Materials Chemistry

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Module - 1
Lecture - 3
Preparative Routes Conventional Precursor Technique – II

In the last lecture, we looked at the importance of precursor method, as I emphasized in the last lecture, precursors are a very convenient route, and wet chemical route to prepare complex metal oxides. So, you start in solution, but you end up with the crystalline solid, where the atoms and the anions take their position in the right symmetry. So, this involves both kinematic approach as well as thermodynamic approach, in precursor method I distinguished between solid solution precursors and simple precursors. Today, before I discuss more with the simple precursors, I just wanted to touch one more example to refresh our idea about solid solution precursor. Just to recap what is the importance of it, and then we will look more into the simple precursor routes.

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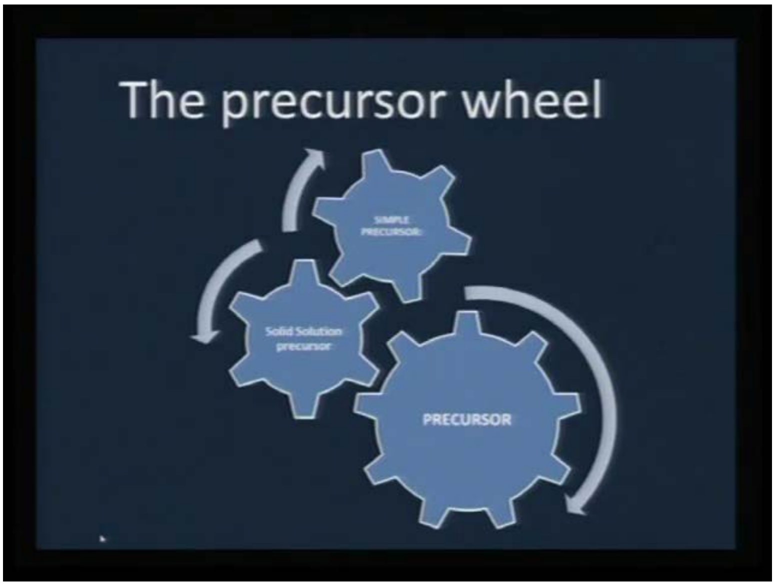

The precursor wheel

And this is the precursor wheel as I put it in simple form. Lot of precursors can be used to bring about the metal oxide formation. But one route is a solid solution precursor route, another route is simple precursor route.

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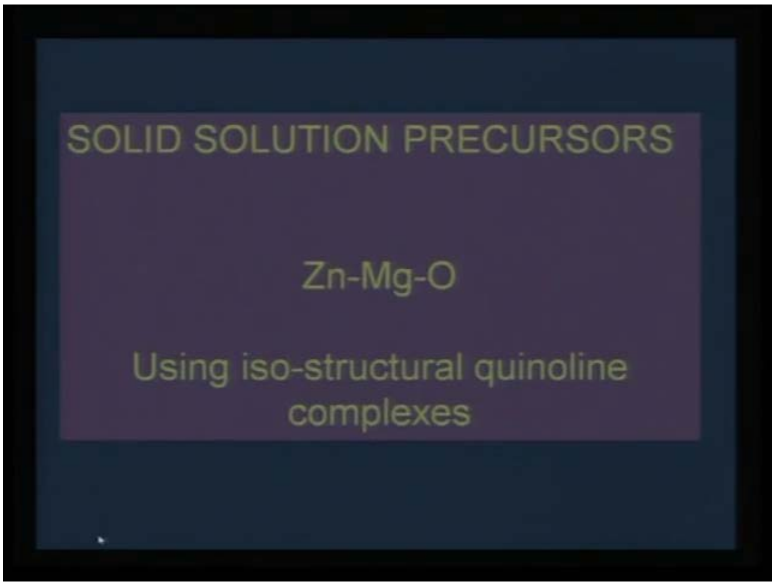

SOLID SOLUTION PRECURSORS

Zn-Mg-O

Using iso-structural quinoline complexes

So, just one more example on solid solution precursors, we can think about zinc, magnesium, oxygen system using the same concept of iso-structural quinoline complexes. In the last lecture I emphasized about the importance of structural similarity, and once you pack all the corresponding atoms into that crystal, then when you decompose it the corresponding metal oxide that you get will also have the finer and atomic level doping can be achieved, using such a principle.

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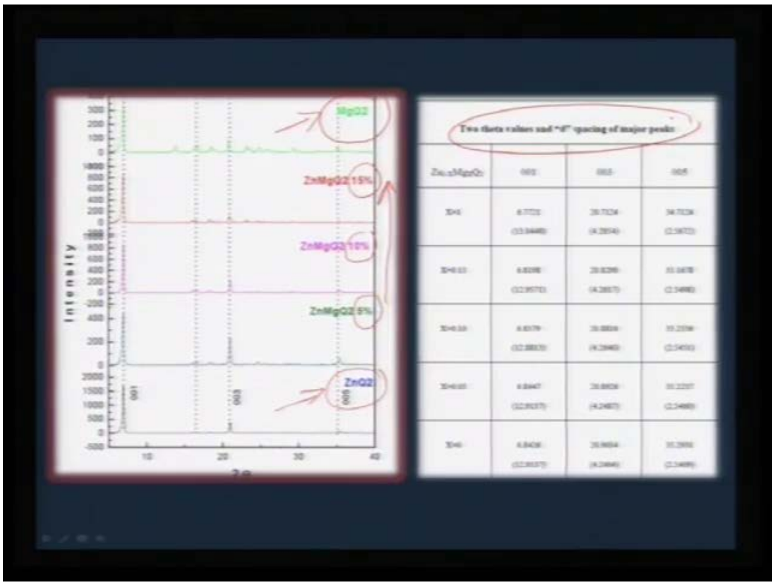

Two theta values and "d" spacing of major peaks

Now, this cartoon shows how the X-ray similar patterns can be exploited for making solid solutions. As you see here, this is zinc Q 2 and zinc Q 2 is nearly cubic in it is X-ray pattern, because you have only three obvious are major peaks and they are nearly equidistance. So, just by looking at the precursor X-ray, one can guess what sort of crystal symmetry it can have and in this case, because of a equidistant peaks, you can easily map it to be a cubic.

Because of higher symmetry you get very less peaks whereas, when it is more complex you get more peaks. Now, look at magnesium Q 2, if you take magnesium Q 2 again, there is a similarity between Z and Q 2 and magnesium Q 2 and therefore, this gives us a privilege to dope, magnesium and zinc together. So, the next three solid solutions are with varying percentage of magnesium from 5 to 15 percent, so you can keep varying it.

And as you see here, all this precursors are having this low degree reflections or low reflections at around 7 degrees, so once you ensure that such a solid solution precursor is made, then you can try to look at the possibility of converting this into the corresponding oxide. The values, the major peaks are all listed here as you can see, they are all closely matching, therefore we can say that they resemble the same crystal symmetry.

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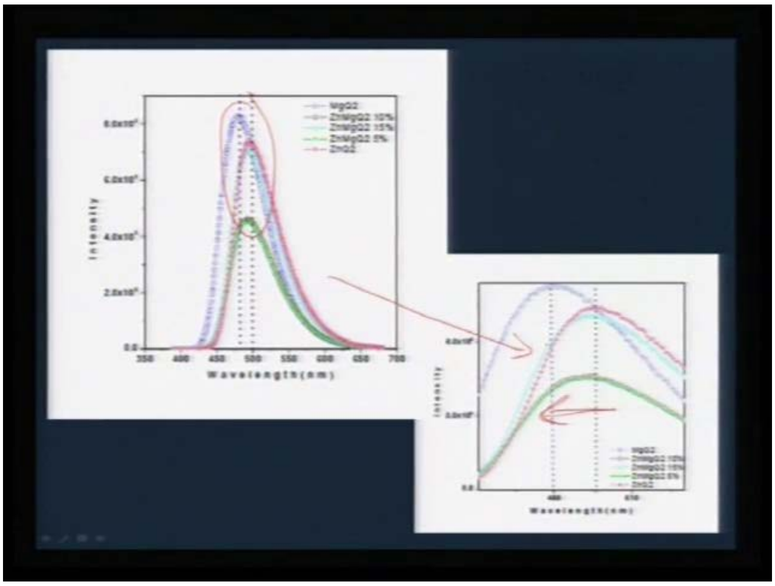

And if you take the precursor itself, they are highly photoluminescence, specially zinc Q 2, therefore when you put magnesium Q 2, you can try to see whether there is any systematicity with the doping concentration of magnesium. And as you would see here very clearly, this is the expanded version of this region, just to highlight that as you dope magnesium in zinc Q 2 you can see, the peak maximize shifting towards the blue region, which you would expect. Because, magnesium has a different size, and it is also showing emission near to bluish green. So, you can you can take clue from P L that magnesium is indeed getting doped, that is why you see the peak shift.

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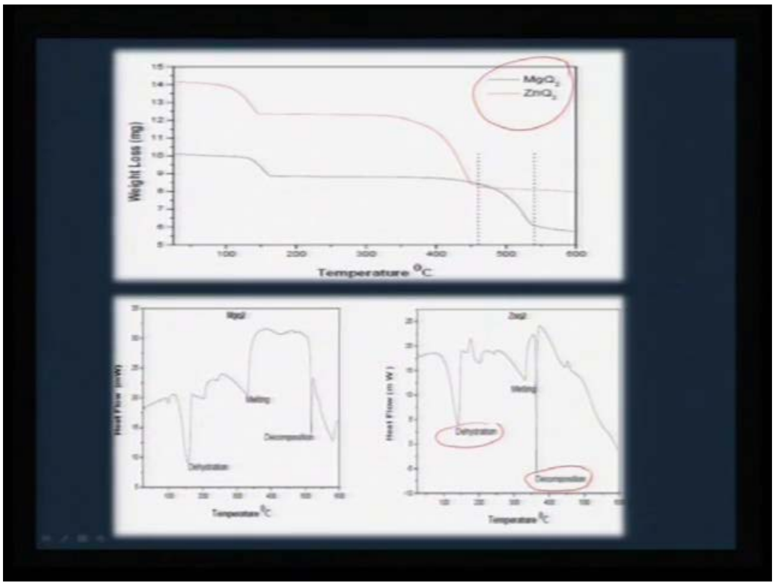

And if you look at the thermogravimetry, it gives you idea about how you can translate this quinoline 2 oxide, by taking magnesium Q 2 and zinc Q 2. If you look at the thermogravimetric zinc Q 2 is decomposing somewhere around 450 degree C, whereas magnesium Q 2 is decomposing around 550 degree C. So, you need to have some idea about how the precursors decompose on their own, by just having a idea of zinc Q 2, suppose you are decomposing the precursors at 500.

What it means is you are going to have a incomplete decomposition, therefore analysis of thermogravimetric traces is very important. And as you would see here the DSE plot is clearly showing, the dehydration step and the decomposition step and melting before decomposition all are prominent; and this gives an idea how we can translate it into the oxide.

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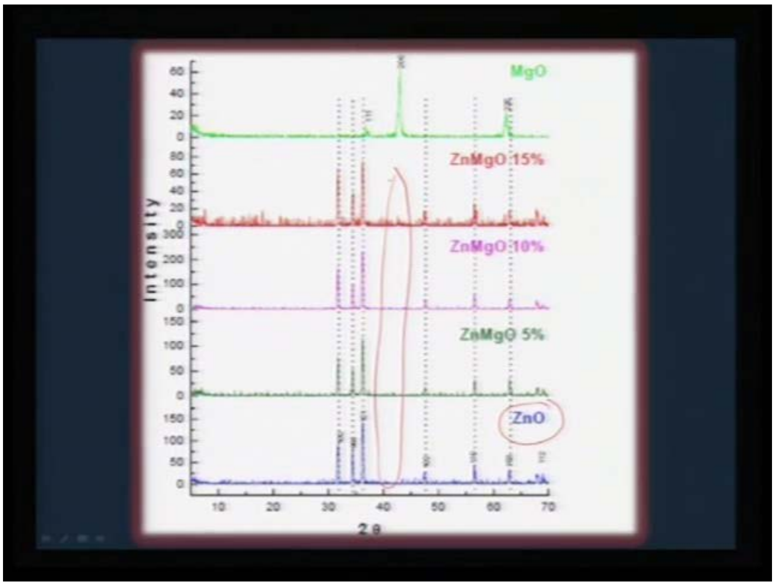

And this particular X-ray diffractogram shows, how zinc oxide with magnesium oxide can be ably substituted. And as you would see here up to 15 percent, there are no traces of any peak of magnesium that is coming here, which means absolutely magnesium is going into the zinc oxide lattice. Therefore, you can say that magnesium is getting substituted and it is not a phase separation, so this is a very useful way that you can try to dope magnesium into zinc oxide.

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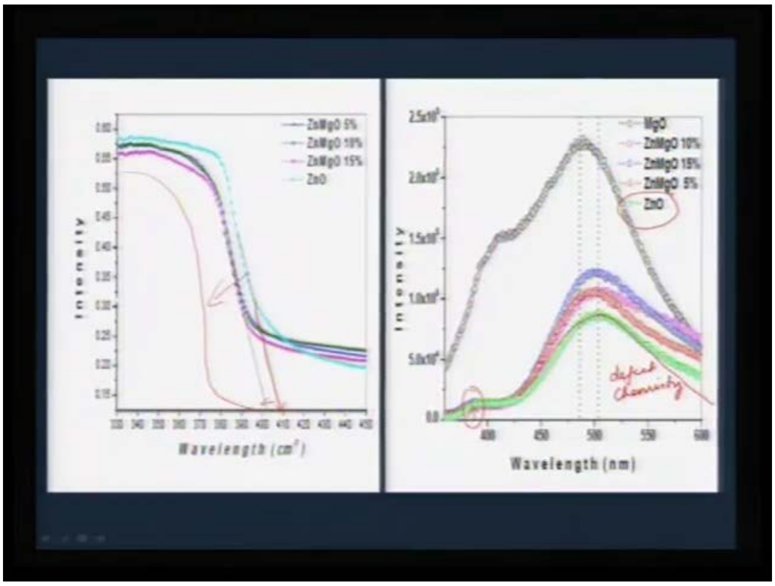

And the absorbance spectra also clearly shows that, there is a blue shifted absorbance, and as you would see zinc oxide is absorbing, which is denoted by this curve. And there is a shift towards the blue, with periodic doping of magnesium and since, magnesium oxide is a high band gap material, magnesium oxide itself would come somewhere around here. And therefore, progressively you can see the bandage is shifting towards the blue region. But, what we have to understand, the P L emission does not seem to really give the necessary feature that we look for.

For example, zinc oxide is showing this band to band emission, which is very useful and which is very conclusive of zinc oxide particles, they show a very small peak and then a very broad peak around 500, this is due to defect chemistry. And as a result we can see, irrespective of magnesium oxide doping the defect induced emission is much more compared to band to band emission. So, we may be able to prepare at low temperature, we may be able to prepare the same thing using a novel method, but what is important to understand is how we can get this surface free defects, and that is very critical. So, just mere consolation of a low temperature synthesis or a solid solution approach, does not guarantee the end product what you desire. It may be compositionally good, but then there are defects which are intricate with the precursor model, so this we need to bear in mind.

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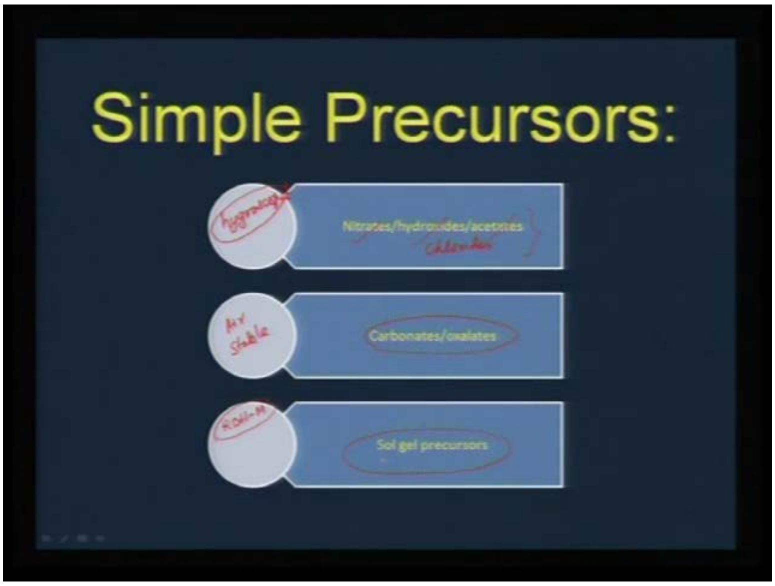

Simple Precursors:

Nitrates/hydroxides/acetates

Carbonates/oxalates

Sol gel precursors

And when we come to a simple precursors, we are now going to talk about several combinations. We can talk about nitrates, hydroxides, acetates or even chlorides, all substituent metals for example, if I take metal 1 and metal 2 corresponding nitrates I expect those two blend together, so that I can get the resulting oxide by decomposing it. But, there are some nitrates which have a very clear crystal symmetry. Therefore one can go for such match also, and these are more or less hydroscopic that is why I grouped this together hydroscopic.

And because nitrates, hydroxides and acetates, sometimes are hygroscopic, even chlorides we can add here; and because of that the use of a nitrate precursor or chloride precursors are very much restricted. Because, if you are going to bring two metal sols, then hygroscopic ones will react as a result you would not get a perfect control over the stoichiometry. Whereas, carbonates and oxalates are mostly they are air stable, and as a result it is better for us to use oxalates or carbonates as precursors. Because, even when you try to weigh those starting materials, you can precisely weigh that, therefore the error involved in your stoichiometry will be very less.

And thirdly the most used among precursors is sol-gel precursors, I will come to this shortly from now, sol-gel precursors are mostly alkoxides, when you treat any metal with a alcohol, then you can get metal alkoxide. And therefore, that is largely used, but as the name itself suggest, there is a phase which where you get a sol phase. And then you progressively take it to a gel phase and then it brings about a metal oxygen framework, which will serve as a good precursor for getting metal oxide. So, I am going to take you through all this three examples, with the several approaches, so in the next few slides I will give a representative idea of how these simple precursors can be used.

First one as an example I want to quote how zinc oxide can be made, zinc oxide is not only used in classical electrical conductivity or sensor applications of UV radiation, it is also used in variety of other application. Therefore, for some applications you need a very stringent control on the stoichiometry or purity, there are certain applications where you really do not need such phase purity. For example, if you are looking at a fastening the colour, for any equipments (( )) applications.

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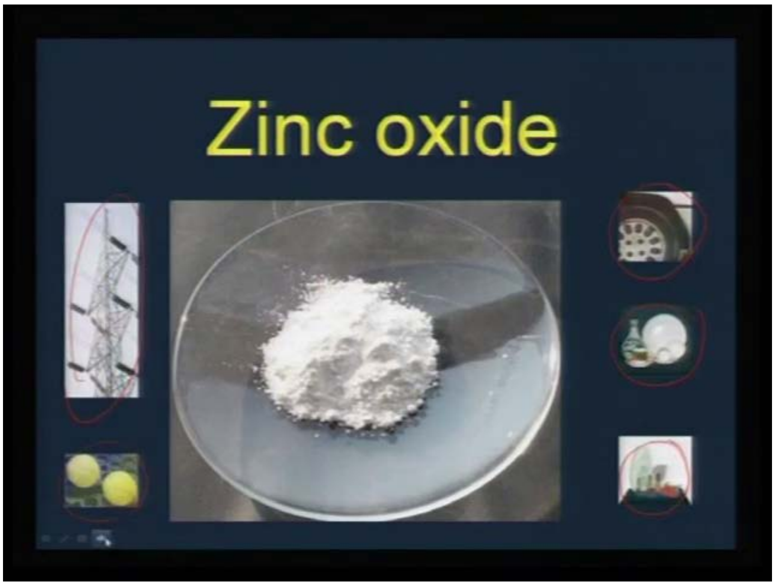

Zinc oxide is used because in all these polymers, you need to put the zinc oxide to filter or to observe the UV radiation, so that the coatings or the colouring agents that are added are not degraded. So, to fasten the colour zinc oxide is used as a pigment, in cosmetics it is used as a base, because you can make a very fine zinc oxide and it is non toxic. And in ceramics you can use it, it is also used to bring a good blend between brass and rubber, therefore zinc oxide comes as a very good one.

But, zinc oxide is not just used as a additive, but zinc oxide also has a very peculiar application as a search arrester, for high voltage applications zinc oxide is a very potential one. Now, zinc oxide is a white powder and there are many ways we can prepare that, I will just show you how simple precursors can be used and how it can transform distinctly.

This particular cartoon tells us, that zinc oxide thin films can be made by merely spin coating or spray coating, zinc nitrate solution, zinc acetate and zinc chloride solutions. So, you can just spray it and then decompose that into a film, and as you would see here in this left cartoon this is the region where you need to get all the reflections in the right intensity. And as you would see here, the chloride precursors are very poorly represented and then the acetate precursors, but what you see here as a good crystalline phase is coming from nitrate.

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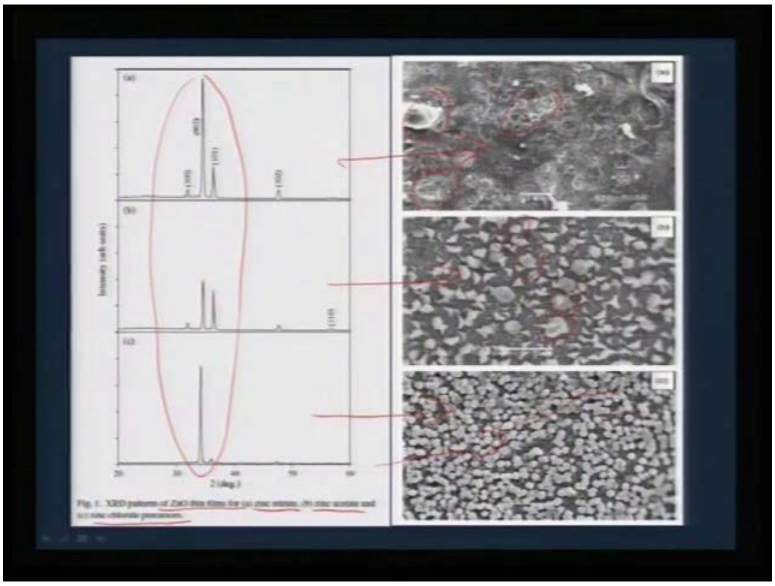

Fig. 1. XRD patterns of ZnO thin films for (a) zinc nitrate, (b) zinc acetate and (c) zinc chloride precursors.

So, among nitrate, chloride and acetate, it gives us a very clear clue that nitrates can be considered as a very useful one, because it gives a crystalline phase. And corresponding thin film also, you can see the morphology completely changes, in case of chloride, because the chlorides do is, escape during the heating process. They give discontinuous grain growth, therefore you do not see any grain growth which is continuous; and although there morphology looks attractive, but electrical continuity is missing between the grains.

And therefore, this particular film might lack percolation, and in the case of chloride based ones, you see lot of segregations or larger particles which are crystallizing. So, this is not a smooth growth, comparatively nitrate appears to be much better, but then there are also lot of voids and the films are not very smooth. So, precursors can be used, but then we should have in mind the limitation that comes along with every precursor, but all these precursors can be decomposed in less than 300 degree centigrade.

And if you look at this films there transmittance, technically the transmittance has to be somewhere around 90 percent, so you would expect a fall like this, for your absorbance spectra. Or in most cases using PLD or MBE method you can get a transmittance up to 80 percent, but using this precursors you can see that the transmittance is going down very abruptly. And therefore, the quality of this films are not very resolved as in the case of PLD, however when you look at the band gap, band gap clearly shows that it corresponds to 3.3. So, for a electrical resistivity purpose, all the films seem to match with the desired values whereas, for photonic application or for other applications, which are critical with the microstructure we seem to see a very inferior film.

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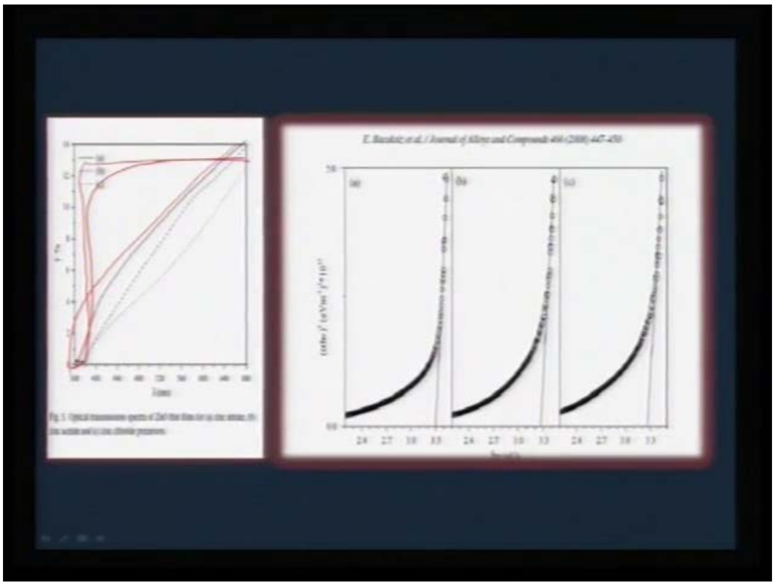

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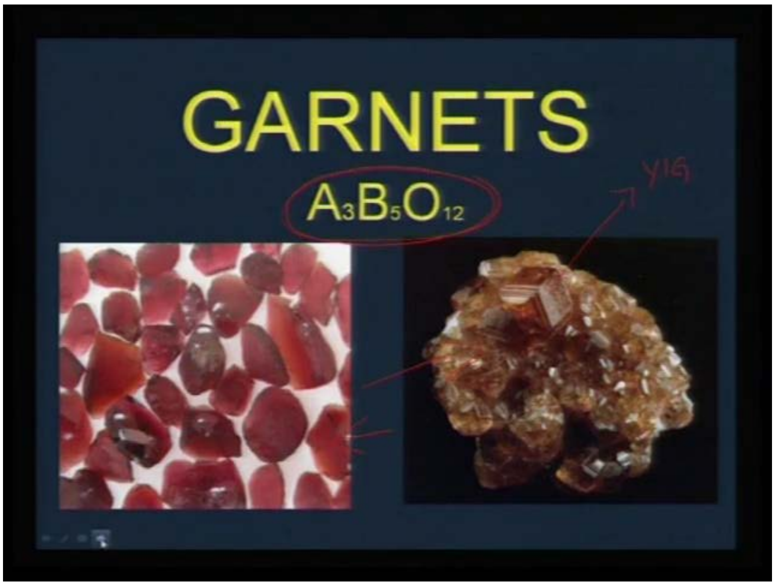

GARNETS

$A_3B_5O_{12}$

YIG

Let us take another example of garnets, garnets are those which have A3B5O12 sort of stoichiometry, and these are all garnet crystals naturally occurring. For example, this is nothing but YIG crystals which occur in nature, and to make such crystals or powder it is very, very difficult, because it involves very stringent thermodynamic requirements.

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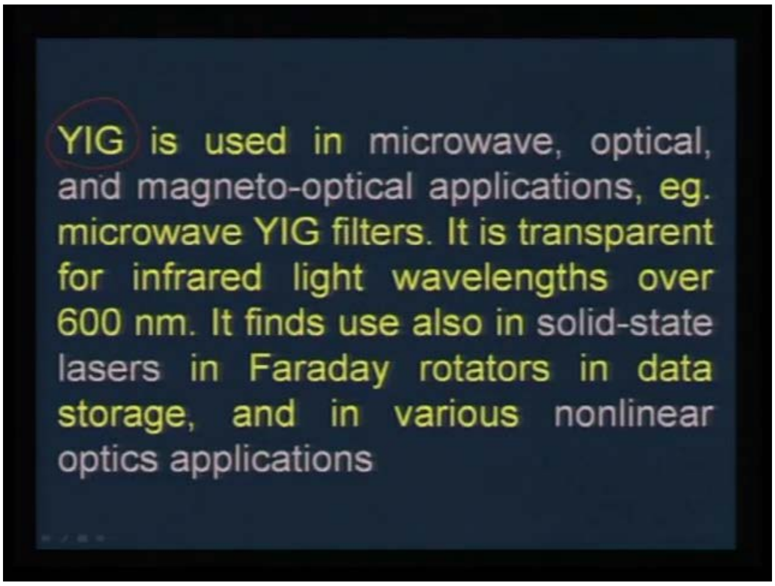

YIG is used in microwave, optical, and magneto-optical applications, eg. microwave YIG filters. It is transparent for infrared light wavelengths over 600 nm. It finds use also in solid-state lasers in Faraday rotators in data storage, and in various nonlinear optics applications

So, how do we achieve that for example, K case of YIG which is iron garnet, this has very wide range of applications including microwave, optical, magneto-optical applications and also in non-linear optic applications it has been used.

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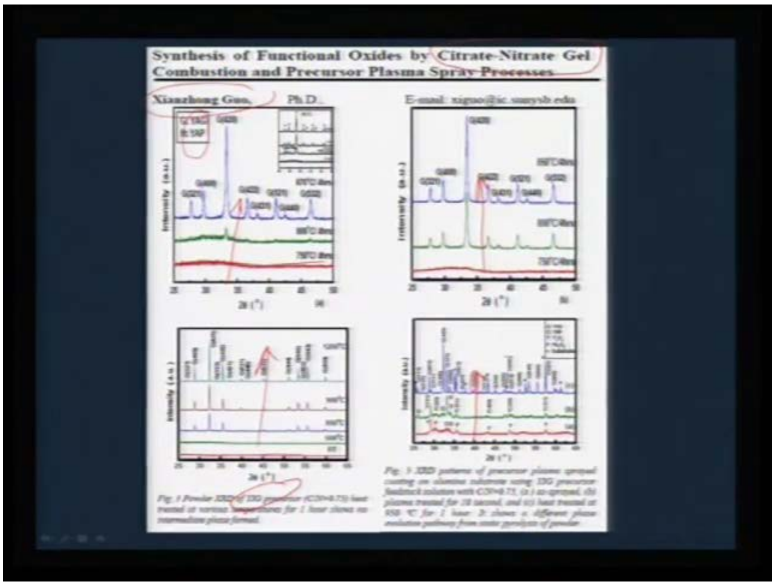

Synthesis of Functional Oxides by Citrate-Nitrate Gel Combustion and Precursor Plasma Spray Processes

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Now, how do we do that, one example is using a citrate-nitrate gel, because when you try to deposit such layered structure with complex stoichiometry, it is always important to go for a slower method rather than a rapid method, because you can get much more stoichiometrically stringent or controlled stoichiometry in the final oxide. So, citrate-nitrate gel is one of the best methods, why we can use citrate nitrate gel is, they almost behave like a combustion mixture.

Because, citrate forms the fuel part, nitrate forms the oxidizer part, but the best part here is instead of keeping it in solution, you can isolate that as a solid, as a result it is possible to isolate a solid, which can act as a precursor to give the corresponding oxide. And that this is the difference between the regular combustion process, which I discussed in one of the earlier lectures, and the combustion that comes out of a citrate nitrate gel.

So, if we do a thermal decomposition, you would see exothermic peak coming and that is mainly, because of the reaction between the fuel and the oxidizer in the gel. Now, as an example quoted by this person, we can actually use a yttrium, aluminium, garnet or we can also make yttrium, ion, garnet. So, we can make this precursors using citrate-nitrate gel and then as you would see in the room temperature mostly they will remain amorphous.

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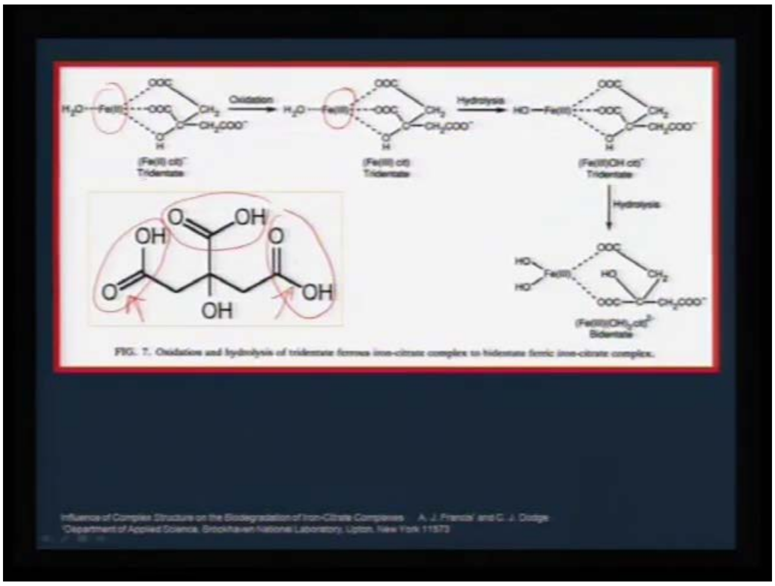

FIG. 7. Oxidation and hydrolysis of tridentate ferrous iron-citrate complex to bidentate ferric iron-citrate complex.

Influence of Complex Structure on the Biodegradation of Iron-Citrate Complexes A. J. Francis¹ and C. J. Dodge
¹Department of Applied Science, Brookhaven National Laboratory, Upton, New York 11973

Because, they actually undergo sol-gel reaction where, a disordered metal oxygen bonds are made, so in your order to crystallize this, you have to heat and this is a usual protocol in the sol-gel chemistry. Therefore, if you keep heating it, you can get very good phase or a single phase compound, but sufficiently at lower temperatures. So, this is one approach by which one can make complex oxides, I will come to the chemistry of this sol-gel, in the later slides in this lecture.

Citrate is very useful mainly because if you look at the structure of a citric acid, you have a carboxylic group here, you have carboxylic group here and then there is another carboxylic group also here. When metals are brought in closer proximity, these two carboxylate groups can actually bind like a dentate, so it is mostly a bi-dentate, therefore you can easily cleave to the metal ion. And as you would see here, for ion tridentate, ion 2 citrate, you can see a complication of this form.

And on oxidation it transforms to ion 3 centre and this sort of citrate complexes usually brings about a three dimensional network. So, when you have that this set of complexation in three dimensional picture, once you start heating it all these organics will start leaving away. And therefore, you are essentially leaving a metal oxygen network, which is more reactive to form the corresponding oxide. So, that is the philosophy of using citrate legend, because the binding capacity is very high, and therefore you can build a three dimensional network of this complexes.

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SPINEL OXIDES

Gamma Fe_2O_3

Another example is Spinel oxides, that is gamma Fe2O3, which is a very popular oxide, and usually it is reddish brown in colour. And gamma Fe2O3 is magnetic although another phase is also magnetic that is magnetite phase that is Fe3O4, gamma iron oxide is particularly important for recording purposes. As you would see here making this sort of needle shape or acicular shaped, iron oxide is very, very difficult. Therefore, if you are successful then this can find applications in magnetic recording industry.

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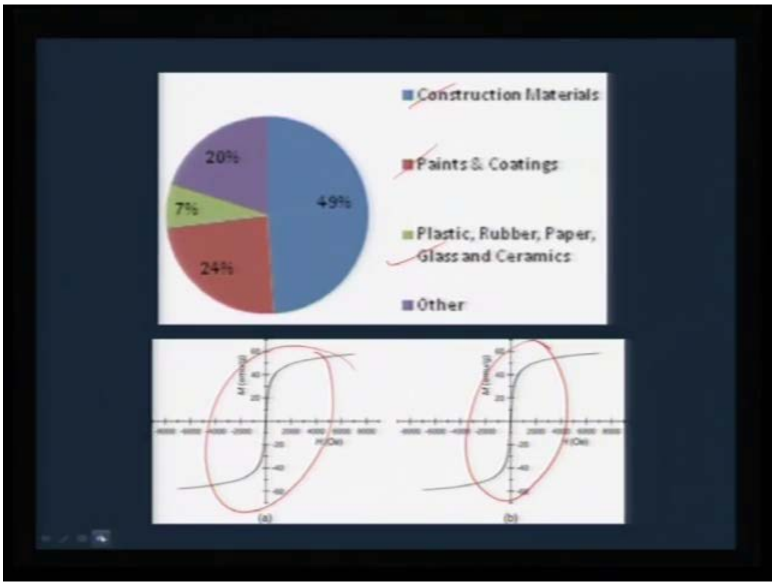

There are other applications of iron oxide apart from the magnetism that it holds, it is used in several industries mostly as pigment also.

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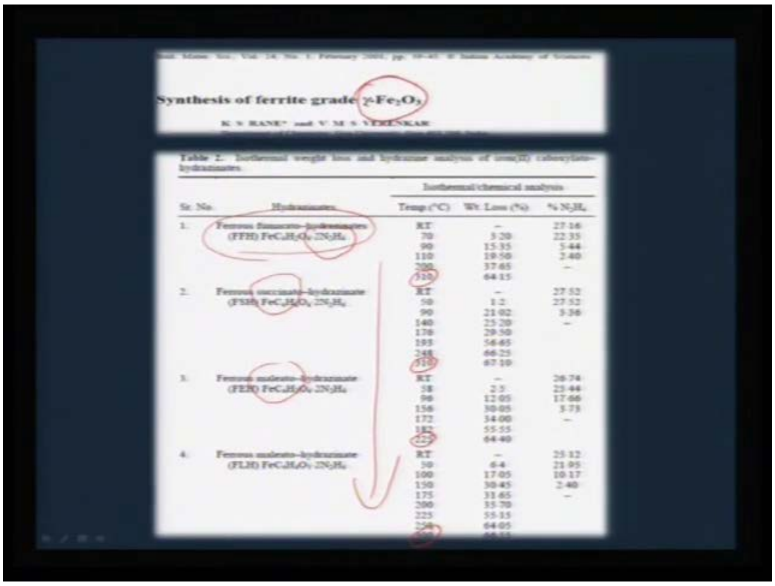

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Synthesis of ferrite grade γ-Fe_2O_3

K S RANE* and V M S VERENKAR

Table 2. Isothermal weight loss and hydrazine analysis of iron(II) carboxylato-hydrazinates.

		Isothermal/chemical analysis		
Sr. No.	Hydrazinates	Temp (°C)	Wt. Loss (%)	% N_2H_4
1.	Ferrous fumarato–hydrazinates (FFH) $FeC_4H_2O_4 \cdot 2N_2H_4$	RT	–	27.16
		70	3.20	22.35
		90	15.35	5.44
		110	19.50	2.40
		200	37.65	–
		310	64.15	
2.	Ferrous succinato–hydrazinate (FSH) $FeC_4H_4O_4 \cdot 2N_2H_4$	RT	–	27.52
		50	1.2	27.52
		90	21.02	3.36
		140	25.20	–
		170	29.50	
		195	56.65	
		248	66.25	
		310	67.10	
3.	Ferrous maleato–hydrazinate (FEH) $FeC_4H_2O_4 \cdot 2N_2H_4$	RT	–	26.74
		58	2.5	25.44
		90	12.05	17.66
		156	30.05	3.73
		172	34.00	–
		182	55.55	
		225	64.40	
4.	Ferrous malonato–hydrazinate (FLH) $FeC_3H_2O_4 \cdot 2N_2H_4$	RT	–	25.12
		50	6.4	21.95
		100	17.05	10.17
		150	30.45	2.40
		175	31.65	–
		200	35.70	
		225	55.15	
		250	64.05	

But, I will just highlight, how simple precursor route can be used for making this compounds for example, a series of compounds have been reported by varnekar group. And this one is Ferrous fumarate hydrocenate, in other words use fumaric acid and make complex which will readily form and you can remove the water of crystallization with hydrazine of crystallization, and that is what you call it as ferrous fumarate hydrocenate. And similarly you can use succinic acid or maleic acid, and you can form a series of hydracine precursors.

What is the use these precursors as you would see here, the final decomposition temperature is somewhere around 300 that means, you can make all this iron oxide precursor below 300. And when you do that, the best part is you can stabilize gamma iron oxide, and gamma iron oxide incidentally is a low temperature phase, and it is a ferromagnetic phase. When you try to heat this iron oxide to very high temperature, you lose the magnetism, therefore gamma iron oxide transforms into a alpha phase and as a result you lose the magnetic property. So, to stabilize this gamma iron oxide you need a chemical route, which will stabilize only the low temperature phase.

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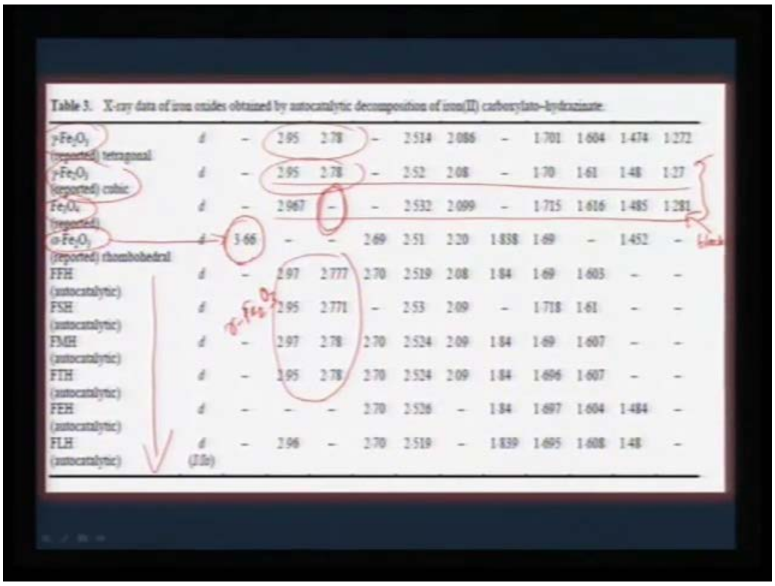

Table 3. X-ray data of iron oxides obtained by autocatalytic decomposition of iron(II) carboxylato-hydrazinate

γ-Fe$_2$O$_3$ (reported) tetragonal	d	–	2·95	2·78	–	2·514	2·086	–	1·701	1·604	1·474	1·272
γ-Fe$_2$O$_3$ (reported) cubic	d	–	2·95	2·78	–	2·52	2·08	–	1·70	1·61	1·48	1·27
Fe$_3$O$_4$ (reported)	d	–	2·967	–	–	2·532	2·099	–	1·715	1·616	1·485	1·281
α-Fe$_2$O$_3$ (reported) rhombohedral	d	3·66	–	–	2·69	2·51	2·20	1·838	1·69	–	1·452	–
FFH (autocatalytic)	d	–	2·97	2·777	2·70	2·519	2·08	1·84	1·69	1·603	–	–
FSH (autocatalytic)	d	–	2·95	2·771	–	2·53	2·09	–	1·718	1·61	–	–
FMH (autocatalytic)	d	–	2·97	2·78	2·70	2·524	2·09	1·84	1·69	1·607	–	–
FTH (autocatalytic)	d	–	2·95	2·78	2·70	2·524	2·09	1·84	1·696	1·607	–	–
FEH (autocatalytic)	d	–	–	–	2·70	2·526	–	1·84	1·697	1·604	1·484	–
FLH (autocatalytic)	d (Å)	–	2·96	–	2·70	2·519	–	1·839	1·695	1·608	1·48	–

γ-Fe$_2$O$_3$

black

As you see here gamma iron oxide the reported value is very peculiar, where you get 2 X-ray diffraction peaks at 2.95 and 2.78. It can also be in cubic phase, where it is again 2.95 and 2.78, but closely related iron oxide peak is nothing but Fe3O4, but Fe3O4 almost has the same reflection as that of gamma Fe2O3. Only thing one peak would miss here and this is the only peak that distinguishes between Fe3O4, and gamma Fe2O3, why it is important, because both are magnetic, however Fe3O4 is actually a black compound.

So, it is easy for us to guess, whether it is a Fe3O4 or Fe2O3, but X-ray can be very deceptive, therefore the only clue that you get here is this one. So, knowing this particular phase, if you follow all the precursors, fumaric, succinate or maleic based precursors, you would see here almost all the precursors are showing only selectively gamma Fe2O3 phase. So, this is a very highly selective precursor that can be used for stabilizing, only the low temperature phase.

If you need high temperature phase, then you need to use a different precursor altogether, one more thing we need to understand, if you are transforming this to a very high temperature, then you are actually going to lose the property, and alpha Fe2O3 will come. And the best way to distinguish alpha Fe2O3 is you will get a peak at 3.666, so once that, then you can understand that part of your gamma Fe2O3 has transformed into alpha. So, here is an example, where we see a phase can be stabilized only at low temperature, and for which you need to take a corresponding precursor. All precursors does not necessarily give the high temperature phase, so you need to have a mechanism by which you can control the exothermicity.

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PEROVSKITES

Another example of perovskite compound, as you see here is a metal ion, which is actually in the A site, and another metal ion is there B these are the dark blue ones, which are nothing but your B cation, and these are your oxygens in the corners of the octahedral. So, making this compound again is a big challenge, I will just leave one example to show, how simple precursor can be used.

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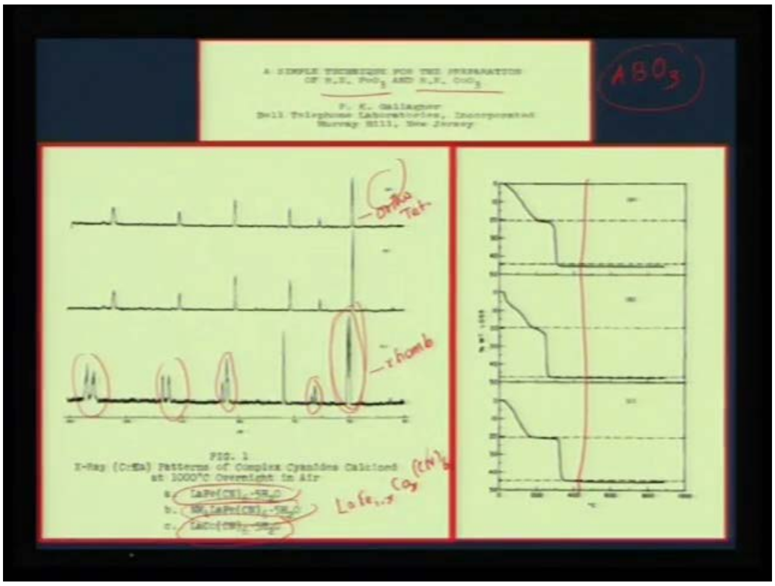

A SIMPLE TECHNIQUE FOR THE PREPARATION
OF R.E. FeO_3 AND R.E. CoO_3

P. K. Gallagher
Bell Telephone Laboratories, Incorporated
Murray Hill, New Jersey

FIG. 1
X-Ray (CrKα) Patterns of Complex Cyanides Calcined at 1000°C Overnight in Air

a. $LaFe(CN)_6 \cdot 5H_2O$
b. $NH_4LaFe(CN)_6 \cdot 5H_2O$
c. $LaCo(CN)_6 \cdot 5H_2O$

This is a very old paper published in 70's by Bell labs by Gallo gate, I presume that he passed away in the last decade, but one of the finest material scientist, who really worked on a variety of metal oxides systems. One of his paper shows how we can make rare earth ferrites and rare earth cobalt tests, both have A B O 3 sort of structure, and as you would see here they have used cyanide precursors.

Take for example, case a is here and this is lanthanum iron, hexazinone precursors and this precursor seemingly has a correlation to lanthanum covered it, because they almost are X-ray similar. Only thing the major peaks in this case, in the case of cobalt is split almost all the peaks that you see is split, therefore what you assume there is from orthorhombic, it is getting transformed to rhombohedra. If you have 200 percent peak, which is your largest peak, that is usually resembling a rhombohedral, whereas this is your orthorhombic or tetragonal symmetry.

So, you can index this, but what you see here in all this cases, you can get a X-ray isomorphous pattern, therefore you can even make changes between La Fe 1 minus x cobalt x C n 6. This sort of mixtures can also be made, because you have X-ray similarity, nevertheless the point I want to make here is even cyanide based precursors can become useful. As you would see here that the decomposition is almost over well below 400 degree C, and there are no reports where you can find making A B O 3 structures with such fairly low temperatures. So, low temperature process gives you advantage to get finely reactive powders, which can be cindered to theoretical density. So, that is the advantage of using low temperature precursors to get these oxides.

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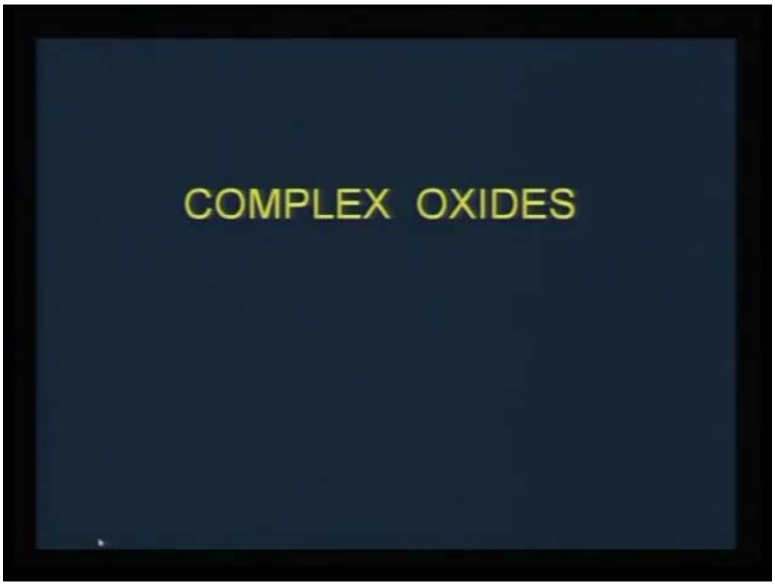

COMPLEX OXIDES

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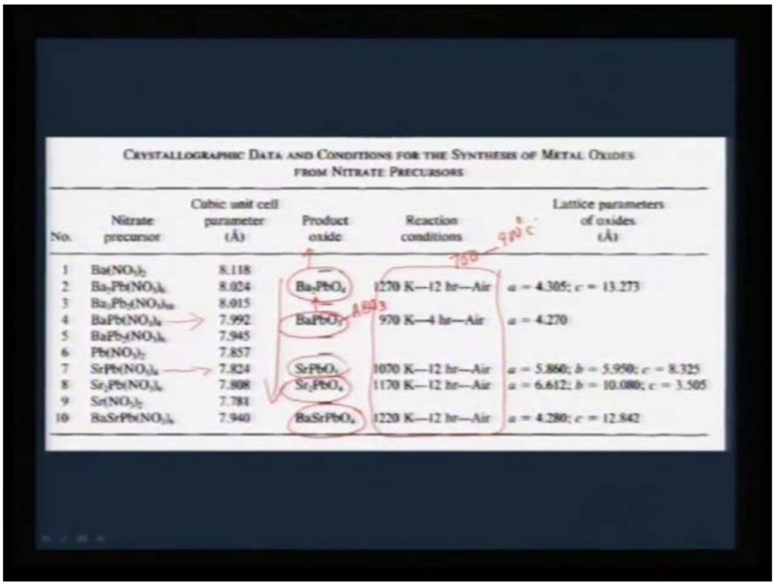

CRYSTALLOGRAPHIC DATA AND CONDITIONS FOR THE SYNTHESIS OF METAL OXIDES FROM NITRATE PRECURSORS

No.	Nitrate precursor	Cubic unit cell parameter (Å)	Product oxide	Reaction conditions	Lattice parameters of oxides (Å)
1	$Ba(NO_3)_2$	8.118	—		
2	$Ba_2Pb(NO_3)_6$	8.024	Ba_2PbO_4	1270 K—12 hr—Air	$a = 4.305$; $c = 13.273$
3	$Ba_3Pb_2(NO_3)_{10}$	8.015	—		
4	$BaPb(NO_3)_4$	7.992	$BaPbO_3$	970 K—4 hr—Air	$a = 4.270$
5	$BaPb_2(NO_3)_6$	7.945	—		
6	$Pb(NO_3)_2$	7.857	—		
7	$SrPb(NO_3)_4$	7.824	$SrPbO_3$	1070 K—12 hr—Air	$a = 5.860$; $b = 5.950$; $c = 8.325$
8	$Sr_2Pb(NO_3)_6$	7.808	Sr_2PbO_4	1170 K—12 hr—Air	$a = 6.612$; $b = 10.080$; $c = 3.505$
9	$Sr(NO_3)_2$	7.781			
10	$BaSrPb(NO_3)_6$	7.940	$BaSrPbO_4$	1220 K—12 hr—Air	$a = 4.280$; $c = 12.842$

Some more examples on complex oxides. And I will give you some example of how nitrates or hydroxides can be used as a precursor, for example you take the case of barium BaPbO3 this is nothing but the A B O 3 type of oxide, and we can actually build upon this using a Ruddlesden and popper series. Ruddlesden and popper series says that, with every addition of another barium you go from BaPbO3 to Ba2PbO4 and we can further keep going adding stackings of the a side cation based oxides as inter layers.

So, we can build on this sort of systems for example, strontium lead oxide, then you can go for another homologous series that is Sr2PbO4 and so on. Now, if we know this X-ray similarity of this precursors, then you can even make a mixed metal precursor for example, if you look at BaPbO3, this is your nitrate precursor which is 7.91 and strontium is 7.824. So, they are having close structural dimension as a result, we can use this as a precursor for making the compounds.

Only thing is when you use simple precursor, sometimes you may not be able to bring down the calcinations temperature in that case, you have to go for very high temperatures. As you see in this case you have to play around between 700 to 900 degree C, to achieve, this the perovskite compounds.

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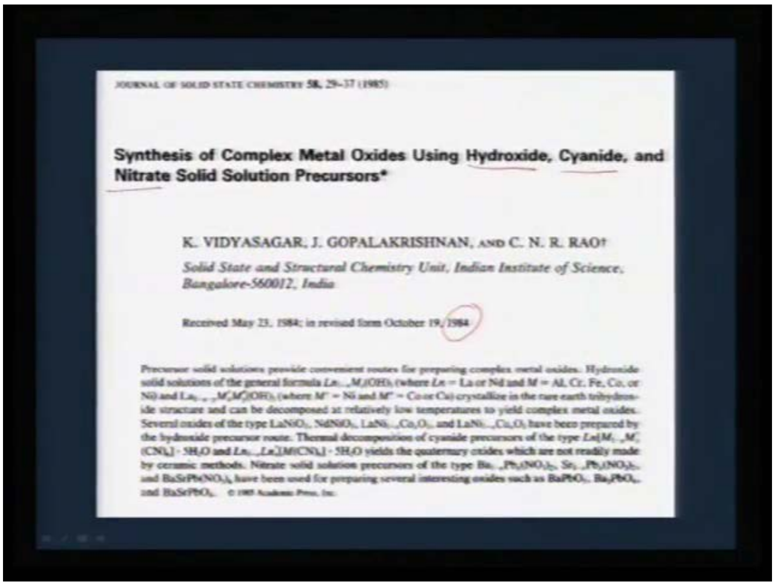

JOURNAL OF SOLID STATE CHEMISTRY 58, 29–37 (1985)

Synthesis of Complex Metal Oxides Using Hydroxide, Cyanide, and Nitrate Solid Solution Precursors*

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Received May 23, 1984; in revised form October 19, 1984

Vidyasagar and co-workers as earliest 84, they have use hydroxides, cyanides and nitrates as precursors to prepare complex metal oxides, I will give you some more example on that.

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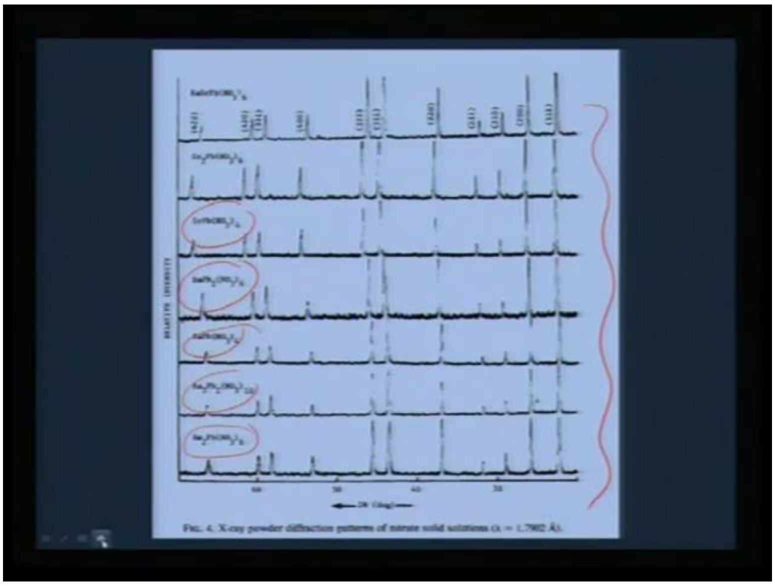

FIG. 4. X-ray powder diffraction patterns of nitrate solid solutions (λ = 1.7902 Å).

For instance, if you look at lanthanum hydroxide, a lanthanum hydroxide and lanthanum aluminium hydroxide both are showing same X-ray isomorphous nature, and as a result you can try to make lanthanum aluminates. Similarly, lanthanum nickel hydroxide, lanthanum cobalt hydroxide, they all seem to have the same crystal symmetry.

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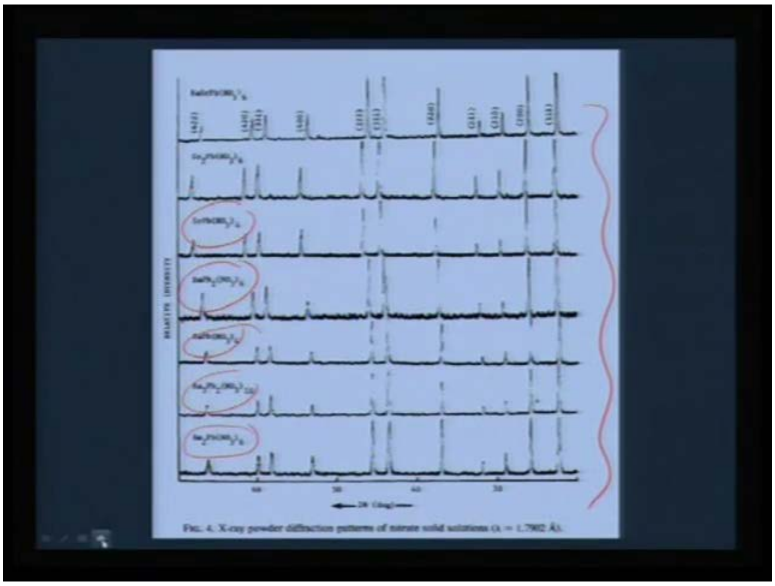

FIG. 4. X-ray powder diffraction patterns of nitrate solid solutions (λ = 1.7902 Å).

And this can be usefully transformed into the corresponding perovskites, and here again as I show to you in the view graph of this X-ray datas. You can see the nitrate precursors all having same X-ay morphology, and as a result a variety of solid solutions can be made mixed metal oxides.

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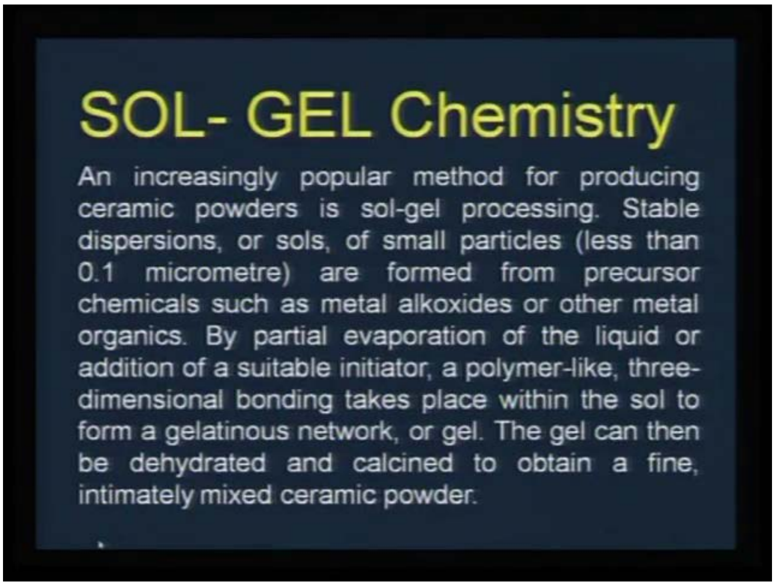

SOL- GEL Chemistry

An increasingly popular method for producing ceramic powders is sol-gel processing. Stable dispersions, or sols, of small particles (less than 0.1 micrometre) are formed from precursor chemicals such as metal alkoxides or other metal organics. By partial evaporation of the liquid or addition of a suitable initiator, a polymer-like, three-dimensional bonding takes place within the sol to form a gelatinous network, or gel. The gel can then be dehydrated and calcined to obtain a fine, intimately mixed ceramic powder.

I will come to the last example that of sol-gel chemistry, of all the precursors sol-gel chemistry is still thriving mainly because although the cost and the stringent requirements for sol-gel processing is not that simple. And it often involves expensive starting materials, yet sol-gel precursors give a lot of advantage. What is the advantage number 1, it can be used for not just making metal powders, but it can be used for making metal oxide films also.

So, the same precursor in solution form can be decomposed to get powders or it can be decomposed to make films, therefore in thin film approach, one of the very well studied method from chemical processing is sol-gel method. Therefore, it is better to understand little bit on how the sol-gel processing works, let look at the definition of what it is, an increasingly popular method for producing ceramic powders is sol-gel processing. Stable dispersions or sols of small particles are formed from precursor chemicals, such as metal alkoxides or other metal organics.

By partial evaporation of the liquid or addition of a suitable initiator, a polymer like three dimensional bonding takes place, within the sol to form a gelatinous network or gel; and the gel can be dehydrated and calcined to get intimately mixed ceramic powder. So, this is nearly a three step process, where you have sol, formation, then you gel it and the gel builds up a three dimension network, on decomposition gives a metal oxide.

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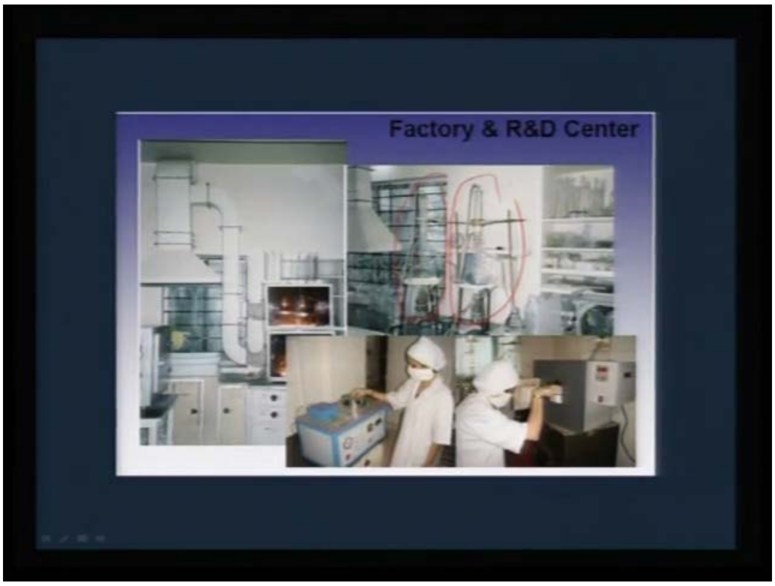

Factory & R&D Center

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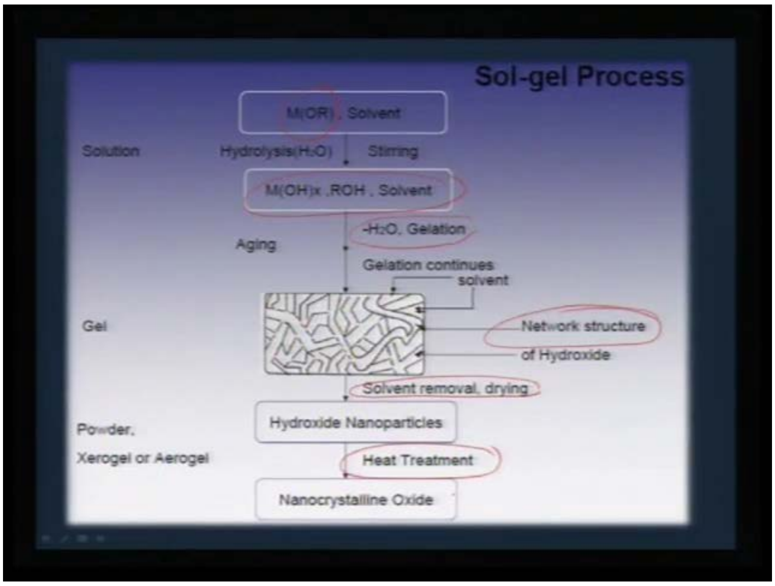

Sol-gel Process

M(OR) , Solvent

Solution

Hydrolysis(H_2O) Stirring

M(OH)x ,ROH , Solvent

Aging

$-H_2O$, Gelation

Gelation continues

solvent

Gel

Network structure of Hydroxide

Solvent removal, drying

Powder, Xerogel or Aerogel

Hydroxide Nanoparticles

Heat Treatment

Nanocrystalline Oxide

Sol-gel a route usually can be scalable, we can go for bulk quantities as well as this particular cartoon shows, how even in a factory or R and D centre you can do this scale up. And as you see here these are all the set up for sol-gel process, and it is possible for us to get even kilogram quantities, so large scale process, but it can be translated into industrial scalable process.

The step that is involved in sol-gel processing, as I told you it is as three step process, first is taking the corresponding metal oxide in a solvent, and hydrolyzing this metal alkoxide to get metal hydroxide. And this metal hydroxide actually is will be a gelatinous precipitate, which has to be gelated, which means by careful removing of this water molecules, it is possible for us to gel it. And this gelation sometimes can take even days, and therefore you got to be very patient with this gelation process.

And when the gelation occurs there is a network that is getting found, which is usually a three dimensional network; and on carefully removing the solvent, then you can actually get the hydroxide particles and heating that further, you will get nanocrystalline oxides. So, if you are looking for very finely divided oxides and of controlled morphology, then sol-gel process is a very good approach. In the next few slides we will see some examples of how we can make such sol-gel derived powders and films.

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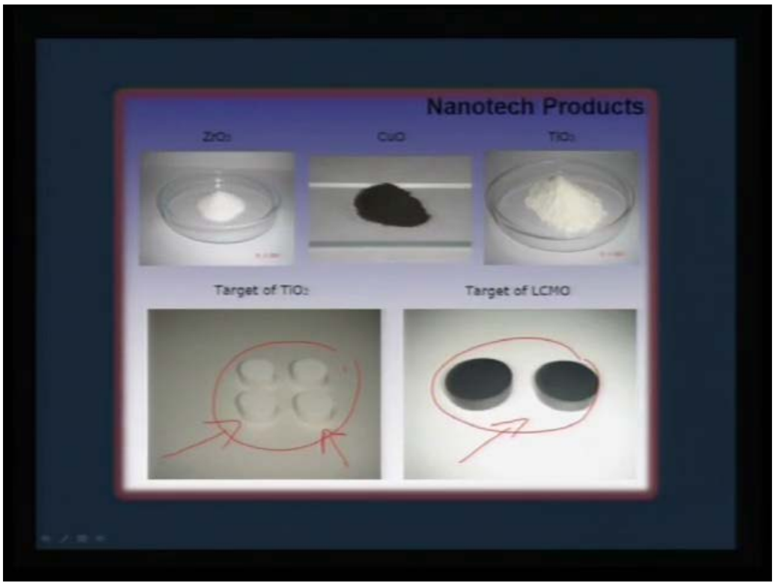

Nanotech Products

ZrO_2

CuO

TiO_2

Target of TiO_2

Target of LCMO

So, in the next slide we see, several products can be made metal oxides like zirconium, copper oxide, titanium and as you see here a range of compounds can be made. And one of the specialities of this compound is, compounds are you can actually control the size such a way, to make circular disc for other applications can also be worked out.

Therefore, it is very important when we try to transcend from a powder to other forms, we need to know, whether we have a finer control on the size dispersion.

One of the chief advantage of sol-gel process is you can control the size so much, so that they will be nearly mono size and as a result centring of this of compounds to make as disc for other applications becomes very useful. In the other precursor cases, sometimes the size distribution of the metal oxide particles are very, very less, and as a result it is not easy to make such compacts. And therefore, sol-gel is still being used in industries to make targets, these are targets could be used for sputtering or for pulsed laser deposition, or for MBE sort of applications. And sol-gel is still considered to be the most popular method by which mono sized oxide particles can be made, so with this reference to it is application.

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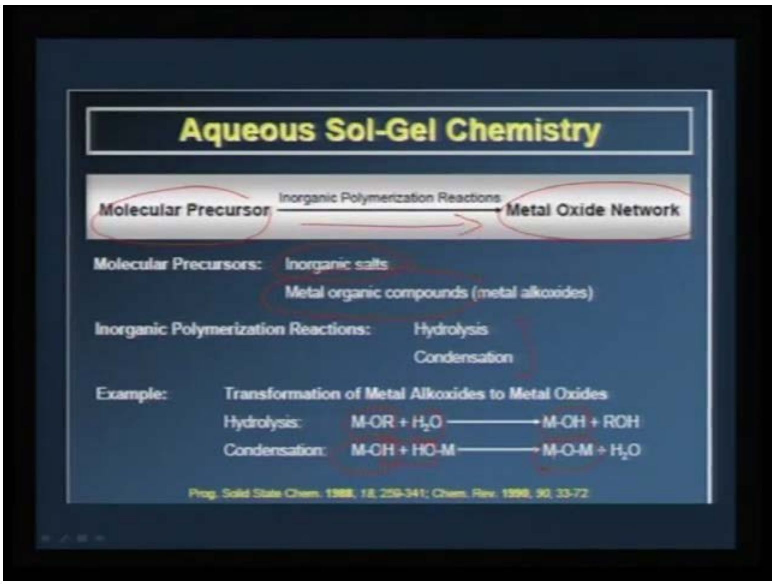

Aqueous Sol-Gel Chemistry

Molecular Precursor $\xrightarrow{\text{Inorganic Polymerization Reactions}}$ Metal Oxide Network

Molecular Precursors: Inorganic salts
Metal organic compounds (metal alkoxides)

Inorganic Polymerization Reactions: Hydrolysis
Condensation

Example: Transformation of Metal Alkoxides to Metal Oxides

Hydrolysis: $M\text{-}OR + H_2O \longrightarrow M\text{-}OH + ROH$

Condensation: $M\text{-}OH + HO\text{-}M \longrightarrow M\text{-}O\text{-}M + H_2O$

Prog. Solid State Chem. 1988, 18, 259-341; Chem. Rev. 1990, 90, 33-72

Let us see some examples of nonaqueous routes to metal oxide nanoparticles, using sol-gel why we are talking about nonaqueous, because once you do it in solution route, which involves water. Then sometimes the end product can have influence, because of the water content, therefore if we can totally make it organic it is much more a refined technique than using aqueous route to get these powders.

So, aqueous sol-gel chemistry is usually making a molecular precursor, and then you try to use reagents to polymerize it and then get the metal oxide network. And molecular precursors are mainly metal organic compounds or they are inorganic salts, and a polymerization as I told you in the previous slide it involves two main process, one is hydrolysis and the other one is condensation process. Examples of hydrolysis, you take alkoxide and you hydrolyse you get metal hydroxide, metal hydroxide and condensation actually it involves a elimination of a water molecule, therefore you will get metal oxygen framework and that you can build it for making it into a bulk form.

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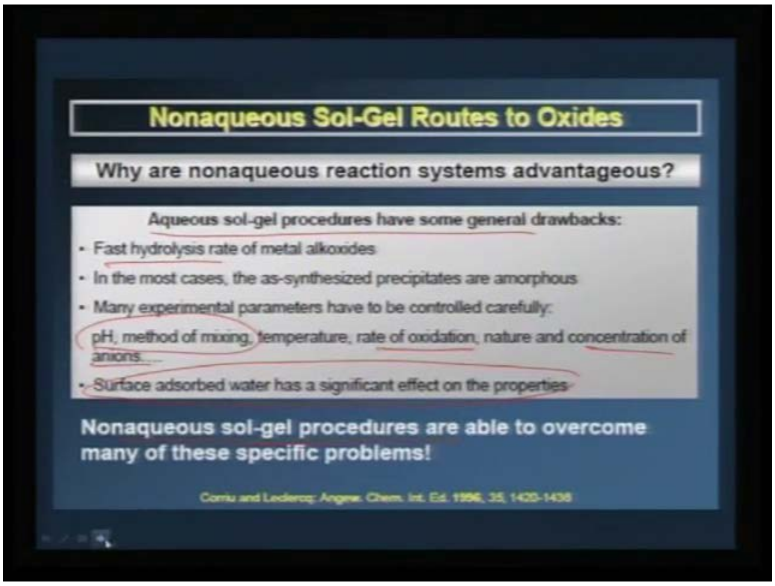

Nonaqueous Sol-Gel Routes to Oxides

Why are nonaqueous reaction systems advantageous?

Aqueous sol-gel procedures have some general drawbacks:

- Fast hydrolysis rate of metal alkoxides
- In the most cases, the as-synthesized precipitates are amorphous
- Many experimental parameters have to be controlled carefully:
  pH, method of mixing, temperature, rate of oxidation, nature and concentration of anions....
- Surface adsorbed water has a significant effect on the properties

Nonaqueous sol-gel procedures are able to overcome many of these specific problems!

Corriu and Leclercq; Angew. Chem. Int. Ed. 1996, 35, 1420-1436

Why nonaqueous reagents are reaction is advantageous, because in the case of aqueous sol-gel procedures you have problem with fast hydrolysis and sometimes, they are very much dependent on pH and the rate of oxidation concentration of anions, all this matters in aqueous chemistry. Therefore, if we use a nonaqueous method for sol-gel preparation, it will be much more viable and last of it as I mentioned to you earlier, surface absorbed water has a significant role on the oxide properties. Therefore it is better to deal with the nonaqueous protocol, nonaqueous sol-gel procedures, they can actually overcome several of this disadvantages.

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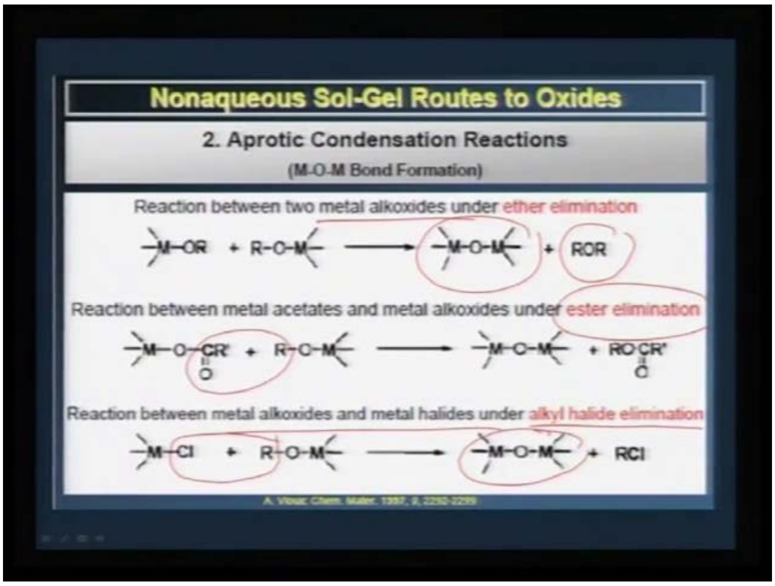

Nonaqueous Sol-Gel Routes to Oxides

2. Aprotic Condensation Reactions

(M-O-M Bond Formation)

Reaction between two metal alkoxides under ether elimination

$\equiv M-OR + R-O-M\equiv \longrightarrow \equiv M-O-M\equiv + ROR$

Reaction between metal acetates and metal alkoxides under ester elimination

$\equiv M-O-C(=O)R' + R-O-M\equiv \longrightarrow \equiv M-O-M\equiv + ROC(=O)R'$

Reaction between metal alkoxides and metal halides under alkyl halide elimination

$\equiv M-Cl + R-O-M\equiv \longrightarrow \equiv M-O-M\equiv + RCl$

A. Vioux Chem. Mater. 1997, 9, 2292-2299

For example, what set of techniques can be used or combinations we can use, we can actually use a metal alkoxide and think of a ether elimination, if we can do a ether elimination then we can build a metal oxygen framework. Or we can try to look for a ester elimination and in such a case, you can actually get a metal oxygen framework of this kind; or we can go for metal oxide and metal halide under alkyl halide elimination. So, we can try to distinctly eliminate this, I can get the metal oxygen framework. So, without water, without hydrolysis step, we can go for these elimination reactions, and we can still bring about the same final product.

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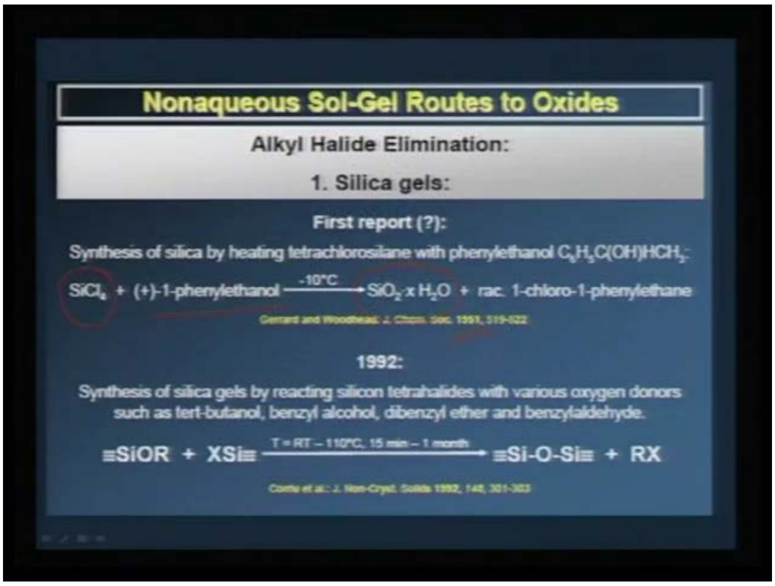

Nonaqueous Sol-Gel Routes to Oxides

Alkyl Halide Elimination:

1. Silica gels:

First report (?):

Synthesis of silica by heating tetrachlorosilane with phenylethanol $C_6H_5C(OH)HCH_3$:

$SiCl_4$ + (+)-1-phenylethanol $\xrightarrow{-10°C}$ $SiO_2 \cdot x\,H_2O$ + rac. 1-chloro-1-phenylethane

Gerrard and Woodhead: J. Chem. Soc. 1951, 519-522

1992:

Synthesis of silica gels by reacting silicon tetrahalides with various oxygen donors such as tert-butanol, benzyl alcohol, dibenzyl ether and benzylaldehyde.

$\equiv SiOR + XSi\equiv \xrightarrow{T = RT - 110°C,\ 15\ min - 1\ month} \equiv Si-O-Si\equiv + RX$

Corriu et al.: J. Non-Cryst. Solids 1992, 146, 301-303

A alkyl halide was actually reported very early as 1951, and where they have used silicon tetra chloride, and a treated with phenylethanol, you can get the silica framework. This was one of the best examples of sol-gel process, which was reported and this was picked up in late 70's and 80's, sol-gel became a very good method for making metal oxygen framework, or porous metal oxides.

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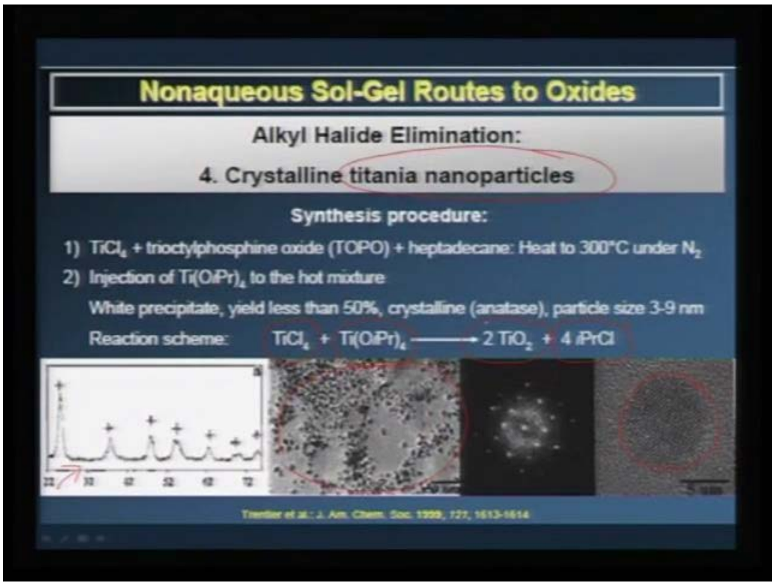

Nonaqueous Sol-Gel Routes to Oxides

Alkyl Halide Elimination:

4. Crystalline titania nanoparticles

Synthesis procedure:

1) $TiCl_4$ + trioctylphosphine oxide (TOPO) + heptadecane: Heat to 300°C under N_2
2) Injection of $Ti(OiPr)_4$ to the hot mixture

White precipitate, yield less than 50%, crystalline (anatase), particle size 3-9 nm

Reaction scheme: $TiCl_4 + Ti(OiPr)_4 \longrightarrow 2\,TiO_2 + 4\,iPrCl$

Trentler et al.: J. Am. Chem. Soc. 1999, 121, 1613-1614

This was the first report of a silica gel formation and then we can actually think of making several nano particles with different approaches, one is titania nanoparticles, as you would see here the nanoparticles are nearly mono disperse and of very very fine structure. And you can also see the lattice fringes of each titania particle, and the broadening of this X-ray clearly shows that they are nano sized in nature.

How do we do that, take titanium chloride it is very important, these are a very reactive, therefore it has to be done in inert atmosphere. If you just expose titanium chloride in air, it will immediately convert into titania sol. So, titanium tetrachloride and titanium propoxide if you try to do that, then you can get a alkyl halide elimination all you get straight away is titania, and those are very finely divided. So, this is one way that we can prepare a titania nanoparticle using a non-aqueous sol-gel route.

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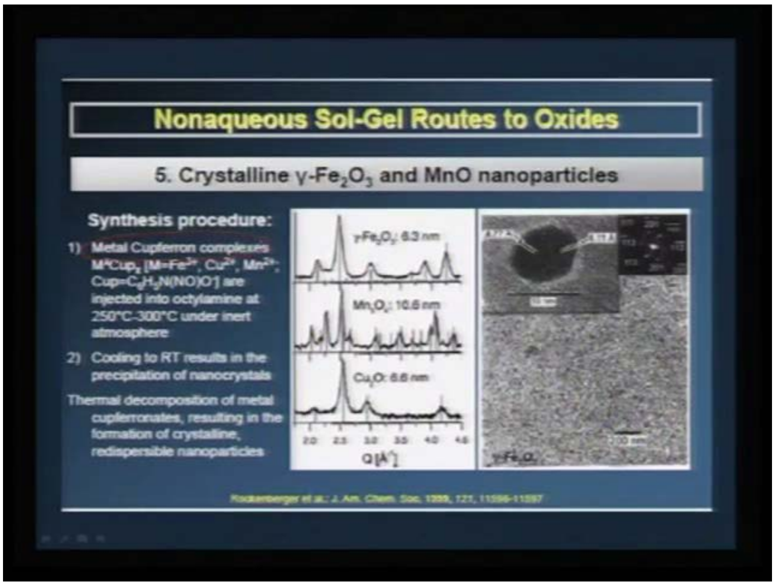

Nonaqueous Sol-Gel Routes to Oxides

5. Crystalline γ-Fe_2O_3 and MnO nanoparticles

Synthesis procedure:

1) Metal Cupferron complexes M^xCup_x [$M = Fe^{3+}$, Cu^{2+}, Mn^{2+}; $Cup = C_6H_5N(NO)O^-$] are injected into octylamine at 250°C-300°C under inert atmosphere
2) Cooling to RT results in the precipitation of nanocrystals

Thermal decomposition of metal cupferronates, resulting in the formation of crystalline, redispersible nanoparticles

Rockenberger et al.: J. Am. Chem. Soc. 1999, 121, 11595-11597

Similarly, we can actually take other organic compounds like metal cupferron complexes of iron, copper and manganese and then try to do a sol-gel approach. You can see here cuprous oxides can be made manganese Mn3O4 gamma Fe2O3 all these can be made, but in this case we are not actually using R O H. So, sol-gel method does not necessarily demand a metal alkoxide, you can also start with any other organic precursor.

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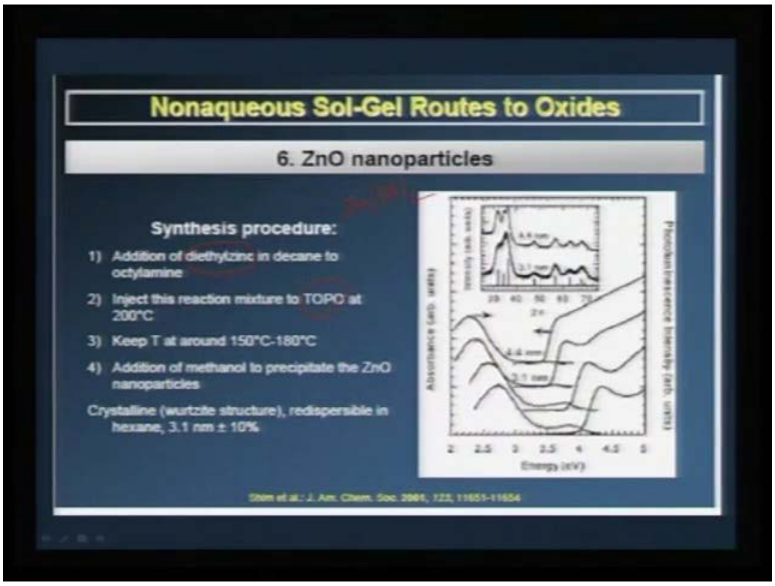

Nonaqueous Sol-Gel Routes to Oxides

6. ZnO nanoparticles

Synthesis procedure:

1) Addition of diethylzinc in decane to octylamine
2) Inject this reaction mixture to TOPO at 200°C
3) Keep T at around 150°C-180°C
4) Addition of methanol to precipitate the ZnO nanoparticles

Crystalline (wurtzite structure), redispersible in hexane, 3.1 nm ± 10%

Shim et al.: J. Am. Chem. Soc. 2001, 123, 11651-11654

Zinc oxide nanoparticles can also be made using sol-gel route, and in this case you can actually take diethylzinc, this is Zn Et twice and try to react it with the TOPO, which is a solvent. And then one can get zinc oxide nanoparticles with very good crystallinity, so this is another approach by which zinc oxide can be made.

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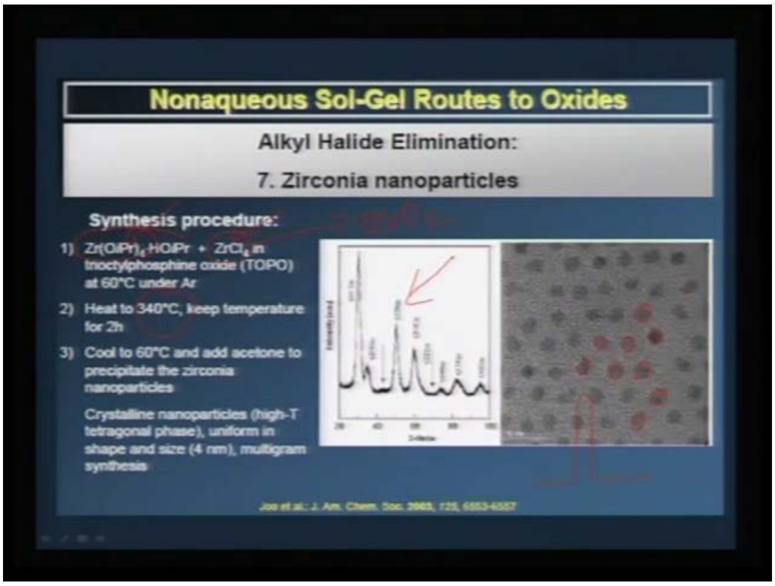

Nonaqueous Sol-Gel Routes to Oxides

Alkyl Halide Elimination:

7. Zirconia nanoparticles

Synthesis procedure:

1) $Zr(OiPr)_4 \cdot HOiPr$ + $ZrCl_4$ in trioctylphosphine oxide (TOPO) at 60°C under Ar
2) Heat to 340°C, keep temperature for 2h
3) Cool to 60°C and add acetone to precipitate the zirconia nanoparticles

Crystalline nanoparticles (high-T tetragonal phase), uniform in shape and size (4 nm), multigram synthesis

Joo et al.: J. Am. Chem. Soc. 2003, 125, 6553-6557

Again zirconia, this is a very useful high temperature material, how do we make zirconia, take zirconyl isopropoxide and zirconyl chloride, if we try to add this again you get the alkyl halide elimination, in the straight away you can make zirconia. As you would see here, each of this is a zirconium particle and they are almost mono size, so if you look at the histogram of this, you would see a very narrow distribution of the particle size. So, in a very selective way, with circular morphology you can get zirconia nanoparticles.

And not only that you, if you look carefully at the X-ray zirconia shows a cubic phase, it is very important to stabilize a cubic phase zirconia, under this conditions, therefore this is one of a very proven method by which you can make zirconia nanoparticles. But, the only thing the handling becomes a problem as I told you all these are very expensive precursors, but if you are looking for mono size dispersions, then you have to use a costly chemicals. So, that is the stringent requirement in sol-gel route again.

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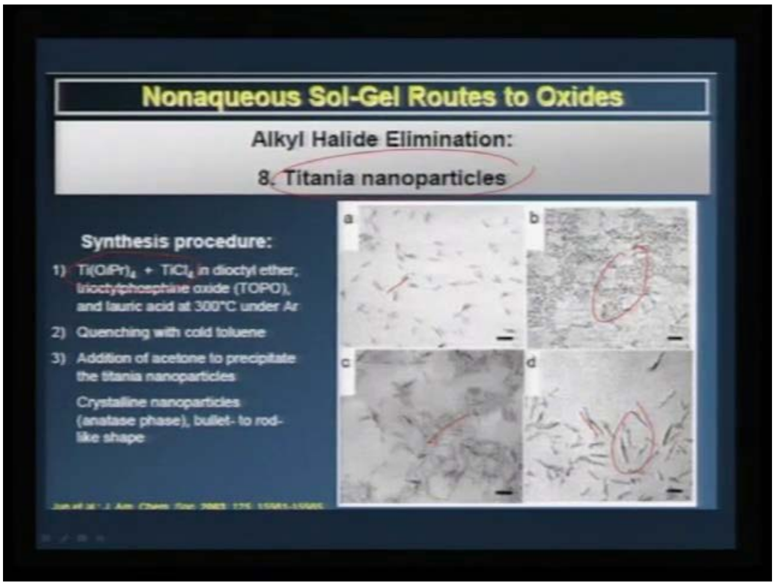

Nonaqueous Sol-Gel Routes to Oxides

Alkyl Halide Elimination:

8. Titania nanoparticles

Synthesis procedure:

1) $Ti(OiPr)_4$ + $TiCl_4$ in dioctyl ether, trioctylphosphine oxide (TOPO), and lauric acid at 300°C under Ar
2) Quenching with cold toluene
3) Addition of acetone to precipitate the titania nanoparticles

Crystalline nanoparticles (anatase phase), bullet- to rod-like shape

Jun et al.: J. Am. Chem. Soc. 2003, 125, 15981-15985

Again titania nanoparticles the methodology is the same, use titanium chloride and titanium isopropoxide, you can see the sort of rod shaped nanoparticles are formed. And these are actually formed with different temperature and gelation, the gelling time is accu pneumatic growth approach. And therefore, you can actually restrict the gel formation, over a period of time and depending on the gel formation, you can actually determine the length and breadth of your nano rods. Therefore, that this gel ageing is very important while you transform it into an oxide.

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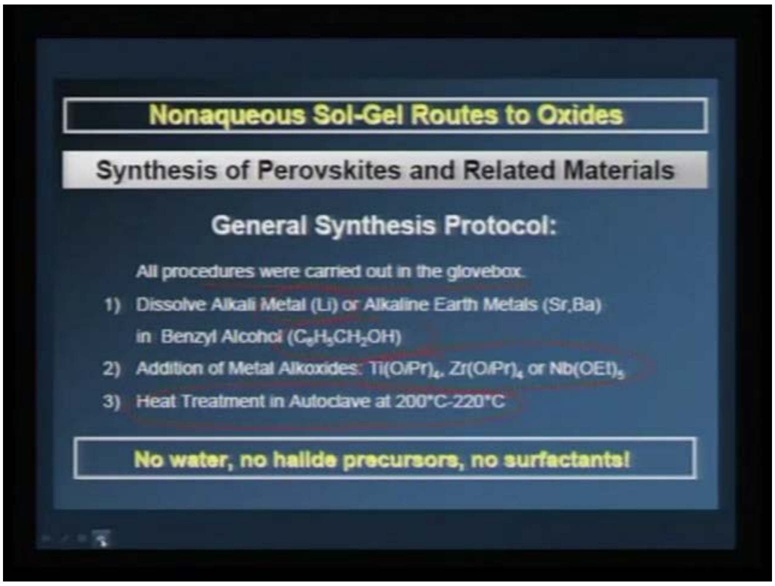

Nonaqueous Sol-Gel Routes to Oxides

Synthesis of Perovskites and Related Materials

General Synthesis Protocol:

All procedures were carried out in the glovebox

1) Dissolve Alkali Metal (Li) or Alkaline Earth Metals (Sr,Ba) in Benzyl Alcohol ($C_6H_5CH_2OH$)
2) Addition of Metal Alkoxides: $Ti(OiPr)_4$, $Zr(OiPr)_4$ or $Nb(OEt)_5$
3) Heat Treatment in Autoclave at 200°C-220°C

No water, no halide precursors, no surfactants!

So, synthesis of perovskites and related materials, in general the synthesis protocol is all procedures are to be carried out in glove box, so this is one stringent problem. And we can actually try to make other combinations, like making a lithium oxide or other perovskites, we can follow a general protocol, where we can mix metal with benzyl alcohol. And then react it with this sort of perovskites to get mixed metal oxides. And how do we do that, if we are wanting to control the size and shape of this crystals, general procedure that is suggested is to put it in a autoclave and heat it. I will show you one or two examples of how such mixed metal oxides can be made, specially for oxides like perovskites.

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Nonaqueous Sol-Gel Routes to Oxides

Typical Procedure: Synthesis of $BaTiO_3$

Take for example, barium, barium it is a metal and it is very, very reactive, therefore you need to keep it in a glove box and dissolve it with benzyl alcohol. And once you do that, then you can dissolve barium into benzyl alcohol as a clear solution and then you can mix it with titanium propoxide, all this has to be done inside the glove box. Otherwise, the exposure of barium to air it will catch fire, and titanium will go into TiO2 we have missed, therefore it has to be handled with care. And this is how it will look like, the barium dissolved in benzyl alcohol, initially it looks like this and then it dissolves into a clear solution. And this solution has to be mixed with titanium isopropoxide, and this is your autoclave and you can maintain this with a pre treatment at 200 degree C, you will get a white powder of barium titanet.

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Nonaqueous Sol-Gel Routes to Oxides

Dissolution of metallic Ba in Benzyl alcohol

Clear, transparent solution

$Ti(O\mathit{i}Pr)_4$

Heat treatment in the autoclave

White precipitation – Centrifugation and Washing: White powder

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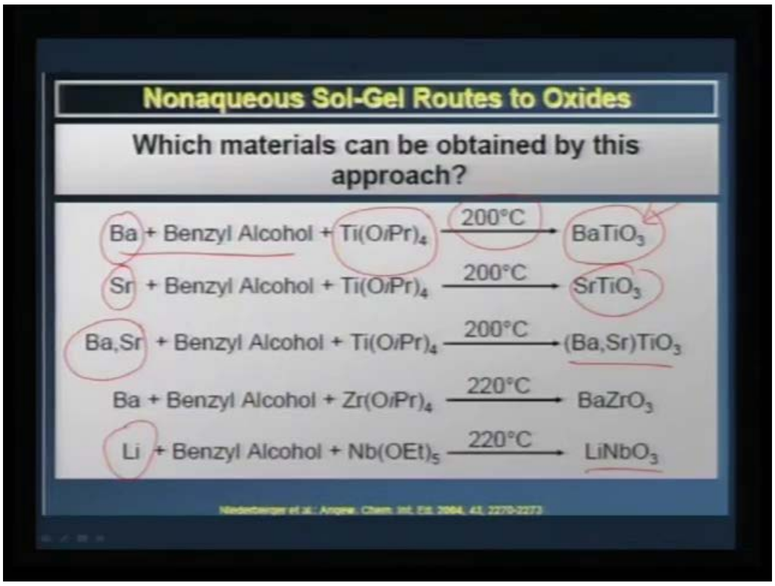

Nonaqueous Sol-Gel Routes to Oxides

Which materials can be obtained by this approach?

$$Ba + \text{Benzyl Alcohol} + Ti(O\mathit{i}Pr)_4 \xrightarrow{200°C} BaTiO_3$$

$$Sr + \text{Benzyl Alcohol} + Ti(O\mathit{i}Pr)_4 \xrightarrow{200°C} SrTiO_3$$

$$Ba,Sr + \text{Benzyl Alcohol} + Ti(O\mathit{i}Pr)_4 \xrightarrow{200°C} (Ba,Sr)TiO_3$$

$$Ba + \text{Benzyl Alcohol} + Zr(O\mathit{i}Pr)_4 \xrightarrow{220°C} BaZrO_3$$

$$Li + \text{Benzyl Alcohol} + Nb(OEt)_5 \xrightarrow{220°C} LiNbO_3$$

Niederberger et al.: Angew. Chem. Int. Ed. 2004, 43, 2270-2273

And this is the general protocol that is followed, so barium titanet if you want, start with barium metal mix it with benzyl alcohol and add it to titanium propoxide, heat it in a autoclave at 200 degree C you get barium titanet. But, the advantage of using this in a alcohol in a autoclave is that, you are not only not only generating a high pressure, but you are also lowering the temperature. So, at high pressure you are able to stabilize all this high temperature phases.

So, this is one way a modified high pressure route, I will talk to you about the hydrothermal process in the later lecturers. Similarly, if you want strontium titanet you have to start with strontium and barium strontium, mixed titanets you can do that and again lithium niobate, then you start with lithium; and you can try to take the corresponding alkoxide.

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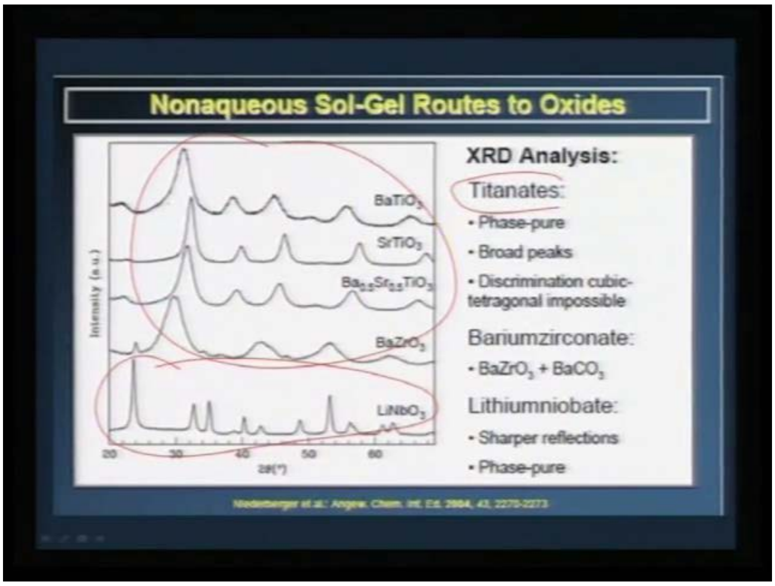

Nonaqueous Sol-Gel Routes to Oxides

XRD Analysis:

Titanates:

- Phase-pure
- Broad peaks
- Discrimination cubic-tetragonal impossible

Bariumzirconate:

- $BaZrO_3 + BaCO_3$

Lithiumniobate:

- Sharper reflections
- Phase-pure

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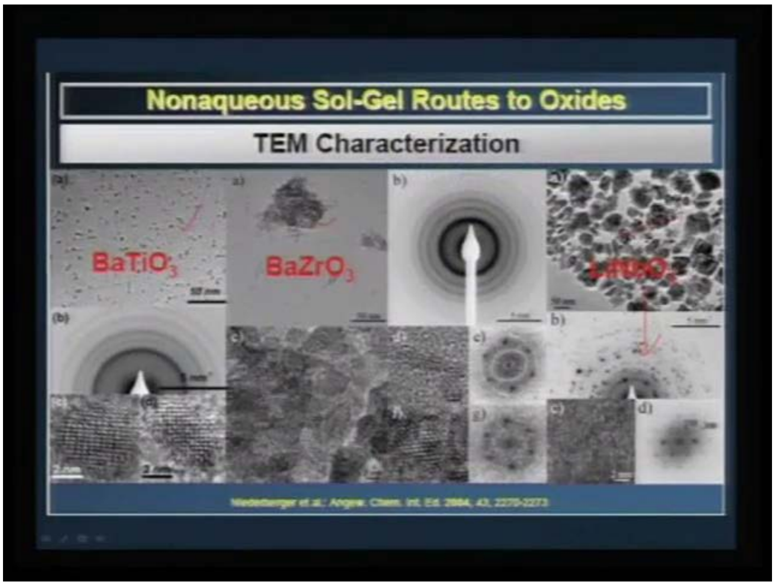

Nonaqueous Sol-Gel Routes to Oxides

TEM Characterization

Niederberger et al.: Angew. Chem. Int. Ed. 2004, 43, 2270-2273

So, this is one way you can try to make this compounds, as you would see here lithium niobate shows a very nice crystalline one. Whereas, in the case of titanets, these are phase pure, but the broadening, X-ray broadening shows that they are really in a nano size.

And these are all some of the view graphs that I wanted to show, just to say what sort of particles that we can get and whether, they are crystalline or this can be mapped with the TEM pictures. These are the TEM morphology of the particles. And in this case lithium niobate gives a polycrystalline ring pattern, whereas barium titanet gives a polycrystalline ring pattern. But, not with this dots, this shows that the order or the symmetries distorted little bit, whereas in this case you can see that the powders are nearly amorphous, they have just started crystallizing. So, all this informations you can get from the TEM picture.

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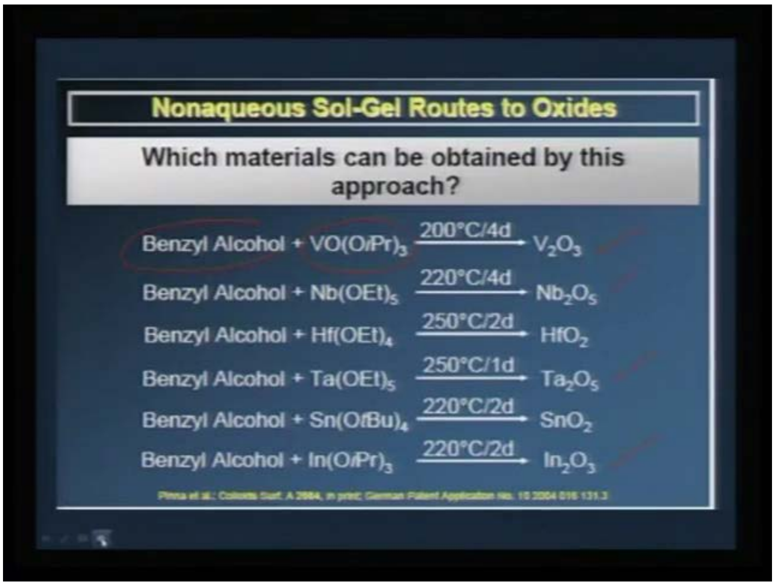

Nonaqueous Sol-Gel Routes to Oxides

Which materials can be obtained by this approach?

$$\text{Benzyl Alcohol} + \text{VO(O}i\text{Pr)}_3 \xrightarrow{200°\text{C}/4\text{d}} V_2O_3$$

$$\text{Benzyl Alcohol} + \text{Nb(OEt)}_5 \xrightarrow{220°\text{C}/4\text{d}} Nb_2O_5$$

$$\text{Benzyl Alcohol} + \text{Hf(OEt)}_4 \xrightarrow{250°\text{C}/2\text{d}} HfO_2$$

$$\text{Benzyl Alcohol} + \text{Ta(OEt)}_5 \xrightarrow{250°\text{C}/1\text{d}} Ta_2O_5$$

$$\text{Benzyl Alcohol} + \text{Sn(O}t\text{Bu)}_4 \xrightarrow{220°\text{C}/2\text{d}} SnO_2$$

$$\text{Benzyl Alcohol} + \text{In(O}i\text{Pr)}_3 \xrightarrow{220°\text{C}/2\text{d}} In_2O_3$$

And we can also make simple oxides, take benzyl alcohol and put vanadyl isopropoxide in a autoclave, then you can get vanadium oxide, niobium oxide, tantalum oxide, indium oxide, all this can be done with a precised control on the geometry, and shape of these particles. As you would see the X-rays are very clearly showing that, and you can also find out at low temperature when you heat these samples, they are amorphous in nature, but they crystallize when you take it to high temperature.

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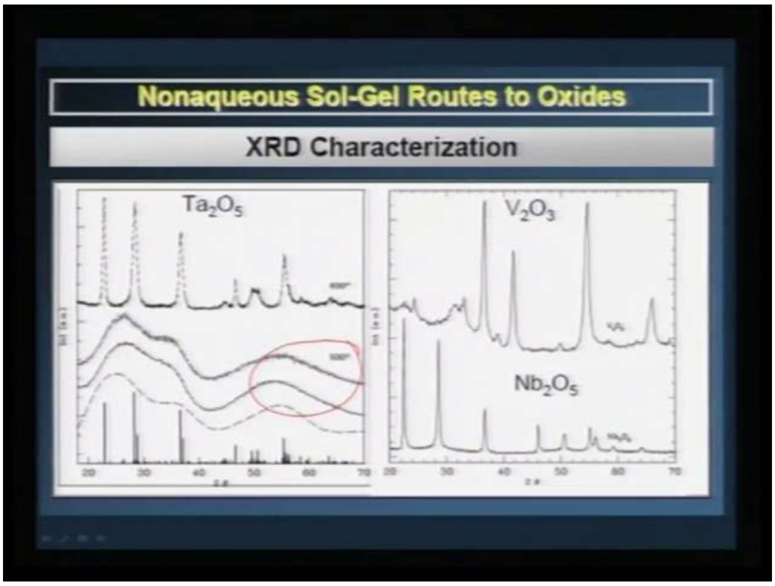

Nonaqueous Sol-Gel Routes to Oxides

XRD Characterization

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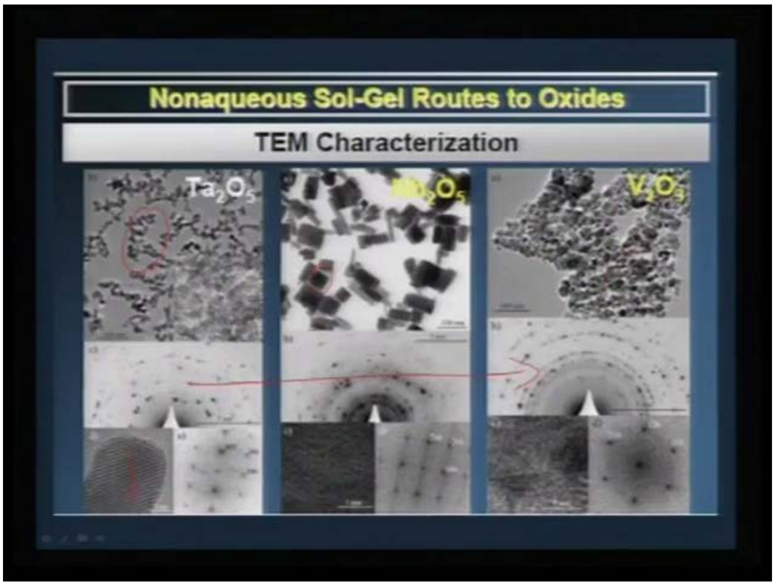

Nonaqueous Sol-Gel Routes to Oxides

TEM Characterization

These are the TEM characterization results, which shows that sol-gel process has a size and shape control, therefore you can see tantalum oxides, very nice lattice fringes of this is seen. And almost all cases you would see a polycrystalline feature, and here you can see square or rod shaped particles, here again V2O3 particles are agglomerated. And similarly, we can show tin oxide, the tin indium oxide and nice indium oxide particles can be formed using TEM.

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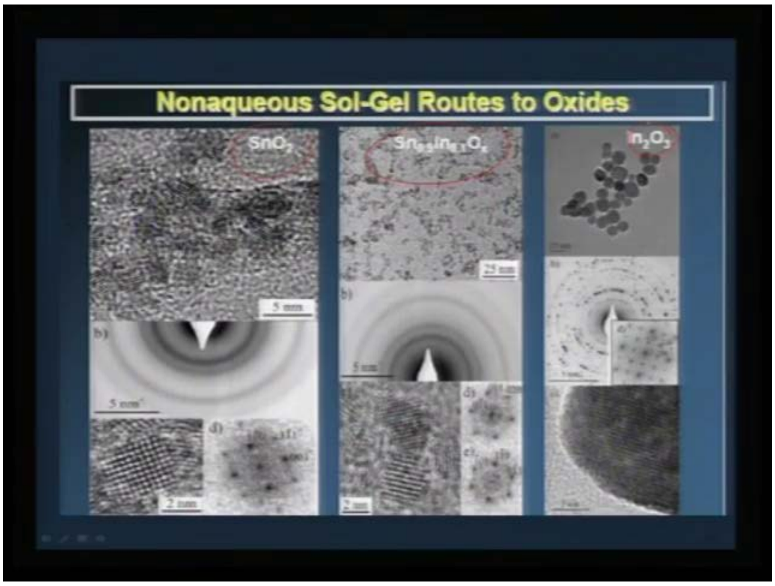

Nonaqueous Sol-Gel Routes to Oxides

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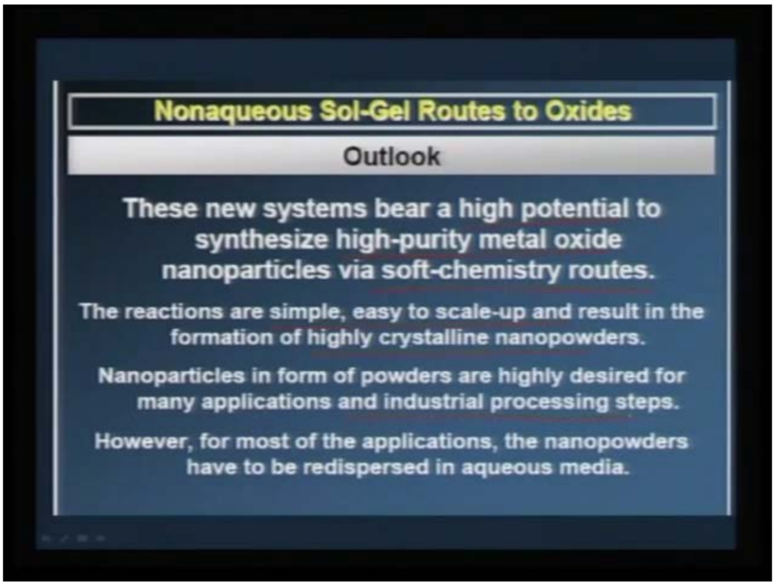

Nonaqueous Sol-Gel Routes to Oxides

Outlook

These new systems bear a high potential to synthesize high-purity metal oxide nanoparticles via soft-chemistry routes.

The reactions are simple, easy to scale-up and result in the formation of highly crystalline nanopowders.

Nanoparticles in form of powders are highly desired for many applications and industrial processing steps.

However, for most of the applications, the nanopowders have to be redispersed in aqueous media.

So, in brief sol-gel process can be a very useful method for precursors, these systems bear a very high potential for making high purity metal oxides, via soft chemistry route. And therefore, among the precursor routes, sol-gel precursor route is one of the very coveted and more used method, the reactions are simple easy to scale up. And they form highly crystalline nanopowders, nanoparticles in form of powders are highly desired for applications, as a result sol-gel can be used for scaling up operations.

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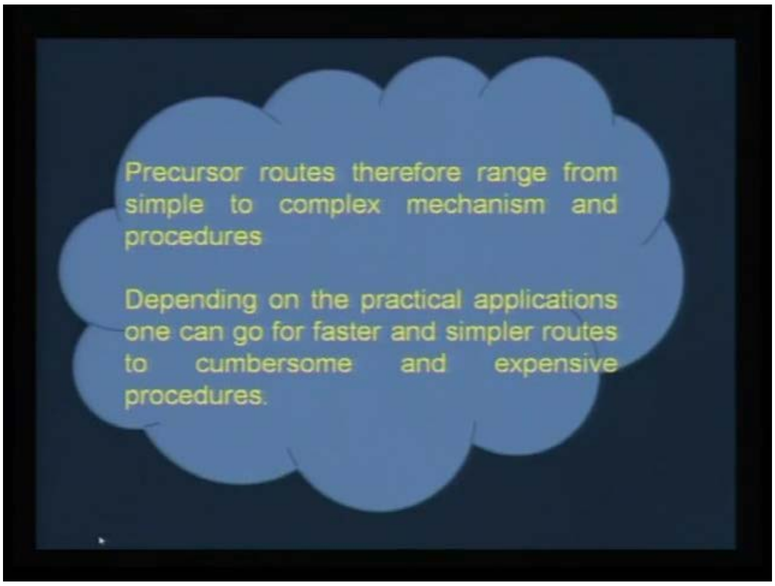

Precursor routes therefore range from simple to complex mechanism and procedures

Depending on the practical applications one can go for faster and simpler routes to cumbersome and expensive procedures.

To sum up on these 2 lectures on precursors, I just want to make two comments, one is precursor routes, therefore range from simple to complex mechanism and procedures. So, as you saw, examples of simple precursors, like nitrates, hydroxides, some of these can have X-ay similarity, we can widen the scope of solid solutions, but usually they are cheaper, and therefore you can try to make the corresponding oxides at a fairly low temperature. But, when you look for high purity and mono size, and lot of other stringent requirement on your final products, you need to go for sophisticated methods, but there are given take in each approach.

So, there are certain things that the sol-gel chemistry approach lacks, which you can take it from simple precursor route, and as I told you solid solution precursor route is one of the other approach which really stands of, but then there again there may be compromise in the issue of the final properties. So, precursor routes can give us a lot of dimension to making new metal oxides, there may be some phases which may not be known, but precursor routes can help us understand and help us synthesize, such new stoichiometries or new phases. Mainly because what is achieved at high temperature can be realized at low temperature, as a result it provides a new pathway to stabilize meta stable phases also. So, we need to take a all this issues into consideration, when we try to look at making new stoichiometries and new metal oxide combinations.