Non - Metallic Materials

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Module - 09

Characterization of structure, composition, and microstructure of non - metallic materials

Lecture - 46

Introduction of spectroscopic technique: UV - VIS spectroscopy

Welcome to my course Non-Metallic Materials and we are in module number 9 Characterizations of structure, composition and microstructure of non metallic materials and this is lecture number 46 introduction to spectroscopic technique and particularly we will be talking about the UV visible spectroscopy.

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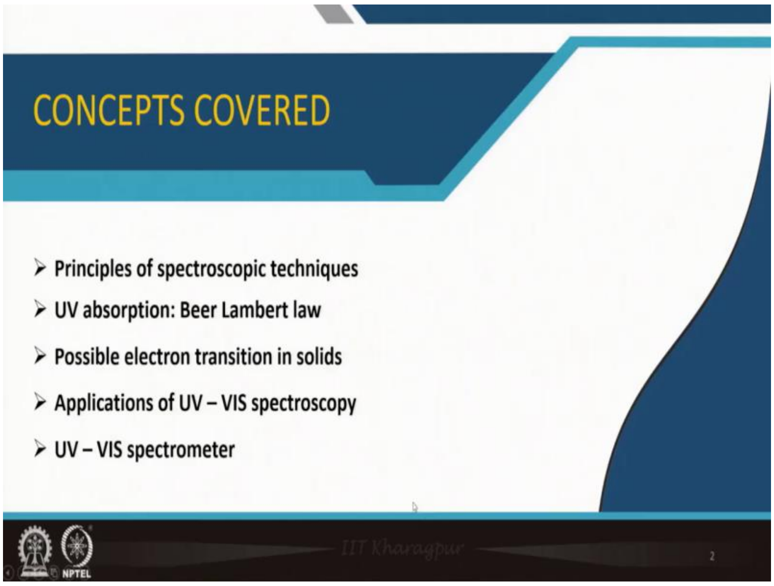

CONCEPTS COVERED

- Principles of spectroscopic techniques
- UV absorption: Beer Lambert law
- Possible electron transition in solids
- Applications of UV – VIS spectroscopy
- UV – VIS spectrometer

So, first I will introduce the principles of spectroscopic techniques and then some details about UV absorption and Beer Lambert law. Then we will talk about possible electron transitions in solids and application of UV visible spectroscopy not a exhaustive one.

But certain important things applicable to non metallic materials will be covered and UV visible spectrometers what is there in that will be introduced. Now the data that you generate out of the UV visible spectrometer. In a separate class I have taught that how to get meaningful information just for a simple transmittance versus lambda data in the optical visible wavelength and the reflectance data altogether.

You can calculate the refractive index extinction coefficient as a function of lambda, you can calculate the Band gap of the material, you can calculate the porosity of the material, you can very precisely calculate the thickness. So, in a separate chapter we have analyzed that how to make use of this type of data what do you get out of a UV visible spectrometer.

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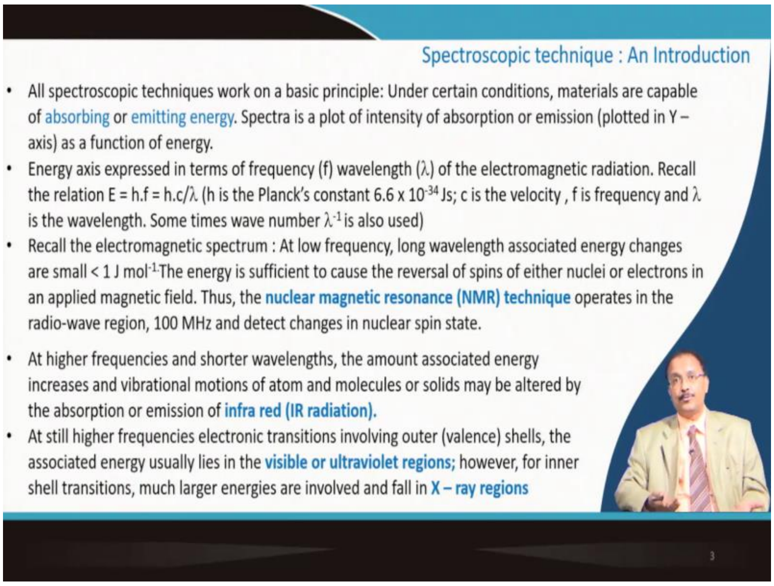

Spectroscopic technique : An Introduction

- All spectroscopic techniques work on a basic principle: Under certain conditions, materials are capable of **absorbing** or **emitting energy**. Spectra is a plot of intensity of absorption or emission (plotted in Y – axis) as a function of energy.
- Energy axis expressed in terms of frequency (f) wavelength (λ) of the electromagnetic radiation. Recall the relation $E = h.f = h.c/\lambda$ (h is the Planck's constant 6.6×10^{-34} Js; c is the velocity , f is frequency and λ is the wavelength. Some times wave number λ^{-1} is also used)
- Recall the electromagnetic spectrum : At low frequency, long wavelength associated energy changes are small < 1 J mol^{-1}. The energy is sufficient to cause the reversal of spins of either nuclei or electrons in an applied magnetic field. Thus, the **nuclear magnetic resonance (NMR) technique** operates in the radio-wave region, 100 MHz and detect changes in nuclear spin state.
- At higher frequencies and shorter wavelengths, the amount associated energy increases and vibrational motions of atom and molecules or solids may be altered by the absorption or emission of **infra red (IR radiation).**
- At still higher frequencies electronic transitions involving outer (valence) shells, the associated energy usually lies in the **visible or ultraviolet regions;** however, for inner shell transitions, much larger energies are involved and fall in **X – ray regions**

So, you know that all spectroscopy technique, not everything I will be covering in this course was some of the spectroscopic technique like UV visible, like infrared X ray photoelectron spectroscopy Raman spectroscopy to some extent will be covered in this course.

So all spectroscopy technique they work on a basic principle that under certain condition the materials are capable of absorbing or emitting energy. So, this spectra so called spectra is a plot of intensity of absorption or emission plotted usually in the y axis as a function of energy.

So, energy axis is defined in terms of frequency which is denoted as f or wavelength lambda of the electromagnetic radiation you are talking about, you may recall the relation equal to h into f where f is the frequency h is a Planck’s constant. So f is replaced by c by lambda c is the velocity of the electromagnetic radiation, f is a frequency, lambda is the wavelength sometimes 1 by lambda is also used then we call this is a wave number.

So, at low frequency long wavelength associated with the energy change or small it is much less than 1 Joule per mole. But this energy is sufficient to cause the reversal of the spin either nuclei or the electrons in a applied magnetic field, because this is basically an electromagnetic radiation.

So the Nuclear Magnetic Resonance for example, which is NMR I will not be covering it in this course that operates in the radio wave region typically 100 megahertz and detect the change of the nuclear spin state, which is so important for the polymer synthesis people who synthesize polymers.

Which is very important at higher frequency and shorter wavelength the amount of associated energy increases and vibrational motion of the atom and molecules of solids may alter by absorption or emission of the infrared. So, we will talk about the infrared spectroscopy in my next lecture.

At still higher frequency if you go electronic transition involves outer valenceiate associated energy, which is usually lies in the visible or ultraviolet regions. So, this topic this today's topic is based on that UV visible spectroscopy for inertial transition much larger energy is involved that is an extra region. So, we talk about x ray photoelectron spectroscopy as a part of another lecture.

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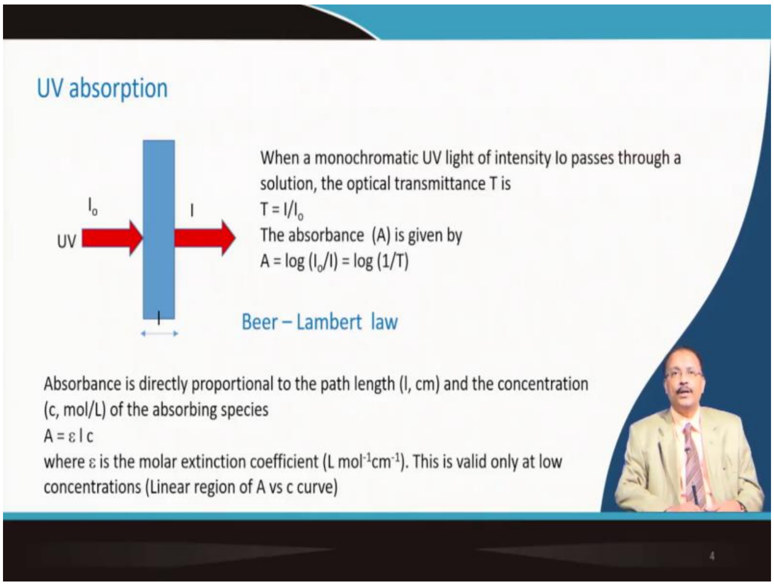

UV absorption

When a monochromatic UV light of intensity Io passes through a solution, the optical transmittance T is
$T = I/I_0$
The absorbance (A) is given by
$A = \log (I_0/I) = \log (1/T)$

Beer – Lambert law

Absorbance is directly proportional to the path length (l, cm) and the concentration (c, mol/L) of the absorbing species
$A = \varepsilon l c$
where ε is the molar extinction coefficient ($L\ mol^{-1} cm^{-1}$). This is valid only at low concentrations (Linear region of A vs c curve)

So, first let us have a look of UV absorption and first consider a monochromatic x ray sorry monochromatic UV light intensity is I 0 that is passes through a solution. So, you have a pivot here and it is filled with a solution. So, the optical transmittance is defined as T. So, the T is the intensity whatever you are getting with respect to the intensity that is incident I by I 0. Now if you consider the absorbance so absorbance is log of I 0 by I, so it is log of 1 by T.

So the Beer Lamberts law that says that the absorbance is directly proportional to the path length, so where from it is passing it is path length. And the concentration of the solution the solute concentration in the solution which are basically the absorbing species which leads to this absorption, so that the transmittance goes down. And here this term epsilon is the molar extinction coefficient and from this relation you can see that dimension is L mole per mole per centimeter.

So, this relation this A equal to epsilon into L into c this is valid when the concentration is low. So, this is a linear relationship who plot A versus c it is a linear relationship and from the slope you can if you know the value of l from the slope you can calculate the value of epsilon. So, it is only valid at the lower concentration of the solute.

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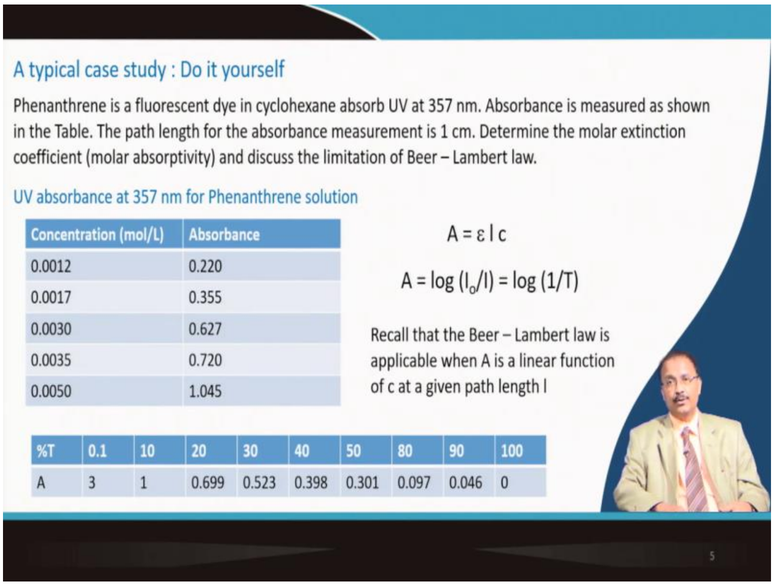

A typical case study : Do it yourself

Phenanthrene is a fluorescent dye in cyclohexane absorb UV at 357 nm. Absorbance is measured as shown in the Table. The path length for the absorbance measurement is 1 cm. Determine the molar extinction coefficient (molar absorptivity) and discuss the limitation of Beer – Lambert law.

UV absorbance at 357 nm for Phenanthrene solution

Concentration (mol/L)	Absorbance
0.0012	0.220
0.0017	0.355
0.0030	0.627
0.0035	0.720
0.0050	1.045

$$A = \varepsilon l c$$

$$A = \log (I_0/I) = \log (1/T)$$

Recall that the Beer – Lambert law is applicable when A is a linear function of c at a given path length l

%T	0.1	10	20	30	40	50	80	90	100
A	3	1	0.699	0.523	0.398	0.301	0.097	0.046	0

Let us take an a example, so we have taken a typical dye a fluorescent dye and which is dissolved in cyclohexane, the dye name is phenanthrene it is a fluorescent dye dissolve in cyclohexane and it absorbs UV at monochromatic UV or 357 nanometers. So the absorbs absorbance is measured as shown in the table, so concentration versus absorbance.

So, you have this table the path length is given as 1 centimeter the value of L. Now we will have to determine the molar extinction coefficient sometimes it is called molar absorptive and also you will have to comment on the Beer Lambert law. So, here you can do this percent transmission it is log of 1 by T. So, you know the percent T, so you can calculate the absorbance and this these are the typical values that you will get.

So the Beer Lambert law it says A equal to epsilon into l into c and A is defined as log of I 0 by I; that means, log of 1 by t. So, you can just work it out so you remember that what you will have to do that absorbance will have to plot with the concentration and you will have to remember that this Beer Lambert law is applicable only when A is a linear function of c.

So, from the slope of this linear curve you can calculate the value of epsilon. In fact, if we have this 2 value you can always calculate the slope, you have y 1 and y 2 you have x 1 and x 2. So, the slope is y 2 minus y 1 by x 2 minus x 1. So, you can easily calculate the value of epsilon, but you can go ahead and plot it in a proper way do a linear fit and estimate the value and compare with the value that you can readily say.

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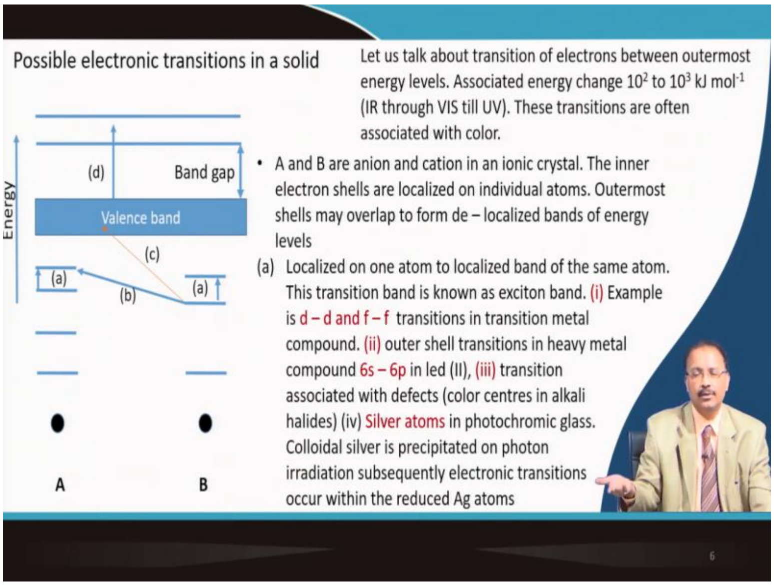

Possible electronic transitions in a solid

Let us talk about transition of electrons between outermost energy levels. Associated energy change 10^2 to 10^3 kJ mol^{-1} (IR through VIS till UV). These transitions are often associated with color.

- A and B are anion and cation in an ionic crystal. The inner electron shells are localized on individual atoms. Outermost shells may overlap to form de – localized bands of energy levels

(a) Localized on one atom to localized band of the same atom. This transition band is known as exciton band. (i) Example is d – d and f – f transitions in transition metal compound. (ii) outer shell transitions in heavy metal compound 6s – 6p in led (II), (iii) transition associated with defects (color centres in alkali halides) (iv) Silver atoms in photochromic glass. Colloidal silver is precipitated on photon irradiation subsequently electronic transitions occur within the reduced Ag atoms

Now in case of a solid there are various possible electron transition that can take place. So, let us talk about the transition of electron between outermost energy level, because it is the energy is low this electromagnetic energy it is starting from say red region to UV region. So, about 200 to 900 nanometer or 800 nanometer that we are talking about.

So, this associated energy if you can calculate this is about 100 to 10 to the power 2 to 10 to the power 3 kilo Joules per mole and that is why it is IR through visible till UV. So, this kind of transition often as I also described earlier it is related to color. So, we can consider A and B A maybe A cation and B maybe an anion and vice versa. So, inner electron shells are localized as you can see these are all localized shell and outermost shell they may overlap. So, to form a de localized band of energy.

So, first let us took take a look of this a transition. So, it is localized on 1 atom to the localized band of the same atom, so this kind of transition I am talking about here also it is possible from the this atom to the same localized atom. So, various possibilities are there it could be a d-d or f-f kind of transition in case of transition middle cation is involved.

It could be a outer shell transition in case of heavy metal, say for example 6 s 6 p that type of transition could be there. Transition associated with defects color center in alkali halides that also gives this a type of transition or a practical application silver in the photochromic glass you will know that when UV is absorbed, then you get a darkening in the photochromic glass.

So, that is nothing but precipitation of colloidal silver and once UV is done then again it is transparent. So, those kind of electronic transition which occur in the reduced silver iron these are the specific example of this type of transition.

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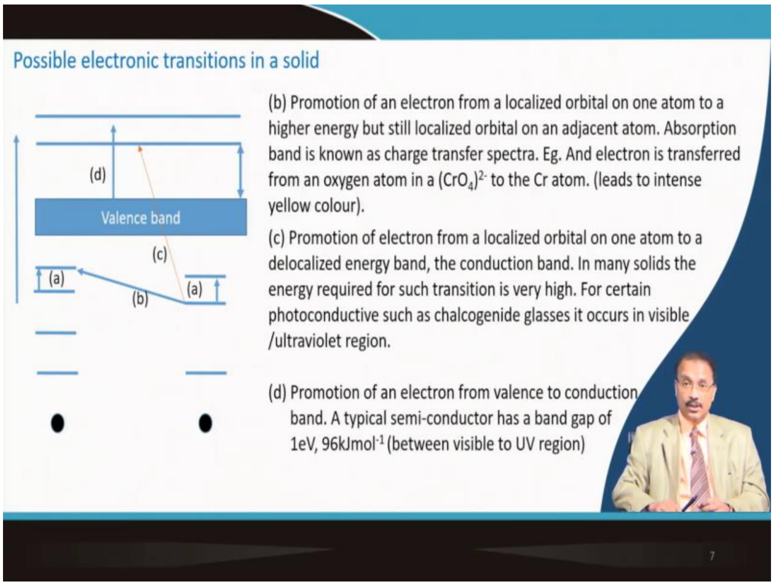

Possible electronic transitions in a solid

(b) Promotion of an electron from a localized orbital on one atom to a higher energy but still localized orbital on an adjacent atom. Absorption band is known as charge transfer spectra. Eg. And electron is transferred from an oxygen atom in a $(CrO_4)^{2-}$ to the Cr atom. (leads to intense yellow colour).

(c) Promotion of electron from a localized orbital on one atom to a delocalized energy band, the conduction band. In many solids the energy required for such transition is very high. For certain photoconductive such as chalcogenide glasses it occurs in visible /ultraviolet region.

(d) Promotion of an electron from valence to conduction band. A typical semi-conductor has a band gap of 1eV, 96kJmol^{-1} (between visible to UV region)

Second is this b type promotion of an electron from a localized orbital on 1 atom to a higher energy level, but still localized orbital on the adjacent atom. So, these absorption band is known as charge transfer spectra. Now an electron is transferred say from oxygen in this chromite radical C r O 4 to the central chromium atom and it leads to a very bright yellow color.

So, this kind of transition is also possible from here to here. Third one is the promotion of the electron from a localized orbital on 1 atom to a delocalized energy band is the conduction band, in many solid the energy for such transition is very high. But for certain photoconductive material like chalcogenide it occurs in the visible or ultraviolet region, otherwise in many of this so called ceramics you do not have this much energy.

So, in the UV visible region this energy is not sufficient and finally it is a band to band transition promotion of electron from one balance band to the conduction band a typical semiconductor has a bandgap say at 1 electron volt. So, 96 kilo joule per mole ah, so that is in between visible and UV region. So this type of transition that is possible in a solid state material.

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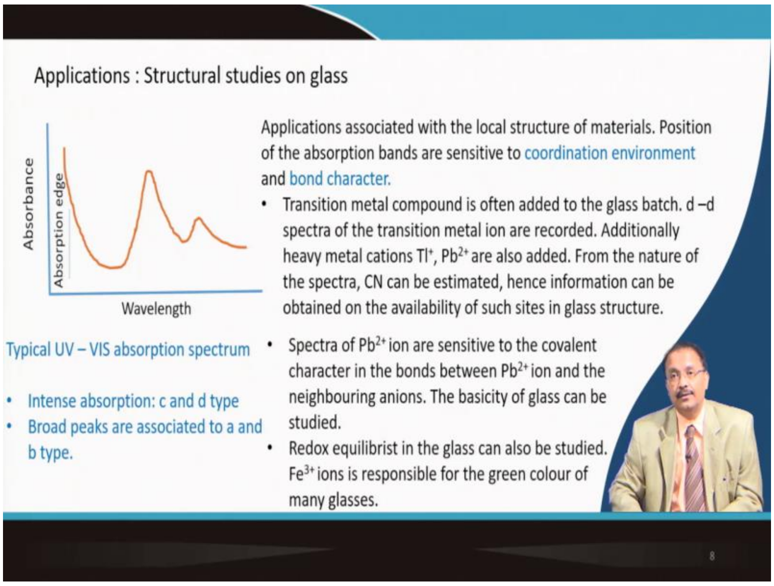

Applications : Structural studies on glass

Typical UV – VIS absorption spectrum

- Intense absorption: c and d type
- Broad peaks are associated to a and b type.

Applications associated with the local structure of materials. Position of the absorption bands are sensitive to coordination environment and bond character.

- Transition metal compound is often added to the glass batch. d –d spectra of the transition metal ion are recorded. Additionally heavy metal cations Tl^+, Pb^{2+} are also added. From the nature of the spectra, CN can be estimated, hence information can be obtained on the availability of such sites in glass structure.
- Spectra of Pb^{2+} ion are sensitive to the covalent character in the bonds between Pb^{2+} ion and the neighbouring anions. The basicity of glass can be studied.
- Redox equilibrist in the glass can also be studied. Fe^{3+} ions is responsible for the green colour of many glasses.

Now one can apply this absorbance spectra. So, it typically visible absorption spectra you can see it here and we can use this to study the structure of the glass, glass already you know you have studied glass part of the other lecture. So, here we are seeing that there is an intense absorption which is could be c type or d type whatever I shown earlier.

So, this is in the UV region and the broad peak here this absorption is the hypothetical material that is associated to either a or b type of transition which we talked about. So the application that is associated with the local structure of the material position of this absorption bands are sensitive to the coordination environment and the bond length.

So, this feature is actually used in order to understand the structure of the glass. So, transition metal compound they are often added in the glass batch for the coloration effect right. So, for different types of color if you want to have within the glass you add it the transition metal oxides. So, this d-d spectra of the transition metal ions are recorded, additionally heavy metal cation like tellurium or led they are also added in glass batch.

So from the nature of the spectra the coordination number can be estimated. How exactly it is done this is not part of this lecture, but this is just for your information the coordination number and the bond distance short bond distance that can be gotten from this absorption peak. So, this information can be obtained and availability of this type of sight of this cation that can easily identified from this absorption spectra of this pertinent glasses.

So spectra of led plus 2 they are very sensitive to the covalent character of the bond between led ion and the neighboring anions. So, that eventually can identify the basicity of the glass that also can be studied by UV visible spectra. The other important thing is the Redox type of cation that is present particularly for the optical fiber you do not want any kind of coloration. So, I ironoxide this plus 3 iron in plus 3 where responsible for green color in many glasses.

So the glass fibre if you do this UV visible spectroscopy then that will give you an idea that whether it is free from those kind of transition metal cation ah. So, there this kind of thing can be used.

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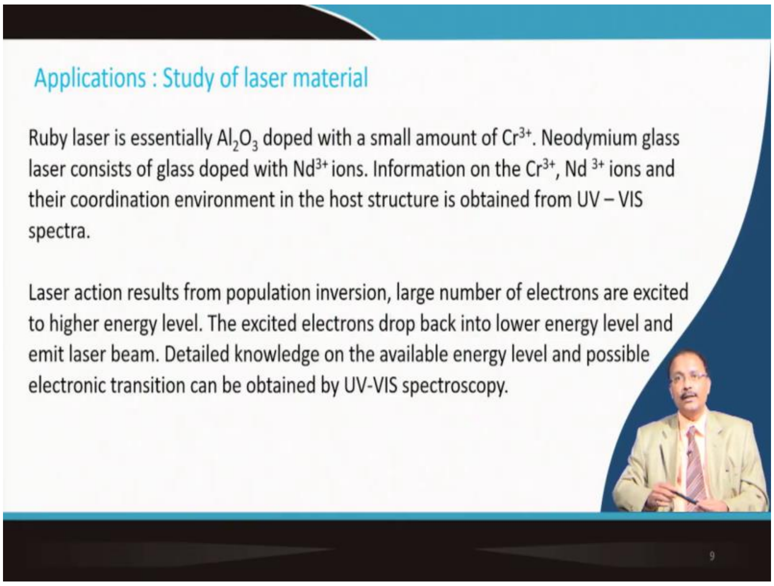

Applications : Study of laser material

Ruby laser is essentially Al_2O_3 doped with a small amount of Cr^{3+}. Neodymium glass laser consists of glass doped with Nd^{3+} ions. Information on the Cr^{3+}, Nd^{3+} ions and their coordination environment in the host structure is obtained from UV – VIS spectra.

Laser action results from population inversion, large number of electrons are excited to higher energy level. The excited electrons drop back into lower energy level and emit laser beam. Detailed knowledge on the available energy level and possible electronic transition can be obtained by UV-VIS spectroscopy.

We have also talked about the laser material aluminum oxide with small amount of chromium oxide or neodymium glass laser it consists glass doped with neodymium ion. So, information on chromium ions, neodymium ions and they are coordination involvement in the host structured that is obtained from UV visible.

So, the laser action results from the population inversion we already talked it about in one of my earlier lectures. So, large number of electrons are excited to higher energy level, the excited electron they drop back to the lower energy level and emit the laser beam. So, the detailed knowledge of the available energy levels and possible electron transition this can be obtained by the so called UV visible spectroscopy.

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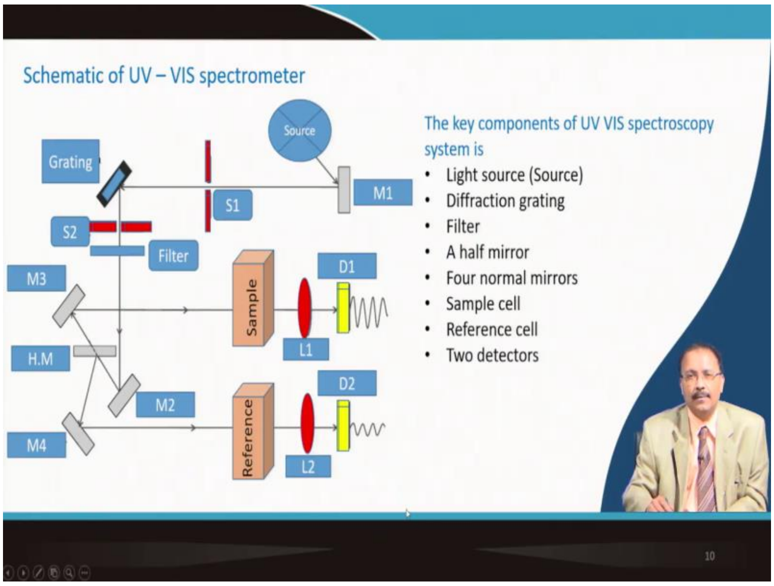

Schematic of UV – VIS spectrometer

The key components of UV VIS spectroscopy system is

- Light source (Source)
- Diffraction grating
- Filter
- A half mirror
- Four normal mirrors
- Sample cell
- Reference cell
- Two detectors

So, if you see the schematic of a UV visible spectrometer it looks something like this, it looks little bit complicated, but it has main sources like you have a light source and this light source starting from UV and other type of sources, so different lamps are there. Then you have a diffraction grating which is nothing but a prism which can make it monochromatic.

You have filter a half mirror somewhere here and 4 normal mirrors 1, 2, 3, 4 and you have sample cell and reference cell for liquid or for solid sample and you have 2 lens and 2 electronic detectors. So, that constitutes your spectrometer to study this material.

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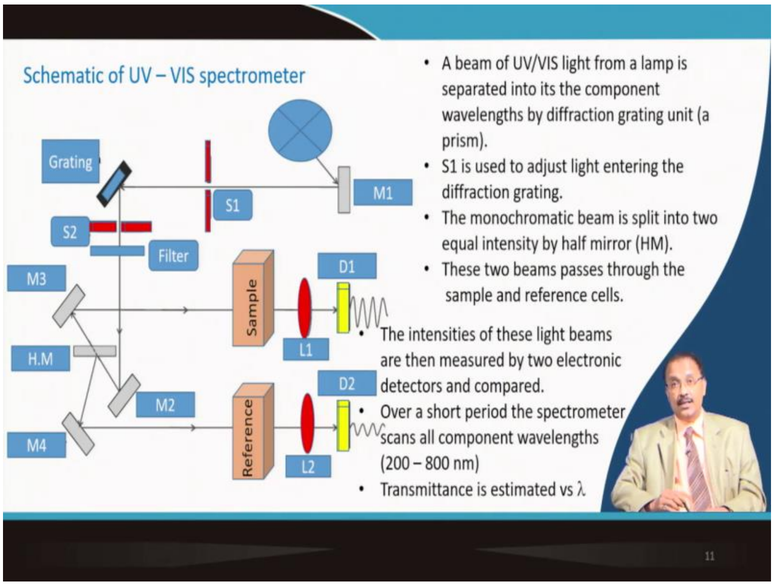

Schematic of UV – VIS spectrometer

- A beam of UV/VIS light from a lamp is separated into its the component wavelengths by diffraction grating unit (a prism).
- S1 is used to adjust light entering the diffraction grating.
- The monochromatic beam is split into two equal intensity by half mirror (HM).
- These two beams passes through the sample and reference cells.
- The intensities of these light beams are then measured by two electronic detectors and compared.
- Over a short period the spectrometer scans all component wavelengths (200 – 800 nm)
- Transmittance is estimated vs λ

Now first a beam of UV or visible that is separated it is component wavelength using this diffraction grating, because you know that in diffraction it will make in a prism it will make it monochromatic. So, this let S 1 is used to adjust the light which is entering into the diffraction grating, then the monochromatic beam is split into 2 equal intensity.

So, one is going here and then this half mirror one is going here and coming to the reference and another one is going to the sample. So, the monochromatic beam is split into 2 equal intensity by this half mirror and this two beam passes through the sample and reference cell.

So, the intensity of these light beams are then measured by 2 electronic detector say D 1 and D 2. So, over a short period of time the spectrometer scans all component wavelengths starting from 200 to 800 nanometer and each time your sample is here and a reference material is here this intensities are compared and basically what you get a transmittance as a function of lambda which you scanned.

In case of reflectance something similar is happening but this thing is this configuration is little bit changed ah. So, that reflectance spectra is actually recorded. So, reflectance and transmittance if it is there then absorbance also can be estimated, so basically reflectance and transmittance are measured in a automated modern UV visible spectrometer.

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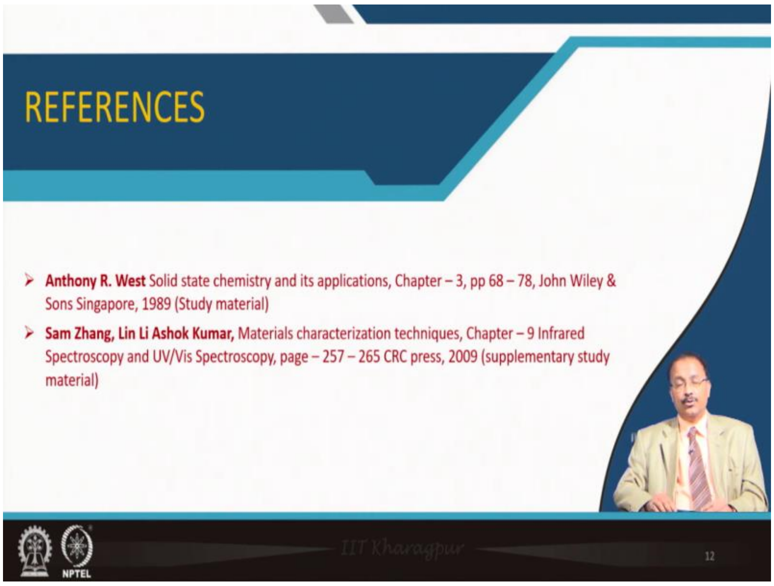

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- **Anthony R. West** Solid state chemistry and its applications, Chapter – 3, pp 68 – 78, John Wiley & Sons Singapore, 1989 (Study material)
- **Sam Zhang, Lin Li Ashok Kumar,** Materials characterization techniques, Chapter – 9 Infrared Spectroscopy and UV/Vis Spectroscopy, page – 257 – 265 CRC press, 2009 (supplementary study material)

So, the part of this lecture you can read from a book by Anthony R. West Solid state chemistry chapter 3 and also material characterization technique by Zhang, Lin Li and Ashok Kumar chapter 9, the chapter says infrared spectroscopy and UV visible spectroscopy.

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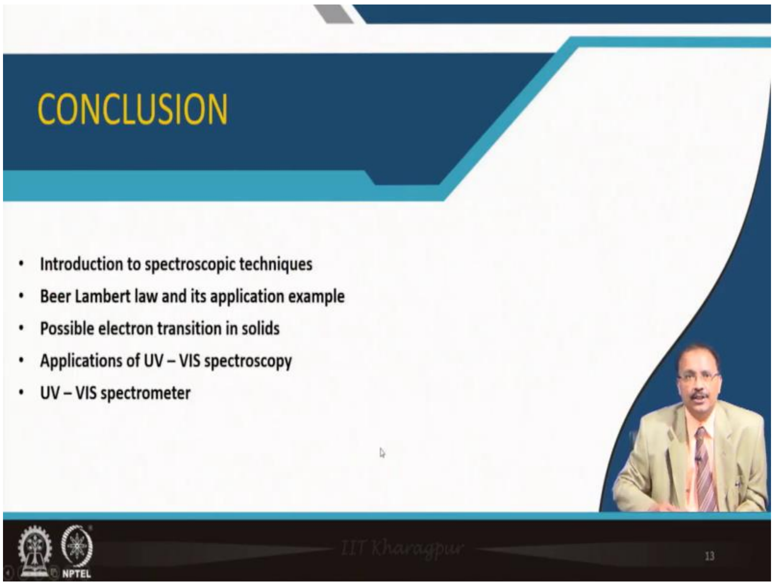

CONCLUSION

- Introduction to spectroscopic techniques
- Beer Lambert law and its application example
- Possible electron transition in solids
- Applications of UV – VIS spectroscopy
- UV – VIS spectrometer

And in this particular lecture we introduce different spectroscopy technique mostly we talked about NMR, we talked about UV visible, IR and extra photoelectron spectroscopy. And then we define what is this Beer Lambert law and it is application example then possible electron transitions in solids they were illustrated. And two prominent applications of UV visible spectroscopy we have highlighted. And finally a very basic look at a modern UV visible spectrometer is illustrated.

Thank you for your attention.