Nanotechnology Science and Applications
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Lecture - 08
Zirconia (ZrO_2)

Hello in this class, we are going to look at the material Zirconia. We are looking at this material in the context of nanomaterials in general and in particular in the context of Thermodynamic aspects associated with nanomaterials. This is just an example of a material where you can see these effects, presumably you can look at other materials and see somewhat similar effects in certain cases, and this is just to show you what is possible and what can happen when you go to the nanoscale. So, it is in that context that we look at it.

So, interestingly zirconia is a material that we do not talk about much at home. So, when you are discussing something with your friends, you are discussing things with your maybe family members about any substance at home or materials at home and so on; you do not tend to talk about the materials zirconia. Interestingly though, you will find through the examples that I am going to show you, that it is a material that is very commonly being used by us. It is being used in various applications that we are familiar with; it is just that we are not aware that zirconia is sitting there.

And we talk of coal, we talk of carbon, we talk of a hydrogen economy, we talk of semiconductors, we talk of silicon; so many other materials we tend to talk about which are even somewhat technical kind of materials as opposed to commonplace materials like wood and maybe construction materials like concrete. But this is a material which is there, very much present in many of the activities that we involve ourselves in, but we do not hear about it much, we are not aware of it much.

So, in fact, through these examples, I believe you are going to be quite surprised at where all we run into zirconia.

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Diamond

Cubic Zirconia
“American Diamond”

First of all, I am pretty sure we have all heard of diamond and how interesting it is and how expensive it is and so on. There is another version of gemstone so to speak, which is nothing, but Cubic Zirconia. So, if you actually in Indian context certainly, I mean people refer to it as the American diamond. I am not really sure what the origin of this phrase is, but in India, if you go to many of these stores where they make this kind of jewellery, where they make say a necklace which is filled with these kinds of artificial diamonds as they called, they tend to call them as American diamonds.

If you actually go to some of the Foreign countries you will find it being referred to as the American, I mean sorry the as cubic zirconia only they do not really refer to it as the American diamond, but this is something that is used in a gemstone.

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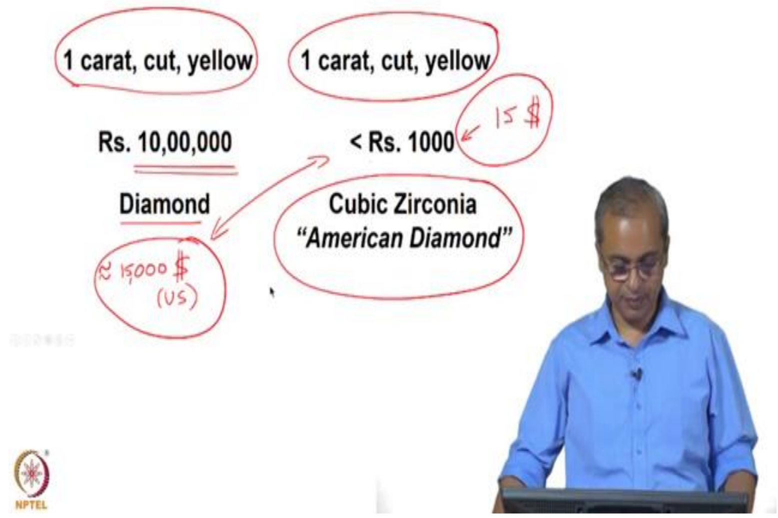

1 carat, cut, yellow

Rs. 10,00,000

Diamond

≈ 15000 $ (US)

1 carat, cut, yellow

< Rs. 1000

15 $

Cubic Zirconia
“American Diamond”

And interestingly, just to give you some idea of what we are dealing with here. If you took the pure diamond, the real diamond and you actually we do not get this kind of a specification of that diamond. Then apparently as per current market rate, so we are looking at about a million rupees about 1 million rupees. So, about so, that is if you divide that by about 70 which is what the US dollar rate is.

So, you are looking at say 100,000 by 7; so, it is about 15000 dollars, so roughly approximately 15000 dollars, 15000 US dollars. And, if you look at the cubic zirconia which is also called the American diamond as I said, then you are looking at a price which is 3 orders of magnitude less in cost. So, it is only about for a similar specification, it is cost is only about 1000 rupees and so, that is actually is just about 15 dollars.

So, you can see the difference, I mean one is 15000 dollars, the other is just 15 dollars. And in fact, for a common person such as myself, I would not know the difference. If in fact, if anything that few times that I have been shown materials, I mean gemstones made of cubic zirconia versus the real diamond; I always thought that the cubic zirconia sample looked better, it looked much more glittery to mean to view.

And, but that apparently is not the market value for it and the market value is based on some other arbitrary aspects such as availability and so on. So, incidentally, I mean many of these things are interestingly priced because I think if the availability is rare, people assume that it has value and that is a very strange way of associating a value with it. So, for example, like if you are aware of it, I am not sure if you are aware of it, but in at one point in time historically in Europe; it turned out that when they have just about sort of discovered aluminium; and it was very difficult to make aluminium at that point in time.

So, it used to be that royalty would eat with aluminium plates and then the less important guests at an official dinner would eat with the silver plates or gold plates and so on. Then of course, how things have completely changed today; aluminium is like one of the cheapest materials that is out there. And you are extremely unlikely to see anybody who remotely considers them themselves to be royal, to actually be using aluminium utensils.

So, that is the way things have changed, but that is just an aside; it is interesting to see how a value is ascribed to different things and that is the kind of price differences we are talking about. So, is it suddenly possible that the value of diamonds could fall; well if you look at science fiction, you will see that the there is a belief that it is the right kind of conditions to form diamond exists. at the center of a gas gaseous planet such as Saturn or Jupiter where there is very high-pressure high temperature and a significant amount of carbon.

So, science fiction stories have been written, I think there is one by Arthur C Clarke where they suggest that there is a huge diamond sitting in the middle of one of those planets and as a result the price of diamond fall. So, that is just an aside, but that tells you how things are valued. So, in our case, our interest is in the fact that zirconia is used as a gemstone and presently that is the kind of value it has.

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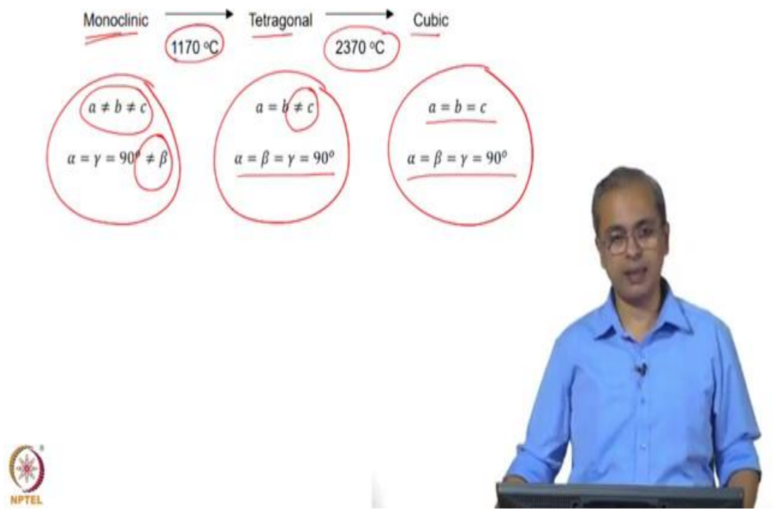

Monoclinic → Tetragonal → Cubic

1170 °C

2370 °C

$a \neq b \neq c$

$\alpha = \gamma = 90^{\circ} \neq \beta$

$a = b \neq c$

$\alpha = \beta = \gamma = 90^{\circ}$

$a = b = c$

$\alpha = \beta = \gamma = 90^{\circ}$

If you take zirconia, it can actually exist in different crystal structures, it can be monoclinic, it can be tetragonal and it can be cubic. So, these are different phases of zirconia. And you can see the transformation temperatures at 1170°C, the monoclinic phase goes to become the tetragonal phase, and then above 2370°C, you get the cubic phase. So, these are the three phases that we tend to see of monoclinic, tetragonal, cubic zirconia; and you can also have amorphous versions of zirconia.

And as always you can always find ways to make one phase stable at different conditions and so on. And, but in general, if you take zirconia and you look at it at room temperature, you will find the monoclinic phase. So, this is what you will see and these are some of the symmetry aspects associated with these three phases that you see here. Of course, the cubic phase means the 3 lattice parameters, lattice constants are the same and the three angles are all equal to 90°s. So, that is the cubic phase.

The tetragonal phase has a little less symmetry than the cubic phase. So, one of the lattice parameters is not equal to the other 2 lattice constants and, but the angles are all 90°s. And then when you come to the monoclinic phase, you have this variation. So, the 3 lattice constants are not equal to each other $a \neq b \neq c$ plus you also have one angle which is not equal to 90°. So, you can see a steady drop in symmetry from as you come from cubic to tetragonal to monoclinic.

So, that is just to give you some idea of the system that we are dealing with and what we see is that at room temperature the monoclinic phase is stable. The idea that we are going to actually discuss through this class is the fact that as you go to the nanomaterial regime, a nanoscale regime of this exact same material. And then you look at the different phases that are stable, you will find that there is an interesting change in terms of which phase is stable at the room temperature.

So, and that change in stability of the phases has been directly affected by the fact that it is now at the nanoscale, and that is the impact of nanoscale activity with respect to the thermodynamic stability of phases that are present.

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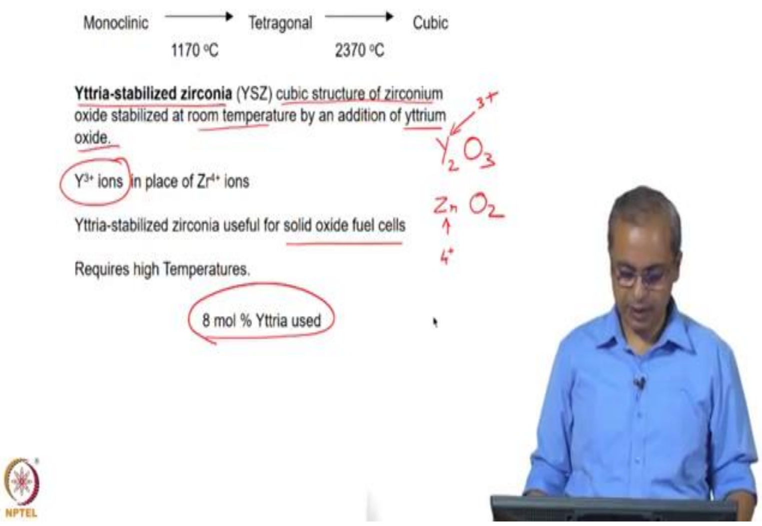

$$\text{Monoclinic} \xrightarrow[1170\,^{\circ}\mathrm{C}]{} \text{Tetragonal} \xrightarrow[2370\,^{\circ}\mathrm{C}]{} \text{Cubic}$$

Yttria-stabilized zirconia (YSZ) cubic structure of zirconium oxide stabilized at room temperature by an addition of yttrium oxide.

Y^{3+} ions in place of Zr^{4+} ions

Yttria-stabilized zirconia useful for solid oxide fuel cells

Requires high Temperatures.

8 mol % Yttria used

So, you can actually get something called yttria-stabilized zirconia, which is a cubic structure of zirconium oxide stabilized at room temperature and that is done by adding yttrium oxide. So, yttrium oxide is Y_2O_3 and you can see here that the yttrium is a trivalent ion in this case. So, you have 3+ ions as opposed to ZrO_2, where zirconium is 4+.

So, this is 4+ oxidation state here Y is 3+. So, it turns out that to some° you can put these 3+ ions into the 4+ ion site and which means that there have to be some vacancies on the oxygen sites to ensure that; there is charge balance, you cannot have charge neutrality, there is it has to be a charge-neutral material, the nature will try to get it to be charge neutral and it ends up that you have oxygen ion vacancies.

And because of these vacancies you actually have better oxygen transport in some of this yttria-stabilized zirconia. So, it is actually used for solid oxide fuel cells and for that particular reason. And usually, it will be something that is stabilized using 8mol% yttria. So, this is the way in which it is done, 8mol% yttria is used and that keeps it stable.

And it still has this situation where you have to actually operate it at high temperature and only at that high temperature the oxygen ion conductivity is sufficient that you can use this material for the purposes that this intended. It is used in multiple places; this is just an example and I will touch upon it again as we go through the discussion.

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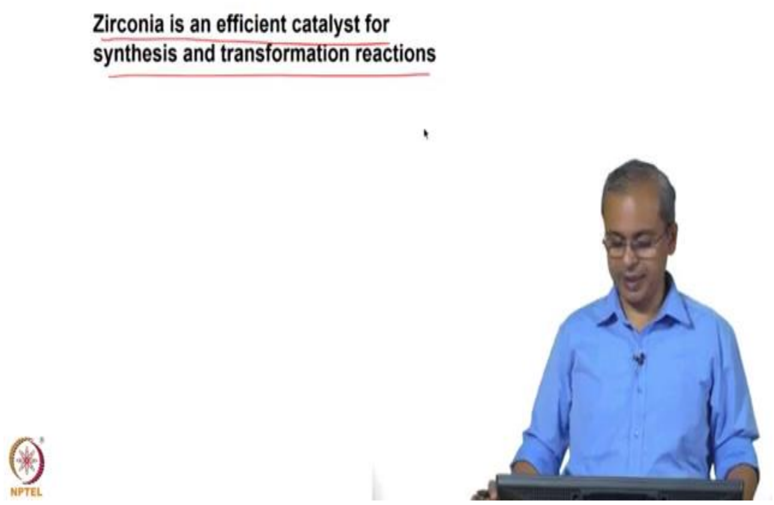

Zirconia is an efficient catalyst for synthesis and transformation reactions

It is also an efficient catalyst. So, it is quite stable and it is able to catalyze a number of organic reactions. So, under those conditions, it is quite stable and at you know, if fine enough particle size, it has enough surface energy that it is able to catalyze a number of organic synthesis reactions. So, zirconia is used as a catalyst in a number of applications.

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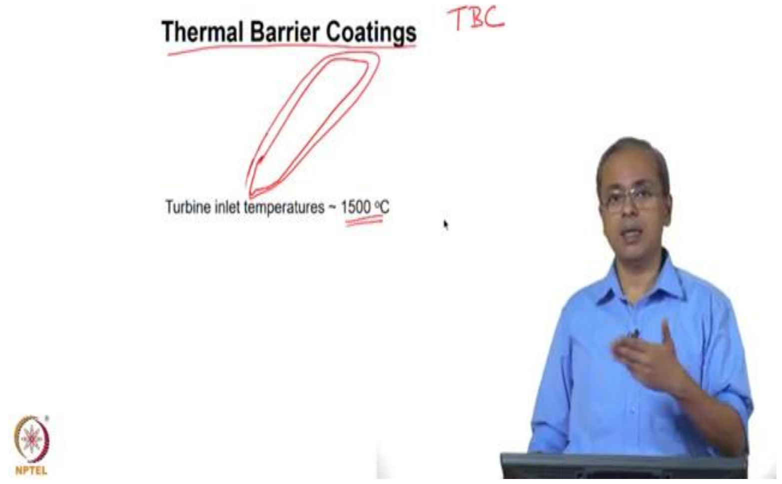

Thermal Barrier Coatings TBC

Turbine inlet temperatures ~ 1500 ºC

Because it is a sort of ceramic material and it is also quite it is capable of handling temperature differences to a fairº; it is used in something called a thermal barrier coating. An often, in fact, abbreviated as TBC. So, there is a lot of people who work on these coatings. So, this is used on turbine blades. So, you have a blade-like that, some kind of a blade.

So, turbine blade and so, it is used as a coating on top of this blade; on the side that is going to face the incoming gases. The incoming gases are typically very hot. So, you can see temperatures of the order of 1500º C. And so, even though you have materials that can actually handle high temperatures, they deteriorate fast under those high-temperature conditions.

So, thermal barrier coatings are one additional layer of coating that is put on top of this turbine blade; which ensures that it takes the brunt of the high temperature. So, the maximum high temperature is handled by it; and then a distinctly lower temperature reaches the is what is experienced by the main structure of the blade and in this process, it helps protect the blades. So, a lot of electricity that we get which uses turbines often has this coating of zirconia being put on this turbine blade.

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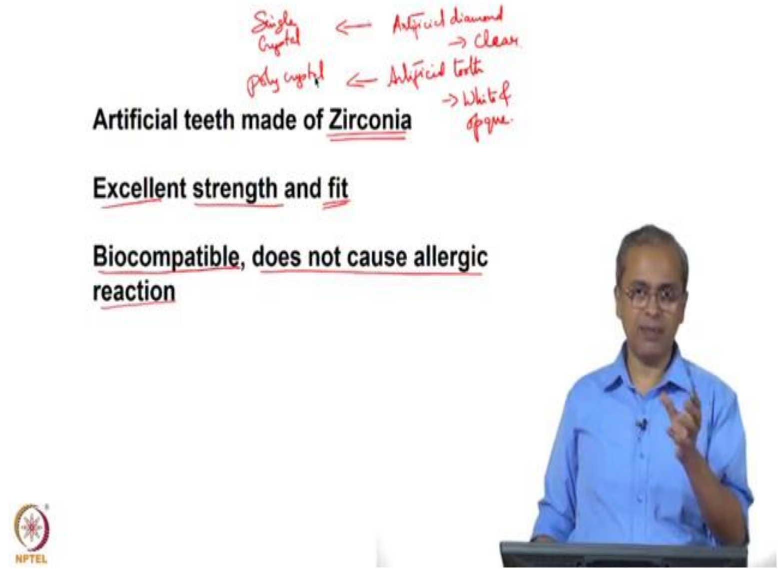

Single Crystal ← Artificial diamond
→ Clear

poly crystal ← Artificial tooth
→ White & opaque

Artificial teeth made of Zirconia

Excellent strength and fit

Biocompatible, does not cause allergic reaction

Artificial teeth, again a product that you may have seen it at your home, I mean maybe at depending on the dental situation amongst various people at home; maybe you may have older people or even middle-aged people who require some artificial tooth to be put into their system. And, it turns out that artificial teeth are made of zirconia; the interesting thing is the zirconia here has exactly the same kind of texture and look and color as our teeth. So, if you actually see somebody with an artificial tooth made of zirconia you would not know the difference, it is very difficult for you to know the difference.

It has got excellent strength. And so, when you, chew on food and you bite onto various food it is able to handle things very well, just the way your normal tooth would do and it fits very well to our mouth. Particularly, because it is going to be in your mouth, it is going to be in contact with your gums and the food that you eat is going to go is going to be chewed by it; it is very important that this material be biocompatible and in it turns out that zirconia is biocompatible. It is also important, that it does not cause allergic reactions, and this is also true with zirconia it does not cause allergic reactions.

Now, again it is very interesting to see, that we saw an example a short while ago in this class; where we were saying that zirconia is used as a gemstone. So, now, if you look at say a diamond even if you are not even examined it closely, you do I mean have the sense that it is some kind of a crystal-clear material which has a lot of internal reflections and so on. And then it glitters as you I mean it gives off a lot of reflections when you show it in light. But in principle, it is something that has a tendency to look transparent at some level and at some inherent level you are seeing some level of transparency with different reflections coming off of it. So, when the zirconia is used as a gemstone, it is actually being used in a manner where it mimics the diamonds look. And so, therefore, it also shows some level of transparency and so on.

But when you use it as a tooth, you are actually using it as an opaque material which is white in color. So, as artificial diamond it is clear; artificial tooth it is white and opaque. So, it is white and opaque when it is used it is as artificial. So, how does that happen, it happens for multiple reasons; the primary reason it will happen is based on whether it is a single crystal or a polycrystal. So, typically the gemstone would be a single crystal, where it is being used as a gemstone it would be a single crystal. And so, it would have perfect crystalline order from one end to the other; and being a ceramic since it has a very large bandgap, it does not absorb the incident radiation, it does not absorb visible light.

So, visible light goes right through it and therefore, you see it has a transparent material. It still has, when it is used as a tooth, as an artificial tooth it is still the same material, it still has the same bandgap which is the large bandgap. So, technically even as artificial tooth it should actually not absorb any light you should actually see a transparent artificial tooth. You do not see that, you actually see a white tooth and the reason that is the case is because it is polycrystalline; in this case, it is single crystal, this case it is polycrystalline, polycrystal.

And because it is a polycrystal with a fine crystallite size, the light that enters this system undergoes a lot of different reflections due to all those discontinuities that are there that the boundaries between the different small crystals; as a result, you end up seeing a lot of light being reflected right back. And so, even though inherently it is a transparent material you end up seeing it as an opaque material. So, that is how it is and it is no different than really if you take powdered glass it suddenly looks opaque it whereas, if you take a single sheet of glass it looks transparent.

So, that is sort of the idea here and that is what it is. So, it is used for artificial teeth for all these reasons that it is biocompatible and does not cause allergic reactions, it fits very well, looks exactly like your tooth.

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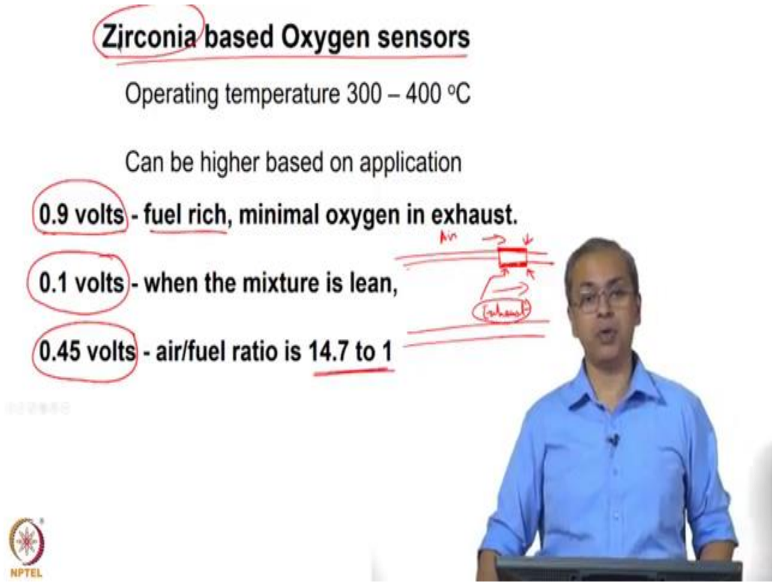

Zirconia based Oxygen sensors

Operating temperature 300 – 400 °C

Can be higher based on application

0.9 volts - fuel rich, minimal oxygen in exhaust.

0.1 volts - when the mixture is lean,

0.45 volts - air/fuel ratio is 14.7 to 1

Zirconia is also used for oxygen sensors. So, again a product that we use quite extensively, we do not realize that we use it. So, most modern automobiles have an oxygen sensor. So, if you have, commuted in any form from your home to your college or place of work you have used either a bike or a car or some four-wheeler or a bus or some such form of transport; in any modern construction of those vehicles in the exhaust line, there is an oxygen sensor.

And typically, that oxygen sensor is made out of zirconia. The purpose of the oxygen sensor is that in olden days when they first came up with the automobiles they would simply put in a certain amount of fuel and a certain amount of oxygen, and that would burn it to generate energy and then you would have your vehicle running.

Now, with increasing conscious feeling that we have to be environmentally friendly when we operate our vehicles; we would like to operate our vehicle with as minimum amount of fuel as possible. So, to do this we want to ensure that the fuel that enters the engine is completely burnt, you do not want unburnt fuel coming off the exhaust of the vehicle; because if it is unburnt you are inefficiently using your fuel. So, that is the thing you wanted completely burnt.

It is also true that as your vehicle is moving, we are often applying a brake, we are accelerating, we are decelerating, etcetera. So, the amount of fuel that goes into the engine increases decreases comes to halt a lot of different things are happening in the engine continuously. It is not that the engine is operating at a single fixed operating point that is not the way it works.

Continuously the operating point of the engine is changing, in the typical driving cycle that most of us experience. So, it is very important that for you to run the engine efficiently, the amount of fuel that goes in should be matched with the amount of oxygen that goes in or air that goes in and this match should be at some appropriate value. So, the fuel is completely burnt.

So, we can actually look at three different scenarios; one is called burning rich which means you are actually having a lot of fuel relatively less amount of air and therefore, you will have some wasted fuel in your exhaust. You could also be burning it the other end of the spectrum which is burning lean, which means you send in a lot of air, you burn the fuel completely and then you get a fair amount of air in the exhaust, and then there is an in-between position.

Now if you want to burn, if you want the engine to if the purpose of this exercise is to make the engine run as efficiently as possible, you want to run it closer to the lean side. So, you are completely burning the fuel. On the other hand, maybe, if you are converting your car for race applications, you may choose a different operating point where the engine should run.

So, that is the kind of fine-tuning that people do when they convert a vehicle from a say, typical consumer vehicle to something that they want to put it for a race. So, they will try and see that you know, they would change the fuel-air ratio. So, that if they are doing it scientifically that is what they would do; that is one of the things that they would do they would adjust the fuel-air ratio. So, they are getting maximum power for example. So, something like that they would have to do.

So, now how does the oxygen sensor work, you basically have a pipe in which the I will remove this, this is a pipe, through which the exhaust is going. In this you will have a sensor and that sensor is attached here and you have a small electrode here and you will also have a small electrode here and then it continues. So, the inner side of this sensor sees the exhaust stream that is it sees this exhaust, the inner side of this sensor. So, it is seeing the exhaust; the outside of the sensor is seeing air, ambient air it is what it seems.

So, now, if you go to high enough temperature which is what this sensor is going to be sitting at especially given that it is an oxygen ion conductor, zirconia. You will see a potential difference between this side and this side; you will see a potential difference if the oxygen ion concentration on either side is different. So, if you have different oxygen ion concentration inside the exhaust pipe compared to the oxygen ion concentration, I mean oxygen concentration on the outside of the pipe then you will see a potential difference.

So, now when you run fuel-rich, what you are doing is you are sending in a lot of fuel-air which means you are completely consuming the oxygen, you have excess fuel in the exhaust stream. So, which means in the pipeline, the exhaust pipe you will see a stream which is mostly fuel, very little to no oxygen; on the outside, you have a lot of air, lot of oxygen. So, since the chemical potential of oxygen is high on the outside and it is minimal to 0 on the inside; you see a potential difference and that is the potential difference that you measure.

So, it turns out to be about 0.9 volts. If you go the other extreme if you send excess air into the engine then you will find a situation where the exhaust stream also has a fair amount of air, what is outside the exhaust stream also has a fair amount of air. So, there is not much of a potential difference between the inside and the outside. So, then you see 0.1 volts going closer to 0. Any in-between position you have, you have some ratio that you are working on. So, this is a typical ratio that many engines might try to use and, in that case, you will start seeing voltages somewhere in the middle.

So, what you can do is and which is what the car manufacturers do, they will select the ratio of fuel to air that they would like their engine to operate at. And this information is fed into the computer in the car, and the potential from the oxygen sensor is also fed into the exhaust I mean into the computer in the car. And instructions are given that you should try to keep mixing the fuel and air such that it stays, that potential stays close to some value. So, they have set 0.45 volts, then what it will do is as you accelerate and decelerate, the engine will keep on the car will keep on adjusting the amount of fuel going in and the amount of oxygen going in to keep pulling it back towards the 0.45-volt operating point.

So, it will mix the fuel and air, increase the air or decrease the air, etcetera and try to keep it at that 0.45 volt. So, this is how you can ensure that the engine behaves in a consistent manner as the vehicle operates over a wide range of operating conditions. And you must understand that the vehicle operating conditions are changing several times every second, maybe 5 6 times every second, the requirements are changing.

So, that fast this feedback loop should be, you should get this feedback from the sensor that fast and you should get the computer to respond accordingly, get change the fuel-air ratio immediately. But this is what goes on in a modern automobile and this is fairly commonly done and it is based on zirconia. So, again it seems to be a one-term material which we have not heard about.

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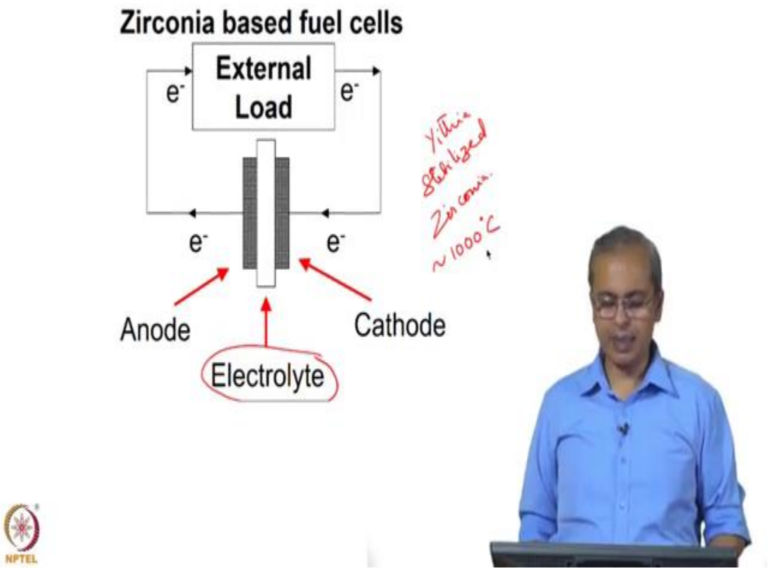
Zirconia based fuel cells

This is also used as I said, for fuel cell applications and you can see here the idea is the same, you have an electrolyte; this electrolyte is based on this yttria-stabilized zirconia and it is an oxygen ion conductor. So, in that sense, if the main thing that it does here is also that same thing that it does in the exhaust sensor that you saw in the automobile oxygen sensor in the automobile. Except that here it is not just sensing the potential difference; it is actually conducting the oxygen ions and enabling the reaction to happen. And, it ends up that this fuel cell will operate at about height at high temperatures around 1000°sC. So, that is the way in which it works.

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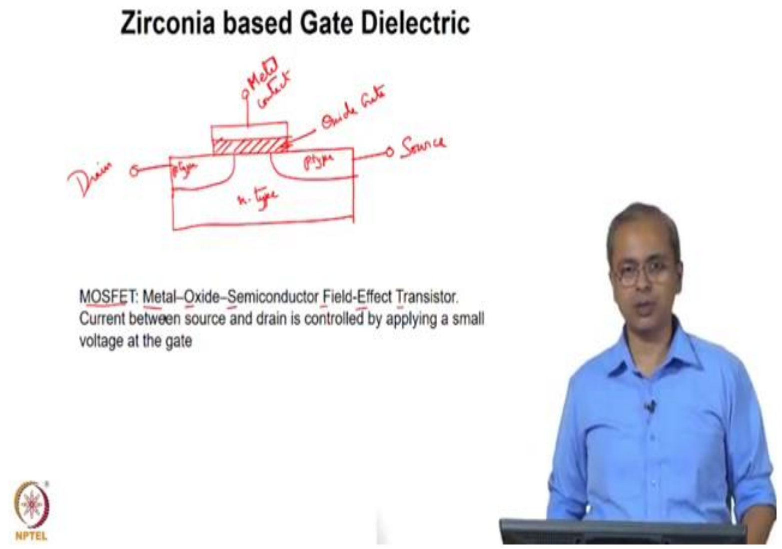
Zirconia based Gate Dielectric

MOSFET: Metal–Oxide–Semiconductor Field-Effect Transistor. Current between source and drain is controlled by applying a small voltage at the gate

Zirconia is also used as a gate dielectric. So, it is used for something called a MOSFET which is the, it is an acronym for a short form for Metal-Oxide-Semiconductor-Field-Effect-Transistor. So, this is a general idea here and it looks something like this. So, we have a p-type semiconductor here, you also have another p-type semiconductor, this is n-type and then this is a gate oxide gate which would be made of zirconia and then you have metal contact.

So, this would serve as a source and this would serve as a drain and you can control the current that goes from the source to the drain by applying a potential across this gate. So, this gate would either restrict the flow of current between the source and the drain or allow the current between the source and the drain; and it is in that form that process that it functions as this transistor behavior. And, there is a metal oxide there is a metal, there is an oxide and there is a semiconductor and using the field we are enabling this to operate as a transistor. So, zirconia is used in this context.

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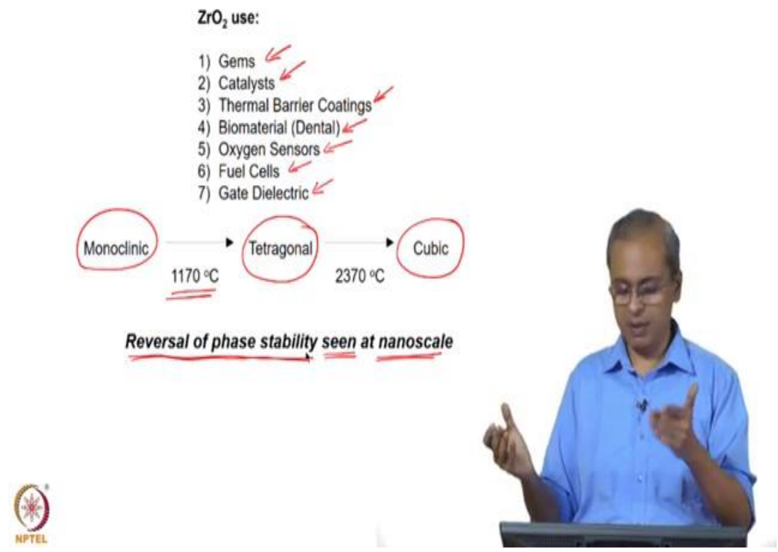

ZrO_2 use:

1) Gems
2) Catalysts
3) Thermal Barrier Coatings
4) Biomaterial (Dental)
5) Oxygen Sensors
6) Fuel Cells
7) Gate Dielectric

Monoclinic → Tetragonal → Cubic

1170 °C

2370 °C

Reversal of phase stability seen at nanoscale

So, we see again that zirconia seems to be some kind of a wonder material. It is getting used for all these things; it is used for a gem as a gem, it is used as a catalyst, it is used for thermal barrier coatings, biomaterial applications, dental applications; so to speak oxygen sensors in automobiles, similar concept being used in fuel cells and as a gate dielectric. So, this is a wide range of things, this is used inside the human body, it is used in vehicles that we use, it is used in medical applications for oxygen sensors and also for our vehicle or applications, it is used in semiconductor devices, catalysts for organic synthesis and of course, for decorative applications such as gems.

Now the important thing is as I said there is this monoclinic phase which is stable at room temperature all the way up to about 1100ºC, nearly 1200ºC; then there is a tetragonal phase which is stable from there for another 1000ºC. So, till about 2300, 2400ºC the tetragonal phase is stable and after that the cubic phase is stable.

So, the interesting thing is that what is observed in the system is that if you take this system. So, all this when I say this phase is stable at room temperature, it turns out that this stability is something that is noticed when you are looking at large crystal structures of this system. So, large crystal structure zirconia at room temperature is monoclinic, at large crystal structure zirconia at about 1000 to 2000ºC is tetragonal and the same large crystal structure zirconia past about 2400º c is cubic in nature. But when you take the same material and you go to the nanoscale of it, you simply and so, you are done nothing other than change the crystal size, no other change you are making. You are not changing the composition in any way; you are simply changing the crystal size. If you change the crystal size, it turns out that suddenly there is a reversal of phase stability, that is seen at the nanoscale.

So, this is very important it may not seem like much, but what it means is that a different phase is now stable at room temperature which you were not expecting it to be; and that is very important because the properties of the material change because the phase has changed. Therefore, at room temperature you can now have zirconia giving you completely new properties, which you otherwise did not expect from zirconia at room temperature and 1-atmosphere pressure; and therefore, you can do something new some new application you can use the same zirconia material for. So, that is the beauty of it and that has happened simply by going to the nanoscale.

So, let us a look a little bit more on why this has happened, see when you say phase stability the idea of phase stability is intricately connected to the thermodynamic aspects of it. So, that is the thermodynamics decides which phase is stable under what conditions. So, you look at thermodynamic properties and particularly you look at free energy and then this phase which has the lowest free energy is the one that is stable and under those conditions.

So, when you say that there is a reversal of phase stability, it means that something has happened to the thermodynamics of the system. That the thermodynamics of the system has changed in some manner and that is the reason why some other phase is now showing you free energy that is the lower value and as a result that is the phase that is now stable at room temperature.

So, you can ask the question has the thermodynamics changed? The direct answer to it is no. The thermodynamics is thermodynamics it is sort of a fundamental law nothing changes there. So, as I mentioned one of the issues we see when we learn thermodynamics is that we tend to see equations written in a certain way and which often is the case because that equation is associated with a certain system under certain conditions.

And as a result, the same system under some totally other conditions may have a few more terms in that equation which are relevant only under those conditions. Whereas, if you come back to your regular conditions those other terms may not be relevant. And as a result, when you write the equation in the macroscopic scale you can actually write a lot of other terms there, all of which will evaluate to values close to 0 and as a result we can neglect them.

It is just that in the typical thermodynamics book they do not write all the terms and say all these there are this other 4, 5 terms I can write; and all the other 4, 5 terms are all 0 and therefore, we are left with these 3 terms. You often do not see that explicitly stated, if you actually looked around in the book and read the words carefully you will see hints that is what they are referring to and generally that seems to work fine.

But when you go to the nanoscale suddenly you find these additional terms which were evaluating to 0 are now no longer evaluating to 0. And since they are getting some larger and larger value more significant value, they suddenly affect the total outcome of that equation and therefore, the value you are getting for that equation is now different. And now that it is a different the result that you see the impact that it has is now beginning to become different. So, that is the idea that we are going to explore a little bit.

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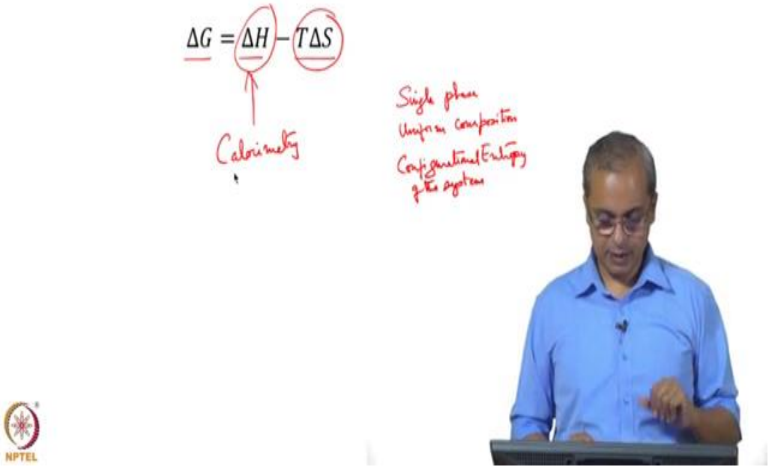

So, if you see here, we write

$$\Delta G = \Delta H - T\Delta S$$

this is the way we write our free energy changes in the typical case that we discuss. Now we always say that for whichever phase is stable the free energy is the lowest and so, you are looking for the lowest free energy.

So, if you are comparing a system, where the chemistry is the same you are not changing, it is a single-phase system. It is single phase, it has uniform composition and within the phase of course, since it is a single-phase it is all the same crystal structure and so on. Then you do not have much impact of and if you are comparing two such single-phase systems; you are comparing one single-phase system. In this case, we are comparing the monoclinic system to the tetragonal system both of zirconia.

Then as long as you have not changed the composition in any way, zirconia, zirconia whether it is monoclinic or tetragonal; and therefore, aspects associated with configurational entropy of the system. Aspects associated with the configurational entropy of the system are not that important to us, because you are not really changed it is not like you have introduced a new element into the system and therefore, you need to look at the randomness of the system etcetera. So, largely it does not seem to be involved.

So, the impact of the sort of the $T \Delta S$ term in the overall scheme of things is it is not as pronounced in any different manner; so, to speak between the macro scale and the nanoscale, so to speak. On the other hand, it turns out that ΔH the enthalpy has some dependence, actually a significant dependence to some° on the crystal size; and this is something that we need to understand.

And that is the reason why this dependence is so much dependent on the crystal size, that at large crystal size, the crystal size dependence reduces to 0. And then you only see the ΔH. Whereas, of any transformation between one phase and the other phase; when you go to smaller crystallite size, you see the same transformation ΔH still being present, but you also have a crystal size effect showing up in the ΔH and that affects the outcome, so to speak. And therefore, it is interesting to follow changes in ΔH as you go to smaller and smaller crystal sizes and that, of course, is done using calorimetry.

And we saw that in our previous class, we discussed calorimetry to some° to understand what is happening there, how is that measured, why is it significant and so on. So, the calorimeter is used and I also told you at that time that when you are looking at thermodynamics of the system calorimeter is a very important tool, a very useful tool that conveys many things to us.

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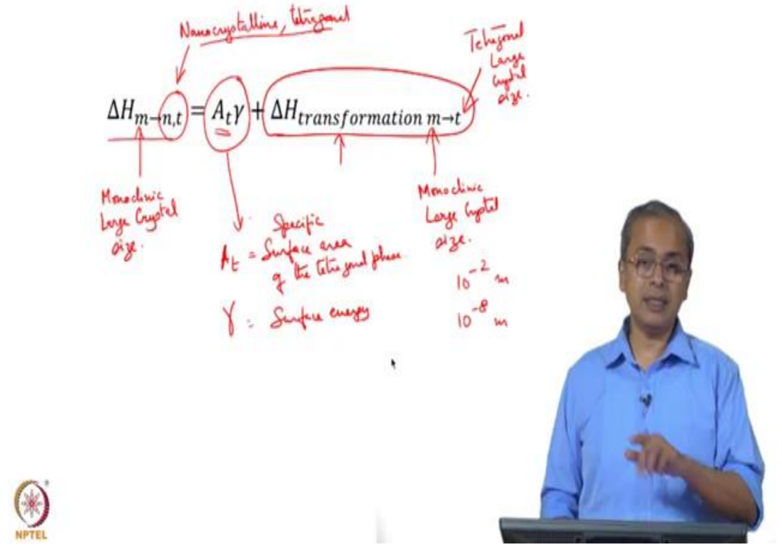

Nanocrystalline, tetragonal

Tetragonal Large crystal size.

$$\Delta H_{m\to n,t} = A_t\gamma + \Delta H_{transformation\ m\to t}$$

Monoclinic Large Crystal size.

Monoclinic Large Crystal size.

A_t = Specific Surface area of the tetragonal phase

γ : Surface energy

10^{-2} m

10^{-8} m

So, if you look at a transformation. So, you have ΔH monoclinic, in this case, I have put m small subscript as m and this is nanocrystalline, tetragonal. So, this is monoclinic. So, normally this is this term is what we would get, the when you do this transformation from monoclinic to tetragonal. So, this is monoclinic to tetragonal. So, please see the difference, this term here the second term that I have now put in a circle is monoclinic large crystal size to tetragonal large crystal size that is what this is.

So, I will just write that here large crystal size, this is also a large crystal size; whereas, what you have on the left-hand side of the equation is monoclinic also large crystal size to tetragonal but nanocrystalline size. So, you can see that when you normally took, I mean when you normally take the monoclinic zirconia of large crystal size; and you put it in a calorimeter and then you start heating it up and finding out what heat is going in and what transformation is happening and so on. What you are actually getting and what you are actually measuring is the term that I have circled here, which is the ΔH of transformation from monoclinic large crystal size to tetragonal large crystal size.

And this ΔH is what you would plug into the

$$\Delta G=\Delta H-T\Delta S$$

and that is where you will get all the other decisions you will make based on that. What is there, that is missing in that information is this A t comma t and that is the where A t is the surface area or we will say specific surface area, because we are always going to look at it on a per unit mass basis or per unit mole basis; so specific surface area of the tetragonal phase. And the γ is surface energy.

So, you can see here. So, we have if you are looking at a specific surface area. So, that is essentially the area I mean that 1 gram of that material would correspond to. So, clearly when the crystal size is larger, so the same 1 gram will now have a certain amount of surface area associated with it. If you keep reducing that crystal size and therefore, you will have many more small crystals, you will have higher and higher surface area for the same 1 gram of that material.

So, the area goes up dramatically for the same weight of the material, the same number of moles of the material; and the area goes up dramatically when you go from a crystal size of say 1 centimeter to a crystal size of say 50 nanometers or 100 nanometers. So, when you go down. So, you are looking at going from 10^{-2} meters to 10^{-8} meters. So, that is a radius; radius is going from10^{-2} meters to 10^{-8}.

So, you are looking at 6 orders of magnitude difference in radius and therefore, you are looking at say 12 orders of magnitude difference in the surface area. So, you will you do a πr^2. So, 10^{-6} you would have 10^{-12}. So, you will have 12 orders of magnitude. So, a huge difference in surface area, so that is the significant thing. And therefore, even if the γ is small because the A becomes very large for the same mass, so same number of moles, this term starts becoming very significant.

So, you can see this is what I said when I said that in thermodynamic systems and thermodynamic discussions; we have additional terms available in the equation which we do not highlight, normally. Because many times for most of our discussion we would have dealt with systems where this specific surface area is so, negligible that it impacts on the system is irrelevant. So, we only talked of terms where the impact, their impact is relevant is significant to the discussion.

And so, therefore, in most of the other situations where we would have run into this equation, we would not have written down A t γ. So, that term would itself would not be there although technically it is there, it is just that it is contribution is negligible, this mini skew. Suddenly you see it is contribution is very significant and as a result, you start seeing a huge impact on the transformation.

And so, interesting interestingly what happens is you can do this monoclinic to tetragonal, monoclinic to cubic, monoclinic to amorphous. So, all these kinds of things you can calculate using calorimetry typically you to drop solution calorimetry for this there is one I will show you a reference where they have done and very extensive study of this system.

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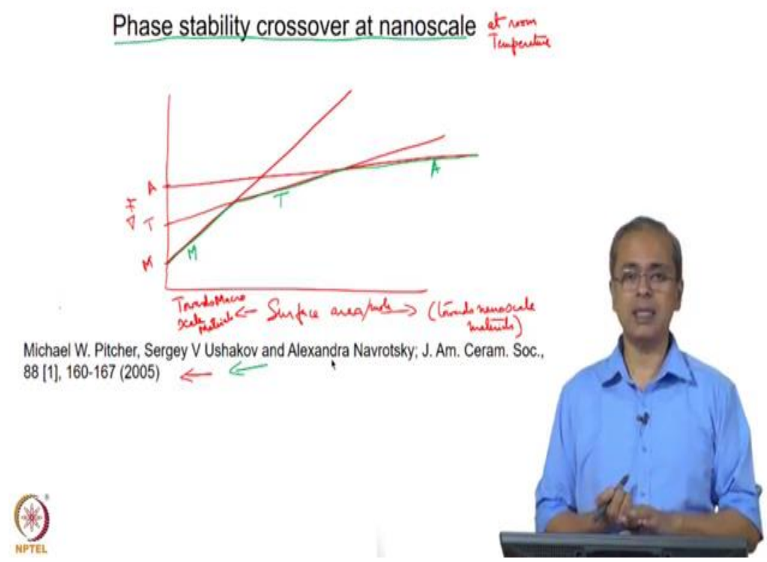

Phase stability crossover at nanoscale

Michael W. Pitcher, Sergey V Ushakov and Alexandra Navrotsky; J. Am. Ceram. Soc., 88 [1], 160-167 (2005)

And so, that reference is out here. So, you can go and see this it is a 2005 paper in the journal of American ceramic society, where they have done a significant amount of work in this area. You can actually see how carefully they have done their experiments; I mean so much thought has gone into everything like you know, what is the state of water there? How they are handling the water there and so on and they are able to get this information.

So, basically what they do is just to show you a trend of what kind of information they get. So, they have surface area here and you have this ΔH data out here. And what you will see is that; so, this if increasing surface area or surface area-specific surface area, surface area per mole. So, increasing surface area means you are going to smaller and smaller crystal size. So, this means you are going to nanomaterial size towards nanoscale, this side is towards macro scale materials.

So, actually, it turns out that you will see, at the macro scale you will see monoclinic, you will see tetragonal and you will see amorphous. Cubic we are not plotted here, because in their system they tend to see this they are not able to see cubic at the room temperature. So, this is all at room temperature, at the nanoscale at room temperature at or near room temperature is what you are looking at.

So, normally this is what you would see at room temperature you will see, a monoclinic phase that is the most stable, then you would see tetragonal and then if you manage to get amorphous scale, amorphous material that this is what you would see. Now what happens is ΔG is the same like I said the ΔH transformation is the same, it is just that the surface area contribution, surface area energy contribution to the H term the enthalpy term is different for each of the phases. So, the γ for each of the phases is different. The γ for the monoclinic is different, tetragonal is different, and amorphous is different; and as a result of the γ as you and that is the slope.

So, the slope is the γ. So, if I say that the monoclinic phase changes it is enthalpy as a function of surface area like this; Then the slope of this line is that γ, that we are looking at in that equation. So, it turns out that they see something like this for monoclinic, they see something like this for tetragonal and they see something like this for amorphous. So, they see that the γ value for the three different phases is different.

And so, as you keep increasing, so it is impact is two impacts the slope of that line as of; and therefore, the change in enthalpy as a function of the surface area of that sample which is basically again as a function of the size of that crystals and as you go towards the nanoscale that line keeps going. And so, you see these three different positions of these lines as a result of the surface energy associated with those respective phases.

Now, as I said the stable phase is one where the ΔG is the lowest and in this case the ΔH would have to be the lowest, if you are assuming the TΔS term is relatively impacting, I mean relatively the same for all the conditions. So, then, therefore, you see that the lowest, the phase with the lowest ΔH is the monoclinic phase up to this point; then the tetragonal phase is lower and then the amorphous phase is lower. So, this is the work that these people have done and this reference that you see here, they have done this in great detail and they are able to show you something like this. More specific details you see there you will have to look at this reference, but this is the general result that they have obtained, and they show that these three phases are showing you; so, at under different.

So, when you are at the macro scale the monoclinic phase is stable, which is what we are typically seeing when you do phase stability measurements at room temperature with macroscopic materials. When you go to smaller and smaller sizes, the tetragonal phase becomes stable; and that is what you see as you go to nanoscale. And even smaller scales of sizes when you go the amorphous phase starts becoming stable.

So, therefore, whereas, at room temperature previously; monoclinic was most stable, tetragonal was less stable. When you go at room temperature when you now go to the nanoscale; tetragonal is more stable monoclinic is less stable. And this is what they are referring to as Phase stability crossover at nanoscale. And this is a very nice work, which very nicely puts together the activity involved in trying to convey this. So, what we have seen here is that nanoscale and therefore, nanomaterials have interesting implications on the thermodynamics associated with the system, in which we are exploring this nanoscale.

And it really depends on that system it, in this case, the surface energy terms ended up in this situation, that you saw this phase reversal; it may or may not be true in all systems. So, you will have to investigate it in your system of interest or lookup values in the literature and see if that suggests that such a reversal could exist. And if you did the right kind of experiments using, calorimetry and so on; you will be able to put together the data and therefore, draw plots of this nature which will be able to show you this difference of phase stability. And so, this conveys in a very nice way what, how nanoscale impacts the thermodynamics.

And so, in this course we are now looking at, primarily looking at nanoscale impact of nanoscale on various properties and the relevance of that impact. As I told you at the end of the day if there is no difference between the nanoscale and the macro scale then the nanoscale is not interesting to us. If everything at the nanoscale looks exactly the same as it does at the micro-scale, then why waste our time and effort trying to create the nanomaterial at all. The whole subject is interesting to us only because things at the nanoscale look very different from what they do look at the micro-scale. Then it is interesting to first find out what is the difference, can we use the difference to some interesting application and also understand why there is that difference.

So, this set of classes that we had, this one and the few 2, 3 ones before this, are all looking at the thermodynamic aspect of the nanoscale and how you analyze it, where you see a difference and why there is a difference. So, with this, we will halt, we will look at other aspects from our next class.

Thank you.