazol-2-yl)benzene†

Bijayalaxmi Jena and S. Sundar Manoharan*

Hydrogen bonding was evaluated mainly, from a T G diagram, this is a benzimidazol molecule, which is attached to a phenyl ring in 1 2 position, it is attached. So, you would see this imidazole can either be intramolecular hydrogen bonded or in intermolecularly hydrogen bonded, in this case there is a intramolecular hydrogen bonding, this case intermolecular hydrogen bonding.

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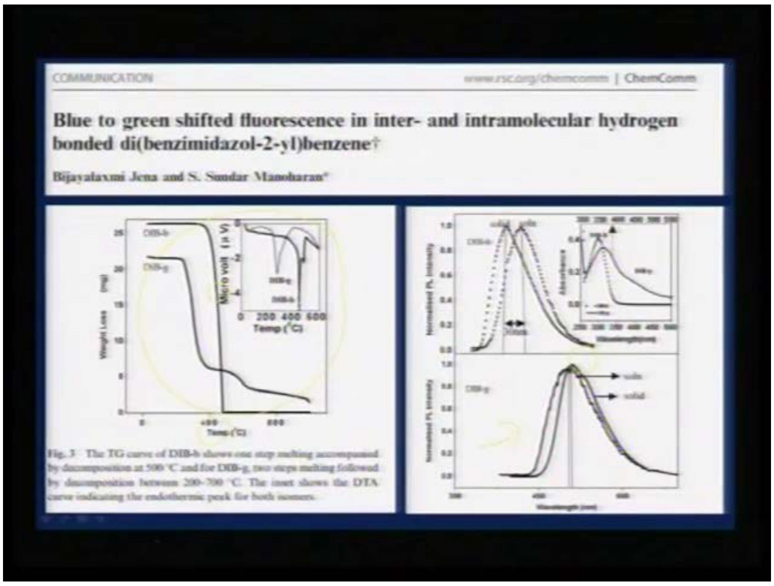

COMMUNICATION www.rsc.org/chemcomm | ChemComm

Blue to green shifted fluorescence in inter- and intramolecular hydrogen bonded di(benzimidazol-2-yl)benzene†

Bijayalaxmi Jena and S. Sundar Manoharan*

Fig. 3 The TG curve of DIB-h shows one step melting accompanied by decomposition at 500 °C and for DIB-g, two steps melting followed by decomposition between 200-700 °C. The inset shows the DTA curve indicating the endothermic peak for both isomers.

You can clearly see between these 2 isomers, the T G pattern is very different, the one which is actually hydrogen bonded with other molecules intermolecular hydrogen bonding shows a very high decomposition temperature, compared to intramolecular hydrogen bonding. So, such information’s you can easily find out, but without this information, it would have been a partial justification of hydrogen bonding, if you are just shown the change in the P L emission between a solid, for the intramolecular hydrogen bonded and the intermolecular hydrogen bonded samples. So, T G can provide a vital information.

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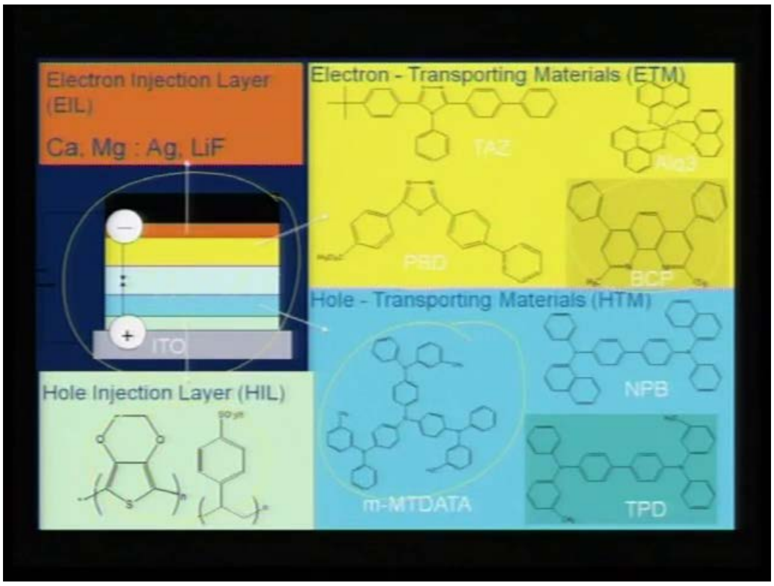

Electron Injection Layer (EIL)

Ca, Mg : Ag, LiF

Electron - Transporting Materials (ETM)

Hole - Transporting Materials (HTM)

Hole Injection Layer (HIL)

And same here, in the case of oled applications as you know several molecules are made, several molecules are there and each of this molecules are actually deposited in these layers, but we are actually looking for, making new organic molecules, when we make this sort of a oled device one of the important criteria is it has to be amorphous. So, one of the important criteria’s in this oled fabrication is when you make these organic films, you should not crystallize.

If it crystallizes then the electrical connectivity will be lost and as a result, you need to make amorphous films of this organic molecules to provide a electrical continuity. So, when you actually deal with polymers, you do not have this problem, because when you evaporate these organic molecules, they found essentially a very good connectivity because they are amorphous. But, when you go for crystalline organic materials, when you fabricate this, there will be electrical discontinuity as a result the device operation will fail, even after a first cycle it, it cannot be sustained.

So, one of the problem involved in organic L E D is to make, thermally as well as electrochemically, they should be a more rigid molecule rather, it should withstand several heating cycles or several current cycles. So, the emphasis is to actually make a bigger organic molecules, bigger the molecule more the molecular weight, less the crystallization temperature in other words, you can actually improve on the decomposition temperature or the melting temperature. So, in the melting temperature is pushed far further, then you can actually make a much better films.

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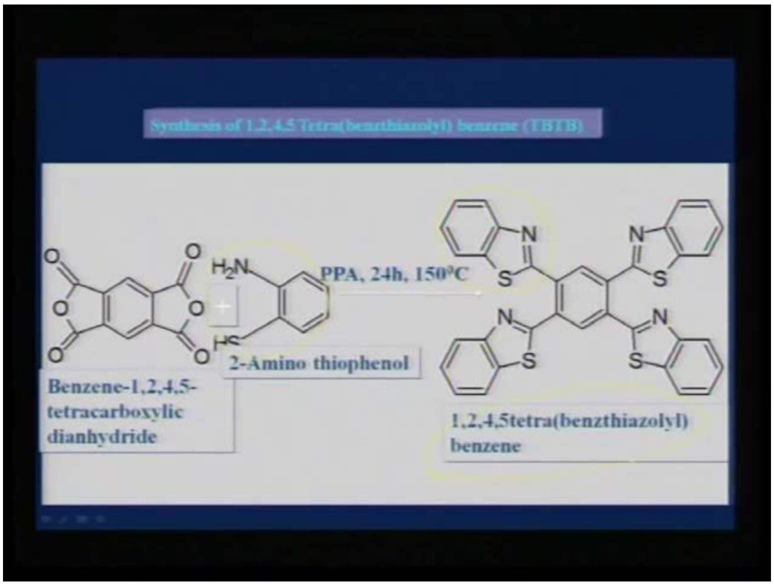

Synthesis of 1,2,4,5 Tetra(benzthiazolyl) benzene (TBTB)

Benzene-1,2,4,5-tetracarboxylic dianhydride

2-Amino thiophenol

1,2,4,5tetra(benzthiazolyl) benzene

So, for that matter, if you can take benzene tetracarboxylic dianhydride, as your starting material, you can try to put 2 amino thiophenol and using this 2 amino theophenol, you can essentially make a compound like this, as you would see that, the dianhydride is now substituted with the 4, such benzthiazolyl molecules. So, what you are essentially doing is instead of just adding one molecule for this, you are substituting 4 as a result, you make a bulky organic molecule.

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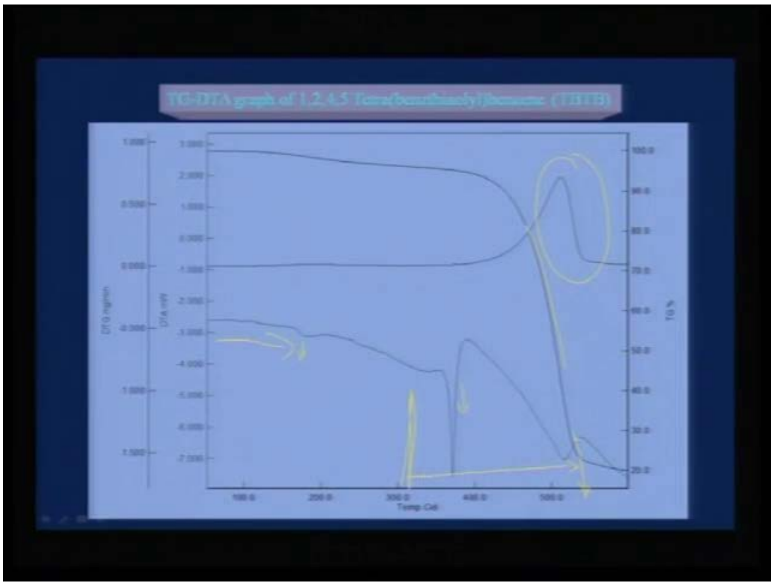

TG-DTA graph of 1,2,4,5 Tetra(benzthiazolyl)benzene (TBTB)

And as you would see from the T G pattern here, typically 1 or 2 benzthiazolyl substituted molecules will have the melting point somewhere here, but you can see that the melting point and the subsequent decomposition temperature is pushed by at least 150 degree c. So, if this is a single step melting point, which involves decomposition somewhere around 550 degree c.

So, these are molecules, which are recommended for oled application, because they will not crystallite easily and spoil the device application and you would see here, this is the D T G pattern, which is corresponding to the single step decomposition here. And this curve is nothing but your differential thermal analysis curve D T A, which first shows some gas concision and then it shows melting and then the decomposition. So, all this are easily mapped in the combined technique.

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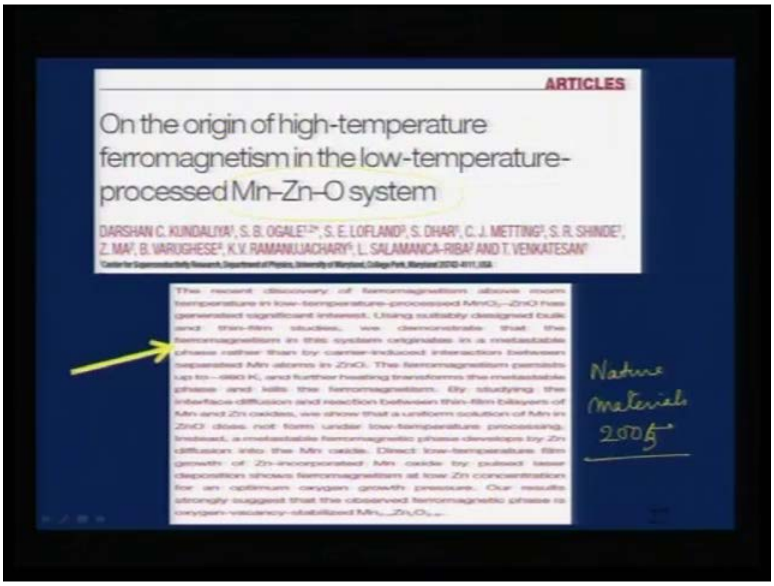

ARTICLES

On the origin of high-temperature ferromagnetism in the low-temperature-processed Mn–Zn–O system

DARSHAN C. KUNDALIYA[1], S. B. OGALE[1,2*], S. E. LOFLAND[3], S. DHAR[1], C. J. METTING[1], S. R. SHINDE[1], Z. MA[2], B. VARUGHESE[2], K. V. RAMANUJACHARY[4], L. SALAMANCA-RIBA[2] AND T. VENKATESAN[1]

The recent discovery of ferromagnetism above room temperature in low-temperature-processed MnO_2–ZnO has generated significant interest. Using suitably designed bulk and thin-film studies, we demonstrate that the ferromagnetism in this system originates in a metastable phase rather than by carrier-induced interaction between separated Mn atoms in ZnO. The ferromagnetism persists up to ~980 K, and further heating transforms the metastable phase and kills the ferromagnetism. By studying the interface diffusion and reaction between thin-film bilayers of Mn and Zn oxides, we show that a uniform solution of Mn in ZnO does not form under low-temperature processing. Instead, a metastable ferromagnetic phase develops by Zn diffusion into the Mn oxide. Direct low-temperature film growth of Zn-incorporated Mn oxide by pulsed laser deposition shows ferromagnetism at low Zn concentration for an optimum oxygen growth pressure. Our results strongly suggest that the observed ferromagnetic phase is oxygen-vacancy-stabilized $Mn_{2-x}Zn_xO_{3-\delta}$.

Nature materials ~~2006~~ 2005

So, it is very useful to analyze and to recommend the sort of materials, that you need in one of the modules, I have coated this example where, simple T G can actually bring about a great amount of insight into mechanism, that is of fundamental as well as application oriented studies. In this there was a confusion about the magnetism, that was happening at room temperature in manganese doped zinc oxide and this is a paper published in nature materials, in the year 2006 sorry, 2005. So, you can refer to this particular paper to understand, how would simple T G analysis can be used to resolve such a Mysterious behavior.

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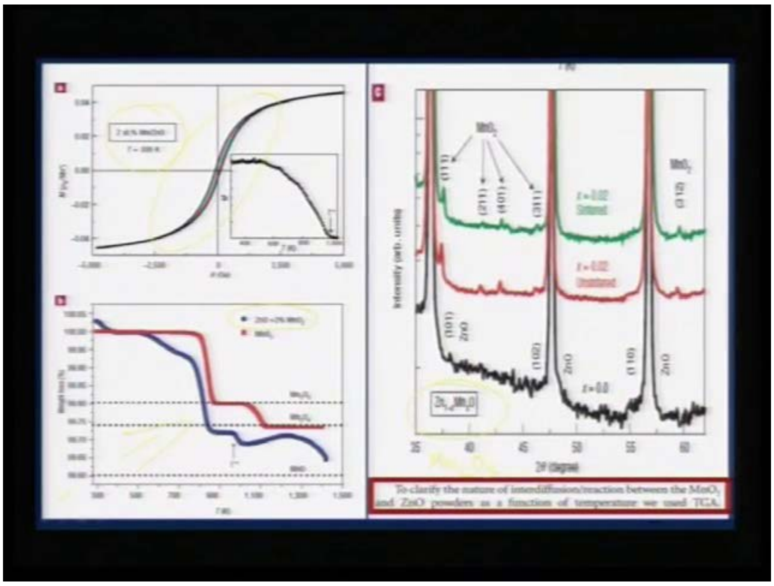

To clarify the nature of interdiffusion/reaction between the MnO_2 and ZnO powders as a function of temperature we used TGA.

In this samples as you would know zinc oxide is a semiconductor, it is not a magnetic compound, but just substituting 2 percent of manganese itself is not a magnetic ion, further and you can still see a room temperature low. So, in that case, it was thought that, a new system has emerged in for device applications called as dilute magnetic semiconductors, but later it was understood, that it is not as a substitution oriented magnetism, but it is some other impurity, which is giving the origin for this magnetic curve.

And what was finally, used to resolve this mystery was the T G plot here as you would see simple thermogravimetric to make a composite of 2 percent M n O 2 grounded with zinc oxide. Finally, went on to prove that, it is not manganese, which is substituting in zinc oxide rather, it is some amount of zinc, which is going into manganese oxide, in other words in M n 2 O 3 phase, which is actually responsible for such a magnetic origin.

So, it is very, very vital all the way, it look simple, not many would even call this as a prima facie important characterization tool, but you would see, that a simple technique can really alter confusion that, prevents in the scientific community. Therefore, T G mapping is very important, now I will take you through some issues related to differential scanning calorimetry.

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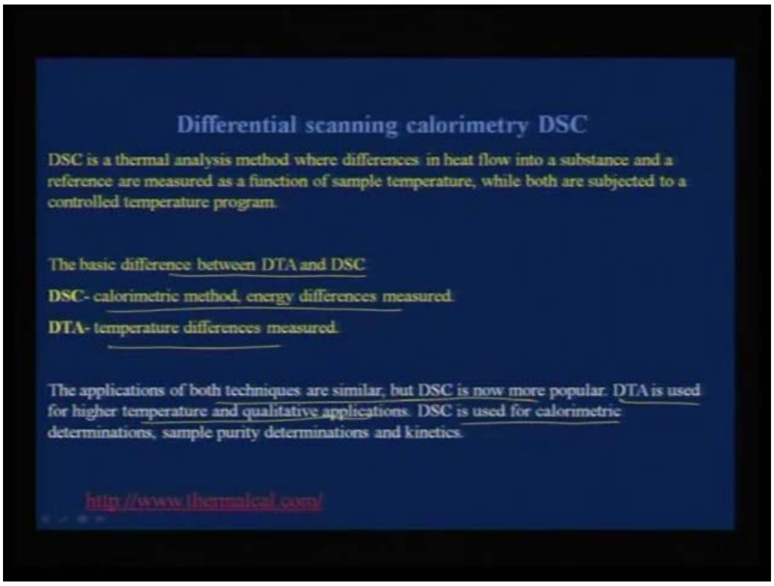

Differential scanning calorimetry DSC

DSC is a thermal analysis method where differences in heat flow into a substance and a reference are measured as a function of sample temperature, while both are subjected to a controlled temperature program.

The basic difference between DTA and DSC

DSC- calorimetric method, energy differences measured.

DTA- temperature differences measured.

The applications of both techniques are similar, but DSC is now more popular. DTA is used for higher temperature and qualitative applications. DSC is used for calorimetric determinations, sample purity determinations and kinetics.

http://www.thermalcal.com/

Because, here you can quantify more results, as I told you there is a basic difference between D T A and D S C, this is a here temperature differences are measured whereas, here the heat flow from or out of the system is sampled is actually measured. Applications of both the techniques are similar whereas, D S C is more popular, because it a it can give you understanding onto the heat exchange, that is happening whereas, D T S conveniently used, because you can go down go up to very high temperatures.

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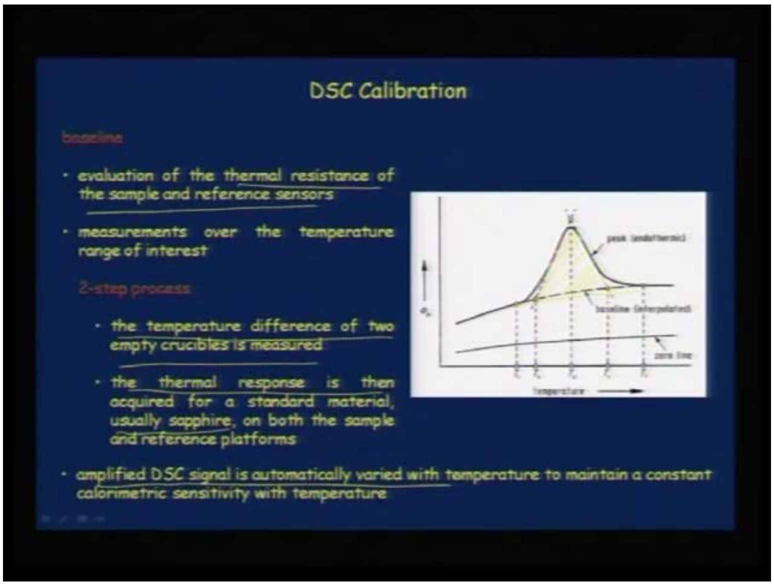

DSC Calibration

baseline

- evaluation of the thermal resistance of the sample and reference sensors
- measurements over the temperature range of interest

  2-step process

  - the temperature difference of two empty crucibles is measured
  - the thermal response is then acquired for a standard material, usually sapphire, on both the sample and reference platforms
- amplified DSC signal is automatically varied with temperature to maintain a constant calorimetric sensitivity with temperature

In D S C one of the things that, you need to do is calibration, you cannot just take the result at its phase value and do the quantification. So, the baseline correction is very important, for example, if you get endothermic peak like this, this is the way you try to deconvolute the peaks where, you try to draw this baseline and then you do this peak corrections, such a way that the area, under the curve is a measure of the amount of heat that is either taken or released.

So, essentially you can determine, the heat capacity or you can determine the delta h of fusion or delta h of combustion, all this can be maximized, therefore, baseline correction or there estimation of the area, under the peak is very, very important. So, evaluation of the thermal resistance of the sample and reference sensors, need to be taken care, it is a 2 step process the temperature difference of the 2 empty crucibles have to be first measured. And then that thermal response is then acquired for a standard material specially, using sapphire, sapphire because melting point is above seventeen hundred degree c. Therefore, you use sapphire as the sample calibrant, amplified D S C signal is automatically varied with temperature to maintain a constant calorimetric sensitivity with temperature.

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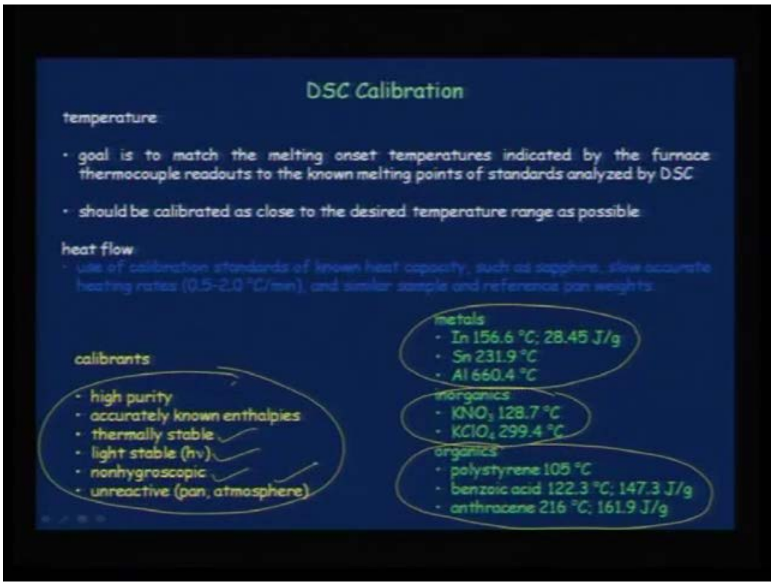

DSC Calibration

temperature

- goal is to match the melting onset temperatures indicated by the furnace thermocouple readouts to the known melting points of standards analyzed by DSC
- should be calibrated as close to the desired temperature range as possible

heat flow

- use of calibration standards of known heat capacity, such as sapphire, slow accurate heating rates (0.5-2.0 °C/min), and similar sample and reference pan weights

calibrants

- high purity
- accurately known enthalpies
- thermally stable
- light stable (hν)
- nonhygroscopic
- unreactive (pan, atmosphere)

metals

- In 156.6 °C; 28.45 J/g
- Sn 231.9 °C
- Al 660.4 °C

inorganics

- KNO_3 128.7 °C
- $KClO_4$ 299.4 °C

organics

- polystyrene 105 °C
- benzoic acid 122.3 °C; 147.3 J/g
- anthracene 216 °C; 161.9 J/g

D S C calibration can be done with the variety of calibrants for example, you can, you have dealing with high temperature samples, you can use metals and if the sample is metal, then you can use metal. As a some inorganics are also good for as calibrants K N O 3 potassium perchlorate organics for example, polystyrene benzoic acid anthracene can be used. And one of the important point is the calibrant should be of high purity, they should be thermally stable, they should not undergo changes with the light, they should be nonhygroscopic, which is much much more important and it should not react with the pan or with the atmosphere, that is possible.

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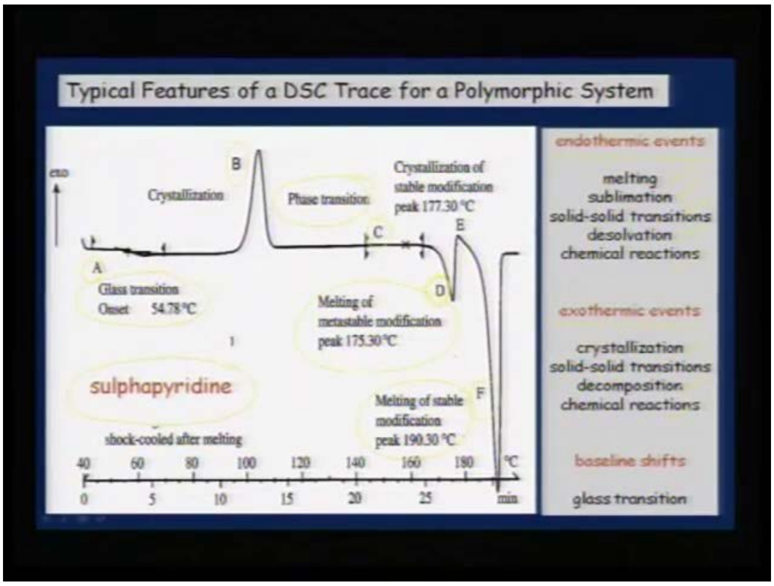

Typical Features of a DSC Trace for a Polymorphic System

endothermic events

melting
sublimation
solid-solid transitions
desolvation
chemical reactions

exothermic events

crystallization
solid-solid transitions
decomposition
chemical reactions

baseline shifts

glass transition

There are typical features, that can be understood from a D S C curve for a polymeric system, for example, if you take sulphapyridine. So, many useful informations that you can get, number one you see a small change in the slope, which actually refers to glass transition, that is step A and in sequence, B it is actually a crystallization from A melt to a crystallite crystallization, which is of a phase transition. And then, here you actually have a melting of metastable modification, that is happening in even D, which is the end of the mid peak.

And then the melting after stable modification, which is another end of the mid peak, so you start with one sample. And then you actually take it through crystallization, after crystallization it goes into a metastable form, which is nothing but your phase transition, which is your event c where, you do not seem anything particular. But, then you see again 2 successive end of the mid peak that relates to 2 different metastable phases, before the sample finally, decomposes.

So, endothermic events are melting sublimation solid transition desolvation chemical reactions, exothermic peaks are crystallization, decomposition and chemical reactions baseline shifts are mostly due to glass transition, as you would see here. Baseline shifts are very, very milder and therefore, you need to be very careful while analyzing it. But, you should also understand any ups and downs in the D S C curve, that it will mean something is happening for example, several artifacts can be recognized.

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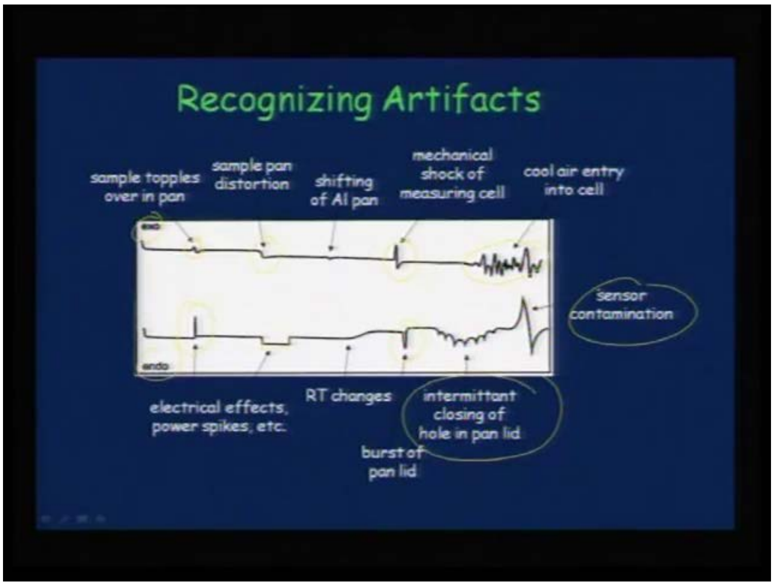

Recognizing Artifacts

Both in the exo peak as well as endo peak, in the exo peak in the sample topples, over in the pan, then you get a fluctuation like this or sample pan is distorted or if you have a mechanical shock of the measuring cell or if the flow of air is leaked out, then you would see this sort of noise coming up.

Similarly, in the endo peak, if you see some set of a plateau like this, it is not exo or endo actually, it is electrical spikes. And spikes can come like this, you also have burst of the pan lid. So, several artifacts can come in a typical D S C, which we should be watchful. And in D S C predominantly, you are talking about the thermal stability where, you can analyze several of these events, which are happening or you can measure the heat flow depending on the nature of a peak or you can look at the chemical purity, you can look at the phase transitions, all this informations, you can get from a D S C curve.

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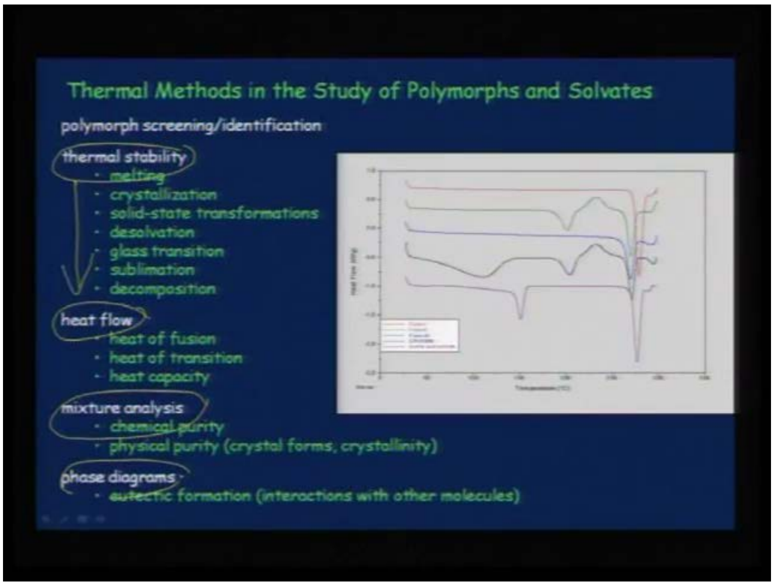

Thermal Methods in the Study of Polymorphs and Solvates

polymorph screening/identification

thermal stability
- melting
- crystallization
- solid-state transformations
- desolvation
- glass transition
- sublimation
- decomposition

heat flow
- heat of fusion
- heat of transition
- heat capacity

mixture analysis
- chemical purity
- physical purity (crystal forms, crystallinity)

phase diagrams
- eutectic formation (interactions with other molecules)

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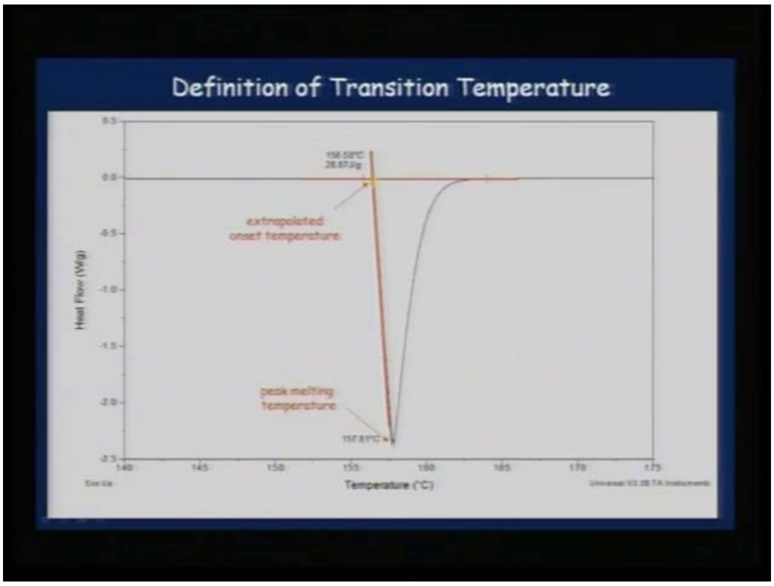

Definition of Transition Temperature

If you are looking at a typical endothermic peak, which is transition temperature actually the onset of this has to be linear, if your peak is to be assist, it can also be a non-linear curve, it can be more Gaussian in such case it tells something different. So, this is the onset of the transition and this is the peak of the transition. In this case, if it is a melting, then this is the weakest down.

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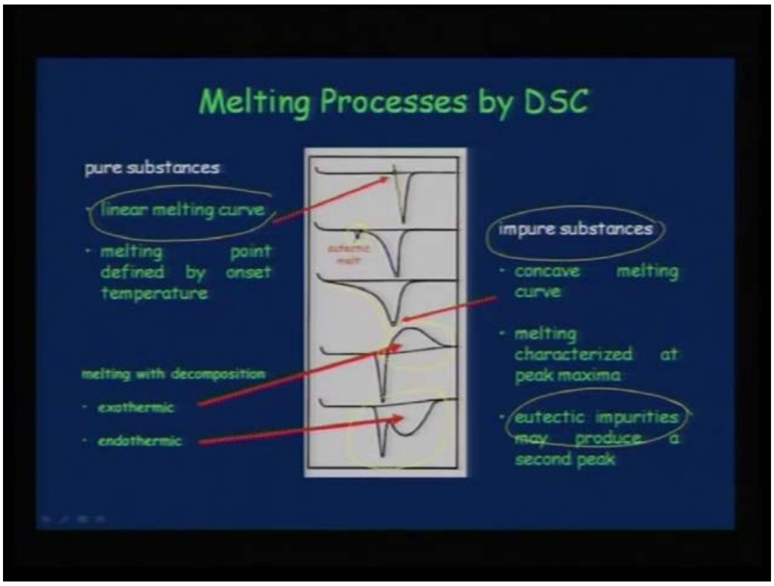

Melting Processes by DSC

pure substances

- linear melting curve
- melting point defined by onset temperature

melting with decomposition

- exothermic
- endothermic

impure substances

- concave melting curve
- melting characterized at peak maxima
- eutectic impurities may produce a second peak

And if you are sample is pure, then there will be a linearity here, if your sample is impure for example, then you would see the onset is actually more with the curvature that means, the sample is impure. And if suppose, there is some other eutectic impurity, that is there it will also show of like another small peak, if there is a endothermic peak, that is melting followed by a exothermic decomposition, it would come out like this, if it is a endothermic decomposition followed by melting, then it would come out like this.

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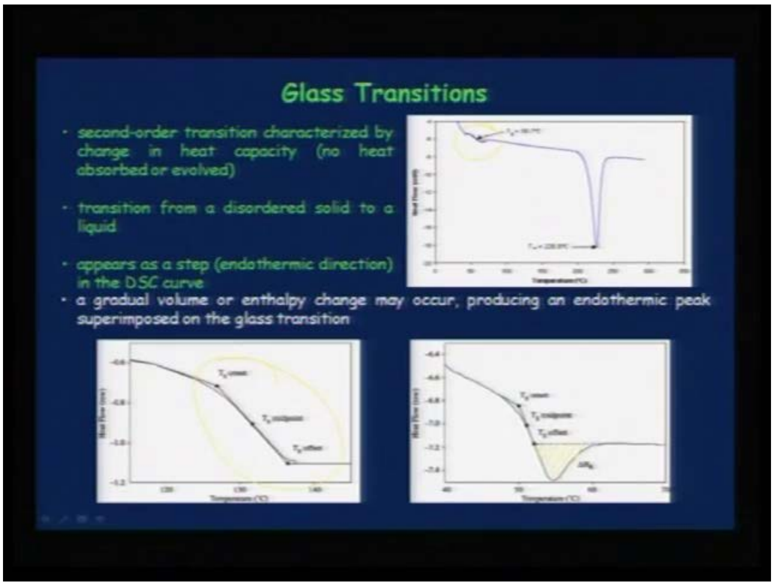

Glass Transitions

- second-order transition characterized by change in heat capacity (no heat absorbed or evolved)
- transition from a disordered solid to a liquid
- appears as a step (endothermic direction) in the DSC curve
- a gradual volume or enthalpy change may occur, producing an endothermic peak superimposed on the glass transition

And in that case actually glass transitions, although they are look very minimal one can actually try to resolve to find out whether, there is a linearity in the slope, which indicates, there is a glass transition and in such case, if you do the baseline correction, you will be able to see, what is the enthalpy, that is involved in this glass transition.

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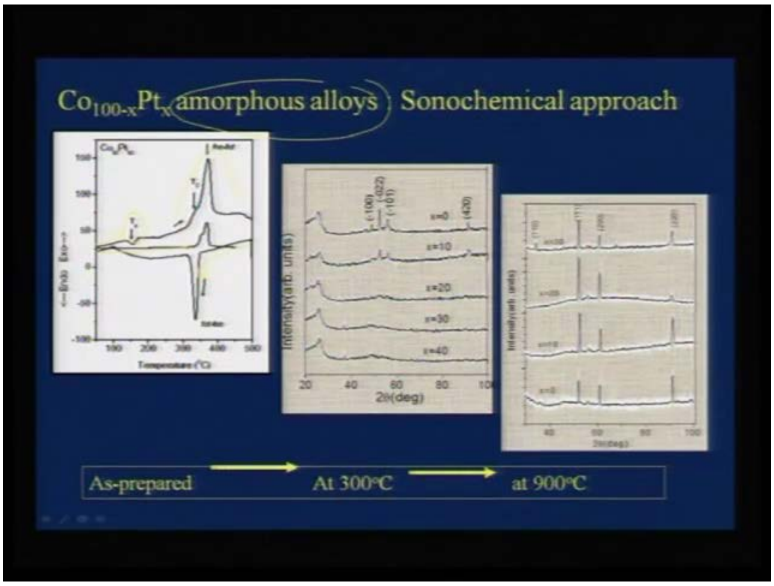

$Co_{100-x}Pt_x$ amorphous alloys : Sonochemical approach

As-prepared → At 300°C → at 900°C

This one of our own work, where you take amorphous alloys of cobalt platinum and if you try to heat that sample, you can map what set of transformation, that is happening for example, if you do this forward run, there is a glass transition, which amounts to a good endothermic peak. After that there is a exothermic peak, which actually corresponds to crystallization, which is a F C C to F C T transformation. So, it is a exothermic peak, so when you cool this sample again, you see the same thing happening where, F C F C T is now reversible to F C C.

So, this phase transitions is a reversible one therefore, on the cooling, you would see a reversible curve, but once you go again for the next run, you can see because of the previous proto you know sweep, the area of this curve has tremendously reduce, which means most of the sample as got crystallized. So, this much information, you can get about, amorphous alloys, about it is glass transition about the crystallization processes and whether it is a reversible or a irreversible transformation.

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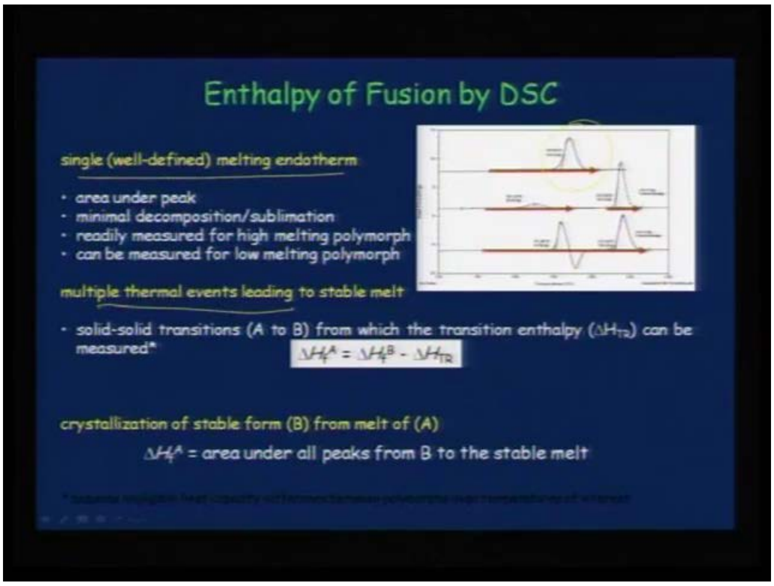

Enthalpy of Fusion by DSC

single (well-defined) melting endotherm

- area under peak
- minimal decomposition/sublimation
- readily measured for high melting polymorph
- can be measured for low melting polymorph

multiple thermal events leading to stable melt

- solid-solid transitions (A to B) from which the transition enthalpy (ΔH_{TR}) can be measured*

$$\Delta H_f^A = \Delta H_f^B - \Delta H_{TR}$$

crystallization of stable form (B) from melt of (A)

ΔH_f^A = area under all peaks from B to the stable melt

So, all this information, you can get from D S C curve enthalpy of fusion, for example, you can try to measure, it could be a multiple thermal steps or it could be a single melting step and the delta H of fusion can be measured.

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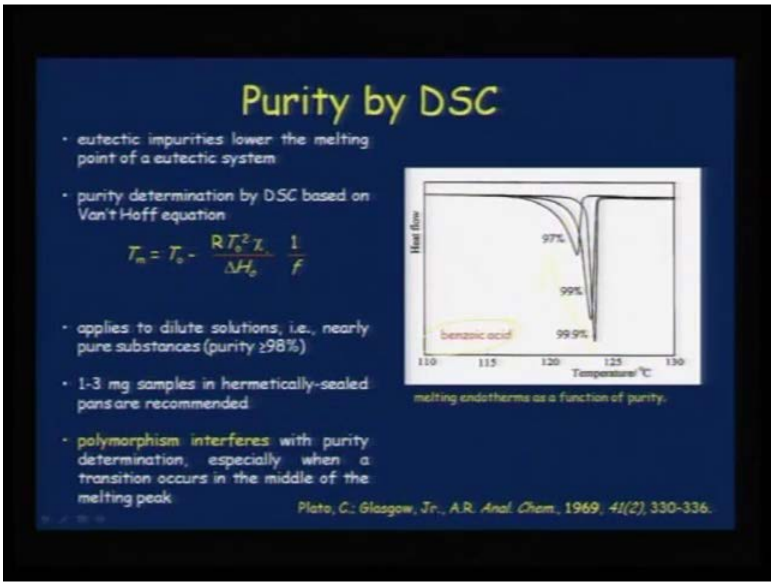

Purity by DSC

- eutectic impurities lower the melting point of a eutectic system
- purity determination by DSC based on Van't Hoff equation

$$T_m = T_o - \frac{RT_o^2\chi_i}{\Delta H_o}\,\frac{1}{f}$$

- applies to dilute solutions, i.e., nearly pure substances (purity ≥98%)
- 1-3 mg samples in hermetically-sealed pans are recommended
- polymorphism interferes with purity determination, especially when a transition occurs in the middle of the melting peak

melting endotherms as a function of purity.

Plato, C.; Glasgow, Jr., A.R. *Anal. Chem.*, 1969, *41(2)*, 330-336.

And I would also show one more example, how purity can be determined, for example, if you take benzoic acid, depending on the purity of this samples, the endothermic peak will actually shift. So, that will tell you the sort of purity of your sample.

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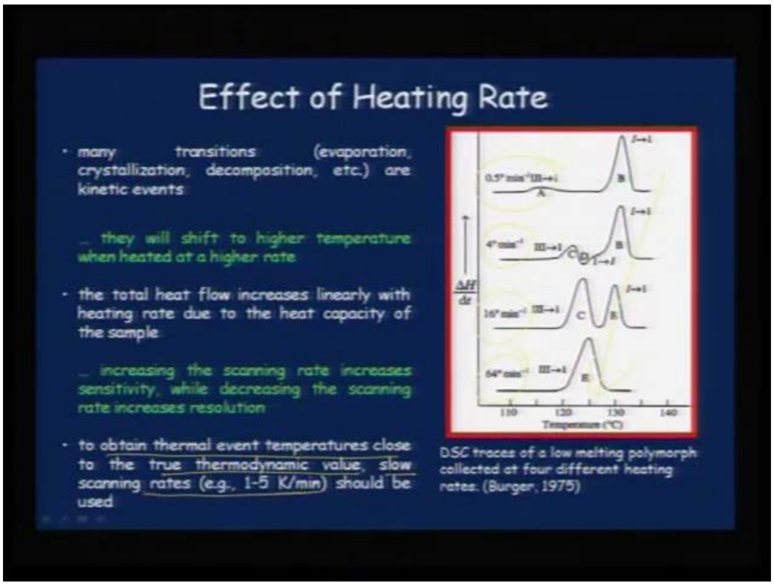

Effect of Heating Rate

- many transitions (evaporation, crystallization, decomposition, etc.) are kinetic events

… they will shift to higher temperature when heated at a higher rate

- the total heat flow increases linearly with heating rate due to the heat capacity of the sample

… increasing the scanning rate increases sensitivity, while decreasing the scanning rate increases resolution

- to obtain thermal event temperatures close to the true thermodynamic value, slow scanning rates (e.g., 1-5 K/min) should be used

DSC traces of a low melting polymorph collected at four different heating rates. (Burger, 1975)

So, this is a good measure by which, you can measure that purity and lastly, I will touch up on the heating rate, suppose you heat the sample at 0.5 degree, then you get a single peak and then one peak here. If you increase the sample heating rate, you can see same transformation, but it is actually giving a very different protocol. So, to obtain thermal events, close to the true thermodynamic value, the recommended heating rates are 1 to 5 degree per minute, that is what is recommended and it has to be done at a very, very slow purging rate of your air or argon atmosphere. Otherwise same process, but you get a confusing D S C curves, lastly I would also like to touch upon this issue.

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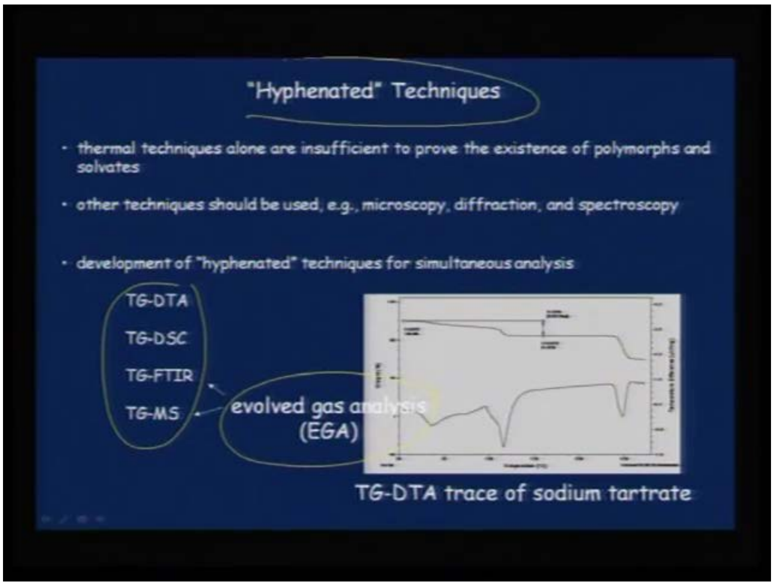

"Hyphenated" Techniques

- thermal techniques alone are insufficient to prove the existence of polymorphs and solvates
- other techniques should be used, e.g., microscopy, diffraction, and spectroscopy
- development of "hyphenated" techniques for simultaneous analysis

TG-DTA
TG-DSC
TG-FTIR
TG-MS

evolved gas analysis (EGA)

TG-DTA trace of sodium tartrate

That T G can be combined with F T I R or it can be combined with mass spec. So, you can evaluate the evolved gases, for example, calcium oxalate carbonic heater, carbon dioxide comes, carbon dioxide can be measured using a i r cell. So, all this multiple techniques or hyphenated techniques, can be studied using this protocol.

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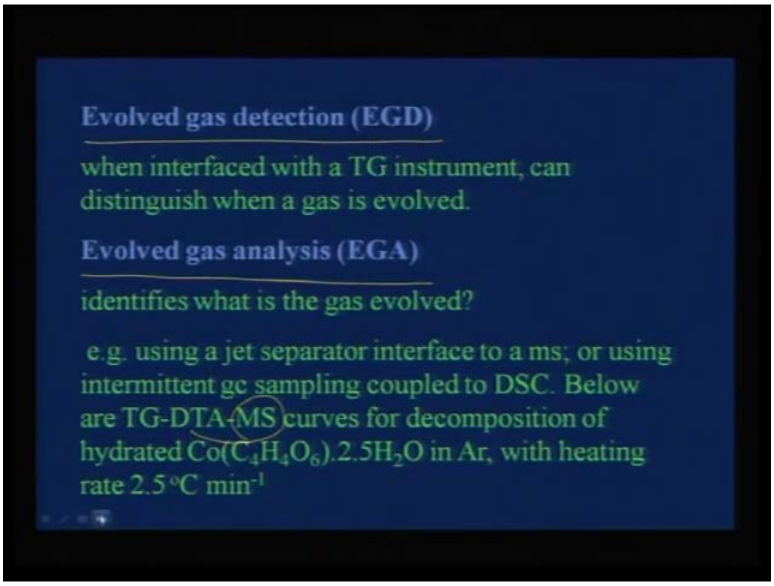

Evolved gas detection (EGD)

when interfaced with a TG instrument, can distinguish when a gas is evolved.

Evolved gas analysis (EGA)

identifies what is the gas evolved?

e.g. using a jet separator interface to a ms; or using intermittent gc sampling coupled to DSC. Below are TG-DTA-MS curves for decomposition of hydrated Co($C_4H_4O_6$).2.5H_2O in Ar, with heating rate 2.5 °C min^{-1}

So, in that way evolved gas analysis, evolved and evolved gas detection, can be achieved using a mass spectra or it can be connected to a online G C gas chromatography.

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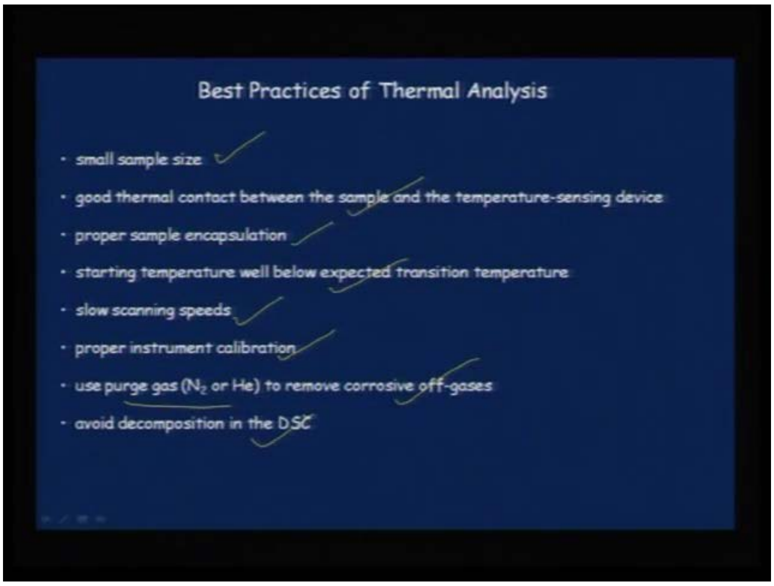

Best Practices of Thermal Analysis

- small sample size
- good thermal contact between the sample and the temperature-sensing device
- proper sample encapsulation
- starting temperature well below expected transition temperature
- slow scanning speeds
- proper instrument calibration
- use purge gas (N_2 or He) to remove corrosive off-gases
- avoid decomposition in the DSC

So, best practices of thermal analysis, use small sample size, good thermal contact between sample and sensing device, proper sample encapsulation when you are talking about D S C. And starting temperature well below, expected transition temperature slow scanning speeds, proper instrument calibration and then purging gas should not be corrosive and avoid decomposition in the D S C. So, these are the best practices with which one can get very useful information, there are several groups, both in chemistry and physics where, they use the thermogravimetric essentially to resolve many, many fascinating features that happened during, the various such activities.