Physics of Functional Materials and Devices

Prof. Amressh Chandra
Department of Physics
Indian Institute of Technology Kharagpur

Lecture – 02, Week 1:
Introduction to solid state materials – From conventional to functional

Welcome to the second lecture of the course Physics of Function Materials and Devices. In the first lecture, I gave you a brief introduction to the materials that we will be studying in this course, and their applications we also saw the importance of this course and why did I chose this topic. Now, let us go a bit further and start seeing the next type of materials which will be investigated during this course and they will also be explained in detail. These are ceramics. So, we will be talking about various types of ceramics, what are their classifications? What are the properties of these ceramics which make them so important that if you look around yourself they are everywhere. That is why you will see that ceramics have the large number of applications.

Once we complete ceramics, we will move to the next class of materials which are termed as composites. After defining what are composites, we will see the various types of composites which are there, why they are there, what is their importance, how we characterize them, what are their properties, and finally, we will try to give a series of applications where these composites are being used in today's world. So, let us start with the topic of ceramics. What are ceramics? The definition of ceramics is they are a class of materials which are inorganic materials, which are prepared at high temperatures.

This is something which you must understand. High temperatures are not like 100° or 200° C. They are in the range of 700°, to 800° C. They can go up to 1500° or so. So, they are prepared at very high temperatures.

We saw yesterday what are crystalline materials, what are polycrystalline materials, and what are amorphous materials. Amorphous materials can also be glassy-type materials. So, ceramics can be crystalline, they can be single crystal or they can be polycrystalline which is the most common. So, you will find that the ceramics that we will be studying in this course will have a polycrystalline nature. They can also be glassy or they can also be amorphous.

That means they have short-range ordering which we discussed in the first lecture. In addition, you will find a class of ceramics that can be both crystalline and glassy in nature. Some of the examples that you see around ceramics are: clay, bricks, glass, tiles, and types of cement. These are the ones that you can if you see around the place where you are sitting you will see it. But if I go to more scientific and things which are more intricate, then you will find that these ceramics are used as dielectrics, they are oxide ceramics used in sensors, they are used as cladding in optical fibers, they are used as shields, shields of various type.

You will see that even the bulletproof jackets that you have heard about have dispersed ceramics in them. So, the ceramics actually act as a shield towards incoming projectiles. So, there are the large number of applications for these ceramics. You must understand certain points regarding the ceramics before we proceed further. And some of these points are that you will see ceramics are brittle, they are very dense.

So, they have a very high density that means, they are hard and because they are very hard the result is that they are strong and they resist corrosion. Traditionally ceramics were based on clay and so, what you would do you would take a clay then give it a shape be it be in a shape of an earthen pot and you would give it a shape and then take this pot put it in a furnace and then heat it. And then once this clay comes out of the furnace it would cool down and as it cools down you will find that you will get hard material or the shape would be retained and that is the way you have been seeing in various places the earthen pots are fabricated. You can have utensils which are based on ceramics and ceramic potteries are very very famous in different parts of the world and they are used for many years. and even the colors which you see can be obtained by dispersing a second type of particles in the host ceramic matrix and that is the indication which I am giving which will be the stepping stone towards defining the topic composite that you will be mixing two different types of materials and then bringing them together to give you a new material.

For the time being let us consider the term ceramics. So, conventionally they were based on clay, but it is not true anymore. Most of the ceramics which you see around have different types of materials that are used and then they are fabricated at high temperatures. For example, piezoelectric ceramics. You have heard about the term piezoelectric.

What does it mean? It means that you apply pressure and you will get electricity out of it. And these are everywhere which you see right from gas lighters to you in kitchens or the sensors in your automobiles which sensors which actually sense the vibrations and then study the vehicle against these potholes. So that you as a passenger do not feel the jerks which may be introduced because of a bumpy road. So that is the range of application of these ceramics and they are made using a ceramic which is called lead zirconium titanate. So what is that ceramic that is used everywhere, that is $PbZr_{1-x}Ti_xO_3$.

So this is ceramic and this material has a structure which is called ABO_3 type. So this is the ABO_3 type material. What do I mean by ABO_3 type material? You will see it in coming slides. So modern-day ceramics can be based on oxides or they can be independent of oxides there you do not need to have oxygen in it. So only oxide ceramics don't need to be there. You can have oxides or you can have a combination of the two. As they are prepared at very high temperatures they are considered as refractory type materials. So they can withstand very high temperatures because suppose if a material is prepared at 1200° C that means it will be stable up to 1200° C. So if you use that material at up to 800° C that material will remain stable because it was formed at 1200° C. So 800° C is not a very low temperature it is a very high temperature we are talking about.

So, you prepare a material at let's say 1200° C and then use it at 100° C, 200° C, 400° C, 500° C, and 600° C, it remains stable and therefore, they are extremely useful in today's world and for the applications which for which they are being investigated and hence they are refractory type materials. If we look around you will see that our life today revolves around ceramics. You will find ceramic-based electronic components in our computers to high-end TVs we watch ceramics are everywhere, okay. Let me give you the first quick assignment for today's class. Can you make a list of ceramics? which I have not mentioned till now but are seen routinely around you.

So I have discussed a series of ceramics and various materials that are used as ceramics. But I have very carefully and knowingly avoided mentioning some of the ceramics that are in and around us. So, if you look around you, can you make a list of these ceramics, which have not been mentioned till now, but you see them routinely around you. If you can do that that means, you understand what is going on in the class and then you will enjoy the class even further. As I mentioned lead zirconium titanate is an ABO_3 type of structure.

What do I mean by ABO3 type of structures? These structures are the ones for the unit cell of the material. What is a unit cell? Unit cell is an entity that when repeated gives you the lattice of the material. So ABO_3, what is ABO_3? ABO_3 means that A is one type of an atom, B is the second type of atom and oxygen is the third atom which is there in the unit cell. Now you can arrange these atoms in different configurations. If you arrange them in different configurations you will get different types of unit cell and these unit cells when repeated will give you lattice, but if I have different configurations and then I build the lattice the shape of the lattice would be different and hence the material which will be formed will have a different shape and the result would be that the properties of these materials would be very different.

This is actually defined by the term crystal structure. So, if you have various types of atoms you can arrange them in different types and they will give you different types of crystal structures we will now try to understand the common crystal structures that you study or that you find in ceramics. Some of the common crystal structures that the ceramics actually manifest are the AX type or the rock salt structure. The second is zinc blende, the third is perovskite type structures and if you go to slightly complicated structures then you can go to spinel type structures. So, till now what we have seen crystals of ceramic consists of atoms located at a lattice point and crystals should be charged neutral then only it is stable.

This we have been studying from our school days for a stable material the condition which should be followed is that it should be charge neutral. So, the number of positive and negative ions must be same. What does it mean the contribution coming from positive ions and from the negative ions must be equal. Let us take an example of an ABO_3 type material which is barium titanate. It is one of the most common examples which you have.

What is the valency of barium? Barium is 2^+. What is the valency of titanium? Titanium is 4^+. So what is the positive charge which is the total positive charge that is 6^+. What is the valency of oxygen? 2^-. How many oxygens are we considering? 3^-.

So, what will be the total negative charge that you will get is 3 into 2^- that is equal to 6^-. What number of positive charges? 6 plus. Several negative charges? 6 minus. Total charge? 0.

They are canceling each other. So what you get is a charge-neutral condition and that is a fundamental thing that you must remember whenever you try to make any material if a material is not fulfilling the condition of charge neutrality it will probably remain in an unstable state. Very rarely you will find materials that are charged but they are stable. Some materials can remain stable for a certain time and then they will transform into new phases and then they will become again charge neutral. But more often you will find that you will have this condition fulfilled which is the fundamental thing one should remember. Sometimes you will find that people talk in terms of the equal number of cations and anions rather than saying you have the equal number of positive charges and negative charges people talk that you have equal number of cations and anions.

What is a cation? It is a type of ion that has a deficiency of negatively charged electron. So what how will a cation be formed? It will be formed when an atom loses one or more than one electron. So you give electron. This results in an overall positive charge on that ion. So you can have calcium, you can have sodium, you can have titanium, you can have iron.

Iron can be in 2+ state or 3+ state and many more. You can actually list them. So you will understand what we actually mean by cations and how many electrons are they giving out. Anion, what is an anion? These are the type of ions that have excess amount of negatively charged electron. So cation gives electron, anion accept electrons.

So these are the types of ions that are formed when the atom gains one or more electrons. So they will accept the electron. So you can have OH^-, you can have Cl^-, you can have F^-, iodine, bromine etcetera. So you can also list them. Now hopefully you understand what I mean when you have ABO_3 type of structure.

So, A is what? Is it a cation or anion? Can you answer? What is B? B is a cation or anion. Can you answer? And similarly, what will you consider? Oxygen is a cation or anion. You must answer this and then you will understand why people say in terms of equal number of cations and anions. So you will understand the concept where some people talk in terms of charge neutrality whereas some people talk in terms of an equal number of cations and anions. So let us talk about the structure which is commonly studied and it is one of the most famous examples which is taken that is the perovskite structure.

It is mostly ABO_3, that was conventionally used, but now with the advent of perovskite-type solar cells the term ABO_3 is slightly being replaced by ABX_3, and therefore, this terms ABX_3 has been written here. But to start with we will consider that you are going to have an ABO_3 type of structure which is a conventional structure that was considered. The first perovskite material that was actually investigated is not barium titanate, it is calcium titanate because it is found in the earth's crust. So, this was the first perovskite material that was studied and then as we moved along materials that had similar structure or behavior as calcium titanate were put into the classification of perovskite materials and then now you have a broad classification which is used as ABO_3 type of structure. So, in a, for example, this structure means what the A atoms are at the cube edges.

So, you have 8 A atoms. How many B atoms? This is at the body center. So, B is at the body center position. How many atoms? You see only one atom. How many oxygens? So, if you see oxygens, you can clearly see that there are 6 oxygen which are at the face centers. So, what should have been the molecular formula for this? You should have actually written 8A + 6O and 1 B, but this is not the way people write it.

So, people do not write it as 8A1B6O. What do we write? We write ABO_3. This means what? This means that there is only 1 A atom, there is only 1 B atom and there are 3 oxygen atoms. This is what is meant by the formula unit. So, where what is this? How do we get this ABO_3 structure? This is coming from because if you have a unit cell and you are making a lattice. In a lattice, you do not have only one unit cell.

You will have a unit cell which is here. On top of this unit cell, there will be one unit cell. Below this unit cell, there will be a unit cell. Then it will be there will be on the right, there will be on the left. So, you will have a unit cell on top of this, you will have a unit cell on the right, the bottom, the back side, and the left side.

So, you have all these unit cells. For example, if you take this corner atom, which is A, this is going to contribute to, how many unit cells? It is going to contribute to the unit cell. There are how many unit cells? Four above. So, if one is on this side, this is also sharing this line, one is on this side, then on this side, then on this side, and similarly on the back side. So, what is the contribution this atom has to a given unit cell? That is only one-eighth. So, the contribution of a given atom to one unit cell in this configuration which is shown on the left side of the screen is one-eighth.

There are how many atoms? There are eight atoms. So, the total number of atoms that you will have would be 8 into one-eighth which is equal to 1 and that is how you get one A atom. But if you look into the B-Lan atom in this unit cell, this is in the body center. So, it is not being shared by any other unit cell on the left, on the right, on the top, on the bottom, in the front or in the back. So, it is not being shared by any, it is being shared only by the one given unit cell and therefore, you have one B atom. Similarly, you can see that the oxygen atoms are being shared by how many? You are sharing them in a way where you will find that half into 6 is equal to 3 atoms.

I have given you a brief answer to this and not explained in detail how oxygen atoms are coming out to be 3. If you have understood the concepts of sharing of A atom between the 8 unit cells, you should be able to tell me how this half into 6 is actually coming in. If you do not understand, then we will discuss this in the online doubt solving session. But try to solve it, you will really enjoy it and then you will understand the concept completely. The next type of structures which are there are the spinal type of structures where you will find that they have the formula unit AB_2X_4, where A is a divalent cation, B is a trivalent cation.

Trivalent means 3 cations plus and X can be oxygen, it can be selenide or it can be sulfur or anything. So, if you look into the structure, you will find that the spinal unit cell is made up of 8 face centered cubic cells, where the anions that is mostly oxygen occupy the face center FCC lattice points. The divalent that is 2 plus cations occupy one-eighth of the tetrahedral voids, whereas the trivalent cations occupy the half of the octahedral voids. Also the inverse spinal structures have the same chemical formula units. But if you go around and try to see what how many types of spinal structures we have, you will be amazed to see there are so many and they are finding large number of applications.

For example, you have $MgAl_2O_4$, you have Mn_3O_4, you have $ZnFe_2O_4$, you have $FeCr_2O_4$ and there are many more. Can you list them? Similarly, you can have nickel ferrites, cobalt ferrites, and manganese oxides of different types which are examples of inverse spinal structures. But if you go to a book, the first structure that is mostly discussed is the rock salt structure which is an AX-type crystal structure. A very simple structure that was found in a large number of materials right from the times people started understanding the arrangement of atoms, and the lattice formation, they started seeing these kinds of arrangements in a large number of materials. The first structure that was actually quite extensively investigated was the rock salt structure which is the structure of NaCl, where you have two types of ions A and X, A is a cation and A is an anion.

The common examples are sodium chloride and cesium chloride. The coordination number of NaCl crystal is 6. What do we mean by coordination number? So, if I take a given ion, you will find that there are 6 nearest neighbor atoms or ions surrounding it. So, there are 6 nearest neighbours. So 1, 2, then you have 3, you have 4, you have 5 and you have 6.

So, the coordination number of NaCl crystal is 6. So, you can find for every there will be 6 nearest numbers and for a cation, there will be 6 anions surrounding it and vice versa.

So, you will see that the ratio between these two atoms is defined in terms of radius ratio that is defined as R cation upon R anion. And the radius ratio in NaCl is in between 0.434 to 0.712 that is you go from one material to the other, but if they have rock salt type structure the radius ratios would be similar.

So, you will take the radius of the cation and then you will divide with the radius of the anion and you will find that this is the ratio you are talking about. What does it tell you? So, this value of 0.43 and 0.712 what does it tell me? Will the radius of anion be smaller than that of cation or vice versa? Just have a thought and you will understand what do we mean by this. Cation should be larger or smaller or anion should be smaller or larger.

This is the question I am asking you and you should be able to answer that by seeing these two values which you should obtain. Then you can move from another AX type material that is CsCl, cesium chloride which has a similar structure as that of AX type structure. You can move on to the zinc blend structures these are also called wurtzite structures. When sulfide ions reside at FCC structures this results in a zinc blend unit cell. If sulphide ions reside at HCP it results in a wurtzite type structure.

So, there are two types of zinc blend structures. So, here I have taken the example of zinc sulfide and you can find that there are the large number of materials that can have wurtzite-type structures. So, try to find them. What is the typical characteristic of zinc blend structures? You have the radius ratio which is in the range of 0.714 divided by 1.70 which is equal to 0.44. So, this is a typical zinc blend structure of zinc sulfide. Suppose, I change zinc and sulfide both and then try to find the new radius ratio the values would be different, but this is the typical range of values that you will obtain. For example, you can calculate the radius ratio for silicon carbide, you can zinc telluride and you will find that these materials will have similar order of radius ratio. And the various properties of these materials are mentioned which I have also discussed in the previous slide. Different applications of these ceramics range from cutting tools.

So, you can use a ceramic actually to cut a ceramic because the ceramics are very hard. So, to cut a very hard material you may need a harder material. So, if there is a ceramic which is itself very hard you have to cut it what will you do? You will need a harder material. So, you will need a harder ceramic.

So, ceramic can be used to cut a ceramic. So, you can use them as cutting tools. They can be used to cut silicon wafers and most commonly they are used during oil drilling because when you drill down you need to have blades or the drill which is going down which needs to be very very hard and should be able to sustain high temperatures as well as pressure. Therefore, ceramics are finding extensive applications in cutting tool area. Then if you go into niche applications they are being used in sensors, they can be used as gas sensors, humidity sensors, they can be used as alarms or they can also be used as any kind of VOC sensor. What is that? Volatile organic compound that means, these gases which can be volatile even at room temperature and they can be hazardous to human health.

So, ceramics are being used in that kind of sensors. And their use in refractories has already been discussed earlier why they are being used in refractories because they themselves are refractory type materials prepared at very high temperatures and hence they will be used in refractories some common examples are high-temperature furnaces. Other examples are money-minting applications, you will find that ceramics are finding a lot of applications in automobile engines, they are finding in automobiles as vibration sensors and that is resulting in a trillion-dollar industry. They are also being used in aerospace turbine blades, nuclear fuel rods, lightweight armors, and stealth coatings, too they can also be used in applications which is for food processing that you can have food processing units based on ceramics. So, you can see from cutting tools to aerospace turbine blades to nuclear applications. You find the use of ceramics is enormous, it is everywhere and that is why we will also be focusing a lot on the synthesis of ceramics, their characterization, and then their applications as we move along in this course.

So, let us summarize what we have seen today. We have discussed the class of materials which are called ceramics. After defining the term ceramics, a certain number of ceramics were discussed and you will find that the classification of ceramics is mostly done based on the arrangement of anions and cations in different nature. That means, what is the crystal structure and the type of anion and cations which are there that result in those kinds of crystal structures? So, based on that we have classified the types of ceramics. You have also seen that these ceramics have wide applications and the applications are there because you can tune their physical properties and chemical properties.

Why can we choose the physical property? They have a wide range of tunable physical and chemical properties. Why do they have different physical and chemical properties? Because if you change the atoms that are combined together to obtain a ceramic, the properties would be different. For example, I can have the same perovskite-type structure, but I have barium titanate that is $BaTiO_3$ and instead of barium suppose I use lead, then I have lead titanium oxygen in this structure and I get $PbTiO_3$. So, these two materials are different. The structure is similar, they are both perovskite type structures, but the structures are different, and hence their physical properties would be different.

That is what we have discussed that as we move from one type of material to the other, the properties would be different and hence their applications would be different. These are the references that were followed in today's lecture and you will get more details about the topics that were covered in today's lecture from these references. In the next lecture, I will start a new topic which is the introduction to another class of materials that are called composites. Thank you very much.