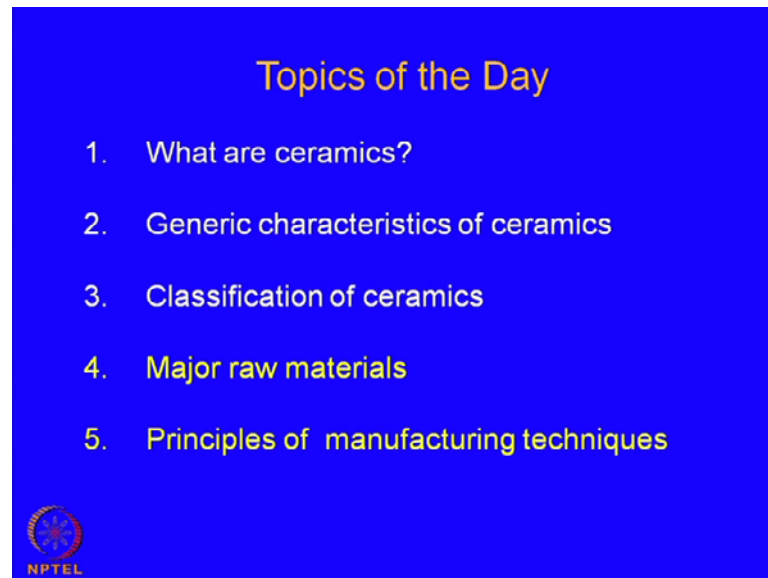


Advanced Ceramics for Strategic Applications
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Lecture - 2
Introduction (Contd.)

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Topics of the Day

1. What are ceramics?
2. Generic characteristics of ceramics
3. Classification of ceramics
4. **Major raw materials**
5. **Principles of manufacturing techniques**



This is the continuation of my earlier lecture, the so called introductory lecture, where I try to introduce the subject and the scope of the subject, the materials to be covered, the distinction between traditional as well as advanced ceramics. In my earlier lecture, I started with some topics like definition of ceramics and then we discussed the generic characterization of the ceramic materials, classification of ceramics; this part we have just completed, but two more topics, which I intend to cover could not be covered. So, in this lecture, I will be covering these two points. The major raw materials, how we can get the raw materials for both for traditional ceramics as well as advanced ceramics and then basic principles of manufacturing techniques as far as the ceramics is concerned. We will be discussing these points later on as an individual lecture. But now for the time we will give you some introductory comments.

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Raw Materials (For Traditional Ceramics)

- 1. Plastic materials**
 - Assist forming process (deform easily without rupture, retain the imposed shape)
 - Example: Clays, talc.
- 2. Fluxes**
 - Melts at a relatively low temperature, reacts with other components, producing a viscous (glassy) liquid, which act as a hard binder on cooling.
 - Example: Feldspar.
- 3. Fillers**
 - Provides a rigid component to aid in forming and firing.
 - Confer some very important physical properties (i.e. thermal expansion).
 - Example: Silica, calcined clay (grog), alumina, lime etc.

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Raw materials, particularly for the traditional ceramics and normally naturally occurring raw materials, they are available in nature in different form of minerals. We purify them to some extent and just directly use them for processing of different products. So, what are those products? There are there three components of natural traditional ceramics. One is called the plastic materials. It has a property of deformation. Once you make or once should add some water to this kind of minerals, particularly called clay minerals containing kaolin, talc and so on. When you mix them with some water, it forms a plastic mass. This plastic mass can be deformed without much pressure. Even with hand pressure, you can deform them and it will not crack.

So, the material, which is basically brittle ceramics materials as we have discussed are basically brittle, but if you make a kind of mixture or fine powder with some amount of water, it forms a plastic mass and it can be deformed quite easily. However, there is only specific type of raw materials, which produces this kind of plasticity and they are called plastic materials or plastic raw materials. All ceramics materials do not produce or do not give rise to this kind of a property. That also we will discuss. So, it is the clay minerals, which is normally give rise to this property and they are called plastic materials.

So, they assist in forming process, deform easily without rupture, and retain the imposed shape. Examples, as I just mentioned, with the clay, kaolinite and talc. So, that is one of the major components of traditional ceramics. The second component of the traditional

ceramics is called fluxes. There again, raw materials available from nature. Some minerals and their property are or their properties are they melt; they have relatively low melting point, and reacts with other components of the mixture. For example, the plastic mass, a clay, and produce a viscous or a glassy liquid. So, when you fire of them or heat them at high temperature, everything does not melt. Only the fluxes melt easily and they form a glassy mass. So, this glass also acts as a binder, which acts as a binder on cooling. So, the liquid, the glassy as it is known is a viscous liquid and on cooling, it solidifies and binds the rest of the (()). So, fluxes is the second component of the traditional ceramics products or raw materials for the products and the example is feldspar. When the composition and other things we will discuss may be at a later stage, but this materials is basically containing some alkali metals like sodium oxide or potassium oxide. So, (()) that is why the names are (()) per a show (()) feldspar per and they acts as a flux.


The third component is called fillers, which do not melt so easily and at the same time, do not produce the plastic mass when it is mixed with water. So, this is actually brittle material, but hard material and therefore, it produces or develops strength after firing (()). It provides the rigid component to aid in forming and firing because this is the forming. One step is forming and we will discuss the basic principles of fabrication in a few minutes. So, this is the filler material and confers some very important physical properties, for example, thermal expansion, strength and so on.

The example is actually sand. The examples are actually sand or aluminum oxide or sometimes lime or even a fired material of this plastic mass, the clays, which are called grog. So, these are actually brittle material, do not have the plasticity, but provides the strength to the body or to the product, which we are trying to make. So, these are three different raw materials primarily used for traditional ceramics. One aspect must be noticed or must be remembered that all these raw materials are actually available in nature. We do not have to synthesize specifically or produce these compounds specifically for the purpose. They are available in nature. Just we can collect it from the mines and purify it to some extent, little bit is needed, so that the unwanted component of the materials are excluded and purer variety of the particular compound is used as raw material for traditional ceramics.

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Specific Compounds under Electroceramics Group

Function	Application	Specific Compounds
Electrical	Multilayer Capacitor, Microwave capacitors	BaTiO ₃ , SrTiO ₃ , TeO ₂ , Ba(Mg ₁₀ Ta ₂₀)O ₃ , Ba(Mg ₁₀ Ta ₂₀)O ₃ , BaTi ₄ O ₉ , Ba ₂ Ti ₉ O ₂₀ etc
	FERAM	(Ba, Sr)TiO ₃
	Ceramic Packages,	Al ₂ O ₃
	Piezoelectric Sensor/ Actuator	Pb(Zr _x Ti _{1-x})O ₃ (PZT); Pb(Mg ₁₀ Nb ₂₀)O ₃
	Thermistors, Varistors	NiO, MnO, CoO, BaTiO ₃ , ZnO
	Gas Sensors, Humidity Sensor	SnO ₂ , ZnO, MgTiO ₃
Magnetic	Oxygen Sensor and Solid Oxide Fuel Cell	ZrO ₂ (La, Sr)MnO ₃ , LaCrO ₃
	Miniature Transformer Core Microwave Magnetic Devices e.g. circulator, isolators, inductors,	(Ni, Zn)Fe ₂ O ₄ (Mn, Zn)Fe ₂ O ₄
	Recording media and heads, ferro-fluids	γ-Fe ₂ O ₃ , CrO ₂



However, the situation is quite different, if we are talking about advanced ceramics. The very basic characteristics of the advanced ceramics, particularly the raw materials of the advanced ceramics are they are very pure. They are pure oxides, pure compounds, pure carbides, pure nitrides, pure silicides, and borides. So, they are individual compounds and many of them, except oxides, many of them do not occur in nature. Therefore, you need special represent techniques or synthesizing techniques to prepare these oxides. Because, until and unless you get these materials in pure form and in compositions or the desired compositions or the design compositions, they do not produce the right kind of property, which we are looking for.

Therefore, when we are talking about the raw materials for the advanced ceramics group, all of them, most of them I would say, most of them are synthesized. You need different techniques to prepare them. But, the examples of the compounds, particularly the oxides, when you are talking about electro ceramics group, that is one sub group of advanced ceramics, here is a least of the compounds which are useful and we exploit different properties to make different devices like this. If you are talking about the electrical properties, one application area is multilayer capacitors or microwave capacitors. As we have discussed, most of the oxides have insulators. But then every oxide or every compound cannot be use as a multilayer capacitor or a microwave capacitor. They need certain specific properties. These capacitors materials which can be used for multilayer capacitors, we will discuss the exact details of the multilayer capacitors and what are the

characteristics required for this particular device at a later stage. But, for the time being, let us see what are the different compounds normally used for multi layer capacitors, because these compounds are known to have very high dielectric constant. Not only they are insulators but they have very high dielectric constant. So, one of the very important compound, once again not available in nature, but can be synthesized by special techniques is barium titanate. Barium oxide and titanium oxide together forms a compound, which is called barium titanate. A similar material is also strontium titanate. Barium is replaced by strontium and therefore, we get another compound strontium titanate. So, these are two mixed oxides, while there is a simple oxide like tantalum oxide also can be used as a capacitor material because of its high dielectric constant.


Now, if you talking about microwave capacitors, they need very another very important property because the energy loss at very high frequency is like microwaves. It should not be very high. Not only that, that means the dielectric loss must be very low. The higher is the frequency, that is very critical parameter to be considered. Normal multilayer capacitors like barium titanate or strontium titanate is normally not used in microwave capacitors, but one uses more complex oxides with some different kind of composition and stoichiometry, like barium magnesium tantalate, barium magnesium tantalate another compound with different compositions. I think there is a mistake. One should be titanium and one should be titanium and another should be tantalum.

In addition to that you have barium titanium oxide, another stoichiometry and this also another stoichiometry. So, these are some of the materials of specific composition, specific crystal structures and so on, and defect chemistry, all these things are important to give rise to microwave properties. There is another device, which is very common in the electronics these days, which is called a FeRAM. The random access memory and fe stands for ferroelectric, ferroelectric random access memory and the material which is used for that purpose is barium strontium titanate. It is a solid solution of barium and strontium titanates. Normally, it is prepared or it is used in the form of thin films and not in bulk material.

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	Ceramic Packages,	Al ₂ O ₃
	Piezoelectric Sensor/ Actuator	Pb(Zr _x Ti _{1-x})O ₃ (PZT); Pb(Mg ₁₀ Nb ₂₀)O ₃
	Thermistors, Varistors	NiO, MnO, CoO, BaTiO ₃ , ZnO
	Gas Sensors, Humidity Sensor	SnO ₂ , ZnO, MgTiO ₃
Magnetic	Oxygen Sensor and Solid Oxide Fuel Cell	ZrO ₂ (La, Sr)MnO ₃ , LaCrO ₃
	Miniature Transformer Core Microwave Magnetic Devices e.g. circulator, isolators, inductors,	(Ni, Zn)Fe ₂ O ₄ (Mn, Zn)Fe ₂ O ₄
	Recording media and heads, ferro-fluids	γ-Fe ₂ O ₃ , CrO ₂



Then, you have ceramic packages. Well, we will discuss what is the purpose of the ceramic package, how it is fabricated, and what are the basic requirements of ceramic package. But, for the time being, it is insulating property of the ceramics, which is utilized for ceramic packages. In fact, ceramic packages are used as an envelope for the silicon micro chips. All the silicon micro chips have to be covered with some kind of a cover and it should be isolated from the environment, because it is very very sensitive. Not only that, but there is a need for electronic connectivity between the micro chip and the outside circuit. So, ceramic package provides that particular function. It actually insulates different connections or connecting wires or connecting strips between the semiconductor chips and the outside circuit and at the same time alumina is also fairly high conducting, thermal conducting compared to other material. It is also chip.

So, alumina is the material of choice for ceramic packages. Extensively used in micro electronics industry. Other property of the ceramics is also important. For example, piezoelectric property. I mentioned earlier that piezoelectricity means, we generate voltage, electrical voltage as we apply mechanical stress. So, those materials are again very useful or many sensors as well as actuators and these are the compounds; barium zirconium titanium oxide or barium zirconium titanium or in short p z t or lead magnesium manganate. These are some of the materials which possess piezoelectric property and they can be used for the sensor and actuators. The reverse is also true. As I just mentioned, piezoelectricity means you generate voltage against mechanical stress.

The converse is also true. You apply electric field and generate mechanical strength. So, the dimension gets changed as you apply the electric field. So, by those forces, you can make a vibration. You can make them to vibrate. You can make the material to vibrate by applying an electric field. So, you can produce noise. Conversely, you can sense the noise. The noise can be sensed by this kind of sensor.


Thermistors and varistors, these are another variety of electronic devices. Once again utilizes some of the properties of ceramics and ceramics oxide. For example, the semiconducting property of nickel oxide, manganese oxide, cobalt oxide and barium titanite, and doped barium titanite. This is not pure barium titanite. Barium titanite, if it is doped with some amount of other oxides, it can be semiconducting. So, this can be used as what we call thermistors, where the resistance changes quite significantly with temperature. Varistor is another variety of material, where the register changes with voltage and that is again has a very important implications or application area, particularly for (()) protection. So, the material which is used for this purpose is zinc oxide. Semi conducting property of some of the oxides can also be used for sensing the presence of gasses, particularly, the reducing gasses or combustible gasses. So, gas sensors can be used by, for the use of exploiting the conductivity, variation of conductivity, electrical conductivity as a function of gas concentration of oxides like tin oxide, and zinc oxide. Then humidity sensor. Humidity sensor can also be measured. Humidity can be measured by a porous ceramics like magnesium titanate or aluminum oxide. There, we actually measure the variation of capacitors as a function of, create the humidity of the environment.

You can make oxygen concentration sales or electro chemical sales using some of the solids, from the solid oxides, like particularly zirconium dioxide. Zirconium dioxide has a very interesting property. It is, appears z partially stable zirconium is a tough ceramics, where stabilized zirconia, fully stabilized zirconia which some calcium addition, calcium oxide addition or yttrium oxide addition, it generates or enhances the oxygen ion conductivity. So, it is no longer an electronic conductor, but an oxygen ionic conductor. So, any ionic conductor can be used as an electrolyte and that electrolyte can be used to fabricate the electro chemical cell.

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Specific Compounds under Electroceramics Group

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	FERAM	(Ba, Sr)TiO ₃
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	Miniature Transformer Core Microwave Magnetic Devices e.g. circulator, isolators, inductors,	(Ni, Zn)Fe ₂ O ₄ (Mn, Zn)Fe ₂ O ₄
	Recording media and heads, ferro-fluids	γ-Fe ₂ O ₃ , CrO ₂



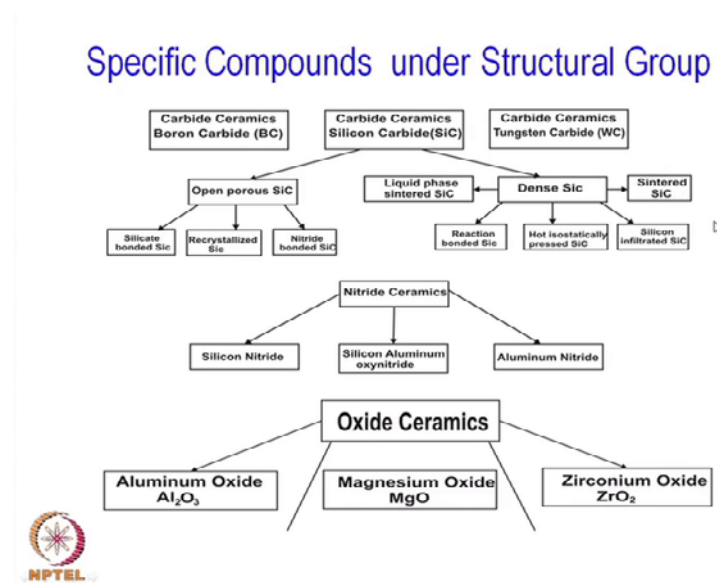
Now, in this case, this oxygen cell, oxygen concentration cell is used to major the oxygen concentration of different environments like gaseous environment or even it can be used in liquid steel. The oxygen content of the liquid steel can be used. So, zirconium is a very important oxide in the area of advanced ceramics. There is another device again using zirconium, it is called solid oxide fuels cell. That solid oxide fuel cell actually generates power. As you burn some fuel electro chemically, not thermally, but electro chemically, if you burn some fuel, you allow oxygen and fuel to combine electro chemically and as a result, you can generate some e m f. So, that is can be used as a source of power and this is one of the very important application area for non conventional sources and where hydrogen can be burned and you can generate power without polluting the environment. We do not generate carbon dioxide by combustion of petroleum gas and so on. So, that is another area of ceramics applications of electro ceramics, which is coming up. Lanthanum chromate is also a part. It is used as an electrode for this solid oxide fuels cell.

In addition to be electrical properties, we have a host of a magnetic property or magnetic materials. They may be primarily used for miniature transformer core. In fact, with the use of ceramic magnetic, the transformer or the size of the transformer have come down by many (()) compared to the so called transform cores made of iron silicon alloys. So, instead of iron silicon alloys, of course iron silicon alloys is still used in very high power transformers, but miniature transformers, for the purpose of different electronics

component, I think the only solution is ceramic magnets. Either in the radio frequency range or in the microwave range. So, these of the ferrites. It is called as ferrites having a final structure. We will discuss these structures later on, but these are the compounds.

It is a solid solution of nickel ferrite and zinc ferrite. In fact, $\text{NiO} \cdot \text{Fe}_2\text{O}_3$ or zinc $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$, they form a solid solution of these two ferrites and is used extensively in the microelectronic circuits. Similarly, is the case with magnesium ferrite. Well, magnetic tapes and magnetic recording is another very important area of electronics industry and the material, once again the oxides and we can classify them again advance ceramics are $\gamma\text{-Fe}_2\text{O}_3$ and chromium oxides Cr_2O_3 . These are materials normally used for the recording media and recording heads. Of course, there are other materials these days can be used. It is in the form of fine powder dispersion or in the form of a tape. So, these are different compounds. I am basically giving you the idea, what are the different compounds when you talk about advanced ceramics, particularly, this sub group of electro ceramics.

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We have also another sub group. I have shown this picture in slightly difference context. But, here we have considering, basically the materials. The specific compounds under structural group, where the mechanical property is important. There are oxides no doubt. Here are some of the oxides, pure oxides. Aluminum oxides, magnesium oxide, zirconium oxide, I am just mentioning because of the toughness and these are insulating


materials and fairly strong and cheaper materials and these are mostly available from nature. Aluminum oxide, magnesium oxide, zirconium dioxide, they are all minerals which can be obtained from the natural resources, but they need some purification. They need some beneficiation; they need because impurity content affects the property quite significantly. So, the impurity must be removed. So, once you get from the natural resources, it needs different kind of purification techniques. Mostly chemical purification and mineral ratio. So, mineral ratio followed by chemical purification is the normal technique by which we can get these raw materials from nature.

However, there are host of other structural ceramics compounds or structural ceramics used, the compounds used in structural ceramics. I mentioned some of them earlier like boron carbide, silicon carbide, and tungsten carbide. Then you have difference forms of silicon carbide and aluminum nitride, silicon aluminum oxynitride, and all these things do not occur in nature. So, you have to prepare them specially to get these compounds. So, the raw materials, the preparation of the raw materials itself is a technology there. So, it just cannot be done only by beneficiation or chemical purification. It needs synthesizing. Synthesizing the compounds artificially. So, silicon and carbon has to be allowed to react together or silicon and nitrogen has to be allowed to react, aluminum and nitrogen has to be allowed to react under certain conditions and then only you can get these pure compounds. Then afterwards they can be fabricated following certain rules and get the different shapes, desired shapes either in bulk form or in the form of thin films or thick films or some strips depending on what is the requirement of the particular application.

So, the basic difference between the raw materials of the traditional ceramics and the raw materials for the advanced ceramics, one can conclude that all the raw materials for the advanced ceramics have to be specially prepared and synthesized following different synthesizing techniques, which I will discuss in a few minutes, whereas, the raw materials for the traditional ceramics are available from nature. Normally available from nature with little bit of modification one can go to the product. That is the basic difference as far as the raw materials are concerned.

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PREPARATION TECHNIQUES	
➤ Pure Oxides:	Chemical Purification Sol-gel Synthesis Hydrothermal Synthesis Spray Pyrolysis, CVD
➤ Mixed oxides:	Solid state synthesis Co-precipitation Sol-gel synthesis Hydrothermal synthesis, CVD
➤ Non-oxide Compounds:	Carbothermal Solid – gas reaction Solid state reaction Decomposition organo-metallic comp. CVD



Now, we come to the preparation technique. What is the basic preparation technique used for both for traditional as well as advanced ceramics. Well, if you are talking about pure oxides, primarily for the advanced ceramics group, which I have just discussed, there are different techniques by which one can make high purity oxides. Chemical purification is one of course one root. For example, if you are talking about aluminum oxide, you can just take the oxide, then remove iron oxide and purify it properly, so that, pure form of aluminum oxide can be available to you, even for the advanced ceramics material or advanced ceramic problems. There is a technique. We will once again discuss this thing later, what are the different consideration what is the basic synthesis technique. But, there is a technique called sol-gel synthesis solution followed by gelation. So, it is a solution chemistry root. You take the elements in the solution form and it may be an aqueous solution, but many a times, most of the times, it is non aqueous solution and alcoholic medium and then slowly hydrolyzed them, so that, the material or the hydrated material or gel forms in a very form, in a nano structure form and slowly one can heat it to high temperature, so that we can get very fine, almost nano size powders.

One has to remember, for any ceramics product, powders is the starting material. So, you need different sizes of powder, and different morphology of powders. Some may be spherical in size, some are angular in shape, and some may be cuboids or hexagonal structures. So, different materials are available in different geometric forms, but their sizes have to be controlled. Preferred things is, one needs a fine powder as possible.


Finer the particle or starting material, it becomes easier for the fabrication or particularly, it can be sintered or fired at a relatively low temperature. So, lower temperature means you save energy. Therefore, starting materials need to be fired and most of the time, the particles will be finer than 1 micron size and these days, we are talking about nano size particles as well. So, sol-gel is one technique by which we can make either micron size or nano size particles of different oxides or mixed oxides. We will come to that also. Hydrothermal synthesis is another area. It is not sol-gel, but you take a solution and then heat as well as pressurize. So, it is a combination of heating and pressurization. By that process also you can crystallize very fine oxides within the liquid environment or some kind of a liquid process.

Then, there is a two processes called spray pyrolysis and c v d. c v d is short form of chemical vapor deposition. Normally, c v d is also another technique by which one can make fine powders. Spray pyrolysis, you just take some, again a solution and spray it or sprinkle it inside a hot chamber or in a flame, so that, the particles, the droplets immediately gets decomposed in the hot environment and produces the powders, produces the solid particles, which are very fine. c v d is also the same thing. More or less the same thing but slight difference. It is a chemical vapor deposition inside the chamber and you decompose it. The chemical is supplied in a form of a vapor and that vapor at high temperature is decomposed and you get oxides.

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PREPARATION TECHNIQUES

- **Pure Oxides:**
 - Chemical Purification
 - Sol-gel Synthesis
 - Hydrothermal Synthesis
 - Spray Pyrolysis, CVD
- **Mixed oxides:**
 - Solid state synthesis
 - Co-precipitation
 - Sol-gel synthesis
 - Hydrothermal synthesis, CVD
- **Non-oxide Compounds:**
 - Carbothermal
 - Solid – gas reaction
 - Solid state reaction
 - Decomposition organo-metallic comp.
 - CVD

 NPTEL

So, that oxide can be deposited in the form of thin films or thick films and so on. So, you can deposit it on a substrate or you can have freely standing particles. So, these are you use for pure oxides. You have a number of mixed oxides, as I mentioned few minutes back. We need different kind of mixed oxides like barium titanate, spinels or ferrites, nickel oxide, iron oxide, barium oxide, titanium oxide, strontium oxide, titanium oxide and so on. So, they have also to be synthesized following special techniques. One very simple technique is what we call a solid state sintering or solid state synthesis. If you want to make, for example, a barium titanate, you just add barium oxide in the form of carbonate, barium carbonate and then mix it with titanium dioxide and heat it to high temperature. So, at high temperature there is a reaction, high temperature chemical reaction between barium oxide and titanium dioxide and you get a second compound in the form of a mixed oxide called barium titanate.

Similarly, if you want to make a ferrite, a magnetic material, magnetic ceramics, you take Fe_2O_3 , pure form of Fe_2O_3 and then other oxides like zinc oxide, manganese oxide, nickel oxide and so on and heat it to an appropriate temperature. Normally, above 1000 degree centigrade and maybe in a controlled atmosphere to some extent, so that, the stoichiometry can be maintained properly and you get at the end of the firing, you get a compound, mixed oxide compound. So, this is one of the very simplest ways to make mixed oxide and large number of ceramic oxides had been prepared by this technique.

However, one of the difficulties is that, you start with fine powders, but after the synthesis, after the sintering or after the high temperature reaction, these powders will grow and you end up with relatively large sized particles. So, you may not be able to use it properly for its fabrication. Therefore, solid state sintering techniques are not normally preferred these days. Instead, we go for fine powders, so that, the sintering, final sintering, final shaping can be done at a relatively low temperature and also you get much finer grain size. We will discuss these things at a later stage, what is the importance of the grain size, what is the importance of the initial particle size or the starting particle size, all these things we will discuss at a later stage. But, these are the different techniques by which one can make mixed oxide powders.


There are other sol-gels, which had been used for pure oxides. Once again can be used for mixed oxides and the advantage is, you get much finer powders. Sometimes, one can get very fine, but spherical powder, which is very rare occasion actually and in special

occasion, you get to need spherical, you need spherical powders for certain advantages. There is another technique once again from the chemical root not the solid state root. It is called co precipitation, which is very common to the chemists. You precipitate or you take a mixed ion solution, in which both the different ions and metallic ions are present and then you add some precipitating agent, so that, both these ions gets precipitated in the stoichiometry ratio whatever we need. So, by this process also co precipitation has become a very important technique for making some of these synthetic raw materials used in advanced ceramics.

Hydro thermal as well as c v d can also be used. Hydrothermal c v d can also be used for this technique, except that, instead of pure oxide we make mixed oxides. However, non oxide compounds like carbides, nitrides, oxynitrides and so on, they are little difficult to prepare. It is not so easy to prepare them under normal conditions. So, sol-gel and co precipitation, these kinds of techniques are not normally used for non oxide compounds.

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PREPARATION TECHNIQUES	
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➤ Mixed oxides:	Solid state synthesis Co-precipitation Sol-gel synthesis Hydrothermal synthesis, CVD
➤ Non-oxide Compounds:	Carbothermal Solid – gas reaction Solid state reaction Decomposition organo-metallic comp. CVD



Instead, we go for carbothermal reaction. Basically, carbothermal reaction is an oxide mixed with carbon and heat it to high temperature is normally exothermic reaction. By that process, the metal carbides can be formed. That is very common technique for making carbides, whether it is silicon carbide, tungsten carbide and so on, they are mostly made by so called carbothermal process, which is nothing but mixing with carbon and then heating in an environment in order atmosphere, so that, the carbon does not get

oxidized in presence of oxygen. So, oxygen should not be allowed when the reaction is going on. Since, if you are talking about nitrides or even carbides, carbon can be taken in the form of solid carbon or gaseous, may be carbon dioxide, sorry, carbon monoxide or some hydrocarbons. Hydrocarbons can be taken as a source of carbon and then it can be allowed to react with some metals, so that, the carbides can be formed.

Solid state reaction, of course is always possible and in many cases, solid state reactions, for example, if you are talking about a oxynitride, so you can take an oxide and then a nitride, silicon oxynitride if you want to make, then you can make from aluminum nitride and silicon. So, these two can be or silicon nitride and aluminum oxide. So, one can make that kind of solid state reactions. Once again, in all these things, because these are non oxides, oxygen has to be excluded. Oxygen presence, presence of oxygen should not be there and therefore, that is an important criterion. Whatever you do, whether it is a solid state reaction, solid gas reaction, carbothermal reaction, decomposition of organo metallic compounds, this is another, so whatever you do, you have to exclude oxygen. The presence of oxygen must be avoided to make non oxide compounds. It is good; obvious. So, there are many organo metallic compounds, which can be directly decomposed or (()) to form some of these non oxide materials, either carbides, nitrides, silicides, borides and so on. c v d, once again can be used for this purpose.


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MANUFACTURING / PROCESSING OF CERAMICS

❑ Important steps

1) Batch Preparation of Powdery Raw Materials:

- In case of traditional ceramics most of the raw materials are naturally occurring minerals, which need to be beneficiated.
- For advanced ceramics, normally synthetic raw materials (specially prepared powders of different compositions) are used as the raw materials.
- Control of both chemical composition and particle size and sometimes particle shapes are of tremendous importance.

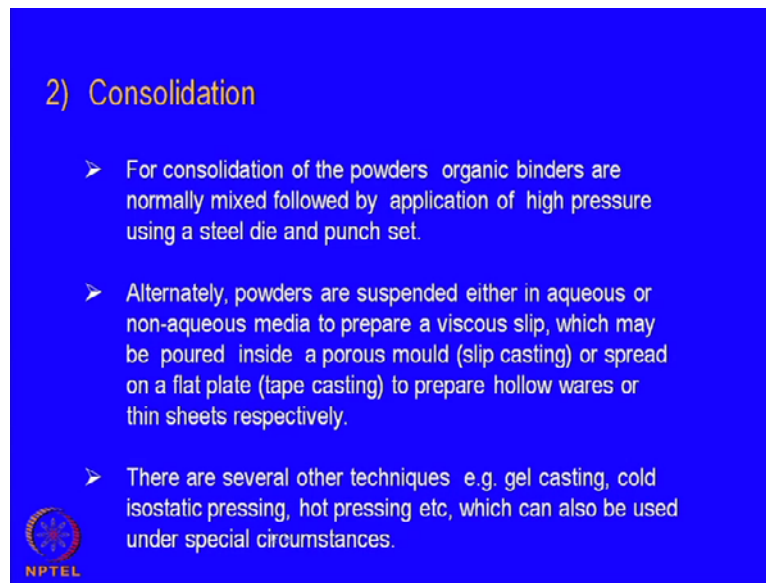


So, having discussed the various type of raw materials, basically the different compounds required for the preparation of the both traditional ceramics and advanced ceramics, let us try to see the basic steps necessary for the manufacturing or the processing of ceramics products or how exactly some products can be made. The important steps are like this.

As I mentioned earlier, our starting material is always powdery. It is not lumps. Even if the lumps are available, it has to be ground to a very fine powder. So, the starting material is always powder and since most of the cases, ceramics or ceramics materials do have a high melting point. So, melting is always avoided because it is a very high temperature process and it is not economic and therefore, melting is always is avoided. But, we start with powders and at the same time, this powder must be consolidated enough, so that, at the end of the process, end of the fabrication process, you do get a geometrically sound material or mechanically sound material, right. So, this is your first step. So, you have to prepare some batch, that is, you mix some different materials if you want to take mixed oxide for example, in appropriate proportions must be mixed together, so you form batch preparation for the powdery raw material. What you do in case of traditional ceramics, most of the raw materials as mentioned already are naturally occurring minerals, which need to be beneficiated. For advanced ceramics, normally synthetic raw materials or specially prepared powders of different compositions are used as the raw materials. So, these are the raw materials and the basic difference between traditional and advance.


Control of both compositions and the particle size and sometimes particle shapes are of tremendous importance. As I mentioned, the chemical composition is important; particle size is important, so that, you have the final particle. So, there your starting material has less pores or less open spaces between the particles, so that, consolidation and their mechanical strength and development becomes easy at a later stage. Then we have different shapes of the particles, sometimes spherical, sometimes more angular, or sometimes little cuboids kinds of shapes. Many times we can get, depending on the crystal structure you can get hexagonal crystals. So, shapes are also important depending on the particular nature of the raw material and the product you want to make.

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2) Consolidation

- For consolidation of the powders organic binders are normally mixed followed by application of high pressure using a steel die and punch set.
- Alternately, powders are suspended either in aqueous or non-aqueous media to prepare a viscous slip, which may be poured inside a porous mould (slip casting) or spread on a flat plate (tape casting) to prepare hollow wares or thin sheets respectively.
- There are several other techniques e.g. gel casting, cold isostatic pressing, hot pressing etc, which can also be used under special circumstances.



Then, the next thing is, once having got the composition, powder composition, you have to consolidate. That means, you have to give it a shape. The shape is done. The consolidation, the powders, normally are mixed with some organic binders, so that, in the green condition, in the ceramics terminology, green means without fire, which has not been heated in the room temperature. Whatever you do, it is actually green processing or the shapes which you get in the room temperature, these are actually called green ceramics. In Green ceramics, the powder cannot be loose. They have to adapt each other and therefore, to facilitate that, you get some organic binders. They are mixed following and followed by application of high pressure using a steel die and punch, so depending on the shape and size you need you have a steel die and punch or a mould in which this powder is compressed under high pressure. The pressures, depending on the size and shape and the kind of quality of the product you make, at times you have to prepare thousands of tons of pressure or load to consolidate them. So, this is one of the simplest ways to make the powders, consolidate the powders or give a shape to the powders.

Alternately, powders are suspended in aqueous or non aqueous media to prepare a viscous slip. So, the powders, this fine powders, when you suspend in a liquid medium, normally a kind of electrolyte, water is good electrolyte also for some material and poured inside a porous mould. Then this slip, a thick suspension is poured inside a porous mould, normally made, in case of traditional ceramics, the porous mould is made of plaster of paris. So, you control the porosity and because of the capillary reaction, the


water which is, in which the material is suspended the particle is suspended, preferentially that water will be absorbed, will be soaked or absorbed inside the porous, because of the capillary reaction and the powders will get a skin form, a skin on a surface of these mould.

So, particularly for prepare hollowware, if you are talking about a hollowware, like cup or a vase or that kind of thing, if you are making a hollowware, you can always or even a sanitary ware, that can be made by slip casting using a porous mould. However, a very similar technique can also be used for making very flat shapes. For example, electronics, we have discussed about the packaging techniques or the multilayer capacitors for which we need a very thin sheet of ceramics. A very thin micron size thick, few tens of microns of thick ceramics or thin ceramics, I would say, so these thin ceramics can also be made by starting with a viscous slip and that viscous slip, of course in this case, most of the time it is not an aqueous slip. It is non aqueous slip, a non aqueous slip made with the volatile liquid or volatile solvent, so that slip can be sprayed on a flat surface and you can form a flexible tape. These tapes, because basically it is a composite, it is a composite of some polymeric material in which very fine particle of ceramics are dispersed, So, that tape is flexible to start with and then you heat it to high temperature when these volatile compound or the polymorphic binder will go away or will evaporate out or volatile out and then you get a stiff, very thin ceramics. So, that is also another technique by which thin sheets can be prepared.

Finally, there are several other techniques, for example gel casting, cold isostatic pressing, hot pressing, etcetera which can also be used under special circumstances. Well, gel casting is also a very similar technique like slip casting, but the compositions are different. But, this again a suspension of fine powders, ceramics powders in some gel, gelatin or gel consistency. Material of gel consistency we have discussed earlier, sol-gel technique. So, it is actually a gelation process, by which the material gets slowly consolidated and then one can fire it at high temperature. Cold isostatic pressing, instead of a (()), what we call a slip casting, we have earlier said high pressure, here it basically (()) slip casting and cold isostatic pressing means, a pressure from all corners or all four sides and that can be available with the use of a liquid, a high pressure well or even, mostly oil. We use oil inside that, the material, the powder in the form of a, inside a bag, flexible bag you put it there and then pressurize the liquid, so that a uniform pressure is

applied from all sides. That has its own advantage, because if pressure distribution is not uniform and we have an inhomogeneous poured size to start with, at the sintering stage and or the firing stage, there will be non uniform porosity and that will be a source of with asso, so far the strength is concerned. So, that is the reason one uses an isostatic pressing. Even this is called cold isostatic pressing and even one can use hot isostatic pressing. So, you apply isostatic pressure and at the same time, simultaneously you heat the temperature, heat the material at a high temperature. So, in this case, of course one cannot use a liquid because it involves high temperature and therefore, one have to use a hot gas, hot gas environment. So, hot isostatic pressing is one of the latest techniques and most of the high performance ceramics are made by this hot isostatic pressing. It is quite expensive, but it has its own advantages.

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- Firing / Sintering
 - As the melting point of any ceramic material is relatively high they are normally not melted cast to generate a shape.
 - Instead, the consolidated powders are heated to a high temperature for a phenomenon called "Sintering" In this process the consolidated fine particles form strong inter-atomic bond with the neighbouring particles to form mechanically strong ceramic products.
- Finishing
 - Under certain circumstances sintered ceramic articles require post sintering finishing operation primarily for adhering to dimensional accuracy and surface finish.


Finally, the third stage is basically firing or sintering. That is what the final or pre final stage you can say. As the melting point of any ceramic material is relatively high, they are normally not melted and cast to generate a shape. So, in metals, melting and casting is a very common technique for making some shapes. But, ceramics being high temperature material, normally it is not melted and given a shape or cast in a mould. Of course, in some cases we do that. Certainly we do that for very special purposes of refractory or of course, glass is another way. But, we do not discuss glass here. We are basically discussing ceramics products. Now, instead of melting and casting, the consolidated powders; sorry, there are some mistakes here; are heated to a high

temperature for a phenomenon called sintering. In this process, the consolidated fine particles form strong inter atomic bond with the neighboring particles to form mechanically strong ceramics products. This is a common technique, whether we consolidate it by cold isostatic pressing or slip casting or tape casting, ultimately all ceramic materials have to be heated to appropriate temperatures, approximately, let say 80 percent of its melting temperature.

There are different techniques or different mechanisms of sintering. If time permits, we will discuss that later on, but there are specific techniques where sintering techniques or the strengthening techniques of the powders are different for different materials. We will try to look at it at a later stage. So, after sintering, the material becomes mechanically strong and useable; its actual useable form. Before that, the powders are not normally used. The last technique or the last process step is called finishing. That is very true. Not always, particularly for advanced ceramics or structural ceramics materials, because for structural ceramics, surface finishing is also very important. Surface finish has a very important role, as far as the application is concerned and of course, dimensional tolerance, because you are going through different processes.

Maintenance of dimensional tolerance sometimes becomes difficult and therefore, there is a need of surface finishing or finishing of the dimensions, primarily, you know, to match the requirements of the dimensionality. Under certain circumstances, sintered ceramics articles are required post sintering finishing operation, primarily for adhering to dimensional accuracy and surface finish. These are the two things very important for structural ceramics material, because most of this are engineering components, either a large component or a fine component and they need conforming to the dimensional tolerance, sometimes very critical dimensional tolerance are very necessary and therefore, we need finishing operation as well after sintering.

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So, these are the four different steps by which powders, which are prepared by some special techniques as mentioned earlier, can be converted to a product. The product which needs, which have the necessary mechanical strength, surface finish, dimensional tolerance and of course, different kind of designs and configurations.

I think that completes or my discussion on the introductory part of this course. This course gives you an overall background of what we are going to discuss in much more details at a later stage. In the next class, will be discussing about the structures. We have discussed some of compositions of different materials for different purposes, some of the properties and so on. Now, we have to understand how this property gets developed; why this properties are there; why some ceramics are insulating or conducting or others are super conducting; some have magnetic property and others do not have that kind of property; some are very strong, but others are not so strong. So, we need to understand the structure property relationship and therefore, we start with structure, basic structure of some of these compounds and slowly develop into how these structures provides you the properties and we can explain some of the properties we look for.

Thank you.