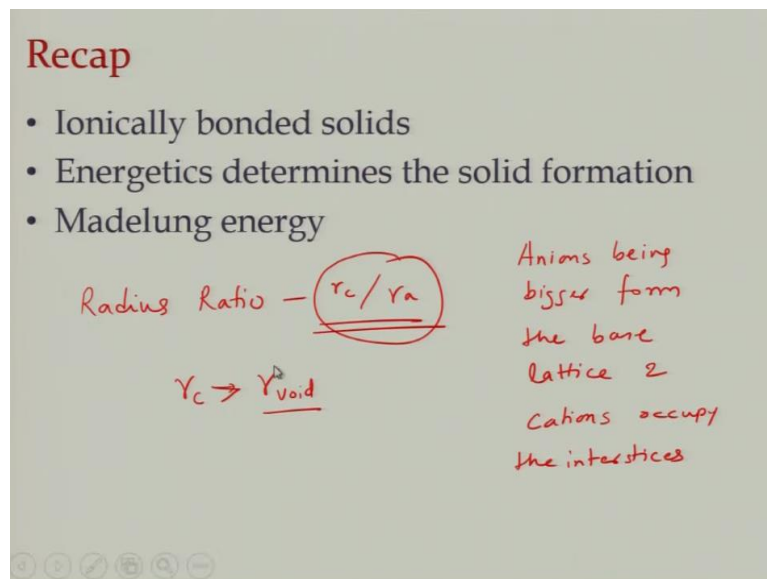


Fundamentals and Applications of Dielectric Ceramics
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Lecture No 06
Pauling's rule and crystal structure of ceramics

Welcome again to this new lecture of the course, Fundamentals and Applications of Dielectric Ceramics. So, let us just first recap the previous lecture.

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Recap

- Ionically bonded solids
- Energetics determines the solid formation
- Madelung energy

Radius Ratio - $\frac{r_c}{r_a}$

$r_c \rightarrow r_{\text{void}}$

Anions being bigger form the base lattice & cations occupy the interstices

In the previous lecture, we initiated our discussion on ionically bonded solids. Where solids form on the basis of differences in the electronegativity of cations and anions, where generally ionically bonded solids are, so ionically bonded solids are those which contain atoms of two different types, that is cations and anions, which have vast difference in electronegativity.

And the energetics of the bond formation will determine the solid formation, so we looked at how, for example, in case of sodium and chlorine, it is energetically favorable to form sodium chloride structure, crystalline solid, which is ensemble of atoms arranged in certain fashion over sodium and chlorine remaining in the gaseous form. And because we gain in terms of energy, the structure is more stable and there is something we worked out the expression also energy derivation.

There is something called as Madelung energy, which is essentially a manifestation of the bond energy of the solid, so lower the bond energy of the, so more negative the potential energy of

the system is, higher the bond energy will be and more the properties such as melting point and elastic modulus, etc. and lower the coefficient of thermal expansion will be and we saw that empirically based on that expression, in a very simple fashion that how, for example solid like magnesium oxide or zirconium oxide or aluminum oxide will have higher, is likely to have higher value of bond energy as compared to something like sodium chloride or lithium fluoride.

And then we started to look at Pauling's rules. And we saw, how the radius ratio of cation to anion determines the structure formation and this is basically assuming first that anions being bigger, from the base lattice and cations occupy the interstices. And interstices that we have seen, you can have tetrahedral, octahedral, but it is not necessary to have only tetrahedral and octahedral, you can have triangular coordination, you can have cubic coordination, you can have 12-fold coordination, 2-fold coordination.

And the kind of coordination that you will have is determined by r_c/r_a and the fundamental reason behind that is that anion should not touch each other, they should remain little away from each other and that is why the size of cation is little bigger than size of the void, slightly bigger than the size of ideal void, okay. But then there are ranges for each of the void and as long as the sizes between that range, it will most likely follow that kind of coordination.

Sometimes there are exceptions because of bonding, because if the material has tendency to form a covalent bond and covalent bonds are highly directional in nature. Sometimes these rules are broken.

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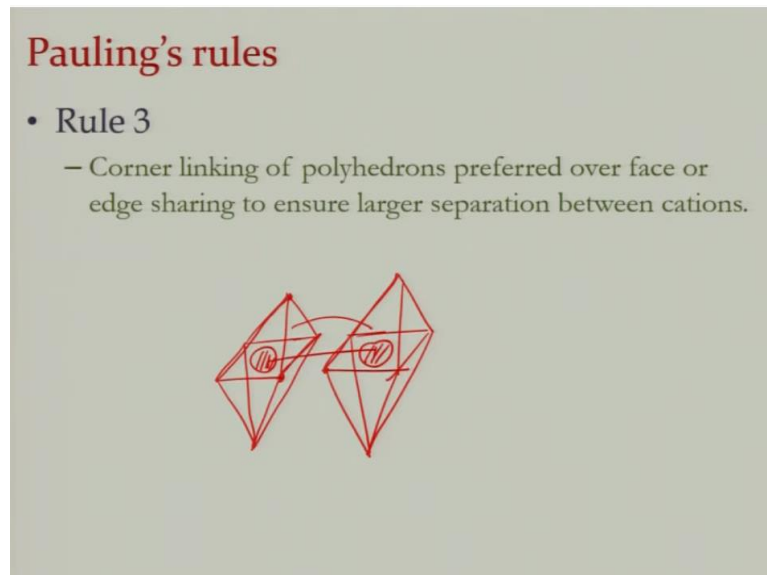
Pauling's rules

- Rule 2
 - Preservation of charge neutrality

$$\begin{array}{l} M^{\oplus} O^{\ominus} \\ \hline \end{array} \Rightarrow \text{solid is charge neutral}$$
$$\begin{array}{l} Al^{3+} O^{2-} \\ \hline 2 \quad 3 \end{array} \quad \begin{array}{l} Fe_2 O_3 \\ \hline \end{array}$$

Second Rule of Pauling's is that charge neutrality in a solid must always be preserved. So, if you have a solid M_xO_y , so M_x and O_y should be in such that so that solid is charge neutral, okay. So, if you have Al for instance and oxygen, then Al is 3+ and oxygen is 2-, as a result stoichiometric solid will be Al_2O_3 . Similarly, Fe_2O_3 and so on and so forth. Solids are charged neutral and this charge neutrality has to be maintained.

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Third thing is about the corner linking of polyhedra. So, corner linking of polyhedra is basically, so just think like that, so you have, let us say, octahedral like this, okay. And you have another neighboring octahedra, okay. So, all of these have cations sitting at the center, let us say both of them have cations sitting in the center. These polyhedra in the solid, so you will form variety of polyhedras right, these polyhedras have, they can be connected at the edge, they can be connected at the corners, they can be connected at the face.

They can share the faces, they can share the edge, they can share the corners, and generally, you will see if they are connected over corners, then the distance between these cations is larger as compared to if they are connected at the face or the edge. As you can see from this very clearly, if you connect these two over the faces, the cations will come closer to each other. If you connect them on the edges, they will again be closer to each other, but if you connect them over the corners, they will be farthest.

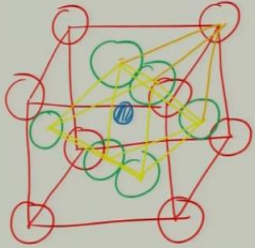
So this basically minimize the electrostatic repulsion between the cations. So, to minimize the electrostatic repulsion between the cations, corner linking of polyhedra is preferred over face or edge sharing between the polyhedras.

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Pauling's rules

- Rule 4
 - In a crystal containing different cations, those of high valence and small coordination number tend not to share polyhedron elements with one another such as in materials like BaTiO_3 .

$\begin{array}{cc} \downarrow & \downarrow \\ 2+ & 4+ \end{array}$



The diagram illustrates the crystal structure of barium titanate (BaTiO₃). It shows a central titanium atom (blue sphere) surrounded by six oxygen atoms (green spheres) forming an octahedron. This octahedron is coordinated to a barium atom (red sphere) at the center of a larger cube. The barium atom is coordinated to six oxygen atoms (red spheres) forming a cube. The diagram shows that the barium and titanium polyhedra are staggered, meaning they do not share any common polyhedral elements, which is consistent with Pauling's fourth rule.

And the fourth rule is, if you have crystal which contains different cations, different cations for example, barium titanate. So, you have barium with 2+ valence, okay and titanium with 4+ valence, alright. So, if you have a crystal with different cations like this, then those of high valence and small coordination number, tend not to share polyhedral elements with one another, such as in barium titanate. So, you will see for example, in barium titanate, so this is barium titanate structure as we will see later on in more detail.

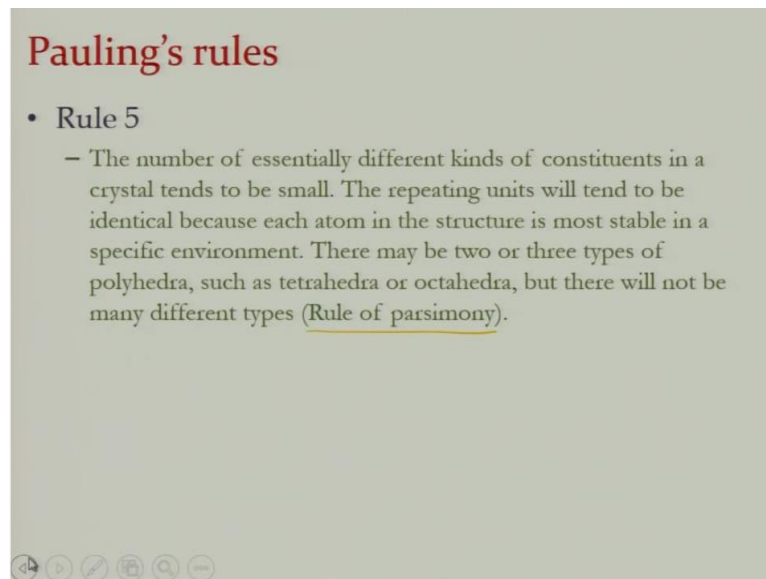
So, these are all barium atoms, these are all oxygen atoms and somewhere in between you will have tiny titanium atoms. So, titanium atom in this case is coordinated by this polyhedra or octahedra, alright, whereas barium atom is coordinated by, I use a different color, so this is barium atom. Barium atom is coordinated by this atom, this atom and then, so you have 1, 2, 3 and then you have four more crystals around it. So you will have total of 12 neighbors.

So you can see that titanium polyhedra is neighboring the barium polyhedra not the titanium polyhedra. So there is a sort of staggered polyhedra, so polyhedra of titanium then polyhedra of barium, polyhedra for titanium followed by polyhedra for barium followed by polyhedra for titanium and that is how the polyhedras are arranged in a staggered fashion. So they do not share, they have different polyhedra for each of the cations.

Polyhedra for titanium is different, polyhedra for barium is different, but they are touching each other at face or edge depending upon the configuration and that also ensures that the polyhedra for titanium and polyhedra for barium are separated from like ions. So, barium barium

polyhedra is separated, typically mediated by a titanium polyhedra. And that also ensures that there is a farthest distance between the two polyhedras.

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Pauling's rules

- Rule 5
 - The number of essentially different kinds of constituents in a crystal tends to be small. The repeating units will tend to be identical because each atom in the structure is most stable in a specific environment. There may be two or three types of polyhedra, such as tetrahedra or octahedra, but there will not be many different types (Rule of parsimony).

And then we have rule number five which is number of essentially different kinds of constituents in a crystal tends to be small, the repeating units will tend to be identical because each atom in the structure is most stable in a specific environment. There may be two or three different types of polyhedra, such as tetrahedral or octahedra, but there will not be too many different types.

So, what it says is that, it is unlikely to have too many different kinds of polyhedra, I mean it is possible to have tetrahedra and octahedra, but very unlikely you will have tetrahedra, octahedra, triangular, FCC, so this is called as rule of parsimony, parsimony means frugal, frugality. So, basically there will be least possible variations of polyhedra in the system than to have, otherwise it will create a very open structure, that open structure may not be favorable, open structure or closed structure may not be favorable.

But again, this is more of a guideline rather than, again it has to be determined only by the electro statistics and energetics rather than anything else, okay. So, these are the five Pauling's rules. The most important thing is electro statistics that cations and anions should be away from each other, they should not touch each other and solids should be charged neutral and the electro statistics is basically manifested in the arrangement of polyhedra in such a fashion, so that energy is minimum.

And then radius ratio determines that a certain kind of polyhedra coordination is preferred over other, just to ensure that anions are a little away from each other and cations are also away from each other.

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Bond strength

- Ratio of valence of an ion to its co-ordination

$$\text{Bond strength} = \frac{\text{Valence of the ion}}{\text{Coordination number of ion}}$$

- In a stoichiometric and charge neutral solid, the bond strength of cations must be equal to those of anions.

Handwritten example for Al_2O_3 :

Cation $\frac{3}{6} \Rightarrow \frac{2}{4}$ Anion

Handwritten example for ZnO :

$\frac{2}{4} = \frac{2}{4}$ — 6 or 8 X X

And another thing that is important to understand is the bond strength in these. Bond strength allows you to determine the charge neutrality and the coordination environment with respect to. So, basically, bond strength is defined as ratio of valence of anion to its coordination. So, bond strength for a given ion is valence of that particular ion divided by coordination number of that ion. So, in a stoichiometric and charge neutral ceramic, the bond strength of cations must be equal to those of anions, this ensures that you have charge neutrality.

So, for example, if you take ZnO, okay. ZnO has, in its cubic form, Zn has valence of 2+ and the coordination number of zinc is 4. What it means is that oxygen also have valence of 2 and its coordination number also has to be 4, so, that the bond strengths are equal, so that that solid remains charge neutral. You cannot have oxygen coordination number of 6 or 8, it is not possible, okay. It will rule out the charge neutrality, it will violate the charge neutrality.

Now if you go to, for example, Al_2O_3 , okay, in case Al_2O_3 , aluminum has a valence of 3, it has a coordination of 6, what it means is that, oxygen has a valence of 2, it will have a coordination number of, they will have different combinations in this case, okay. But this coordination is necessary to ensure the charge neutrality, okay. So, this is for cation, this is for anion. So, this is how this bond balance rule helps you in determining whether you got it right or not.

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Typical Ceramic Crystal Structures

- Compounds based on cubic closed packing (CCP or FCC) of ions
- Compounds based on hexagonal closed packing (HCP) of ions
- Other structures with some deviations from above two.

Now, let us look at some of the typical ceramic structures, which are followed by a lot of dielectric materials and let us see what these structures are. So, generally, the structures are based on cubic closed packing of ions, that is anions, which means anions will form a base lattice, which is FCC structure or cubic closed packed and cations will occupy interstices in them. You can have structures in which anions will make HCP lattice based on hexagonal closed pack structures.

And again cations will occupy the interstices and you can have some other deviations such as cubic packing, just the cubic packing or some of the forms of packing, let us see what these structures are.

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Compounds with FCC Packing of anions

- Rocksalt structured compounds
- Antifluorite (A_2X) & Fluorite (AX_2) Structures
- Zinc Blende (MX) Structure
- Spinel Structure

So, we first begin with compounds with FCC packing of anions, we will look at four structures

here, we will look at rock solid structure compounds, which are basically rock salt sodium chloride, then we will look at fluorite structure, anti-fluorite structured compounds, we look at zinc blend structures and we look at spinel structures. These are the four structures that we will look at.

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Rock Salt Structured Compounds

- NaCl type (MX Type)
- Examples
 - MgO, FeO, CaO, NiO, MnO
- Radius ratio, r_c/r_a : typically between 0.414 - 0.732
- Co-ordination
 - Cation: 6 ✓
 - Anion: 6 ✓
- 100% occupancy of octahedral sites
- Crystal Structure: FCC

Handwritten notes:
 r_c/r_a (with arrow pointing to 0.414 - 0.732)
 6-fold (with arrow pointing to Co-ordination)
 Each host ion
 ↓
 one octahedral void
 FCC → 4 atom
 4 Oct. void

Rock salt structured compounds are basically sodium chloride type materials. In this, they are many examples. So, in addition to sodium chloride we have oxide such as magnesium oxide, iron oxide, nickel oxide, calcium oxide, manganese oxide, most of these binary oxides will follow this kind of structure which is rock salt structure. And if you look at the radius ratio for these, it generally lies between point 0.414 to 0.732.

So, if you do this home exercise by yourself, just take the cation radius anion radius for these examples, okay. So r_c/r_a you can calculate for these, it generally will fall within the range 0.414 to 0.732. 0.414 is at the edge of octahedral, 0.414 is the ideal size of octahedral void. 0.732 is the ideal size of cubic void. So, which means, the coordination number that we will have in this case is six fold, octahedral is six fold coordination.

So, we will have six fold coordination in this case, so, we will have six fold coordination. This is eight fold, but it will remain six fold because at the edge of eight fold, okay. So, in this case, the cation coordination will be six fold and by definition of bond strength, anion coordination will also be six fold because it is stoichiometric because M:X is 1:1, which means they have similar valence. If they have similar valence, they will have similar coordination number as well.

And here what happens is that, you know that in FCC materials, for each host ion, you will have one octahedral void, right. So, FCC has four atoms and it has four octahedral voids, which means 100% occupancy of octahedral voids. So, X kind of atoms will make FCC lattice and all the octahedral voids will be filled by M atoms and crystal structure eventually is FCC.

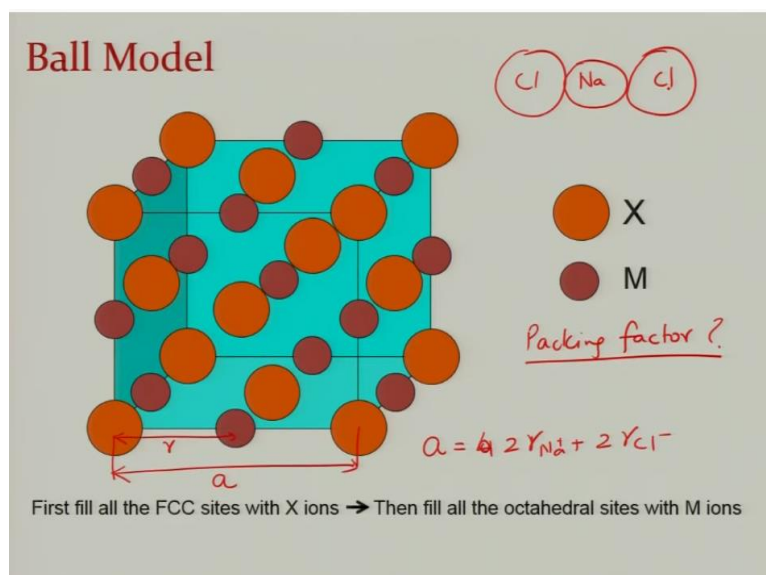
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Radius ratios

Compound	r_c (nm)	r_a (nm)	r_c/r_a
NaCl	0.102	0.181	0.564
MgO	0.072	0.140	0.514
SrO	0.118	0.140	0.842
NiO	0.069	0.140	0.492
FeO	0.078	0.140	0.557

So, this is the radius ratio table, you can have a look at it later and calculate it and see. So, you can see that most of the ratios are between 0.414 to 0.732.

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So, this is the sort of typical ball model that we see. So, first fill all the interstices with all the FCC sites with X ions. So, these are face entered cubic positions, X ions go there. Then, we fill all the octahedral voids, where are the octahedral voids? In the body center and at the edge

center. So, we fill all the octahedral voids with the M ions and this is what basically makes a MX structure, okay. You can calculate the packing density. So, packing factor you can calculate yourself, it will be different for different solids.

Now it is left to you as a home exercise to work out whether this packing structure will be smaller or larger than the FCC crystal, okay. And the lattice parameter will be given by this, this is the lattice parameter and this is the distance between the sodium and chlorine atoms, okay. So basically $a = 2r_{\text{Na}} + 2r_{\text{Cl}}$, right, and this will be lattice parameter and in this case, I have shown the atoms to be away from each other, but in reality, they will be touching each other.

So, this will be chlorine, this will be sodium and this will again be chlorine. This is how the configuration will be.

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Rock Salt Structured Compounds

- Lattice type: FCC and motif will be M at 0 0 0 and X at $\frac{1}{2}$ 0 0
- Four formula units per unit cell
- Bond Strength

M ↓

0 0 0
 $\frac{1}{2}$ $\frac{1}{2}$ 0
 $\frac{1}{2}$ 0 $\frac{1}{2}$
0 $\frac{1}{2}$ $\frac{1}{2}$

X -

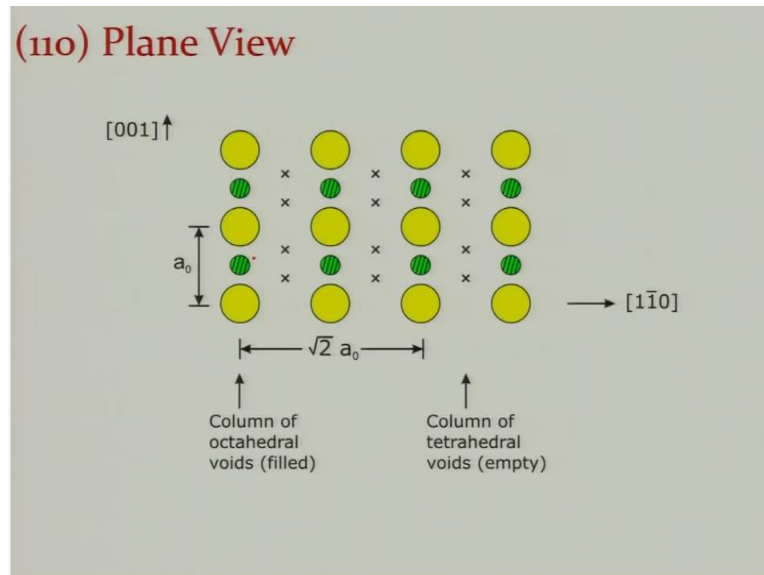
$\frac{1}{2}$ 0 0
0 $\frac{1}{2}$ 0
0 0 $\frac{1}{2}$
 $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$

Okay, so, this is how the structure is going to look like. So, the way you define the lattices, lattice type is FCC and the motive will be M at (0,0,0) and x at (1/2,0,0), what this will mean is that you have four atoms at M (0,0,0), (1/2,1/2,0), (1/2,0,1/2), and (0,1/2,1/2). And x will be at (1/2,0,0) okay. One is at (1/2,0,0) what is the other type? (0,1/2,0) another will be at (0,0,1/2), and then last one will be at (1/2,1/2,1/2). You can see that these positions are shifted by (1/2,0,0) with respect to the previous one, right.

So, you have added (1/2,0,0) to (0,0,0) if you add half here then this will become 1, 1 is equivalent to 0, so this becomes (0,1/2,0). Similarly, (0,0,1/2) so, it is basically displacement

of half to each of the atoms, okay. So, when you define FCC you just have to write at (0,0,0) and (1/2,0,0), it automatically means that you will have translation vector accordingly. You have four formula units per unit cell and you can satisfy the bond strength principle by yourself, okay.

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So, this is a rock salt structure and this is how you can view the structure in different ways, so this is 110 plan view, you can see that you have columns of octahedral voids, which are filled, but columns of tetrahedral voids, which are empty. So, different ways of representing the structure.

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Fluorite/Anti-fluorite Structures

- Formula: M_2X : Anti-Fluorite; MX_2 : Fluorite
- Examples
 - Anti-Fluorites: Na_2O , K_2O , Li_2O
 - Fluorites: CaF_2 , ZrO_2 , ThO_2 , CeO_2 , RuO_2
- Co-ordination according to radius ratio:
 - Anti-Fluorite (r_c/r_a : 0.225-0.414)
 - r_{Li} : 0.059 nm, r_{Na} : 0.099 nm, r_O : 0.14 nm
 - Cation: 4 →
 - Anion: 8 →
 - Fluorite (r_c/r_a : 0.732-1.0)
 - U: 0.1 nm, Zr: 0.084 nm, Ce: 0.097 nm, O: 0.14 nm
 - Anion: 4 →
 - Cation: 8

$\frac{4}{8} = \frac{2}{4} O_2$

Then second structure is fluorite or anti-fluorite structure. In this case, fluorite structure is basically MX_2 kind of structure and M_2X is anti-fluorite structure. So, anti-fluorites are

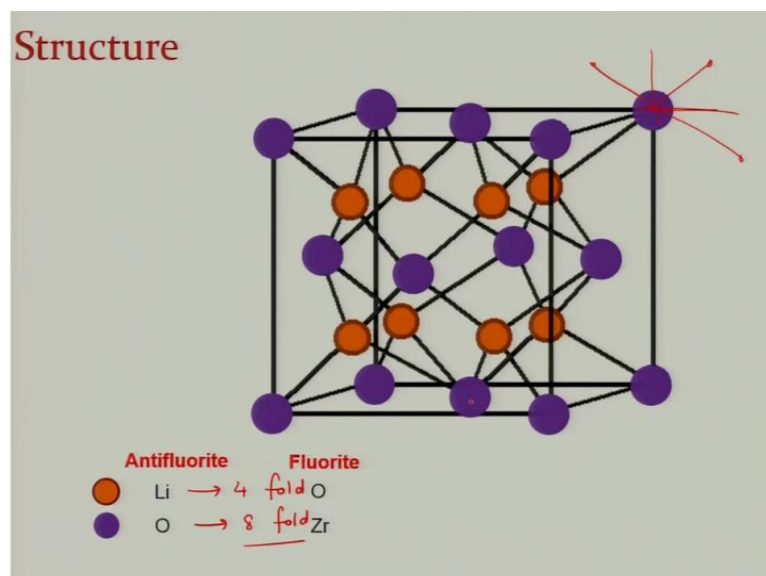
generally sodium oxide, potassium oxide, lithium oxide. Fluorites are generally calcium fluoride, zirconium oxide, thorium oxide, ruthenium oxide, etc. So, again the coordination number goes as per radius ratio, for anti-fluorite structure, r_c/r_a is 0.225 to 0.414.

So, lithium is for example 0.059 nanometers, sodium is 0.099 nanometer and so on and oxygen is 0.14. So, generally, so in these structures' cations will have four fold coordination and anions will have eight fold coordination, okay. Cations are very small as compared to anions, you can see the difference is very small. In case of fluorite structure, it is a little bit different.

For example, atoms like uranium, pretty big atoms, 0.1 nanometer, zirconium 0.084 nanometer, cerium 0.097 nanometer as compared to oxygen, they are pretty big. So, in this case, the radius ratio is such that so that you will have cations will have, sorry its other way round, anions will have four fold coordination and cations will have eight fold coordination, this is how the structure is going to be like. So, this is a typo here so, it is eight fold and four fold, so, its other way round.

And this again you can verify using the bond strength rule, I mean, alright, in this case UO_2 , your cation has a valence of four, right, it has a radius ratio which falls in the range 0.732, which means it is eight fold, right, which means your anion has a valence of 2, its coordination number has to be 4, okay. And likewise in the previous case.

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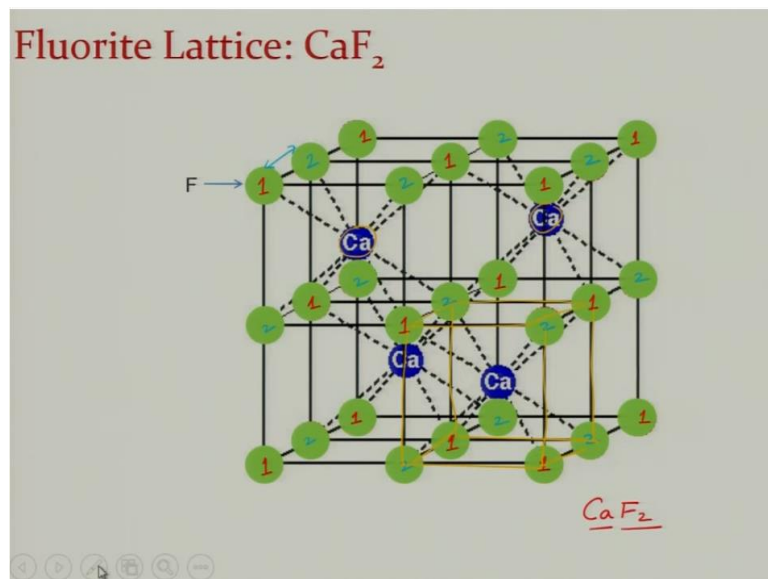
So, here the structure is like this, this is the anti-fluorite. In case of anti-fluorite, oxygen atoms occupy the face center positions and lithium atoms are in tetrahedral voids, all the tetrahedral

voids are filled, so you can see that lithium is four fold and oxygen will be eight fold, this is oxygen you have one lithium atom here, but each corner atom is surrounded by 8 unit cells, okay. So there will be 8 lithium atoms surrounding it in all the eight directions.

So there will be one here, one here, so one here, one there, one there, one there and then of course, they will be in the front as well. So, four in the front, four in the back, you will have total of eight atoms surrounding it. So, you will have unit cell, one unit cell on this side, one unit cell on the front side, two on the front and four on the back, so all of them will contribute one atom each, as a result it will have eight fold.

When you go to fluorite structure, it is opposite to that, in the fluorite structure, oxygen will be, so this atom will become oxygen and this atom will become zirconium, or uranium or whatever it is, okay.

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You can represent the fluorite structure little differently, since we are saying that lattices made by the anion, it can be represented in a different form. The fluorine makes FCC lattice, okay, so this is the first fluorine lattice, number 1, number 1, number 1, number 1, number 1, number 1, number 1, number 1, okay. This is the first fluorine lattice, the second floor in lattice is since you have CaF₂, you have 2 fluorine ions and 1 calcium ion, alright.

So one FCC lattice is made by one type of fluorine ion, second FCC lattice is made by these fluorine ions. This is also a fluorine lattice, okay. Because one lattice will give you only four ions, alright. Another lattice will give you four ions and you can see that the first lattice has

shifted with respect to the second lattice by this vector, okay. And then, when you put these 2 FCC lattices together into each other, it is a representation of, as if you have put eight cubes.

So, you can see that this is one cube, so there is one cube on the front. So, this is first cube that you form, right. This is the first cube, then you have second cube on the back, third cube on the side, fourth cube on the back side, and then four cubes on the top, it is like eight cubes on top of each other and the way calcium goes in it, since calcium has now eight fold coordination, eight fold coordination is nothing but cubic coordination, okay.

So, basically calcium goes into these cubic voids, these are cubic voids. So two on the front diagonally, two at the bottom diagonally rotated by 90 degrees, okay. This is how this lattice is, so this is a real representation. The lattices are made by anions, the cations go into the cubic voids, this is the real representation of CaF_2 lattice. It is a little difficult to visualize, but this is how you visualize in reality.

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Fluorite & Antifluorite structures

- Lattice type: FCC
- Motif - X: 0 0 0, M - $\frac{1}{4} \frac{1}{4} \frac{1}{4}$ and $\frac{3}{4} \frac{3}{4} \frac{3}{4}$ and vice versa for fluorite structure
- Four formula units per unit cell.
- The structure shows corner sharing of tetrahedra.
- Large void in the center of unit cell → good ionic conductors

- Batteries and fuel-cells

$A_2 X \rightarrow 2 \text{ FCC-A}$
 1 FCC-X
 $A X_2 \rightarrow 1 \text{ FCC-A}$
 2 FCC-X

So, basically you can say the lattice in both cases the FCC type, the motive for anti-fluorite, is X is at (0,0,0) and M is at (1/4,1/4,1/4) and (3/4,3/4,3/4). When you say you have eight atoms, which means you have two FCC lattices; one is made by this, second is made by this, okay. So, in total you have three FCC lattices. In case of anti-fluorite one FCC lattice of anion, two FCC lattices of cations. In fluorite structure, two FCC lattices of anions, one FCC lattice of cation, okay, intermingled into each other.

Otherwise, they will not make FCC structure, all of them have to follow FCC structure. So,

the moment you have this A_2X , you will have two FCC lattices of A, 1 FCC of X. The moment you have AX_2 , you will have 1 FCC of A and 2 FCC of A. This is how it has to follow the, sorry the color is little dull, so A_2X , AX_2 , 2 FCC lattices of A, 1 FCC lattices of X, 1 FCC of A and 2 FCC of X. This is how it has to be, okay.

So, basically A_2X and AX_2 are sort of inverse of each other and both of them have four formula units per unit cell, the structure has basically corner sharing of tetrahedra and since there is nothing in the octahedral place, they don't have, they have a big void at the center of the unit cell and that is why many of these materials are very good ionic conductors. So, they are used for batteries and fuel cells, lot of fluorite structure materials are used for batteries and fuel cells.

So we have run out of time now. We have discussed sodium chloride and fluorite structured compounds, in the next class we look at the sphalerite and spinel structured compounds before we looked at perovskites, which are very important for dielectrics and then we look at some cases of hexagonal structured compounds before we finish the structural part. Okay, so thank you very much.