An Introduction to Materials: Nature and Properties
(Part 1: Structure of Materials)
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Lecture – 03
Correlation between bond and physical properties

So, we are going to start with a new lecture let me just recap the last lecture.

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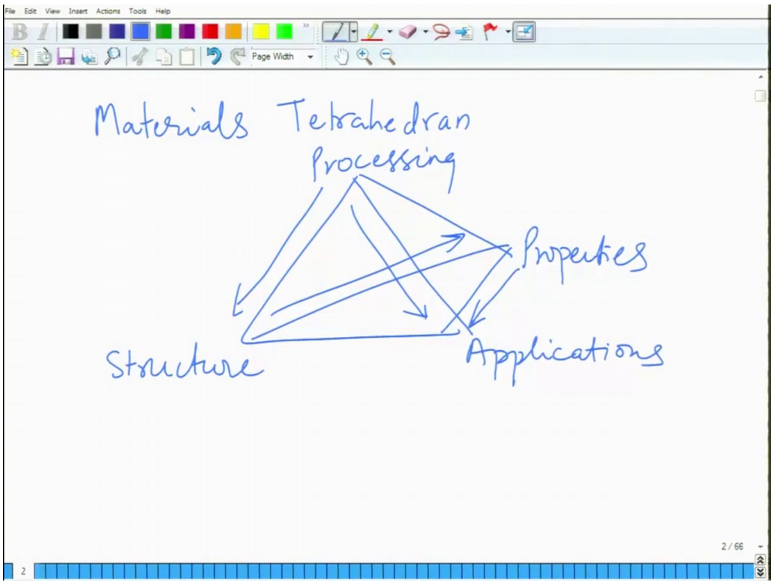

In the last lecture we learned about, so, let me write again materials tetrahedron and basically this was about you know you can make it a tetrahedron like this and on 1 hand you have properties of materials, on another hand you have applications, on this side you have structure and then you have proper processing.

Now, processing is very important here because, processing of excess structure especially the microstructure and structure affects the properties a micro structure and nano structure crystal structure is normally something which is it does not change significantly and un until you do some special kind of processing like non equilibrium processing. So, undermost processing method the crystal structures does not alter.

Ah the phase fractions may alter and the microstructure may alter which will give rise to change in the properties and that will affect the applicability of the material. So, this is how these things are related, processing is also related to applications because processing is related to cost and ease of processing and manufacturability. So, this tetrahedron basically shows you interrelation between 4 important aspects of materials engineering and then we discussed about classification of materials.

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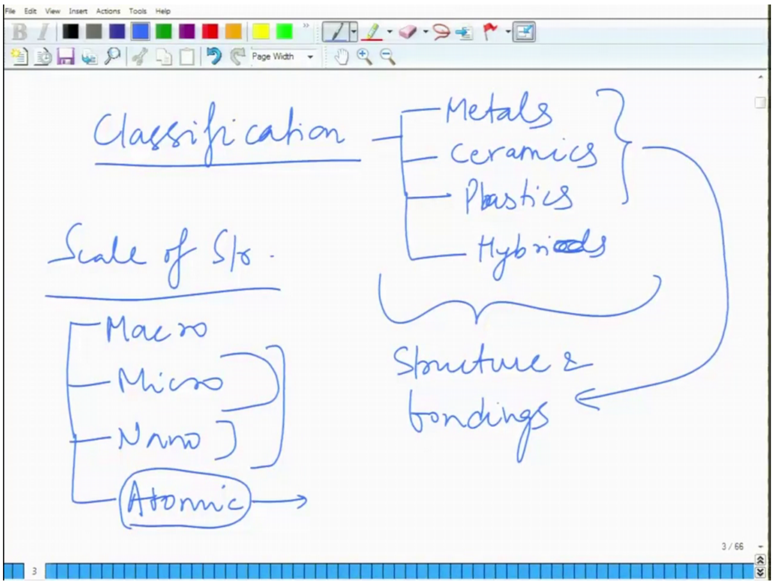

So, classification of materials was basically in 4 categories metals and there are alloys ceramics polymers or let us say plastics polymers in last tumors and then we had hybrids ok. Now these are these are basically on the basis of type of materials in the sense they metals are strong and ductile and they have high electrical and thermal connectivity, but they are not very good they do not have good corrosion resistance ceramics; on the other hand have very high strength, but they have very poor ductility they are very brittle and they have low cost in thermal expansion and poor electrical and thermal conductivity. Plastics are man ductile they can be stretched to long lengths they also have good toughness they have corrosion resistance, but their high temperature properties are suspect and the hybrids are something which you intentionally make. So, this classification of materials basically is not only because of properties, but properties are because of structure and bonding.

So, this classification the basis behind this lies in structure and bonding; as we will see metals are metallically bonded and because of bonding they are malleable in ductile most ceramics are ionically and covalently bonded that is why ceramics are hard and brittle and strong ah. Plastics are mix of covalent bonding and secondary bonding of van der Waals bonding and that is why they are softer and hybrids are mixture of both of them, so they may have differential area.

But this particular classification of these 3 categories is primarily related to the bonding in metal and materials and then we looked at the scale of structure. So, when we talk about structure has various scales. So, first a scale is the macro, second is micro, third is nano fourth is atomic. Now it is so in the context of materials engineering we are interested in micro structure which is the structure and distribution of phases grains grain boundary etc, impurities inclusions at micron level or some micron level scale nano structure could be again related to same as micro structure then the formation of nano crystalline phases nano crystalline structures.

So, micro and nano something are something which can be by microscopy and they have very profound in fact impact on the properties of materials. Fourth is atomic structure this atomic structure is something which is not which is innate to materials, materials tend to adopt atomic structure based on the bonding and based on energy calculations as I saw and I showed you that atoms have to have certain equilibrium distance. So, based on the energetic, they tend to adopt certain configurations which determine their properties.

So, what we will do next is we will go backwards we will start looking from the atomic structure and then go to nano, then go to micro and nano structures so, but before we go to atomic structures let us just get into bonding, we were looking at it last time and we defined a term called as bond energy.

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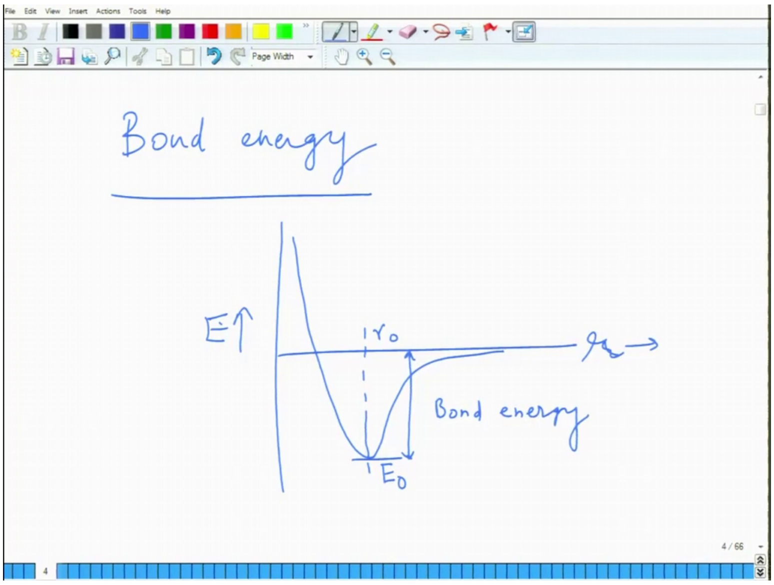

Bond energy

Which is the energy of the bonds corresponding to so if you have a plot like that ah. So, this is the separation distance r, this is the energy e and energy corresponding to the separation distance at which energy is minimum.

This is the bond energy of the materials and this bond energy has profound correlation with the properties basic properties of materials. So, let me now get into the bonding, there are 3 kinds of bonding that we primarily come across or study first is ionic bonding, second is covalent bonding and third is metallic bonding and then there is something, so these are all primary bonding methods ok.

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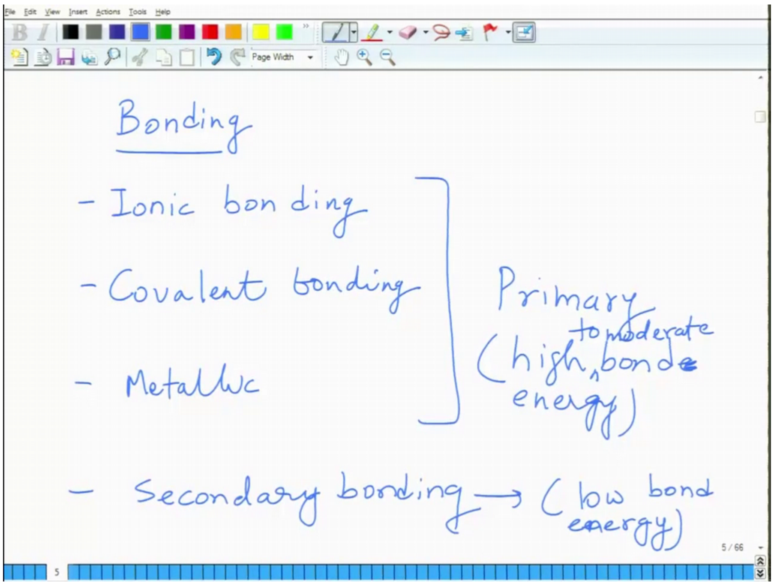

Bonding

- Ionic bonding
- Covalent bonding
- Metallic

Primary (high to moderate bond energy)

- Secondary bonding → (low bond energy)

So, this is called as primary then there is another class of bonding which is called as secondary bonding and the reason for this classification is because primary bonding is typically characterized by high bond energy, high to moderate bond energy, high to moderate bond energy and secondary bonding is characterized by low bond energy.

So, I will show you the bond energy magnitudes later on as we move on, but there is a substantial difference between bond energy of 2 things and that is why materials which are purely covalently or ionically or mechanically bonded they are stronger than what heals which are secondary bonded, so let us look at the ionic bonding to begin with ok.

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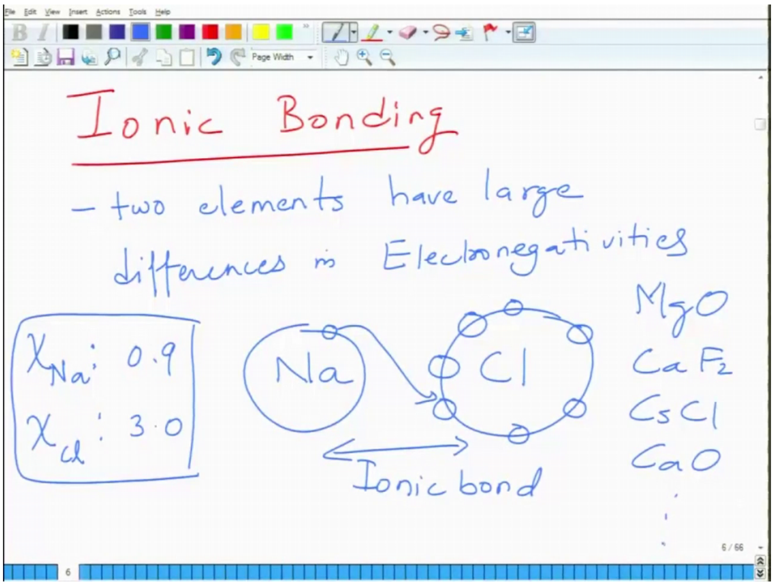

Ionic Bonding

- two elements have large differences in Electronegativities

χ_{Na} : 0.9

χ_{Cl} : 3.0

MgO

CaF_2

$CsCl$

CaO

⋮

So, ionic bonding happens when 2 elements have large differences in their in electro negativities. So, for example you take example of sodium and you take the example of chlorine, sodium has 1 extra electron in it is outer shell chlorine has 7 6 and 7, so to complete it is 8 electrons it borrows 1 electron from this side. So, that sodium becomes a stable chlorine becomes a stable and a bond formed between 2 of them is called as ionic bond and let me just tell you the energies of the values of electro negativity.

So, chi of sodium has a value of about 0.9 and chi of chlorine has a value of roughly 3. So, this difference is substantial difference between the 2 and this is related to the bond energy so and that is why ionic bonds are typically very strong. So, if you had. So, other examples of these materials could be any. So, you have magnesium oxide which is ionically bonded solid, you have calcium fluoride, you have cesium chloride you have calcium oxide variety of these materials they are all ionically bonded materials and that is why they have they tend to have high strength high melting point.

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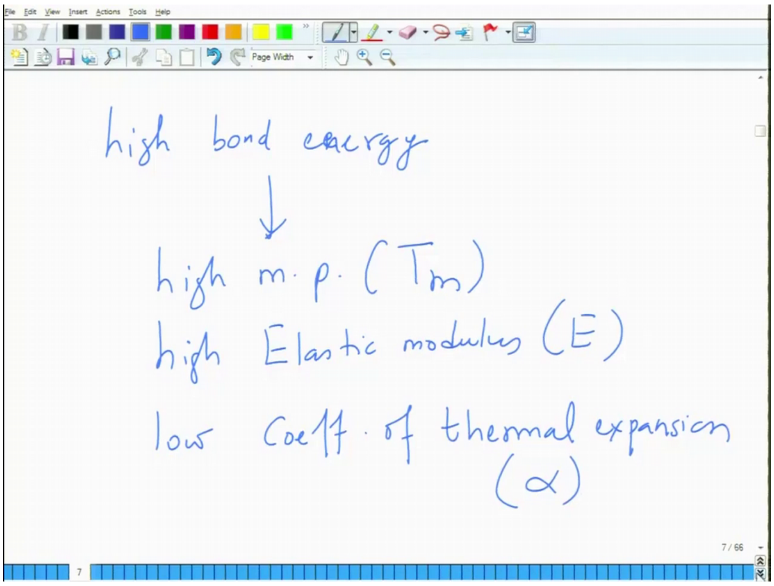

high bond energy

$\downarrow$

high m.p. (T_m)

high Elastic modulus (E)

low Coeff. of thermal expansion (α)

So, basically I would say here high bond energy implies in this case high melting point, high drastic modulus low coefficient of thermal expansion and most ionic solids as a result have these characteristics. Then you have will go into details of ionic bonding a little later when we study the ionically pointed material structures. So, I am not doing mathematical treatment, right.

Now, I am just giving you a qualitative treatment at this stage and then second is covalent bonding.

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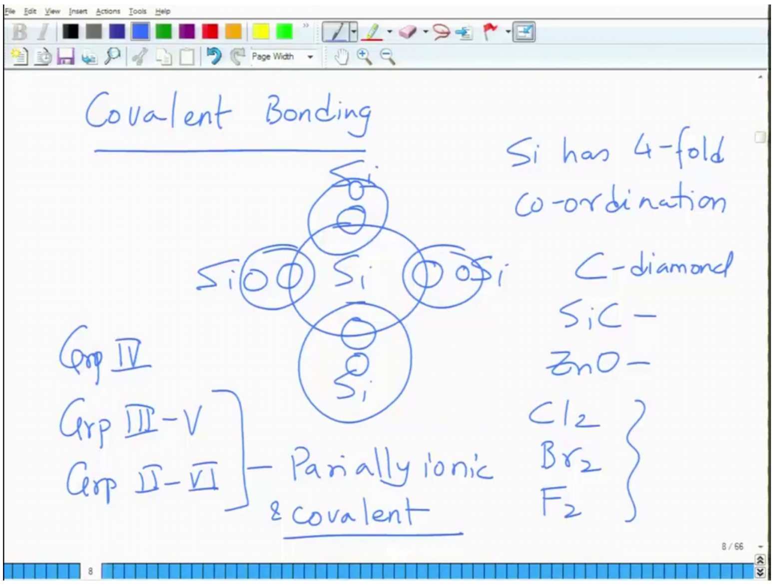

So, for example you take silicon. Silicon has how many unpaired electrons 4, silicon tends to share it is electrons with neighboring silicon atoms. So, this is not this is not give and take that is sharing. So, neighboring silicon will have 1 electron here it will pair similarly this silicon will have 1 electron here they will pair, this will have 1 electron here it will pair and likewise this silicon on the outside will also be pairing with 4 neighbors ok.

So, as a result silicon is silicon has a fourfold coordination. So, it pairs up every silicon atom in the silicon lattice is in the silicon structure is paired up with 4 silicon atoms it has 4 neighbors. So, as to have this covalent bonding and this is called as and so only silicon but there are a lot of other elements which have this kind of characteristics. So, silicon is 1 carbon basically diamond has this kind of structure silicon carbide, zinc oxide which is an oxide which is partially ionic but it also has a very strong covalent character ah.

So, all these materials they are covalently bonded gases such as Cl 2 Br 2 F2 all of them tends to be covalently bonded group 4 element. So, base in terms materials group 4 group 3 5 semiconductors and group 2 6 semiconductors they tend to have very strong covalent character. So, these 2 also have ionic character, but they are partially ionic and covalent.

So, these materials like silicon oxide zinc oxide silicon carbide and zinc oxide they have ready they have quite strong covalent character, again they have similar characteristics they have high bond energy, covalent bond typically is characterized by high bond energy as a result covalent materials also have similar characteristics.

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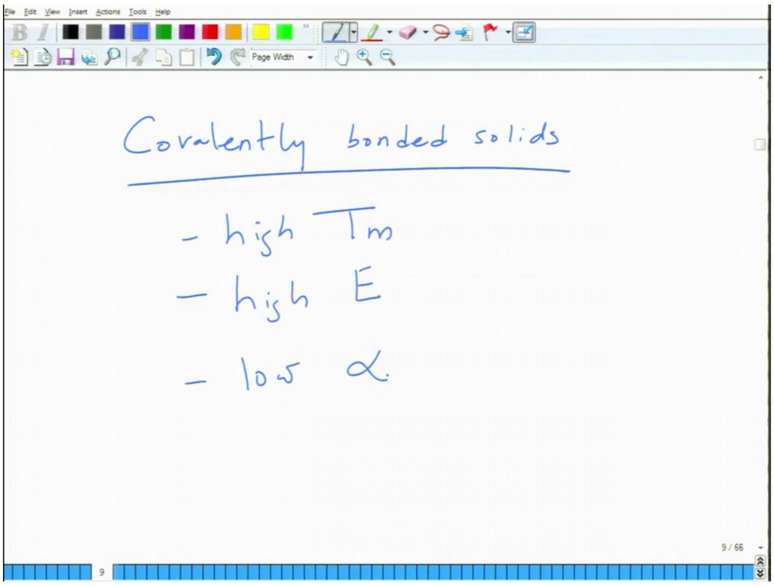

Covalently bonded solids

- high T_m
- high E
- low α

Covalently bonded solids have high tm high e which is basically elastic modulus and low alpha coefficient thermal expansion and also write in the previous slide tm e and alpha all right. So, the third bonding which is there which is now primary nature is called as metallic bonding and most metals have this kind of bonding present all matter. In fact, all metals are bonded with metallic bonding.

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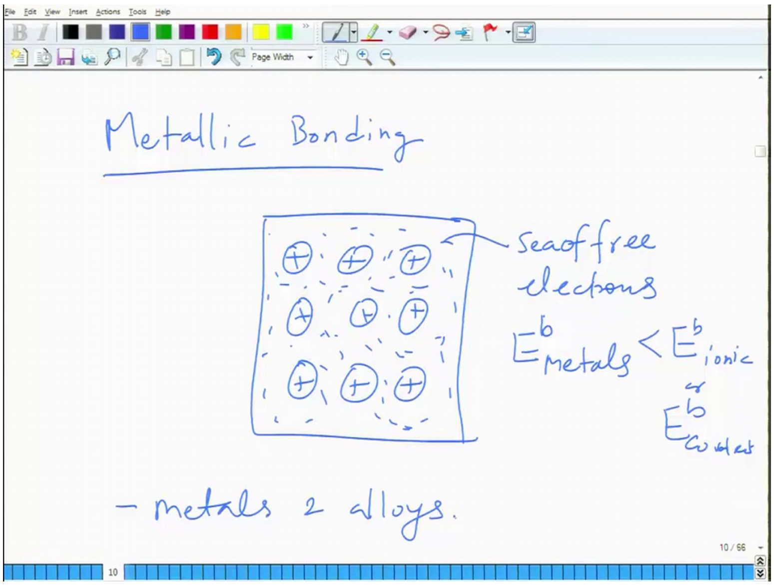

Metallic Bonding

Sea of free electrons

$E^b_{metals} < E^b_{ionic}$ or $E^b_{covalent}$

- metals & alloys.

So, what you have here is basically suppose this is the volume in which atoms are there these are all atoms. So, positive coarse are atom are left behind and these are surrounded by this resilience of electrons, which are the basically the villains unpaired electrons. So, this is you can say a sea of free electrons and because this is a sea of free electrons, there is no as such like ionic or covalent kind of bonding the bonding is the bond energy is the e metals.

Let us say, I write it as EB ok, bond energy of metals is lower than typically EB ionic or covalent, it is not always true but in most cases it is true metals have lower bond energy as compared to ceramics which are ionically covalently bonded, but metallic bond is fairly strong stilts are very weak it is very strong as compared to secondary bond and this is typically bonding in metals and their alloys ok.

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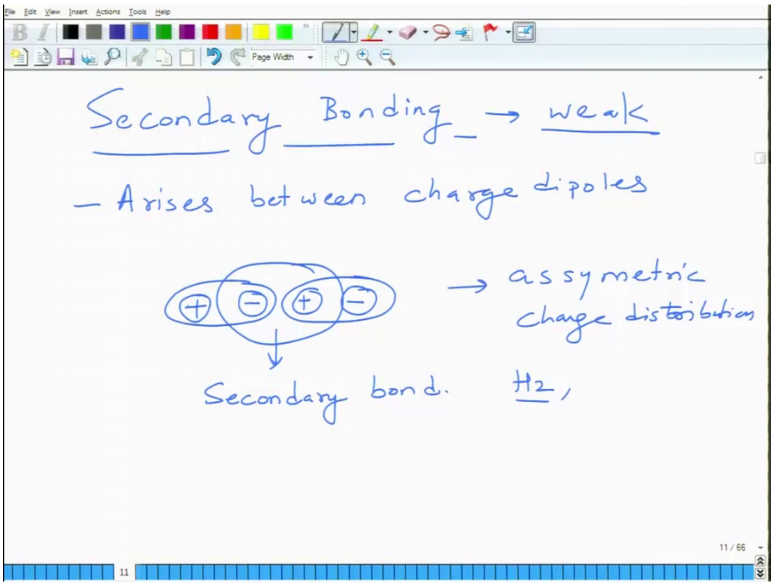

Secondary Bonding → weak

– Arises between charge dipoles

→ assymetric charge distribution

Secondary bond.

H_2,

So, now the other kind of bonding that we discussed was called a secondary bonding, this is basically weak weaker than the primary bonds and this basically arises from interaction between charged dipoles on the surface, as a result so for example, you can have you can have things like let us say you have something situation like this where. So, normally what happens to that center of negative and center positive charges will coincide.

But let us say you have a center of positive charge here and centre of negative charge here and similarly you have a neighbor which also has similar kind of configuration center a positive charge here, center of negative charges here these 2 attract each other they form what is called as a secondary bond ok. So, this is because of asymmetric, let us say a symmetric charge distribution and that is when you have a symmetric charge distribution you will have formation of electric charge dipoles ok.

So, this happens in things like hydrogen most of the gases have this kind of van der Waals kind of a structure, because they have very weak water molecules are second rebounded. Then second type could be you have present for example, in polymers you have these polymer chains.

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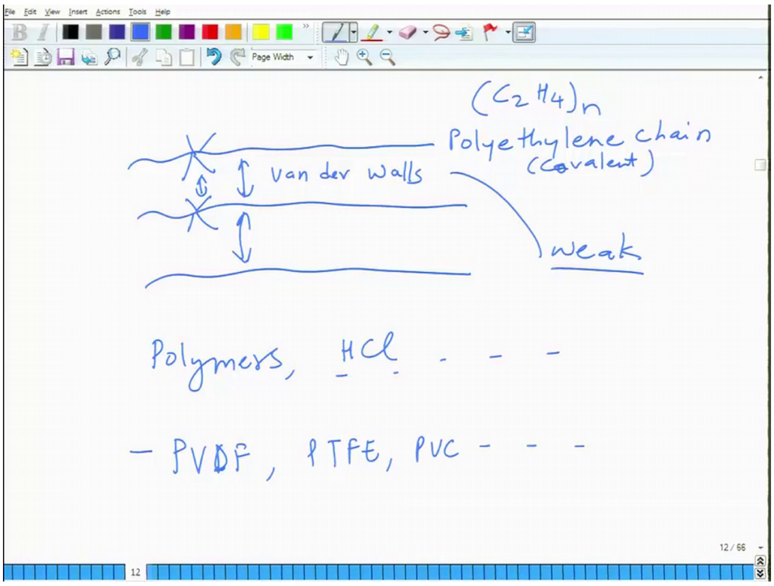

So, let us say these are all at polyethylene chains ok. So, basically C2H4 n ok, these chains are all covalently bonded. So, within chain you have covalent bonding, but between the chains the interaction is van der Waals. So, since in polymer chains are randomly oriented that is why polymers a little malleable, because the interaction between chains is very weak. So, this is for example so this is this could happen because if you have you know these chains will have branching the groups will be present.

Similarly, you have groups present here there is some interaction between these groups on both sides and again that is secondary in nature, this happens in polymers things like HCl. So, organic many organic compounds have this kind of behavior. So, this is basically and this could be because of permanent dipole moment, so materials which can have ah. So, things like water things like various polymers PTFE, PVDF, PVC is a material permanent dipole moment is still it is the polymer.

So, you can also have examples are PVDF or you can have p PVC some of them may have permanent moments some of them may not have permanent moment, but still you will have this secondary bonding. So, now, let me come to some energies. So, for example, let me compare some compounds like. You have lithium fluoride.

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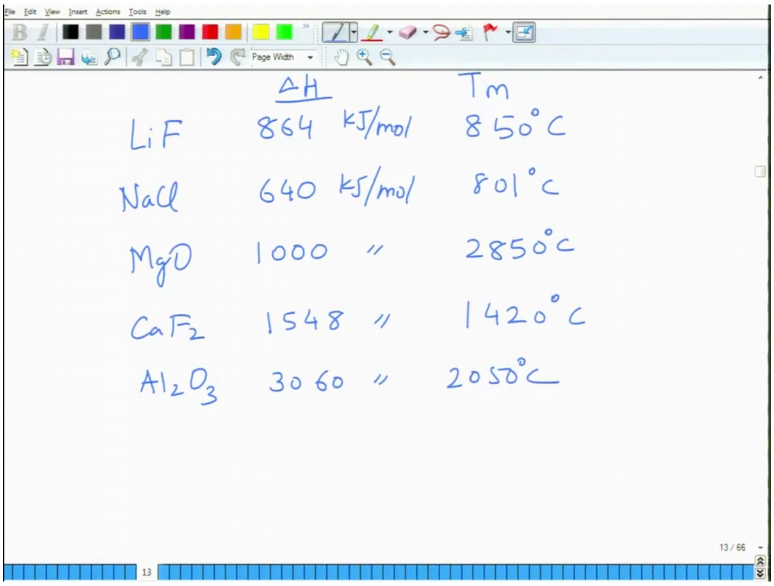

	ΔH	T_m
LiF	864 kJ/mol	850°C
NaCl	640 kJ/mol	801°C
MgO	1000 〃	2850°C
CaF_2	1548 〃	1420°C
Al_2O_3	3060 〃	2050°C

So, lithium is from top of the variable on the left florid is right on the right side then you have sodium chloride.

Then let me take example of magnesium oxide then let me take example of calcium fluorite and then let us take example of Al2O3, now you will see that now this bond energy is related to enthalpy of atomization let us say. So, if I take the values this is for example, 864 kilo joule per mole, on the other hand the value for NaCl is 640 kilo joule per mole, on the other hand magnesium oxide is a value which is 1000 calcium fluorite has a value of 1548 and aluminum oxide has a value of 3060 these values can be found in any standard text for sample raghavanx by materials.

Now, which of these you expect to have highest melting point and which of these you expect to have the lowest melting point. So, as you as you as you suggested al through earlier Al2O3 will have highest melting point. So, it is melting point is 2050 degree centigrade. So, let us say this is Tm and this is delta h basically the you know enthalpy of atomization which is nothing, but related to bond energy.

So, and NaCl by this token should have the lowest melting point it is melting point is 801 degree centigrade lithium fluoride has a 850 degree centigrade, MgO has twenty 850 degrees centigrade and calcium fluoride has 1420 degree centigrade, there are some exceptions in the middle, but by and large this rule follows.

There are a lot of other reasons you see the melting point is related to the atoms themselves the behavior of character of atoms. So, bond energy is 1 important factor, but by and large this is true with the exception of calcium fluoride here you can see that as you increase the bond energy the melting point increases and this is true about melting point boiling point and similarly you will have a decrease in the coefficient thermal expansion.

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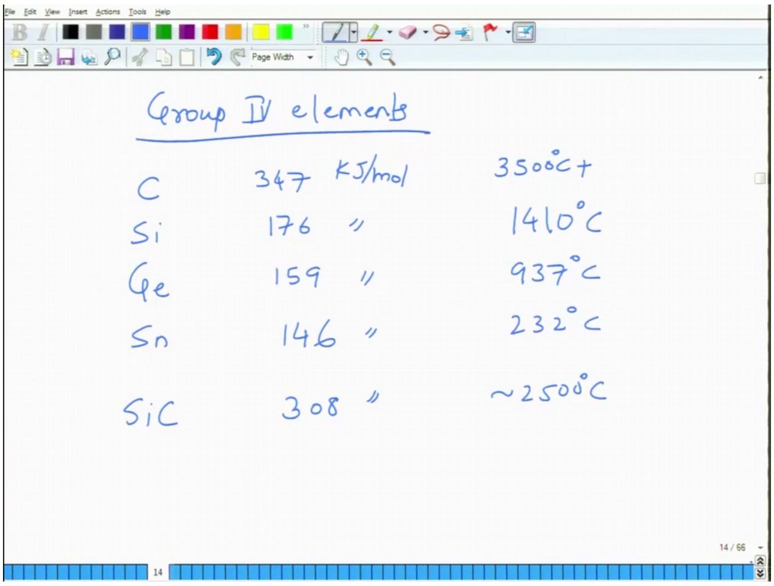

Group IV elements

C	347 KJ/mol	3500°C+
Si	176 "	1410°C
Ge	159 "	937°C
Sn	146 "	232°C
SiC	308 "	~2500°C

So, if I now compare the fourth group elements, let us say 4 elements in group 4 elements we have carbon, we have silicon, we have germanium and we have grayton 10 and if I look at the bond energy diamond has 347 kilo joule per mole, silicon has 176, germanium has 149 and tin has 146 and I compare this with another material which is silicon carbide which has 308 and if you look at the values of melting point diamond is about 3500 degree centigrade plus it is difficult to measure the diamond diamonds melting point because it is too high.

Silicon has 1410 degree centigrade this has 937 degree centigrade this has 232 degree centigrade and this has about 2500 degree centigrade. So, you can again see the compounds which have lower bond energy they have a lower melting point and this is true if you compare the values to these as well. So, of course, you can see that the bond energy. So, this is enthalpy of atomization not exactly the bond energy bond energy ies related to that, but the sequence is fairly the trend is fairly similar.

What you get there is also true here, if I look at certain metals for example, do not compare the values of 2 compounds directly because that may not be very comparable directly, but that says let us compare some metals such as copper let us say gold. Let us say aluminum, I am just going to talk about the engineering metals nickel zinc tungsten and iron I am going to stop here.

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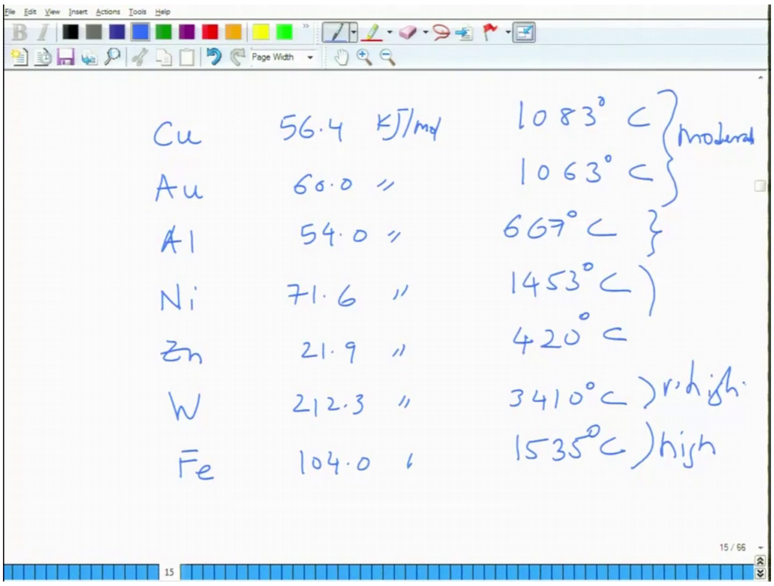

Cu	56.4 KJ/mol	1083° C	moderat
Au	60.0 "	1063° C	
Al	54.0 "	667° C	
Ni	71.6 "	1453° C	
Zn	21.9 "	420° C	
W	212.3 "	3410° C	v. high.
Fe	104.0 "	1535° C	high

So, copper has a bond energy of 56.4 kilo joule per mole, gold has a value of 60 aluminum has the value of 44 nickel has a value of 71.6, zinc has a value of 21.9 tungsten has a value of 212.3 and iron has a value of 104 and by our experience we know which has highest melting point of these. So, tungsten has highest melting point of these it is melting point is 3410 degree centigrade which is very high, of course you know that it is 1535 degree centigrade, aluminum we know it is 667 degree centigrade, copper is 1083 degree centigrade and gold as 2163 degree centigrade, nickel is again high bond energy it is melting point is 1453 degree centigrade and zinc of course, is very low it is 420 degree centigrade.

So, you can see again the correlation these are all moderate bond energy metals the melting point is about 1000 a lower, aluminum is on slightly lower side nickel is nickel iron there on higher side they have moderate melting points zinc is of course, very low. So, this is moderate this is high this is very high ; now of course, if you compare with ceramics if you for example, if you compare with diamond. Diamond has a boundary of 347 and if you compare tungsten is a value of 212 and they have similar melting points.

Bond energies for different classes of materials are not exactly comparable because, they have lot of other factors to go behind; but by and large for the same category of materials there is a trend that as the bond energy increases the melting point increases and this is also to about the boiling point ah. So, this is how it will so to summarize this part.

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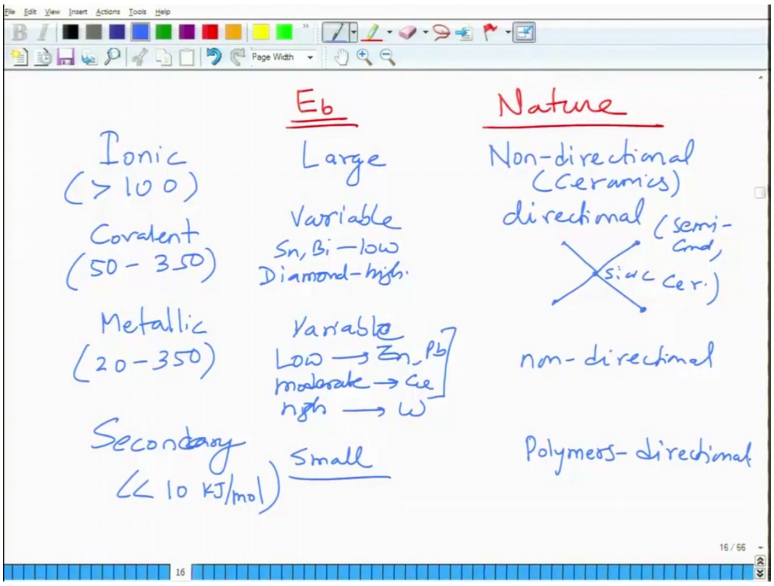

	Eb	Nature
Ionic (> 100)	Large	Non-directional (Ceramics)
Covalent (50 - 350)	Variable Sn, Bi — low Diamond - high.	directional (semi-Cond, Si, C cer.)
Metallic (20-350)	Variable Low → Zn, Pb moderate → Cu high → W	non-directional
Secondary (<< 10 KJ/mol)	Small	Polymers- directional

I would say I would write 3 kinds of bonding ionic covalent metallic and secondary and let us first talk about the bond energy Eb. So, Eb for ionic bond is typically large ok; Ev for covalent bonding is variable, because for something like bismuth or tin it can be low. So, for tin bismuth it is low, but for diamond it is high for ionic bond it is typically large, but there are some compounds like NaCl for which it is not very high, metallic bonding it is variable again low moderate high ok.

The low will be things like zinc lead moderate will be for things like copper and high will be for things like tungsten ok. So, of course, defining the boundary is not very easy and secondary bonding is very small, it will have a bond energy which will be less than 1x kilojoules per mole. So, typically it is less than 5 to 10 kilo joule per mole. In fact, it is even lower than that. So, ionic we are looking at typically values greater than 100 covalent we are looking at values which are between 50. Let us say 350 metallic again will be anywhere from 20 to 350 and these will be very low less than 10.

Of course less than 10, but typically on the lower side they would be less than 1 kilo joule per mole and another thing that you want to know is the nature. Now ionic bond typically is non directional it does not have particular the externality, on the other hand covalent bond is very directional. So, if you look at silicon for example, silicon this is central silicon atom it is 1 bounded by 4 silicon atoms, these silicon atoms are also bounded by 4 silicon atoms.

So, as a result of maintaining these 4 bonds it has to follow a certain geometrical framework and that is why covalent bonds tend to be very ah, because it requires sharing it has to be very direct it is very directional in nature. So, this is silicon or carbon for example, silicon or carbon. So, this is directional in nature typically this you will see in ceramics or this could be semiconductors also as well as ceramics metals of course, is non directional and because of this moderate bond energy that is why metals are ductile also.

If bond energy was very high they would not be deforming very easily. So, most metals are moderate or low bond energy that is very different they deform easily and this is basically secondary bonding tends to be in polymers. F or example, it is its directional because it is between the chains ok. So, that is why it is directional or it could be intra intermolecular as well, all right.

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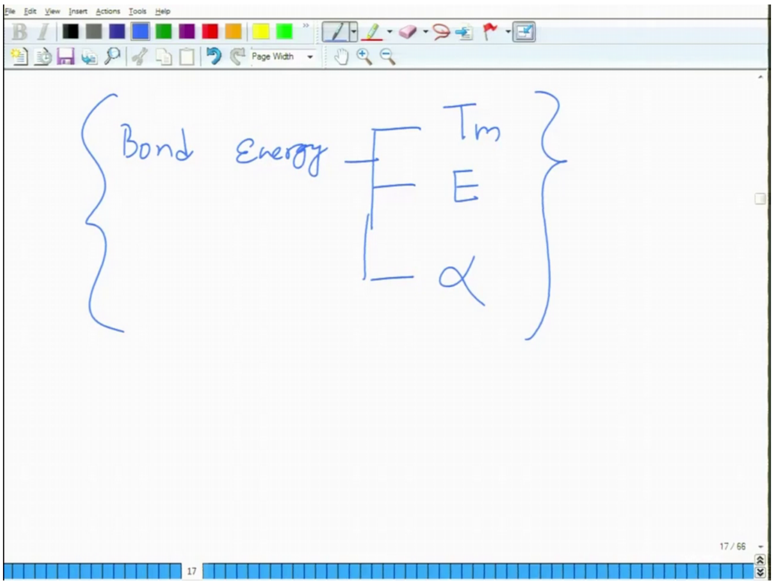

So, some properties of course you know bond energy, I have told you that bond energy has it has correlation with Tm it has correlation with the modulus of elasticity and it has no correlation with alpha. So, I do not need to repeat this you have already been told. So, we will finish this part here and we will move on to the next part.