Materials Chemistry
Prof. S. Sunder Manoharan
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture - 9
Preparative Routes
Conventional Solid State Technique

So, we are in this module 1 and I would like to place emphasis on one of the important issue that governs materials chemistry that is the philosophy of a synthesis. Which is a inseparable issue as far as those working on materials. So, I call this as a philosophy of synthesis.

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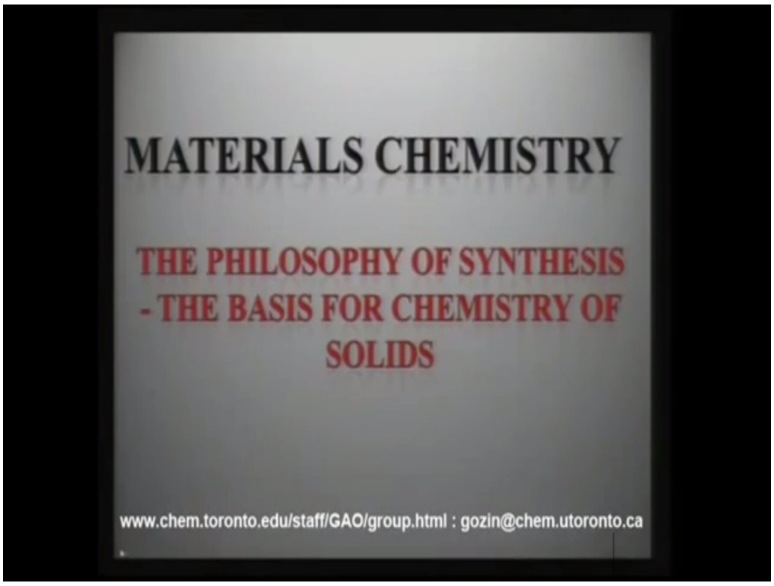

MATERIALS CHEMISTRY

THE PHILOSOPHY OF SYNTHESIS - THE BASIS FOR CHEMISTRY OF SOLIDS

www.chem.toronto.edu/staff/GAO/group.html : gozin@chem.utoronto.ca

The basis for chemistry of solids, before we go into the details of other slides I wish to record the contributions from Gaussian and his group. Specially I have taken most of the resource material from his a group website. Therefore, I would like to place my acknowledgement for the resource material that I have taken form his group.

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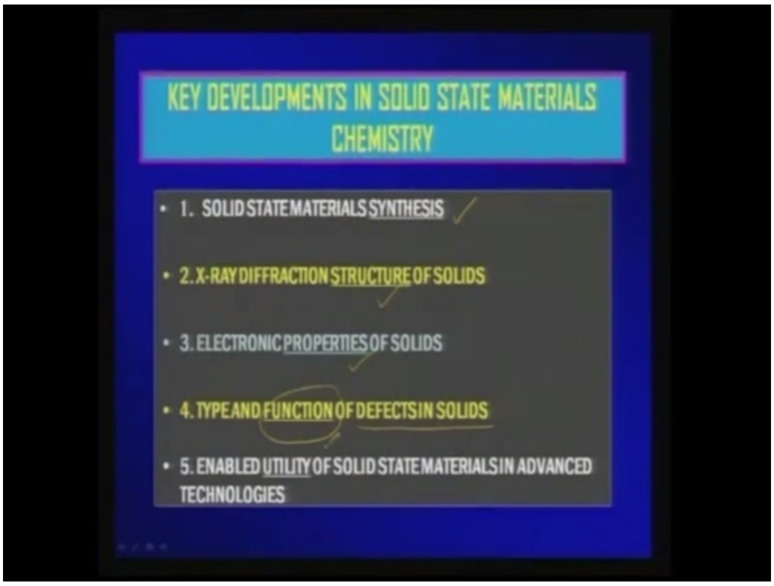

KEY DEVELOPMENTS IN SOLID STATE MATERIALS CHEMISTRY

- 1. SOLID STATE MATERIALS SYNTHESIS
- 2. X-RAY DIFFRACTION STRUCTURE OF SOLIDS
- 3. ELECTRONIC PROPERTIES OF SOLIDS
- 4. TYPE AND FUNCTION OF DEFECTS IN SOLIDS
- 5. ENABLED UTILITY OF SOLID STATE MATERIALS IN ADVANCED TECHNOLOGIES

When we come to solid state materials chemistry, we are mainly concerned about few issues number 1, as I pointed put in the inaugural lecture synthesis of solids plays a very important role. And if we need to have an idea of the synthetic strategy, the most of fundamental understanding that we require is that of structure of solids. So, once you know the structure you can design, what set of chemical approach that you need to take to synthesize this materials. And once you have a handsome grip on the structure and the way you need to make this material, it is possible to correlate that to the property of solids.

So, structure and property together would help us in deciding what sort of functional application that we are looking for. And one of the main contribution factors to the chemistry of solids is the electronic properties of solids. The key developments in solid state materials chemistry is to do with synthesis and second structure, and the properties. And one of the things that really holds this whole study of solids together is the function of defects. In solids defect chemistry plays a very important role whether we have to accept it reluctantly or, so the function of defects do play a important role.

So, in combination with the defects in solids the properties and structure will determine what set of utility that we can think of. So, utility of solid state materials in advanced technologies can be realized, if one knows how to synthesize a particular structure of a solid. And if you are able to fine tune the properties with the help of the intrinsic defects in the solids.

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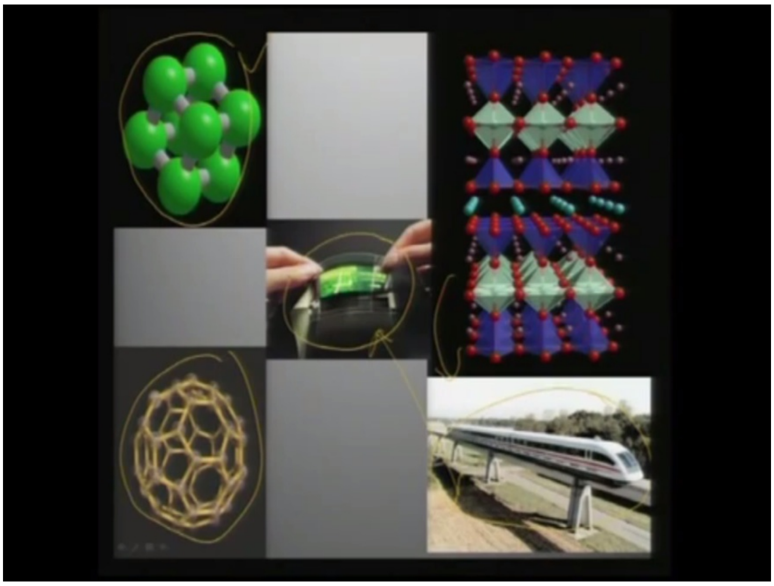

In the next cartoon I just want to tell you that fundamental understandings of materials chemistry has to do with knowing the different classes of compounds. And not only knowing the basics of the structure, but one can also come across several new phases serendipities in the materials chemistry field. And once we come stumbled at new ideas and new molecules or new solids, then we can actually translate that in applications. For example, this is a application of a magnetically levitated train which as come from the basic understanding of super conducting solids, which were not existent these are not available in nature, but then you by knowing the structure and property you can make this materials.

And another group of compounds are this organic materials or organic molecules, which are solids which can be translated into display materials. So as far as this are the functional applications are concerned one can start with the basic understanding of structures in solids or by stumbling at some new phases, new solids you can actually translate that to the waste applications.

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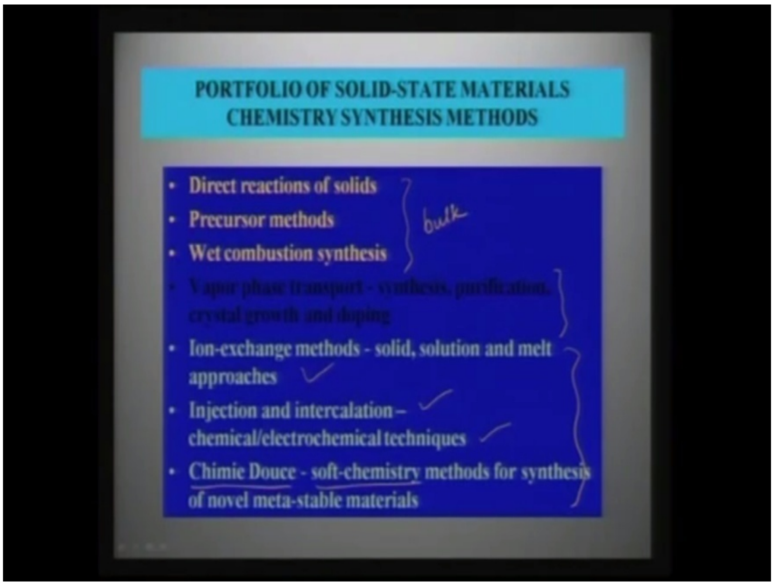

PORTFOLIO OF SOLID-STATE MATERIALS
CHEMISTRY SYNTHESIS METHODS

- Direct reactions of solids
- Precursor methods
- Wet combustion synthesis
- Vapor phase transport - synthesis, purification, crystal growth and doping
- Ion-exchange methods - solid, solution and melt approaches ✓
- Injection and intercalation – chemical/electrochemical techniques ✓
- Chimie Douce - soft-chemistry methods for synthesis of novel meta-stable materials

bulk

Now, when we think about material synthesis first we need to understand making materials is a big word, and the group of people who are engaged in making solids are host of groups, who involved in variety of solid state materials chemistry synthesis. Now, here I have listed some of the portfolio of this synthetic methods, and purposely I have grouped them into some categories. One of the main and the most simplest approach to solid state synthesis is the direct reaction of solids which is not very, very intricate it does not call for very stringent application, but then once you get a feel for it is easier for to make many materials. Therefore, these are grouped under 1 direct reaction of solids precursor methods, or wet combustion synthesis by this you can actually try to solids in bulk.

And another group of compounds that you can make is through vapor transport synthesis, which is not a very rigorously a solid state method, but then it’s another approach by which you can actually aim for synthesis, purification, precursor growth and doping. Then you stumble at variety of wet chemistry roots which we call it as a soft chemistry or as French people call it as chimie douce these are soft chemical approaches by which without making much modification, you can bring in a variety of new properties into a existing solid. And these are called as novel meta stable phases, which you can realize using soft chemistry roots. And this also involves intercalation, we can also try to synthesize material using a electro chemical techniques which is not a very hot protocol.

Therefore, this can also be considered as a soft chemistry root and again ion exchange methods are also soft chemistry approaches. So, here we are talking about direct solid solid interactions and then we can also think of using wet chemistry roots to prepare solids.

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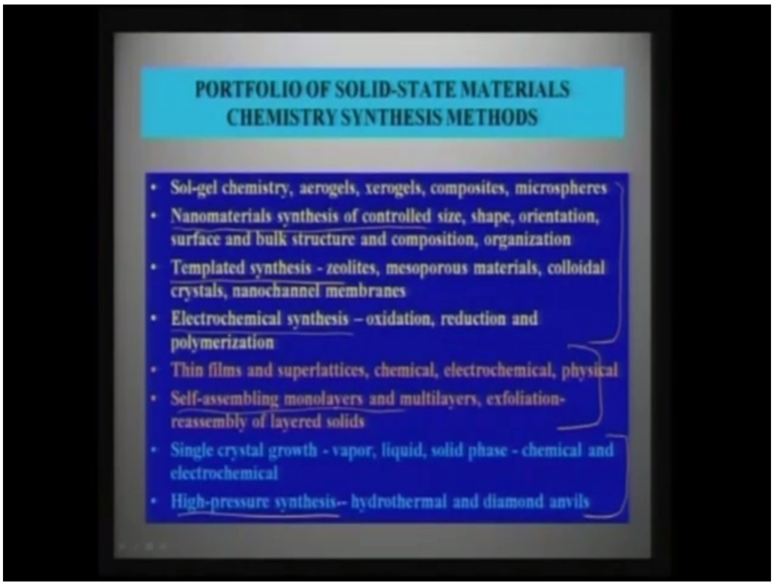

PORTFOLIO OF SOLID-STATE MATERIALS CHEMISTRY SYNTHESIS METHODS

- Sol-gel chemistry, aerogels, xerogels, composites, microspheres
- Nanomaterials synthesis of controlled size, shape, orientation, surface and bulk structure and composition, organization
- Templated synthesis - zeolites, mesoporous materials, colloidal crystals, nanochannel membranes
- Electrochemical synthesis – oxidation, reduction and polymerization
- Thin films and superlattices, chemical, electrochemical, physical
- Self-assembling monolayers and multilayers, exfoliation-reassembly of layered solids
- Single crystal growth - vapor, liquid, solid phase - chemical and electrochemical
- High-pressure synthesis-- hydrothermal and diamond anvils

And there are other host of methods that are available and this list is ever growing. For example, sol gel synthesis aerogels for composites then again in the last decade we have witnessed many reactions based on nano materials, for controlled size shape and orientation. And then you have template synthesis for zeolites, mesoporous materials, colloidal crystals and so on. And we can also aim for electro chemical synthesis, oxidation reduction, and polymerization methods all this are grouped under wet chemical roots. And each synthetic approach distinguishes itself in stabilizing a particular phase, or a group of solids that we are looking for.

Another popular root for making solids which often the physics, the principles are involved. Therefore, physicists often work on these methods these are based on thin films using either chemical methods or physical methods, and then the most popular one now is the self assembling monolayers, which we call it as Sam for making solids. Of course, the most traditional way of making solids in the in the earlier decades is the single crystal growth for making high pure solids. And also one can use high pressure synthesis for making solids using either dry approach or wet approach. So, there are different ways in which we can make this solid state materials, and we will take some time in the subsequent lectures to see how this solids can be made using different functional groups functional approachs.

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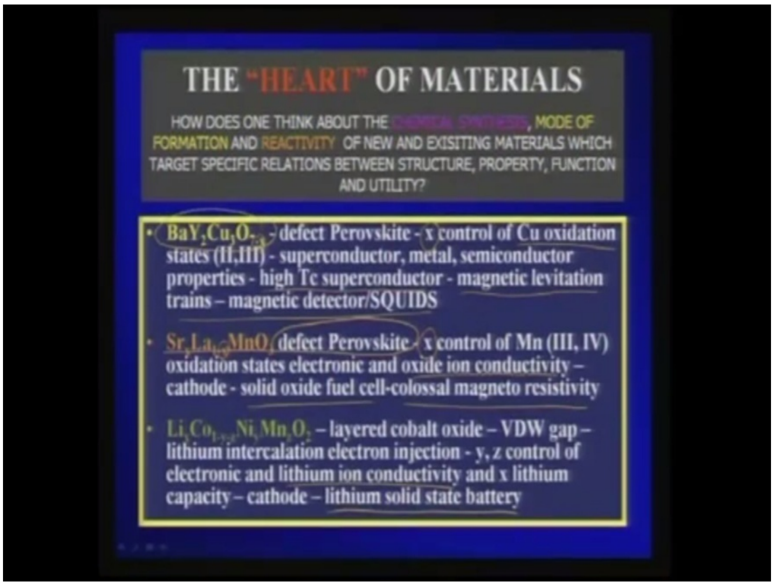

THE "HEART" OF MATERIALS

HOW DOES ONE THINK ABOUT THE CHEMICAL SYNTHESIS, MODE OF FORMATION AND REACTIVITY OF NEW AND EXISITING MATERIALS WHICH TARGET SPECIFIC RELATIONS BETWEEN STRUCTURE, PROPERTY, FUNCTION AND UTILITY?

- $BaY_2Cu_3O_{7-x}$ - defect Perovskite - x control of Cu oxidation states (II,III) - superconductor, metal, semiconductor properties - high Tc superconductor - magnetic levitation trains – magnetic detector/SQUIDS
- $Sr_xLa_{1-x}MnO_3$ defect Perovskite - x control of Mn (III, IV) oxidation states electronic and oxide ion conductivity – cathode - solid oxide fuel cell-colossal magneto resistivity
- $Li_xCo_{1-y-z}Ni_yMn_zO_2$ – layered cobalt oxide – VDW gap – lithium intercalation electron injection - y, z control of electronic and lithium ion conductivity and x lithium capacity – cathode – lithium solid state battery

The heart of materials is how does one think about the chemical synthesis, the mode of formation and reactivity of new and existing materials, which target specific relations between structured property function and utility. Therefore, this form the core of the materials chemistry approach, now to name a few I just want to bring this candid illustration of yttrium barium copper, this is the most highly studied super conducting phase. This is a defect prostate and all you see here is that x what we see here is what is controlling this super conducting property here, and this is based on in other words this x will control the copper oxidation state between 2 and 3. And that will make either the material super conducting or it will make it metal or semi conducting.

So, this is one of the group of oxides which really stands as a explicit example to show how chemical synthesis is a very vital protocol in realizing applications of many of the solids. Now, by carefully maintaining the synthetic route we can control the phase purity and we can realize this high T c super conductors, which actually can be used for the application like this. And there is another group of compound which is again a perovskite and this is also a defect in this perovskite and here again the x factor plays a very important role. And this x will control in this case not copper, but here manganese between 3 and 4 oxidation state, which actually determines the oxide ion conductivity or the solid oxide fuel or the colossal magneto resistivity. This is another very interesting compound, where the chemical synthesis has really been established to control different properties as far as the applications are concerned.

Another group of compounds which are layered cobalt oxide where you create a Van der waals gap and lithium can be intercalated in this layers as a result, you can control the lithium ion conductivity, and you can also look at the solid state battery applications. So, these are a class of compounds where the chemical synthesis has been laid a lot of emphasis because of their functional importance.

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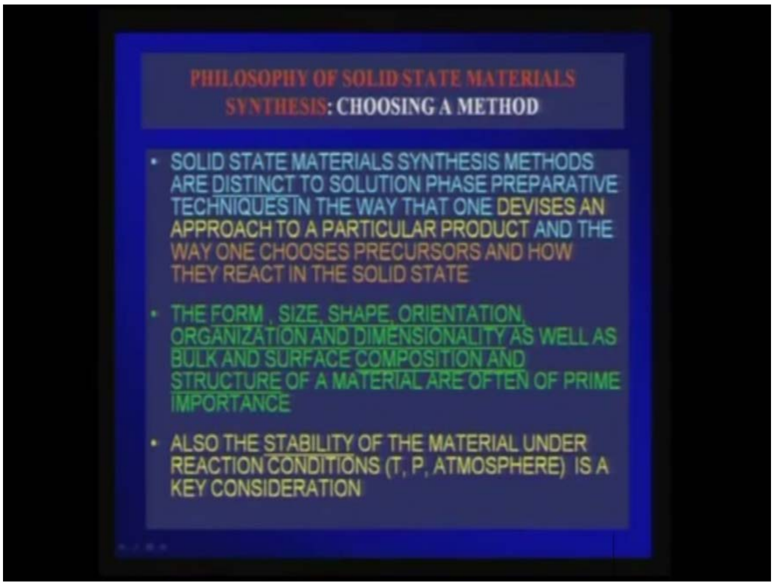

PHILOSOPHY OF SOLID STATE MATERIALS SYNTHESIS: CHOOSING A METHOD

- SOLID STATE MATERIALS SYNTHESIS METHODS ARE DISTINCT TO SOLUTION PHASE PREPARATIVE TECHNIQUES IN THE WAY THAT ONE DEVISES AN APPROACH TO A PARTICULAR PRODUCT AND THE WAY ONE CHOOSES PRECURSORS AND HOW THEY REACT IN THE SOLID STATE
- THE FORM , SIZE, SHAPE, ORIENTATION, ORGANIZATION AND DIMENSIONALITY AS WELL AS BULK AND SURFACE COMPOSITION AND STRUCTURE OF A MATERIAL ARE OFTEN OF PRIME IMPORTANCE
- ALSO THE STABILITY OF THE MATERIAL UNDER REACTION CONDITIONS (T, P, ATMOSPHERE) IS A KEY CONSIDERATION

Now, when we think of the philosophy of solid state material synthesis, choosing a method is very, very important. The solid state material synthesis methods are distinct to solution phased preparative techniques, in the way that one devices an approach to a particular product and the way one chooses precursors, and how they react in the solid state. So, there is a basic difference between the synthetic approach for making solid state materials compared to solution phased preparative techniques. The form the size shape, orientation, organization and dimensionality, as well as bulk and surface composition, and structure of a material are often of prime importance. Also the stability of material under reaction conditions that is temperature, pressure, and the atmosphere is a key consideration for making solid state materials.

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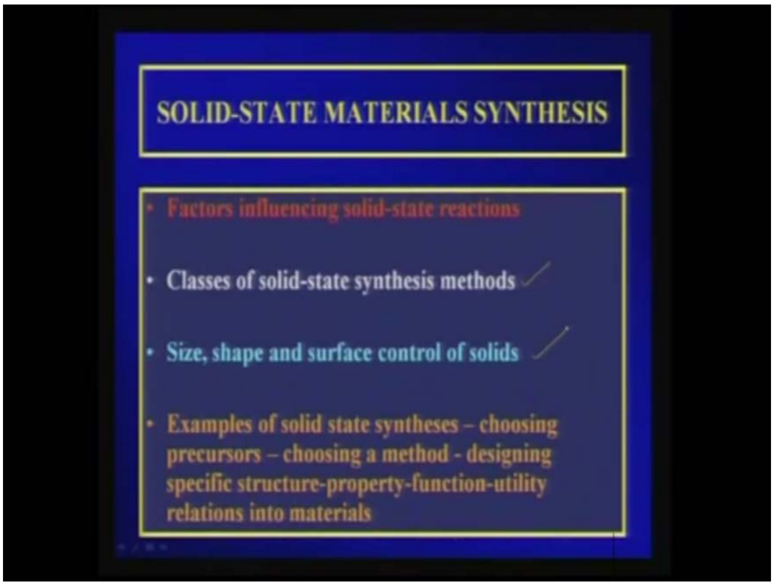

SOLID-STATE MATERIALS SYNTHESIS

- Factors influencing solid-state reactions
- Classes of solid-state synthesis methods
- Size, shape and surface control of solids
- Examples of solid state syntheses – choosing precursors – choosing a method - designing specific structure-property-function-utility relations into materials

Therefore, the factors that influence solid sate reactions are many and this can be governed during the synthesis the classes of solid state synthetic methods are of important. And other things that control these material synthesis is size shape and surface control of solids. For example, the solid state synthesis choosing the precursor, choosing a method designing a specific structure property all this governs the solid state material synthesis.

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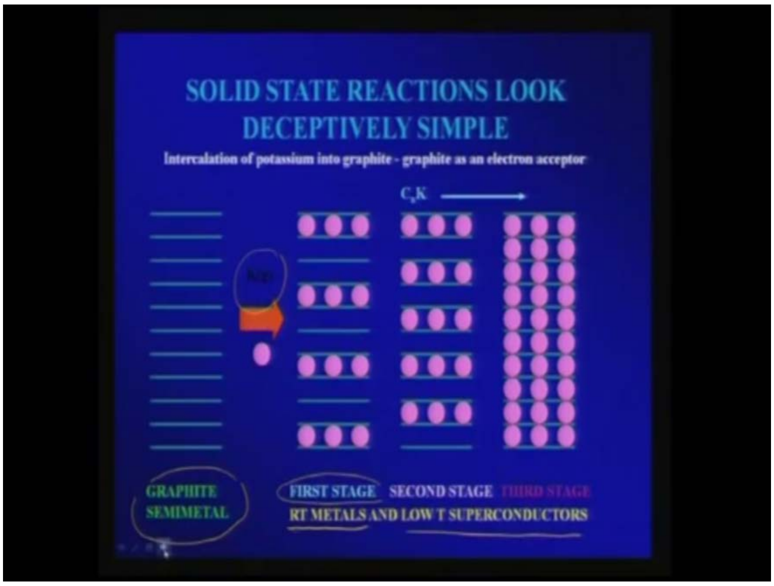

SOLID STATE REACTIONS LOOK DECEPTIVELY SIMPLE

Intercalation of potassium into graphite - graphite as an electron acceptor

Now, when we think of the synthesis we always think is very easy because it does not involve much of wet chemical route. Therefore, we often think solid state chemistry synthesis is often a very simple phenomenon, but what we see is it looks deceptively simple, but when you actually go through the protocol you will find that it is extremely important to have a hands on experience on solid state chemistry.

For example, you take graphite which is a semi metal and if you start doping potassium, actually this is a intercalation that is happening and your try to pump in the potassium as gaseous molecule. When they arrive between the graphite sheets, this is what happens the potassium ions get intercalated between graphitic sheets and what happens in their first stage, selectively they occupy at random and then as you keep on increasing the concentration of the potassium ions. You would see they go from room temperature metal all the way up to low temperature super conductors now how much of potassium that you control, determines what sort of property that you are looking for. So, it is a simple graphitic semi metal, but the way you progressively go on doping potassium, determines whether the material can transient to a normal metal or to a super conductor. So, this is very important to understand that solid state principles are looking easier…

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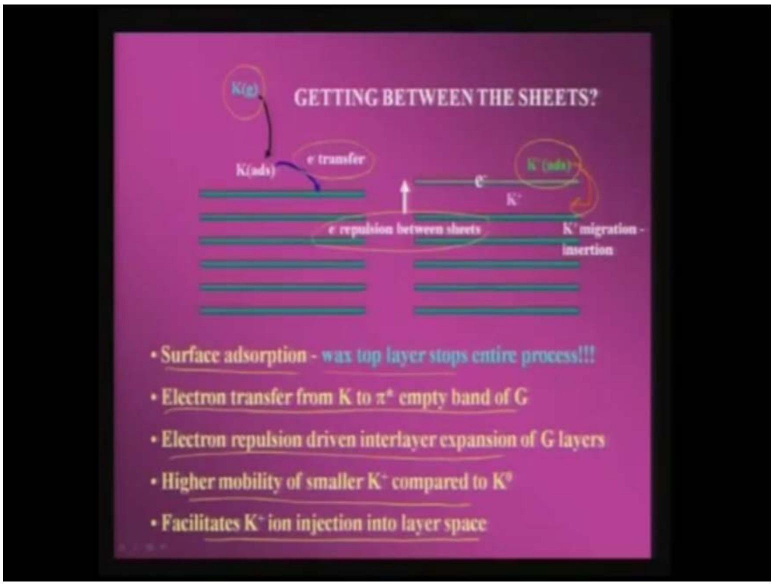

GETTING BETWEEN THE SHEETS?

- Surface adsorption - wax top layer stops entire process!!!
- Electron transfer from K to π^* empty band of G
- Electron repulsion driven interlayer expansion of G layers
- Higher mobility of smaller K^+ compared to K^0
- Facilitates K^+ ion injection into layer space

But they are more involved for example, if you look at the same reaction more carefully in a mechanistic way, you would see that initially the potassium is sent as gaseous phase and they get absorbed. And during absorption there is a electron transfer, and after the electron transfer, the potassium ions gets absorbed. And then there is a migration insertion of this potassium ions, which are absorbed on the surface into the graphitic sheets. Then because of this lot of other things can happen a electron repulsion between the sheets can come because you are trying to accommodate a potassium ion between the graphitic sheets. As a result your graphitic layers get deformed.

So, several things happened here for example, surface absorption sometimes this waxing top layer can actually sort of hinder the whole process, but if you selectively do the absorption then that transforms to a electron transfer form potassium to pie star empty band of graphite. And then electron repulsion between inter layer leading to expansion of the graphitic layers, higher mobility of the smaller k plus compared to k 0 will also alter the graphitic sheet alignment. And then this facilitates k plus ion injection into the layer space, so many mechanisms happened in a simple reaction between a gas phase, gas solid interface.

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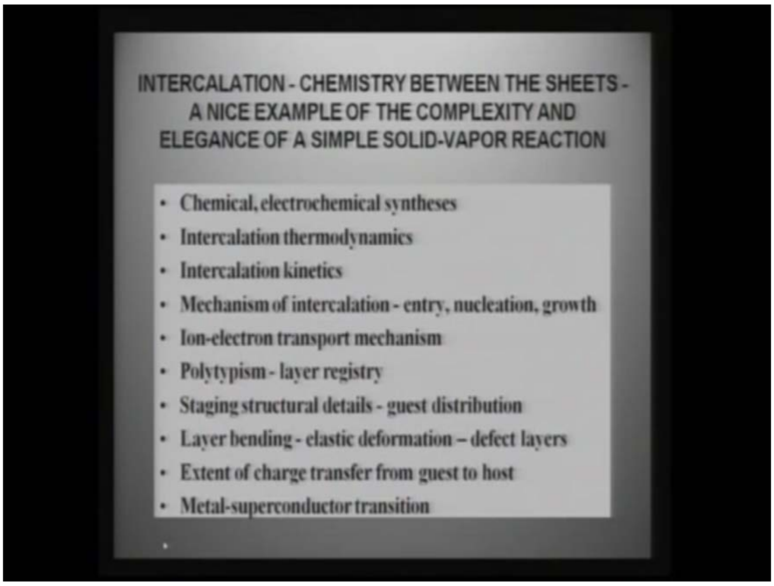

INTERCALATION - CHEMISTRY BETWEEN THE SHEETS - A NICE EXAMPLE OF THE COMPLEXITY AND ELEGANCE OF A SIMPLE SOLID-VAPOR REACTION

- Chemical, electrochemical syntheses
- Intercalation thermodynamics
- Intercalation kinetics
- Mechanism of intercalation - entry, nucleation, growth
- Ion-electron transport mechanism
- Polytypism - layer registry
- Staging structural details - guest distribution
- Layer bending - elastic deformation – defect layers
- Extent of charge transfer from guest to host
- Metal-superconductor transition

And therefore the mechanism of any solid state chemistry synthesis is quite involved. Now, in this intercalation chemistry between the sheets, this nice example of a solid vapor reaction, if we sum up all the mechanism that is happening you can see it is not just one or two. There are more than ten reactions, that are happening in a simple solid vapor reaction. For example, the most important once which can affect the property of graphitic stuff is the gas distribution as a result you can see the layer bending, and elastic deformation of the defect inducing graphitic layers. And then it transforms the whole material from a metal to a super conducting transition.

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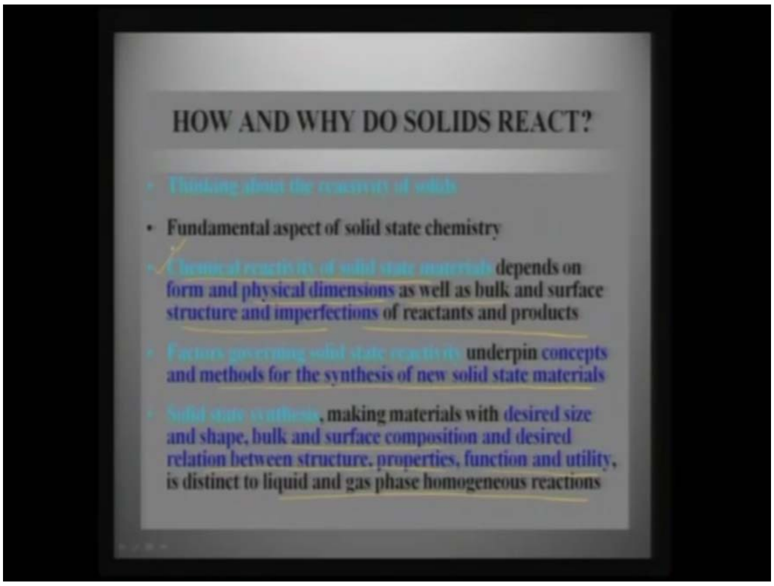

HOW AND WHY DO SOLIDS REACT?

- Thinking about the reactivity of solids
- Fundamental aspect of solid state chemistry
- Chemical reactivity of solid state materials depends on form and physical dimensions as well as bulk and surface structure and imperfections of reactants and products
- Factors governing solid state reactivity underpin concepts and methods for the synthesis of new solid state materials
- Solid state synthesis, making materials with desired size and shape, bulk and surface composition and desired relation between structure, properties, function and utility, is distinct to liquid and gas phase homogeneous reactions

So, how and why do solids react what is the fundamental understanding about the reactivity of solids. Now, when we probe into this reasons one of the thing that we need to understand is when we look at solid state chemistry synthesis, the chemical reactivity of the solid state material is very important. And this depends on the physical dimensions as well as the bulk and surface structure, and imperfections of reactants, and products. All these decides whether such a chemical synthesis can be achieved with precision. Therefore, the individual reactivity of the reactants play a important role, and second the factors governing solid state reactivity underpin concepts and methods for the synthesis of new solid state materials.

So, once you know the individual reactivity of this reactants then you need to know what sort of synthetic approach that you need to take in order to get this new materials. And solid state synthesis making materials with decide size and shape bulk and surface composition and decide relation between structured properties function, and utility is distinct. And this is certainly quite different from the liquid and gas phase homogeneous reactions. So, what we need to understand is the chemical reactivity and the factors governing such reactivity underplays a very important role in the synthesis.

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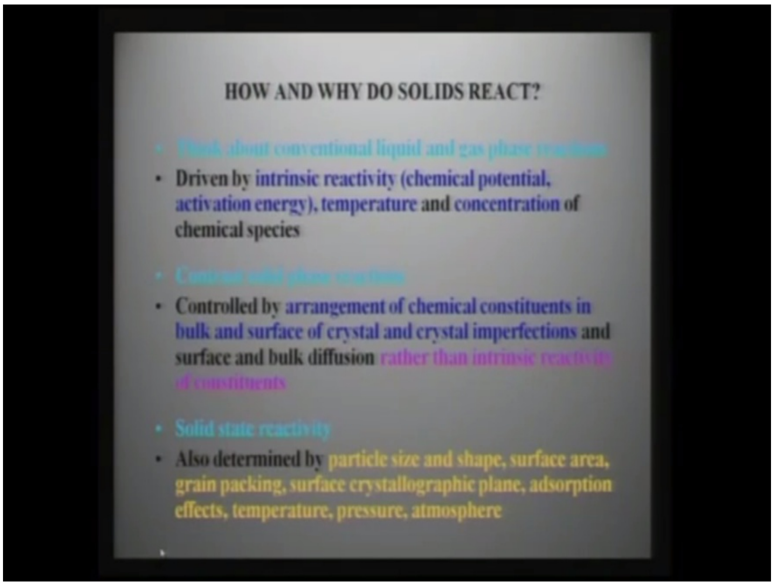

HOW AND WHY DO SOLIDS REACT?

- Think about conventional liquid and gas phase reactions
- Driven by intrinsic reactivity (chemical potential, activation energy), temperature and concentration of chemical species
- Contrast solid phase reactions
- Controlled by arrangement of chemical constituents in bulk and surface of crystal and crystal imperfections and surface and bulk diffusion rather than intrinsic reactivity of constituents
- Solid state reactivity
- Also determined by particle size and shape, surface area, grain packing, surface crystallographic plane, adsorption effects, temperature, pressure, atmosphere

Again when we talk about the reactivity now we need to think about conventional liquid and gas reaction. Usually they are driven by intrinsic reactivity such as chemical potential activation energy temperature and concentration of the chemical species. Where as in contrast to that is the solid phase reactions, and in solid phase reactions we are talking about the chemical constituents and we are talking about crystal imperfections, and the diffusion rather than intrinsic reactivity of the constituents. So solid state reactivity is also determined by the particle size, shape, surface area, grain packing, surface crystallographic plane and so on. So, all this underlie the reactivity of solids.

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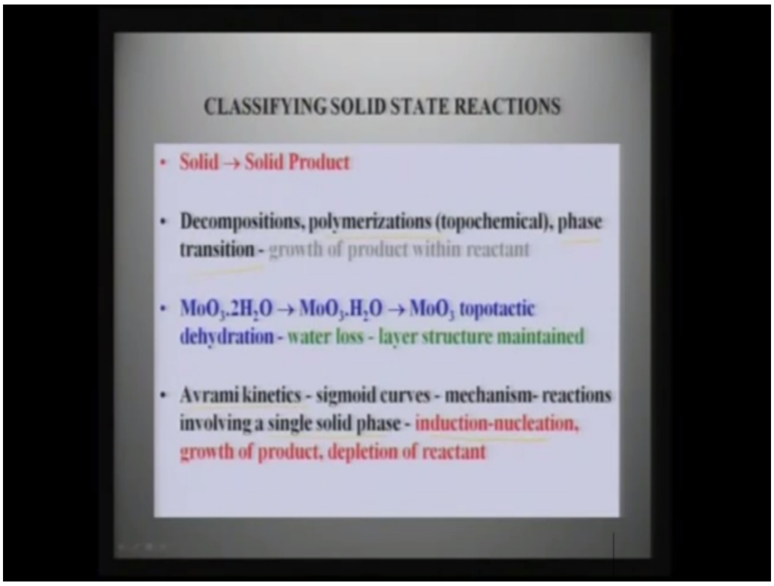

CLASSIFYING SOLID STATE REACTIONS

- Solid → Solid Product
- Decompositions, polymerizations (topochemical), phase transition - growth of product within reactant
- $MoO_3.2H_2O \rightarrow MoO_3.H_2O \rightarrow MoO_3$ topotactic dehydration - water loss - layer structure maintained
- Avrami kinetics - sigmoid curves - mechanism- reactions involving a single solid phase - induction-nucleation, growth of product, depletion of reactant

Now, we can actually classify what sort of solid state reactions happen or the reactivity of solids, and how the chemicals synthesis progresses. There different ways we can realize the synthesis, first of all we can think of a solid converting to a solid, this is one of the ways of realizing a solid state material. And the simplest example is that of a decomposition reaction, it could be simple decomposition conversion of say calcium carbonate to calcium oxide, which is a solid to solid product conversion or it could be a polymerization reaction or it could be a phase transition reaction.

One of the classic example of this sort is taking molybdenum tri oxide, which is usually a di hydride and if you heat this it transforms to a mono hydride. And then it goes through a topo tactic reaction to give MoO3 and this beauty here is it is a topo tactic reaction, involving a water loss. This can be actually monitored based on Avrami kinetics and we can talk here about the single solid phase interaction, where induction nucleation growth product and depletion of reaction can be studies at one stretch.

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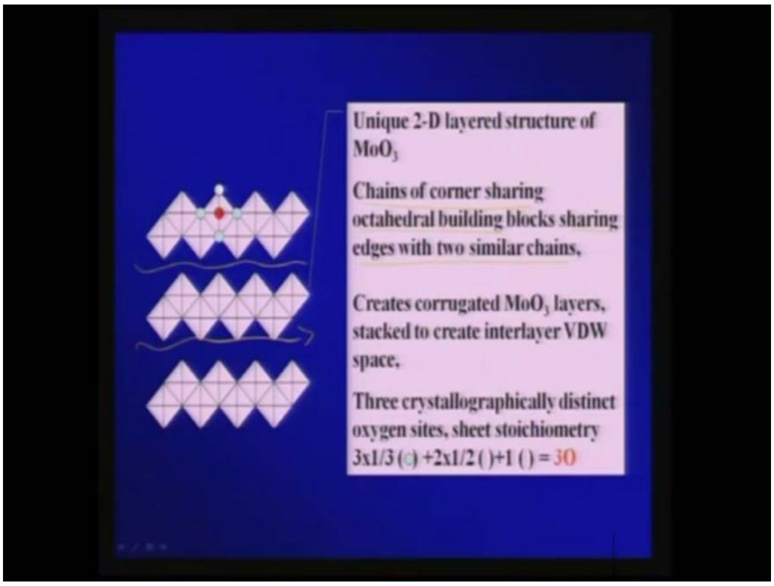

Unique 2-D layered structure of MoO_3

Chains of corner sharing octahedral building blocks sharing edges with two similar chains,

Creates corrugated MoO_3 layers, stacked to create interlayer VDW space,

Three crystallographically distinct oxygen sites, sheet stoichiometry 3x1/3 (○) +2x1/2 ( )+1 ( ) = 30

For example, if you take this example of unique two dimensional layered MoO3 you can see there are chains of corner sharing octahedral building blocks, and they are shared by edges with two similar chain. These are the corner shared ones which are edge shared here and they make two similar chains like this, and this set of arrangement makes a layer where in you can actually bring about intercalation between this MoO3 layers. One of the example is that of introducing tungsten ion into this, and once this MoO3 layers are staged, then they create a inter layer Van der Waals space where in intercalation and de intercalation can be achieved.

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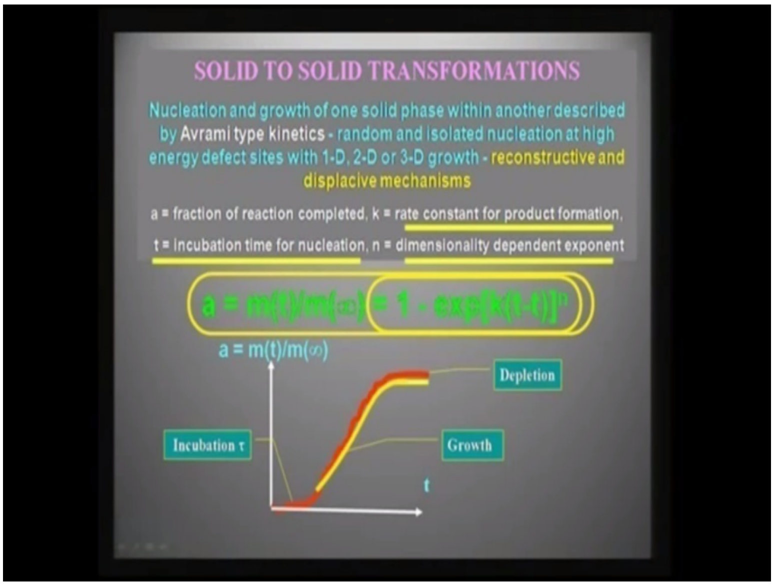

SOLID TO SOLID TRANSFORMATIONS

Nucleation and growth of one solid phase within another described by Avrami type kinetics - random and isolated nucleation at high energy defect sites with 1-D, 2-D or 3-D growth - reconstructive and displacive mechanisms

a = fraction of reaction completed, k = rate constant for product formation,

t = incubation time for nucleation, n = dimensionality dependent exponent

$$a = m(t)/m(\infty) = 1 - \exp[k(t-t)]^n$$

In general the solid to solid transformations can be studied by Avrami kinetics. So, the nucleation and growth of one solid phase with in the other can be described by this kinetics where random and isolated nucleation at high energy defect sights, with one dimensional two dimensional or three dimensional growth can be studied expressions. For Avrami kinetics is based on this expression where the fraction of the reaction that is completed is equated to this term exponential term that is 1 minus e to the power k t minus tau whole power n. Where tau is the incubation time for nucleation and n is the dimensionality depend exponent and k is your rate constant.

So, in the initial phase you will see that the conversion is very slow, so which we call it as a incubation which is determined by tau. And then there is a phase where the growth of this solid state phases occurring, which is in this plato and then once the reaction is complete it goes through a depletion time. So, this can be equated to the Avramic kinetics and in solid state synthesis one can effectively study the kinetics kinetic parameters and the growth can be monitored.

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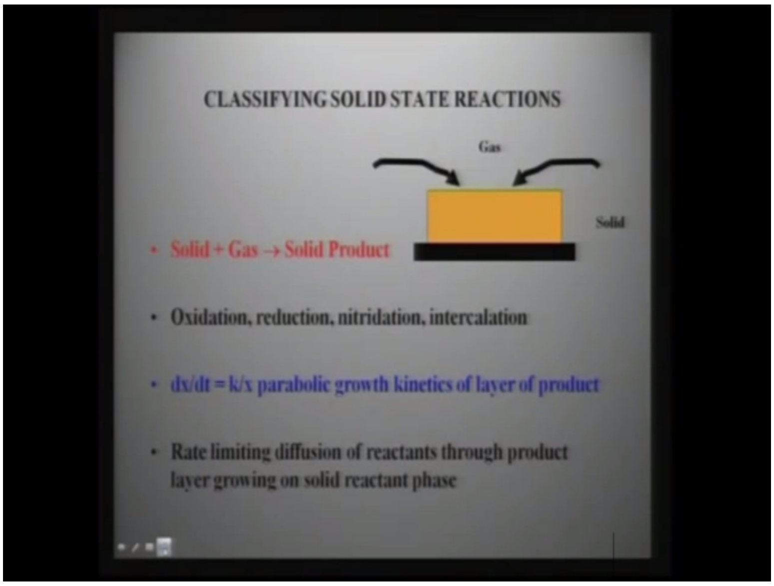

CLASSIFYING SOLID STATE REACTIONS

- Solid + Gas → Solid Product
- Oxidation, reduction, nitridation, intercalation
- $dx/dt = k/x$ parabolic growth kinetics of layer of product
- Rate limiting diffusion of reactants through product layer growing on solid reactant phase

If you look at gas solid reaction then we can study how a gas is getting absorbed. For example, if we have solid and we allow gas to come and get absorbed, now we can have many sort of reactions happening like this examples are oxidation reactions, reduction reactions, nitridation and intercalation. All this reactions can happen on a static solid phase and gas is getting absorbed either it can defuse or it can replace. So, many things can happen for example, we can passivate a metal, metallic layer or a oxide layer using nitrogen.

So, nitrogen gas can get absorbed and something like this can happen, as you keep on adding or passing gas you can see the surface is getting modified and the growth can proceed systematically to completely convert the solid phase with a gas that you are passing. So, rate limiting diffusion of reactants through product layer growing on solid reactant phase can be achieved using this sort of solid gas reaction.

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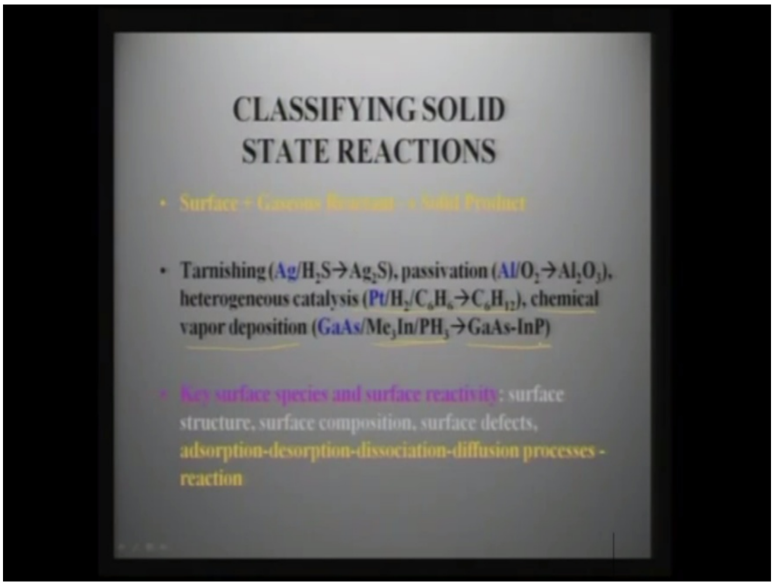

CLASSIFYING SOLID STATE REACTIONS

- Surface + Gaseous Reactant → Solid Product
- Tarnishing (Ag/$H_2S \rightarrow Ag_2S$), passivation (Al/$O_2 \rightarrow Al_2O_3$), heterogeneous catalysis (Pt/H_2/$C_6H_6 \rightarrow C_6H_{12}$), chemical vapor deposition (GaAs/Me_3In/$PH_3 \rightarrow$ GaAs-InP)
- Key surface species and surface reactivity: surface structure, surface composition, surface defects, adsorption-desorption-dissociation-diffusion processes - reaction

And we can also classify the solid state reaction based on other examples. For example, in this case again absorbing H2S on silver to form silver sulphide is a solid state reaction, or passivation of aluminum by oxygen giving aluminum oxide is a another solid state reaction involving surface, and gaseous reactant. We can also look at the conversion of benzene to cyclo hexane as one of the heterogeneous catalyst reaction, where hydrogen is absorbed on to platinum and then it reacts with benzene to give C6H12 or there could be chemical vapor deposition. Where you can take gallium arsenate and you can you can pump in this gaseous reactants to form gallium arsenate indium phosphate semi conductors. So, key surface species and surface reactivity where absorption, desorption, dissociation and diffusion process are achieved and by this way you can get new phases.

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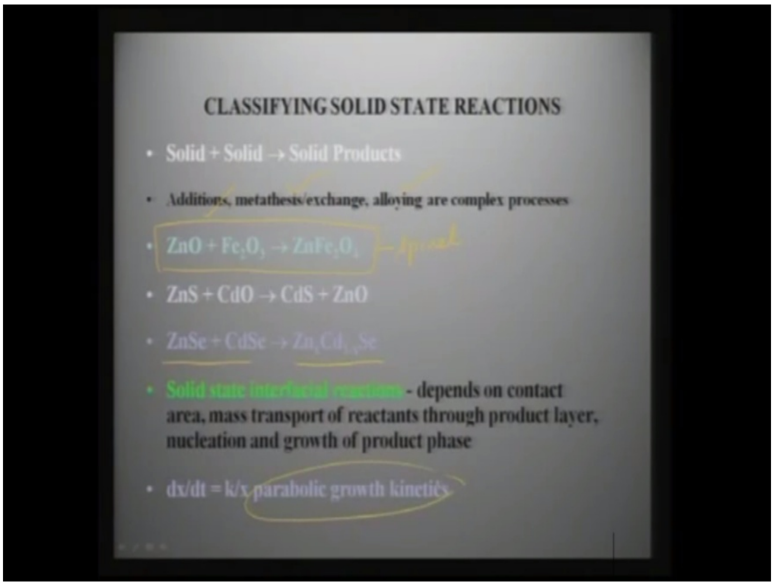

CLASSIFYING SOLID STATE REACTIONS

- Solid + Solid → Solid Products
- Additions, metathesis/exchange, alloying are complex processes
- $\boxed{ZnO + Fe_2O_3 \rightarrow ZnFe_2O_4}$ – Spinel
- $ZnS + CdO \rightarrow CdS + ZnO$
- $ZnSe + CdSe \rightarrow Zn_xCd_{1-x}Se$
- Solid state interfacial reactions - depends on contact area, mass transport of reactants through product layer, nucleation and growth of product phase
- $dx/dt = k/x$ parabolic growth kinetics

There are other solid state reactions where in solid plus solid can give solid products some of the examples are addition reaction. In this addition reaction you have zinc oxide and Fe2O3 forming zinc ferrate, in other words this is a spinel compound so this is a solid solid reaction yielding another solid, or you can go for a metathesis, or exchange reaction where you take zinc sulphate and treat it with cadmium oxide, you can actually get cadmium sulphate and zinc oxide. So, this is a metathesis reaction or you can go for allying where you take zinc selenide, and you add cadmium selenide then you can get a solid solution such as zinc cadmium selenide. So, solid state interfacial reactions depends on contact area mass transport of reactants through product layer, nucleation and growth of product phase. This again can be systematically governed or monitored through a parabolic growth kinetics.

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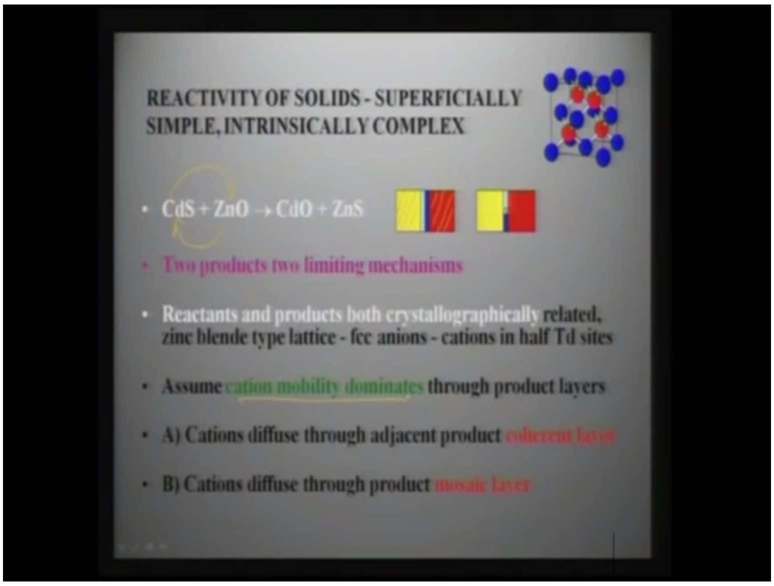

REACTIVITY OF SOLIDS - SUPERFICIALLY SIMPLE, INTRINSICALLY COMPLEX

- $CdS + ZnO \rightarrow CdO + ZnS$
- Two products two limiting mechanisms
- Reactants and products both crystallographically related, zinc blende type lattice - fcc anions - cations in half Td sites
- Assume cation mobility dominates through product layers
- A) Cations diffuse through adjacent product coherent layer
- B) Cations diffuse through product mosaic layer

Here is a another example of cadmium sulphate zinc oxide which I mentioned the metathesis here this is very interesting because both the reactants, what we have and the product they all have the same crystal structure. But the reaction that is proceeding is of a very integrate nature, we take the surface of cadmium sulphate and then we have zinc oxide, but what happens here is both cadmium has to go into zinc and zinc has to go into cadmium, such a way that you have the anions exchanged. In other words in this case this is these are the anions so you have the anion close packing that is intricate, but cadmium has to diffuse into the zinc sight. And zinc has to diffuse into cadmium side, it looks very simple, but then it is a diffusion controlled mechanism where the cationic mobility dominates this conversion process. So, this is a classic example of how diffusion controlled mechanism holds very important role in the solid state synthesis.

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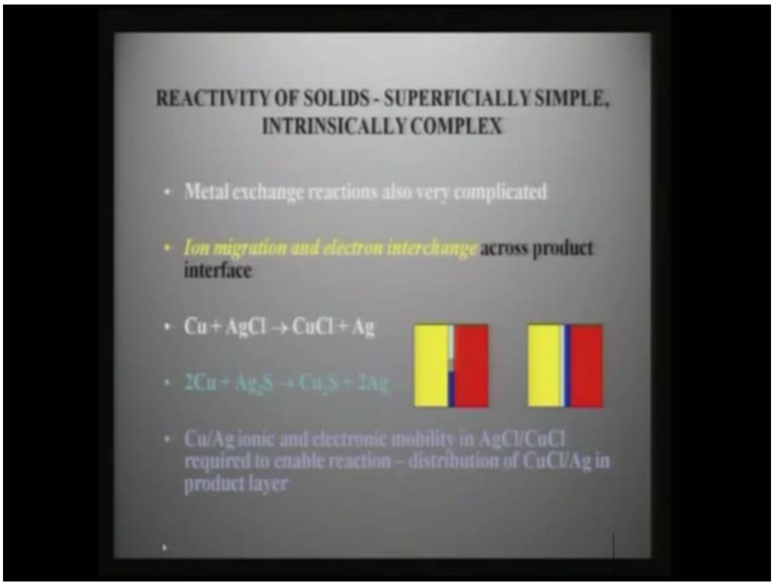

REACTIVITY OF SOLIDS - SUPERFICIALLY SIMPLE, INTRINSICALLY COMPLEX

- Metal exchange reactions also very complicated
- *Ion migration and electron interchange* across product interface
- $Cu + AgCl \rightarrow CuCl + Ag$
- $2Cu + Ag_2S \rightarrow Cu_2S + 2Ag$
- Cu/Ag ionic and electronic mobility in AgCl/CuCl required to enable reaction – distribution of CuCl/Ag in product layer

Here is another reaction where the metal exchange reaction is also achieved and this can look very simple, but again this is very complicated. For example, you take copper and silver chloride giving copper chloride and silver or copper treated with silver sulphide giving copper sulphide and silver metal. This is purely based on ion migration and electron exchange inter phase. So, two things are happening one is the ionic mobility is there and also there is a electronic mobility. So, as much as the ionic mobility is happening between this two inter phases. Now, there is also electron mobility that is to be taken into consideration because it has to happen that way for this new reaction products to be achieved. So, this again looks very simple its intrinsically very complex process.

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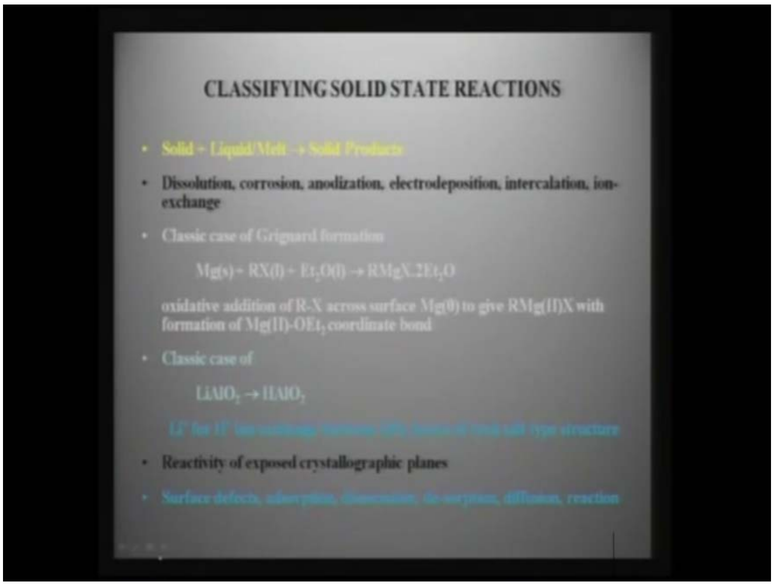

CLASSIFYING SOLID STATE REACTIONS

- Solid + Liquid/Melt → Solid Products
- Dissolution, corrosion, anodization, electrodeposition, intercalation, ion-exchange
- Classic case of Grignard formation

  $Mg(s) + RX(l) + Et_2O(l) \rightarrow RMgX.2Et_2O$

  oxidative addition of R-X across surface Mg(0) to give RMg(II)X with formation of Mg(II)-OEt_2 coordinate bond
- Classic case of

  $LiAlO_2 \rightarrow HAlO_2$

  Li^+ for H^+ ion exchange between AlO_2 layers of rock salt type structure
- Reactivity of exposed crystallographic planes
- Surface defects, adsorption, dissociation, de-sorption, diffusion, reaction

Take for example, another solid state reaction, let us take a example of solid with a liquid or a melt giving solid products. The best example in this case is the gridnant reagent formation take the case of magnesium metal, which is a solid and then you have RX that is alkyl halide which is liquid and then you also have ethane which is liquid. Now, to form this solid product you actually have to go through several fundamental steps, which looks simple, but it is very intricate. Another classic example of solid liquid melt is your hydrogen incorporation in lithium aluminum hydrate, where lithium ion for hydrogen ion exchange between AlO2 layers are achieved, and this is also very sensitive reaction. Basically these are controlled by surface defects absorption dissociation and other diffusion mechanisms.

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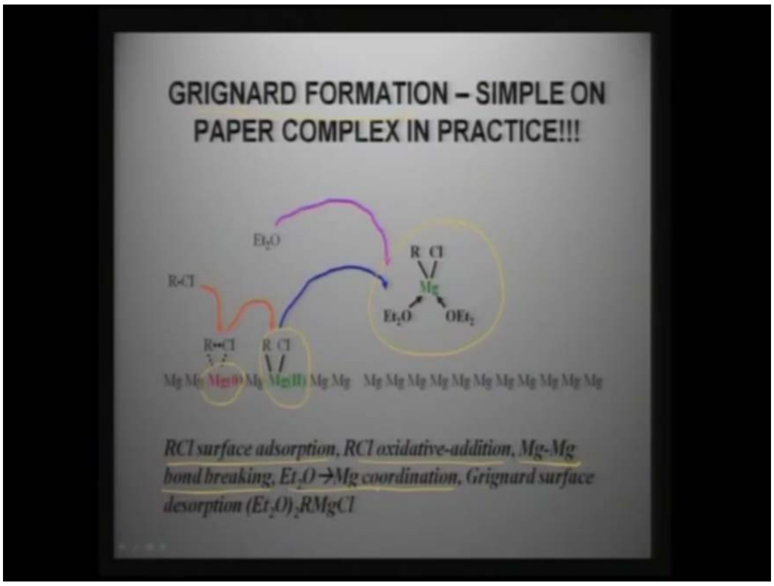

GRIGNARD FORMATION – SIMPLE ON PAPER COMPLEX IN PRACTICE!!!

RCl surface adsorption, RCl oxidative-addition, Mg-Mg bond breaking, $Et_2O \rightarrow Mg$ coordination, Grignard surface desorption $(Et_2O)_2RMgCl$

Just to show what all the various steps that happens in solid state synthesis, you take again the example of grignard formation. In this case actually the alkyl halide actually gets absorbed in the initial reaction with magnesium metal, which is having a zero valance. Now, once bonds are formed now this sort of species is formed which now is taking another molecule of either, and this is now getting dethatched from the magnesium metal surface.

So, so many things happen one is the RCl surface absorption and then a oxidative addition that is happening and then magnesium magnesium bond breaking occurs. And after that you have the ether getting coordinated to magnesium and then the grignard surface de subs form the magnesium metal. So, many things happen but it looks as though it is a very, very easy process, but the solid state chemistry that is involved is really peculiar there.

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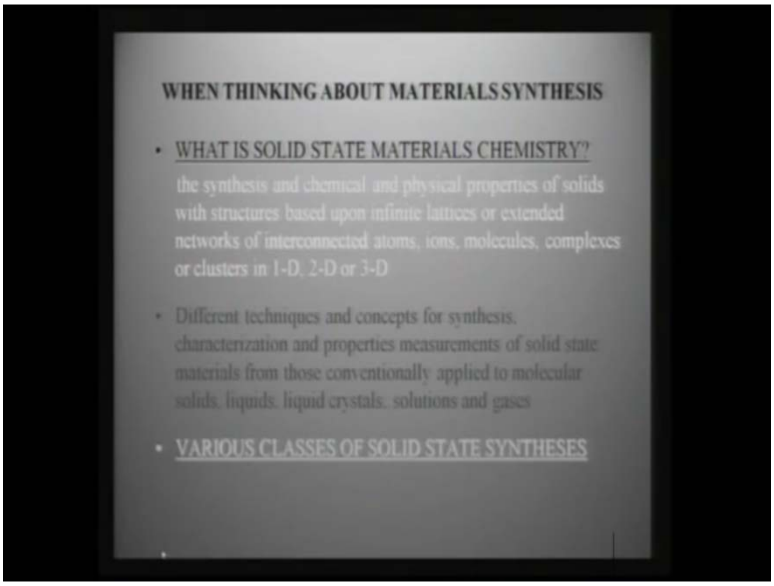

WHEN THINKING ABOUT MATERIALS SYNTHESIS

- WHAT IS SOLID STATE MATERIALS CHEMISTRY?
  the synthesis and chemical and physical properties of solids with structures based upon infinite lattices or extended networks of interconnected atoms, ions, molecules, complexes or clusters in 1-D, 2-D or 3-D
- Different techniques and concepts for synthesis, characterization and properties measurements of solid state materials from those conventionally applied to molecular solids, liquids, liquid crystals, solutions and gases
- VARIOUS CLASSES OF SOLID STATE SYNTHESES

So, when thinking about material synthesis what is solid state materials chemistry all about? It is the synthesis and chemical and physical properties of solids which structures based upon infinite lattices or extended networks of interconnected atoms ions molecules complexes or clusters in 1-d, 2-d and 3-d. So, it is a quite involved mechanism.

Different techniques and concepts for synthesis characterization and properties measurements of solid state materials from those conventionally applied to molecular solids, liquids liquid crystals solutions and gases. Fundamentally this solid state approach is very, very different from what we usually encounter with the molecular solids. And we can therefore, play around with a various class of solid state synthesis depending on the type on end products that we are looking for. So, this brings us again to focus what sort of approach what we are using, the slides which is showed in the initial part of the lecture.

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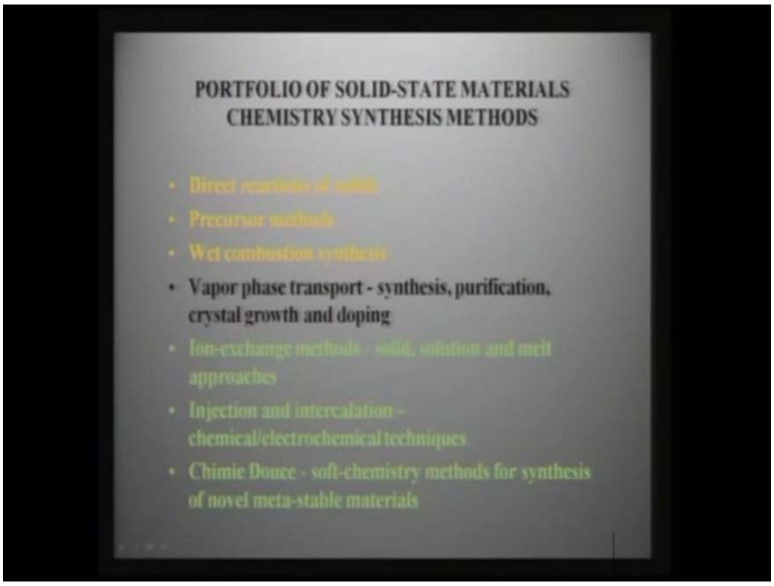

PORTFOLIO OF SOLID-STATE MATERIALS CHEMISTRY SYNTHESIS METHODS

- Direct reactions of solids
- Precursor methods
- Wet combustion synthesis
- Vapor phase transport - synthesis, purification, crystal growth and doping
- Ion-exchange methods - solid, solution and melt approaches
- Injection and intercalation – chemical/electrochemical techniques
- Chimie Douce - soft-chemistry methods for synthesis of novel meta-stable materials

Again we come to the portfolio of solid state materials so we need to go based on the reactivity of the solids, based on the functional application, based on the reactivity of the starting materials or the structure we can play around with host of preparative route. Not only this, but think front routes.

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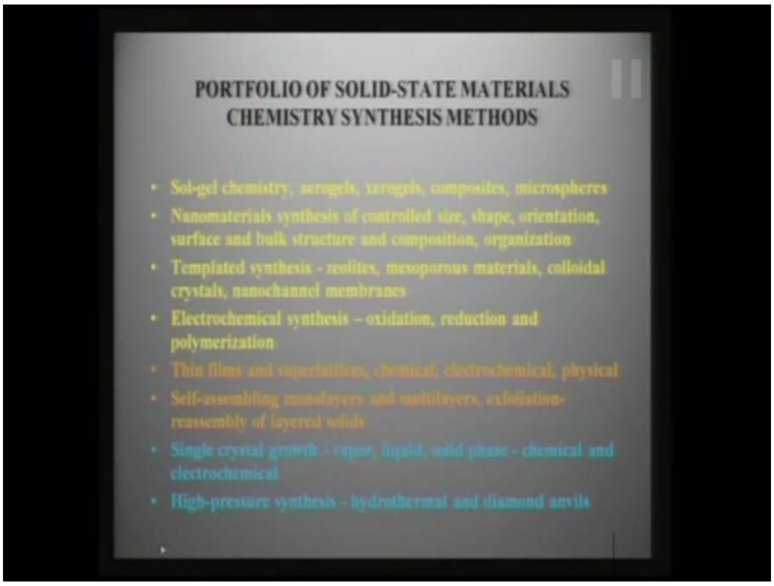

PORTFOLIO OF SOLID-STATE MATERIALS CHEMISTRY SYNTHESIS METHODS

- Sol-gel chemistry, aerogels, xerogels, composites, microspheres
- Nanomaterials synthesis of controlled size, shape, orientation, surface and bulk structure and composition, organization
- Templated synthesis - zeolites, mesoporous materials, colloidal crystals, nanochannel membranes
- Electrochemical synthesis – oxidation, reduction and polymerization
- Thin films and superlattices, chemical, electrochemical, physical
- Self-assembling monolayers and multilayers, exfoliation-reassembly of layered solids
- Single crystal growth - vapor, liquid, solid phase - chemical and electrochemical
- High-pressure synthesis - hydrothermal and diamond anvils

Nano approaches can be made in order to realize different sort of chemical compounds.

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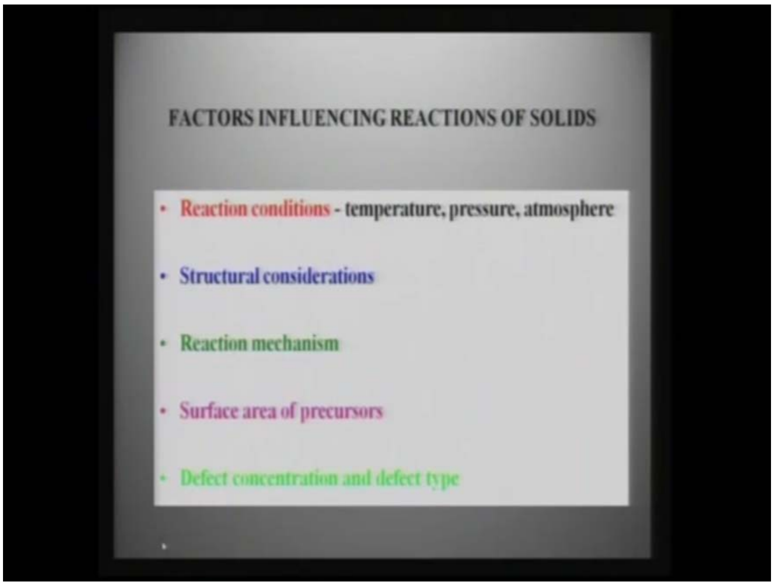

FACTORS INFLUENCING REACTIONS OF SOLIDS

- Reaction conditions - temperature, pressure, atmosphere
- Structural considerations
- Reaction mechanism
- Surface area of precursors
- Defect concentration and defect type

So, in one sense we can brief briefly sum up to say that the factors influencing reactions of solids involves reaction conditions temperature, pressure and atmosphere, structural considerations reaction mechanism, surface area of precursors, defect concentration and defect types.

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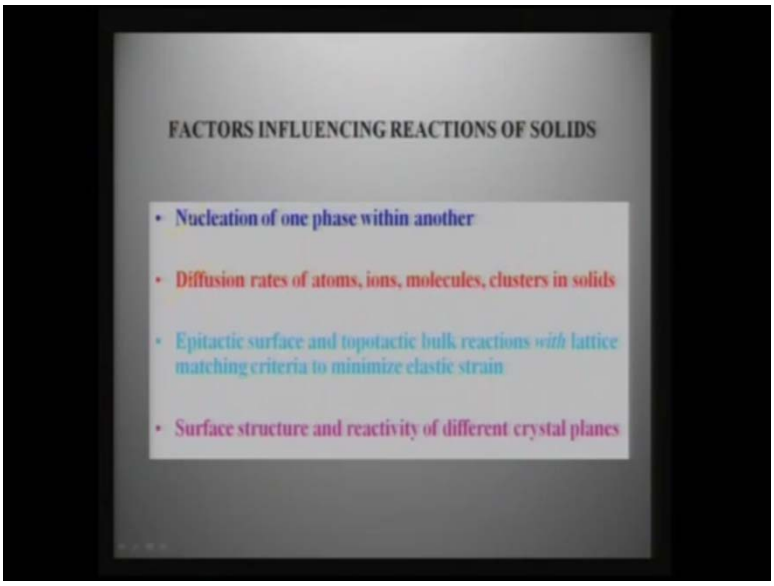

FACTORS INFLUENCING REACTIONS OF SOLIDS

- Nucleation of one phase within another
- Diffusion rates of atoms, ions, molecules, clusters in solids
- Epitactic surface and topotactic bulk reactions *with* lattice matching criteria to minimize elastic strain
- Surface structure and reactivity of different crystal planes

Nucleation of one phase within the other diffusion rates of atoms, ions, molecules, clusters and solids. And then we can talk about so the epi tactic surface and topo tactic bulk reactions with the lattice matching criteria to minimize a elastic strain. And then surface structure and the reactivity of different crystal plates. So, so many factors do effect the solid state synthesis and specially to make new functional materials all this issues have to be taken into consideration.

I will now take you to through some of the reactions, which stands as a architect for solid state reactions. One of the classic example is the formation of magnesium Al2O3 Al2O4 which is a spinal. And how this formation of this compound can be monitored, now this can be kinetically monitored let us take the single crystals of Mgo Al2O 3 when they are kept glued to each other surface and then one can monitor. How the formation of the spinal can be achieved?

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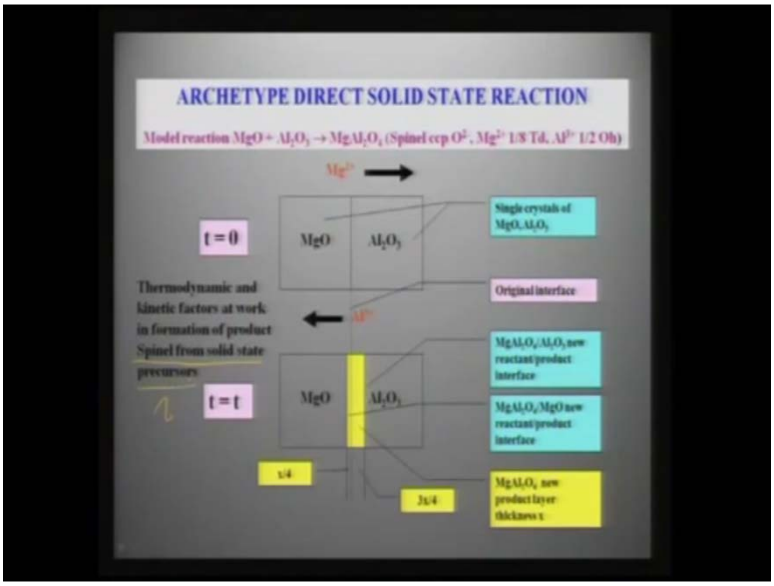

ARCHETYPE DIRECT SOLID STATE REACTION

Model reaction $MgO + Al_2O_3 \rightarrow MgAl_2O_4$ (Spinel ccp O^{2-}, Mg^{2+} 1/8 Td, Al^{3+} 1/2 Oh)

Thermodynamic and kinetic factors at work in formation of product Spinel from solid state precursors

The model reaction is Mg O plus A l 2 O 3 giving Mg Al 2 O 4 and this is a spinal which is a cubic close piped one, made of oxygen close packing. Now, here the beauty is magnesium has to go into one-eighth of the tetra Hedral vides, and aluminum has to go into half of the octahedral vide selectively. Now, all this has to happen when you just keep one crystal with the other crystal and you start heating it, and this is what happens magnesium has to travel form this interface, this region into the inter phase along this direction and Al 3 plus has to travel in this direction.

So, as this diffusion is happening then you will see progressively at the inter phase a product is forming and this is initially, the original inter phase at time t 0. And once you start heating it you will see this yellow patch that is forming which is nothing but your spinal phase. And this yellow phase is the Mg Al 2 O 4 new product layer thickness and this thickness is actually increasing with time, in such a way that this will amount from this original layer x by 4 times of this will propagate towards the MgO layer and 3 x by 4 times it will be propagating towards the Al 2 O 3 layer.

So, the product front will actually travel in both the directions depending on the mobility and the concentration of aluminum and magnesium respectively. So, if one magnesium has to go in this forward direction then two aluminum has to travel in this direction. As a result you will see the product front is actually growing much faster in the Al 2 O 3 inter phase, rather than the MgO inter phase. So, this can be clearly monitored and time t we can try to see how much of this final phase has grown. So, in this solid state reaction you can see, this is thermodynamic and kinetic factors are at work both are playing a vital role in the formation of this product, this spinal is formed eventually because of the solid state precursor.

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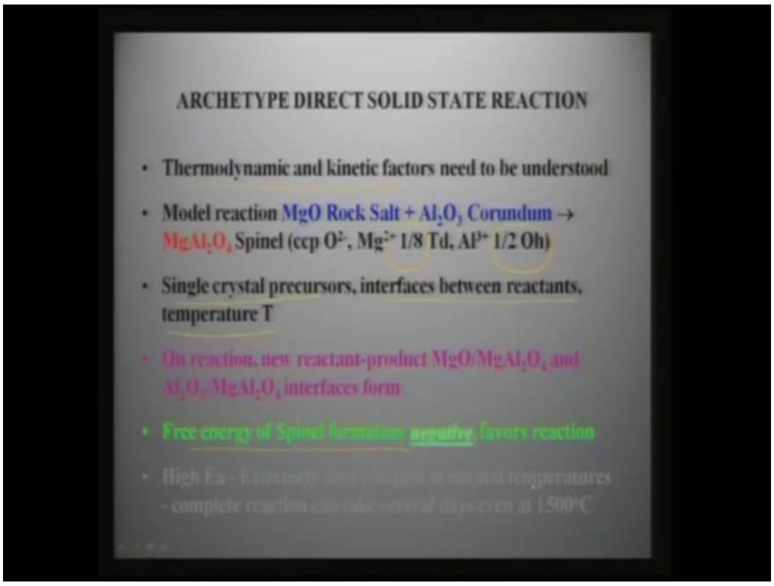

ARCHETYPE DIRECT SOLID STATE REACTION

- Thermodynamic and kinetic factors need to be understood
- Model reaction MgO Rock Salt + Al_2O_3 Corundum → $MgAl_2O_4$ Spinel (ccp O^{2-}, Mg^{2+} 1/8 Td, Al^{3+} 1/2 Oh)
- Single crystal precursors, interfaces between reactants, temperature T
- On reaction, new reactant-product $MgO/MgAl_2O_4$ and $Al_2O_3/MgAl_2O_4$ interfaces form
- Free energy of Spinel formation negative, favors reaction
- High Ea - Extremely slow reaction at normal temperatures - complete reaction can take several days even at 1500°C

So, what are all the issues that are happening during this solid state reaction, number 1 is thermo dynamic and kinetic factors are to be understood, how they are they can limit this formation. Number 2 we should know the side occupancy and therefore if you know the side occupancy then we will also know whether the ionic size is suitable for such a solid state reaction to happen. And then we should know the single crystal precursor whether they are ((Refer Time: 40:00)) whether they are defect free and the inter phases between the reactants and the temperature that is applied for this reaction to occur.

On reaction new reactant product that is Mgo Mg Al 2 O 4 and Al 2 O 3 Mg Al 2 O 4 inter phases form. And progressively as you see here in this type of reaction the free energy of spinal formation is always negative and therefore, it favours reaction. And the high energy of activation means extremely slow reaction at normal temperatures. But you can see this reaction rate is enhancing if you are going to increase the temperature to fifteen hundred degrees centigrade.

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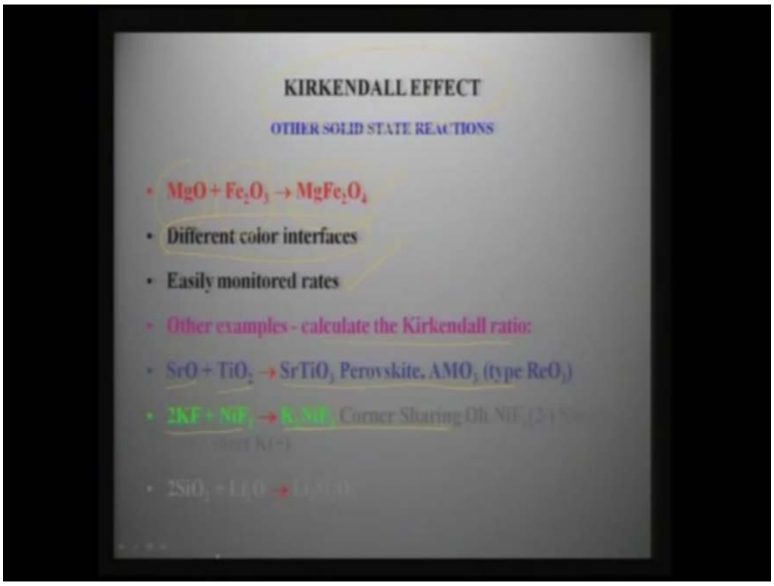

KIRKENDALL EFFECT

OTHER SOLID STATE REACTIONS

- $MgO + Fe_2O_3 \rightarrow MgFe_2O_4$
- Different color interfaces
- Easily monitored rates
- Other examples - calculate the Kirkendall ratio:
- $SrO + TiO_2 \rightarrow SrTiO_3$ Perovskite, AMO_3 (type ReO_3)
- $2KF + NiF_2 \rightarrow K_2NiF_4$ Corner Sharing Oh [illegible]
- $2SiO_2 + Li_2O \rightarrow$ [illegible]

Similarly, one can actually follow the reaction kinetics of Mg Fe 2 O 4 which is spinal again, and this is popularly known as a Kirkendall effect because in one case MgO is a color less solid and Fe 2 O 3 is a brownish orange solid. And together it will give you a brown solid and it is very easy if you take a Mgo crystal and Fe 2 O 3 crystal and you try to keep at the inter phase and start heating it, you will see different color inter phases happening at that point. And therefore, you can easily monitor the kinetics of such reaction which is ha nothing but the Kirkendal effect. And there are other examples to such process and we can calculate the kirkendal ratio for example, reaction involving strontium oxide and Ti O 2 gives you Sr Ti O 3 and we can take 2 KF plus Ni F 2 which is K 2 Ni F type of structure and so on.

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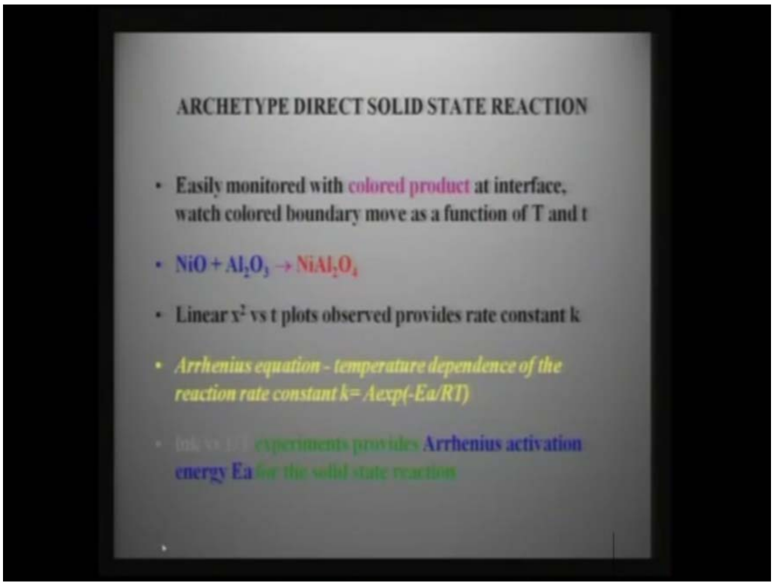

ARCHETYPE DIRECT SOLID STATE REACTION

- Easily monitored with colored product at interface, watch colored boundary move as a function of T and t
- $NiO + Al_2O_3 \rightarrow NiAl_2O_4$
- Linear x^2 vs t plots observed provides rate constant k
- *Arrhenius equation - temperature dependence of the reaction rate constant k= Aexp(-Ea/RT)*
- lnk vs 1/T experiments provides Arrhenius activation energy Ea for the solid state reaction

So, we can also try to monitor based on the colored inter phases there are other examples to that end. Easily monitored with colored product such inter phase for example, nickel oxide which is a green oxide and Al 2 O 3 is color less, together it will form a faint green form a blue oxide nickel Al 2 O 4. Again here in this case we can determine the reaction kinetics using Arrhenius plot, and we can try to monitor the energy of activation of this reaction.

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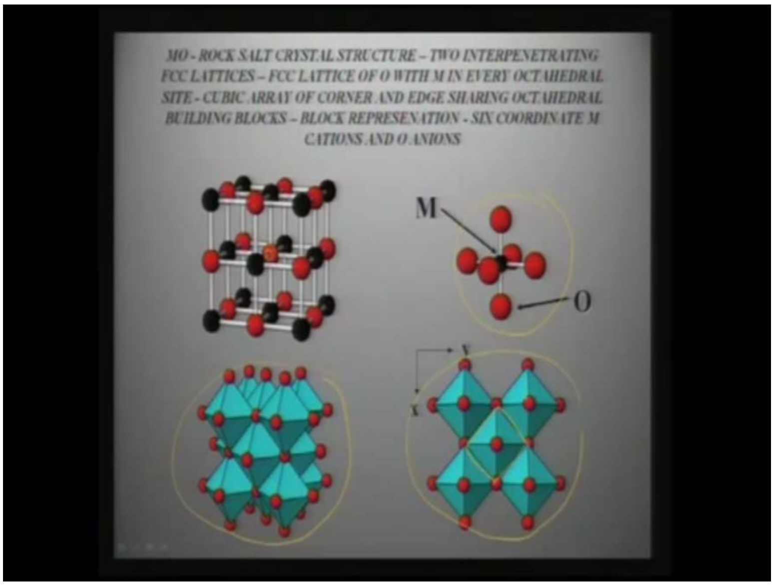

MO - ROCK SALT CRYSTAL STRUCTURE – TWO INTERPENETRATING FCC LATTICES – FCC LATTICE OF O WITH M IN EVERY OCTAHEDRAL SITE - CUBIC ARRAY OF CORNER AND EDGE SHARING OCTAHEDRAL BUILDING BLOCKS – BLOCK REPRESENATION - SIX COORDINATE M CATIONS AND O ANIONS

If you take for example, two rock solids for example, this is the famous NaCl structure Mo rock salt crystal structure, this looks simple, but actually this is too inter interpenetrating FCC lattices. FCC lattice of oxygen with M in every octahedral side and therefore, they form a cubic array of corner and edge sharing octahedral building blocks. And if you actually look at the structure it is very important to understand how this reactions proceed because with in this FCC lattice, you will see two rock salt lattices mixed together. One is with the red core as your center which is octahedral coordinated and second is this black sphere, which is octahedral coordinated to six red spheres.

So, it can either be a MO 6 octahedral or OM 6 octahedral and together they can form either a cornered shared polyhedral or they can form a edge shared polyhedral. This is edge shared because the edges of this octahedral is actually in phase with 4 other octahedral. So, to make either a cornered shared octahedral or edge shared octahedral, solid state reaction has to be very selective it cannot give mixed ones, but it is very selective dependent on the type of rock salt structure that you are using. What sort of the cation that cation anion that you are looking for will determine, whether you get a cornered shared or a edge shared polyhedral.

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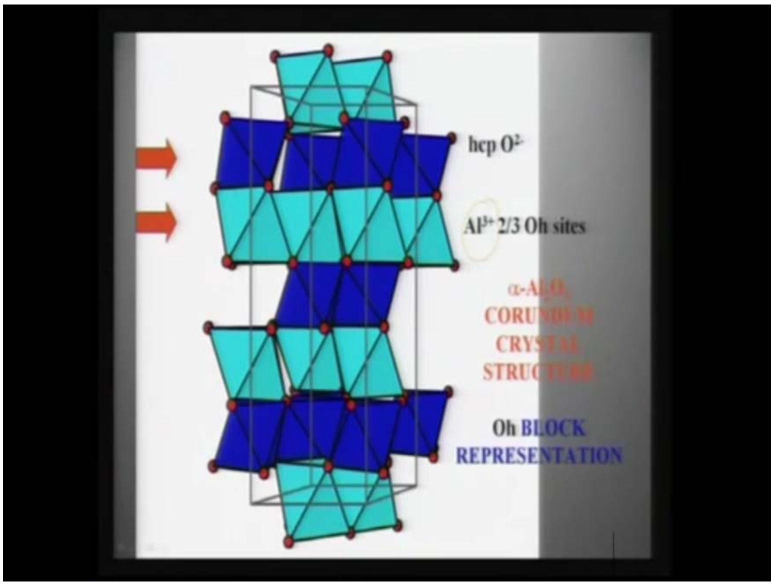

Again corundum structure is there, this is a octahedral block representation of Al 2 O 3 which is having corundum structure, where this is made out of a hexagonal close packing of oxygen, where two-third of the octahedral sides are occupied by Al 2 O 3. So, this is again a very selective site occupancy so if any doping has to be happening, then it has to go in to this selective sites of this octahedral sites, where aluminum is doped and that will determine the property of the substitute solids.

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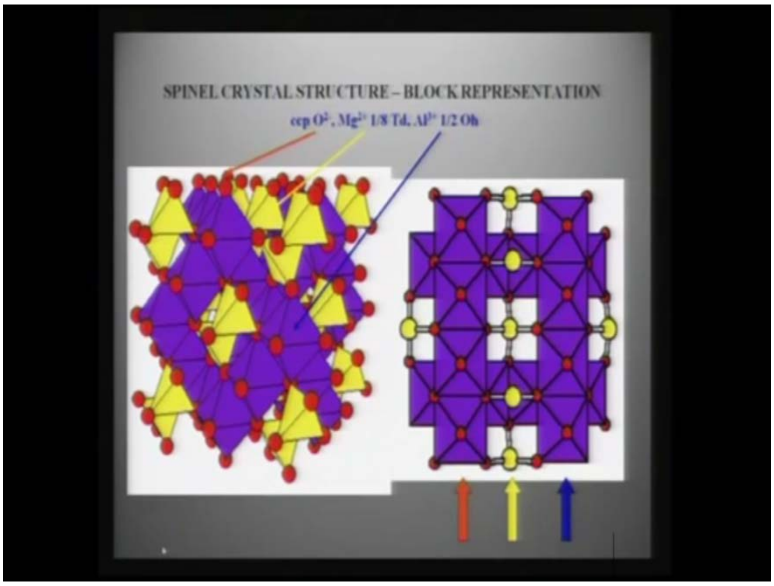

SPINEL CRYSTAL STRUCTURE – BLOCK REPRESENTATION

ccp O^{2-}, Mg^{2+} 1/8 Td, Al^{3+} 1/2 Oh

Spinal crystal structure is another good representation of how the solid state reaction happens this is another complicated crystal structure. Where the whole network of spinal structure is made out of oxygen close packing, where one-eighth of the tetrahedral voids is occupied by Mg 2 plus and half of the octahedral voids are occupied by Al 3 plus. So, trivalent metal ion occupies the octahedral site and the di valiant metal ion occupies the tetra valiant site. And here again the diffusion or the solid state reaction is a time consuming process because each of this metal ions have to go and occupy the respective sites. It’s not possible for the aluminum to occupy the tetra hedral site therefore, this solid state reaction conditions has to be optimized such a way that a effective occupancy of magnesium and aluminum in tetrahedral, and octahedral voices is achieved respectively.

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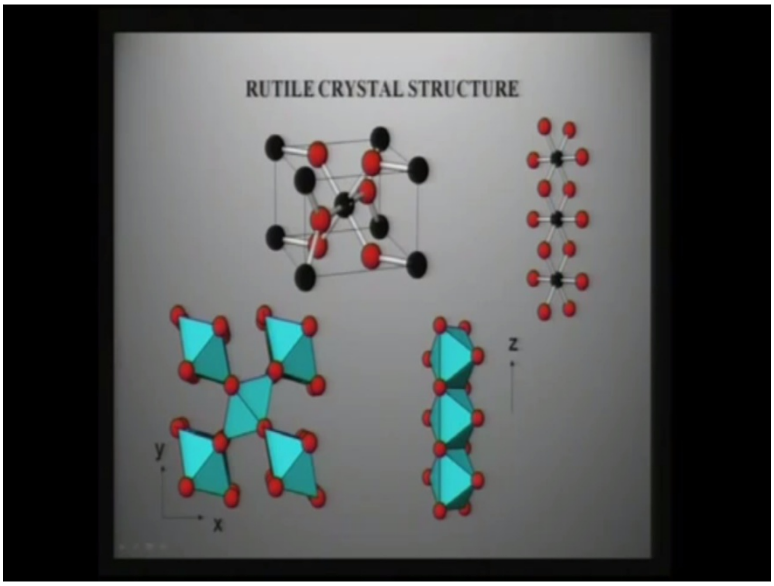

RUTILE CRYSTAL STRUCTURE

And another very important structure in material chemistry is rutile structure, where you have the metal ion which is actually a coordinated to 4 other oxygen’s in this fashion. And they can be edge shared or they can be phase shared or corner shared depending on size of metal ion.

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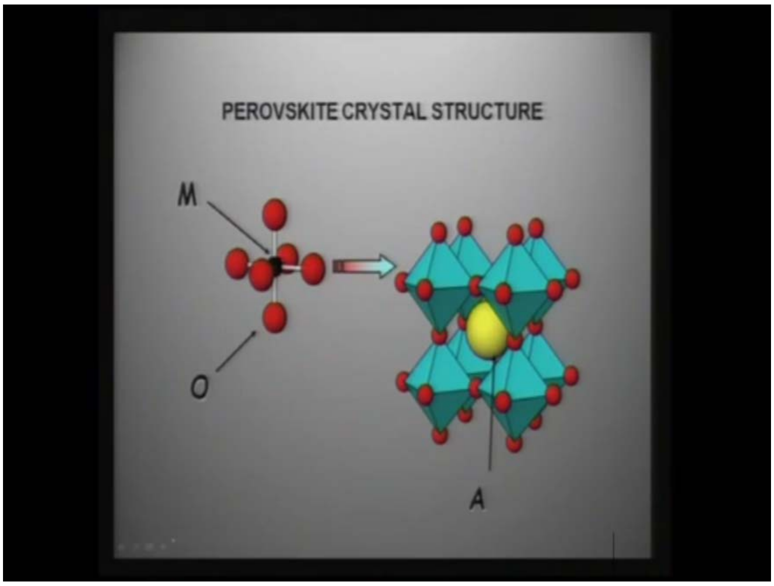

PEROVSKITE CRYSTAL STRUCTURE

And the anion that you are looking for the next important class of compounds which takes our attention in solid state synthesis is the Perovskite crystal structure. This again comes from a a MO 6 octahedral and this MO 6 octahedral forms the corner shared polyhedral stuff. So doping selectively for the metal sight is very important technique where solid state chemistry synthesis can play a vital role.

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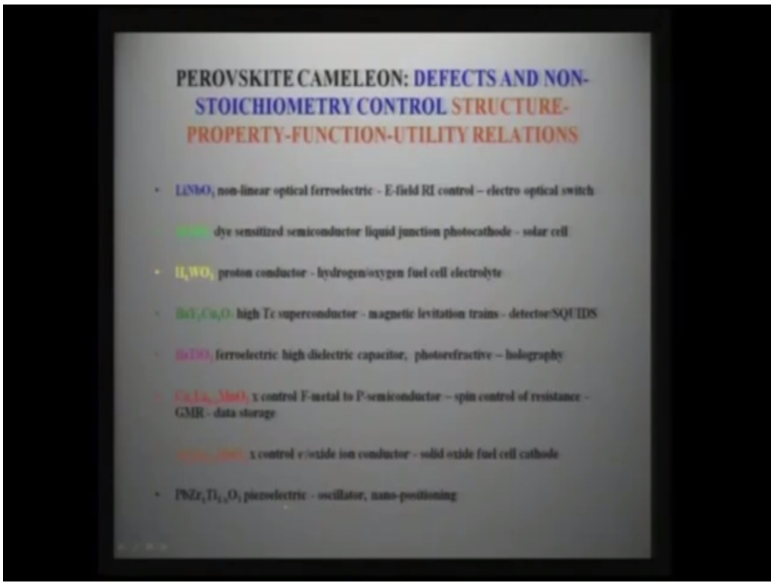

PEROVSKITE CAMELEON: DEFECTS AND NON-STOICHIOMETRY CONTROL STRUCTURE-PROPERTY-FUNCTION-UTILITY RELATIONS

- $LiNbO_3$ non-linear optical ferroelectric - E-field RI control – electro optical switch
- [illegible] dye sensitized semiconductor liquid junction photocathode - solar cell
- H_xWO_3 proton conductor - hydrogen/oxygen fuel cell electrolyte
- [illegible] high Tc superconductor - magnetic levitation trains - detector/SQUIDS
- [illegible] ferroelectric high dielectric capacitor, photorefractive – holography
- $Ca_xLa_{1-x}MnO_3$ x control F-metal to P-semiconductor – spin control of resistance - GMR - data storage
- [illegible] x control e/oxide ion conductor - solid oxide fuel cell cathode
- $PbZr_xTi_{1-x}O_3$ piezoelectric - oscillator, nano-positioning

And therefore, its is actually called as a Perovskite Cameleon because you can very easily modify the property of this Perovskite by carefully doping either into the oxygen site or the metal site. And therefore, defects and non stoichiometry control the structure property and as a result the utility relations. There are classic examples of this perovskite compounds one is lithium neobit which is a non-linear optical ferroelectric, which is used in electro optical switch. As you can see here the Perovskite lattice can be still maintained with a penta valiant niobium, and a mono valiant lithium, still they can stabilize a Ab O 3 type of structure or this can be a di valiant and a tetra valiant cation, strontium titanium these are di sensitize semi conductor used in solar cells Sr Te O 3.

And then we have Hx WO 3 which is a proton conductor and this is used in hydrogen oxygen fuel cell as a electrolyte, where you can carefully try to dope hydrogen in a WO 3 matrix. As I told you earlier we also have other Perovskite for example, this high T c super conductor and then barium, titanium which is a ferro electric we can use it for holographic applications. And we have lanthanum magnetite doped with magnesium as I told you earlier this is used for spin control of resistance and used in data storage, lanthanum strontium magnetite used in solid oxide fuel cell as cathods because it is a good oxide ion conductor.

And we can also make several perovskite compounds like Pb Zr Ti O 3 which is used for piezopelectric applications use in Af Mn so on. So, so many different sort of compounds and you can see a variety of cations that you can dope maintaining this structure, but you can end up with a range of properties from magnetism to conductivity to ionic mobility, you can for any sort of property. And the precise control of the size and shape of this materials will help in the utility applications.

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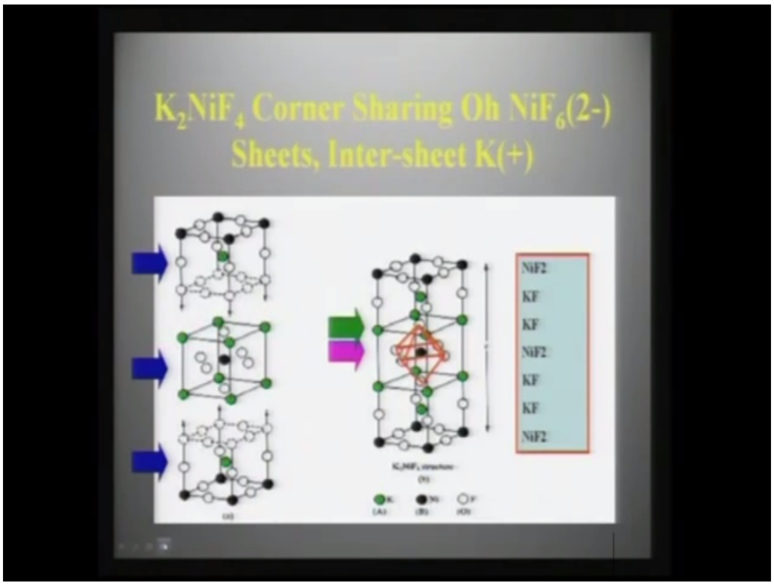

K_2NiF_4 Corner Sharing Oh NiF_6(2-) Sheets, Inter-sheet K(+)

K 2 Na 4 is another group of structure, which is important in this materials chemistry where you can see this as a repeat layer of Ni F 2 KF KF Ni F 2 KF KF Ni F 2 and so on. So, you this is a special case of perovskite that you can make where you have this Ni F 2 sheets with a inter sheet of K plus that is stabilizing this K 2 F structure.

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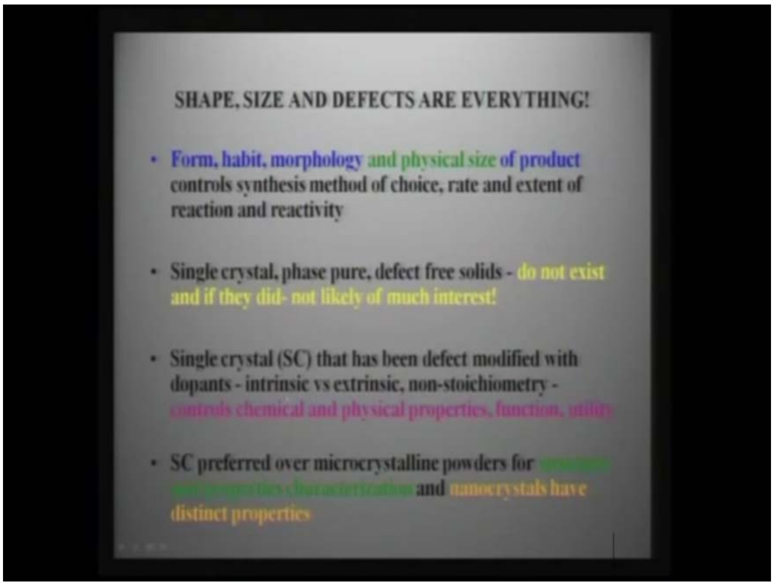

SHAPE, SIZE AND DEFECTS ARE EVERYTHING!

- Form, habit, morphology and physical size of product controls synthesis method of choice, rate and extent of reaction and reactivity
- Single crystal, phase pure, defect free solids - do not exist and if they did- not likely of much interest!
- Single crystal (SC) that has been defect modified with dopants - intrinsic vs extrinsic, non-stoichiometry - controls chemical and physical properties, function, utility
- SC preferred over microcrystalline powders for structure and properties characterization and nanocrystals have distinct properties

So, in essence we are actually looking at few issues that are fundamental to the solid state synthesis, size, shape and defects are everything so to say. The morphology and physical size of product controls synthetic method of choice, rate and extent of reaction and reactivity. Single crystal phase pure defect free solids they do not exits and if they did not likely of much interest. Single crystals that has been defect modified with dopends which are intrinsic extrinsic and this can control the chemical physical properties the function and utility.

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SHAPE IS EVERYTHING!

- Microcrystalline powder Used for characterization when single crystal can not be easily obtained, preferred for industrial production and certain applications, where large surface area useful like control of reactivity, catalytic chemistry, separation materials, energy materials
- Polycrystalline shapes like pellet, tube, rod, wire Super-conducting ceramic wires, ceramic engines, aeronautical parts, magnets
- Single crystal or polycrystalline film Widespread use in microelectronics, optical telecommunications, photonic applications, coatings – protective, antireflection, self-cleaning
- Epitaxial film – multilayer superlattice films - lattice matching, tolerance factor, elastic strain, defects important for fabrication of electronic, magnetic, optical planarized devices
- Non-crystalline, amorphous, glassy – fibers, films, tubes, plates No long range translational order – just short range local order - control mechanical, optical electrical magnetic properties like fiber optic cables, fiber lasers, optical components
- Nanocrystalline – below a certain dimensions properties scale with size Quantum size effect materials – electronic, optical, magnetic devices - discrete electronic energy levels rather than continuous electronic bands – also useful in nanomedicine like drug delivery, imaging contrast agents, cancer therapy, and fuel, battery, solar cell materials

And therefore, when we when we look at this combinations we can single out to say that shape determines the solid state synthetic approach. So, if you are looking for micro crystalline powder then where ever single crystal cannot be used and it is not preferred for industrial production, you can resort to a powder form and certain applications where large area useful for control of reactivity, catalytic chemistry, separation materials and energy material can be achieved just with micro crystalline powder.

Suppose, you want poly crystalline shapes like pallid, tube, rod and wire then we can go in for such a chemical process, where we can get that for applications like super conducting ceramic wires ceramic engines magnets and so on. Then you can think of single crystal or polycrystalline film you know, if we are looking for use in micro electronics, in optical communication, photonic applications we can go for epical film. If we are looking for photonic and electronic applications or we can go for glassy substances fibers films and so on for a range of opto electronic applications and so on. So, in all this we see that the role of chemical synthesis is actually based on the sort of utility that you are looking for. So, based on that you need to modify your chemical applications.

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SMALL!

SUPERCONDUCTING HELICAL FLEXIBLE NANOCABLES!

SIZE AND SHAPE AND SURFACE IS EVERYTHING IN THE SOLID STATE NANOMATERIALS WORLD

Lastly I just want to finish with this beautiful figure this are nothing but super conducting helical flexible nanocables. And these are actually formed by chemical synthetic roots size and shape, and surfaces everything in the solid state. And specially at this time it is more on the nano materials world. So, with this I finish and then we can look at a several chemical approaches in the upcoming lectures.