Non - Metallic Materials
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Module – 03
Diffusion, phase transformation in non – metallic materials, glass and glass - ceramics
Lecture – 14
Phase transformation of non–– metallic materials

Welcome to my course Non-Metallic Materials. And today, this is part of module 3, Diffusion and phase transformation in non-metallic materials, glass and glass ceramics, which is on Phase transformation of non-metallic materials.

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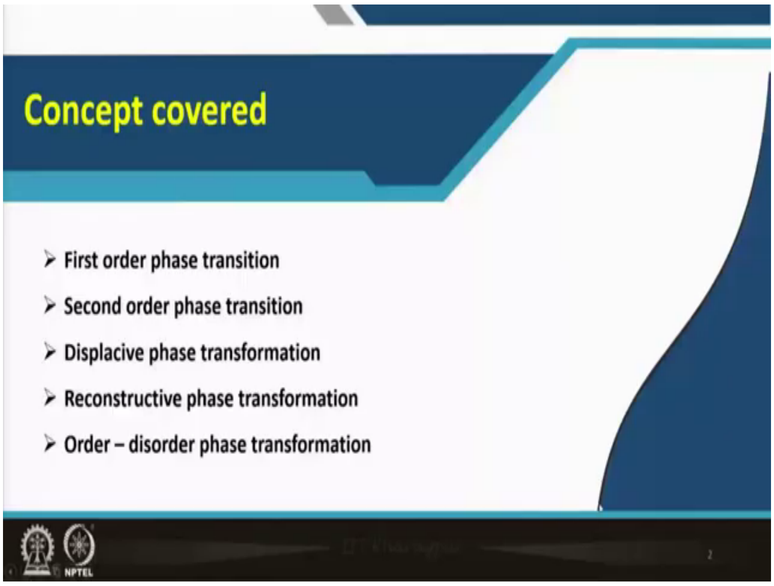

Concept covered

- First order phase transition
- Second order phase transition
- Displacive phase transformation
- Reconstructive phase transformation
- Order – disorder phase transformation

Now, we will clarify the concept of the first order phase transition as well as second order phase transition with special emphasis on oxide materials. Then we will be talking on the displacive and as well as reconstructive phase transformation, and finally, order-disorder type of phase transformation.

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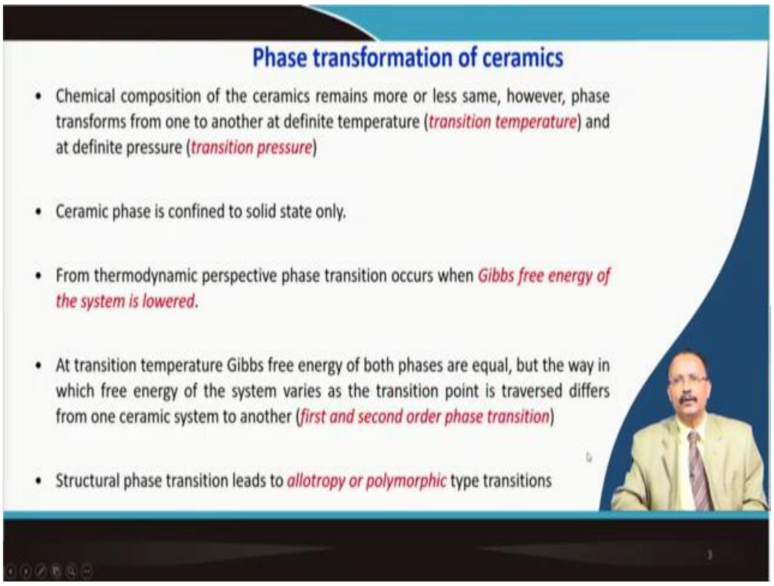

Phase transformation of ceramics

- Chemical composition of the ceramics remains more or less same, however, phase transforms from one to another at definite temperature (*transition temperature*) and at definite pressure (*transition pressure*)
- Ceramic phase is confined to solid state only.
- From thermodynamic perspective phase transition occurs when *Gibbs free energy of the system is lowered*.
- At transition temperature Gibbs free energy of both phases are equal, but the way in which free energy of the system varies as the transition point is traversed differs from one ceramic system to another (*first and second order phase transition*)
- Structural phase transition leads to *allotropy or polymorphic* type transitions

Now, this is related to the concept that I introduced while I was teaching phase diagram. We talked about single component system, and we talked about the polymorphic phase transformation as well as allotropy, we mentioned this term. So, the chemical composition of this ceramics they more or less remain same, but actually the phase transforms, so the crystal structure is different across a temperature when you cross a particular temperature.

So, at lower temperature the ceramic is having one particular phase when you cross the temperature we call it is a transition temperature, then it assumes a different phases. It also applies for pressure under low pressure, it may have one type of phase, composition does not change, but at higher pressure it assumes different types of phase different crystal structure; so, this kind of phase transformations that is known as polymorphic phase transition when the composition does not change.

In case of oxide material, we are particularly restrict ourselves to solid phase, and the thermodynamic concept, the perspective of this type of phase transition is of course, the Gibbs free energy of the system must be lowered. So, at the transition temperature then Gibbs free energy for both the phase the transformed phase or the phase which is to be transformed they are equal.

But the way they changes the traverse this temperature or pressure zone depending on that we call this is a first order or second order phase transition which will be clear in my next slide, clarified in my next slide. And the structural phase transition that basically leads to allotropy when you have say single component system or it could be polymorphic in case of a binary system for example.

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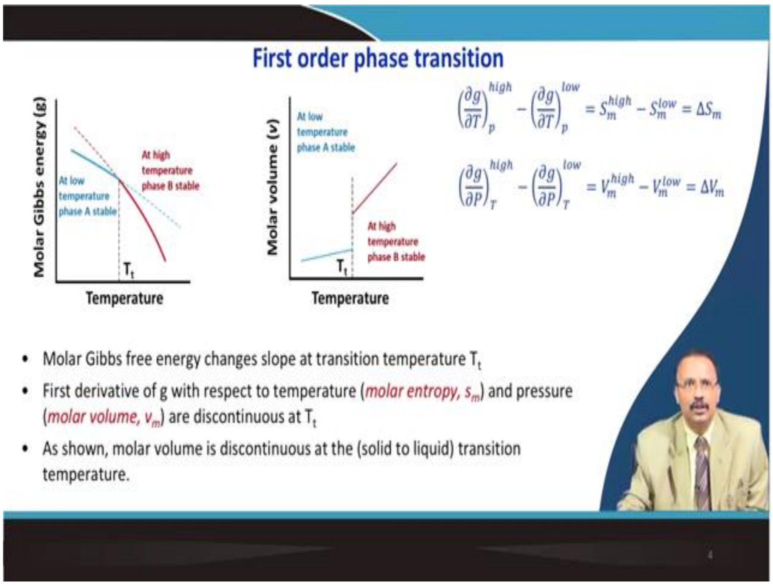

First order phase transition

$$\left(\frac{\partial g}{\partial T}\right)_p^{high} - \left(\frac{\partial g}{\partial T}\right)_p^{low} = S_m^{high} - S_m^{low} = \Delta S_m$$

$$\left(\frac{\partial g}{\partial P}\right)_T^{high} - \left(\frac{\partial g}{\partial P}\right)_T^{low} = V_m^{high} - V_m^{low} = \Delta V_m$$

- Molar Gibbs free energy changes slope at transition temperature T_t
- First derivative of g with respect to temperature (*molar entropy, s_m*) and pressure (*molar volume, v_m*) are discontinuous at T_t
- As shown, molar volume is discontinuous at the (solid to liquid) transition temperature.

Now, this view graph is shows the plot of molar Gibbs free energy as a function of temperature. So, as you can see that this molar Gibbs free energy it changes its slope at a particular temperature and this is your phase transition temperature T_t. So, it changes the phases.

So, it is basically a solid to liquid types of phase transition. So, at lower temperature the solid phase this is having a lower free energy as compared to liquid that is why it is stable. And at high temperature you see the liquid phase that is having lower free energy as compared to the solid. So, that is why liquid is stable.

Now, we will call this kind of phase transition as a first order phase transition, when the first derivative with respect to temperature that you can deduct that if you have a derivative of g as a function of temperature at constant pressure, this is nothing but molar entropy. I leave it on you, just to prove it.

And if you do the same thing with pressure then it is nothing but molar volume. So, at this transition temperature both the molar entropy and pressure that are discontinuous. So, then we call this is a first order phase transition. So, it is a typical example as you can see that I am cooling a liquid from its molten phase, so exactly at the transition temperature which is nothing but the freezing temperature here you can see.

And this is also the melting temperature. So, here suddenly the specific this molar volume that is discontinuous at the transition temperature which is in line to the way I have derived the first order phase transition. So, it is discontinuous in nature.

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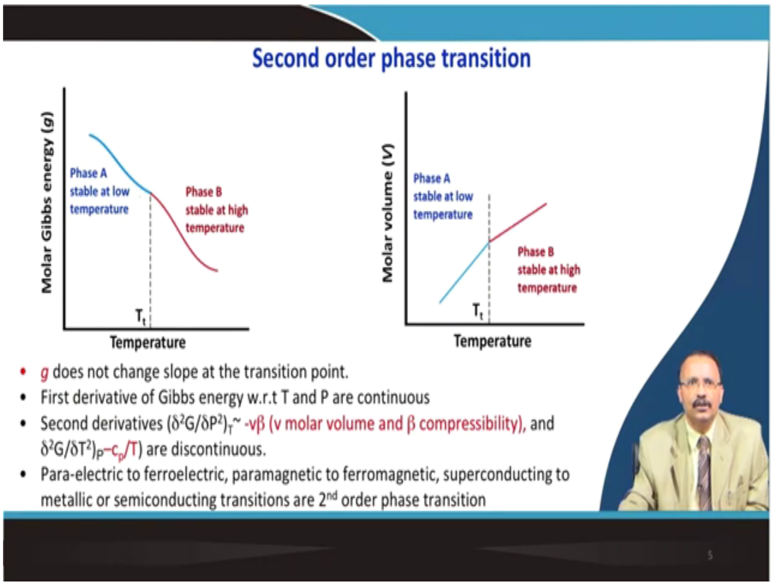

Second order phase transition

- g does not change slope at the transition point.
- First derivative of Gibbs energy w.r.t T and P are continuous
- Second derivatives $(\delta^2G/\delta P^2)_T$~ -vβ (v molar volume and β compressibility), and $\delta^2G/\delta T^2)_P$–c_p/T) are discontinuous.
- Para-electric to ferroelectric, paramagnetic to ferromagnetic, superconducting to metallic or semiconducting transitions are 2nd order phase transition

Now, you go to the second order phase transition, you can see that the g does not change slope at the transition point. So, it is not changing the slope. The first order the first derivative of the Gibbs energy with respect to both temperature and pressure they are continuous, but the second derivative.

So, you can do the second derivative del 2 G by del P square which one can show this is nothing, but molar volume and compressibility product, so v is your molar volume and beta is the compressibility. And also delta 2 G by del T square at constant P which is nothing but specific heater constant pressure divided by T both these are discontinuous. So, one example I have shown that you see the molar volume here the second derivative this is discontinuous in case of a second order phase transition.

And many many oxide system the non-metallic materials they undergo this second order phase transition. Para electric to ferroelectric phase transition we will be talking about in this course. Paramagnetic to ferromagnetic phase transition, super conducting to metallic type of phase transition or superconducting to semiconducting phase transition, these are all second order phase transition as far as the destination goes.

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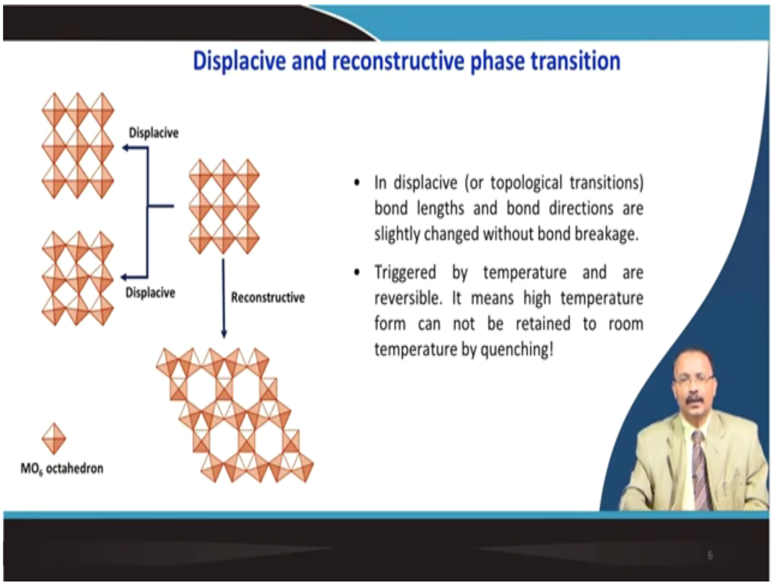

Displacive and reconstructive phase transition

- In displacive (or topological transitions) bond lengths and bond directions are slightly changed without bond breakage.
- Triggered by temperature and are reversible. It means high temperature form can not be retained to room temperature by quenching!

Now, another type of phase transition one can demark from displacive and reconstructive phase transition. Now, in case of displacive phase transition which is also termed as topological transitions; the bond length and bond angle they are slightly changed, but the bond breakage does not take place.

And this is usually triggered by temperature and they are reversible in nature. So, once is formed to the another phase, again you cool it down lower temperature the same phase you will get back. So, if you have one phase at high temperature this also means that if you quench the sample, if you just quench it, then you cannot retain that high temperature phase because immediately it will get transformed.

So, this schematic shows the way it is done. So, either as you can see this octahedral arrangement this is elongated. So, that is one type of displacive phase transition or this can be little bit twisted, so the angle is twisting. So, this is also displacive in nature.

So, if you reduce the temperature, again it will go back to its original position. But this is very much different as compared to your reconstructive phase transformation. There are lot of bond breakages taking place and once it forms it is not reversing back to its original position.

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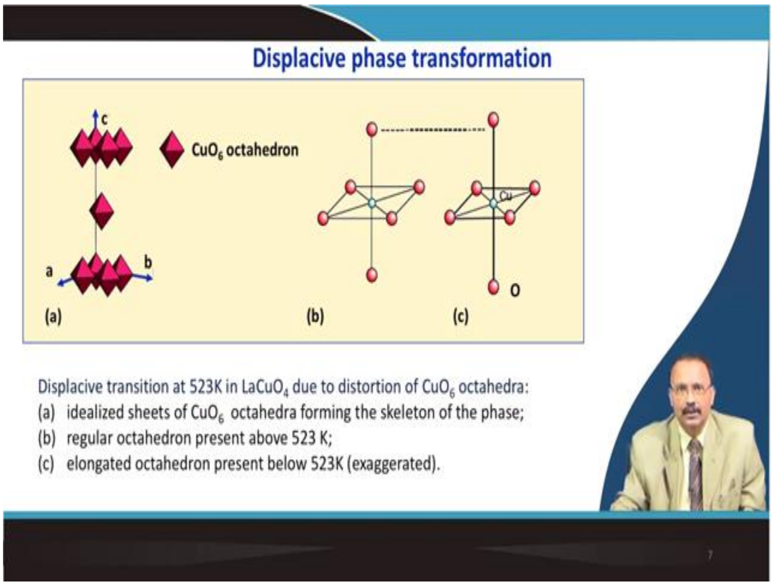

Displacive phase transformation

Displacive transition at 523K in $LaCuO_4$ due to distortion of CuO_6 octahedra:

(a) idealized sheets of CuO_6 octahedra forming the skeleton of the phase;

(b) regular octahedron present above 523 K;

(c) elongated octahedron present below 523K (exaggerated).

I will site some example I am sorry. So, some example for example, you take lanthanum copper oxide $LaCuO_4$. And this is having some kind of structure like this and the copper oxygen octahedra as you can see, the oxygen are in the corner and out of plane oxygen is there and your copper is sitting at the octahedral position. So, there is a slight change in this bond length you can see the bond length has changed. So, the idealized sheets of CuO 6 octahedra, this actually form the skeleton of the phase.

And the regular octahedron present, this present at a temperature above 523. And once you cool it down below 523 then this bond length is slightly increased. Although, it is an exaggerated scale, but still you can see the increase of the bond length no massive change in the structure is taking place.

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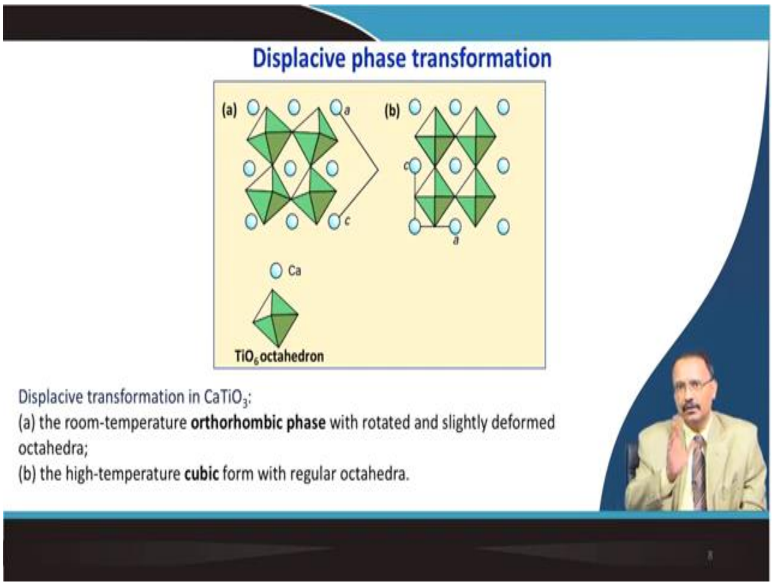

Displacive phase transformation

Displacive transformation in $CaTiO_3$:
(a) the room-temperature **orthorhombic phase** with rotated and slightly deformed octahedra;
(b) the high-temperature **cubic** form with regular octahedra.

Another example is calcium titanate which is known as perovskite. At room temperature it is having orthorhombic phase and it is slightly distorted below I mean beyond the transition temperature and it forms a high temperature cubic phase with a regular kind of octahedra. So, this is a typical example for displacive type of phase transformation.

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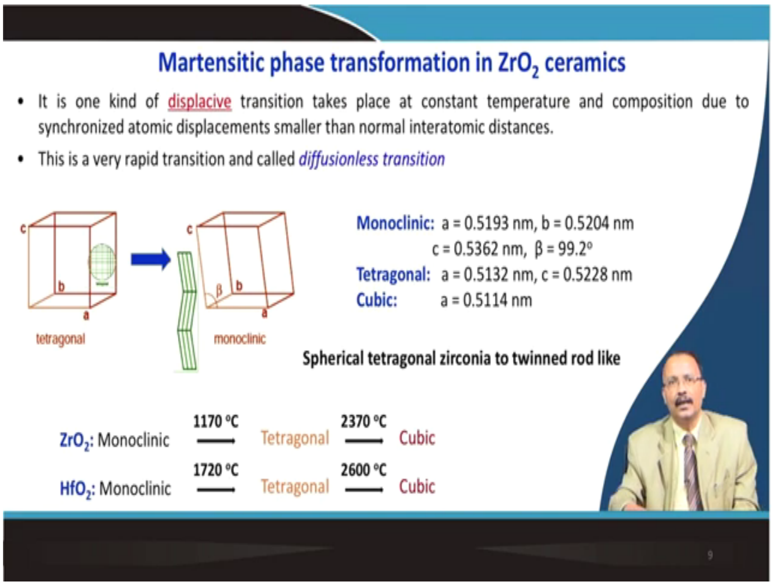

Martensitic phase transformation in ZrO_2 ceramics

- It is one kind of displacive transition takes place at constant temperature and composition due to synchronized atomic displacements smaller than normal interatomic distances.
- This is a very rapid transition and called *diffusionless transition*

Monoclinic: a = 0.5193 nm, b = 0.5204 nm, c = 0.5362 nm, $\beta = 99.2^\circ$
Tetragonal: a = 0.5132 nm, c = 0.5228 nm
Cubic: a = 0.5114 nm

Spherical tetragonal zirconia to twinned rod like

ZrO_2: Monoclinic $\xrightarrow{1170\,^\circ C}$ Tetragonal $\xrightarrow{2370\,^\circ C}$ Cubic
HfO_2: Monoclinic $\xrightarrow{1720\,^\circ C}$ Tetragonal $\xrightarrow{2600\,^\circ C}$ Cubic

So, in line to this a martensitic phase transformation can be also described which is another type of displacive phase transition, but it is something similar to the metal system. So, this actually takes place at constant temperature and composition, and this is due to synchronized movement of the atomic displacement and very small atomic distances it actually crosses during this transition. So, this is very rapid kind of transition with a small synchronized atomic movement.

So, monoclinic is a stable phase at room temperature and it changes to tetragonal phase and when you cool it down from tetragonal to monoclinic phase transition takes place. So, in monoclinic form this is having a twin rod like structure, you know what is twinning by this time I already described in one of my lectures. And your tetragonal phase is spherical it has wide implication in ceramic refractories, so that is why it is important this zirconium phase transition.

So, in monoclinic you know the crystal structure is a and c, that is not equal tetragonal a is equal to b, but not equal to c, but the angles are 90 degree and cubic all are equal. So, there is a volume strain that takes place when the transition takes place from cubic to tetragonal or sorry cubic to tetragonal to monoclinic and this kind of volume stress is detrimental for the use in refractory.

So, you must stabilize the ZrO_2 get rid of this volume strain which happens due to this kind of martensitic phase transition. Similar, example can also be cited for hafnium oxide, although the temperature range is different as you can see.

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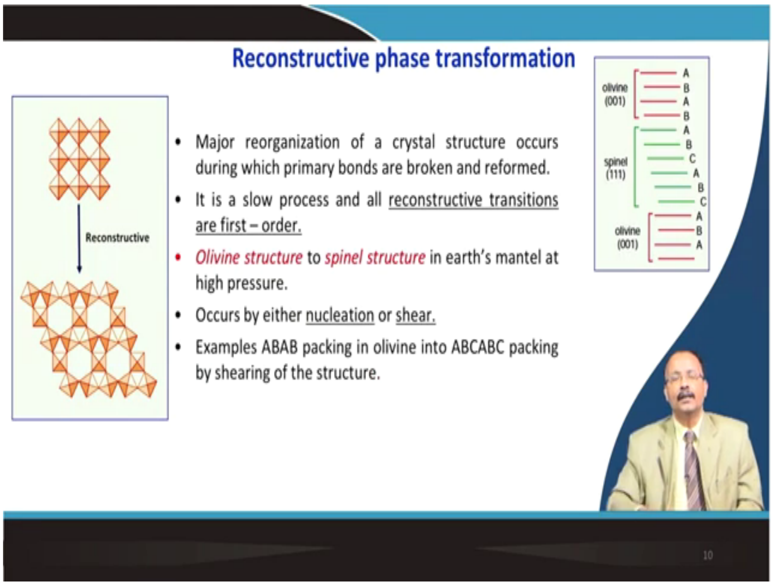

Reconstructive phase transformation

- Major reorganization of a crystal structure occurs during which primary bonds are broken and reformed.
- It is a slow process and all reconstructive transitions are first – order.
- *Olivine structure* to *spinel structure* in earth's mantel at high pressure.
- Occurs by either nucleation or shear.
- Examples ABAB packing in olivine into ABCABC packing by shearing of the structure.

In case of reconstructive phase transition, major change in the crystal structure that takes place. So, bonds are broken, they are reformed, and all these types of reconstructive phase transitions they are first order. So, define the first order in couple of slides back. So, one example is olivine structure to spinel structure that is under the earth's mantle at very high pressure it is happening it is not a function of temperature, but mostly under a pressure.

And a nucleation and or shear this is the either I mean this kind of phase transition is related to either nucleation or shear. So, one example as you can see that in olivine they are hexagonal kind of packing ABAB kind of packing, and then it transform to spinel type of packing which is cubic ABCABC type of packing. And the shearing of the structure that is also taking place that is apparent from this. So, this is a typical extra example of reconstructive phase transition.

Similar thing also happens in silica system both reconstructive and displacive phase transition is a classic example. So, as a part of the reconstructive phase transition it transformed to cristobalite and tridymite phase, and there are several displacive phase transition for silica.

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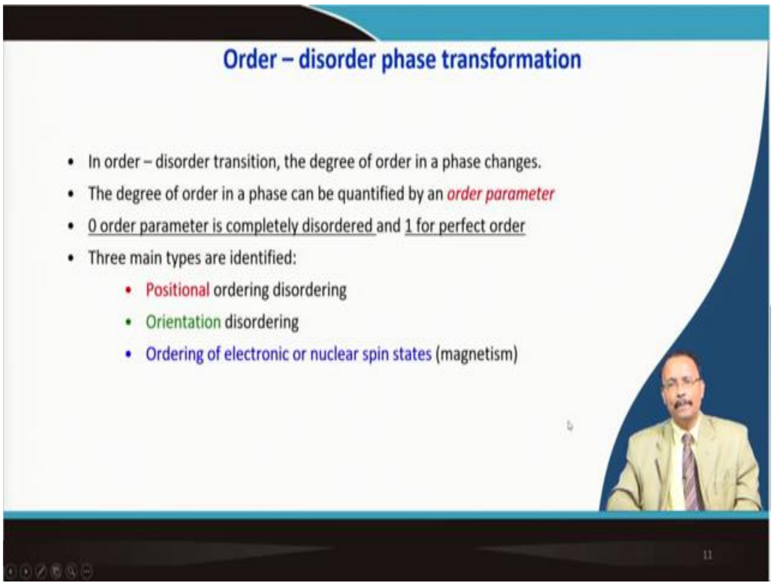

Order – disorder phase transformation

- In order – disorder transition, the degree of order in a phase changes.
- The degree of order in a phase can be quantified by an *order parameter*
- 0 order parameter is completely disordered and 1 for perfect order
- Three main types are identified:
  - Positional ordering disordering
  - Orientation disordering
  - Ordering of electronic or nuclear spin states (magnetism)

The third and important transition which is known as order-disorder kind of phase transition; so, in order-disorder kind of phase transition the degree of ordering of a phase that is changed and I will just explain in a moment that what exactly is this kind of degree of ordering. And of course, the degree of ordering that is you can define as with the order parameter. So, usually 0 is completely disorder system and when the order is 1 then we consider it is a perfect ordering system.

So, there are many types of varieties of order-disorder phase transition. The first one that I will be explaining that is a positional ordering or disordering. Apart from that we have orientational order-disorder transformation and also order-disorder transformation which is related to electronic or nuclear spin state that also is important for non-metallic system.

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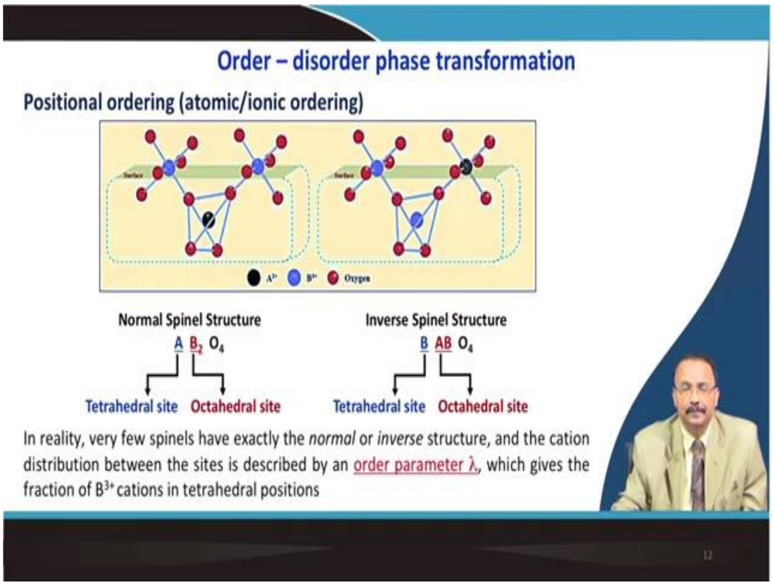

Order – disorder phase transformation

Positional ordering (atomic/ionic ordering)

Normal Spinel Structure

$A\ B_2\ O_4$

Tetrahedral site Octahedral site

Inverse Spinel Structure

$B\ AB\ O_4$

Tetrahedral site Octahedral site

In reality, very few spinels have exactly the *normal* or *inverse* structure, and the cation distribution between the sites is described by an order parameter λ, which gives the fraction of B^{3+} cations in tetrahedral positions

So, we will start with the simple structure of a normal spinel and an inverse spinel structure. So, in normal spinel it is AB_2O_4 structure, where A is a divalent cation which is at its tetrahedral void space of the cubic closed plaque lattice, and B is a octahedral cation which is at its usually it is trivalent cation and you can have a transition or inverse spinel where half of this B cation goes to the A cation site and all A cation goes to this site.

So, the formula changes to $BABO_4$, and we call this is a inverse type of spinel structure. So, the important thing is and this is the example that how it will look like. So, as you can see the tetrahedral void a divalent cation is there the black colored one and this octahedral void a blue color tetravalent cation is there. And in case of inverse spinel this half of B is coming to the tetrahedral site and whole cation in the tetrahedral site goes to the octahedral site.

So, the order parameter lambda is defined in case of mixed spinel structure. So, it is not completely inverse spinel, but part of it is inverse spinel. So, it determines that fraction of this B cation in the tetrahedral position, how much it has come. So, maximum 50 percent it should come, but it is not exactly 15 percent what is the fraction it has come that decides the order parameter which is defined by lambda. So, this is one classic example.

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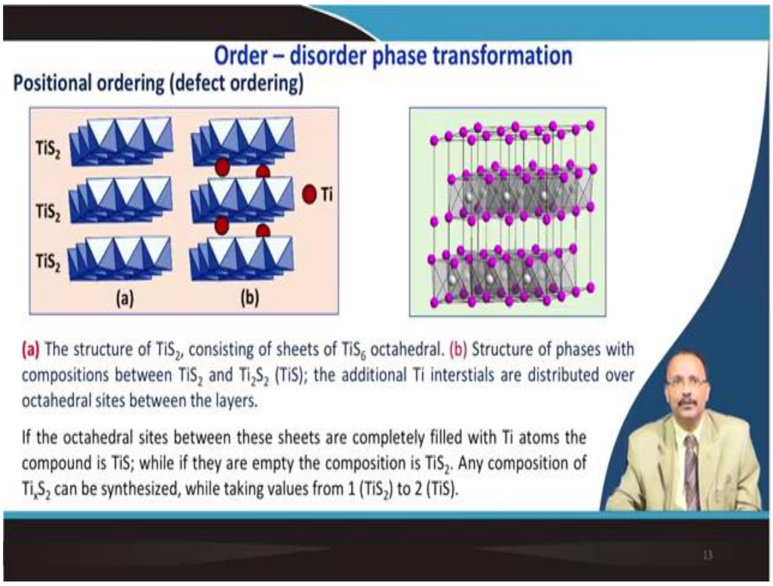

Order – disorder phase transformation

Positional ordering (defect ordering)

(a) The structure of TiS_2, consisting of sheets of TiS_6 octahedral. (b) Structure of phases with compositions between TiS_2 and Ti_2S_2 (TiS); the additional Ti interstials are distributed over octahedral sites between the layers.

If the octahedral sites between these sheets are completely filled with Ti atoms the compound is TiS; while if they are empty the composition is TiS_2. Any composition of Ti_xS_2 can be synthesized, while taking values from 1 (TiS_2) to 2 (TiS).

Another one is related to titanium disulphide and here you can see that this void space they are vacant for TiS_2, and then if it is completely filled by titanium then the formula changes to Ti_2S_2 that is nothing but TiS. So, again the order parameter is defined that how much titania has gone to this octahedral position.

So, if it is completely vacant then you get titanium disulphide. If it is completely filled then you get TiS and the order parameter is in between these two. And this is also initially it was very important material for lithium ion battery, but nowadays some other exotic material has taken its place.

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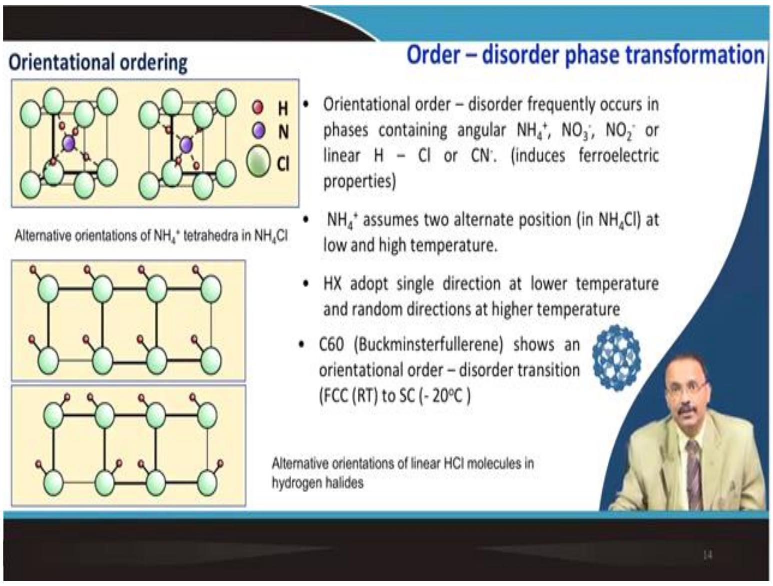

Orientational ordering

Order – disorder phase transformation

- Orientational order – disorder frequently occurs in phases containing angular NH_4^+, NO_3^-, NO_2^- or linear H – Cl or CN^-. (induces ferroelectric properties)
- NH_4^+ assumes two alternate position (in NH_4Cl) at low and high temperature.
- HX adopt single direction at lower temperature and random directions at higher temperature
- C60 (Buckminsterfullerene) shows an orientational order – disorder transition (FCC (RT) to SC (- 20°C)

Alternative orientations of NH_4^+ tetrahedra in NH_4Cl

Alternative orientations of linear HCl molecules in hydrogen halides

Order-disorder type of phase transition can also be orientation type of ordering and particularly if these cations are present like ammonium, then nitrate nitrite, or hydrogen, chloride or cyanide they exhibit this kind of thing. So, for example, here in this case this lattice of ammonium chloride it is assumed by 2 position ammonium chloride NH_4Cl, one is at low and another one is at high temperature. You see that the orientational ordering is completely changed.

And something similar also happens for halide crystal HX, and this is a single direction as you can see this H and Cl, they are alternative molecules HCl molecules they are oriented like this. And then finally, you see that there is a transition where it is relatively disorder, it is random at the higher temperature. So, this is another example.

Another prominent example is the fullerene structure which already I have described in one of my lectures. So, it also exhibits this orientational order-disorder transition at room temperature it is FCC and it transformed to cubic when you cool it down at 20 degree Celsius minus. So, this is another example.

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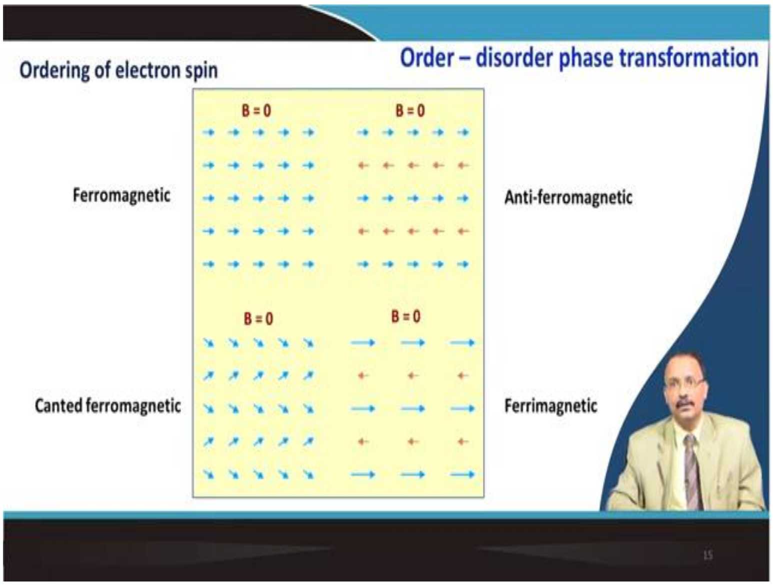

Order – disorder phase transformation

Ordering of electron spin

Order-disorder phase transition is also related to the ordering of electron spin, and in when I will talk about the magnetic materials then you will be seeing that in ferromagnetic material the spin is perfectly aligned when there is no magnetic field involved or when there is no magnetic field then there are alternate direction of the spin. So, the total spin moment is 0.

You can have a canted ferromagnetic structure also where the spin is slightly angled, so that you are getting its cross component in calculating the magnetic moment or it could be ferry magnetic in nature. So, they are all the example of ordering and once you cross the transition temperature then they are in their paramagnetic state, so all this ordering is lost. So, this 0 and 1, this order parameter and disorder parameter this is also relevant for this type of magnetic non-metallic materials.

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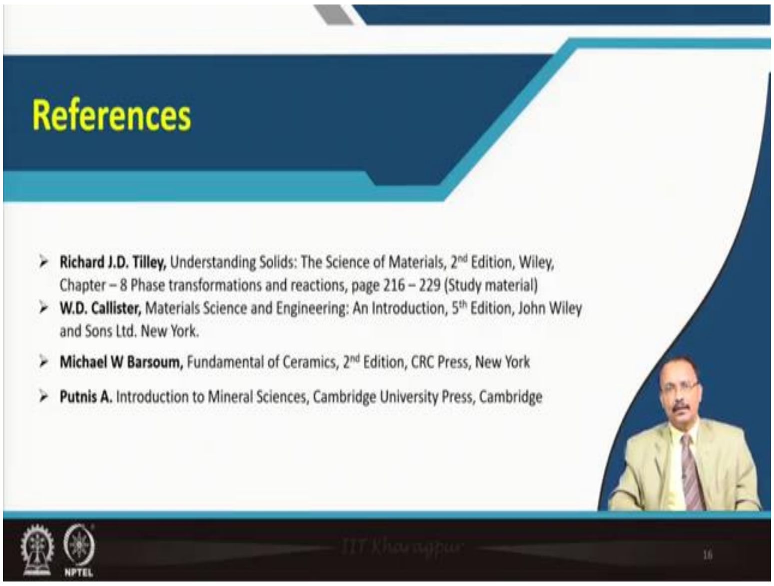

References

- **Richard J.D. Tilley,** Understanding Solids: The Science of Materials, 2nd Edition, Wiley, Chapter – 8 Phase transformations and reactions, page 216 – 229 (Study material)
- **W.D. Callister,** Materials Science and Engineering: An Introduction, 5th Edition, John Wiley and Sons Ltd. New York.
- **Michael W Barsoum,** Fundamental of Ceramics, 2nd Edition, CRC Press, New York
- **Putnis A.** Introduction to Mineral Sciences, Cambridge University Press, Cambridge

So, the topic that is actually covered in this course it is taken from a book by Richard J D Tilley, Understanding of the Solid. And you need to read chapter 8, which the chapter name is Phase transformation and reaction. So, many things are described, but the thing that we have covered you can get a decent description.

Callister book is another one that gives you a very vivid idea for magnetic property or the electric ordering. Michael Barsoum book is also relevant. And this is excellent source Introduction of Mineral Science, Putnis this also gives a decent description of this kind of phase transition which is important for non-metallic materials.

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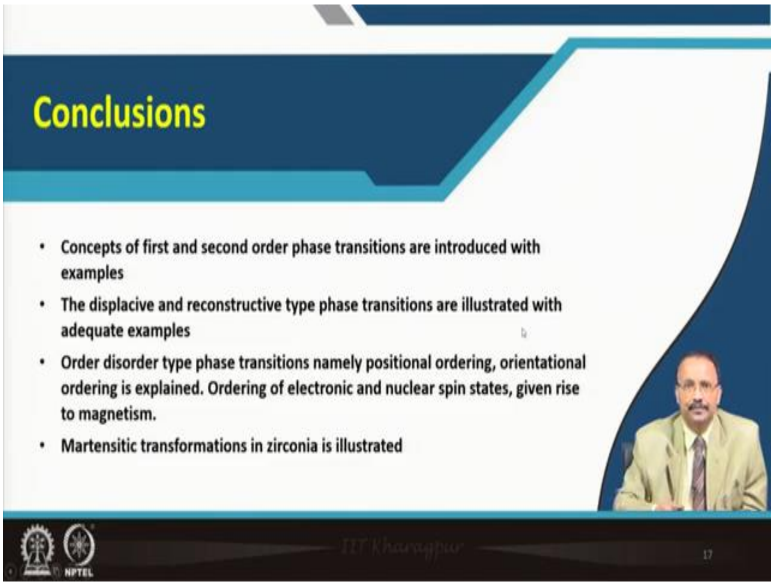

Conclusions

- **Concepts of first and second order phase transitions are introduced with examples**
- **The displacive and reconstructive type phase transitions are illustrated with adequate examples**
- **Order disorder type phase transitions namely positional ordering, orientational ordering is explained. Ordering of electronic and nuclear spin states, given rise to magnetism.**
- **Martensitic transformations in zirconia is illustrated**

So, in this particular lecture, we first introduce concepts of the first and second order phase transitions that is introduced. Then, progressively we talked about displacive and reconstructive type of phase transition. In displacive phase transition there is a slight misalignment of the bond, slight angle change of the bond or the length change of the bond takes place, but in case of a reconstructive phase transition there is severe bond breakage takes place and it is non-reversible.

Then finally, order-disorder phase transition we talked about, particularly positional ordering, orientational ordering is explained, and ordering of the electronic spin defining the magnetic property of the non-metallic materials that has been described. And also part of a displacive phase transition the diffusion less phase transition, diffusion by the way I will be taking in my next class.

And this is diffusion less phase transition only a slight alignment of the slight displacement of the atoms that is taking place in case of zirconia. And this implication in making zirconium refractories that is also explained in this particular lecture.

Thank you so much for your attention.