Physics of Functional Materials and Devices

Prof. Amreesh Chandra
Department of Physics
Indian Institute of Technology Kharagpur

Lecture – 46, Week 11
X-ray Diffraction (XRD)

Welcome to the final lecture of week 11. Till now we have been talking to you about materials, how to make them, how they can be used in various devices. And at each point you have seen that before a material goes into a device it needs to be characterized thoroughly. Some of the common techniques which we have mentioned and routinely used to explain the properties of these materials are X-ray diffraction, X-ray photoelectron spectroscopy, SEM, TEM, UV visible spectroscopy, Raman spectroscopy So, in this final phase of the course, let us develop some basic understanding about these characterization tools and how those are used in characterizing the materials or the devices itself. In today's lecture, I will give you a overview of various types of characterization tools which are used for characterizing solid materials mostly, but many of the techniques which we will mention are also used to characterize the alloys and melts. We will spend most of the time of today's lecture in discussing the technique that is X-ray diffraction, how the data is collected in an X-ray diffractometer and finally, how the data is converted to useful information. If you look into the characterization techniques for various materials. you will find that for our studies most of the times we have been talking about the tools which can be classified under four broad headings. These are diffraction techniques, microscopic techniques, spectroscopic techniques or thermal techniques. If you see the diffraction techniques you have three major diffraction based techniques.

Those are X-ray diffraction, neutron diffraction or electron diffraction techniques. If you go and see the techniques which are useful for microscopic characterization. then they can be classified under two subcategories either you can have optical microscope or you can have electron microscopy. Basically, it is based on the source which you use to take the microscopic picture of the sample. If you have electron microscopy where electrons are used as the source to lead to certain phenomena, then you can have scanning electron microscope, you can have transmission electron microscope or you can have high resolution electron microscopy in TEM or SEM.

In SEM again you can have the secondary electron mode or the backscattered mode. In TEM you can have the diffraction mode or the transmission mode. So, there are various types of techniques and they themselves can have various modes of operation and based on the modes of operation you will get different types of information from a given

technique. If you go to spectroscopic technique you can have NMR or NQR. you can have IR, infrared, you can have RAMAN, you can have EPR, you can have UV vis, Mössbauer or electron spectroscopy.

If you look into the thermal techniques, you can have TG, DTA, DSC, dielectrometry, the thermal mechanical analyzers. Similarly, you can have electrical techniques, you can have magnetic techniques, you can have electrochemical measurements, you can have chemical techniques. So, there are various types of characterization techniques and before a material actually goes into a device, it needs to undergo lot many characterizations give the desired response characteristics before the application in a given device is proposed. When you have a protocol to make a material it is also essential that when you move from one batch of material to the other batch. That means, for example, you are producing material today then you produce the same material after 10 days using the same synthesis protocol you should get the similar output from the characterization of the materials which were fabricated from two different patches.

It is essential that the reproducibility of the materials are checked carefully before you actually start using them in devices. Otherwise what will happen? If the material is having different performance, if they are produced in batches then you can never predict what would be the performance characteristics of a device which is being designed and fabricated by utilizing the material which you are fabricating. If you look into the common techniques such as X-ray, it can itself have various types of uses. For example, if you use diffraction, then it is XRD. If you use the absorption of X-rays and see what happens, you have XRFs, you have XANES or if you use the emission of X-rays, you have XRF, EPMA or PIXE.

Now, if you go back to the initial lectures, you will find that we have seen that the solid materials can be either single crystalline, polycrystalline or amorphous in nature. To differentiate amongst these types of materials, one of the most common technique which is used is the X-ray diffraction measurement. how this technique is actually used let us see now. So, what are we going to have? We will have an incident x-ray beam which will be falling on the material. There are various phenomena's which this incident beam can itself generate.

For example, you can have emission of fluorescent x-rays. or you can have heating of the samples. If you can have samples which are thin enough, then you may actually find that you can see transmitted X-ray beam. If you have a phenomena where the beams are not transmitted, but you have scattered X-rays, then you can have two types of scattered X-rays that where energies are modified. or where energies are not modified.

If the energies are unmodified then you have a coherent scattering or if you have a modified energy of the waves which are coming out then you have incoherent and you can get

competent modified X-ray scattering. If you have electron emission taking place then you can have the competent recoil electron, you can have a photoelectron or you can have an electron and each of this phenomena will give you information about a material. Therefore, you will find that the field of X-rays which was discovered in 1895 is amongst the areas for which maximum number of Nobel Prize have been given. So, you can investigate various types of materials and depending upon their crystal structure and lattice arrangements the X-ray patterns will change and why should it change? Let us see the typical reason why there is a diffraction beam. So, if you see a lattice typical 2D lattice, the interplanar distance is d, you have an incident beam.

So, one of the beam is getting diffracted from the top surface, if you have the coherent beam which is moving and passing and hitting the atom at the second layer. Then this coherent beam has to travel an extra path which is going to give you the path length which is this second beam has to traverse that is equal to $2d\ sin\theta$. Now, this is first beam which is diffracted the second beam is getting diffracted. For constructive interference what should happen? You should have the condition that delta that is the path difference $2d\ sin\theta$ should be equal to nλ and n is an integer otherwise you will have a minima and that is why you have the famous Bragg's law $n\lambda = 2d\ sin\theta$. So, for first order, second order, third order you will have n equal to 1, 2 or 3 and if that is the condition which is satisfied you will get a maxima otherwise you will get minima.

There are various types of X-ray diffraction which are performed and you have various types of experimental arrangements. There are three variables what are those either you change the incident radiation or you change the way you are going to mount the sample or the nature of the sample itself and finally, the way you are going to detect the signal which comes out the sample. If you change the variable like radiation you can have a monochromatic or a variable radiation source. based X-ray. If you change the sample that means, you can have a single crystal or powder crystal or you can have thin film based samples.

You can have detectors which can be radiation counters or photographic films or solid state detectors. If you have wavelength as monochromatic, you have a sample which is powder or single crystalline If you use a counter, then the technique which you are going to obtain is diffractometer. If you have a monochromatic wavelength, then you have a powdered sample and you use a film based detector, then you have the Debye-Scherrer or the Gunier type method. If you have a monochromatic wavelength, use a single crystal. film type detector you can have a rotation Weissenberg or precession based diffractometer method.

If you have monochromatic wavelength single crystal as a sample counters as a detector then you have the automatic diffractometers. If you have a wavelength which is variable sample which is a solid piece, detector which is a film then you have the method which is called as the Lave method of X-ray diffraction studies. So, based on the combination you

can have different experimental arrangements each have their own advantages and disadvantages. We know that X-rays are produced when you have a high energy electron impinging on a substrate that is an anode and you have two types of spectrum which is obtained. There is a continuous radiation over which the characteristic X-ray comes out.

For example, if you have copper K $K\alpha_1$ and copper $K\alpha_2$, then you have the characteristic X-rays coming out of the copper anode. So, it depends on what type of wavelength are you talking about. The typical properties of X-rays are EM waves, wavelengths of the order of 0.04 to let us say 1000 angstrom, they can ionize the medium in which they go through, they can cause fluorescence. they emerge from a tube in straight lines, they can induce secondary radiation and they impact the photographic plate on which they fall.

Hence, the typical block diagram of an XRD unit looks like you have a high voltage generator. So, there you will have high V and current source. from this voltage you have the X-ray tube. which leads to the generation of X-rays. So, then you have the slits through which the X-rays pass, then you have the collimator which make sure that the X-ray beam which are passing through are parallel.

Those fall on the sample, they lead to diffraction which passes through the monochromator and the final beam is collected from the detector which is sent to an amplifier and the processing unit. this is what a classical power diffractometer looks like. So, you have various slits and then you have the detector which receives a signal and feed it to the processing unit. You can have various types of anode materials, you can have copper, cobalt, iron, chromium, you can use various types of filters and various voltages can be obtained using these kind of anode materials. So, depending upon the maximum voltage which can be applied you will have the materials giving you various wavelengths which are characteristic to those anode material.

If you look into most of the X-ray diffractometers mostly you use copper based anodes which have a wavelength of 1.54 nanometers or you can also have various types of anode materials and depending on the wavelength you can apply the incident radiation. The filters are basically used to separate out the wavelengths which can be incident on a material. So, you only want one signal to come out, but if you have a material on which there is an incident radiation then you will have first transition $K\alpha$ then you can have $k\beta$. So, you do not want the rays to fall on the sample because then you will have signals coming out for varying orders of wavelength.

So, then you will get multiple peaks, but those are not coming in from one wavelength, but multiple wavelengths and you do not know how to calculate the lattice parameters because $2d\ sin\theta = n\lambda$ which λ are you considering that becomes difficult to pinpoint and hence you must use filters and ensure that you have a monochromatic incident beam falling on the sample. Let us show you how you prepare the sample. So, if you look into the curve

you will find that the way we make the samples is given in this video. You have a motor vessel, you have your sample, then you crush it fine so that the preferred orientation or any kind of particle inhomogeneity is removed. and you are seeing that the pestle is being actually moved in the figure of 8.

So, that you do not introduce any preferred orientation in the sample. Once you have your powder which is finally, crushed then you collect this powder. Once you collect this powder you have to put it on a sample holder. When you have the powder, please make sure that the powders are not wasted because you have spent lot of time in making even 1 gram of powder. So, the powders are carefully collected.

This is a typical glass slide on which the sample can be made or you can have a glass slide made up of steeps. depending upon what your refractometer allows and which in which configuration you are going to carry out the measurement. So, then you put the powder on the groove in the glass slide. Use another slide to press this powder in the groove so that when the slide is actually being placed in the diffractometer that is at the goniometer stage in the diffractometer, the powder does not fall and the top surface should be plain because the distance that is from the source to the sample and from the sample to the detector should be carefully ensured. For that the sample should be carefully made so that the surface of the sample is plain.

So, you put some more powder so that if there is any gaps remaining those are removed and when you make the slide then automatically the excess powder will come out. You must check that the powders are not coming out and then once the slide is ready you can fix it in the coniometer of a X-ray refractometer. This is a typical Rigaku Miniflex laboratory tabletop X-ray refractometer. So, you can see you have the source of X-ray which is having the green light illuminating, then you put the sample and you have the theta to theta rotation. So, the detector is on the right hand side and the X-ray falls on the sample and the signal is received by the detector and then the detector moves in the 2θ angle and what you see is the diffraction at various angles.

This is the typical way in which you carry out the measurement of the samples. You can see that depending upon the nature of the diffraction pattern either you will have from crystalline, polycrystalline or amorphous or monatomic gases. Once you switch on the diffraction measurement conditions, then you will define in the range in which you would like to carry out the measurement. The source will switch on, the shutters will open, x-rays would then fall on the sample, the diffracted beam will pass through the receiving slit. and hit the monochromator from the monochromator it will then go and reach the detector.

The detector will generate the corresponding signal which is received by the data collection unit. So, a compatible computer with the required software. you can see that for this sample which we are characterizing you have a very sharp peak which indicates that you are talking

about a crystalline material. Once you have the data in the full range using the basic knowledge about the crystallography what are the extension rules you can find out what is the Bravais lattice and the crystal unit cell. By knowing that you will know what are the Wyckoff positions that the atoms would be occupied and you can determine the overall lattice quite easily.

What will happen? If you have this material and then you use certain dopants, the dopants would go and change the lattice positions. If the lattice settings are changed that means, you have some displacements from the initial position at which the atoms were sitting at or occupying then these peaks would shift and by the nature of the peak shift, the nature of the splitting of the peaks or by the appearance or disappearance of peaks you can then get information about the phase the phase transformation or lattice and lattice displacements which are taking place. Once you collect this data you will find that the powder refraction pattern which we were only considering as a technique to determine phase has lot of information. If you analyze the background you can Find out information about the sample, the count and scattering, the amorphous content or local order disorder. If you see the reflections, then you can have the position of the reflection of the peak the nature of the peak profile, the intensity of the peak.

If you see the position of the peak, then using that you can get information about the unit cell parameters, the symmetry, the space group and the phase analysis which is qualitative. If you look into the profile and the shape of the profile you can talk about the particle size, the strain in the lattice. If you look into the intensity, then you can talk about the crystal structure, the atomic positions, the temperature factors, the occupancies and then you can talk about the phase analysis quantify it. So, a data which was only being considered as a way to give information about whether a material is single phase or not actually has large number of other informations intrinsically inbuilt inside it. So, if you have only access to X-ray diffraction technique, then also you can characterize the sample thoroughly and you can derive lot of information about a material.

Let us see the patterns which we have shown. as remember we were talking about the CMR materials the lanthanum manganese oxide strontium doped you can see that the peak intensities are changing. Clearly this is an impact of strontium doping in the lanthanum manganese oxide. So, you already have an information the nature of the splitting of the peaks have changed here you see that the peaks are clearly splitted in this case they are merging and here the asymmetry has nearly vanished. Another indication that there is reorientation within the lattice and the unit cell and you are transforming to a new structure. So, peak splitting, position of peak, intensity of peak just by looking at that we have got critical information about the materials.

You had bismuth strontium ferrite similar information you can see that the peaks here are vanishing. That means, your bismuth ferrite material is changing its shape that is the unit

cell of the material is changing as you go beyond let us say 30 percent of strontium in bismuth ferrite lattice. So, you have can easily talk about the phase transition in these materials. materials as a function of topping. You can also study phase transition as a function of temperature.

Just take an X-ray diffraction pattern for a given composition at room temperature and then carry out the analysis at different temperatures. Plot the unit cell parameters as a function of temperature. You can even find out the nature of phase transition in these materials whether it is first order or second order. If you want to go to much more complicated structures, you can clearly see that they can be easily analyzed and here you will find that there is much more broader peak. So, you are going towards the nano size structures and you have the materials which are in nano dimensions.

Clearly, you must have realized now that X-ray refraction is an extremely powerful technique for understanding the properties of materials and therefore, is one of the most used technique in the field of material science. Generally, if you look into the result or the analysis which one performs using the X-ray data it is quite limited, but if you exploit the full extent of the information which is inbuilt inside a given diffraction pattern, you will be getting lot of information about the material which would be very useful when you start using these materials in devices. To develop further understanding about the field of X-ray diffraction and the technique you can go through the literature and these three books which explain the whole concept very nicely. So, thank you for attending the final lecture of week 11 and in the next lecture of which will be the first lecture of week 12 we will carry on our discussion. on characterization tools for understanding the properties of multifunctional materials. Thank you very much.