Nature and Properties of Materials
Professor Bishak Bhattacharya
Department of Mechanical Engineering
Indian Institute of Technology Kanpur
Lecture 14
Ceramics 1

Okay, today we are going to talk about the ceramics. If you remember that ceramics are the 1st group of the materials with which the civilisation began I told you that it is the old stone age that actually kind of make, the beginning of the civilisation and our use of the materials for building various types of artifacts. And so that is the same thing which has come back after thousands of years in a much bigger way into the civilisation.

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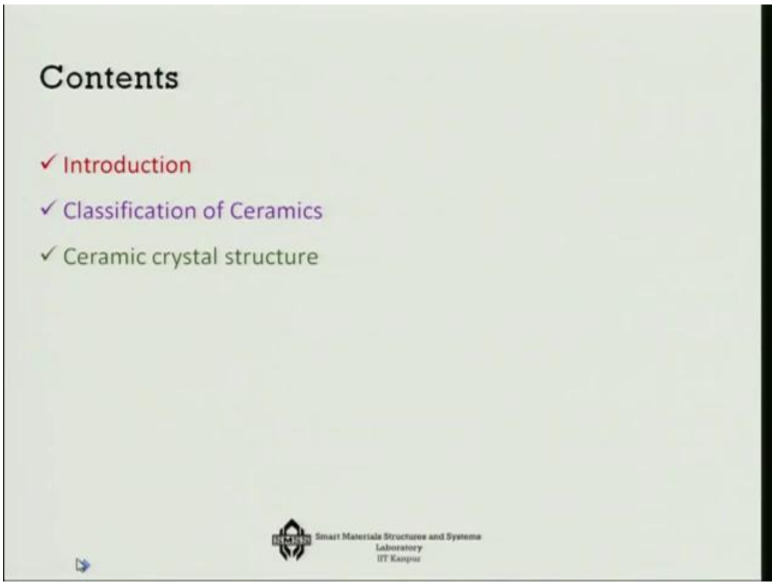

And how it has kind of appeared in our civilisation, how we are today using it, this is what we will be talking about in this series. So 1st we will talk about little bit of introduction, we will talk about the classification of ceramics and then we will talk about ceramic crystal structure.

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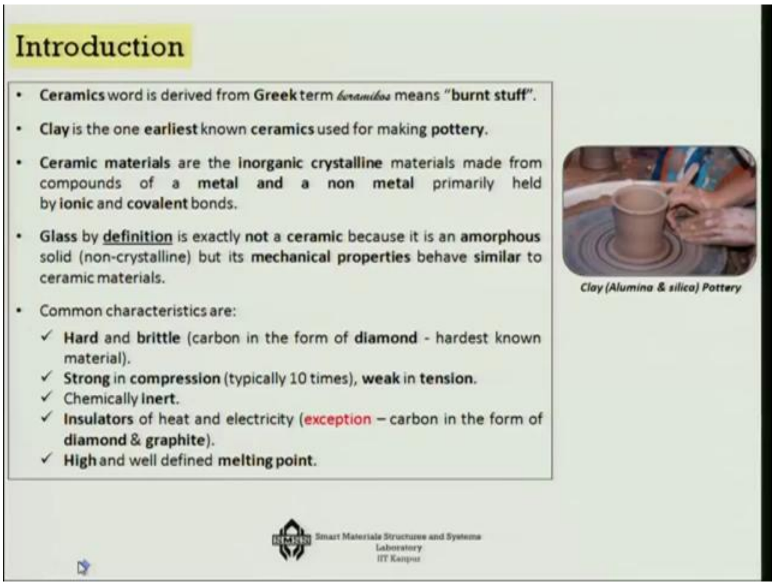

Now the name ceramic as I told you that this whole thing itself is very ancient in nature, the name itself is also having a very ancient root because it is derived from a Greek term "Keramikos", which means actually burnt stuff. And in earlier days when we used to talk about something like ceramic, ceramic was always associated with pottery. So clay is the earliest known ceramic which are used in potteries and that is mostly Alumina and Silica type of material.

Now, ceramic materials are definitely by root, they are actually inorganic crystalline materials and that is very important, which are made from compounds of one metal and a non-metal. So if it is a metal non-metal combination, then that types of ceramics are generally having ionic bonds. And if it is non-metal-non-metal combination, then it is generally having covalent bonds.

Now, glass is also sometimes attached to the same way with ceramic, but glass by definition is not a ceramic because ceramics have definitely distinctive crystalline structure, but glass is amorphous. However, the mechanical properties of glass even though they are amorphous, they are very much similar to ceramic materials. Some of the common characteristics are, both ceramics and glass are hard and brittle.

For example, carbon in the form of diamond is known as the hardest material, strong in comparison to tension, it is actually and sometimes it can be something like 10 times stronger in compression and then in tension, chemically very inert, so if there are chemically active substances, you can very easily keep ceramics or glasses you can use them to contain, they are known to be good insulators of heat and electricity.

In metals you are always getting free electrons to travel to carry the charges, but in ceramics or in glasses that is not their ionic bond or covalent bonds are very-very strong to absorb electrons, so they are insulators of heat and electricity. Only exception could be of because of the special allotropic form of carbon in diamond and graphite. And generally they have very high and well defined melting point.

Melting point, melting temperature of course is also quite high, in comparison to metals it is even higher in fact, that is many of the re-entry vehicles you will find like space shuttles and other things comes back from the space and hence it is subjected to very high temperature, you will see that invariably the surface is made of ceramic tiles, so that it can resist the high temperature.

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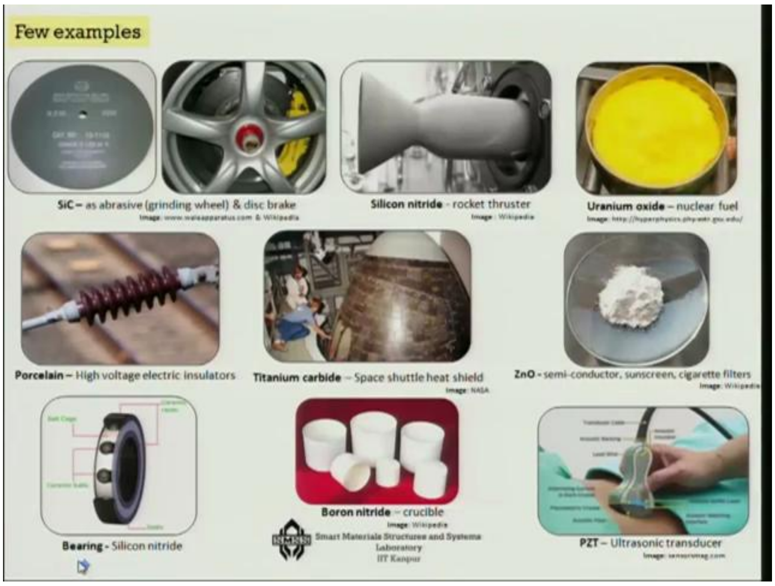

There are many examples, for example the Silicon carbide, which is used as abrasive grinding wheel or you will see it in the disc brake. Then Silicon nitrides, which is used in rocket thrusters, Uranium oxide which is used in nuclear fuels, porcelain very standard in high voltage electric insulators, Titanium carbide space shuttle heat sink, Zinc oxide as a semiconductor, Sunscreen or sometimes even in cigarette filters.

Barings you will get Silicon nitride again, Boron nitride in crucibles and of course Lead Zirconate Titanate one of the smart materials, which is heavily used in the Ultrasonic transducers, so all Ultrasonic tests when you see the crystal that is used inside to generate a high frequency vibration that is nothing but a piezo electric material, which is a ceramic material. Now let us go for different types of ceramics.

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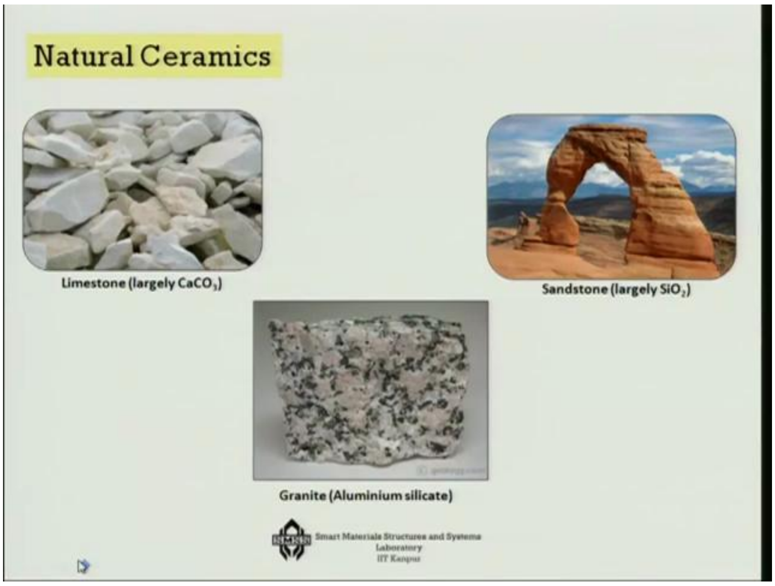

Say 1st of all are the natural ceramics for example, Limestone is mostly Calcium carbonate, Sandstone which is largely Silicon dioxide or Granite which is like Aluminium silicate. So there is a very good actually reserve of ceramic materials in the form of rocks and stones.

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Next is abrasive, typical examples are like Silicon carbide, Tungsten carbide, Alumina aka Or Corundum, Silica sand, they are used to grind or cut away other relatively softer materials.

And they generally because they are used for cutting and sharpening others softer materials, so they have actually very high hardness and pure resistance.

And they are used in form of for example, bonded to grinding wheel by glassy ceramic or an organic resin, something like Tungsten carbide wheel. Or abrasive powders coated on paper or cloth something like sandpapers. So in the form of abrasives they have very large applications for sharpening or shaping or making smooth texture of various types of products.

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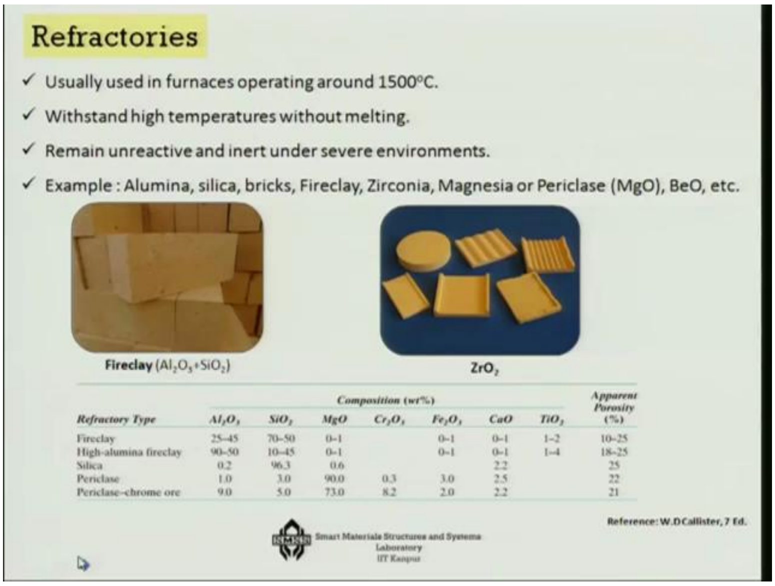

The next one of the biggest application of ceramic materials is in the Refractories. For example, they are used in furnaces operating around 1500 degrees centigrade. If you look at the brick clays when the brick are prepared, the film itself is made of refectory grade of ceramic material. As I told you that they can withstand very high temperature without melting and they remain un-reactive and inert under severe environments.

That is why in addition to not getting molten that inertness makes it suitable for many processes where there are corrosive chemical environments are generated. There are many examples of them like Alumina, Silica, Bricks, Fireclay, Zirconia, Magnesia or Periclase There is a Fireclay which is combination of Alumina and Silica and there is a Zirconia, I will talk about Zirconia later.

So, there are many such things and if you look at it in terms of composition. Suppose Fireclay you will see that most of it is actually Alumina a more importantly of course Silica is also there. In fact, Silica higher than Alumina and then Magnesium oxide, little bit of Iron Oxide, Calcium oxide and Titanium dioxide. If you look at the high Alumina Fireclay, 90% is

Alumina, then 10 to 45 the Silica may vary, again little bit of Magnesium oxide, Iron oxide and Calcium oxide.

Similarly, Silica you will see that mostly it is Silica itself, Alumina comes as an impurity there, then of course Magnesium oxide and Calcium oxide. The other important thing is that the Porosity is generally about 20 to 25% in this type of material. So they are porous and that can reduce the weight of the system at times. In fact, 1 of the Ceramic that I have shown you earlier is actually Aerogel, they are very light because they are highly porous. Okay, so it is also good for various applications like point of view like thermal insulation

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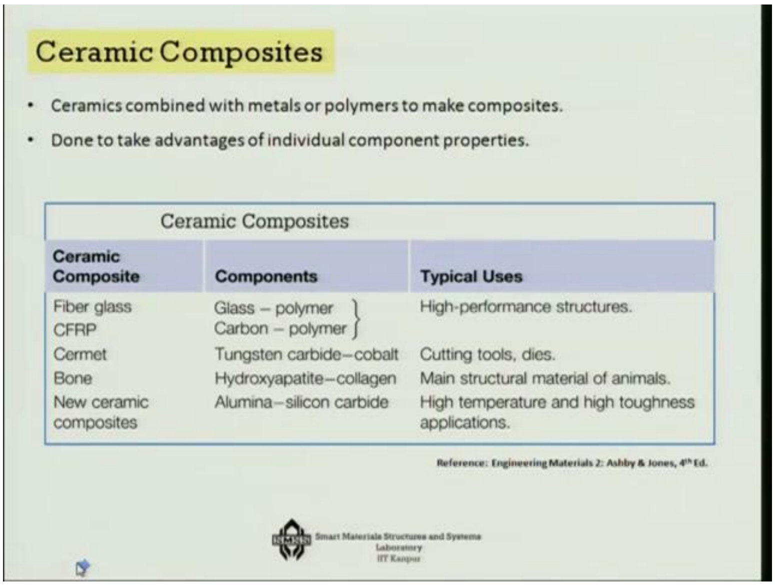

The Ceramic as composites okay, so when we will discuss about composites, we will discuss about ceramics in terms of fibres or also ceramics in terms of matrices. In general, ceramics are very important elements of making composites. You can combine it with metals or polymers to make the composite and that is done to take the advantage of individual component properties.

For example, as fibres, ceramic has quite high modulus of elasticity, so you can take advantage of it and also that in a macro scale, ceramics are generally very brittle. But if you draw them in the fibre form then they are not so brittle and because they are less susceptible to cracks and hence they are very good reinforcement component in composites.

So the ceramic composite like fiberglass is one of the important things, which is a composite of glass and polymer used for high-performance structures. CFRP, carbon is again the reinforcement in the polymer. Cermet, Tungsten carbide is used with Cobalt that is used in cutting tools, then our human bone is one of the best examples of ceramic composites where you have this collagen fibres. So collagen here works like a fibre and hydroxyapatite works like a matrix. There are many new ceramic composites are coming up like Alumina Silicon carbide, which has high temperature and high toughness applications.

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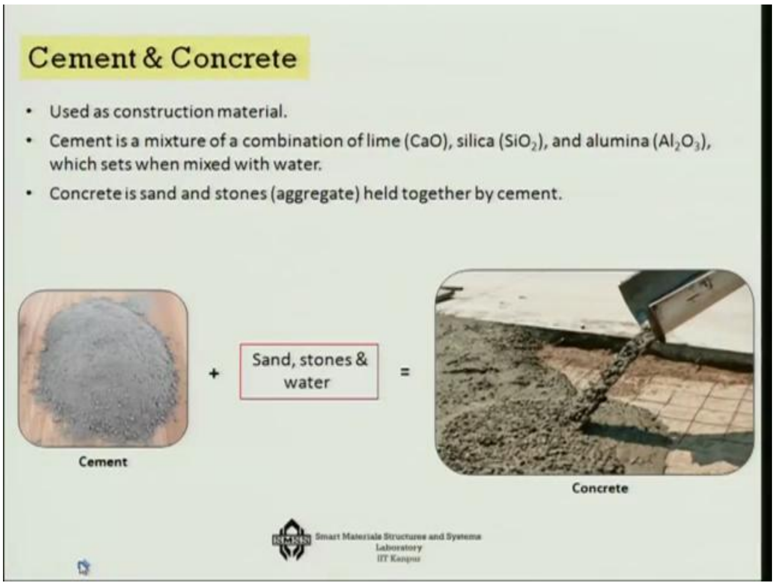

The other vast examples was actually are Cement and Concrete, which is used as construction material. And the cement is basically a mixture of combination of Lime and Silica and Alumina and it sets when it is mixed with water. The concrete is mixture of sand and Sandstone which are like aggregates, which are held together by the cement

So in that sense the stones work like you can say as particle reinforcement in a macro scale kind of similarity to composites, so they work like particle reinforcement. And the cement, the ceramic part of that that is like the matrix in the whole system. So cement and concrete is another very good example of the ceramics.

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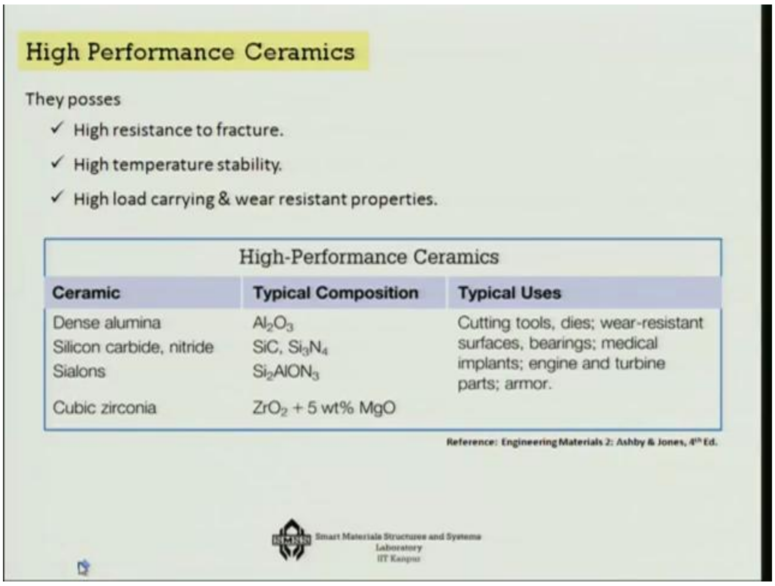

Now there are certain high performance ceramics which has high resistance to fracture and temperature stability, high load carrying and wear resistant property. For example, the dense Alumina, which is used in cutting tools, dyes, wears resistance. Then the Silicon carbide or Silicon nitride is used for surface bearings, medical implants. There is another product which is known as Sialons.

It is a complex composite of Silicon, Aluminium, Oxygen and Nitrogen. And it Sialons are also used in various applications in engineering like engine and turbine parts. Then there is the Cubic Zirconia which is used once again in terms of making cutting tools, dyes and armor sometimes, so these are high performance ceramics. The high performance comes because one has to really it has to undergo very complex chemical processes okay.

And not unlike cement and concrete in this case the ceramics are actually in one of the examples I will show you that the minerals are 1^{st} excavated and then they are very highly filtered, seed and only the pure ceramic materials are actually chosen and then there is a processing and then you make the green circle finally bind them and you get the sample which you use. So all this process, which makes it very expensive as well is it actually adds very high performance parameters to the ceramics.

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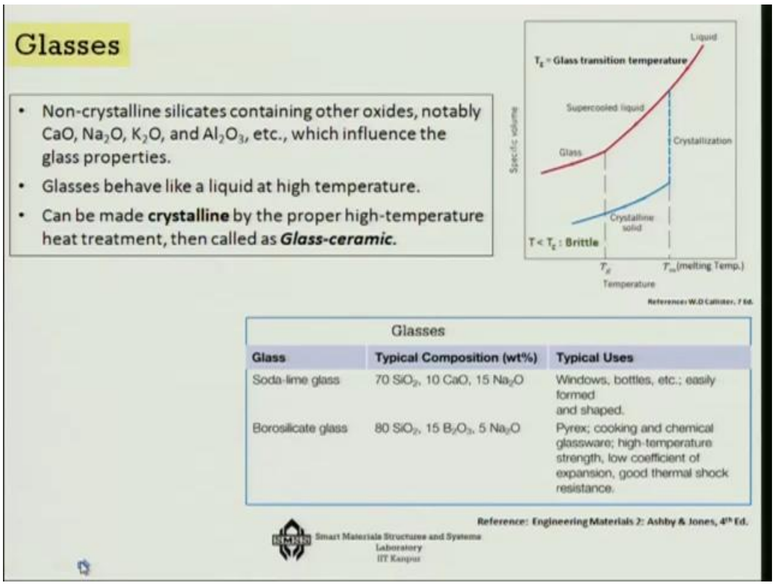

Now, glasses as we have said that they have some very common properties which ceramics although they do not have regular crystal structure, but they are amorphous in nature. But the glasses are actually non-crystalline silicates may be from Calcium oxide, Sodium oxide, Potassium, Aluminium oxide, et cetera.

Many a times actually we make a something which you call Eutectic mixture, so that the temperature required melting it because the key thing is that you have to get various types sides in a matrix ratio and you have to heat it to a high degree of temperature. Now with that, temperature can be reduced or good stoichiometric ratio can actually give a eutectic temperature which is lower and then the whole thing melts.

And after melting, the cooling process is as you can see here that from the liquid if you hold it for a long time at a particular temperature level, then the crystallization takes place and you start to get crystalline solids, but instead of holding it if you start to cool it in fact the first or the better okay.

That means you are simply freezing the fluid, the molecules are moving all around and that mobility suddenly frozen and then that will give you the amorphously glassy structure. And that kind of glassy structure also gives you a very brittle structure mostly because there will be lots of micro cracks that will be there in that super cooling condition.

Now, it this glassy system can also be made crystalline by a high temperature heat treatment. So once again you take it to a very high temperature and when held it and get crystalline form, this is commonly known as glass ceramic. So there are 2 very common types of glasses; Soda lime glass, which is used in windows, bottles and easily forming shaped.

The other one, which is more expensive is Borosilicate glass and that has actually along with the Silica has actually Boron oxide and this is used for Pyrex, cooking and chemical glassware, high temperature strength, low coefficient of expansion and good thermal shock resistance. Then there is a fascinating variety of ceramics, which is known as Piezoelectric electric ceramics.

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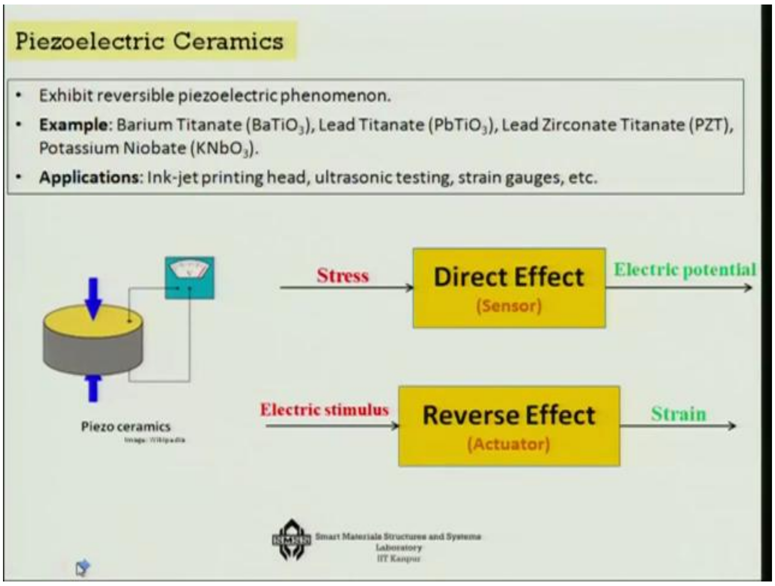

We will certainly devote more time on this, but this is just the beginning of introducing the ceramics, so I will talk very briefly about it now. Now this ceramics are capable of actually generating electricity if you apply mechanical force into it. So you can see it here that you are applying mechanical force and there is a voltage that is generated in the system.

This was actually discovered by the Curie and quite a century before, but now it has lot of industrial applications because of piezoelectric effect, which is very prominent, we call it Giant piezoelectric effect actually in some of these ceramic materials. For example, Barium titanate, Lead Titanic Lead Zirconate or the Potassium Niobate are some of the materials where this effect is very predominant.

So there are 2 types of this piezoelectric effect in the ceramics. One is direct effect, which is used for sensor making like in your many of these cameras you will see it that if there is a stress, then there is a electric voltage that will be generated on the system. And the other is reverse okay that means you apply the electric field and you are going to get strain out of it.

The applications are enormous, some of them are inkjet printing head, ultrasonic testing, strain gauges, various types of sensors, various types of actuators are developed using the piezoelectric ceramics, but there are some very special grade of ceramics. Now we will discuss about the bonding and crystal structure of ceramics.

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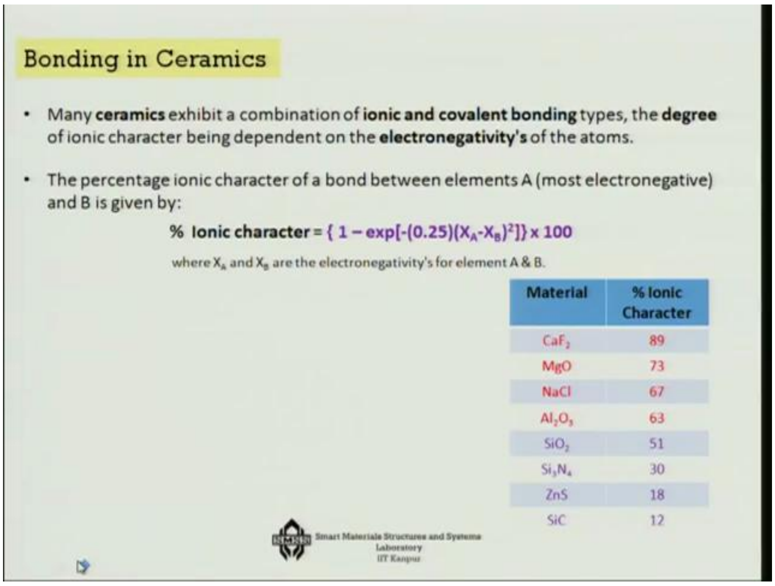

Now as I told you that this bonding in ceramics can be either ionic or covalent bond or can be both actually. So depending on the typical compound, you can actually find out that what is the percentage of ionic character, okay. That means if the elements that are used in the ceramics X A and X B and if the electronegativity, then you can find out that what is the percentage of the ionic character. For example, Calcium and Fluorine, you know their electronegativity so you can find out that it will be 89% ionic in nature.

On the other hand, Silicon carbide you will see that it is mostly covalent bond predominant, so it is about 12% of ionic character. So the elements that makes these ceramic compounds, their electronegativity basically determines that whether it is going to be predominant the ionic bond or whether it is covalent bond. If they are very far apart that means if X A - X A is very high in terms of electronegativity, then will be predominantly ionic otherwise, it will it will be the other way round that is covalent bond.

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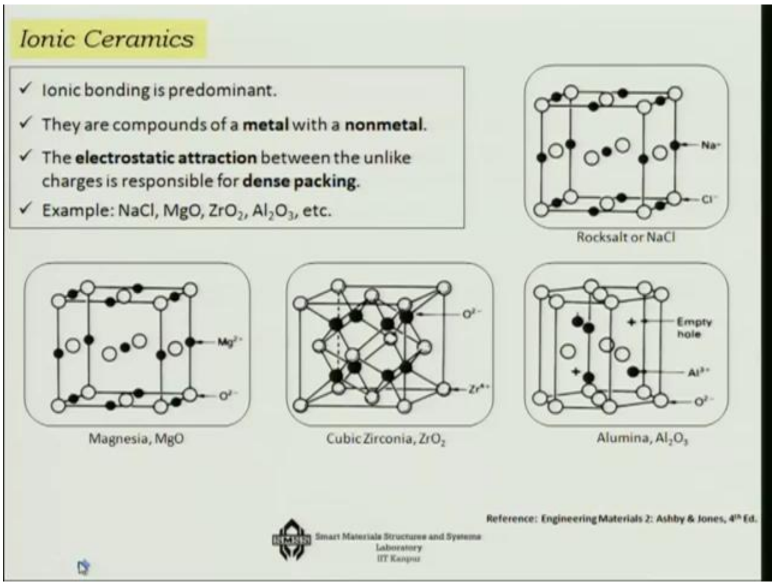

There are very popular examples of ionic ceramic; the common salt that you take is Ionic ceramic Sodium chloride. Then of course Magnesium oxide, Zirconia, Alumina, these are all ionic ceramics. They have actually metal non metal combination and that is what makes these bonds actually the ionic bonding and they are generally because there is electrostatic attraction between the unlike charges, they have very dense packing.

So the density would be very high, so this is the structure of common salt, rock salt, Sodium chloride as you can see, then Magnesia, even Zirconia, which is little more complicated and Alumina, so that is about the ionic ceramics. Now if it is in non-metals for example, Carbon and Silicon then it may create covalent ceramics.

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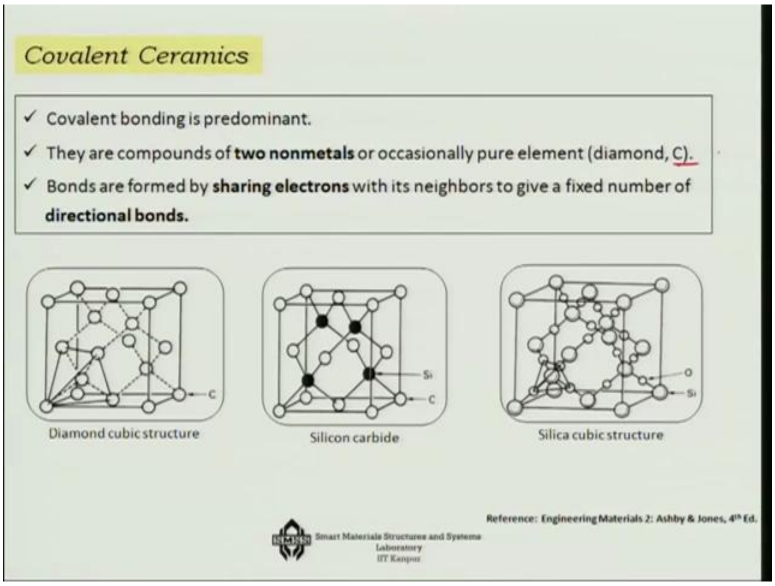

So here the bonds are formed by sharing electrons with its neighbors to give a fixed number of directional bonds because covalent bonds are directional in nature for example, Diamond, Silicon carbide, or Silica cubic structure. Because the bonds are directional, that means these materials even though they are strong, they will be anisotropic because they are along the direction of the bond you expect most thickness than across of the bonds.

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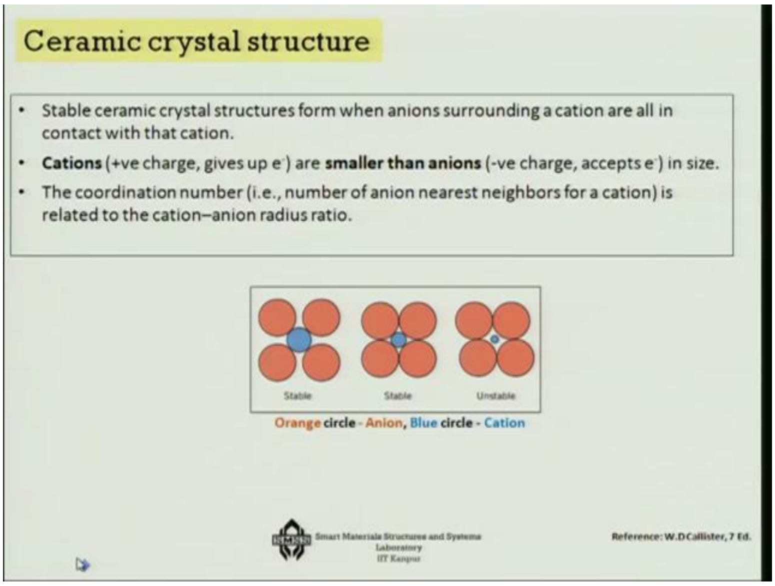

Now, some ceramics crystal structures are actually more stable than the others. Why, because if you look at the ionic bonding based ceramic structures, then you have cations and anions and generally the cations are actually smaller than anions, like there is a cation here and all around there of these anions here okay.

So because this fellow is there in the middle there are various ways in which you can get a 3 dimensional structure, but the most stable will be if they are in touch with each other. If not for example, in this case they are not in touch with each other, whereas you can see these regions, so that may not give stability. And definitely if this happens that anion is not touching the cation then definitely there will be an unstable situation here.

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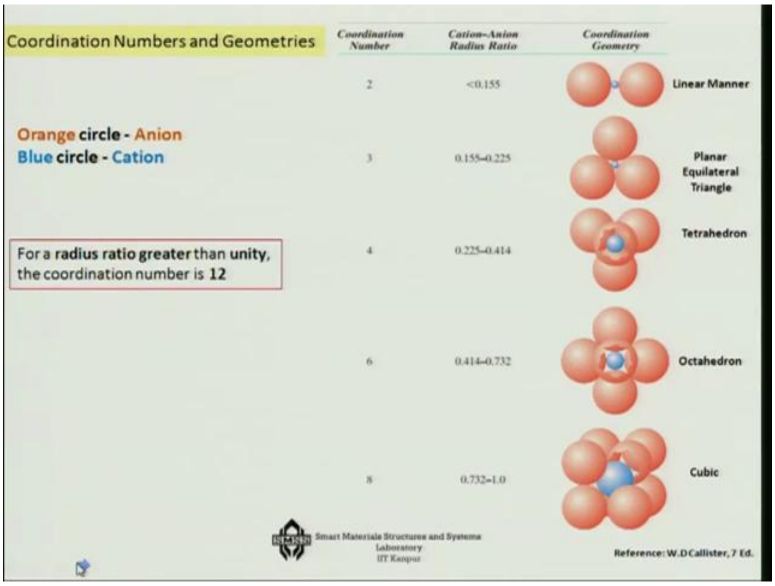

So let us look at it in a much more variations for example, from the coordination number point of view. If there is a linear structure, then you get a coordination number of 2 of anion cation, if it is a planner equilateral triangle something like that, you get a slightly higher coordination number, you get a better packing. If it is tetrahedron that is you can see that all figure them and anion is sitting inside, you get a better coordination number, even better Octahedron 6 or Cubic you get the maximum about 8, so that is how the packing actually changes.

And depending on various types of cation-anion combination, you get actually various types of packing systems, it can go as high as up to 12 in fact so we have shown here up to 8.

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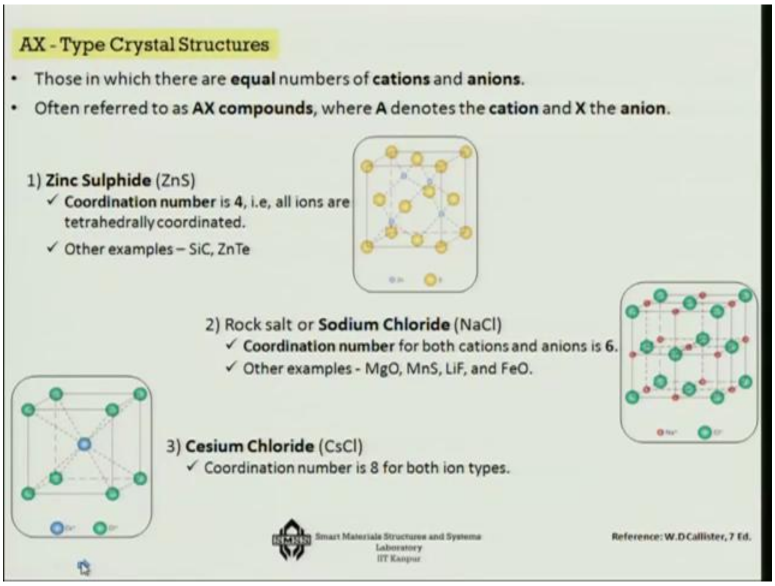

The common crystal structure in ceramics is AX type of a crystal structure, where there are equal numbers of cations and anions that can be referred as AX compounds, where A denotes the cations and X denotes is the anion. For example, Zinc Sulphide equal number so and the coordination number in this case is 4, all ions are tetrahedrally coordinated. There can be other examples like Silicon carbide or Zinc Tallium, so these are similar to Zinc Sulphide in terms of AX compounds.

Other types of AX compounds are Sodium chloride, okay Rock salt and here the coordination number is higher, it is about 6, there are other examples of these types of rock salt structure like Magnesium oxide, Iron oxide, et cetera. Then Cesium Chloride is the 3rd type of system, which has even higher coordination number among the AX type of structures and there are both types of the systems, both shows close to 8, so this is the highest coordination number in the AX structure.

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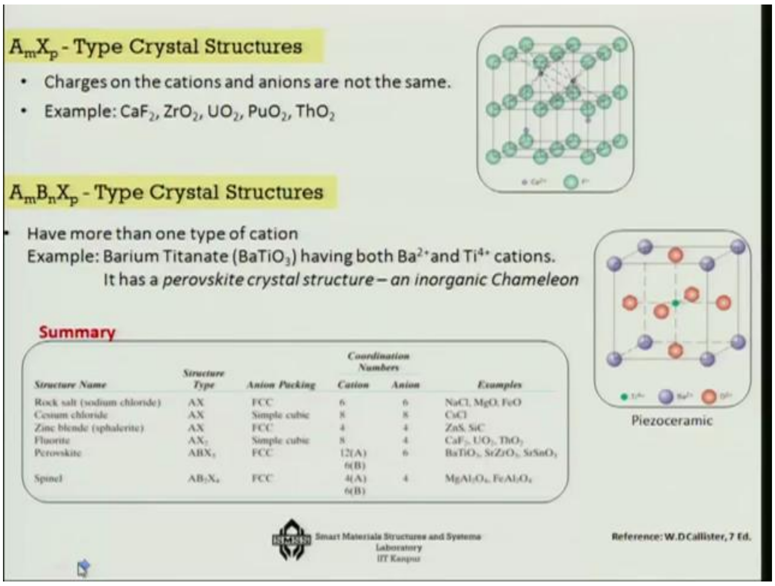

Now, the other possibilities actually A m X p type that means you do not have equal numbers of cations and anions, they have unequal numbers of them. For example, Calcium chloride, Zirconia, okay Thoria, etc, many of these radioactive materials, they belong to this group A n X p group. And the 3rd type, which is even more complicated, is actually A m B n X p group, where you get actually more than 1 type of cation.

Like in distributed Barium and Titanium, 2 cations and oxygen as one anion, so this is also known as Perovskite named after a Russian geologist. And many piezoelectric materials actually show this type of 2 cation system A m B n X p type of a system.

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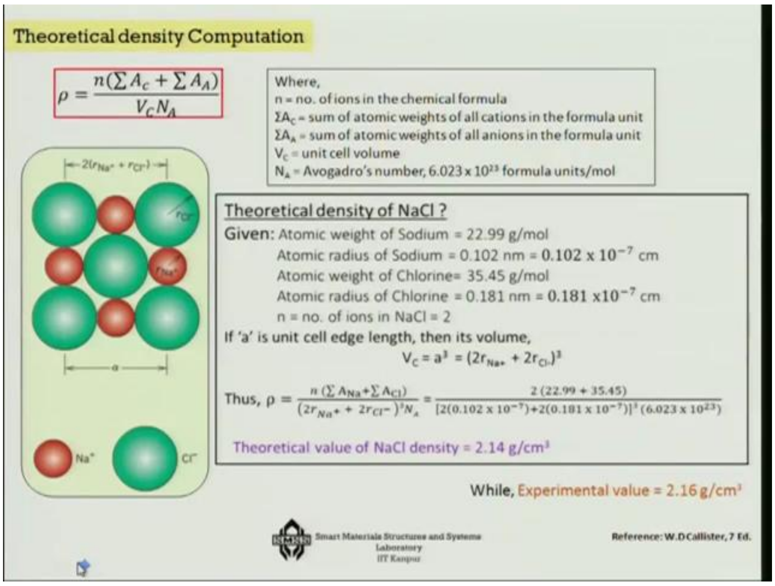

Now, how do I use this to compute theoretically the density of a ceramic compound? So the information that we will require there is that first of all number of ions in the chemical formula, I will explain it soon with the help of an example. And sum of the atomic weights of all combine, some of the atomic weights of all anions, we need cell volume, Avogadro's number.

So let us look into this particular example that can we find out the theoretical density of sodium chloride okay rock salt. What is known to us? What is the atomic weight of sodium? That is 22.99 gram per mole, what is the atomic weight of Sodium that is also known to us about 0.102 nanometre 0.102 into 10 to the power - 7 centimeters, whatever we will put it.

The atomic weight of Chlorine is 35.45 grams per mole and atomic radius of chlorine is bigger, it is about 0.181 nanometre, so this is the anion which is bigger. So as you can see here that these green ones are the Chlorines okay that is your 0.181 nanometre and orange ones are the Sodium okay.

Now the number of iron in NaCl are actually 2 okay Na + Cl -, and if A is unit cell edge length, then what is its volume of you look at it that if you look at the structure of it as you can see here that the this half and this half makes it as double of radius of the Sodium atom and then a full diameter of the chlorine, so that is the unit cell size, so the cube of that that is what is our V c, so now we can find out what should be the density.

The number of ions is 2 that is that 5, the atomic weight if you look at it, cation and anion, so you have 22.99 gram per mole of sodium, 35.45 gram per mole of chlorine of equal proportion, so I can sum it up. And then the size wise you have the that is the size okay that is the unit cell size multiplied by the Avogadro's number because the here you have this in terms of moles.

So the number of that comes in the Avogadro's number, the number of molecules that you have to actually divide and then you are getting the Sodium chloride density as 2.14 gram per centimeter cube and the actual experimental value is about 2.16 grams per centimeter cube.

So that means we are pretty close in terms of the estimation of Sodium chloride in this manner provided that what is the chemical formula of a material and what is the crystal structure of the material, you can actually find out what is the theoretical density of a compound okay.

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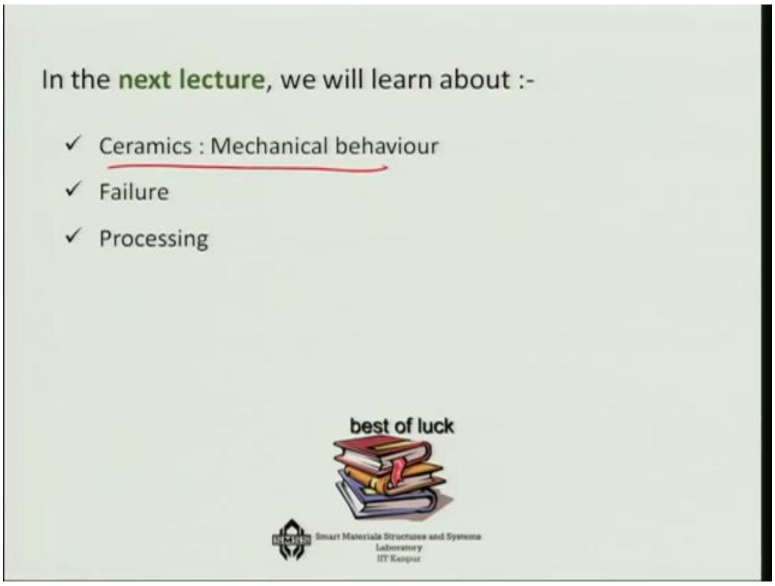

So this is where I think we put an end and in the next lecture we are going to talk about the mechanical behavior of ceramics, we are going to talk about its failure and processing of various types of ceramic materials, thank you.