

Physics of Functional Materials and Devices
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Lecture – 27, Week 7
From magnetic to multiferroic materials

Welcome to the second lecture of this week. In the previous lecture, I gave you a quick overview on the phenomena of magnetism and the origin of magnetism in materials. This course which is functional materials and devices, we had been talking about the term functional, which means that we are looking into a material which has at least two or more than two functionalities in the same phase. So, we should also talk about materials which have two functionalities. In this, what have we talked? We are talking about the magnetic materials. So, obviously we would like to talk about materials which have at least one of the properties as magnetism.

What is the next? And in today's class, I will introduce to you the next and we would like to see and talk about materials which are known as multiferroics. What are multiferroics? And we will focus that at least one of the properties of this material is magnetism. But it also shows additional properties and the coupling between the order parameters of these properties is there. So, if you change one, the other will also respond to these changes.

How do you make these materials? Can you just learn from this course and go into the lab and make a material? In addition to that, can you use the knowledge we obtained during the synthesis protocol lectures of this course and make those materials. We will show that it is very simple to make those materials. And finally, we will talk about the application of those materials. Now the basic idea of a material simultaneously showing ferromagnetism and ferroelectricity was proposed by Curie in 19th century itself. The first material which was showing ferroelectricity was the Rochelle salt and it was discovered in 1920.

But the first multiferroic material which was discovered was nickel-iodine borocite Ni_2O_3 , an alloy. But a detailed and focused studies to find and determine multiferroics started around 1950s in various parts. The first major breakthrough came by the discovery of multiferroic properties in bismuth ferrite and bismuth ferrite-based materials continue to be an important class of multiferroic materials even today. And then people built the theory of these materials, but the term multiferroics was first coined by Schmidt in 1994. What is multiferroic? This is the term which I have used So, many times, but I have not given you the definition.

Let me define it. Multiferroics are those which have two or more than two ferroic properties. What are those ferroic properties? They are ferroelectricity, ferromagnetism, ferroelasticity and ferrotoroidal. In the single phase that means if you have a multiferroic material, it should have at least two of these properties in the same phase. You do not have to move from one phase of the material to the next to get these properties.

Some of the common examples are bismuth ferrite and bismuth manganese oxides. So, you have ferroelectric materials which have a hysteresis loop in the PE curve. You have ferromagnetic materials which have a hysteresis loop in the MH curve and you have multiferrite or magnetoelectric materials which show hysteresis loop both in PE loop or MH loop. And if that is happening, you have a coupling between the order parameters that is either P, there is a coupling between P and M in these materials. So, you have multiferrite materials.

You can have piezoelectricity alone, you can have magnetoelasticity or you can have magnetoelectricity and these are the combinations which you can get. But initially multiferroics were considered for those materials which had two of these ferroic properties. But what you will see that in today's world multiferroics are mostly used for those materials which have simultaneous properties of magnetism and ferroelectricity observed in them. So, what we would have called initially as magnetoelectrics are now known as multiferroics themselves but this is because you get more materials which have a coupling between the magnetic or ferroelectric order parameter. These are the common materials which are found.

Let us see how you can make these materials. For example, you can make a very common material as bismuth strontium ferrite. You would have thought why do not we make bismuth ferrite. I took this example because to show that you can also dope this material. You can have doping of this material and that is what I have chosen and let us take an example of Sr^{2+} and Ca^{2+} as the dopants.

Now what is the valency of bismuth? If you look into the periodic table, you will find that you are considering bismuth as 3 plus, iron in the 3 plus state and oxygen is the 2 minus state and therefore you have equal and you have a charge neutral condition. But the moment I start doping a divalent atom, what happens? You start seeing certain modification in the systems and you may get novel properties because then you will have certain of iron which is in the 3 plus state either transforming into 4 plus state So, that the overall charge neutrality condition is maintained or you can induce certain oxygen defects which can modify the properties and you can have oxygen ion conductors because then the vacancies can hop from one place to the other. So, that is what we want to show that there are various systems which can be doped. You have to choose the application of the materials which you want to make. So, you can just start with stoichiometric amounts of ingredients in nitrate forms.

Then you mix them in distilled water or deionized water and add certain HNO_3 in them So, that you have the whole solution properly dissolved. Stir it for 4 to 6 hours at 100 degrees to ensure homogeneity. Then calcine it, grind it, recalcine to break the agglomerates and then sinter the material and you will get the desired compositions. You can have 5% doping, you can have 10% doping, you can have 15% doping, 20% doping, 25% doping or you can even have 60% doping. So, if you have 60% doping that means bismuth is how much? Bismuth is 0.40, strontium is 0.60, you have iron, oxygen and so, you see 0.40 plus 0.60 is equal to 1. So, you can have various materials.

Similarly, you can even try to make calcium, dope, bismuth, ferrite similar process. What is the first step you will carry out after making a material? You must find out whether a material has actually formed or not. If a material has formed, what will it show? It will show periodic arrangement of atom in the long range. That means the lattice is well defined and you have translational and rotational symmetries that means you will have a building block with well-defined symmetries. If you have a 3D system then the material will fall under one of the 14 Bravais lattices.

So, and they will belong to one of the 7 crystal systems. If that is the case then if you perform the X-ray diffraction measurements you will get certain diffraction patterns and you will be able to index each and every peak of the X-ray diffraction pattern based on the unit cell which you said that the material is stabilizing in. And if you can index all the diffraction peaks and you do not see any other peak that means you have got a pure material and that is what is done and we indicated in the second week when I was teaching you the use of X-ray diffraction to find out whether a material has formed or not. Let us see a typical X-ray diffraction pattern for bismuth ferrite that is shown with X is equal to 0.

Now when you start doping this system you find that for example if you see this region up to a certain region you see that the peak profiles are same but beyond a certain composition you can clearly see that there is modification in the peak profiles. The nature of the peaks changes but they can be indexed by one form or the other which the unit cell takes. So, you can just by looking at the diffraction patterns you can clearly say that as you change the composition of the material there is a structural reorientation and you go and face the condition of phase transition. This is not induced by temperature but induced by the composition of the lattice because you have different size atoms now occupying the lattice positions, they have their Brillouin zone which is different from the case where other atom was dominant in the lattice and hence, they are forcing the nearby atoms to have different order of atomic displacement leading to a phase transition. So, you can also see compositional dependent phase transition in materials.

Now what happens when you make these materials? These are scanning electron microscopes, high resolution imaging. So, we are talking in terms of let us say nanometer

range. This is 1 micrometer; this is 13 micrometers. So, you can clearly see these are individual particles we are talking about.

This is high resolution. We have gone to very, very low dimensions. So, you can clearly see that there are particles which are forming and they have very small sizes. But if you look into all the pictures, they look to be similar at the same level. So, they are similar and have spherical morphologies. This was one way of ferritization.

Then we had studied that you can tune the properties of a material just by changing the temperature at which they are formed. So, let us take an example of Bismuth strontium ferrite with 5% strontium. You calcine them at different temperatures. Let us say 500 degrees, 550 degrees, 600 degrees, 650 degrees and 700 degrees. What do you see? You see that the nature of the peaks does not change significantly.

They are not changing significantly. So, there is no phase transition taking place. The material is forming with same phase and the typical particle size which you can calculate using the shearer formula is of the order of 80 nanometers. But then if you are not seeing any change as a function of temperature why do you want to do this exercise? For this let us look into the SEM pictures once again. For example, this was the Bismuth ferrite sample and then you had the Bismuth strontium ferrite 5% samples.

These two were formed at 500 degrees C. But then as you move from 500 to 550, then 600, then 650 and then 700. You can clearly see that the samples now have a rod like morphologies or particles which are rod like and not spherical in shape. So, you have transformed the particles from rod like to spherical shape as a function of decreasing temperature or from spherical shape to rod like as a function of increasing temperature of fabrication. So, now obviously there is some change and that is significant.

The building block is remaining the same. Please note it is still the same unit cell because X-ray diffraction did not show any major modifications. It is only the size and the shape of the particles which are forming that are changing. So, you can clearly see what you now see is the rod like morphologies of particle. And the change is basically induced by the homogeneous nucleation growth mechanism which we studied in the week where we were talking about the synthesis protocol.

So, what happens? Initially you will get a particle which will try to form but will not be able to form because you have the surface energy and volume energy terms competing and if you do not have reduction in Gibbs free energy, then the particle will go back. But beyond a critical radius, the volume energy term which varies by r^3 and the surface area which varies as r^2 , initially the square term dominates but beyond a critical value, the cube term starts to dominate and then what you see? A new nucleus is formed at r^* and as you increase the temperature further, you find that the material actually grows further and you have the whole system showing a new nucleus and that is why you see transformation

from spherical to rod like beyond a critical temperature and then as you let it grow, you see the growth further. The whole process is driven by the concept that the new nuclei must have a lower Gibbs free energy. Similarly, you can see that same phenomena occurs in calcium doped systems. You can get compositional dependent phase transformations and you can go from one type of unit cell to the other.

Now what did we say? We said that these have-to-have heroic properties that means they should show ferroelectricity as well as ferromagnetism. So, you have PE loops and MH loops. You can see these materials show clear PE loops, So, they have ferroelectricity in them and they also show magnetic loops that means they have ferromagnetic properties. Although the ferromagnetic properties are weak, but if you deconvolute into the paramagnetic and ferromagnetic components, you will find that the ferromagnetic components are still significant. So, now you have a material which is ferroelectric as well as ferromagnetic and that gives this material the term as a multiferroic properties.

If this is the case, then are the order parameters that means polarization and magnetization are they coupled. So, you characterize these materials, for example, this is the dielectric constant measurements as a function of temperature. They show appearance of a peak. Why does a dielectric constant show a peak? It shows a peak because there is a phase transition taking place in a dielectric material. But if you perform the magnetic measurements, you will find that these are the same temperature at which the materials are showing the magnetic transitions.

So the place at which you see magnetic transition is the same place where you see a peak in the dielectric constant. The change in magnetism is M and here it is polarization which is changing, but they are changing at the same temperature and that is the transition temperature. That means there is a coupling between the two. And if this can be used, then for example, we have seen that this material can be used as a ferroelectric material, as a ferromagnetic material or a material which can be both ferroelectric and ferromagnetic. So, by changing one, you can change the other.

Additional examples of why these materials are known as functional materials, these are materials which are also being used in photoluminescence. And these are being driven by the oxygen vacancies which we induce in these materials by having a divalent dopant which forces the material to have the composition as. So, you induce some oxygen vacancies and because of that you can get luminescence properties near the IR region. So, when you choose for example a material which had a spherical shape and compare the photoluminescence with a material which has a rod like morphology, they are very different. And hence you can tune the photoluminescence properties of these materials by just making these materials at different temperatures.

You can clearly see also by changing the doping element. So, we had doped calcium and obtained the study. So, if you change the dopant, now you use strontium, the nature of the PE loop can also be tuned. You can compare the hysteresis loop which you got for bismuth calcium ferrite with that what you are getting for bismuth strontium ferrite and obviously they are different. What has happened? The host matrix, that is the parent is still remaining the same.

It is still bismuth ferrite. It is only that the solute in the earlier case the dopant was calcium 2 plus and here it is strontium. That is changing and because the ionic radius of these two elements are different, their field of force is different and hence the consequences they generate in a lattice becomes different and the response characteristic of the materials also change. That is why you can tune a property of a material by carefully choosing the dopant. I hope now you understand a slightly higher-level topic that is what are multiferroics. You understand that the material synthesis protocols which have been taught to you can be used to make these high-end materials and these materials have applications ranging from photoluminescence, magnetic card readers, dielectrics, sensors, ion conductors, solar cells to even energy harvesting.

So, one material can be used in at least 8 to 10 applications in today's world. So, they are becoming extremely important and you will find if you pick a scientific journal which is dealing with these materials, then new and novel materials are being reported on weekly basis. These are the references which were followed to get the data and information for today's lecture and you can follow them for further understanding. Thank you very much.