Non - Metallic Materials
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Module - 09
Characterization of structure, composition, and microstructure of non - metallic materials
Lecture - 45
Thermal analyses

Welcome, to my course Non-metallic Materials and today, we are in lecture number, module number 9, Characterization of structure, composition, and microstructure of nonmetallic materials. And, this is lecture number 45, where I will discuss the Thermal analyses.

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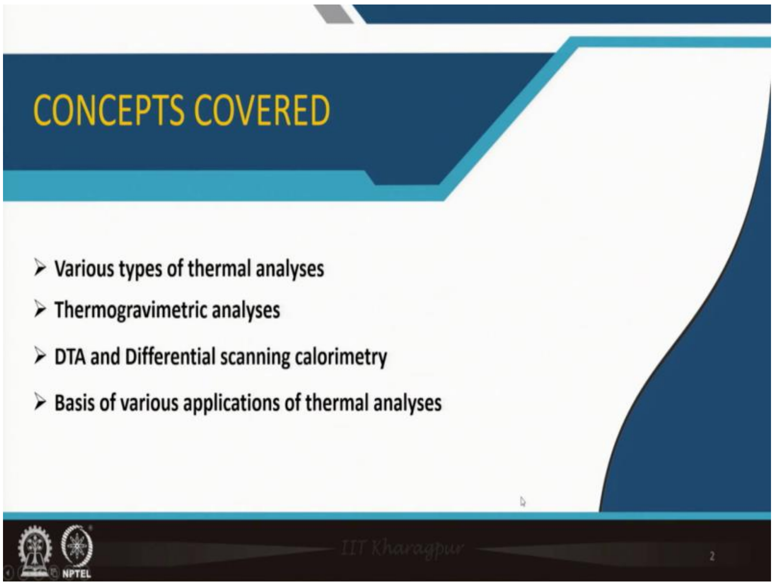

CONCEPTS COVERED

- Various types of thermal analyses
- Thermogravimetric analyses
- DTA and Differential scanning calorimetry
- Basis of various applications of thermal analyses

So, various types of thermal analyses first will be introduced and then we will concentrate on thermo gravimetric analyses followed by differential thermal analyses and differential scanning calorimetry – this two important characterization tool will be described. And, various application that is possible using this thermal analyses that will be covered in this particular lecture.

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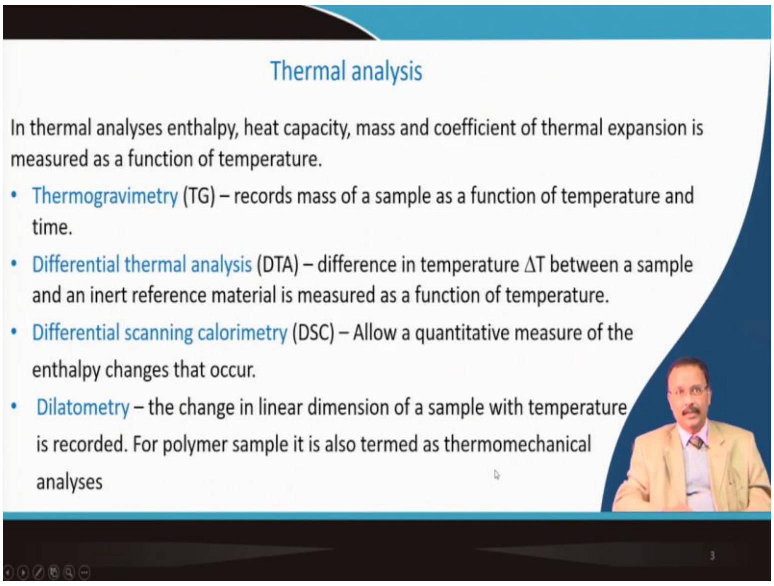

Thermal analysis

In thermal analyses enthalpy, heat capacity, mass and coefficient of thermal expansion is measured as a function of temperature.

- Thermogravimetry (TG) – records mass of a sample as a function of temperature and time.
- Differential thermal analysis (DTA) – difference in temperature ΔT between a sample and an inert reference material is measured as a function of temperature.
- Differential scanning calorimetry (DSC) – Allow a quantitative measure of the enthalpy changes that occur.
- Dilatometry – the change in linear dimension of a sample with temperature is recorded. For polymer sample it is also termed as thermomechanical analyses

So, basically in thermal analyses enthalpy, heat capacity, mass and coefficient of thermal expansions they are measured as a function of temperature and in some instances as a function of time. So, in thermogravimetry, that we record the mass of a sample as a function of temperature and time. In differential thermal analysis: the difference in temperature between a sample and an inert reference material that is measured as a function of temperature.

In case of differential scanning calorimetry it basically allow a quantitative measure of the enthalpy change that occur in the sample. In case of dilatometry, the change in linear dimension of the sample with temperature is recorded. For polymer base sample this kind of measurement is also termed as thermo mechanical analyses.

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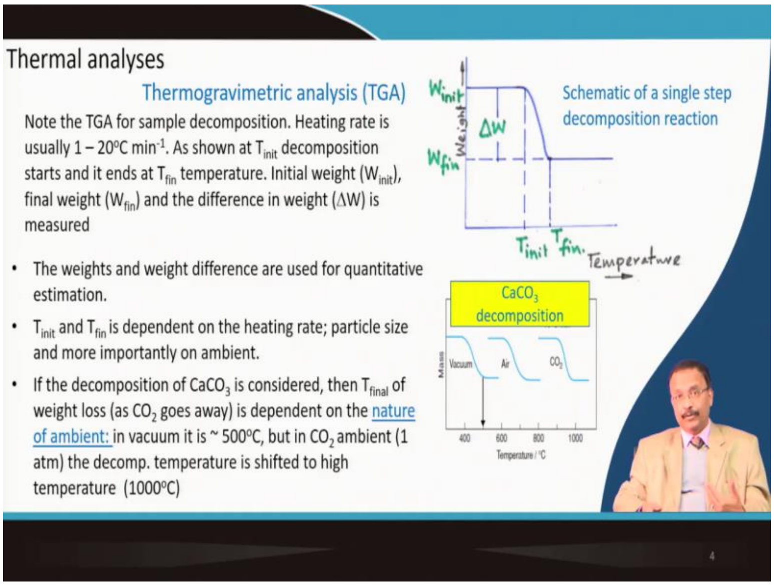

Thermal analyses

Thermogravimetric analysis (TGA)

Note the TGA for sample decomposition. Heating rate is usually 1 – 20°C min^{-1}. As shown at T_{init} decomposition starts and it ends at T_{fin} temperature. Initial weight (W_{init}), final weight (W_{fin}) and the difference in weight (ΔW) is measured

- The weights and weight difference are used for quantitative estimation.
- T_{init} and T_{fin} is dependent on the heating rate; particle size and more importantly on ambient.
- If the decomposition of $CaCO_3$ is considered, then T_{final} of weight loss (as CO_2 goes away) is dependent on the nature of ambient: in vacuum it is ~ 500°C, but in CO_2 ambient (1 atm) the decomp. temperature is shifted to high temperature (1000°C)

Schematic of a single step decomposition reaction

So, a typical thermogravimetric analyses where a decomposition reaction is taking place, there the samples are heated in a constant rate. So, typically 1 to 20 degrees Celsius per minute rate is used. So, if you can see this figure you can see the temperature of initiation of a decomposition reaction this is here and it ends at a temperature which is marked as T fin, right.

So, initial weight was W in it and the final weight after decomposition is W fin and the difference in weight del W that is measured. Basically, this weight change at each temperature is measured. The weights and weight difference they are used for quantitative estimation either absolute weight you can use or the difference in weight you can use.

So, there are various types of presentations and sometimes weight percent weight loss that is also used in the ordinate. And, the initial temperature T init and T final if T fin that is dependent on the heating rate. It is also dependent on the particle size of the material that you are using and more importantly it depends on the ambient that is kept surrounding the sample.

If you consider the decomposition of calcium carbonate T final will be the temperatures where there will be the weight loss completion carbon dioxide completely goes away. So it depends on the nature of the ambient. So, if you do the same experiment in vacuum, see it is about 500 degree Celsius where all the weight is stabilized. So, it forms calcium oxide.

But, if you maintain a pure air ambient, then this temperature increased and if you maintain an ambient which is carbon dioxide at 1 atmosphere this decomposition temperature is shifted to very high temperature about 1000 degree Celsius. So, it is important you will have to report that at what particular ambient this kind of decomposition reaction is taking place.

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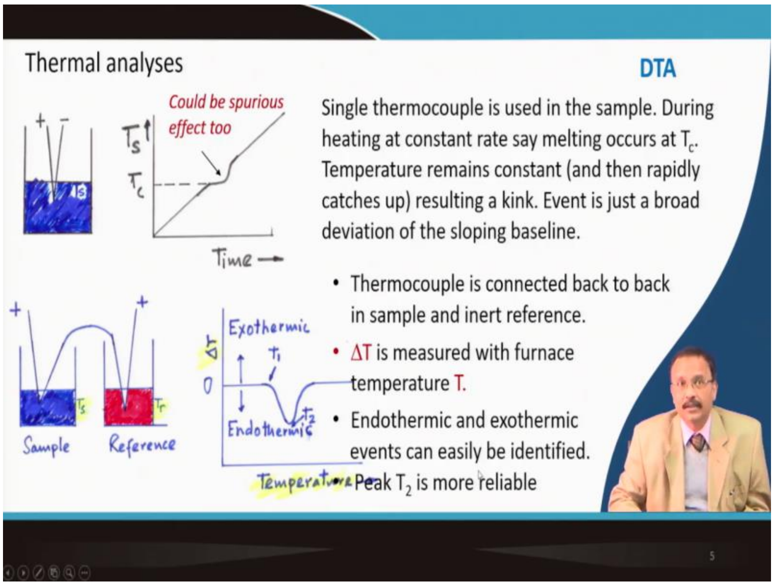

Thermal analyses

DTA

Single thermocouple is used in the sample. During heating at constant rate say melting occurs at T_c. Temperature remains constant (and then rapidly catches up) resulting a kink. Event is just a broad deviation of the sloping baseline.

- Thermocouple is connected back to back in sample and inert reference.
- ΔT is measured with furnace temperature T.
- Endothermic and exothermic events can easily be identified. Peak T_2 is more reliable

Another important thermal analyses is differential thermal analyses. So, consider your sample you kept in a crucible and you have a thermocouple here kept and you are increasing the temperature of this sample. So, sample temperature T s is increased and you have only the configuration is something like this.

So, when a constant heat at a constant rate this temperature is increased say melting takes place at some temperature say at T c this is the temperature melting takes place. So while the whole of it will melt the temperature will remain constant it will take latent heat. So, it will remain constant. So, this will not change.

So, there will be some kind of anomaly at this temperature and again when this reaction is completed then it will again catch up this heating rate. So, it will just be a change in the slope. So, sometimes this slope can be spurious. So, you cannot really identify that this melting transition at what temperature it takes place. So, it could be a spurious change in the slope.

So, you can misinterpret the data. So, therefore, this differential thermal analyses is important where you have your sample and along with that you have an inert material, which does not undergo any kind of reaction without decomposition or whatever, I mean no reaction is taking place.

So, it remains in its pure state there is no phase transition, no polymorphic phase transition nothing is happening to that. And, then you connect the thermocouple back to back and you measure the temperature difference as a function of temperature by putting another thermocouple inside the DTA equipment.

So, del t is measured along with the furnace temperature. So, endothermic and exothermic events can easily be identified because in case of say melting or in case of crystallization, then there will be either an endothermic reaction or it will be an exothermic reaction in case of crystallization. So, that can easily be identified.

Now, you can get for example, in case of endothermic reaction a peak something like that. So, it is having a initiation and it is the completion. So, usually it is difficult to identify sometimes the initiation peak. So, it the reaction can be characterized by the completion peak and you can identify this kind of transition.

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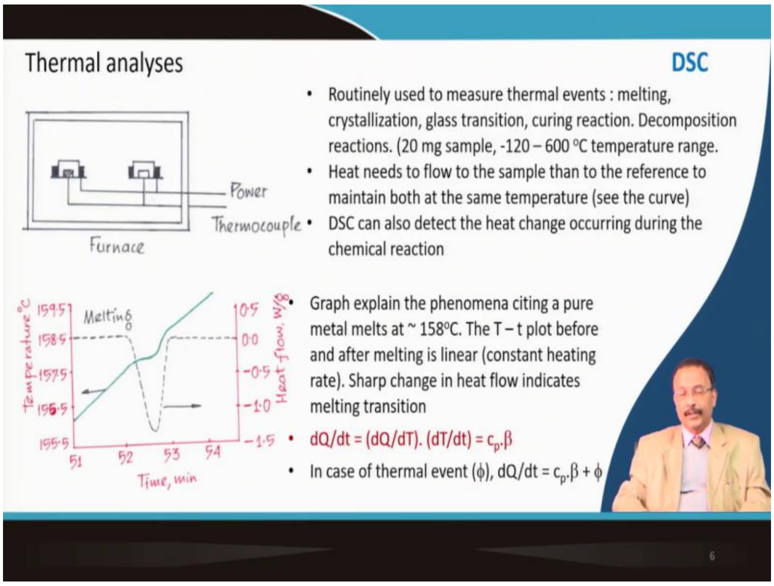

Thermal analyses

DSC

- Routinely used to measure thermal events : melting, crystallization, glass transition, curing reaction. Decomposition reactions. (20 mg sample, -120 – 600 °C temperature range.
- Heat needs to flow to the sample than to the reference to maintain both at the same temperature (see the curve)
- DSC can also detect the heat change occurring during the chemical reaction
- Graph explain the phenomena citing a pure metal melts at ~ 158°C. The T – t plot before and after melting is linear (constant heating rate). Sharp change in heat flow indicates melting transition
- $dQ/dt = (dQ/dT).(dT/dt) = c_p.\beta$
- In case of thermal event (ϕ), $dQ/dt = c_p.\beta + \phi$

So, another similar kind of thing is differential scanning calorimetry. So, these are routinely used for various types of measurement of thermal events including melting, crystallization, blast transition, some kind of curing reaction, decomposition reaction. So, usually about 20 milligrams samples are kept in one of the crucible inside a DTF furnace and the temperature range can be quite wide maybe from minus 120 degree Celsius to 600 degree Celsius.

So, heat needs to flow to the sample then to the reference to maintain both at the same temperature. So, DSC can be used to detect the heat change occurring during the chemical reaction. So, the graph this that explains the phenomena, which cite a melting reaction of a metal, which is occurring at about 158 degree Celsius.

So, if you have the T versus t curve; this is heating curve temperature versus time before and after the melting it is linear. It maintains the constant heating rate, but the sharp change in the heat flow in case of DSC. So, here it is it could be just an some kind of anomaly, but here there is a sharp change in the heat flow that actually identify very clear the melting transition.

So, the rate of heat flow dQ by dt that is dQ by d temperature into d temperature by d time. So, the first one is the specific heat and second one is the heating rate. So, when a thermal event takes place, then your rate of heat flow change with time that is c p into the heating rate plus some thermal event phi. So, that denotes the heat flow change.

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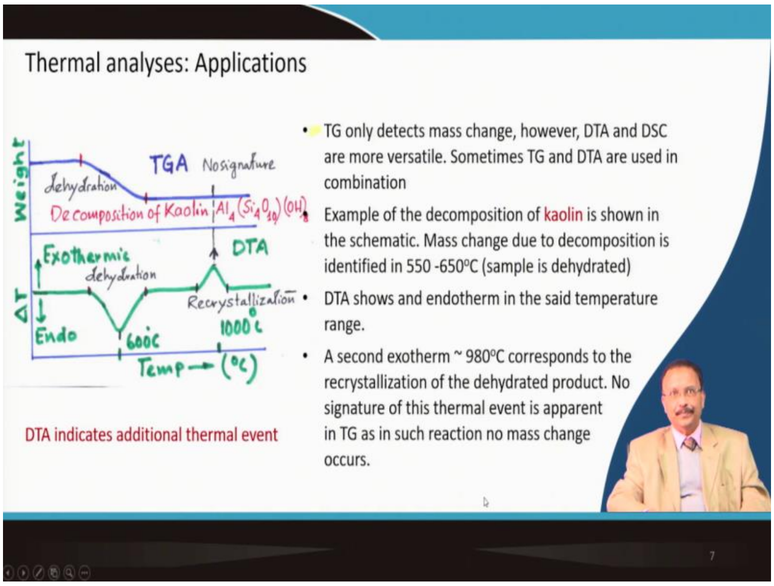

Thermal analyses: Applications

DTA indicates additional thermal event

- TG only detects mass change, however, DTA and DSC are more versatile. Sometimes TG and DTA are used in combination
- Example of the decomposition of kaolin is shown in the schematic. Mass change due to decomposition is identified in 550 -650ºC (sample is dehydrated)
- DTA shows and endotherm in the said temperature range.
- A second exotherm ~ 980ºC corresponds to the recrystallization of the dehydrated product. No signature of this thermal event is apparent in TG as in such reaction no mass change occurs.

So, TG the thermo gravimetric analyses that can detect only the mass change, but your DTA and DSC they are more versatile. So in some of the equipment the thermogravimetry and the differential thermal analyses they are used in combination. So, both are combined in a particular in a single equipment and that is quite versatile in nature. So, here for example, you can consider the decomposition of kaolin that is taking place.

So, mass change due to the decomposition is identified at a temperature about 550 to 650 degree Celsius. So, the sample is dehydrated. And, DTA shows a very broad peak which is endothermic in nature in the said temperature range, but in addition in case of DTA you can see the presence of another peak. So, this is an exotherm which is otherwise there is no signature in the thermo gravimetric analyses.

So, the second exotherm at 980 degree Celsius, that correspond to the recrystallization of the dehydrated kaolin. So, this signature you will not get in thermo gravimetric analyses, because that is there is no mass change is involved in this crystallization, but DTA can detect it. So, DTA is in addition to the thermo gravimetric analyses it can detect additional thermal event in the sample.

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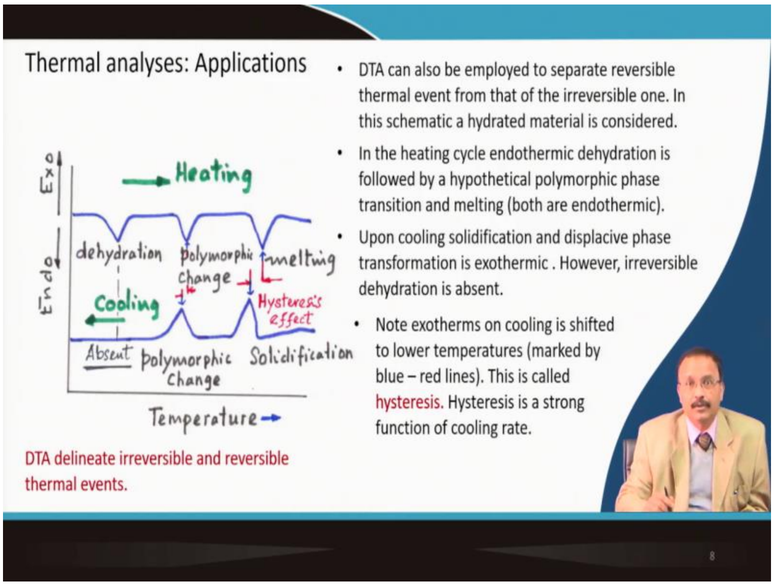

Thermal analyses: Applications

- DTA can also be employed to separate reversible thermal event from that of the irreversible one. In this schematic a hydrated material is considered.
- In the heating cycle endothermic dehydration is followed by a hypothetical polymorphic phase transition and melting (both are endothermic).
- Upon cooling solidification and displacive phase transformation is exothermic . However, irreversible dehydration is absent.
- Note exotherms on cooling is shifted to lower temperatures (marked by blue – red lines). This is called hysteresis. Hysteresis is a strong function of cooling rate.

DTA delineate irreversible and reversible thermal events.

So, in some cases it can be employed to separate the reaction which is reversible thermal event from the one which is irreversible. So, in this particular schematic we have included either schematic of a hydrated material. So, in the heating cycle you can see endothermic dehydration, then a hypothetical polymorphic phase transition; already I described in certain material the crystal structure changes, but this can be dispersive or this can be reconstructive in nature and then there is a melting transition.

So, three types of reaction that you can see it is occurring here in the heating cycle. When you cool it then this melting transition is replaced by solidification and then the polymorphic transition it is displacive in nature. So, again there is a signature for this, but dehydration is a irreversible phenomena.

So, it is it cannot be I mean this is not appeared here. So, it can detect the reaction which are reversible and which are not reversible. So, easily from the DTA relation. Here you can see a little bit of hysteresis.

So, exotherm on cooling is usually shifted to lower temperature that is marked by this arrow. So, as compared to this temperature it is shifted and usually this kind of hysteresis is a very strong function the amount is a strong function of cooling rate.

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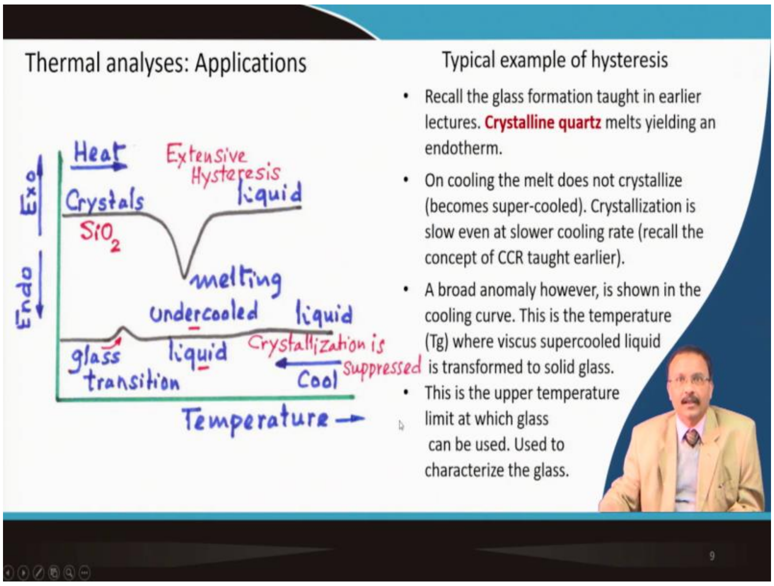
Thermal analyses: Applications

Typical example of hysteresis

- Recall the glass formation taught in earlier lectures. **Crystalline quartz** melts yielding an endotherm.
- On cooling the melt does not crystallize (becomes super-cooled). Crystallization is slow even at slower cooling rate (recall the concept of CCR taught earlier).
- A broad anomaly however, is shown in the cooling curve. This is the temperature (Tg) where viscus supercooled liquid is transformed to solid glass.
- This is the upper temperature limit at which glass can be used. Used to characterize the glass.

So, consider the glass formation that already I have taught. In case of crystalline quartz the melting yields and endotherm right, on cooling the melts they do not crystallize. So, instead they become super cooled in nature. So, crystallization is a slow event at slower cooling rate. So, remember the concept that I talked about in the critical cooling rate is involved.

So, you can cannot see the crystallization peak here in this case in case of glass formation, but a broad anomaly is actually shown in the cooling curve. And, this temperature is known as glass transition temperature where the viscous super cooled liquid that is transformed into a solid glass.

So, this is the upper temperature limit at which the glass can be used already we talked about it. So, this is used this temperature is used to characterize the glass. So, that is the limit when you consider in the heating cycle. So, after that it transform into a supercooled or uncooled liquid. So, that defines the temperature till which you can safely use the glass. So, these things can be detected by a differential thermal analyses plot.

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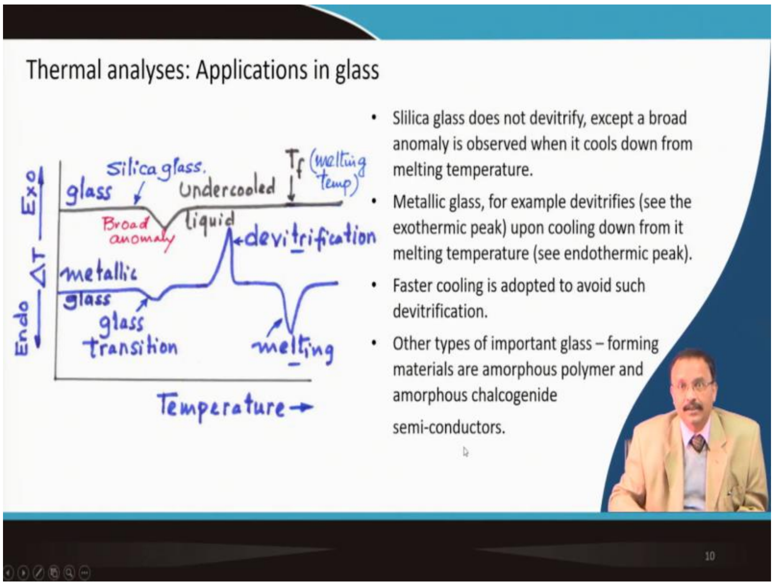
Thermal analyses: Applications in glass

- Slilica glass does not devitrify, except a broad anomaly is observed when it cools down from melting temperature.
- Metallic glass, for example devitrifies (see the exothermic peak) upon cooling down from it melting temperature (see endothermic peak).
- Faster cooling is adopted to avoid such devitrification.
- Other types of important glass – forming materials are amorphous polymer and amorphous chalcogenide semi-conductors.

So, silica glass they do not devitrifies. So, once you melt it then you cool it down it will not crystallize back. So, a broad anomaly only we will see that will correspond the glass transition temperature when you are cooling from the melt. But, if you talk about the metallic glass it devitrifies.

So, you can see in case of metallic glass again you have the signature of glass transition and then there is an exothermic peak. So, that corresponds to the crystallization and once you again farther heat it then it starts to melt. So, faster cooling is adopted to avoid such divert devitrification.

So, in fact, if you cooled the metallic glass from it is melt the very very high rate, then only you can get rid of the crystallization phenomena the devitrification. So, other type of glass forming material they are amorphous polymers and also in some cases amorphous chalcogenide semiconducting materials, they also form glass. That already we talked about while we I taught the glass in part of my earlier lectures.

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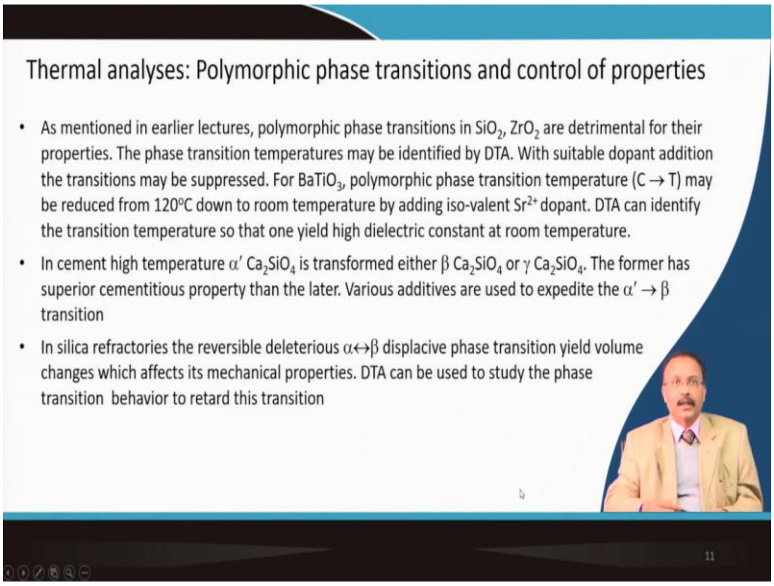

Thermal analyses: Polymorphic phase transitions and control of properties

- As mentioned in earlier lectures, polymorphic phase transitions in SiO_2, ZrO_2 are detrimental for their properties. The phase transition temperatures may be identified by DTA. With suitable dopant addition the transitions may be suppressed. For $BaTiO_3$, polymorphic phase transition temperature ($C \rightarrow T$) may be reduced from 120°C down to room temperature by adding iso-valent Sr^{2+} dopant. DTA can identify the transition temperature so that one yield high dielectric constant at room temperature.
- In cement high temperature α' Ca_2SiO_4 is transformed either β Ca_2SiO_4 or γ Ca_2SiO_4. The former has superior cementitious property than the later. Various additives are used to expedite the $\alpha' \rightarrow \beta$ transition
- In silica refractories the reversible deleterious $\alpha \leftrightarrow \beta$ displacive phase transition yield volume changes which affects its mechanical properties. DTA can be used to study the phase transition behavior to retard this transition

So, the thermal analyses the polymorphic phase transformation identification of those polymorphic phase transition and control of the material property DTA is a very very important characterizing tool. So, polymorphic phase transition as you understand it occurs in case of silicon dioxide, zirconium oxide and usually they are detrimental for their refracted in property refractory based property because of the volume expansion.

So, this phase transition temperature can be identified by differential thermal analysis. Now, you can use suitable dopant you if you remember in case of silica you can use certain dopant, in case of zirconium oxide you can use itria or calcia, doped ZrO 2 also various rare-earth also can be used, so that this kind of phase transition is avoided maybe in case of zirconia at room temperature cubic phase can be stabilized, which will not undergo any kind of polymorphic phase transition.

So, that is good for the property they that these materials are used for. So in those cases DTA is absolutely necessary. Another important material of concern is barium titanate which is used for dielectric material. So, here also polymorphic phase transition takes place cubic to tetragonal already we talked about it.

Now, in case of this polymorphic phase transition that transition temperature the dielectric constant maximizes, right. So, you would like to reduce this transition temperature down to room temperature because otherwise 120 degree Celsius where this cubic to tetragonal phase transition takes place that is too high.

So, you can use some kind of dopant like strontium replacing part of barium to form BST to reduce the transition temperature very close to room temperature by adding a specific amount of the dopant so that the dielectric constant the dielectric property is the maxima at room temperature instead of 120 degree Celsius. So, for this kind of analyses DTA is very important.

Another place where this can be used is the formation of cement. So, in case of cement usually this alpha calcium silicate Ca 2 Si O 4 that can either be transformed to a beta phase beta calcium silicate or gamma calcium silicate. Now, the beta phase this is having beta cementitious property as compared to the gamma phase.

So, usually various dopants are used to stabilize this phase when it cools down from the clinker to room temperatures. So, this transition or the usefulness of this dopant controlling this phase transition that also can be studied by this differential thermal analyses the transition temperature.

Silica refractory you know that reversible alpha to beta transition that introduced lot of volume change. So, this volume change affects their mechanical property as I said. Again, DTA can be used to study this phase transition behavior or whether at all they are suppressed by adding dopant. So, it is indeed very useful.

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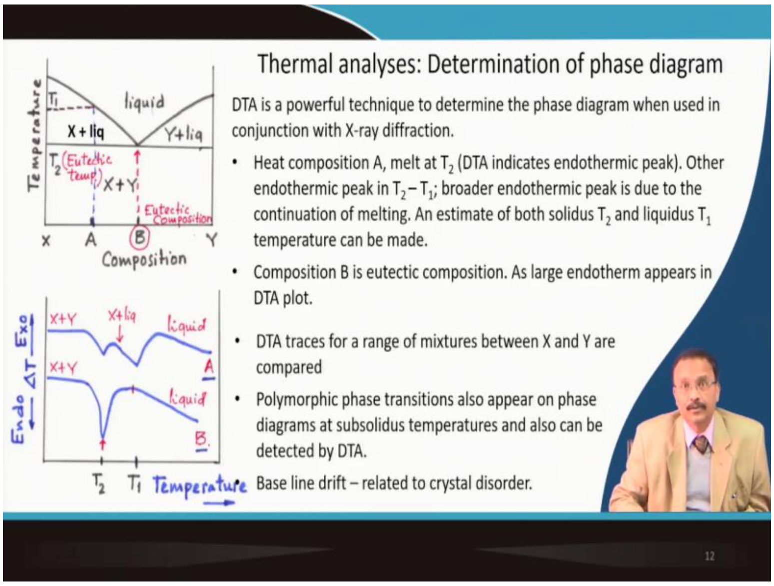

Thermal analyses: Determination of phase diagram

DTA is a powerful technique to determine the phase diagram when used in conjunction with X-ray diffraction.

- Heat composition A, melt at T_2 (DTA indicates endothermic peak). Other endothermic peak in $T_2 - T_1$; broader endothermic peak is due to the continuation of melting. An estimate of both solidus T_2 and liquidus T_1 temperature can be made.
- Composition B is eutectic composition. As large endotherm appears in DTA plot.
- DTA traces for a range of mixtures between X and Y are compared
- Polymorphic phase transitions also appear on phase diagrams at subsolidus temperatures and also can be detected by DTA.
- Base line drift – related to crystal disorder.

This is a very powerful technique to determine the phase diagram. This also I have taught in my other lectures now how to make this kind of phase diagram. Along with X-ray diffraction the DTA can be used to construct this phase diagram. So, here is simple eutectic phase diagram you may remember that is considered here.

So, if you consider the composition A, then it basically melts at a temperature T 2. So, when it melts, then it indicates an endothermic peak a broader endothermic peak, but here you keep on heating it. So, there is a phase mixture of x and liquid and finally, and the liquids thus temperature is reached. So then again this solid phase they are all transformed to liquid phase.

So, another endothermic peak it will appear in between T 2 and T 1 if you are having composition something like this something like a right. So, an estimate of both solidus T 2 and liquidus T 1 temperature can be met and this can be met at any of this composition, right.

All this composition you can mix in different proportion and do the DTA analyses and you precisely get the temperature 1 temperature will be fixed and another one will be varied and you will get the these two temperature very precisely. If you consider the composition which is B, so, this is a eutectic composition. So, in here this two solid will directly be melt and form liquid.

So, only one kind of endothermic which is the same temperature T 2 it will appear here. So, DTA trace for a range of mixture between X and Y, they are compared and also the polymorphic phase transition on the phase diagram that can appear at the sub solidus temperature. So, if something is happening here any polymorphic phase transition takes place, so that also can be identified by the DTA analysis.

So, in other words, with the help of X-ray to know the exact phase composition at least in the solid state you can precisely get the phase diagram constructed by this analyses. Now, the baseline not always the baseline is very straight. So, sometimes the baseline is also sloping. So, if it is a sloped baseline, it is basically related to the crystal disorder and in modern DTA and TGA analyzer there is by in the software you can change the slope you can cancel the slope.

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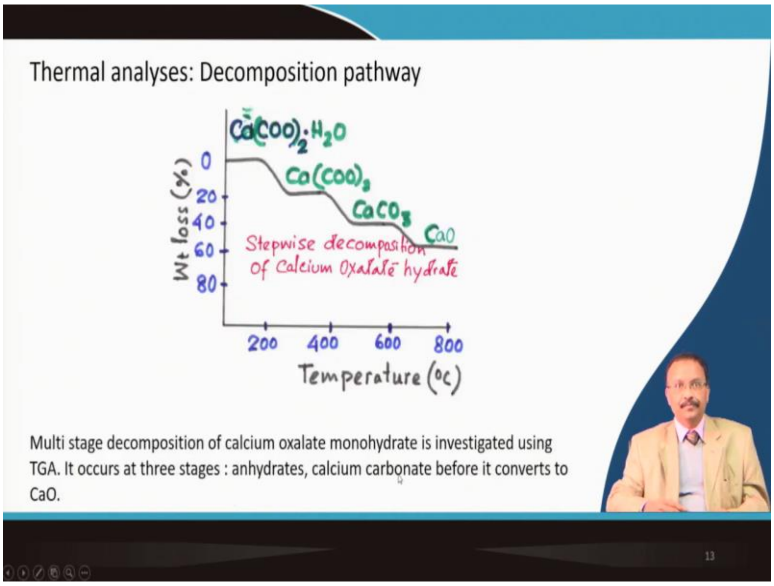

Thermal analyses: Decomposition pathway

Multi stage decomposition of calcium oxalate monohydrate is investigated using TGA. It occurs at three stages : anhydrates, calcium carbonate before it converts to CaO.

The decomposition pathway of a particular material that also can be identified for example, by a TGA analyses here you can see that, calcium oxalate hydrate if you take then it precisely they are decomposed to form three different types of material. So, it basically occurs in stages.

So, first anhydrate form forms, then it transform into a calcium carbonate before it finally, converts to calcium oxide. So, this temperature corresponds to this reactions they can be precisely identified by thermal gravimetric analyses for example.

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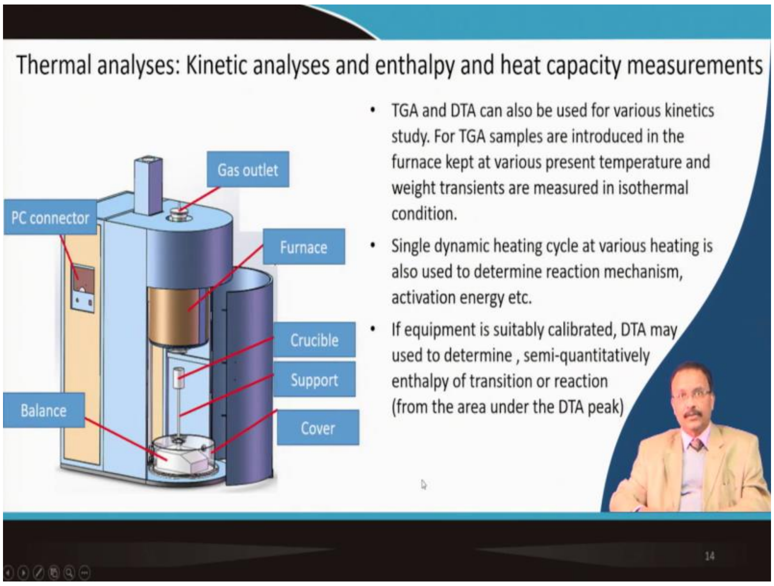

Thermal analyses: Kinetic analyses and enthalpy and heat capacity measurements

- TGA and DTA can also be used for various kinetics study. For TGA samples are introduced in the furnace kept at various present temperature and weight transients are measured in isothermal condition.
- Single dynamic heating cycle at various heating is also used to determine reaction mechanism, activation energy etc.
- If equipment is suitably calibrated, DTA may used to determine , semi-quantitatively enthalpy of transition or reaction (from the area under the DTA peak)

For certain case, a kinetic analyses also can be done in certain material. So, in this case either you can raise the temperature at that particular temperature of concern where the reaction is taking place. And, then for example, in TGA this material is directly inserted to a temperature where a decomposition reaction is taking place.

And then you can start measuring the weight as a function of time, right. So, various temperature you can select and then directly insert your sample right at that temperature and the weight transient you can measure in isothermal condition. And, this data can be used to determine various kinetic parameter which is occurring in this reaction.

Alternatively, a single dynamic heating cycle at various heating rate also one can use to determine the reaction mechanism and from this one can precisely determine the type of nucleation and growth whether it is ever any type or some other type, what is the activation energy, this can be very precisely known by this kind of kinetic analyses.

So, if the equipment is suitably calibrated DTA is also used although it is semi-quantitative way, enthalpy of transition of the reaction and usually it is found from the area under the big which is not part of this lecture. So, that also can be used to measure various other material related parameter, which is helpful to understand the reaction mechanism we are talking about.

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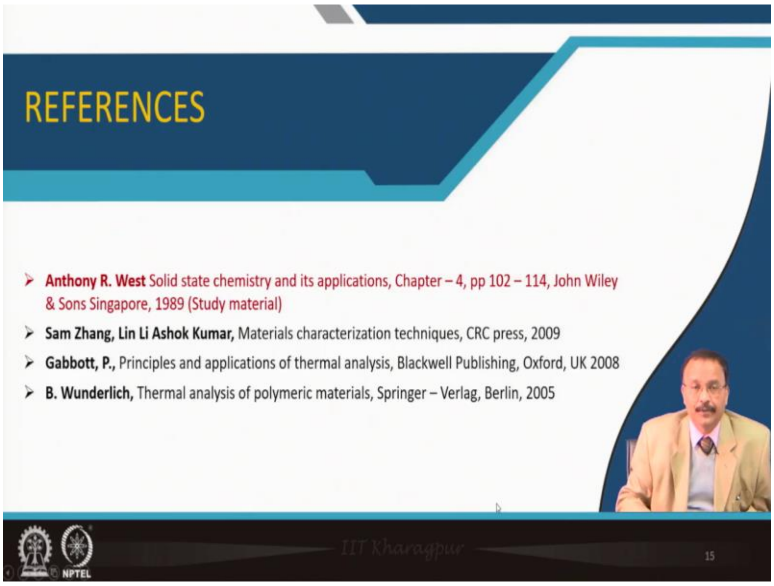

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- **Sam Zhang, Lin Li Ashok Kumar,** Materials characterization techniques, CRC press, 2009
- **Gabbott, P.,** Principles and applications of thermal analysis, Blackwell Publishing, Oxford, UK 2008
- **B. Wunderlich,** Thermal analysis of polymeric materials, Springer – Verlag, Berlin, 2005

So, the study material for this part of the lecture is the book by West – Solid state chemistry and its application, Chapter number 4 and apart from that you can consider the Material characterization technique by Zhang, Lin Li, Ashok Kumar and other references that I have cited here.

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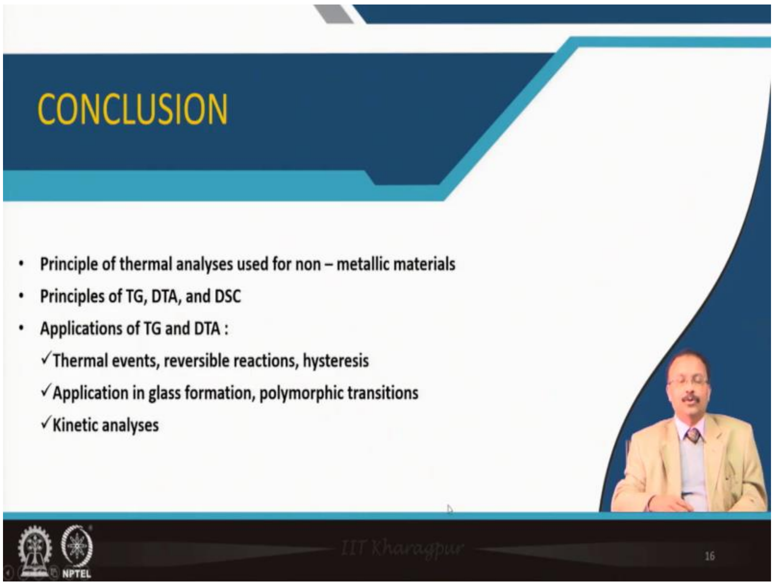

CONCLUSION

- Principle of thermal analyses used for non – metallic materials
- Principles of TG, DTA, and DSC
- Applications of TG and DTA :
  - ✓Thermal events, reversible reactions, hysteresis
  - ✓Application in glass formation, polymorphic transitions
  - ✓Kinetic analyses

So, in this particular lecture the principle of thermal analyses used for nonmetallic materials are introduced, specifically the principle of thermo gravimetric analyses DTA and DSC we have introduced and described. And, in particular the various applications of TGA and DTA we have highlighted the thermal events reversible.

Or reactions the concept of hysteresis, why it is forming, the hysteresis between the cooling and heating cycles the temperature difference, then application in glass formation, polymorphic phase transition, controlling the properties how they are used and finally, kinetic analyses that can also be done using the DTA and TGA measurement and we have talked about it.

Thank you for your attention.