Coordination Chemistry
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Lecture - 28
Spinels

Good evening everybody. Today we will be talking about the another application of crystal field theory, so how we can apply the crystal field theory in case of several oxides.

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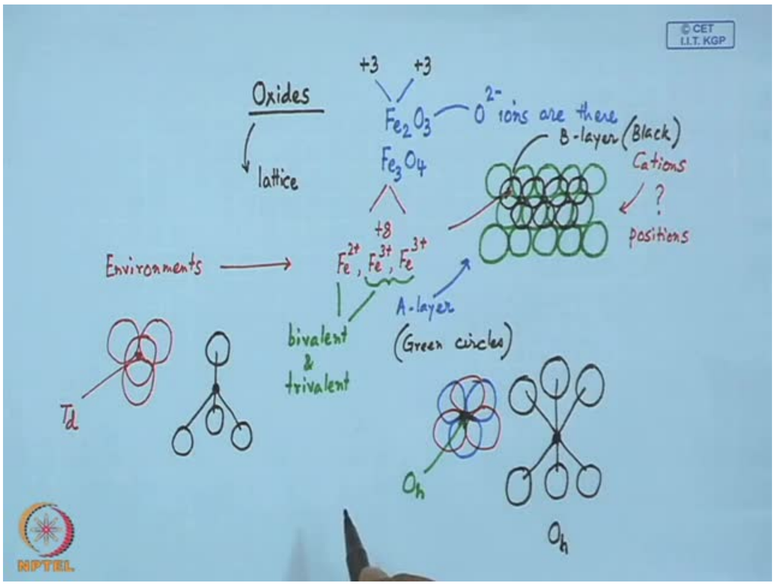

So, those oxides are specially named as some spinels where we will find that easily, when you find that if we have a metal oxide like this Fe2O3 or sometime we can have Fe3O4. So, this particular case when we know the number of oxide anions attached to the metal centre will immediately tells us that what is the corresponding oxidation state of the metal ions present in this oxide lattice.

So, we have the oxides, so we can have the corresponding oxide lattice also in our hand, and several of these oxide anions are closely packed in the solid state. So, O 2 minus ions are there, which are closely packed, that means if we consider these oxide anions as good spheres.

So, these spheres will be side by side to form a closed packed arrangement and this particular arrangement tells us that, if we can have such arrangement in a particular layer, will get some interesting information relative to the occupancy of the corresponding cations. So, if we have anywhere this particular one, which is a particular layer say; A layer. So, if we have this as A layer and all the oxide anions are there, and this oxide anion is a charged one, so somewhere we should have the corresponding cations.

So, how we can locate the corresponding positions? So, these positions to know that where we can place the cations and interestingly, when we can have this cations, such as in this particular case, where we have a total positive charge equal to plus 8. Since we have 4 such spices of O2 minus that means, 4 into minus 2 is equal to 4 negative, 8 negative charges. So, 8 negative charges should be equally balanced by 8 positive charges, from the 3 iron centres. So, obviously we will have one Fe2 plus centre and two other Fe3 plus centres.

So, by knowing the corresponding formula of these oxides, what we come to know is that; we have the corresponding bivalent as well as trivalent cations. So, we have the bivalent and trivalent cations will be there. So, if we get this particular layer arrangement and if we just simply go for the second layer, if this is A layer that means the green circles. These green circles are giving us the A layer and next we can have the second layer that means the B layer. So, we can have the B layer also like this, so by doing so we have the B layer, which are black circles. We get some arrangement where we can focus our attention now, to see the environment of this cations. So, what are the corresponding environments of these cations?

So, if we just look at this particular site, such as this site, how it looks like? It looks like, that means 3 green circles from the first layer and 1 black circle from the B layer. If we see this particular site which can be designated as the corresponding tetrahedral site, how? If we see now that particular one layer, that means this is one oxide anion, this is second oxide anion, this is third oxide anion these three from the first layer. They are forming a triangle and from the top we have the fourth, which is covering this particular cavity and your small cavity or hole within this particular arrangement of force spheres is like this. And it has thus four nearest neighbours, so the arrangement is typically a tetrahedral arrangement. In similar fashion if we go for the other arrangement, where we see that the first layer is similar to that arrangement, that means three of them are there, giving three of these spheres like this.

But, the second layer which will come to cover this particular area will be like this. So, if we have these two layers of spheres arranged together or one after another, will generate a new type of hole here, which can now be levelled as the corresponding octahedral hole. So, this can be now our octahedral hole because in a similar fashion the central cavity can have three spheres from the first layer, that means the A layer and three more from the second layer, that means the B layer. So, I will have the corresponding arrangement as the octahedral arrangement.

So, you have the random arrangement of the spheres in a closed packed way and we are simultaneously generating some positions as the tetrahedral cavity, and some as the octahedral cavity. So, if we have this Fe2 plus and Fe3 plus ions, which are surrounding in this oxide environment, what will happen? We will see in this class of oxides, which are known as the corresponding spinels.

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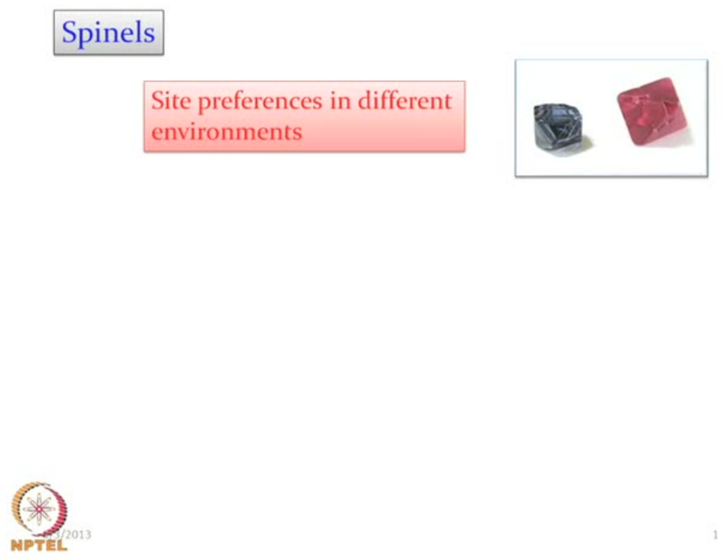

Spinels

Site preferences in different environments

So, spinels can be defined in this fashion, that we have certain arrangement of these oxides lattice around and they are very good material. And color wise they are also giving us several information’s related to the different gems and stones, as well as it is giving us lots of information related to the different types of oxide minerals because naturally these oxide minerals are available. But our interest will lie on the thing that how this particular species, which can be a simple oxide lattice or oxide containing minerals, how they can be colored and they can give rise to beautiful colored gemstones?

So, we can have what we see just now, that we can have two sites; one is a tetrahedral site and another is the octahedral site. So, we can create from the close packing of the O2 minus ions in a solid state structure, with some definite positions of these oxide anions, we can generate the tetrahedral site as well as the octahedral site. So, next if we put the corresponding metal ions, it can be simple alkali metal ions alkaline non-metal ion or the transition metal ion, will see either we are placing that particular metal ion in corresponding tetrahedral site or the octahedral site. But they will have some preference for that and this preference is basically dictated by the preference for their corresponding stabilization, due to crystal film.

So, we can calculate out the corresponding crystal fields stabilization energy, that means the CFSE for finding the site preference of these metal ions. So, if a particular metal ion has more crystal field stabilization in tetrahedral hole or the tetrahedral site, it will basically prefer that particular arrangement, where in the solid state structure that particular cation will sit within the tetrahedral sites. Similarly, if the other cations can have higher CFSE in other oxidation, states such as the trivalent state and if it gives more CFSE values compared to it is other site, it will simply go for the octahedral site in the solid states structure.

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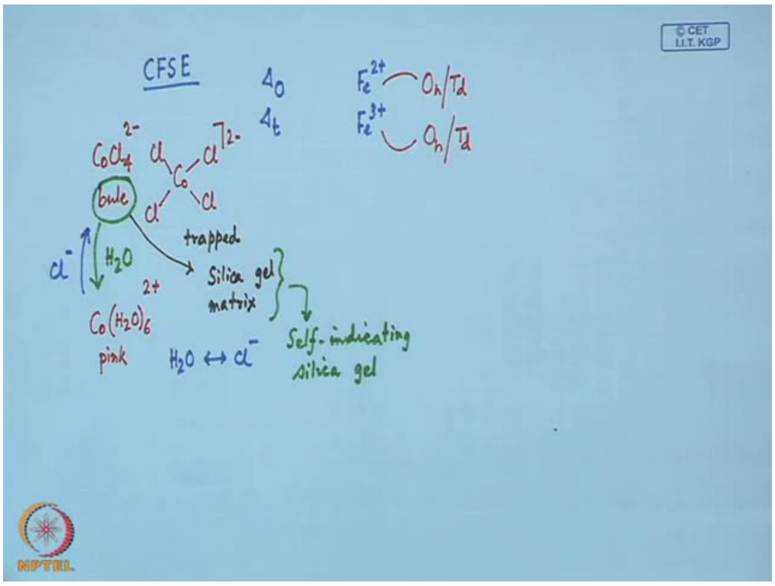

So, this is basically a typical example for the application or establishment of the role of CFSE, in guiding the different structures of these spinels. So, spinels can have a typical environment, where we can find out the corresponding crystal field stabilization with respect to delta o or delta t. The tetrahedral crystal field and octahedral crystal field will tell us where we can place the metal ions, such as Fe2 plus or Fe3 plus, in two different oxide environment. That means the environment we can have, the geometry we can have either octahedral or tetrahedral for this or in case of these also either octahedral or tetrahedral.

So, simple calculation of the CFSE values will immediately tell us, whether we will have the Fe2 plus in the octahedral site or the tetrahedral site, or the Fe3 plus in octahedral site or the tetrahedral site, because we just have seen that CFSE has a beautiful application when we see that tetrachloro cobaltate anion, which is a blue coloured solution or in the solid state also. The compound is blue coloured depending upon the cation what we use to isolate this particular anionic complex. So, this particular complex is basically stabilized in a tetrahedral arrangement of chloride anions.

This particular arrangement is basically responsible for the stabilization of cobalt in tetrahedral geometry. This can also be there if we ns have a solid state arrangement, that means we know that this blue coloured compound and solution, when it reacts with water from the moisture or some aquas environment or moist environment; it basically changes to cobalt hexaaqua form, which is 2 plus and the colour is also changing from blue to pink. So, this chloride environment to the water environment, that means the oxygen environment changing the corresponding different values of this corresponding CFSE and in octahedrals environment this particular arrangement is stabilized.

So, once we change the environment we get a corresponding colour change. So, this tetra chloro cobaltate can be trapped, it is possible to trap within a silica gel matrix to get the corresponding dehydrating agent, which is self indicating. So, by looking at the corresponding color change from blue to pink, we can have a silica gel, which is absorbing some amount of moisture or which is already absorbed some amount of moisture and has changed it is colour from blue to pink. So, it gives us the corresponding self indicating silica gel, where we can utilize this particular colour change for indicating whether the particular silica gel can be used for dehydration or not.

So, by simply changing the corresponding environment, we see the corresponding colour change and this is due to again the corresponding crystal fields stabilization from one environment to the other. Because this particular transformation is reversible and if we can supply C l minus from simple hydrochloric acid or any other source of C l minus, we can revert back to the corresponding condition, where we can have the corresponding CoCl for 2 minus species. But in case of silica gel when moisture is going, it is simply replacing the corresponding cobalt environment or cobalt co-ordination sites or the ligand environment around cobalt.

The C l minus is going away, but it is not leaving the corresponding silica gel matrix it cannot leave the corresponding silica gel matrix, but it will have only competition with the water molecule, with respect to C l minus. So, c l minus will be still there, but it is not coordinated to the cobalt centre. When he put this pink coloured in oven, in air oven at around 100 or 120 degree centigrade, we see that when we remove these moistures at this particular temperature, this water molecules will go out from the cobalt site and these C l minus anions, which are nearby trapped within the silica gel will approach again back to the cobalt site giving the silica gel again the corresponding blue coloration. So, that is the corresponding principle for knowing the self indicating silica gel and how CFSE can help us in changing the corresponding color from one form to the other.

Similarly, in this particular case also the corresponding site preference of any particular metal ion. Say the transition metal ion, which we all know that they are very good coloured when they are having some environment, such as the corresponding oxide environment, which are weak ligands. So, in oxide environment these transition metal ions, if it is there can give rise to some coloration to these solid minerals and minerals like materials. So that is why we should also be able to identify the colour change or the different colors due to the presence of different transition metal ions in some oxide lattices.

So, what are these oxide lattices, which is very well known to us because we can have very stable oxide lattices forming from silica, that means that SiO2 or alumina Al2O3 or the different borates, based on B2O3. So, this anion based oxides we can have and if we can dope the transition metal ions into the solid network or the solid structure of this oxide lattices, will get the corresponding spinels for the different arrangements of different metal ions.

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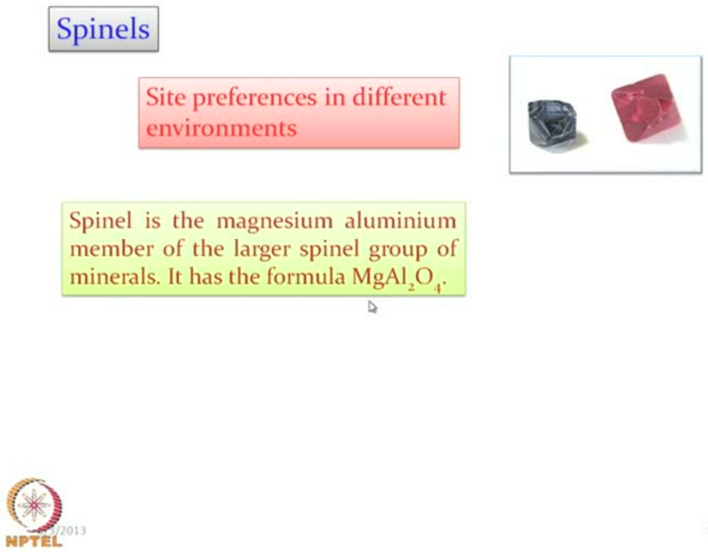

Spinels

Site preferences in different environments

Spinel is the magnesium aluminium member of the larger spinel group of minerals. It has the formula $MgAl_2O_4$.

So, the first one which is discovered in the form of a mineral, which is also known as spinel. So, this is a huge class of molecules where this particular state, it is the corresponding magnesium aluminium oxide. So, this particular species is 1 Mg, 2 aluminium and O 4, like that of are Fe3O4.

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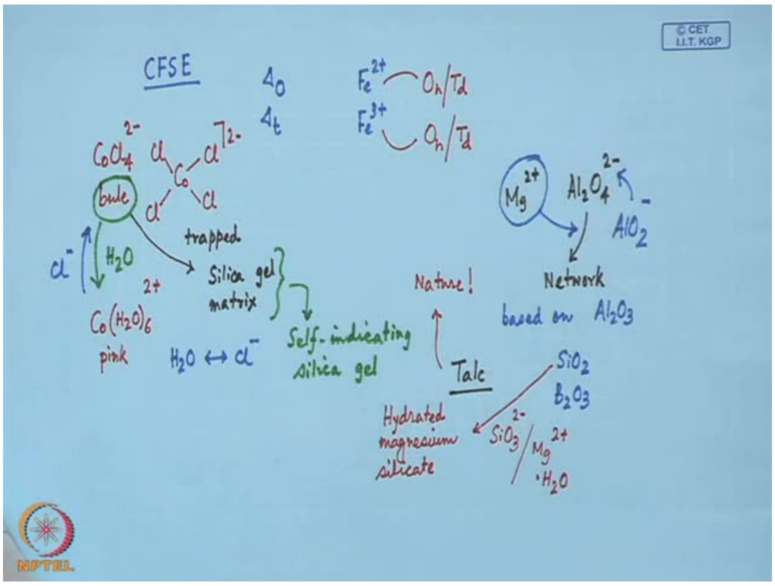

So, this magnesium aluminate, what we can consider over here because the magnesium is 2 plus and this is 2 plus, and our Al2O4 network is 2 minus, so if we have the corresponding network based on aluminium and oxygen. So, in solid state we will have a typical arrangement of this oxide anions and several or some positions are designated, or here marked for the occupation of this aluminium ions over there. Now, several other positions cationic positions will also be available for Mg2 plus and within this lattice magnesium 2 plus will enter and occupy several such positions by sharing the corresponding oxides, as their ligands. So, this particular thing is basically based on a typical alumina structure. So, basically what we can have? We have the alumina it can be alpha alumina, it can be beta alumina or gamma alumina.

So, in this particular alumina network if we just simply can go for, we can create some defect in this particular case, where we can have less number of oxide anions. See, when the ratio is 2 is to 3, where here it is 1 is to 2. So, when we remove some of these oxides around these, so just we basically go for this corresponding species like these AlO2. So, if we have species like AlO2, which is having one negative charge and if we can generate these an (( )) of these can give rise to Al2O4 minus with some charge. So, this can also be something that means some silicate minerals as we all know. So, silicate minerals are all based on SiO2.

Similarly, the borates are also based on B2O3, so these are the basic ingredients or the basic oxide lattices what we can have. And based on that basically we can have the corresponding substitution for the different other types of minerals and the corresponding compounds, and we classified as their solid state oxide and these oxides can be identified for their stabilization, and for any particular type of structure. So, we know that one important mineral what we all know very easily it can have some important applications also, which is talc, which is nothing but hydrated magnesium silicate.

So, these hydrated magnesium silicate for they see that they are based on these silica, that means it is based on the corresponding SiO3 2 minus that this more oxide anions you can have in the structure. And if we can have this and if we put on it the magnesium cation as well as some of these positions are hydrated. That means more number of water molecules are present over there and we thus get talc which nature giving us, which is also naturally occurring. So, nature is giving us this particular mineral and we get the talc which is based on the silicate mineral.

So, if we have the corresponding molecules which are based on the corresponding aluminate structure, which is MgAl2O4 we see that this particular compound can be termed as the spinel structure. So, there are two different types of the spinel structures we can have. In the normal spinel will find that the corresponding typical arrangement for M3O4 would be like this, where the bivalent metal ions will remain in tetrahedral sites and the trivalent ions will be in octahedral sides.

So, we write this in this fashion that M2 the bivalent ions in ted site, that means the tetrahedral sites and the corresponding trivalent ions, that means M3 and here also M3 in octahedral sites.

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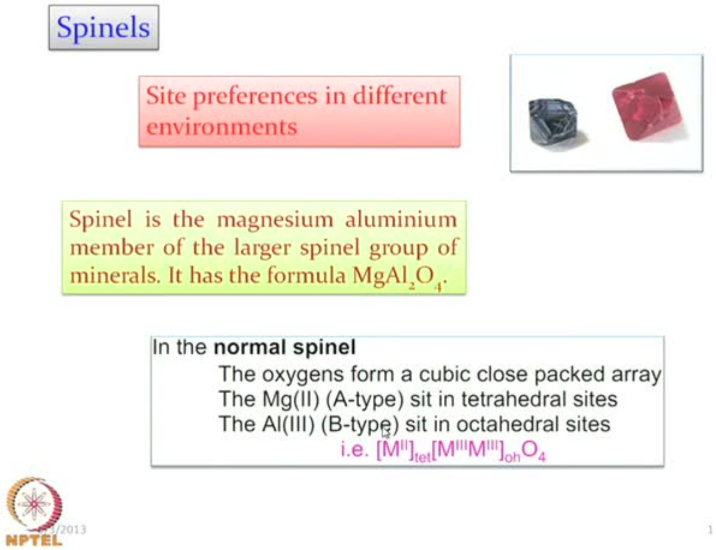

Spinels

Site preferences in different environments

Spinel is the magnesium aluminium member of the larger spinel group of minerals. It has the formula $MgAl_2O_4$.

In the **normal spinel**

The oxygens form a cubic close packed array
The Mg(II) (A-type) sit in tetrahedral sites
The Al(III) (B-type) sit in octahedral sites
i.e. $[M^{II}]_{tet}[M^{III}M^{III}]_{oh}O_4$

So, these two basically compensating the corresponding total positive charge, which is 8 unit and which we can have writing the formula, where M is of one type and the second M is of different type.

So, we have three m ions together with this O 4. So, in normal spinel the oxygens form a cubic closed packed array. What we have just now seen, that the closed packing arrangement of these oxide anions can give rise to two different types of cavities or the sites or holes, where we can put the corresponding positively charged cations. So, if we have in this particular formula of the spinel, that means MgAl2O4. If magnesium is present in tetrahedral sites that means magnesium can have 4 oxide anions in a tetrahedral arrangement. That means we consider these as the A type, that means M in A site and another M in B site, which are two in number and 4 oxygen as the oxide anions.

So, if aluminium is sitting in B type site and sit in octahedral site, so we get the corresponding arrangement, where we have the defined site. That means the smaller bivalent cations will prefer for only 4 ligands within the tetrahedral sites, but the trivalent states of the metal ions such as aluminium, which are having higher charge and small size will be present in the octahedral sites. Thus, giving rise to a structure which will simply call as normal spinel. That means the that means the most preferred arrangement, where the lower oxidation states in in lower co-ordination number and higher oxidation states in higher co-ordination number within the oxide lattice.

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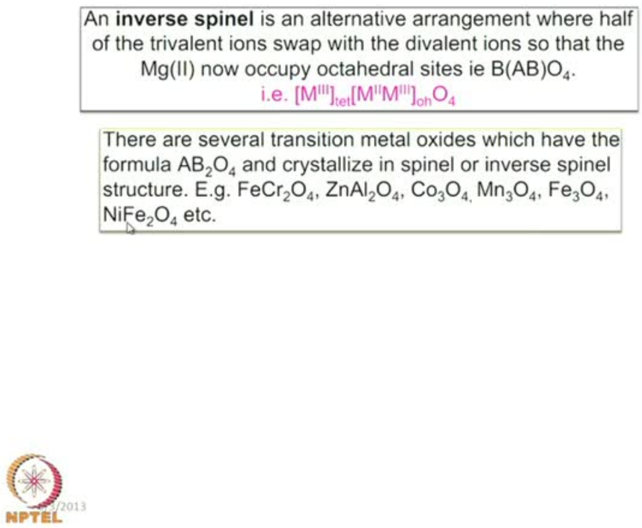

An **inverse spinel** is an alternative arrangement where half of the trivalent ions swap with the divalent ions so that the Mg(II) now occupy octahedral sites ie $B(AB)O_4$.

i.e. $[M^{III}]_{tet}[M^{II}M^{III}]_{oh}O_4$

There are several transition metal oxides which have the formula AB_2O_4 and crystallize in spinel or inverse spinel structure. E.g. $FeCr_2O_4$, $ZnAl_2O_4$, Co_3O_4, Mn_3O_4, Fe_3O_4, $NiFe_2O_4$ etc.

So, what about the alternative arrangement, the other arrangement? So, other arrangement is simply we have to move the smaller cation, that means the bivalent cation from lower co-ordination number to higher co-ordination number. That means from tetrahedral sites to the octahedral sites. This is because by placing this bivalent metal ion depending upon the corresponding electron configuration of the metal ion, we will have more CFSE; that means the more crystal field stabilization energy we can have, if we move the bivalent cation from the tetrahedral site to the octahedral site.

So, this is due to the corresponding preference of stabilization, due to stabilization in terms the corresponding crystal field around the bivalent metal ion. So, substitution can take place as we move one or more of these bivalent sites from tetrahedral to octahedral sites, by substitution of the trivalent metal ions from the octahedral sites. So, definitely this particular movement will proves the 50 percent of these trivalent sites from trivalent metal ions in this octahedral sites to the tetrahedral sites. And thus it gives rise to the corresponding arrangement, what can be termed as inverse spinel arrangement.

So, this is a different arrangement or we can consider it as an alternative arrangement where 50 percent, what I told you that the 50 percent, that means half of the trivalent ions. So, of with the trivalent ions, so that the manganese 2 plus, now occupy octahedral sites in B AB O 4 arrangement. That means the bivalent in site and 50 percent trivalent in a site and another 50 percent trivalent ions in other B sites, the remaining B sites with an arrangement of O 4. So, this particular formula we can level for the inverse spinel and we should be careful while, we will ask the question in this fashion that; what is the particular arrangement? What is showing over here for a particular spinel structure. So, we have to tell that whether this arrangement is for inverse spinel or the normal spinel.

So, there several such spinel arrangements we can have, utilization transition metal ions that means the transition metal oxides we can have. As we can seen the very basic one, what the name comes from for magnesium aluminum spinel. That means both of them where non transition elements, but we can have both the two sites, which are occupied by transition metal ions. Such as in this particular case, where all of them are manganese, where all of them are cobalt, where all of them are iron and half of them can be nickel and the other half is concerning of the iron.

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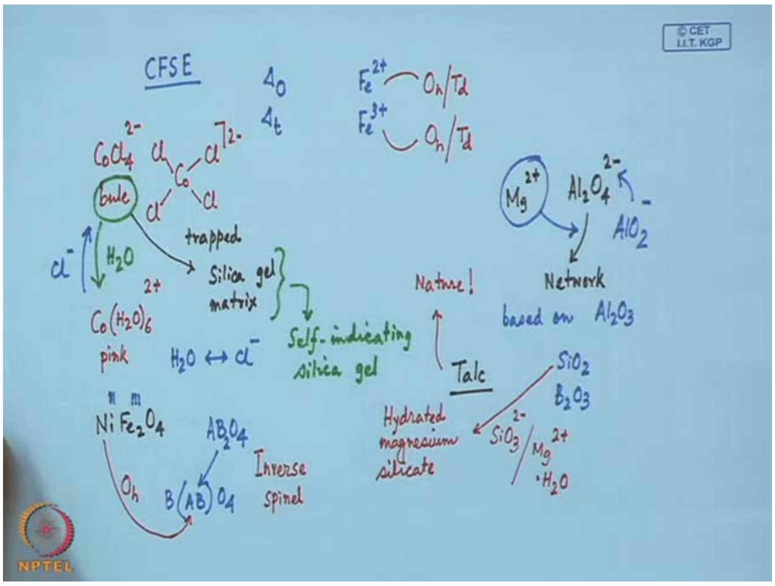

Because in the case of Ni Fe 2 O 4, clearly due to the preference or availability of the metal in that typical oxidation states, we know the nickel can only be present as a bivalent state and iron is in trivalent state.

So, this particular arrangement we can have and this particular arrangement can stabilization this particular formula. What we see that when they are crystallizing, that means we have ABO 4 arrangement, but if we this arrangement we can get that; we have two of this B and one B is here, then we can have AB and O 4. So, we have this metal ion that means the nickel and if this can be moved to the octahedral site because nickel we always know, it can have only the plus 2 oxidation state, and it will have the preference for the corresponding octahedral site. Because is very difficult to get a corresponding situation, where nickel is being stabilized by 4O 2 minus in a tetrahedral arrangement.

So, these particular spices that means NiFe2O4 will give rise to us a corresponding structure, which can be crystallized as corresponding inverse structure. So, we will have inverse spinel for that. So, when this as well as that corresponding zinc aluminums oxide or iron chromium oxide, these are basically the corresponding transition metal oxides, which have the formula obviously AB 2 O 4, but they are crystallizing in normal spinel structure or the corresponding inverse spinel structure.

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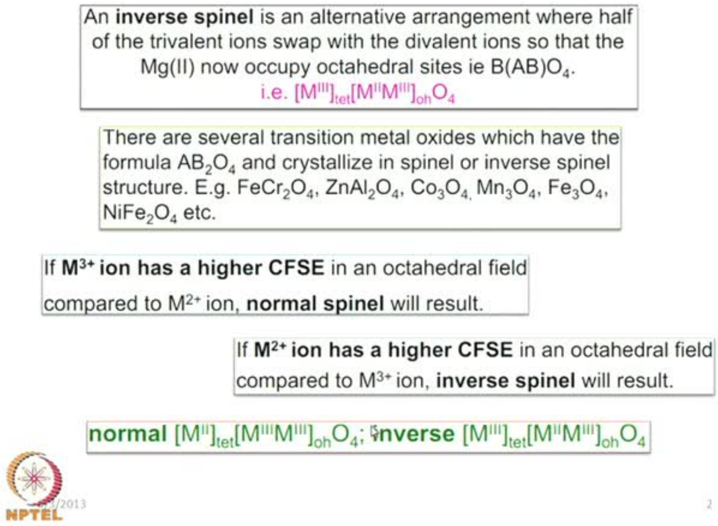

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If **M^{3+} ion has a higher CFSE** in an octahedral field compared to M^{2+} ion, **normal spinel** will result.

If **M^{2+} ion has a higher CFSE** in an octahedral field compared to M^{3+} ion, **inverse spinel** will result.

normal $[M^{II}]_{tet}[M^{III}M^{III}]_{oh}O_4$; **inverse** $[M^{III}]_{tet}[M^{II}M^{III}]_{oh}O_4$

So, if the corresponding M 3 plus ion that means, we have to identify which one is present as a trivalent state and which one is present in a bivalent state. So, if M 3 plus ion has a higher CFSE in a an octahedral field. So, this is the most important definition for formation of the normal spinel that the trivalent state we are having both the two M 3 plus ion in octahedral site.

So, in AB2O4 in both the two metal ions in the trivalent state can give rise to higher values of crystal field stabilization energy and they are two in number, so the stabilization energy will be doubled. So, we get the corresponding stabilization of this M 3 plus ion in octahedral field and we get the normal spinel, and definitely we will push the M 2 plus in the tetrahedral field. But if the reverse thing happen that means, the important criteria for M 2 plus is that, M 2 plus has a higher CFSE in octahedral field. So, we have to compare the corresponding CFSE of M 3 plus in octahedral and tetrahedral field, what we have done earlier.

Similarly, for M 2 plus we have to find out it is CFSE in both the two fields and if it has higher CFSE in octahedral field, compare to M 3 plus ion, we get the corresponding inverse spinel. So, we write down in this fashion what we have seen in this two cases; that normal is M 2 plus in tetrahedral site and inverse M 3 plus in tetrahedral sites. And this resolves basically 50 percent of movement of this M 3 plus from octahedral site to the tetrahedral site because the ratio of metal ions with respective to all this spinel structure is that, we need for charge neutralization, one bivalent metal ion and two trivalent metal ions. So, we cannot remove all the trivalent metal ions from the octahedral sites, but we can have the full occupancy of the trivalent metal ions for available octahedral sites, and 50 percent occupancy of the trivalent metal ions for the corresponding octahedral sites.

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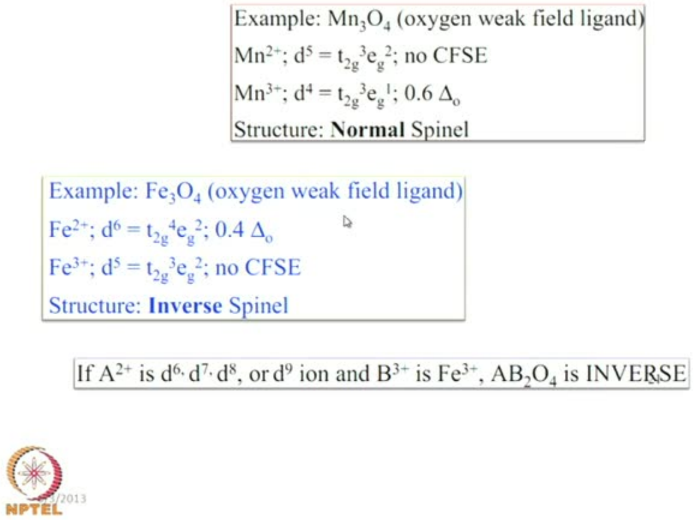

Example: Mn_3O_4 (oxygen weak field ligand)
Mn^{2+}; $d^5 = t_{2g}^3e_g^2$; no CFSE
Mn^{3+}; $d^4 = t_{2g}^3e_g^1$; 0.6 Δ_o
Structure: **Normal** Spinel

Example: Fe_3O_4 (oxygen weak field ligand)
Fe^{2+}; $d^6 = t_{2g}^4e_g^2$; 0.4 Δ_o
Fe^{3+}; $d^5 = t_{2g}^3e_g^2$; no CFSE
Structure: **Inverse** Spinel

If A^{2+} is $d^{6,}$ $d^{7,}$ d^8, or d^9 ion and B^{3+} is Fe^{3+}, AB_2O_4 is INVERSE

So, let us find out this as our examples for finding out the corresponding CSFE. So, we simply find out for manganese spinel, which is Mn3O4 and we have oxygen in weak field and M 2 plus, which is d 5 arrangement. And this in the d 5 arrangement we have the corresponding thing that means, we just simply go for this M 2 plus in octahedral stabilization, we do not have any stabilization because the arrangement is t 2g 3e g 2. We do not have any CFSE, but for manganese 3 plus, which is d 4 arrangement that means, t 2g 3e g 1, 1 electron is removed from e g level, as a result we have a corresponding crystal field stabilization energy of point six delta o. So, the structure would defiantly be a normal spinel, is a very simple calculation where we can calculate out the corresponding CFSE, of the bivalent metal ion in octahedral field and the trivalent metal ion in the octahedral field.

Similarly, for Fe3O4 again oxygen in weak field case Fe 2 plus is giving the stabilization due to t 2g 4e g 2 arrangement, where we can have for this arrangement. We all know that we do not have this particular thing. So, we have this Fe d 6 arrangement for Fe 2 plus. So, Fe 2 plus is giving rise to corresponding stabilization 0.4 delta o and for Fe 3 plus we have no CFSE, and with this results basically the corresponding inverse spinels structure. So, looking at this particular arrangement, for this arrangement because this t 2g 6 and e g 6 is we can have, that Mn 2 plus, how it is going from tetrahedral arrangement. So, this g thing will not there when we put in the tetrahedral arrangement and the tetrahedral stabilization can be converted to the octahedral stabilization, all we know for that.

So, we just simply comparing the corresponding CSFE we can have the two structures, whether it is a normal one or the inverse one. So, the thing is that if we have n 2 plus where it is d 5, d 7, d 8 and d 9 and B 3 plus is Fe 3 plus will result in an inverse spinel. So, inverse spinel structure will be resulting if we have a mixed metal ion thing, where we can have this as Fe, this iron base spinel. And if this iron is Fe 2 plus this is the d 6, this also give rise to the corresponding inverse spinel structure. But in case of other metal ion, apart from this four we have the normal spinel arrangement.

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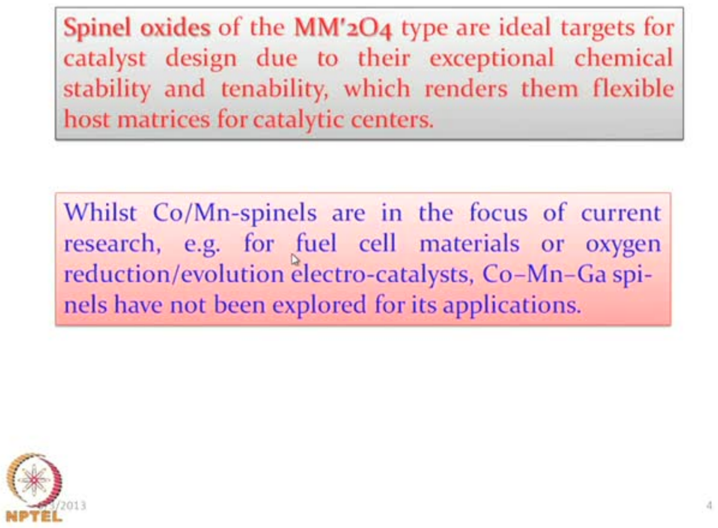

Spinel oxides of the MM'_2O_4 type are ideal targets for catalyst design due to their exceptional chemical stability and tenability, which renders them flexible host matrices for catalytic centers.

Whilst Co/Mn-spinels are in the focus of current research, e.g. for fuel cell materials or oxygen reduction/evolution electro-catalysts, Co–Mn–Ga spinels have not been explored for its applications.

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So, what we get that this spinel oxides, which we can have one in the corresponding A site and two other in the B site. That means one is one particular metal, it can be magnesium or it can be aluminium. So, the formula is M, M prime 2 O 4 is a typical target element for the development of the different types of catalyst also. So, we can design based on these oxides as good catalyst because they are very much stable, they have very good stability, whether chemical stability and tenability, a tenability. That mean we can tune them from one structure to the other and which can be utilized for flexible host matrices, for catalytic center. So, we can have this particular spinel based catalytic system, where the spinels can function as a good catalyst.

Similarly, we all know that the typical arrangement for this spinels cobalt and manganese. That means the cobalt and manganese based spinels are there, which people are working on it for different catalytic arrangement for this particular system, and can also be utilize for fuel cell material for oxygen reduction or evolution. That means how we can evolve oxygen from water or any other oxygen donor system, for fuel cell material preparation and evolution electro catalysts, that when catalytic system is governed by electron transfer.

Similarly, if we put the third metal ion based on this cobalt and manganese spinel, if we put gallium and this sought of spinel arrangement is a difficult one. People are working on it; it has very little application till now. So, if we instead of considering that MM B type of arrangement that means one in A site one in B site and for oxide anion, we can add A and this two are in the B site. That means both manganese and both gallium can be in the B site and they basically render for some different type catalytic arrangement, due to the presence of gallium into the system.

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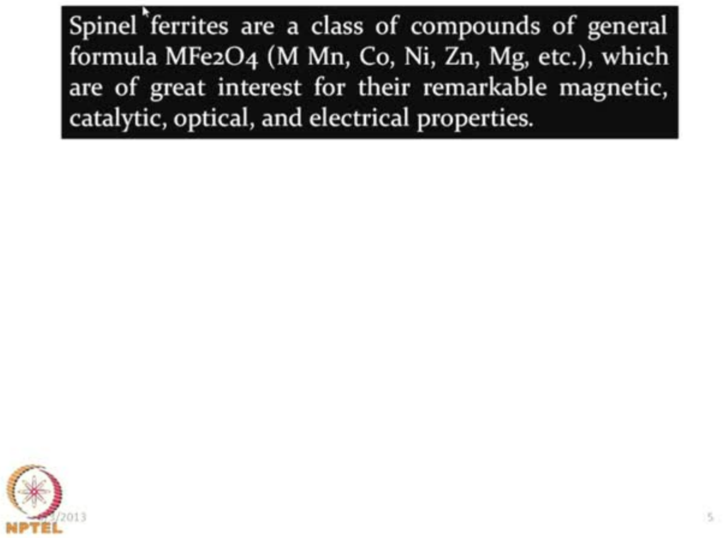

Spinel ferrites are a class of compounds of general formula MFe2O4 (M Mn, Co, Ni, Zn, Mg, etc.), which are of great interest for their remarkable magnetic, catalytic, optical, and electrical properties.

So, other group of molecules like this where M is equal to manganese, cobalt, nickel, zinc and magnesium based on iron that means, what we have seen just now.

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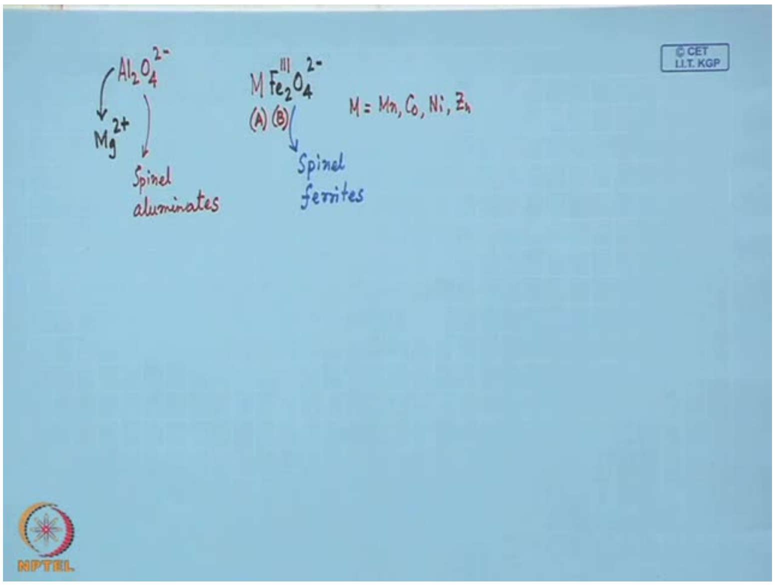

That we have the corresponding system which are based on aluminates. The standard spinal what we know that Al2O4 2 minus where it is attaching with magnesium ion. This basically gives us the corresponding simple spinel, where from we derived the name of the spinel structure. Also, and we can have the similar thing based on iron, where the arrangement is Fe2O4 2 minus, since it is based on iron. So, these spinels this basically the spinels, which are based on, so aluminum oxides are alumina. So, this can be consider as corresponding spinel aluminates, these are spinel aluminates and here we can have the same thing for spinel ferrites.

So, we have iron based spinel structure where the entire network is formed from iron oxides, utilizing iron in trivalent state. So, we can have the different spinel ferrites. So, what we do, we just add the metal in the A site. So, this is M in A site and iron will be in the B site, so we can have the different metal ions. So, luckily we can have all sought of M that means the different M, which can be utilized for these spinel ferrites because they have also very useful applications for this, which can have like this M for manganese. So, the first transition series can utilize for that, we can have cobalt, we can have nickel and we can have zinc. So, starting from the entire series from manganese, cobalt, nickel and zinc we can have this sought of arrangement for ferrite spinels.

So, this can be termed as spinel ferrites or ferrite spinels. They are a class of compounds of general formula, since the ferrites are defined over here like aluminates, so these are ferrites.

So, we have MFe2O4 and including this transition metal ion as well as magnesium, which is the most common metal ion what we found for the spinel structure in tetrahedral environment. They are very important because they are of great interest for their remarkable magnetic, catalytic, optical and electrical properties. So, apart from their catalytic importance, they can be utilized for magnetic properties or magnetic utilization. Several magnetic tapes for storing the voice and forwarding the other data, we can use it as the corresponding magnetic material or magnetic data storing devices.

So, they can have remarkable application in magnetic area, they can have some optical arrangement because they can have some typical optical spectra and some laser or any other thing like ruby laser. We know that, but that is aluminum based, but several like ruby like thing can also be utilized for optical properties; that means optical behavior can be seen with this sought of material. And then electrical conductions can be utilized for their electrical properties.

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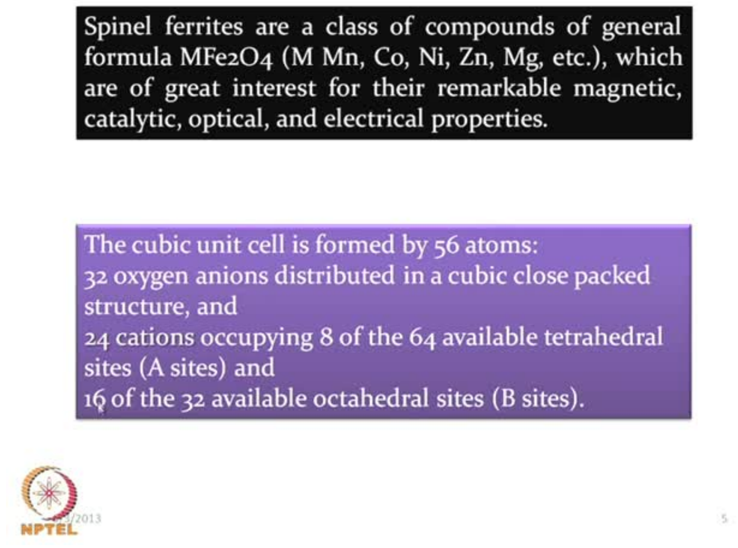

Spinel ferrites are a class of compounds of general formula MFe2O4 (M Mn, Co, Ni, Zn, Mg, etc.), which are of great interest for their remarkable magnetic, catalytic, optical, and electrical properties.

The cubic unit cell is formed by 56 atoms:
32 oxygen anions distributed in a cubic close packed structure, and
24 cations occupying 8 of the 64 available tetrahedral sites (A sites) and
16 of the 32 available octahedral sites (B sites).

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So, they are very useful molecules. So, in a cubic unit cell if we can have, which is form from 56 atoms together with the oxides as well as the corresponding cations. So, apart from that we have 32 oxygen anions and 24 cations altogether we have 56 atoms. So, 32 oxygen anions can be distributed in a cubic closed pack structure. What we have seen at the very beginning of this particular class, where we have the layer arrangement of the different oxide anions. Now, the cations can be placed, how? You have 64 available tetrahedral sites, out of these if we just go for the arrangement of these anions. So, in this cubic arrangement we can have 64 available tetrahedral sites and out of them 8 is occupied as a tetrahedral site.

Similarly, out of 32 available octahedral sites, 16 will be occupied by these cations. So, we can have the arrangements for B and we can have the arrangements for A. So, this is the M A site and these are the M B site, which are so double in number. So, 8 and 16 are there and we have 32 oxygen atom. So, all together by matching the formula also, which is M 8 2 B 2 A 4 which is 8 for the A site, 16 for the B site and 32 for the oxide anions.

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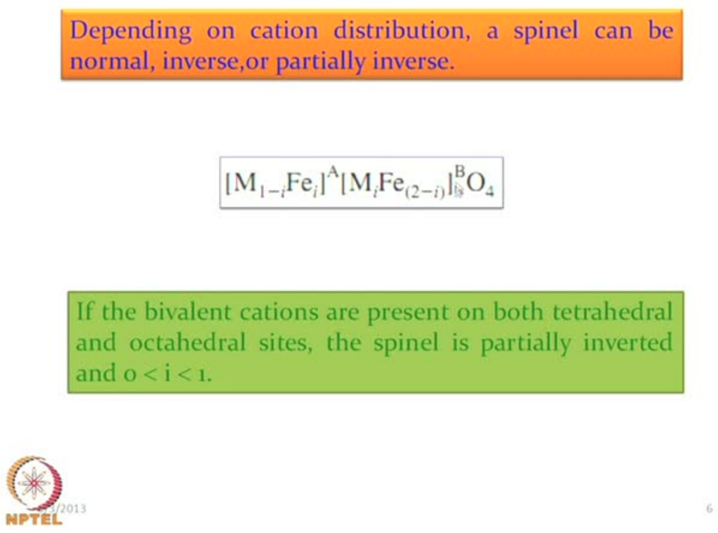

Depending on cation distribution, a spinel can be normal, inverse,or partially inverse.

$[M_{1-i}Fe_i]^A[M_iFe_{(2-i)}]^B_{\text{}}O_4$

If the bivalent cations are present on both tetrahedral and octahedral sites, the spinel is partially inverted and 0 < i < 1.

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So, we can have also the depending on the cation distribution, apart from this two arrangements what we have seen. The normal and as well as the inverse arrangement we can have also a partially inverse structure. Partially inverse structure is nothing but we cannot move the all of one particular type of metal ion. That means the bivalent or the trivalent entirely from the octahedral site to the tetrahedral site or the reverse. So, if we can have one such ferrite base spinel structure, where we see that entirely we can have MFe2O4 structure. This is corresponding A site and this is the corresponding B site. Now, if we can have from this, that means some of these, some percentage of these M.

Not that the entire M we are moving from A site to B site, but certain percentage of this M can be moved from A site to B site, that means the tetrahedral site to the octahedral site. Similarly, of these iron atoms from B site should be moved from this B to A site. So, we have this particular formula for this partially inverse spinel structure.

And if the bivalent cations are present on both the tetrahedral and on the octahedral sites, that means this M. They are present both here as well as here, the spinel is know as partially inverted one and the i value can range from 0 to 1. So, if it is 0, we can have between this normal and inverse one. If it is 1 we can have the other one, but if it is in between, if the i values are in between, we have the partially inverse spinel. So, these partially inverse spinel can also have some important application or important structures for that. And we basically go for these by seeing that that some of this metal ions and be moved from A site to B site, with regular substitution of those metal atoms from B site, which can be pushed from be to A.

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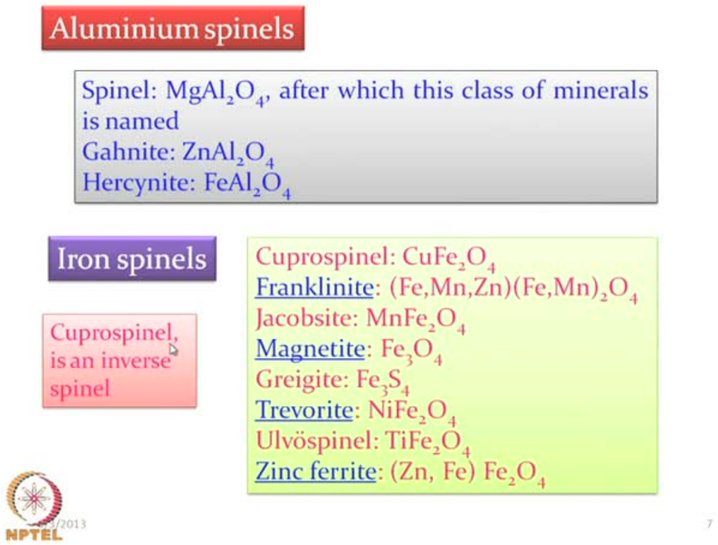

Aluminium spinels

Spinel: $MgAl_2O_4$, after which this class of minerals is named
Gahnite: $ZnAl_2O_4$
Hercynite: $FeAl_2O_4$

Iron spinels

Cuprospinel, is an inverse spinel

Cuprospinel: $CuFe_2O_4$
Franklinite: $(Fe,Mn,Zn)(Fe,Mn)_2O_4$
Jacobsite: $MnFe_2O_4$
Magnetite: Fe_3O_4
Greigite: Fe_3S_4
Trevorite: $NiFe_2O_4$
Ulvöspinel: $TiFe_2O_4$
Zinc ferrite: $(Zn, Fe)\ Fe_2O_4$

So, we can have this structure like this, we can have the aluminium spinels in us. So, based on this what we have seen that aluminium spinels, where that normal spinel structures we can have. And these normal spinels we get that where we have the entire network is forming from aluminium. So, we have when this are forming from magnesium together with aluminium and the normal one, that the spinel structure what we get for the minerals, which is known as the typical spinel one.

Then if we substitute this magnesium position by zinc, we get gahnite. If we substitute zinc site by iron or the magnesium by iron, we get hercynite. So, these are all available naturally some of them has been identify nicely, and we can explore them for their typical applications. Based on the parents structure, which is formed from aluminium and which is formed from iron we can level them as for aluminium spinels or iron spinels.

So, in a similar fashion we can have several such iron spinels in our hand and this iron spinels, the network is forming from the arrangement of iron and oxygen, like that of our arrangement what we get for aluminium. Because we are not getting this arrangement for the typical silica because we need the trivalent state, but silicon is giving the corresponding bivalent state. So, for the trivalent state we can use the corresponding iron.

The first example is very useful one which is nothing but our cuprospinel, where the site is occupied. The A site is occupied by copper, then franklinite where this two, the basic structure is forming not only by iron, but also can by formed by manganese. Similarly, A sites can be substituted by iron, manganese and zinc, any of them can be their to give this particular structure. Then jacobsite is nothing but substituted by manganese by for the A site. Then we can have the magnetite, in magnetite we have both the iron. Then greigite, with we have this particular arrangement is based on sulphur, which is a different class, which is a thio spinel structure and tervorite is based on nickel, then titanium and then zinc and iron.

So, like this, which is griegite that means your oxide lattice has been changed from oxide to sulphite and this cuprospinel can have a typical inverse spinel structure.

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Chromium spinels

So, we can have similarly, the chromium spinels and where the entire structure can be found from the chromium. It is a useful molecule in terms of or compound, in terms of the corresponding mineral application and that we will discuss in our next class.

Thank you very much.