Electroceramics
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Lecture - 40

Here, we start a new lecture again with a new topic all together. So, in the last lecture we discussed another class of Electroceramics, which is rather more exotic in nature and something whose properties have created lot of interest in the research community over decades and that was superconducting ceramics. So, we started with fundamentals of super conductivity, why super conductivity exists, what is super conductivity, what are the things, which lead to the super conductivity.

And we saw that the superconductors were typically two different kinds of superconductors, type one and type two. And early generation superconductors were mostly either metals or metallic alloys and they had T C’s well below 30 Kelvin and that was not very helpful, because in order to use any superconductor, you have to go to liquid helium. And liquid helium is being expensive, they do not they do not make a cut towards you know practical technologies.

Now, the real revolution came in 1986 when Bednorz and Muller discovered, your cuprite oxides having superconductivity at high temperatures about 40 Kelvin or so. And then this lead led to lot of flurry of activities in superconducting research especially using cuprite oxides. And then in then soon after yttrium barium copper oxide was discovered, which had ATC of 92 Kelvin and this was a remarkable discovery because it allowed people to transition from liquid helium to liquid nitrogen.

And this was a major leap in the superconducting research and this made commercial sense as well, because liquid nitrogen is a lot cheaper than liquids helium. And then variety of other materials were discovered having higher T C, then Y B C O, but eventually Y B C O remained choice of material. Simply because of, it is easy of ease of fabrication and it is rather uncomplicated nature as compared to other materials.

And there are some applications, which have emerged on the bases of these superconductors. For instance your magnetically levitated trains, which work on the principle of repulsion of magnetic field. So, as a result, the train floats in the in the rail tracks and there the superconductors, which in superconducting state expel the magnetic field, which is analogous to diamagnetic effect but it is not diamagnetic effect.

And it helps in moving the train rather frictionless in a frictionless manner. And then we discover, we talked about another use that was MRI imaging and that is, again based on superconductors. And there are some other applications which are coming up. Such as, superconducting tapes and wires which can which will of course operate at lower temperatures but they will have zero resistance. Now, another class of materials in this, in the similar league is you know recently, which have been researched for about 10 years or so quite significantly.

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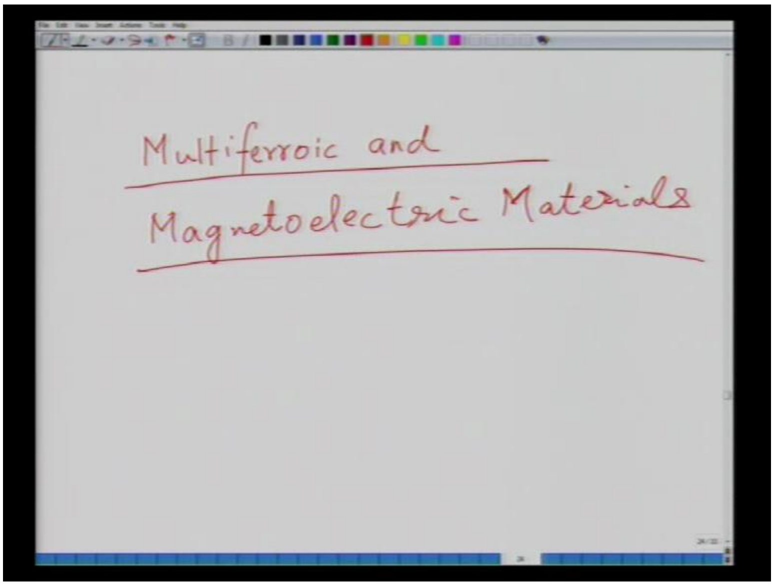

Multiferroic and

Magnetoelectric Materials

And these materials are called as multiferroic and magneto electric materials.

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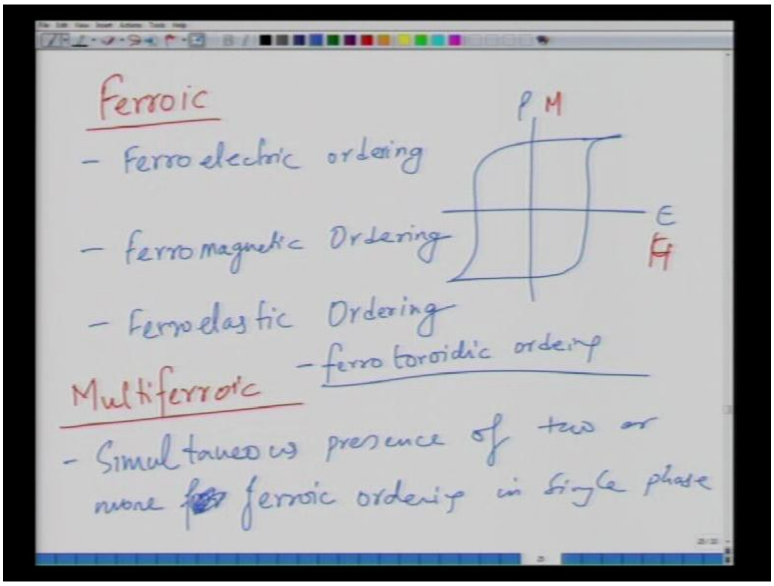

Ferroic

- Ferroelectric ordering
- ferromagnetic Ordering
- Ferroelastic Ordering
- ferro toroidic ordering

Multiferroic

- Simultaneous presence of two or more ferroic ordering in single phase

Now, we know what is a ferroic material? Now ferroic material ferroic material is a material, which has you know ferroelectric ordering. A ferroelectric ordering of course, you know that you know it is it is nothing but coupling of polarization in electric field. So, you have polarization versus electric field plot when you switch a ferroelectric material then you have ferroelectric ordering sorry ferromagnetic ordering I am just being stupid here ferromagnetic ordering.

Now, which has coupling between you know all the parameters like magnetization, and magnetic field. And then you of course have ferro elastic ordering which is nothing but coupling between stress and strain. So, these three order ordering states individually are called as ferroic orderings or materials, which consist of these ordering are called as ferroic materials. Now, naturally a multiferroic material is a material, which has more than one of these ordering present.

So, a multiferroic material would be a material, which has either of these two ordering states present simultaneously in the single phase, so in have so this is a multiferroic material. So, multiferroic material would be defined as, simultaneous presence of two or more ferroic ordering in single phase. Now, this is something as you can understand, it is a very, it is a rare phenomena but it is a very exciting phenomena because it gives rise to tunability of devices by more than one or two, more than one stimuli.

So, for a a multiferroic for instance, if it is ferromagnetic and ferroelectric in nature, it can allow tuning of devices by application of both electrical magnetic field. And both polarization and magnetization are could be controlled by applying magnetic or electric field. So, there is some interdependence of properties, there is some sort of interplay of property and that allows multidimensional devices. You can have multistate memory elements, you can have a spintronic devices etcetera, etcetera.

So, this has opened a flurry of activities to discover materials, which are workable at room temperature, which could be used in these a coveted applications. So, these are three different kind of orderings, which exist in materials. Another ordering which could which you could think is, which has been recently coined is ferro toy toroidic ordering, which is also been thought to exist in these materials. Now, another class, so this is magneto electric and multiferroic and then you have magneto electric.

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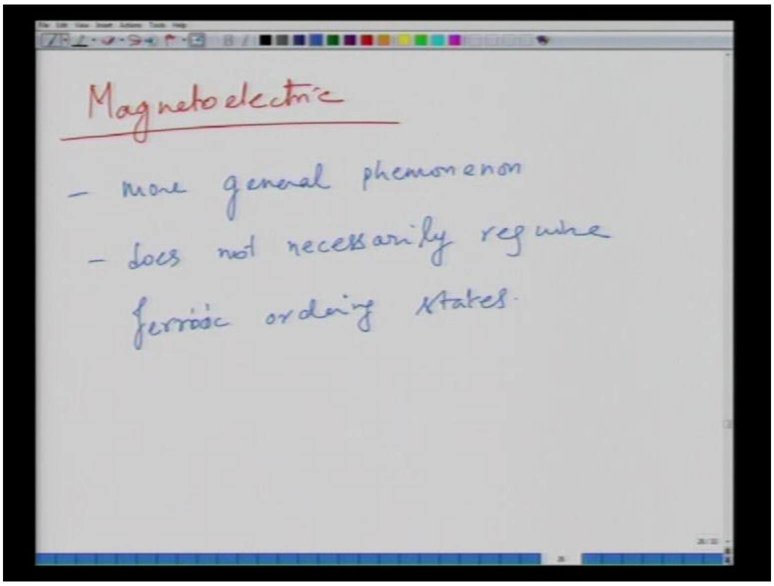

Magnetoelectric

- more general phenomenon
- does not necessarily require ferroic ordering states.

Now, magneto electric is little bit more general than multiferroic, because magneto electric is simply dependence of you do not need to have a ferroic material for this purpose. But, all you need is dependence of magnetic and electrical properties on each other. Whereas in multiferroic, you would require both the ordering states we present but it does not it does not mean that they are very strongly coupled with respect to each other.

So, here magnetoelectric is essentially, it is a more sort of I would say general phenomenon and this is and does not necessarily require ferroic ordering states in the material. All you require is material should be magnetically and electrically polarizable and there should be interdependence. So, for instance you can have a paramagnetic, you can have a material, which is paraelectric and ferromagetic and here, the properties of this material can be you know mediated by something like strain.

So, you do not really require direct coupling, there could be indirect coupling of these properties through some other order parameter such as strain. So, essentially two effects have allowed researchers think of variety of devices, which could come up if these materials were successfully designed and fabricated. And this would allow the development of you know a completely new array of devices, for instance memory sensors and spin walls etcetera.

So, what we are, what we are going to do is that, we are going to discuss the fundamental aspects of these two materials. And then we look at some of the candidate materials which are being researched and at present.

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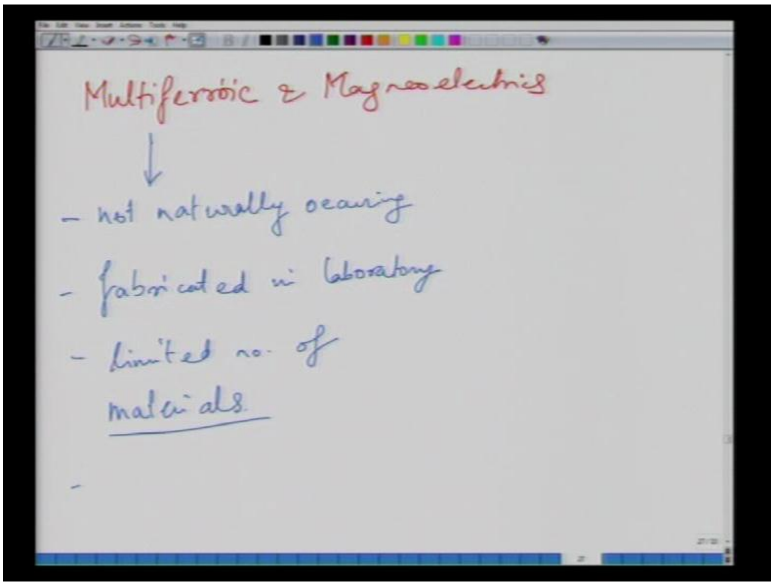

Multiferroic & Magnetoelectrics

↓

- not naturally occuring
- fabricated in laboratory
- limited no. of materials
-

So, the problem is the problem is specially with multiferroics most of them are not naturally occurring. So, as a result the the their availability is limited, so most of them are fabricated in laboratory. On top of that even if you make them in laboratory based on variety of considerations, there are not many materials, which show effect there is very limited limited number of material show this effect.

So, as a result your choice of materials is severely limited and there are other problems with respect to their fabrication as well as their transition temperatures. They show which are often not workable near the room temperature or fabrication could be quite tricky to obtain a single phase, often they come up with many impurities. And this sort of this makes a life of difficult researchers quit difficult, in order to make use them in any useful application.

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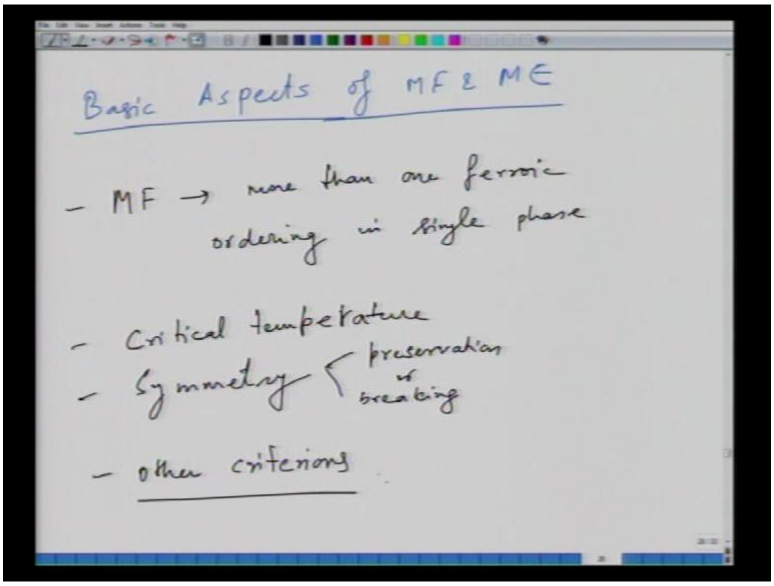

Basic Aspects of MF & ME

- MF → more than one ferroic ordering in single phase
- Critical temperature
- Symmetry { preservation or breaking
- other criterions

So, we will just first discuss the basic aspects of multiferroic and magneto electric systems. So, we will we will discuss the general features, now general features of course, a multiferroic materials must have more than one ferroic ordering in single phase, this is a true definition of a multiferroic material. Another is so which means, you should have either Ferro electricity or ferromagnetism, basically ferromagnetic ordering ferroelectric and magnetic ordering or ferroelectric and ferro elastic ordering or ferromagnetic and ferro elastic ordering.

Typically preferable ones are from the electrical magnetic properties point of view are ferroelectric and magnetic ordering should exist in single phase because ferroelectric materials will anyway be piezoelectric. So, mechanical part is covered in there and if you have magneto instruction that also becomes a part of it. And then you have you know critical temperature, so both of these materials, both of these classes multiferroics, if you have a ferroic ferroelectric ordering.

If you have a magnetic ordering then you have a critical temperature and you also have to consider the symmetry of material. So, critical temperature versus symmetry and whether the symmetry is preserved whether symmetry is broken, this has to be and then of course, you have other criteria such as, whether the material is conducting or so on, and so forth. So, some other criteria's, which we have a look at soon. A typical a general guide to eye to find out the magnetic and non multiferroic and magneto electric materials source so you draw variety of these circles.

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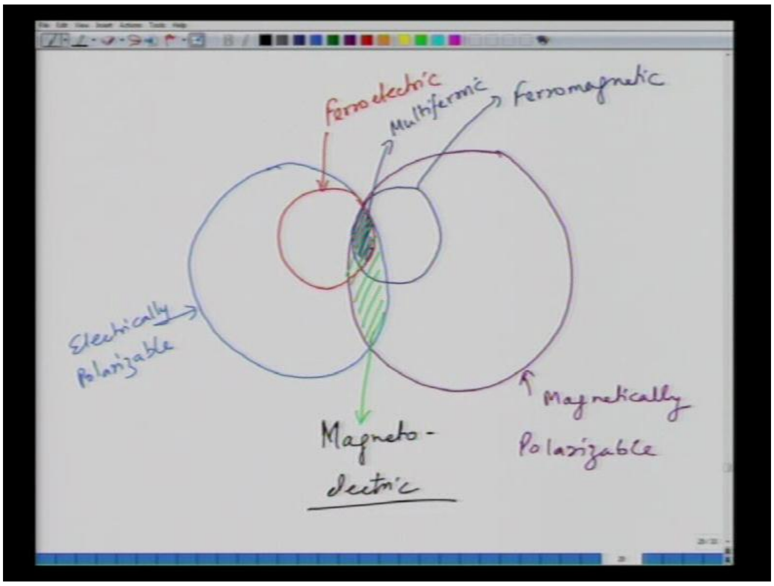

So, you have this for example, one circle which you can refer to as materials, which are electrically, polarizable then you have another circle of materials, which could be you know called as magnetically, polarizable. And anything in between and then you can have something you know within this electrically polarizable. You can have a class which is ferroelectric.

We just change this. So, this is you know ferroelectric. And then I can have another class, which can be you know ferromagnetic and between these I have you know the anything the common materials between ferroelectric, ferromagnetic are going to be this, these and these are going to be you know your multiferroic. And then you have a class of materials, which are these and these are going to be your magneto electric. So, this is a general guide to I to define magneto electric and multiferroic materials.

Now, before we go into further discussion, I will recommend certain papers and books for you to read because there are no books on this topic as such very good books.

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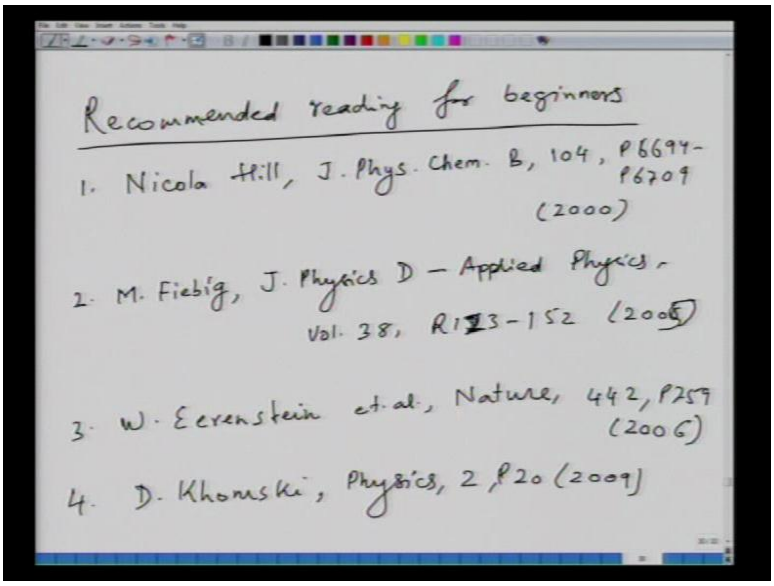

Recommended reading for beginners

1. Nicola Hill, J. Phys. Chem. B, 104, P6694-P6709 (2000)
2. M. Fiebig, J. Physics D – Applied Physics, Vol. 38, R123-152 (2005)
3. W. Eerenstein et. al., Nature, 442, P759 (2006)
4. D. Khomski, Physics, 2, P20 (2009)

So, I would say recommended reading for beginners. And once, you build up certain background, you can of course, look at more papers so recommended reading for instance would be a paper by very nice paper by Nicola Hill. This appeared in journal of physics and chemistry B and volume number is 104, page number is 66942, page 6709 and this appeared in 2000.

And then we have a paper from Manfred Fiebig, this appeared in journal of physics D applied physics and this has a volume 38, page number R151,23 to 152 and this appeared in 2005. And then third paper in this line is a paper by Wilma Eevenstein and co-workers, who published in nature volume number 442, page number 759 and this appeared in 2006. And finally, there is another 1 by D. Khomski in physics journal volume 2, page 20 and 2009.

So, these are some of the papers, which you can go through in order to get some fundamentals understanding of this topic and in the in this lecture most of the content has been taken basic content has been taken from these papers only.

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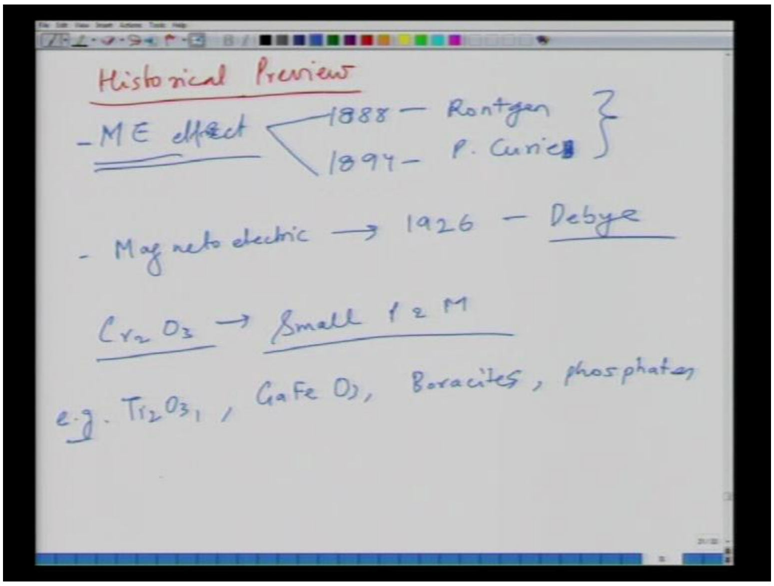

Historical Preview

- ME effect
  - 1888 – Rontgen
  - 1894 – P. Curie
- Magnetoelectric → 1926 – Debye

Cr_2O_3 → Small P & M

e.g. Ti_2O_3, $GaFeO_3$, Boracites, phosphates

So, before we go into the theory, we will have a look at the historical prospective, historical preview. And here, multiferroic effect was discovered in or magnetoelectric effect was (( )) magnetoelectric effect was discovered in 1888 by Rontgen and in 1894 by Pierre curie and these where two independent studies, which discovered magneto electric effect.

Now, what Rontgen discovered was he discovered in materials that a magnetic materials could be a material, when placed in electric field was magnetized and conversely, when they put it in magnetic field, it got polarized. So, this was the discovery made by Rontgen. Pierre curie made the discovery that the he discovered the magneto electric effect in the material, which is effect essentially dependence on magnetic and electrical properties on each other based on its symmetry considerations in material.

So, the two effects were observed independently and quite independently concluding a studies. And the term magneto electric, so in both of these studies they observe by effects, but they did not call this as a magneto electric effect. Rather they just describe the phenomenon. So, the term magneto electric was used in 1926 by Debye. This was the first time when the term was used.

And the first material to show this effect was chromium oxide and this chromium oxide essentially, it showed this small magnitudes of induced polarization as well as magnetization. So, you can say small p and m. And after that, there are flurry of activities and variety of other materials, which were discovered to show for example, TI2O3 and you know gallium ferrite was again studied and then boracites, phosphates etcetera, etcetera. Variety of these materials were studied for the magneto electric effect.

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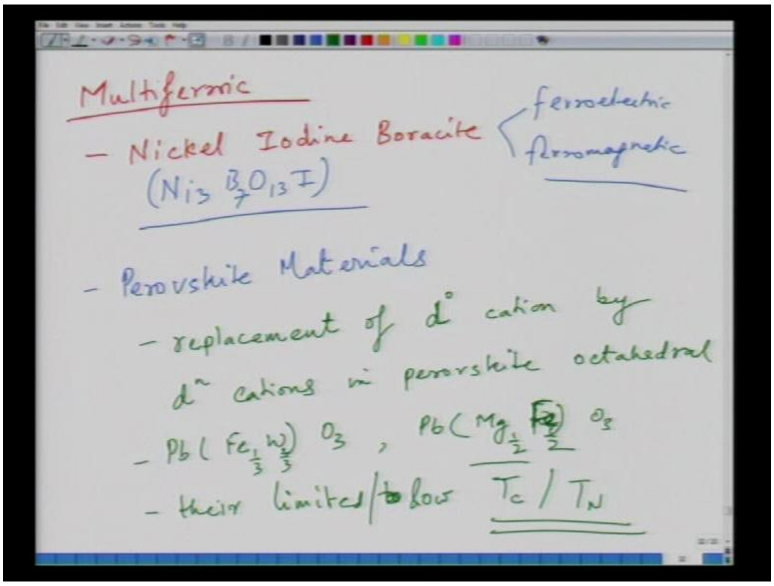

Multiferroic

- Nickel Iodine Boracite { ferroelectric / ferromagnetic
  ($Ni_3 B_7 O_{13} I$)

- Perovskite Materials
  - replacement of d^0 cation by d^n cations in perovskite octahedral
  - $Pb(Fe_{\frac{1}{3}} W_{\frac{2}{3}}) O_3$, $Pb(Mg_{\frac{1}{2}} Fe_{\frac{1}{2}}) O_3$
  - their limited/to low T_c / T_N

As far as the multiferroics are concerned. The first multiferroic discovered was Nickel boracite Nickel Iodine Boracite to be precise, with the formula Ni3 B7O13 I. So, this was the first multiferroic which was discovered and this was simultaneously ferroelectric and ferro magnetic. And subsequently there where many studies, which were made on these compounds.

However, most of them had quite complex structures and an materials were not really very useful from the technological point of view, because the because of small magnitudes of polarization, magnetization as well as the curie temperatures, which were not handy. Now, this sort of led to this research on variety of perovskite materials. In case of perovskite materials Russian scientist took lead sort of they discovered lot of early generation perovskite materials.

And here, what they did was in the perovskite material, this d 0 cation which sits in the ideal phosphate structure at the center of the unit cell. This was replaced by variety of ion. So, essentially the their whole theory was based on replacement of d 0 cation by d n partially filled d orbital cations.

So, cations with partially filled your metals in perovskite octahedral. And their basic philosophy and this lead to variety of compounds and the compounds, which were discovered first for such, compounds were you know Pb Fe W O 3 F e here would be given by 3 w would be 2 by 3 and similarly, another was Pb Mg W O 3 and these would be half half.

So, these were (( )) to mixed perovskite, which gave rise to simultaneous Ferro electricity and magnetic ordering. And here, the ferroelectricity was caused by you know diamagnetic these magnesium and tungsten ions sorry here, it would be iron Iron magnesium. And the magnetic ordering was caused by this iron ion. So, this was the basis of discovery of these materials. However, these materials were a little unsuccessful simply because of their limited or rather I shall say low curie temperature or neel temperatures. So as a result, they did not prove really commercially attractive.

And then subsequently the research focus now, this even after this lot of research was done on multiferroic and magnetoelectric materials, but the real breakthrough started coming in the beginning of this century, when people started talking about these materials again. And these materials were now discovered in you know thin film form. And thin film form somehow, just like it happened with ferroelectric materials. Ferroelectric materials were early in the early stages were studied in the bulk form.

And in the bulk form their properties were somehow limited but in subsequently when with the advent of good deposition technologies people started using them in thin film form of high quality. And then they started observing that you know, properties can be significantly retained or enhanced in the thin film form, if the thin films are of good quality.

And same thing has happened by multi ferroics. Now, there is we have fantastic techniques as we I will discuss in the last lecture, which can give rise to rather defect free layers with very good chemical and structural integrity. And they can give rise to fantastic properties that we otherwise do not notice in the bulk form simply because of, presence of defects like grain boundaries etcetera.

So so, in two thousand three for instance, a paper was published in science by a group of scientists from Maryland and Berkeley. And another places as well and they postulated large other showed large Ferro electricity in a material called bismuth ferrite. And this bismuth ferrite has since, then been researched massively I mean over last 8 years hundreds of paper, thousands of papers have appeared many conferences have been held. And this has also led to massive research in magnetoelectric and multiferroic material.

So, this recent is, it is about past decade has been spent mostly on understanding, their structure property correlation in thin film multiferroics. Along with of course, bulk and single crystals as well.

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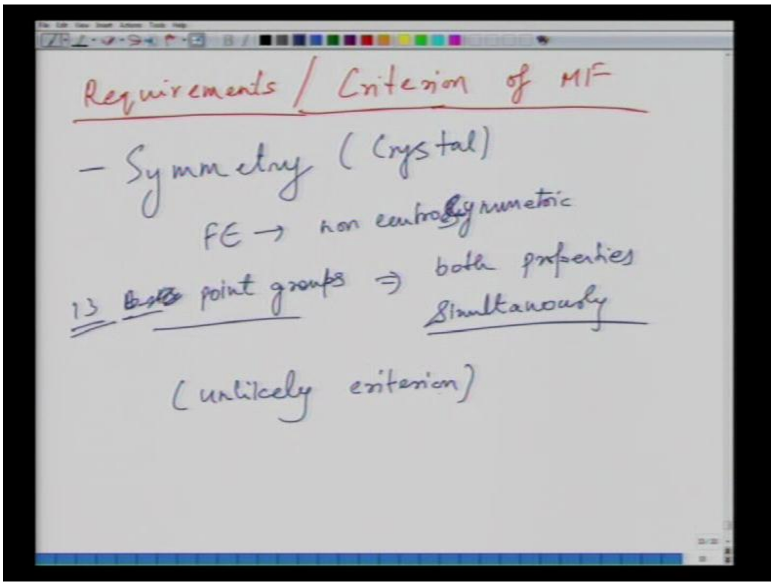

Requirements / Criterion of MF

- Symmetry (Crystal)

FE → non centrosymmetric

13 point groups ⇒ both properties Simultanously

(unlikely criterion)

So So, I will discuss these materials a little later. So, first I will talk about, what is the requirement for a magnetoelectric multiferroic material. So, requirements from the point of view of physics. The first requirement is first criteria that comes to our mind or you can say requirements rather than criterion for multiferroic materials.

Now, in the first criterion that of course, comes to our mind is symmetry and and simply because and this is nothing but crystal symmetry. And this comes to our mind because we know that ferroelectric materials are materials, which do not have a center of symmetry. So, ferroelectric materials are non centrosymmetric. And this is a must requirement for ferroelectricity to prevail.

On the other hand now, there are 31 total out of 31 point groups and out of 31 point groups, you have you know by 11, 11 point groups which are non centro symmetric and which show Ferro electricity or which are polar. And some of them show Ferro electricity. Now, according to calculations for the for simultaneous existence of Ferro electricity ferroelectrical magnetic ordering. You require 13 13 point groups, which can show both properties simultaneously.

Now, this is a large number I mean materials, which belong to these 11 to 13 point groups or let us say 11 point groups, they are very large in number. And out of so out of these, if you have you space group and plain group both of them together, so out of these 13 point groups. So, total 13 point groups include variety of materials and you can form variety of crystal structures. This certainly cannot be a criterion simply because the number of materials, which belong to these point groups is very large.

So, it is a probably or likely that symmetry is going to play up and so symmetry probably is unlikely criterion.

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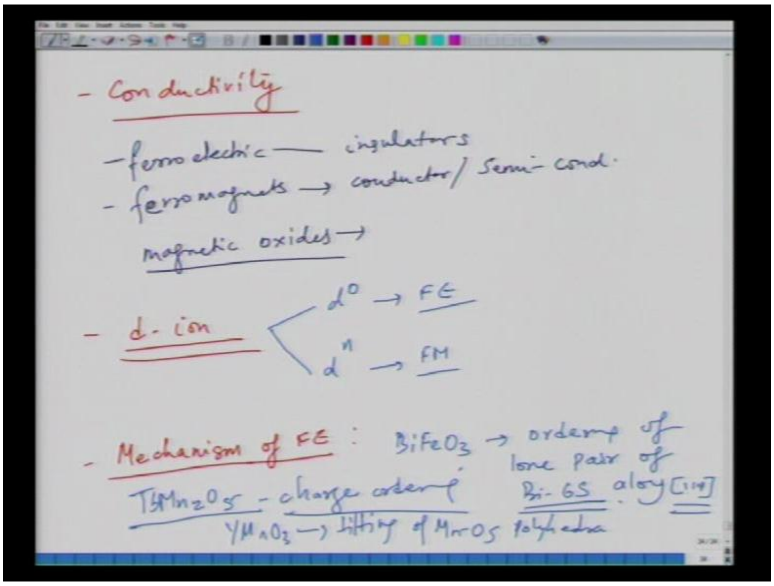

- Conductivity

- ferroelectric — insulators
- ferromagnets → conductor/ Semi-cond.

magnetic oxides →

- d-ion < d^0 → FE, d^n → FM

- Mechanism of FE : $BiFeO_3$ → ordering of lone pair of Bi-6S along [111]

$TbMn_2O_5$ - charge ordering

$YMnO_3$ → tilting of MnO_5 polyhedra

And then another criteria that emerges is the conductivity. Conductivity has emerged as a criteria, because ferroelectrics are typically by definition ferroelectrics are insulators and most Ferro magnets are conductors or a semi conductors. Now, this was thought as one of the criteria however, there are some magnetic oxides, which are which can be highly semiconducting or may be on the on the lower side of semi conductivity, which means having high resistivity or insulators.

So, some of these can be insulating, so this is again thought out as not a very strict criteria. And another criteria is the nature of d ion. Now, this d ion in case of ferroelectric, you would require the d ion to be d 0. In case of Ferro electric, you would you would require so this is for ferroelectric and this is for Ferro magnet.

Now, these two criterions are quite opposite in nature. So, as a result this criterion something, which puts a constraint on these system and it is kind of paradoxical in nature as well, so because of opposite requirement. So, this is something, which is not understood well. And then the other one, you can say is mechanism of Ferro electricity. Now, typically in ferroelectric materials like perovskite materials, you would assume the center of symmetry to be broken by movement of central ions in the octahedral.

Now, here in ferroelectrics in multiferroics the this is not a strictly maintained. So for instance in bismuth ferrite BiFeO3. So, ordering of lone pair of lone pair of electrons of, you can say lone pair of orbitals of bismuth 6S lone pair of electrons of bismuth 6s orbital along 111 is responsible for ferroelectricity. It could be some other mechanism in other materials as well for example, ATBM, TBM2O5, which is another class of multiferroic materials in TBMN2O5, it is the it is the charge ordering, which allows the Ferro electricity to occur.

So, as we can see here the phenomena of Ferro electricity is not now limited to only central displacement of displacement of central B ions in perovskites, but rather it could be anything else as well, so such as such as charge ordering here. Similarly, in y m n o 3 the tilting of polyhedra M N O M, you do not have M N O 5, M N O 6 rather you have M N O 5 polyhedra, so in case of YMnO3. So, tilting of MnO5 polyhedra is responsible for ferroelectricity.

So, the reasons for ferroelectricity now have become different as opposed to, what we had in simple A B O 3 structure. So, as a result there are variety of mechanisms now, for Ferro electricity as against the real normal ferroelectric.

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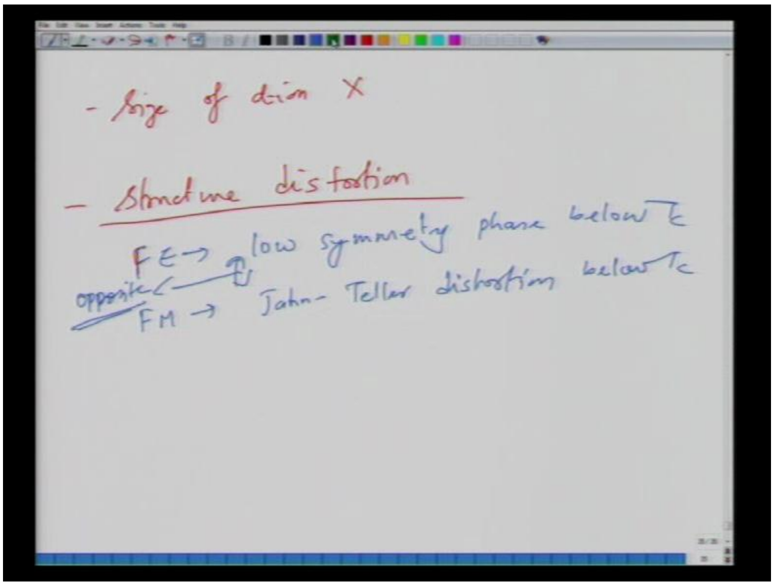

- Size of d-ion ✗

- Structure distortion
FE → low symmetry phase below T_c
opposite ⇕
FM → Jahn-Teller distortion below T_c

Another criteria, which was considered was size of d ion. Now, this is not a very valid criteria simply because there are variety of materials with variety of size of d ions, which show both effects. So, not a very valid criteria, and then you had structured distortion, this is something, which is interesting because in ferromagnetic because in ferroelectrics you require, when you cool across curie temperature. You have this distortion from high symmetry phase high symmetry phase to a low symmetry phase, when you cool it down.

And this low symmetry phase does not have a center of symmetry as a result, your materials ferroelectric. In case of so you your symmetry has to be center of symmetry has to be broken. In case of ferromagnetic material, when you are in ferromagnetic state, you have a Jahn teller distortion. This Jahn teller distortion requires that center of symmetry is maintained.

So, this is this paradoxical or conflicting requirement win requirement of a structure distortion in both of these materials. So, ferroelectrics Ferroelectric will have low symmetry phase below TC and this requires breaking of center of symmetry. And Ferro magnets have Jahn I am talking about oxides only.

So, here we are talking in the context of ceramic materials not in not in the context of metals. And this requires this requires so these two are opposite requirements, because Jahn teller distortion requires center of symmetry to be maintained and low symmetry phase requires center of symmetry to be broken. So, as a result you have conflicting requirement. So, this is something, which is interesting.

Another and so these are few criterions, which have been proposed for these ferroelectric and magnetic ordering for simultaneous existence of these. So, there is no as such, you can say a concise theory, which gives rise to a concise set of criterion. There are variety of set of criterions, which are followed in variety of materials. So, we do not have a clear agreement at the movement by researchers on these. So So, at the movement it is a it is a topic of let us say debate or research.

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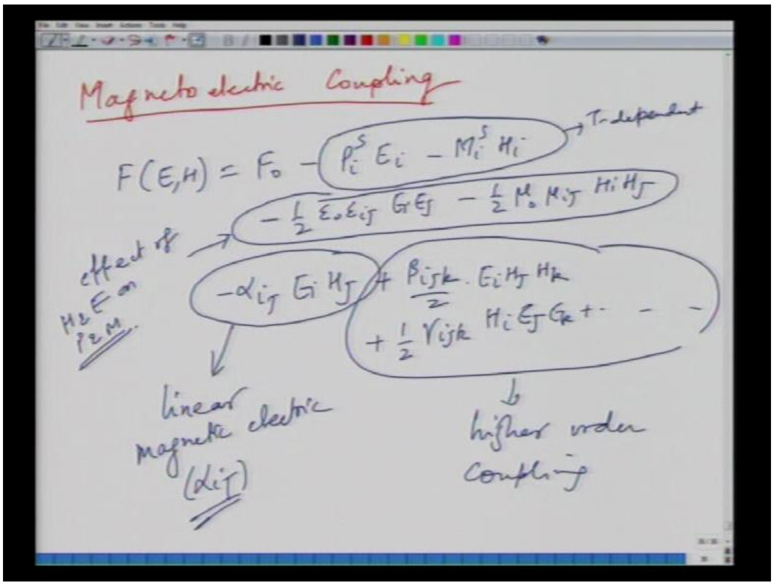

Magneto electric Coupling

$$F(E,H) = F_0 - \left(P_i^S E_i - M_i^S H_i\right) \rightarrow \text{T-dependent}$$

$$- \frac{1}{2}\varepsilon_0 \varepsilon_{ij} E_i E_J - \frac{1}{2}\mu_0 \mu_{iJ} H_i H_J$$

effect of H & E on P & M

$$-\alpha_{iJ} E_i H_J + \frac{\beta_{iJk}}{2} \cdot E_i H_J H_k + \frac{1}{2}\gamma_{ijk} H_i E_J E_k + \cdots$$

linear magneto electric (α_{iJ})

higher order coupling

Now, as far as magneto electric coupling in these materials is concerned. Since, you have these two properties occurring simultaneously. You have coupling of these two properties and this is being given by landau expression. So, you can derive you can write in expression for a free energy in the in terms of electric and magnetic field. So, this would be equal to F E H will be equal to f naught minus P i S M. This would be E i and then minus of M i s H i.

So, you have two terms for polarization of magnetic field dependence linear dependence. And then you have minus of epsilon naught epsilon i j E i E J minus of half mu naught into mu i j H i H J. So, these are again 3rd and 4th term. So, these two terms are linear dependence of polarization temperature dependent basically polarization magnetization depending upon electric magnetic field as well. And then you have these two terms.

So, you have temperature dependent terms for purely magnetization polarization. And then you have these 4th and 5th terms, which are essentially effect of H and E on P N M. Through now, they are because you have this permeability and susceptibility in that. So, these are temperature dependent terms effect of and then you have, what is called as a minus alpha i J E i H J. So, this is the magneto electric term.

So, interdependence of magnetic and electrical parameters, and then you have higher order terms beta i J K by 2 E i H J H k plus half of gamma i J K E H i E J E k and so on, and so fourth. So, all these terms here on the right. They are all higher order terms. Higher order higher order coupling terms and these could be you know about they could be third rent tenses.

What is of importance here is this linear term. Liner magneto electric coupling term here, which is this alpha i J and this is called as liner magneto electric coupling coefficient. And if you so naturally, you can you can get polarization and magnetization from these terms by just differentiating these equations with respect to electric field and magnetic field.

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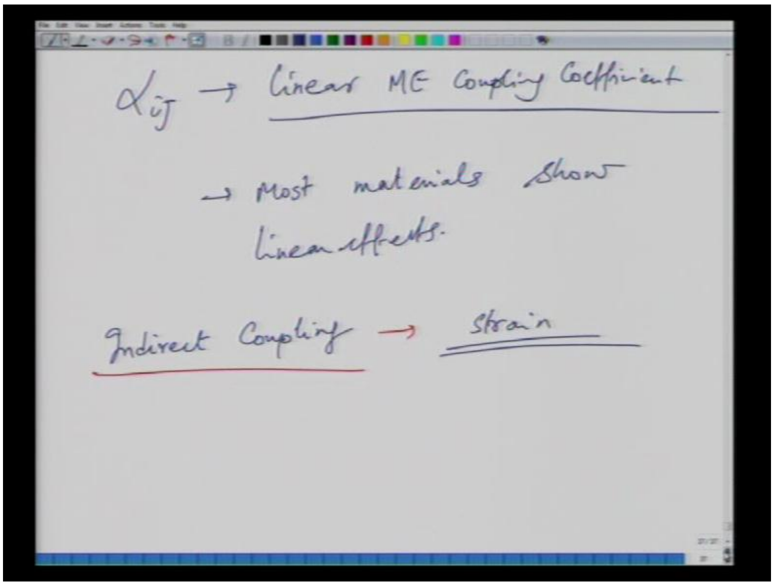

$\alpha_{ij} \rightarrow$ Linear ME Coupling Coefficient

→ Most materials show linear effects.

Indirect Coupling → Strain

So, what you have alpha i J here is, it is called as linear magneto electric coupling coefficient. And we are fortunate that most of the materials show this linear magneto electric coupling, which basically quantifies the dependence of magnetization and electric field or dependence of polarization on magnetic field and in and by large. We are quite fortunate that most materials show linear effects.

Now, how do you how do you, so so this is called as direct coupling. Then you have indirect coupling as well. An indirect coupling is essentially can be mediated by some other order parameter. Such as, by strain and this strain and this has been shown in variety of systems like europium titanate and strontium manganite, where a strain can couple these two order parameters in a single phase ah.

As far as the measurement of these techniques are concerned. You can measure them indirectly including for instance, you can measure them, you can measure the polarization magnetization versus temperature measurement and notice the fluctuation dielectric property is near the magnetic transition or vice versa. You do the dielectric constant versus temperature measurement and notice the fluctuation in the magnetization near transition temperature.

So, this is indirect measurement. Direct measurement include directly measuring the response of material in magnetic or electric response of material in response to applied electric magnetic field. So, these are this is sort of fundamental background of magneto electric multiferroic material. Now, we will look at some of the materials in question.

This is the fundamental of multiferroic materials and magneto electric materials. So, just to have a summary at this point, for a might, magnetoelectric materials are of course, the materials we which have interdependence of magnetic and electrical properties. It does not require materials necessarily to be magneto multi ferroelectric or ferromagnetic. In contrast multiferroic materials is a is a state of materials, where you know, you have to have simultaneous existence of these two order parameters either ferroelectric ferromagnetic or ferromagnetic ferroelastic and so or ferroelastic and ferroelectric.

So, this requires variety of criterions as we discussed. Some of these criterions are quit conflicting in nature, some of this criterions are do not work very well. So, essentially as, we would say the movement, there is no well established theory of multiferroic effect as to, what makes material show a multiferroic effect. And then as far as multiferroic effects of multiferroic materials are concerned.

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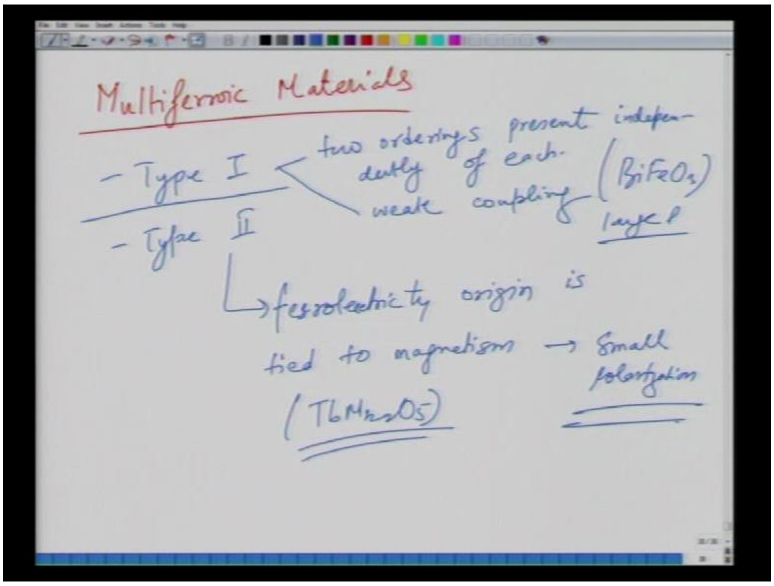

Multiferroic Materials

- Type I < two orderings present independently of each. weak coupling ($BiFeO_3$) large P
- Type II → ferroelectricity origin is tied to magnetism → small polarization ($TbMn_2O_5$)

There are two types of multiferroic materials. And another thing, that is of interest is just to deviate, that is of interest is this alpha i J term. And this alpha i J is the linear magnetoelectric coefficient given that, you have ferroic and ferroic two ferroic ordering is present ferroelectric and magnetic ordering. You have interdependence of magnetic and electrical order parameters. And this can be quite well characterized by this calculation of or measurement of this alpha i J.

And this alpha i J can be measured indirectly or directly. And indirect measurements include the observation of properties near the transition temperatures or you can say observation of, you can say magnetic or electrical properties, near the electrical and magnetic transition temperatures. And direct measurement of course require direct observations of the coupling. Multiferroic materials are further classified in two classes.

So, one is type I multiferroic and another is type II multiferroic. Now, in case of type one multiferroic, you have these two effects, these two ordering steps present independently of each other. So, two orderings present independently of each other. And as a result, they have weak coupling of properties. In case of, type II magnetism, it is the type II magnetism essentially are the materials, which have you know, where the in many cases the magnetism in the material is thought to give rise to Ferro electricity.

So, this is something, which is a very interesting phenomenon. So, as we will as we will see in in the coming slides. So, here in type II multiferroics, what you have is ferroelecticity origin ferroelectricity origin is tied to magnetism. And examples, here are materials like B i F e O 3 are type I and materials like T B M N 2 O 5 are type II kind of materials. Now, this the type I multiferroics typically have large polarization and type II multiferroics typically have a small polarization. So, this is the difference between these II different kinds of multi ferroics.

So, what we will do is that now, we will we will take example of, some of the multiferroic materials. So, we will take examples of only a few of them.

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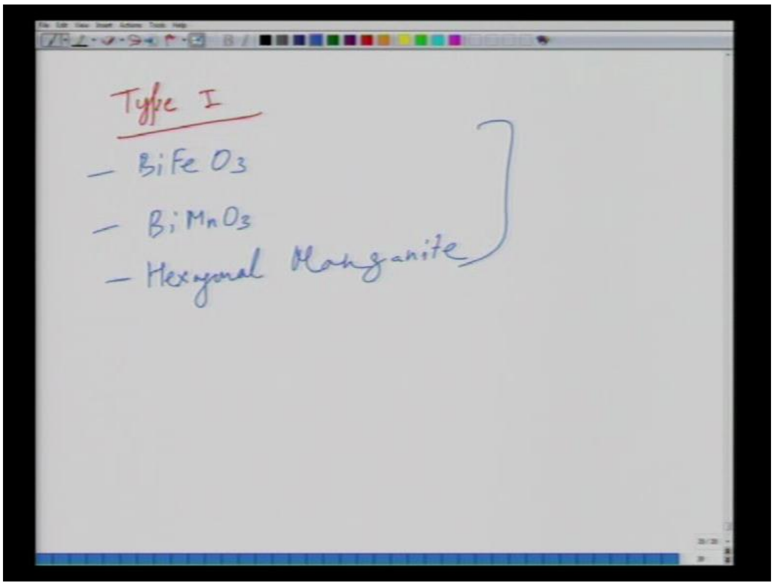

Type I

- $BiFeO_3$
- $BiMnO_3$
- Hexagonal Manganite

So, we will take in case of type I, we will take example of, B i F e O 3, B i M n O 3 and some hexagonal manganites. And then we will move on to the next part.

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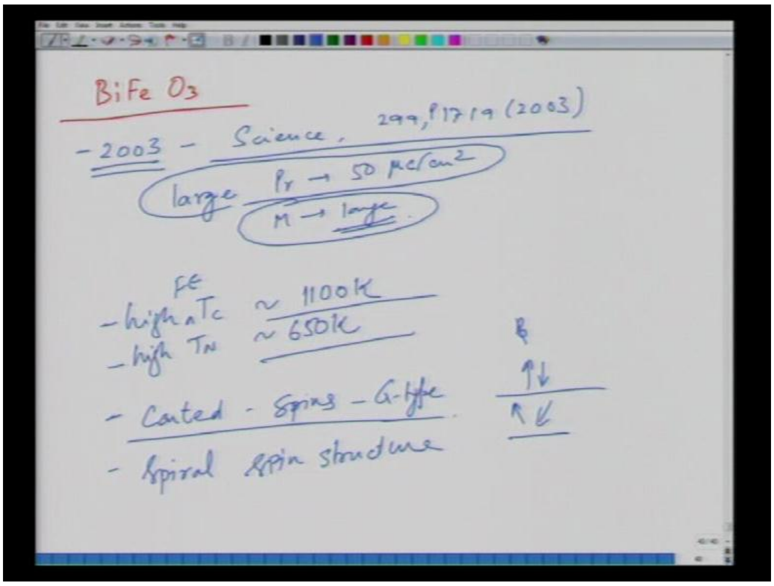

$BiFeO_3$

- 2003 - Science, 299, P1719 (2003)

large $P_r \rightarrow 50\ \mu C/cm^2$

$M \rightarrow$ large.

- high FE T_c ~ 1100K
- high T_N ~ 650K
- Canted - spins - G-type.
- Spiral spin structure

So, we will start B i F e O 3, which is also called as bismuth iron oxide or bismuth ferrite. Now, this is one of the most studied ferroelectric multiferroic materials. Earlier B i F e O 3 was of course, discovered by lot of Russians in 50’s and 60’s, but 2003 mark the year, when a paper in science, which is whose details are 299 1719 page, 2003. A paper in science sparked massive interest in this material, because the material showed large polarization of about 50 micro coulomb per centimeter square and magnetization.

Now, this discovery was true to some extent, because the polarization which was reported was indeed true, but the magnetization which was imported was not true. And later, it was worked out that, this magnetization was because of impurities in the material. However, this material B i F U 3 is very exciting because of, large polarization and one can work his way around in terms of magnetization by tuning the material by doping it with certain certain chemical substituent’s, which can promote magnetic movements or now, why we will we will look at the basic characteristics first.

And then we will go into what can be done to tune this material. So, this materials has high T c of around 1100 k, which is ferroelectric T C. And reasonably high T N, which is of around 650 kelvin. And this is a this is a antiferromagnet with canted spins. Now, this canted spins are spiral in nature as a result typically as, we discussed in antiferromagnetism, you will spins are not perfectly anti parallel. Rather they are little bit inclined with respect to each other.

So, as a result you would expect some magnetism, but because of periodicity of these spins, which is called as g type and this is a g type antiferromagnet. And there are variety of antiferromagnets depending upon the antiparallel in is whether, it is antiparallel in plain is whether, it is antiparallel in sides.

So, this is called as g type antiferromagnet. And this gives size to very small magnetic movement in the material. And there are the strategies, which can be use to so you have a spiral spin structure of g type antiferromagnetic structure. However, this can be broken down by some methods and this material has a rhombohedral structure. So, the structure of this material is something like I will show you in a in a different slide.

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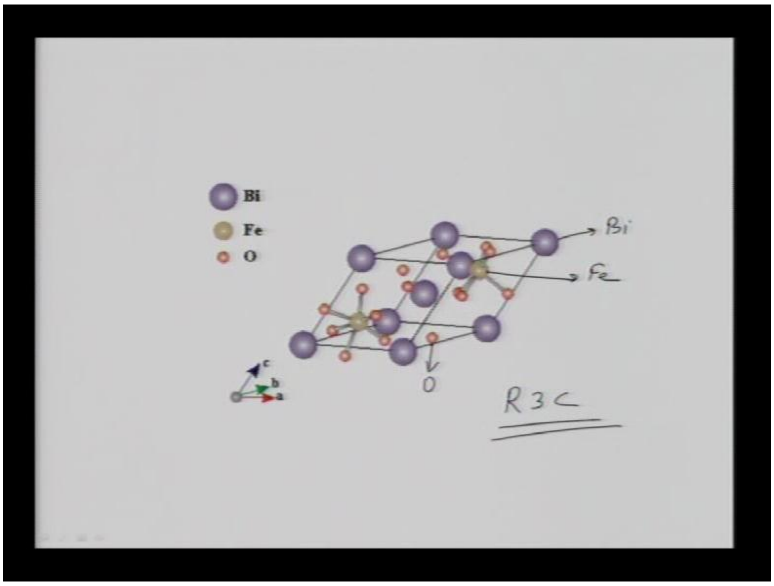

So, this is a structure of this material. So, what you have here is these bigger ions are you know bismuth ions. So, these are your bismuth ions as written there. These are iron ions and these are oxygen atoms. So, this is a rhombohedrally rhombohedral structure with a space group R3C. And this structure changes to of course, high symmetry phase up after the curie temperature, when you heat this material. So, these are the crystallographic aspects of this material.

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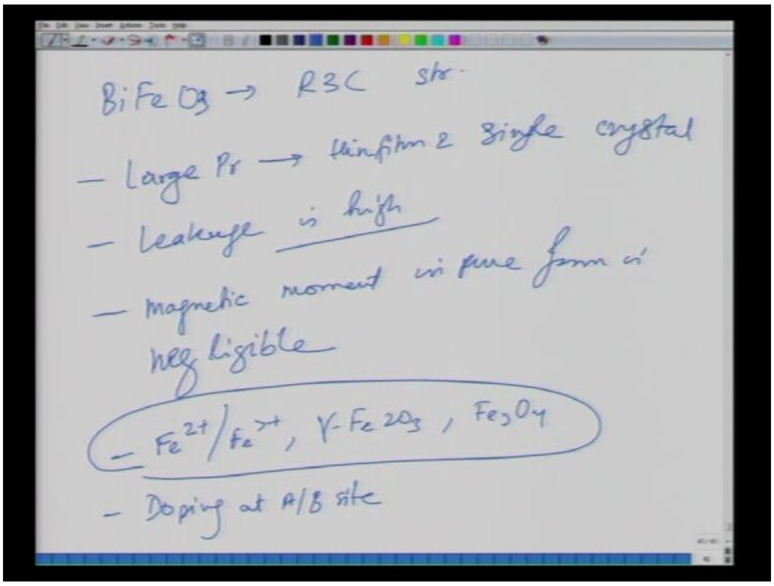

$BiFeO_3 \rightarrow$ R3C str.

- Large Pr → thinfilm & single crystal
- Leakage is high
- magnetic moment in pure form is negligible
- Fe^{2+}/Fe^{3+}, γ-Fe_2O_3, Fe_3O_4
- Doping at A/B site

So, we can write here, B i F e O 3 has a R3C structure. And this so this these are the general parameters of this material. Now, I have told you that in thin film form of this material has been shown to predict high polarization, but the magnetization, which was predicted in that, study was found to be later wrong because of, because the authors did not notice the presence of impurities. However, the material making this material is not easy.

So, although it has large P r in both thin film and bulk single crystal state. The leakage is high. And leakage could be high because of, defects, it could be of impurities, it could be because of, grain boundaries. So, as a result making this material is not easy. So, one has to be really careful in making this material in good quality. And if you can control the magnetic impurity formation precisely then in pure form the magnetic movement is negligible.

So, in order to induce the magnetic movement and this typically this, if you see magnetic movement then this is because of you know F e 2 plus F e 3 plus value fluctuations. You can have F e 2 O 3 kind of impurities gamma F e 2 O 3 or alpha F e 2 O 3 or F e 3 O 4. So, any iron containing impurities which is magnetic in nature can give rise to the observed magnetism in this material. Now, this material can be tuned by variety of things. So, doping at A and B site can be one of the factors to induce certain properties in this material.

So, for instance you can dope it by A size substituents like barium or neodymium or lanthanum or B size substitutes like zirconium titanium etcetera. And these have been reported in the literature to exhibit result in improved or changed properties, in terms of both electrical and magnetic properties. So, there are variety of, so this structure is one of the most well studied structure. You can have a look at variety of journals and literature to find about this material more.

I will not I give you all the studies, but all I have done is, I given you the general features of this material. And this is indeed a very well studied system in terms of properties simply because of, its attractive high curie temperatures and neel temperatures, which make these material very attractive.

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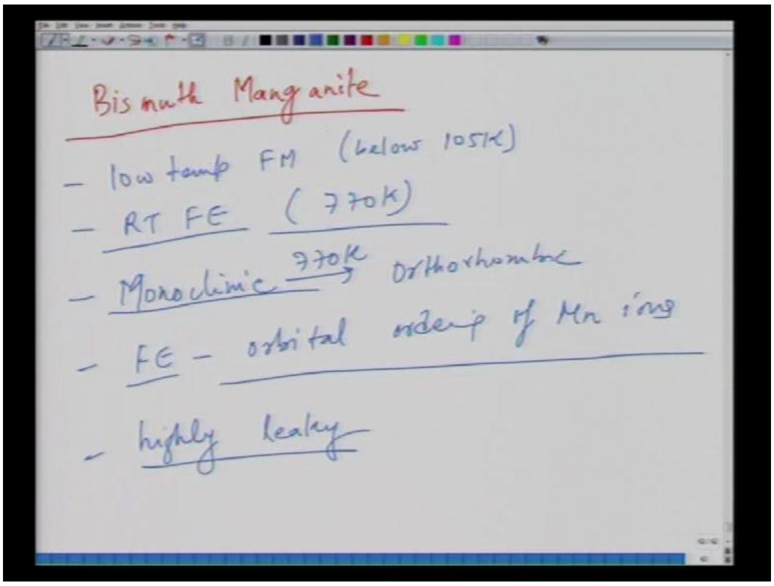

Bismuth Manganite

- low temp FM (below 105K)
- RT FE (770K)
- Monoclinic $\xrightarrow{770K}$ orthorhombic
- FE – orbital ordering of Mn ions
- highly leaky

Another class of material in this category is called as bismuth manganite. And this bismuth manganite is again multiferroic materials. It has it is a low temperature ferromagnet and a room temperature ferroelectric. And it is shows magnetic ordering below 105 k and and ferroelectric T C is happens around 770 k.

The crystal structure of this material is monoclinic in nature and this monoclinic to changes to so monoclinic changes to orthorhombic structure at about 770 k and below monoclinic. You have another low symmetry phase which is triclinic and this material basically has Ferro electricity because of orbital ordering of manganese ions.

So, this is responsible for Ferro electricity or ferroelectric distortion in this material. The problem with this material is this is highly leaky so it is really difficult to make this material in a resistive form because in order to have a ferroelectric effect, you have to have you know high insulation. And this is somehow has been a problem with this material. There are some studies recently, which have in which have reported high resistance in this material in thin film form, but that again depends up on group to group and paper to paper.

So, however there are strategies, which can which can be adopted to make this material more resistive.

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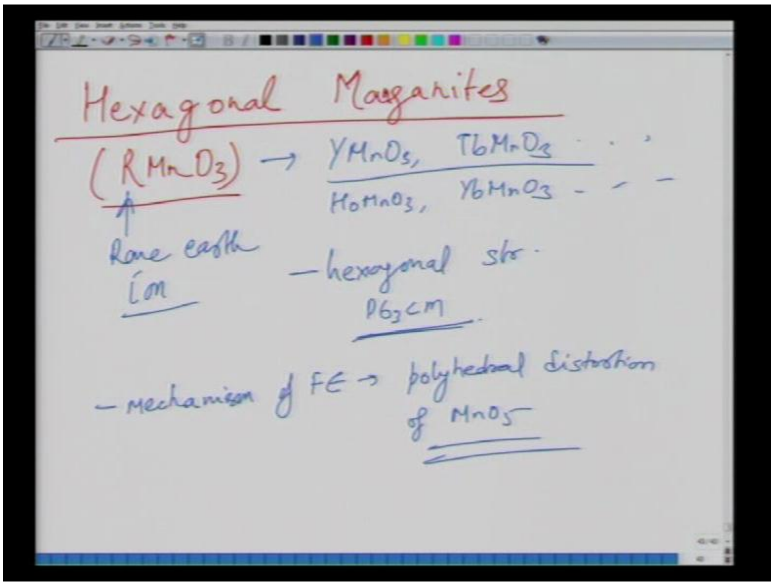

Hexagonal Manganites

$(RMnO_3) \rightarrow YMnO_3$, $TbMnO_3$ . . .

$HoMnO_3$, $YbMnO_3$ - - -

Rare earth ion

- hexagonal str.

$P6_3cm$

- mechanism of FE → polyhedral distortion of MnO_5

And then you have another class of materials, which is hexagonal manganites. And these hexagonal manganites are typically called as you know R M n O 3 kind of materials. And examples of, these are you know Y M n O 3, T b M n O 3 etcetera. Variety of these materials, so so R is you can say a typically a rare earth ion and these are all manganites structured. So, you have hexagonal structure here, I will again show you the hexagonal structure.

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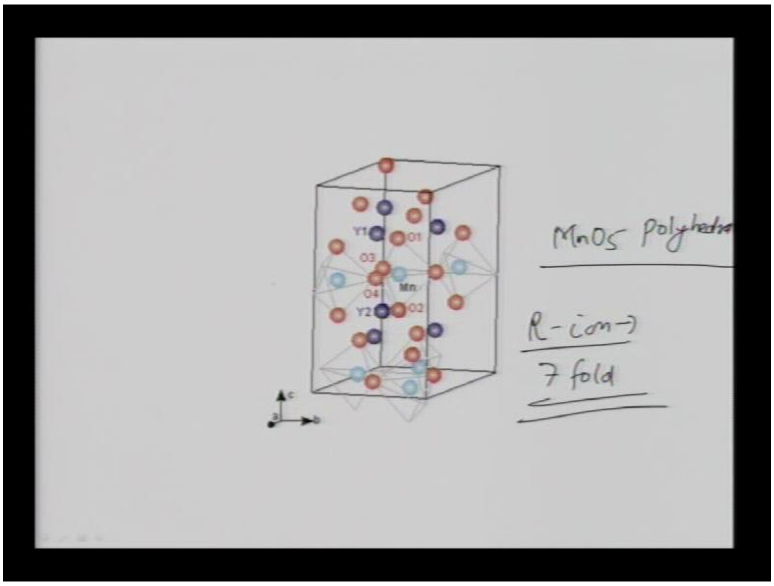

MnO_5 Polyhedr

R-ion →

7 fold

So, this is the hexagonal structure based on A T M manganese oxide. So, you have here, this is the M n O 5 polyhedra. Now here, notice unlike A B O 3 perovskite structure, which is cubic in nature. You have M n O 5, so you have M n O 5 polyhedra. So, instead of having 6 fold coordination, you have a 5 fold coordination of manganese.

Similarly, the bismuth similarly the R ion not bismuth the R ion has a7 fold coordination. So, this coordination is different as compared to A B O 3 structure and you can say this is hexagonal unit cell. And you have these layers of manganese oxides followed by yttrium oxides followed by manganese oxides, so its layered kind of structure which you have here.

So, you can say. So, here these materials, you can have holmium manganite as well, you can have you know Y b M n O 3 variety of these materials are possible. So, and they have hexagonal structure with the space group of P 6 3 C M. This is the space group of these materials. So, here as we are as I have shown in the crystal structure, you have difference in coordination.

This the polyhedral, which you have M n O 5 polyhedra the distortion of these polyhedra is responsible for Ferro electricity in these materials. So, again the mechanism of Ferro electricity is because of, polyhedral distortion of M n O 5.

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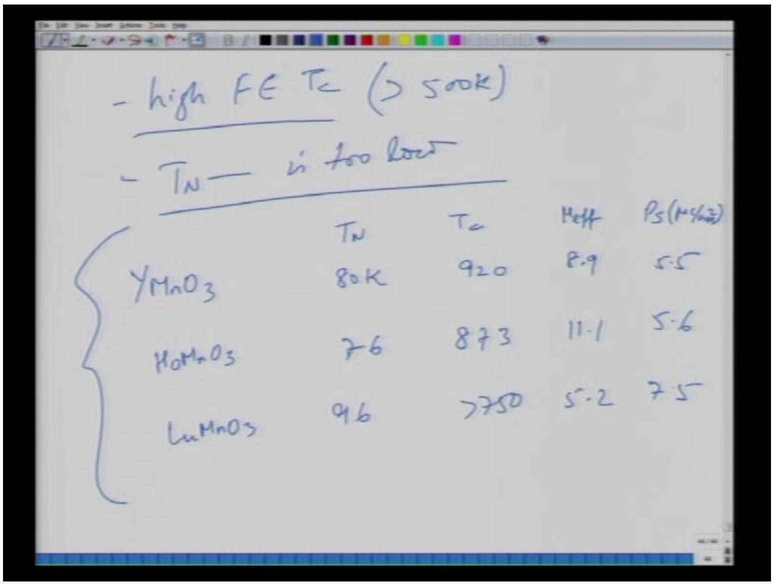

- high FE T_c (> 500K)
- T_N — is too low

	T_N	T_c	μ_{eff}	P_s ($\mu C/cm^2$)
$YMnO_3$	80K	920	8.9	5.5
$HoMnO_3$	76	873	11.1	5.6
$LuMnO_3$	96	>750	5.2	7.5

So, is. So, this is this is this is the difference here, you have with respect to other cubic sort of pseudocubic structures. Now, the advantage with these materials is that they have high ferroelectric condition temperatures, so typically higher than 500 k. However, neel temperature is too low and this is, what makes results in these materials not being very useful for practical applications.

Now, I will show you some materials examples. So for example, Y M n O 3 has ATC as a T N of about you know 80 Kelvin and T C of 920 Kelvin. And this has new effective, you can say 8.9 and polarization in micro coulomb per centimeter square this is 5.5 not too bad. Similarly, you have H O M n O 3 holmium manganite and this has 76 873 11.1 and 5.6. Similarly, you can have L U M n O 3 this has 96 greater than 755.2 and 75 percent so by tuning the composition, you can tune these temperatures as well as the properties.

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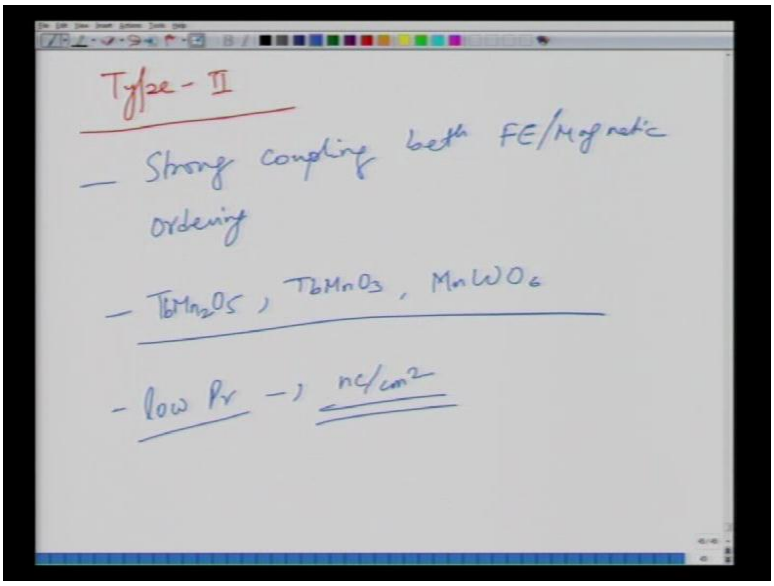

Type - II

- Strong coupling betn FE/Magnetic ordering
- $TbMn_2O_5$, $TbMnO_3$, $MnWO_6$
- low Pr → nC/cm^2

Now finally, another class of material as we said is type II multiferroics. And here, we will not go in great detail, because here Ferro electricity is tied with respect to magnetic structure these materials. So, having a magnetically ordered state is very important, but you have a very strong coupling between ferroelectric and magnetic ordering and so. Examples of, these materials are you know T b M n 2 O 5, T b M n O 3, T b M n O 3 belongs to this class not to the type I class.

So, here I should make a change here. So, not T b M n O 3 this should be type, it is a hexagonal material, but it is type II. So, in that sense hexagonal is common to both of these classes. So, you have and then you have M n W O 6 variety of these materials. And these materials have different reasons for Ferro electricity, which we will not go into detail, but these are the examples of type II multiferroics, where which have a strong coupling of ferroelectric and magnetic properties, but they have low P r of the order of Nano coulombs per centimeter square.

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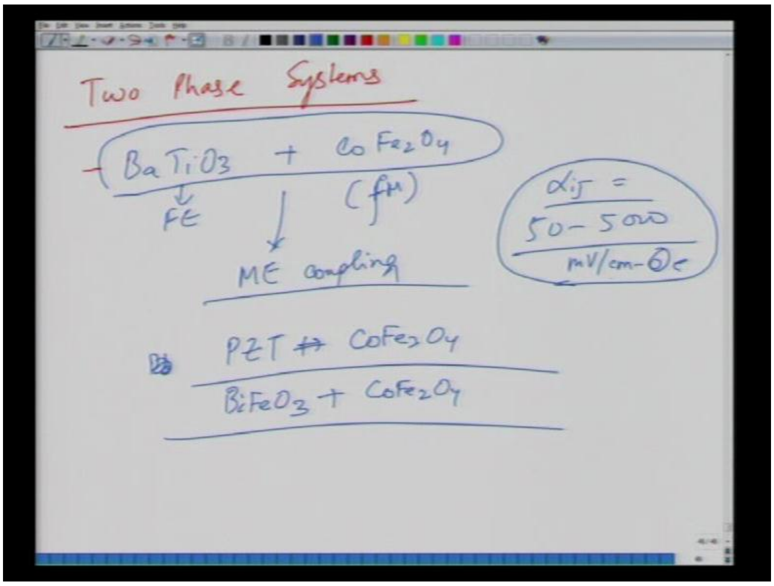

So, about 2 or 3 orders of magnitude is smaller as compared to normal material multiferroics. Finally, what we have is a two phase systems. Now, two phase of course, are artificially made they are not in single phase. So, for instance materials like you know barium titanate, which is a ferroelectric can be mixed with ferromagnet like, ferry magnet like, c cobalt ferrite. And these two when mixed with each other they give rise to coupling through the interface between these two phases. And they have they show magneto electric coupling.

So, of course,, you do not have two properties in the same phase, but you in you artificially put them together. And then create a interphase and which gives rise to coupling between these two properties. And there are variety of these materials titanate cobalt ferrite, you can have P Z T plus C O F e 2 O 4 and then B i F e O 3 plus C O F e 2 O 4.

So, variety of these structures are possible and which have different coupling constants and coupling constants vary from 50 to you know 5000. So, you would say alpha i J, this would vary from milli volt per centimeter (( )). Now, variety of these systems can be made artificially. So, we will we will stop, so this is the end of this module.

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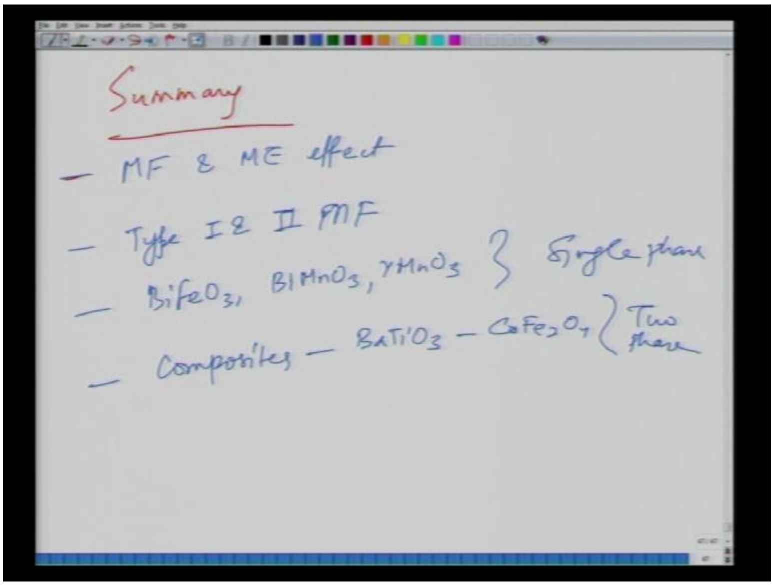

Summary

- MF & ME effect
- Type I & II MF
- $BiFeO_3$, $BiMnO_3$, $YMnO_3$ } Single phase
- Composites – $BaTiO_3$ – $CoFe_2O_4$ } Two phase

What we have so in summary, what we have discussed here is. So, I will just summaries this here. In summary you have fantastic effects like you know multiferroic and magneto electric effects. Multiferroic materials can be magnetoelectric, but magnetoelectric materials are not necessarily multiferroic. For multiferroic materials you need to have simultaneous existence of ferroelectric and magnetic ordering. Unfortunately, these materials are not very commonly available, they are very rare.

So, as a result lot of effort has been put in research and development in developing these materials in laboratories. There is no well understood physics of these materials as to is there a unified theory, which says that these materials are multiferroic these are not. So, this is not a very well established phenomena in terms of physics as yet. However, research has been carried out on variety of materials with lot of emphasis on materials like bismuth ferrite. And some emphasis on other class of materials like bismuth manganite, terbium manganite, yttrium manganite etcetera.

And of course, artificially structured materials like composite sub developed as well, where you do not have multiferroicity in single phase, but you can create artificial multiferocity by mixing these two phases. And through interface meditation, you can create this multiferroic effect or magnetoelectric effect. So, we will we will stop this lecture here.

What I have done is I have basically introduced to a new topic. So, multiferroic magnetoelectric effect type I and II multiferroics, materials like B i F e O 3, B i M n O 3, Y M n O 3. So, I have introduced you to these materials. And then you have composites like barium titanate and cobalt ferrite.

So, this is you know single phase system and this is your two phase or multi phase system. So so this is the end of this lecture in the so this is probably, we are ending the we are nearing the end of this module. In the next module, we will take up the preparation methods of these electro ceramics in general. And then we will finish this module.

Thank you.