Solid State Chemistry
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Lecture - 48
Perovskites and Spinels

Now, I will start third lecture of week 10 of this course. In the last 2 lectures we saw the crystal structures of simple elements and binary compounds. Now I will go to some other crystal structures that are very that are very commonly seen and they have lot of relevance for many solid state materials, especially ferroelectric and magnetic materials. So, these 2 structures are the, that we will discuss in today's lecture are Perovskites and Spinel.

And I will just give the basic structures of perovskites and spinels. It turns out that there is a lot more to these materials than the basic structures that I will be showing, but I just want you to see how these basic structures are constructed. So, week 10 lecture 3 will be perovskites and spinels.

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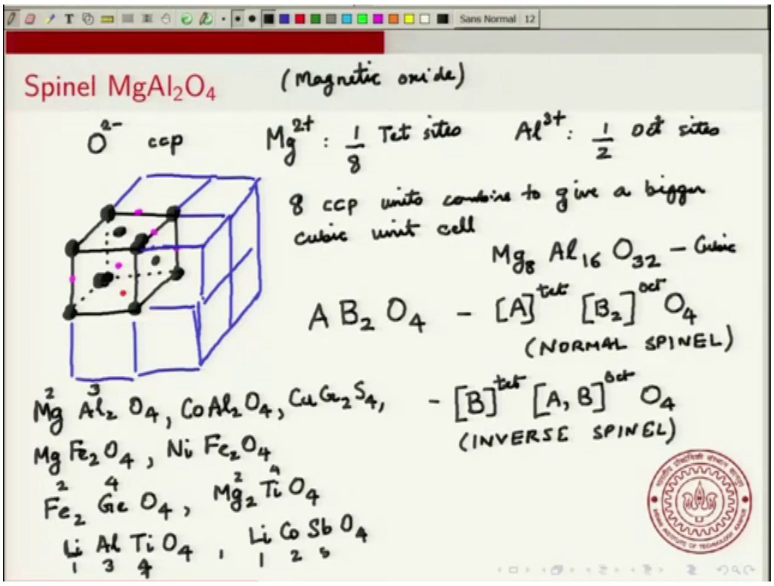

So, let us look at spinel first. So, the spinel the typical material is Mg Al 2 O 4. So, Mg Al 2 O 4 is the typical material for those spinel. These are of interest because these are magnetic oxides.

So, there is an interest in these materials and people try to make different kinds of spinels ok, and try to see their magnetic properties. So, the basic structure of spinel can be understood in the following way. You have oxygen 2 minus the oxide ion that forms a CCP; Cubic Close Packed and now the Mg 2 plus cations, they occupy one-eighth of the tetrahedral sites ok and the Al 3 plus ions ok .They occupy half of the octahedral sites ok.

Now there are a total of 8 tetrahedral sites in one conventional cubic close packed cell ok. Now if you occupy one-eighth of those with one-eighth of the tetrahedral sites; that means, you are occupying only one of the tetrahedral sites ok and you occupying 2 out of the 4 octahedral sites. Now it turns out that way if you do this if you do this, so, you can see it; if you just imagine that you have a that you have a cubic close packed ok. So, let me show a cubic close packed with oxygen's ok.

I will show the oxygen's in black. So, if you take a cubic close pack structure and now if you occupy only one-eight, that is 1 out of the 8 tetrahedral sites ok. And similarly if you occupy a only 2 out of the 4 octahedral sites ok then something happens which is which can be understood quite easily ok. You can see that if you just occupy 1, let us say you occupy this site here, this tetrahedral site here. Now you can immediately see that now the cell will be distorted because, now there is an atom only on this part, but not in the remaining part of the cell.

And so the cell will tend to distort ok. So, similarly, if you want to occupy 2 out of the 8 octahedral sites, so, the octahedral sites I will show them in purple. So, now, you could do it in different ways ok. Let us say you occupy the one at the center and now that is one site, now one more site you have to get by occupying 4 out of the remaining 12 sites ok. And again you can do them and do in different ways and in each case you will get you will get different occupancy.

So, for example, suppose I, suppose you occupy this and let us say you occupy this. So, now, I have half of the octahedral sites are occupied and you can see that now the distribution of material in the cell is not is not symmetric and the cell will tend to distort.

And you can, so there is a natural tendency to distort whenever you have this partial occupancy of tetrahedral and octahedral sites ok. So, what happens is that this individual one close packed subunit is distorted, but then 4 of these, rather 8 of these 8 of these ok. So, there are there are 8 CCP units combined to give bigger cubic unit cell ok. So, what I mean is that now the unit cell for spinel ok. Actually, that contains 8 Mg 16 aluminum and 32 oxygen, ok.

So, this is the actual composition of the unit cell ok. So, that one unit cell it is you can think of it as composed of 8 CCA, 8 of these individual CCP units ok. So, but it is but it is cubic structure and you still have oxygen occupying sites that look like a cubic close packed, but now it is a much bigger cell and Mg will occupy one-eighth of the tetrahedral sites and aluminum will occupy half of the octahedral sites ok. So, this is a structure of spinel; I will just show I will just. So, what you should think is that this same cell is repeating in all directions it repeats 2 times.

So, it repeats this way and then even in this direction it repeats and so this is here. So, this whole this whole this whole cube this bigger cube is the unit cell of spinel ok. And now what happens is that these the octahedral sites are suitably arranged so that the hole so that there is no net distortion on this cubic cell ok. So, the octahedral and tetrahedral sites are symmetrically arranged with respect to this cube and this cubic this larger cube is the unit cell of Mg Al 2 O 4 spinel ok.

Now, if you look at the detailed positions of the anions you can of the cation. So, the anions will always occupy these CCP sites ok. Now the cations will be located in a rather complicated arrangement, I will just show this ok. Well, ok I will not show the detailed arrangement of these cations ok, but basically this is a unit cell of spinel ok. And again I should mention that each of these individual CCP units will actually be distorted because, they have an asymmetric distribution ok, but overall the whole cell will be perfect cube it will be a larger perfect cube ok.

Now, this spinel the, if you look at a general spinel spinel has a formula B AB2O4 ok. And in this in this formula the A is in the tetrahedral sites and B is in the B 2 are in the octahedral sites and of course, the oxygen is in the cubic close packed. If you have this arrangement it is called a normal spinel, normal spinel or simply spinel ok. There is a there is another closely related structure where instead of having A at the tetrahedral sites you have B you have a half of the Bs at the tetrahedral sites and the octahedral sites are partially occupied by both A and B O 4.

So, this is a related structure ok, where the only difference is that instead of having all As at the tetrahedral site, you have B at the tetrahedral site and A and B together occupy the octahedral sites ok. And this is referred to as inverse spinel ok, and this is also structure that is found in found in nature ok. So, let us look at some examples of spinels ok. Now also in this spinel, we now we had Mg had a charge of 2 plus and Al had a charge of 3 plus; so, this Mg Al 2 O 4 ok.

So, the oxidation state of Mg is 2, and that of Al is 3 ok. So, this is referred to as a 2, 3 spinel ok, and there are several other spinels ok. The 2, 3 spinels you can have for example, you can have Co Al 2 O 4, you can have C u C r 2 S 4 ok. So, oxygen is replaced by sulfur and aluminum is replaced by chromium ok. Then you can have Mg Fe 2 O 4, you can have Ni Fe 2 O 4. Then you could have you could have other compounds ok. For example, you could have Fe 2 Ge O 4 ok.

This is a 2 4 spinel and here Ge occupies the well ok. So, this is a 2 4 spinel ok. Then you could have so the oxidation state of Ge is plus 4 ok, and now there are 2 ions ok. Instead of having instead of having Mg instead of having A B 2 you have something like A to B O 4 ok, but the charge on B has to be larger ok. Then you could have you could have spinels such as another example of such a spinel as Mg 2 Ti O 4 ok. There is also a 2 4 spinel ok. Then you could have you could have a more complicated spinel ok. You could have a something like lithium, aluminum, titanate ok.

So, this is also a like a spinel. Now you have a 1, 3, 4, 1 3 4 spinel, but these are also this also forms a spinel structure. Say similarly you could have a something like Li Co Sb O 4, this is a 1 2 5 spinel. So, the I mean a antimony has a oxidation state of plus 5 cobalt is plus 2 lithium is plus 1 and together they add up to minus 8 which is compensated by the by the oxygen they add up to plus 8 which is compensated by the oxide charge ok. So, there are several examples of spinel ok, spinels that are observed that are seen and it is indeed a very common structure it is as I said it is well known as a magnetic oxide ok.

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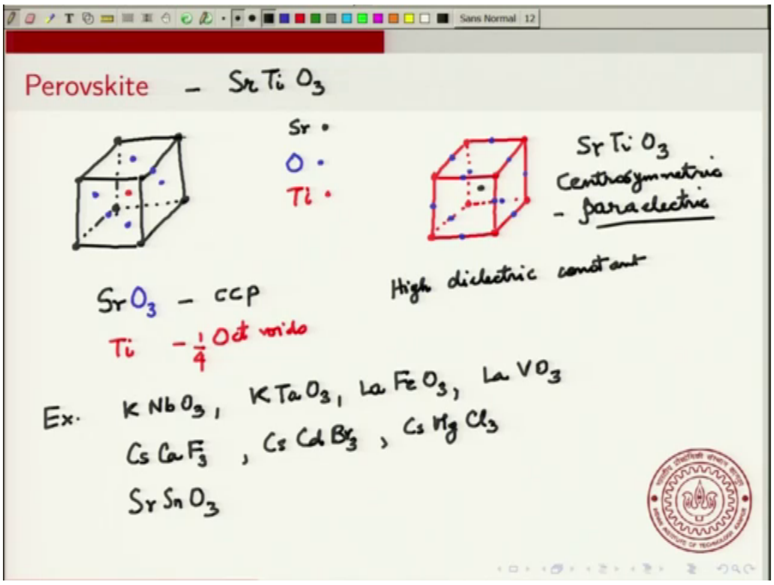

The next structure that I want to talk about is the perovskite structure, and the typical example of a perovskite is strontium titanate ok. Now strontium titanate, now the structure can be understood in the following way. So, you take strontium and form a simple cubed. So, let me color code this. So, I will say Sr is in black. So, we form a simple cube of strontium atoms ok. And now what you do is you put the oxygen atoms at the face centers. So, you have put. So, clearly you have 3 oxygen atoms ok. So, you have 6 oxygen atoms each of them contributes half to this unit cell.

So, in this unit cell you have 3 oxygen atoms ok. So, these are the oxygen and then the titanium you put right at the middle, at the body center of this cube ok. So, this will have the formula Sr Ti O 3 ok. And this is the structure of perovskite this is the basic structure of perovskites. Now you can you can think of this and you can look at the same structure in a slightly different way. So, suppose I put it the Ti atoms at the corners ok. So, if I put the Ti atoms at the corners of the cube then I will have Ti.

So, I am just depicting it slightly differently, so instead of putting strontium at the corners I am putting Ti at the corner. So, I go and you know you can just take this to the next cell and you can complete it ok. So, then the titanium will form a simple cube. And now with respect to the titanium the oxygen atoms ok, will be located at the edge centers ok.

So, the so these are the locations of the oxygen atoms ok, and the strontium will be located at the body center ok. So, I will show it again in black. So, there are 2 equivalent ways of looking at this strontium titanate structure ok.

Now notice that in this in this way of looking at it there is no atom at the face center ok. So, if you form the unit cell using titanium ok. Then you do not have you do not have any atoms at the face centers of this cubed. Whereas, if you form the same unit cell using strontium ok. Then the strontium forms a simple cube oxygen occupies the face center ok, and titanium occupies this octahedral void ok. Now you can really think of this as an Sr O 3 Sr O 3 which is forming a CCP. So, the combination of strontium and oxygen together they seem to form a cubic close pack.

So, if you take if you take both strontium and oxygen together they seem to form a cubic close packed and this titanium is at the octahedral void. So, it is at actually one-fourth of the octahedral voids ok. So, you can also visualize this perovskite structure in this in this manner ok. Now of course, these perovskites materials are very interesting for applications because, they have very high dielectric constants ok. In the case of strontium titanate; strontium titanate it is a centro symmetric, it is centro symmetric. So, it is because it has a high dielectric constant such a material is called a paraelectric material, paraelectric material.

Now, I will tell you a few other materials I mean there are several materials that form perovskites. So, other examples are potassium niobate, potassium tantalite, lanthanum iron oxide, tantalum vanadate ok. Then so, these are oxides. You can also have you can also have things like cesium, calcium, fluoride cesium cadmium B 3 or Br 3, cesium mercury chloride ok. You can also have strontium instead of having titanium you could have tin oxide strontium stannate ok. So, these are all examples of perovskites Now, there is an interesting thing that happens in the case of if instead of strontium titanate you have a barium titanate ok.

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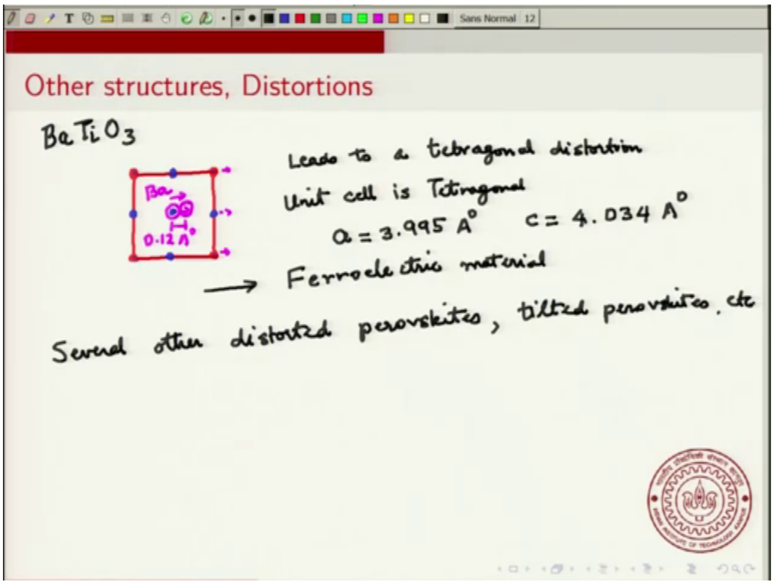

And I will just go to that this has to do with distortions that take place. So, in the case of barium titanate, there is something interesting that happens ok. Now if you look at let us say let us say we look at this structure ok, where you have the titanium at the corners of the cell ok and oxygen at these locations. Now let me just take a planar view of this ok. So, you have titanium at the corners, I am just making a planar representation. You have oxygen at the edge centers ok. And it will also be it will also be located at these edge centers, but at height of half ok, it will also be located here, but that will also be it that will be in the base layer ok.

And now you have the barium atom ok, that is located at a height of half I will show it in purple color ok. So, this is the barium.

Now, this barium atom ok, it tends to distort a little bit to this side ok. So, it moves from the center it moves from the location directly below the oxygen to a location about it just moves by about 0.12 angstroms ok, it just moves a little bit to the right to this point by 0.12 angstroms ok. And now because of this ok, now because of this these titaniums and oxygen they also move a little ok. And what this does is that it makes the cell tetragonal ok. So, it leads to a tetragonal distortion.

So, the unit cell of Bi Ti O 3 is tetragonal ok, and actually there is only a small difference the, a parameter a lattice parameter is 3.995 angstroms whereas, the c lattice parameter is 4.034 angstrom. So, there is only a small distortion ok, very small distortion ok. But this distortion ok, this distortion in the unit cell plays a very important role in the electrical properties ok. So, because of this tetragonal distortion BaTi O 3 is a ferroelectric material ok.

So, it is a ferroelectric is like is the is the analog of a ferromagnetic material, but now instead of applying a magnetic field you apply an external electric field and you have domains of aligned barium titanate unit cells. So, there are several other distorted perovskites

So, several other distorted perovskites ok, there are things like tilted perovskites etcetera ok. And what I want to say is that is that as play around with different materials ok, the perovskite structure gets slightly modified and there are various distortions that form ok. And each of these will give you a slightly different structure and in some cases like barium titanate you can actually you can actually see diagonal distortion. So, this is Ba Ti O 3, Bi Ti O 3 is the is the standard material for ferroelectric applications ok.

So, I will not go I mean there are a whole lot of whole lot of different perovskites and whole lot of different spinels, but I will not be discussing that. I will just I just wanted to give you the basic feel of what a perovskite and what a spinel structure is ok.

So, with this I will conclude this third lecture ok. In the next lecture I will show a slightly different way of looking at structures this is in terms of space filling polyhedral ok. And then and then I will also talk a little bit about alloys, alloys where you have where you have 2 different metals that are mixed and what are the possibilities that can happen when you have alloys, what structures you can get ok.

Thank you.