Materials Chemistry
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Module - 6
Lecture - 5
Phosphor Materials

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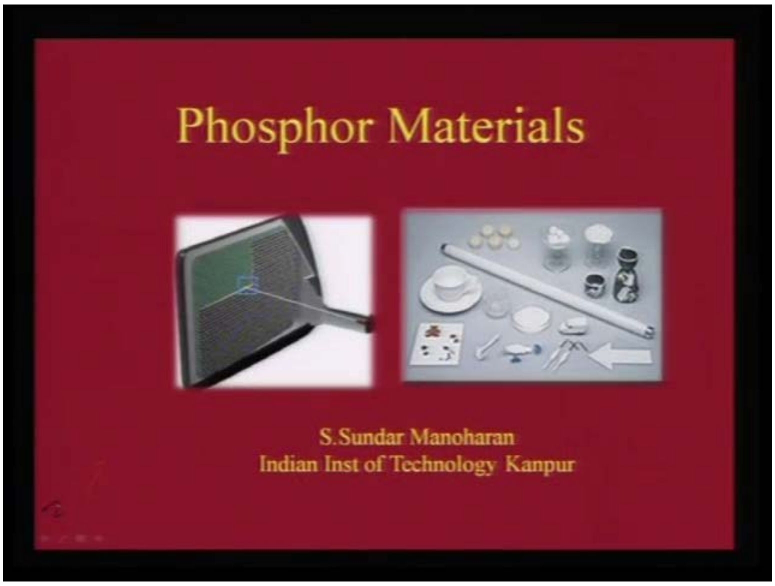

In the past few lectures on photonic materials. We have looked more at the possibility of organic photonics, where organic molecules can be used for optoelectronic applications, specially we have seen the examples of how organic molecules both small molecule and organic polymers, how they can be used for device applications as OLED displays. And also in another lecture we have seen the importance of organic molecules in solar cells. Today I am going to talk to you about a group of inorganic compounds, which is actually holding a billion dollar industry for more than 20 years now.

And they are generally categorized as phosphor materials, and as you would see in the cartoons in the slide, there are variety of applications that you can engineer using this set of molecules or inorganic compounds, they are usually oxides or sulphides. So, in this lecture, I will try outline the importance of this molecules or oxides. And then how this is governing the principle of tuning colours in display devices.

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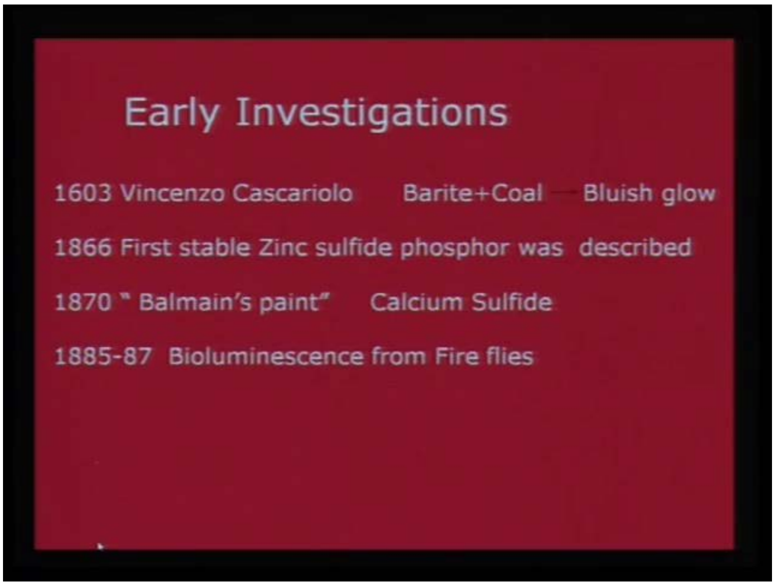

Let me start first with what this phosphor history is all about, and where it emerged from it actually started as early as 1603. We have documents where a Italian scientist he is alchemist actually he found that barite which is nothing but barium sulphate when it is heated with cold, on heating he observed a bluish glow which is actually due to barium sulphite which formed.

So, since then there has been several re-visitation of this issue of glowing materials, 1866 first stable zinc sulphite phosphor was described, and then calcium sulphite was discovered in 1870; and 1885-87 the concept of bioluminescence from fire flies was also observed. So, these are some of the milestones in this phosphor research, and in the last 20, 30 years it has taken a very different turn, and we can look at it.

Before I define what this phosphor material are, and where we can see them operating, just give you basic definition of the different types of luminescence phosphors that are possible. When we say luminescence it means we are talking about light emission, and this can actually come from two process, which are fundamental to photochemistry, and those are called as fluorescence and phosphorescence.

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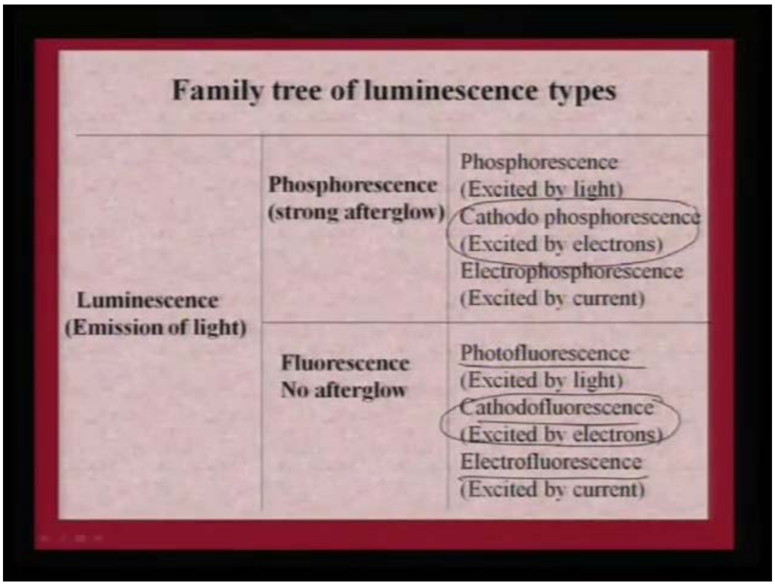

Fluorescence is a fast decaying process, and the decay of this excited molecule happens in the order of 10 power minus 15 seconds therefore, there is no afterglow it just rapidly quenches. Then you have a spin forbidden transition which is called as phosphorescence, and this is because of it is spin forbidden nature, it is a slow emission process therefore, we can call this as a strong afterglow. And in both categories we also have a subsets of this process manifested, one is phosphorescence which is excited by light, cathodo phosphorescence when it is excited electrons, electrophosphorescence when it us excited by current.

Same is true for fluorescence; you have electrofluorescence, cathodofluorescence and photofluorescence. So, as you would see here, the category of light emission actually comes from what is the initiating process, and the case of phosphorous with either cathodo phosphorescence or cathodofluorescence is a well-established one out of all this possibilities. And this is basic to the CRT tube applications which I will come in the next few slides. So, when we talk about luminescent materials, we should also know that how much ever we engineer, the mother nature has also gifted many luminescent materials.

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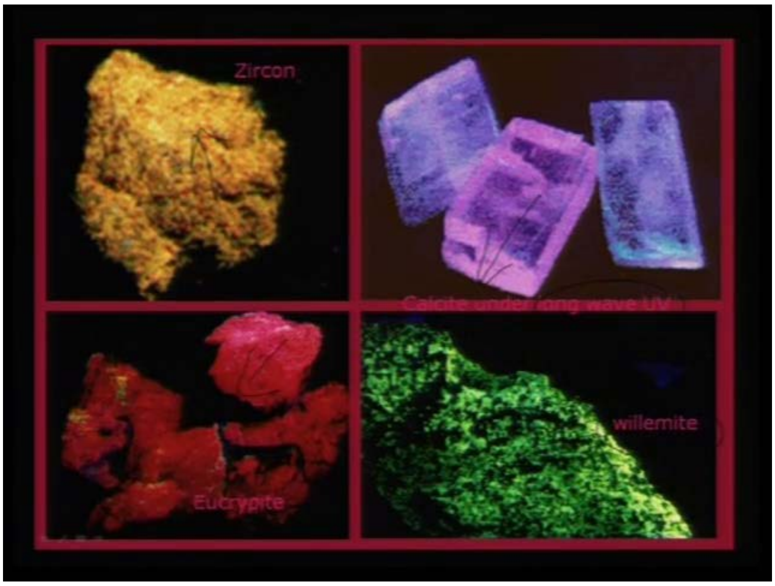

Which are found as it is without even any refining process, you can isolate those luminescent materials in nature. For example, calcite itself is a blue light emitting one, if you can excite it with the long wave UV, so this is a calcite crystal which is glowing under UV radiation. And zircon is here, and that shows a dominating yellow and then you have eucryptite which is mainly a europium doped phosphor, and then willemite is there, then we also have a combination of several of this phosphors, which is available in nature.

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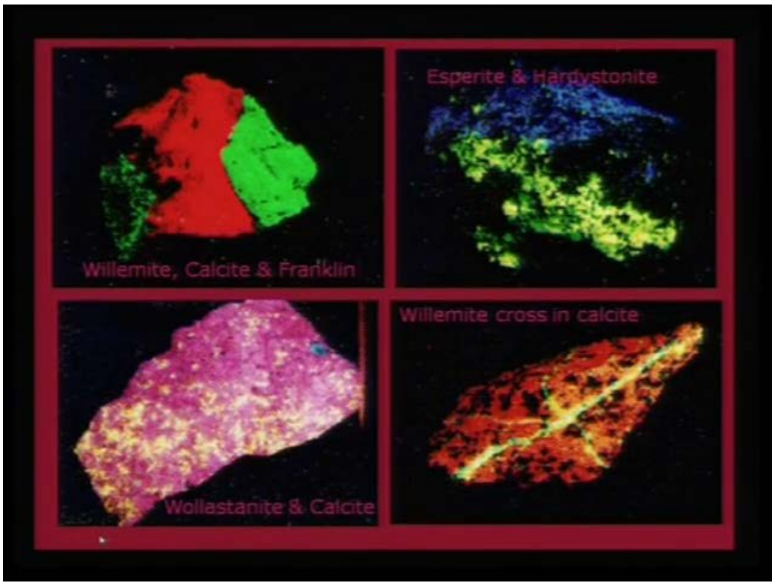

As it is as willemite, calcite, franklin all these are isolated as minerals, so as you would see here under UV radiation several lights with very strong fluorescence can be obtained. But, this you should also respond to cathodo luminescence, some of these materials may not be a active material for the process by which it is driven, either by current or by cathode rays or by photo. So, depending on the nature of application these materials can find use in devices.

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And again this is the example of bioluminescence were the fire fly actually is glowing, this is the fire fly without illuminating the light, but when it is actually luminescing it glows like this. And that the basic compound that is responsible for chemiluminescence or bioluminescence is this compound luciferin which emits in dark. And the basic functional groups here are thio-sol groups, which becomes very important and to isolate this compound it is a billion dollar work. In fact, if you see in commercial catalogues, you would see 1 microgram sold for 100 dollars, so to isolate these compounds are very expensive. Therefore, although it is very highly luminescing with very good quantum efficiency, these molecules have not been used per say.

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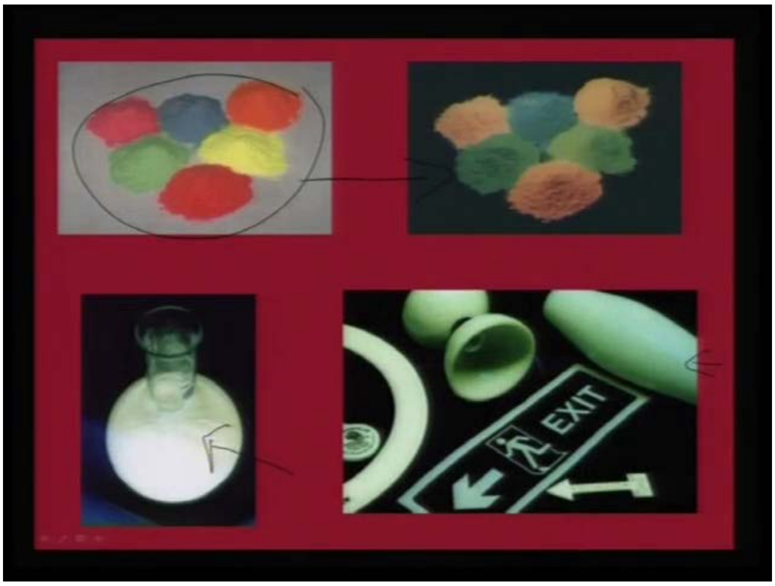

But, apart from the naturally occurring luminescent materials, we also have manmade materials, and you can see all these sign boards and different ceramic components glowing in the dark. Mainly because of a variety of compound that you can prepare, and in the UV light, they show the same colour and in darkness you can see that they are glowing. And it is also possible for us to generate white light emitting phosphors by combination of these colours, so these are manmade phosphors, and this can also find use in device applications. And here is another example of how glow in the dark phosphors can be seen.

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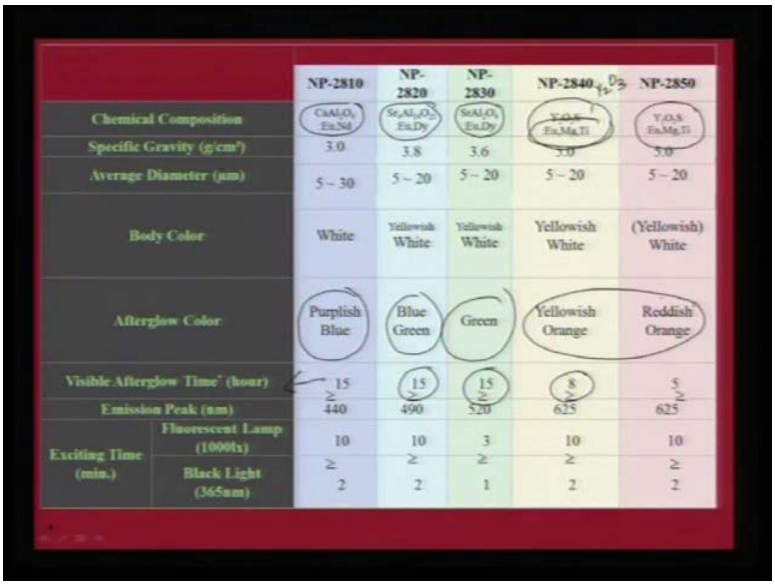

		NP-2810	NP-2820	NP-2830	NP-2840	NP-2850
Chemical Composition		$CaAl_2O_4$ Eu,Nd	$Sr_4Al_{14}O_{25}$ Eu,Dy	$SrAl_2O_4$ Eu,Dy	Y_2O_2S Eu,Mg,Ti	Y_2O_2S Eu,Mg,Ti
Specific Gravity (g/cm^3)		3.0	3.8	3.6	5.0	5.0
Average Diameter (μm)		5 ~ 30	5 ~ 20	5 ~ 20	5 ~ 20	5 ~ 20
Body Color		White	Yellowish White	Yellowish White	Yellowish White	(Yellowish) White
Afterglow Color		Purplish Blue	Blue Green	Green	Yellowish Orange	Reddish Orange
Visible Afterglow Time* (hour)		15 ≥	15 ≥	15 ≥	8 ≥	5 ≥
Emission Peak (nm)		440	490	520	625	625
Exciting Time (min.)	Fluorescent Lamp (1000lx)	10 ≥	10 ≥	3 ≥	10 ≥	10 ≥
	Black Light (365nm)	2	2	1	2	2

Now, just to satisfy our curiosity, I would like to list some of the afterglow phosphors which show phosphorescence during their emission. And some of the candidates are yttrium oxide doped with sulphur, and as you would see this is nothing but Y2O3 one of the oxygen is replaced fully by sulphur. And then the dopants here are europium,, magnesium or titanium, which will actually generate the excited states that will be responsible for the phosphorescence here.

And one thing that I would like to draw you attention is to the visible afterglow time in these phosphors, you can see they can radiate light for over 15 hours,. and that is the speciality of this sort of phosphors. And if you can see the other phosphors they are all mostly alumina based, so it is mostly yttrium based oxides or it is alumina based oxides, and these oxides are usually termed as sam.

If it is strontium aluminium magnesium oxide or bam oxides, so depending on the constituents they form a different story in terms of its light output. As you would see calcium aluminate with europium is very selective for purplish blue, strontium aluminates for blue and bluish green, and then strontium aluminate the lower analogue with europium is specially meant for green fluorescence. And as you would see here red and yellow is mostly to do with yttrium based phosphors.

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And these phosphor materials are mainly used in phosphor labs, and today the latest generation lights or bulbs are the CFL ones, which has a very strong coating of the fluorescence. And as you would see these oxides have a variety of applications, and we will specifically look into phosphors which are used in TV screen. So, what are these phosphors are an established materials technology, compared to liquid crystals and other light emitting polymers.

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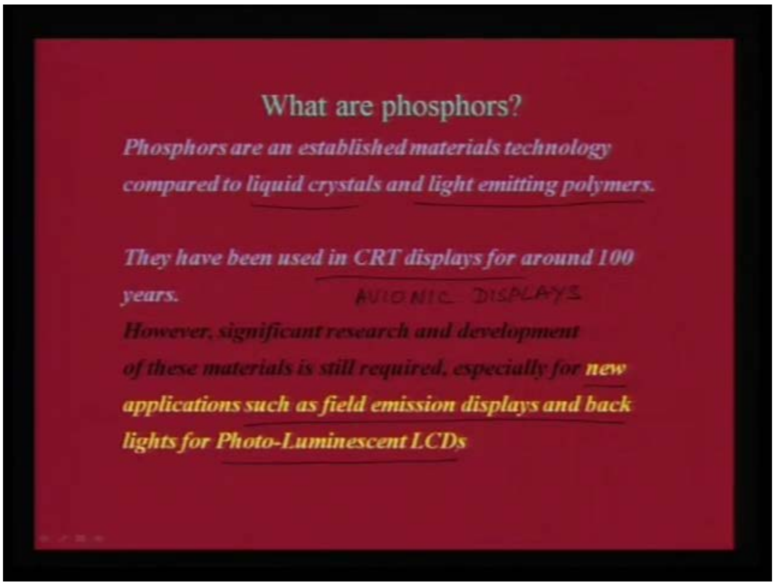

And they have been used in the cathode ray tube displays for around 100 years, now these phosphors are also used in avionic tube applications, and avionic displays. And nothing but all the screens that you see in a cockpit is all totally driven by the CRT tubes, and those CRT tubes are usually 6 inch display stuff. So, all these avionic applications are totally taken over by this CRT phosphors, now new research have actually focused on field emission displays, and on photo luminescent LCDs which are already coming into market, and the phosphors find a special role in that.

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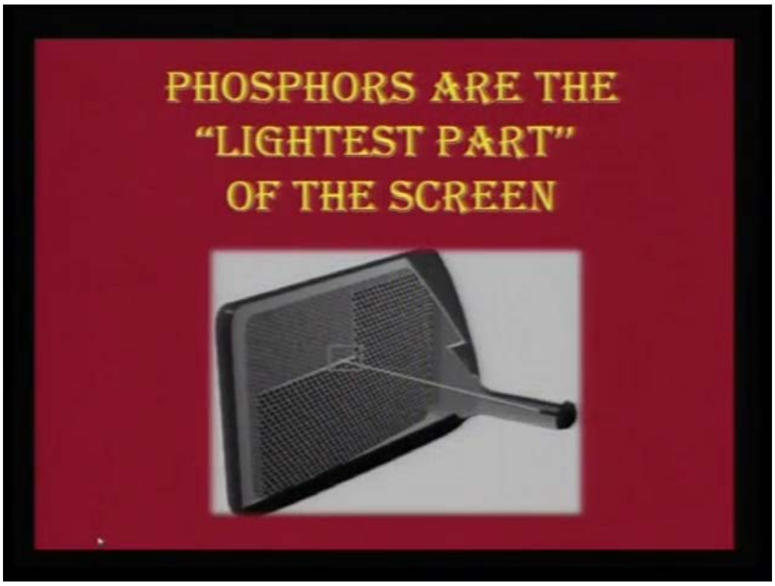

When you look at the CRT tube, now you would wonder where exactly these phosphors come into picture, but actually the phosphors are the lightest part of the screen, as somebody put it. Because, the panel that you are facing which is the class panel is actually containing phosphors in a very, very small units as triads, I will show the contour of how this phosphors are coated on the glass screen.

And this is a very well established technology now; this technology cannot be substituted by even the nanotechnology that we are talking about, because the shear temptation for us would be to immediately try to make these phosphors in nano scale. But, this particular technology is well proven not for nano, but for a micron technology, as I would point out in other slides, you would be convinced that CRT phosphor does not necessarily need a nano phosphor, but you can actually operate with a micron sized phosphor materials. So, in the CRT tube the main display event that is happening is the light that is coming out, apart from all the engineering technology that is there. And the lightest part is nothing but the screen which has the fluorescent material.

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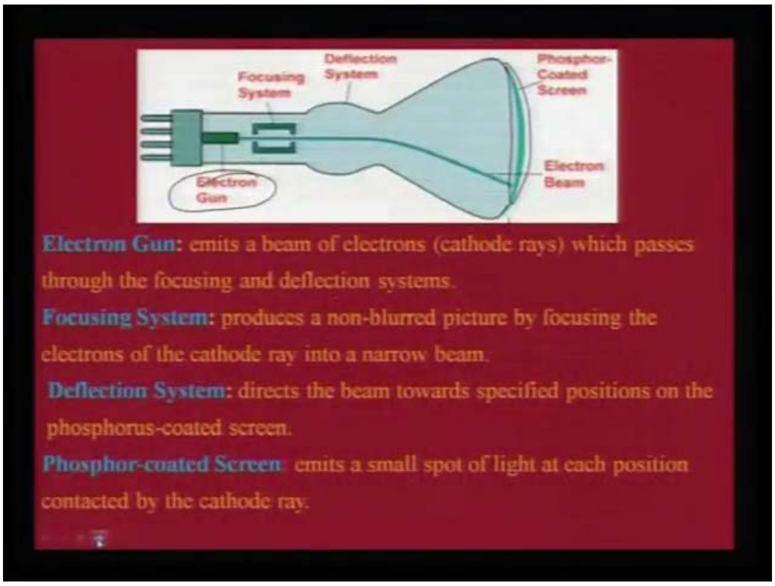

Therefore, this is a simple contour of your CRT tube, this is you cathode ray gun through which you can actually using a deflection system. You can move this electron beam up and down therefore, it scans 100000 times per second, in such a fashion that you get a complete continuous display of your image. And in this place the anode is actually bearing your phosphor coated screen, so anode is nothing but a graphite coating. And on the graphite coating you can pattern these phosphors, so this is where the phosphors lie.

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And to the present generation this may be a old time photograph, because this sort of monitors existed in the early 80s, and these are called the monochrome displays. Today nobody has seen or it is reddened, nobody knows about a monochrome display, but these displays were the first generation displays, when the computer came into picture in Indian market. And as you would see here, we all have lived with just a monochrome display for at least 5 years, and then the technology transcended to full colour display, so we will see those events more carefully.

So, when we look at a cathode ray tube, this is how the simple operation is electron gun actually brings out a ray which is channelized through an add on. So, the direction is along this way, when it goes through this you can actually deflect with a magnetic field and based on the deflection, you can try to scan this electron beam or bend this electron beam wherever you want. So, the cathode ray can actually hit the screen million times in a second, as per the way the deflection is contour.

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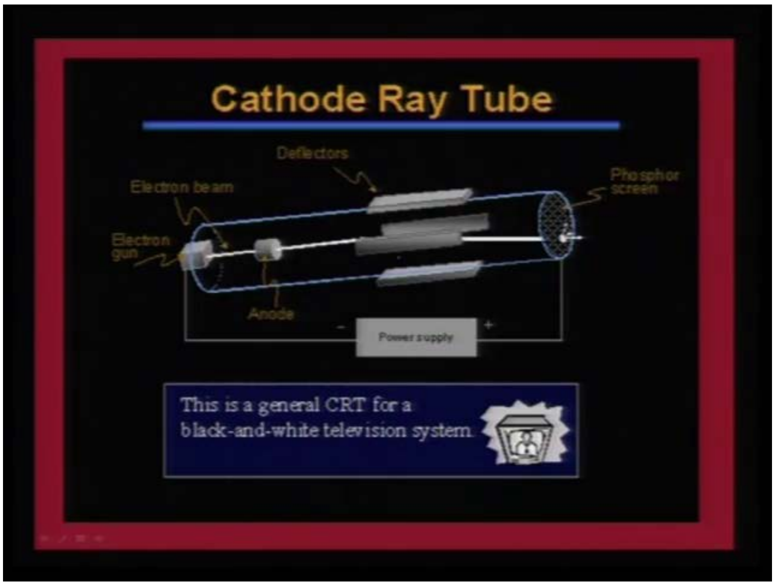

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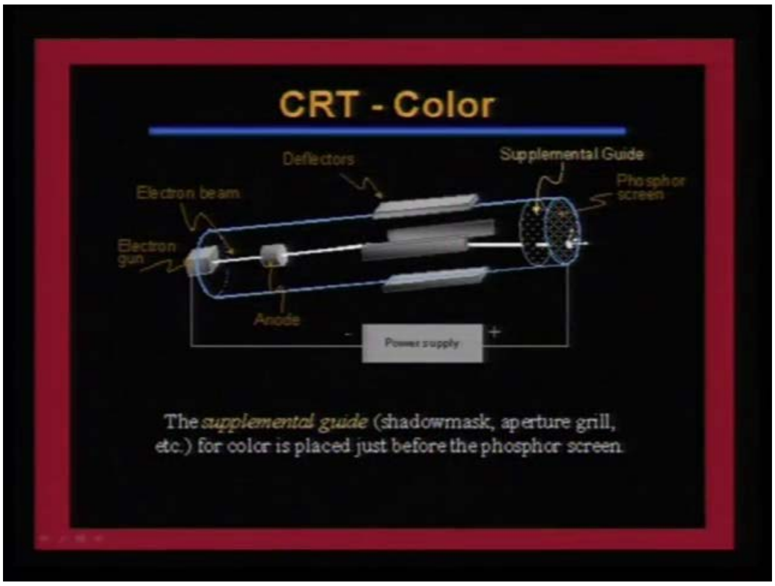

Now, we can do one more thing, we can have a supplement guide in front of the phosphor screen, and in that case you will be able to even channelize through this supplement guide, which has lot of holes. You can channelize how this electron beam can selectively hit some of the phosphor material on the screen, so this supplement guide is also called the shadow mask. And if you have this shadow mask in front of the phosphor screen, then that means, you are talking about a colour monitor system. But, if it is a monochrome material you do not need this supplement screen or a supplemental guide or the shadow mask, so we will see how this shadow mask will work.

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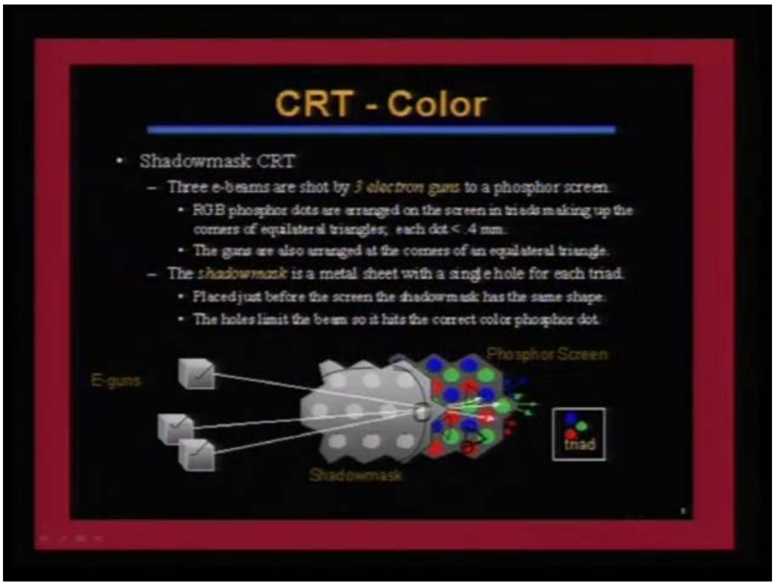

And in case you have a shadow mask like this which is in the gray image, then in a typical CRT colour monitor you would not use just 1 gun, but you would use 3 guns. And each one of this gun is maintained at a different potential to excite the corresponding colour, so the colours are actually made like triads. If you can follow here I can draw a triad like this at any point any given place, so each triad forms a pair. And each of this triad can actually be injected with an appropriate cathode ray which has a different energy, and depending on that the mixing of this colour occurs.

So, if you want more of red colour dominance, then you need to pump in more cathode ray energy, so that you get this on a brighter proportion compared to blue and green. So, in a colour monitor you actually have 3 electron guns doing the job, and each of this gun will go through one single RFS in the shadow mask, which will in turn do the right colour mixing. So, when all these three hit at three different colours, then the actual colour mixing will happen.

And in a typical TV screen, you would see this sort of a panel and each one is separated by few angstrom, thickness. So, in essence you would actually see a triad of this sort, because this will be finally, chipped into micro pixels. So, each pixel would have a combination of triad, so this is how the phosphor coating is actually made on the electrode.

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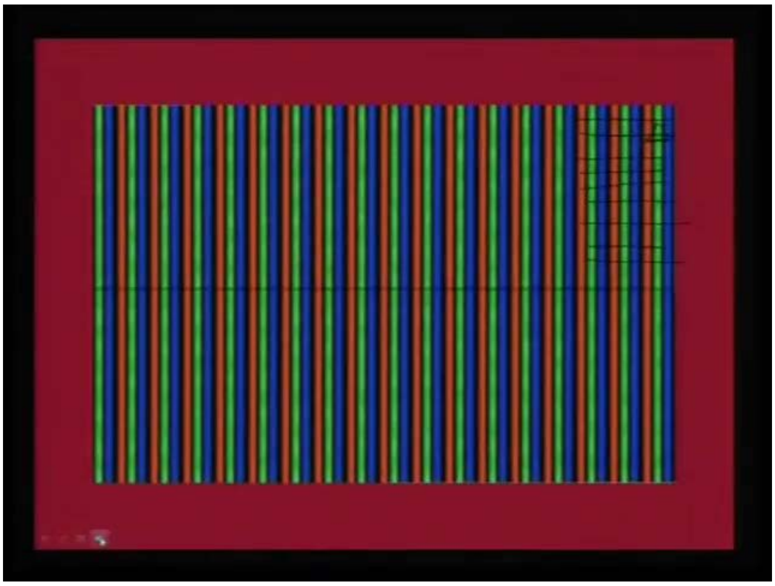

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And the colour mixing as you would know the principle three colours are here, and these colours when they are mixed in equal proportion, then you get white. And this white is a combination of 30 percent of green, 33 percent of blue, 33 percent of red. So, actually there is a way to address to this colour mixing or to the colour purity, so those in the CRT triad never try to talk about phosphor in terms of red, blue and green, but they have coded it. Such a way they know what the colour purity or what is the dominant colour that will emerge out of a particular phosphor. So, the colour coordinate that is recommended for pure white, is 0.33, 0.33, which is actually defined by a CIE diagram.

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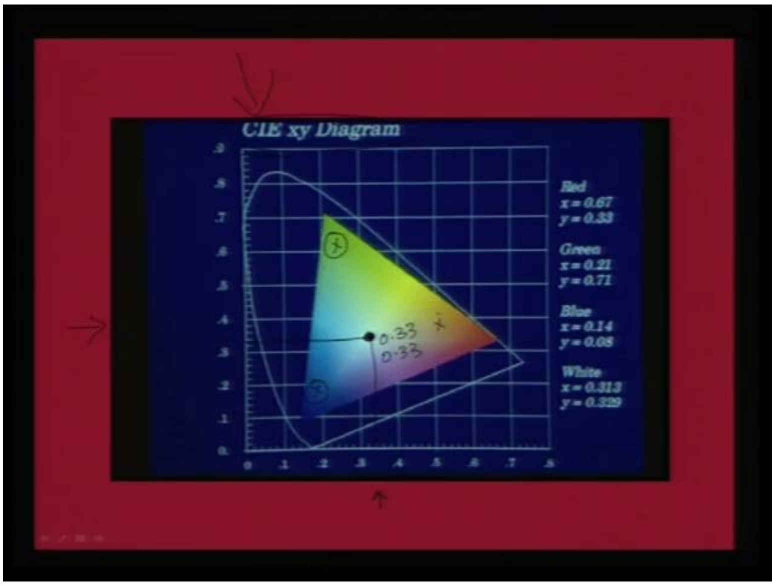

This is a international standard, it is called CIE x y diagram, so you can actually plot the components of blue, red and green in terms of a two dimensional plot. And by this way your x axis value and your y axis value will tell you where exactly you stand for example, the one which we spoke about white should necessarily come here, so this is your white emission. And if the coordinate is somewhere here, then you talk more about a red dominant one, if you x y coordinate is somewhere here then you talk about green or bluish green and so on.

So, this is a very useful parameter to evaluate what sort of a phosphor you make, so whenever you make a phosphor. And you see there is a potential, then necessarily you need to talk about CIE coordinates, then the colour purity is actually defined. Typically these oxides are colourless, those which are used are colourless in ordinary light, but in the presence of UV radiation, you would see that they are glowing. And in cathodo luminescence, actually this will become much brighter therefore, it will give a dominant green, blue and red.

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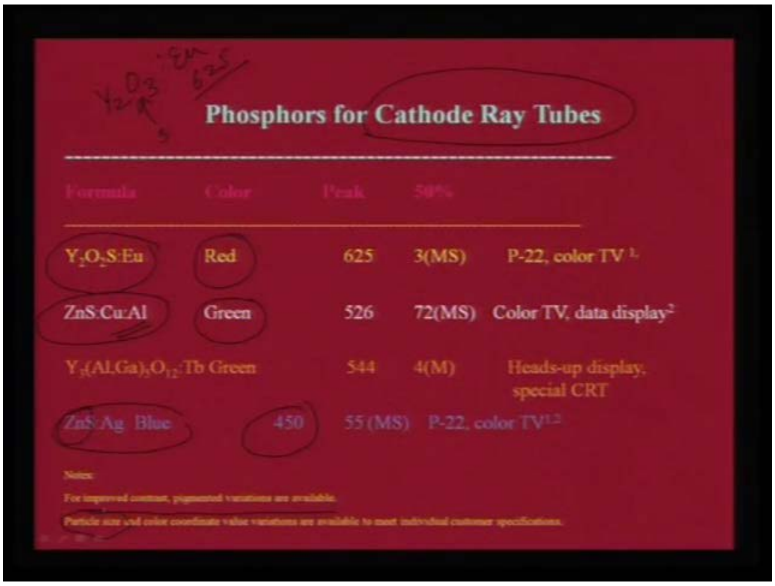

And what are the phosphors that are used for cathode ray tube application, to single out some example which is as of now used in CRT applications. As I told you yttrium oxide or yttrium oxide sulphide with europium doping is supposed to be the most preferred on for red. In fact, yttrium oxide with europium also gives the same 625 nanometre emission, but a proportion of sulphur into oxygen is always recommended, because it improves on the sharpness, and it restricts the degradation therefore, yttrium oxysulfide is preferred.

And as you would see here, the other group which is really taken the show in CRT application is zinc sulphide, the base material or the host is the same zinc sulphide. But, if you actually dope it with choice quantity of copper and aluminium, these are actually doped less than 5 percent. And if you make the right proportion, then you get green for copper, but if you dope it with silver then you get a clear blue emission. So, in the whole issue of CRT phosphors, as you would see in the further slides numbers of examples are given, many compounds have been traded commercially.

And the most important phosphor of all is the zinc sulphide based 1, because zinc sulphide phosphor is actually able to take care of both blue as well as green emission, the red is always unique to yttrium oxysulfide. So, for improved contrast we have pigmented variations that are available, I will come to this in one of slides. And the particle size and colour coordinate variations are available to meet individual customers specification, as I told you in one of the earlier slide; I talked about the strands of red, green and blue phosphors which are actually coated on the front panel.

Therefore, if you want to make such sleek and very narrow width of this phosphor stripes, then the particle size of the starting material is important. Because, you need to make a blend and then you need to need to burn it carefully to make such very sharp strands of phosphors. Therefore, particle size becomes a very unique issue, and it is preferred by different customers who have different technology to dope this phosphors on the glass light.

As you see in this slide again, the whole this is given and of the unique stuff that we see in this CRT phosphors is that, they are coded with the specific numbers. So, depending on the numbers it is possible for us to categorize, what sort of compound is used for that particular application. As you would see here in all this blue emitting phosphors it is silver, but along with silver you also see a chloride ion that is doped, which is actually considered to be a co-activator.

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So, if you want a very strong fluorescence not only you dope with silver, which is the actual dopant and the actual activator. You also use chloride as co-activator which improves on the efficiency of this compound, green ones are those with copper and aluminium and again we have yttrium. And in all this classes you also see, there is a tag attached to it pigmented and non-pigmented, because pigmented brings a different affect in terms of the contrast of these phosphors.

One thing is the bright glow that is luminescence, another thing is the contrast, contrast is actually inversely related to luminescence therefore, we need to have a very sharp control on the contrast also. It is not just a straub like that is coming out, but it has to be very sharp therefore, when we talk about contrast the issue of pigmentation comes into picture, I will show some examples on those slides.

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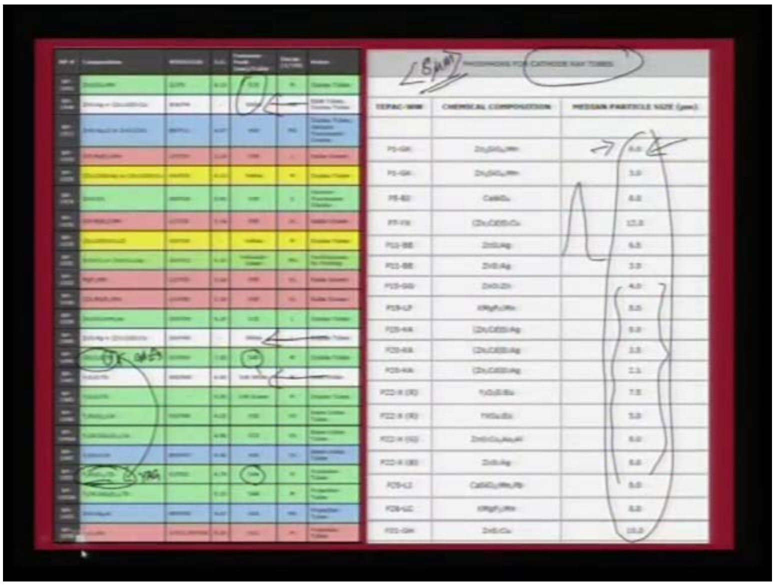

And in this view graph it may not be very easy for you to read through all the numbers, but I am just picking out this column for discussion in the slide. As you would see here, these are all the candidates used over the years for cathode rate tubes, and for those who are engineering this CRT monitors, they usually are very sensitive to the choice of the particle size of this phosphor. So, if we are going to make using a chemical route or by some other route, it is not just important to get the emission peak which is desired for example, 525 you would anyway get when you dope manganese in zinc silicate.

But, you need to achieve the right micron size and it has to be a narrow distribution, if it is a narrow distribution then such phosphor particles can be easily engineered for making this panels. Suppose you have a very wide distribution, then it is very very difficult for putting that as a strand in the front panel therefore, one of the things that I want to point out to you is the average size that is preferred is actually 8 micron.

Because, we are living in a nano world, there is always a temptation for us to talk about nanometre. But, one should also realize that the micron technology is proven and it cannot be shaken that easily therefore, when you talk about CRT the issue is not about nanosize, but the issue is about a very narrow distribution. And what is good for processing is a average micron range of 8 micron, so if you have a 8 micron particle you do not have to really feel bad, but you can only be happy because that is what exactly is preferred for developing the front panel.

And you also see here ((Refer Time: 29:20)) on the left slide, I just want to pick out on few things for example, a phosphor which is highlighted in white; these are the candidates for getting white light phosphors. And what are these candidates, those are a mixture of zinc sulphide doped with silver, and zinc cadmium sulphide doped with copper, such combinations actually gives you white light phosphors, so you can go for that.

Because, if you are looking for application in liquid crystal displays as a backlight emission, then you would rather prefer a white light, rather than red, green or blue. And therefore, there are other combinations for example, if you take yttrium oxysulfide which is doped with terbium from 2 to 5 percent, and then you would end up with white light which has a dominant emission at 545. So, by varying the dopant concentration, it is possible for us to engineer a variety of phosphors and as you would see here, the range is mainly between zinc sulphide or yttrium based oxides or aluminates.

In this case for example, this is a yttrium aluminium garnet doped with terbium then you should be able to get a 544 nanometre green emission, and we can also gamble with several other substitutions, in case of zinc sulphide based compounds. There is one compound which is quite peculiar in this table that is gadolinium oxysulfide doped with terbium again, shows a 545 nanometre emission. And just want to make a correlation between this and this ((Refer Time: 31:19)), in this case this is a YAG compound that is yttrium aluminium garnet whereas; in this case this is only simply a gadolinium oxide.

But both are giving same emission at 545 nanometre and the peculiarity is because of the dopant which is the same that is terbium 3 plus. So, as you would see it is not the host that would control the light emission, but the dopant because of the particular excitations in the d to f transition or f to d transition, which will determine whether this is unique of the dopant or not. And as you would see from the red emission it is always europium, which gives you emission at 620 nanometres, so this is the range of compounds that we have.

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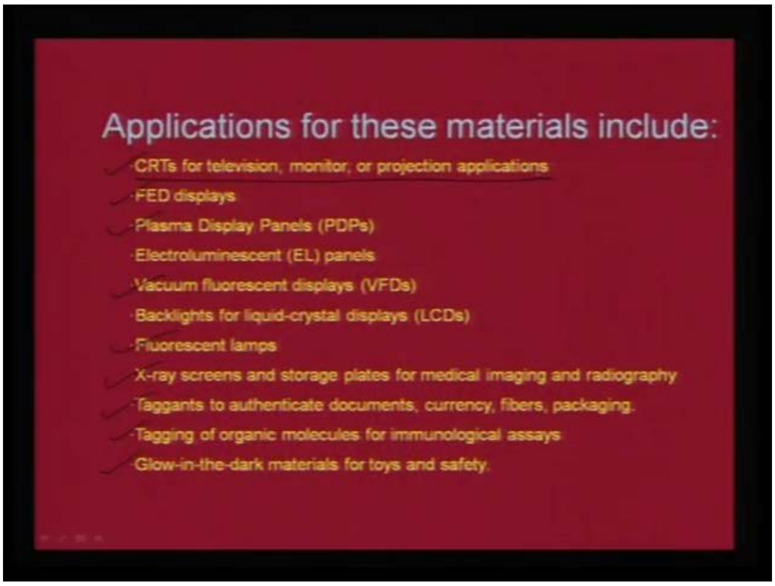

Now, the applications for this material include CRTs, which is the major player in the displays. And then in the last 10 years several groups have come or several applications have emerged, one is FED that is Field Emission Displays which are known for the contrast that it can bring in the image resolution. Or plasma display panels, which has a revolutionized today's modern living room, because you do not need the space it can be wall mounted.

Therefore, plasma display panels are really replacing the conventional CRT tubes, but for a higher cost, the processing of plasma display panel is 3 times more costlier than cathode rate tube. But, from the aesthetic point of view and for making a large panel display, still plasma display panels are counted to be one of the modern technologies. And then of course, these same phosphors can be used in vacuum fluorescent displays, fluorescent lamps, and then X-ray screens.

And storage plates for medical images and radiography, and of late it is also used as taggants in several documentation, even I will show one or two examples on that. And for immunological assay it can be tagged with organic molecules and of course, the issue of phosphorescence is used now, in every bit of application including toys and other safety devices. So, as you would see the range of compounds, it is not limited and several possibilities are there, but chief among them is the application to CRT tubes.

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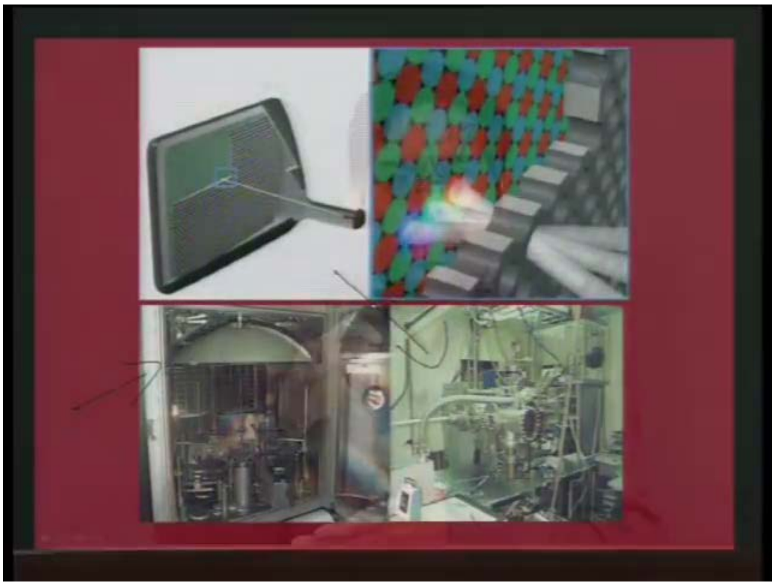

Now, in the CRT tube how do we make it, as you would see from the cartoon that is given below, the CRT tube is actually mounted on the top down position, and you can see the evaporation process is actually happening this way. So, it is a very involved technology and to make one CRT tube it takes several hours, starting from the simple glass panel to making the phosphor, and then to bring in all the electronic component it takes more than 10 hours to bring out one picture tube.

So, it is a very involved issue and as you would see here, the way you try to bring about this triad coating is the speciality of the CRT tube. So, if you can make the right choice and if you can make the right approach to coat this material, then through colour purity and the clarity of the pictures will be extremely impressive as far as the CRT tube is concerned. And coatings can also be made using this sort of vacuum technology set up, and therefore, this also brings in another issue that you cannot go for a very large area. So, CRT tubes are confined only maximum to 29 inch or 32 inch monitors, and bigger than that it is very, very difficult.

Therefore, people are trying to transcend from a CRT application to plasma display panel, because the way that is operating, the principle behind plasma display is very different from CRT. And to manage this deflection of cathode rays in a very focused way, it is very important as a result the CRT application is actually confined to a small area display.

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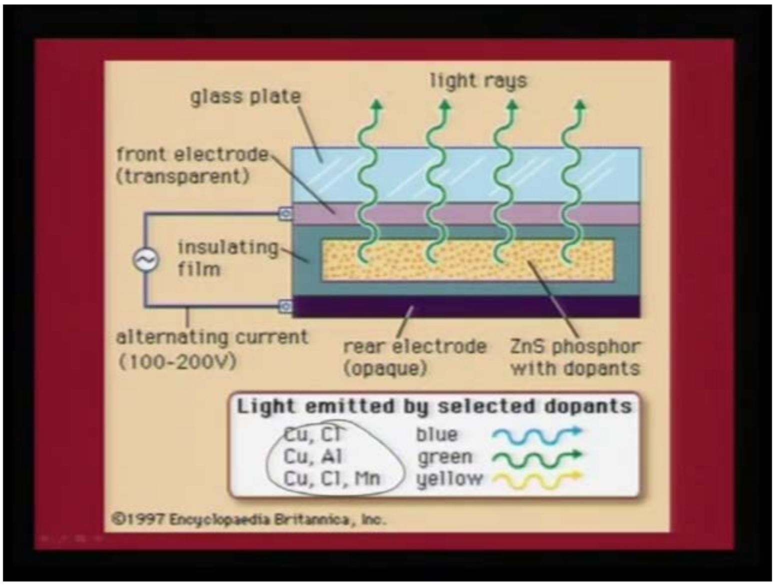

This is how the current induced photoluminescence occurs in a typical phosphor, where depending on the dopant and co-dopant, you can actually get the light output from this displays.

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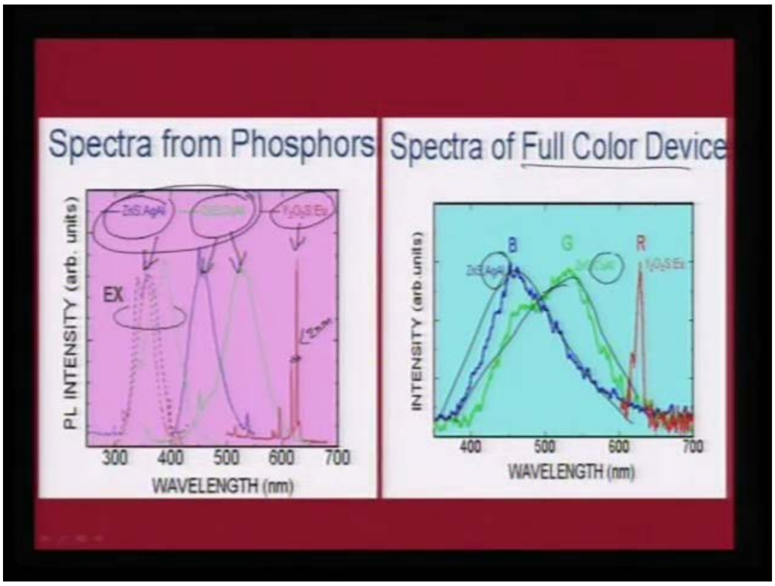

And the spectra from the phosphors actually look like this, the silver doped ones show a blue light here, and the copper doped ones show bluish to bluish green. So, these two candidates give the blue and green component, and as you see here yttrium oxide phosphors doped with europium usually give a very, very strong red light. And if you look at the full with at half maxima, it is only ranging to less than 2 nanometres, which shows how selective this luminescence can be compared to the other two phosphors.

And this is mainly, because of the mechanism of photoluminescence that is operating in the zinc oxide base phosphors compared to yttrium based phosphors. And if you are looking for full coloured display, then what we desire is that it should not be narrow, but it should also have a wide mixing between the corresponding colours. For example, blue should nicely mix with the green component in this fashion, so that the overlap is more, more the overlap then you can try to the white light emission or the full colour display in a better way. Therefore, not just getting a narrow band emission, but mixing of these colours to get the full spectrum is very important. Therefore, the amount of dopant and co-dopant that you add becomes very, very important.

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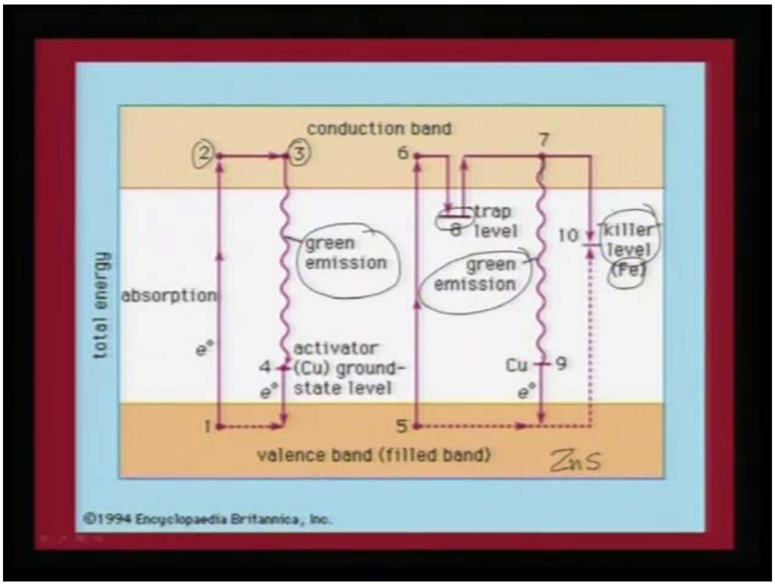

And lastly on the mechanism of how this zinc sulphide based phosphors operate, there are two, three things that can be dominant. One is the electrons are excited to from state 1 to state 2 that is the conduction band, and this can dwell in the conduction band for a short span. And then this can give out green emission, and come back to the copper ground state level and then this can return back to the ground state, so this is one process.

There are other things that are also accompanied with it, because of several processing issues, one is if it is a defect induced one, then the electron gets trapped momentarily in this trap level. And because of the influence of the cathode ray, they do get ejected out and finally, they return giving a green emission. So, there are trap levels and the number of tarp densities or trap levels, do control the quantum efficiency, and the purity to some extent. If we have very little amount of iron that is coming out as a impurity, then this can actually act like a killer. So, this is called a killer level, because any other impurities which are in same comparable atomic level, can actually bring about quenching of this light.

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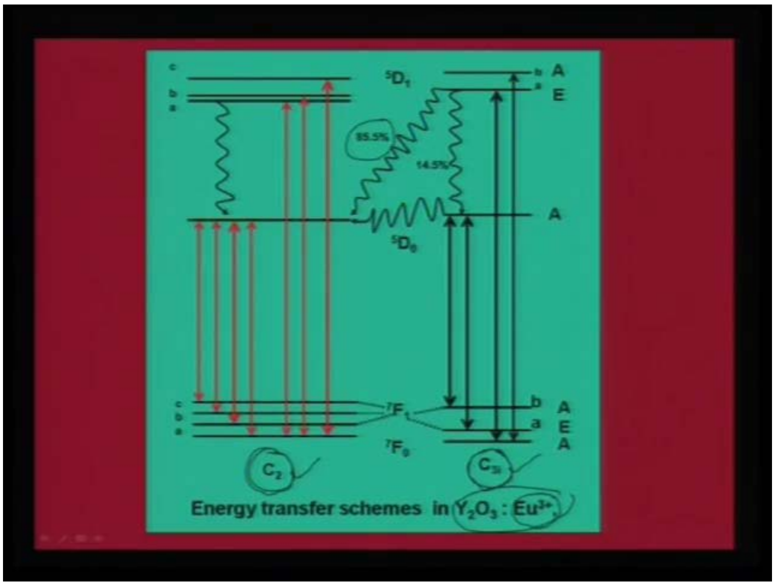

In the case of emission that is happening in the red light based on europium oxide based phosphors, there is a unique issue that is involved. The europium 3 plus can actually go into two different sites in yttria, one is there is nearly 70 percent of sides have C2 symmetry, and then 30 percent of sites have C3i symmetry. Therefore, the europium which is actually doped in yttria can either go to C3i site or it can go to C2 site.

Now, if because there is a invasion symmetry all the europium ions, which are occupying the C3i site actually do not contribute to fluorescence, so only if they occupy the C2 sited then they are more productive in terms of emission. And therefore, this has to be carefully monitored that the occupancy of the europium site is dominated by a C2 based occupancy and in fact, it is possible even to reconvert the C3 occupied sites to C2. And the conversion that is possible is up to 85 percent to C2 symmetry, and those C2 occupied europium sites, actually are responsible for the red emission.

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The same phosphors can also be used for plasma display panels.

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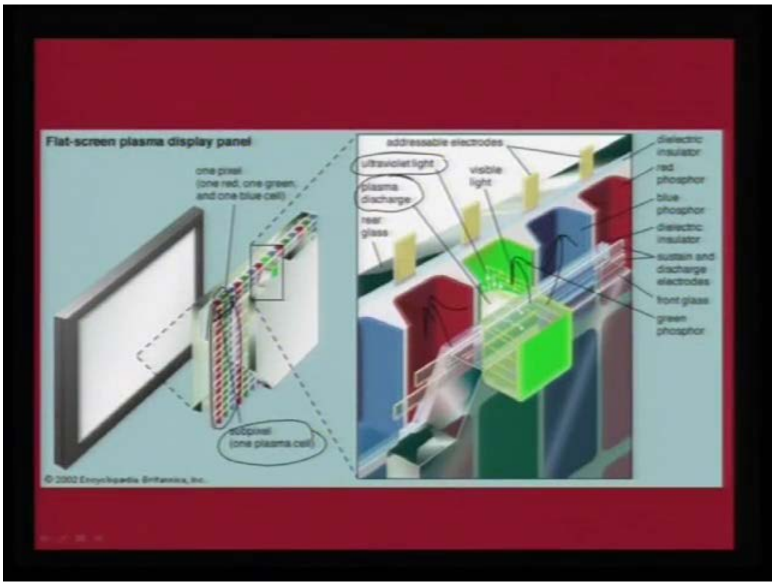

And as you would see, the display mechanism is quite different compared to the CRT applications, and in this case what you see is a plasma discharge. And this plasma discharged is actually brought about by the UV light, and once UV light is generated in the back panel that UV light will shine on the respective ones red, green and blue. And as a result you will get plasma which is generated that will account for the emission of full colour display. So, even in this case the way the red green and blue are mapped is of this fashion as subpixel, and this will constitute one plasma cell.

Therefore, the plasma that is generated will have to have a different mixing co-efficiency between each of this panel, and as a result you will get the proper colour output. So, in plasma display panel, the main mechanism is not the cathode rate tube or the cathode rays, it is the UV light emission which will bring about the colour display. So, here again you have choice materials which are used for plasma display.

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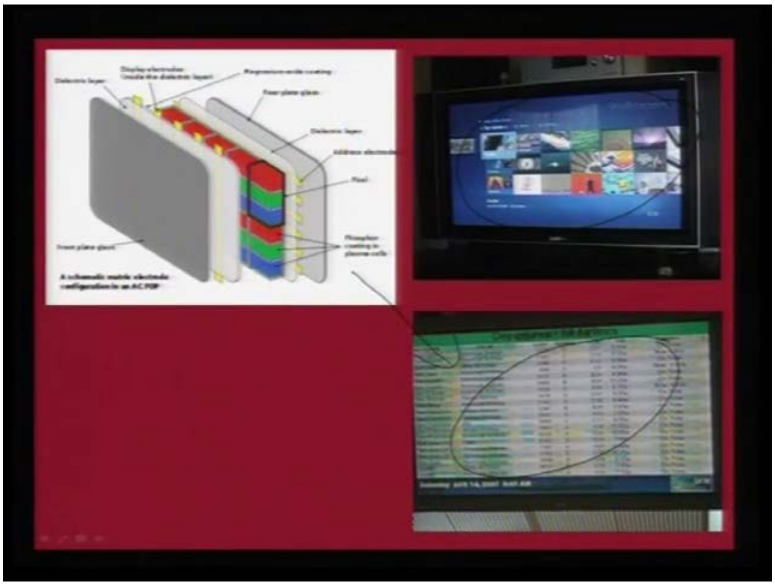

And we have set of such phosphors, which have been proven and as you know that continuous exposure to UV can also result in degradation of this phosphors, or the phosphors can get chocked. And as a result nice display of this sort can become as disfigured like this, so a distorted display like this clearly shows that the phosphors are getting degraded in the plasma display panel. So, this is one of the main problem that you encounter in practical application compared to CRT tube, you have a problem of the phosphor degradation, because of a continuous exposure to plasma, so this has to be taken care.

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Some of the candidates for plasma display panels are borides, aluminates, silicates; this is slightly different from the phosphors that are used in CRT tubes. Main reason is the silicates and aluminates are preferred over the conventional zinc sulphide based phosphors is mainly because of the thermal properties. They are much more rugged for very high heating effect which can happen in the plasma therefore, to with stand the internal heating effects; we actually use a high temperature ceramics, which also have same colour efficiency. Therefore, most of this oxides if you see, they are all insulating or these are high temperature materials, so this is very unique for PDP applications.

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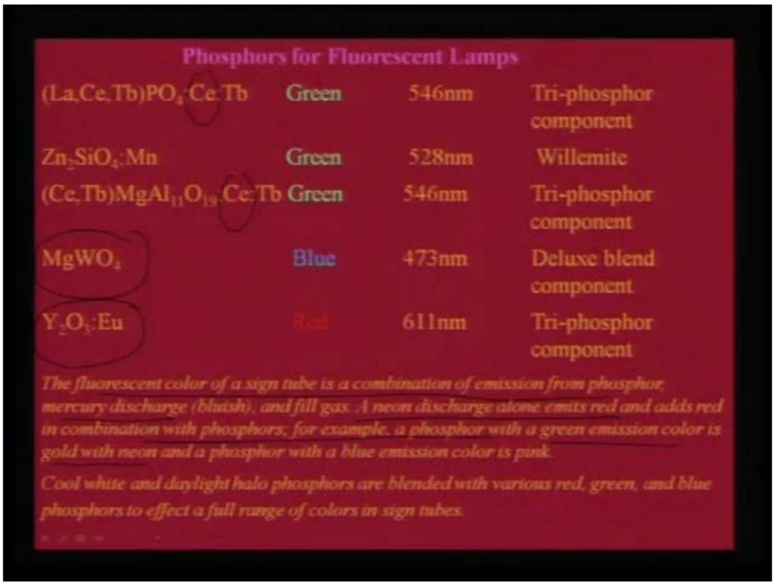

And when we come to fluorescent lamps, you again see that the major contributor is cerium doping, because cerium doped phosphors they respond immediately to mercury plasma that is generated in all the fluorescent tubes, so it has to respond. And cerium is very unique for green emission, you also have magnesium tungsten and then of course, europium based yttria, these are used for blue and red. The fluorescent colour of a sign tube is a combination of emission from phosphor, and the discharge that is taking place.

So, if it is a mercury discharge, then the emission will be mostly dominantly blue in colour, suppose it is a neon discharge alone, emits red and adds red in combination with phosphors for example, green emission colour is gold with neon. So, if you have a neon discharge, then you can get a different emission for the same phosphor compared to mercury discharge therefore, these are being worked out as combinations for mixing.

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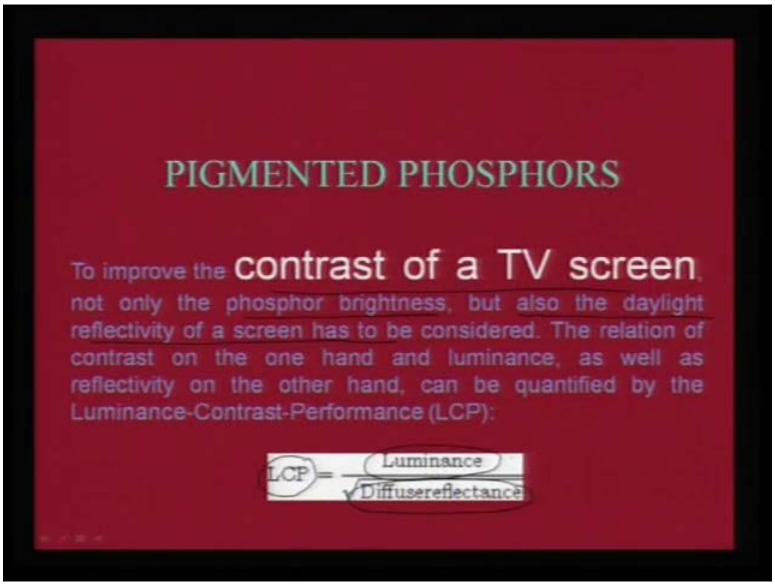

Now, when I talk about the contrast of a TV screen, we should understand the contrast is nothing but the luminescence contrast performance, this is defined as a ratio of your luminescence versus diffused reflectance. Diffused reflectance is actually coming from the stray radiation to improve the contrast of a TV screen, not only the phosphor brightness is important, just because it glows bright does not make it a good candidate.

And because we need to combat with the day light reflectivity of the screen, so the contrast is actually a gamble between the brightness of the phosphor, and the daylight reflectivity. And as a result it is generally agreed that this has to be pigmented, so that the daylight reflectivity can be controlled when the phosphors are glowing.

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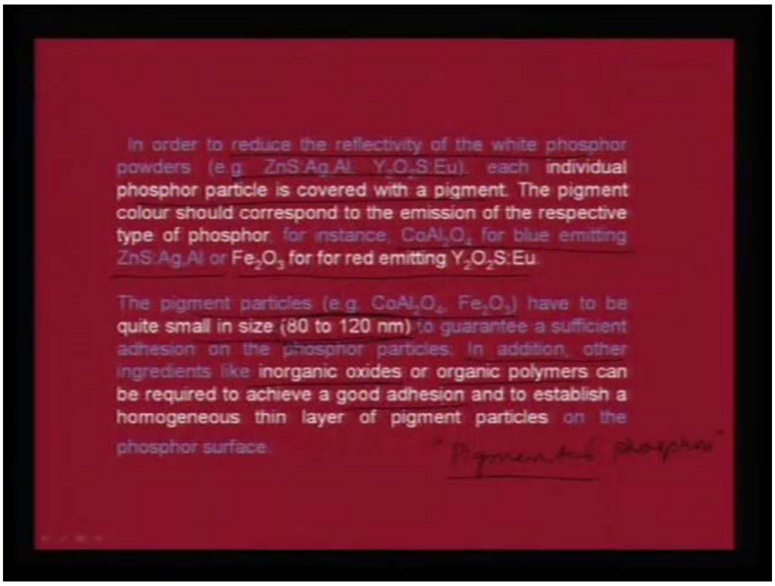

And in order to reduce the reflectivity of the white phosphor powder for example, these are all candidates for white phosphor. Each phosphor particle is covered with the pigment for example, cobalt aluminate is a good pigment for blue emitting zinc sulphide, which is doped with silver and aluminium. Similarly, you can use iron oxide it could be alpha iron oxide powder, which is actually used to control the refractivity as far as the red emitting yttria compounds are concerned.

So, each of this phosphors have to be controlled in order to combat with the day light reflectivity, as a result we have a new generation called pigmented phosphors which are used; and this again depends on the company which is making and the requirements. So, a pigmented phosphor are a very important issue, and here again the pigmentation as you see comes from several coloured inorganic oxides for example, cobalt aluminate is mostly a peacock greenish blue combination.

Iron oxide is predominantly a yellow brown stuff, which is added to control the reflectivity the pigment particles have to be quite small in size. Because, they should not be of a comparable size with the stuff, otherwise the adhesion between the actual phosphor and the pigment will become equal. As a result the narrow range that is preferred for pigmented for particles is of the order of 80 to 120 nanometre. In addition to other ingredients like inorganic oxides you also have organic polymers with a good adhesion, which can actually coat this phosphors for getting more contrast.

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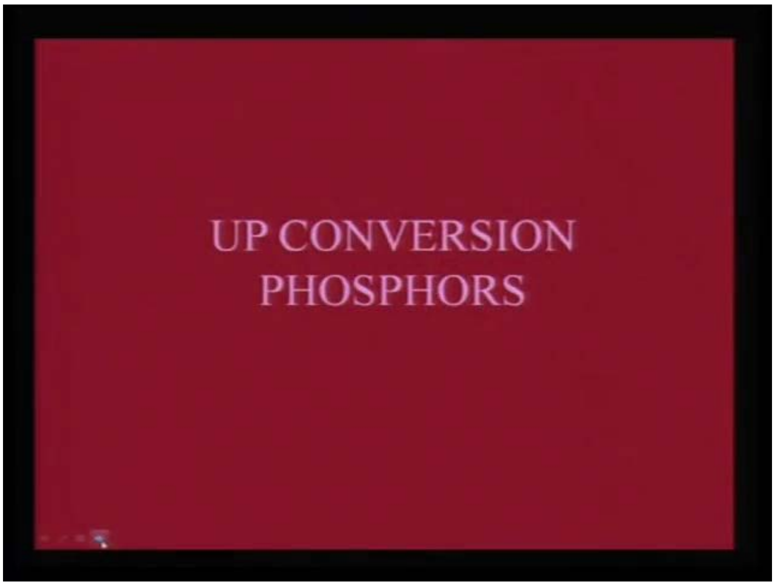

Another example of this phosphors are up conversion phosphors, as we know when we try to use a UV light, then you will get a emission of a higher wavelength, in other words lesser energy. This is actually the Stokes law or Stokes lines, which we have learnt from the spectroscopy, but up-conversion phosphors are actually Anti-Stokes phosphors. Because they take energy in the lower nanometre range, but they actually emit a higher energy emission. And therefore, this up-conversion phosphors are also called as Anti-Stokes phosphors, this up-conversion phosphor are actually used as a anti-counterfeit phosphor. And it is a luminescent material that converts different invisible infrared light into visible light.

The best example is when we try to go through a security zone, usually our identity cards are scanned through some light, and those are usually infrared lights, because that is safer. And as you would see here in the normal light a tag like this, a monogram might have two different lights. So, person who is trying to dupe may try to put a counterfeit like this, but in the infrared actually it has to glow fully same. So, these are special phosphors which will actually take low energy, but will emit in higher energy.

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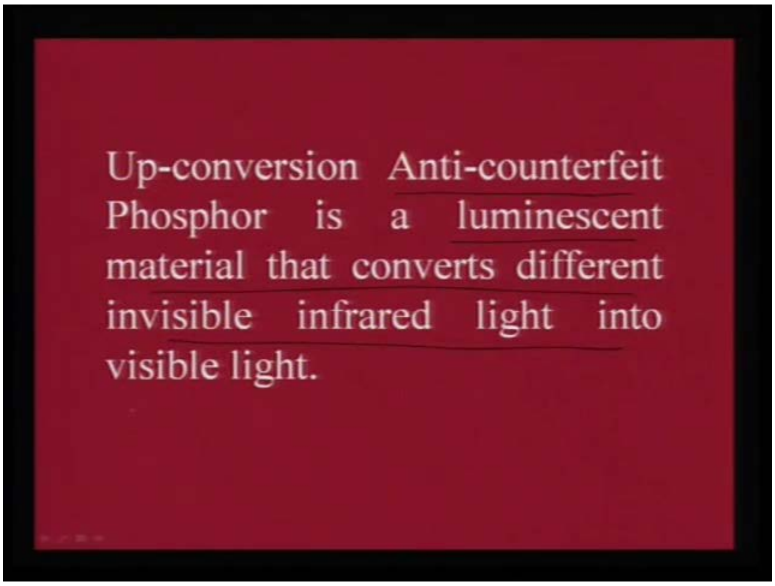

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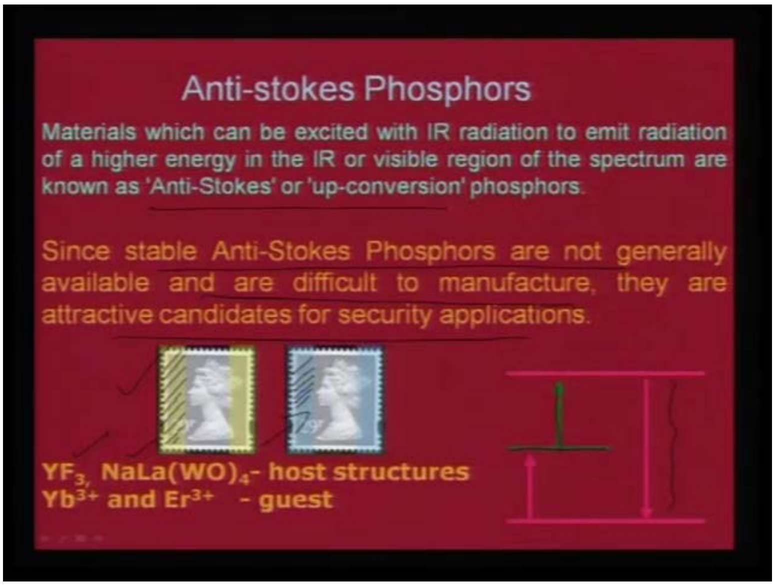

So, this is nearly green, which is actually emitting in blue and these are actually called as two photon process or more than two photon process. So, what happens you have a activator which actually takes it to this level, and there is another co-activator which will push it right this level therefore, the emission will actually be a two photon emission against one photon that your giving, so this is called up-conversion phosphors. Since, stable Anti-Stoke phosphors are not generally available, and are difficult to manufacture they are actually attractive candidates for a security applications. One or two examples of that yttrium fluoride and then sodium lanthanum tungsten, these are very critical to prepare. People who want a dupe cannot easily make it, therefore these are special chemicals which have a controlled emission, and these are also called as Anti Stokes phosphors.

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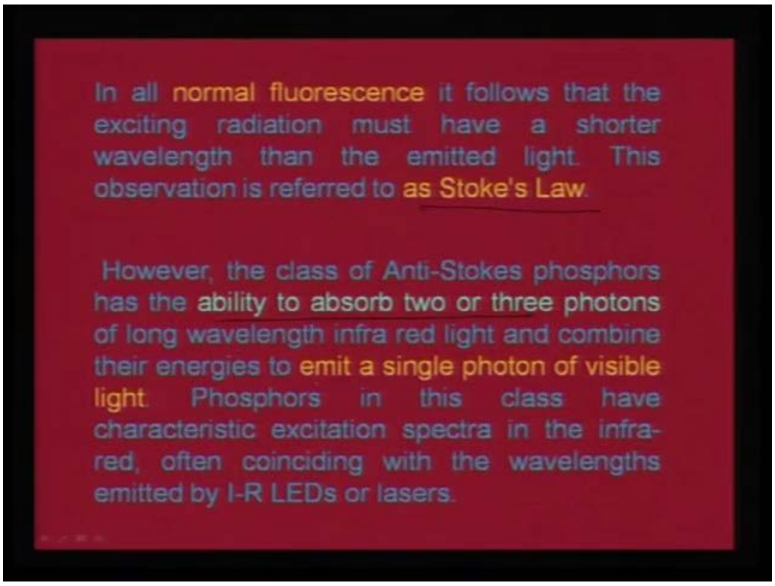

In all normal fluorescence, we know that this is a behaves based on Stokes law however, in Anti-Stoke phosphor, we have two or three photon absorption and they emit a single photon of visible light.

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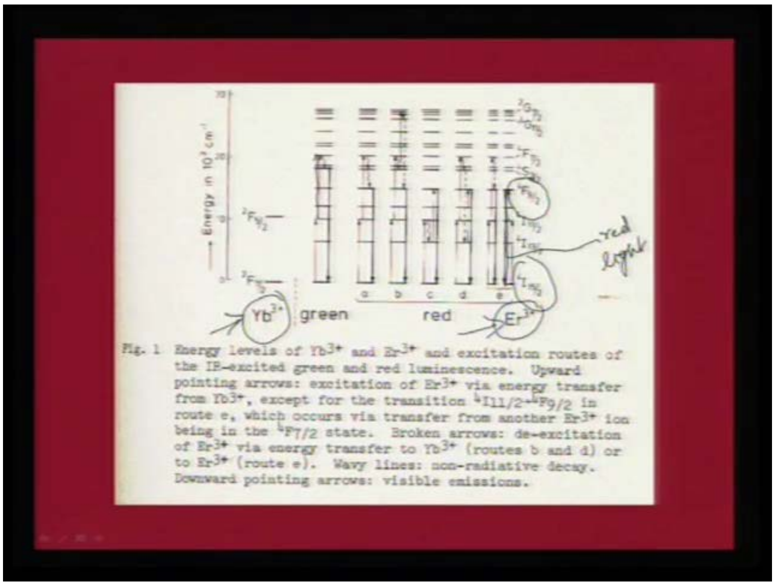

This is another example of how the IR excited phosphors behave; you can see here this is the ytterbium dopant, which actually takes care of the emission from this state 2F7 by 2 state to vF5 by 2 states. But, then you also have a co-doping in the form of erbium, which will actually translate this further to higher energy levels, as a result the emission that we see here from F4 9 by 2 to 4I15 by 2 is nothing but you red light emission. And this is actually engineered by the doping of both ytterbium and erbium as activator, and co-activator.

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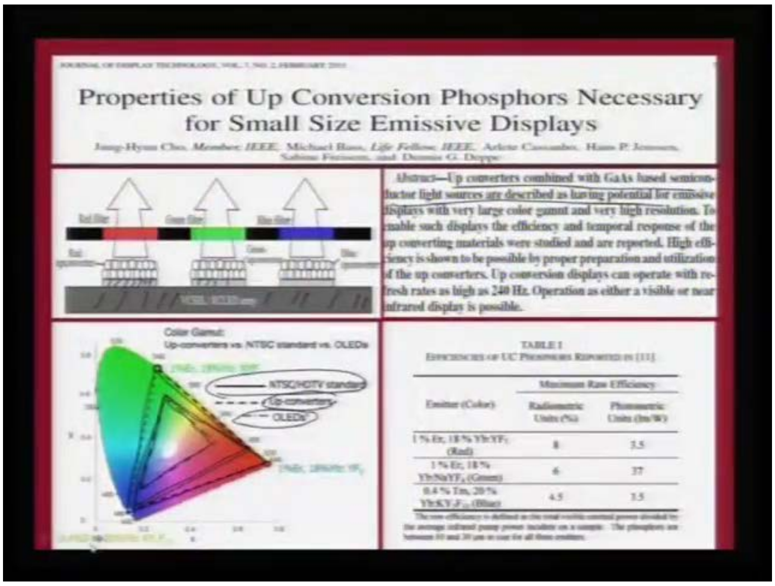

And there are also other examples of up-conversion not necessarily the examples that I showed there, here your actually using a combination of gallium arsenide base semiconductors. And in combination with this phosphors, they can actually do a up-conversion and as you see here, this is your gallium arsenide based panels, and here you can put your phosphor. And then you can get through suitable filters either red, green or blue colours, but in this sort of conversions you would see the phosphor that are used has a much better gamete of colour.

For example, the triangle that we see on the outer side, this is corresponding to the up-convertors what has been engineered here. So, they have much better gamete of colours compared to OLEDs which are highly pure, but at the same time they have very limited colour resource, and then comes your NTSE based phosphors which are in the middle.

So, when you think of several highbred combinations, you see this up-conversion phosphors seem to have a larger scope than the conventional ones.

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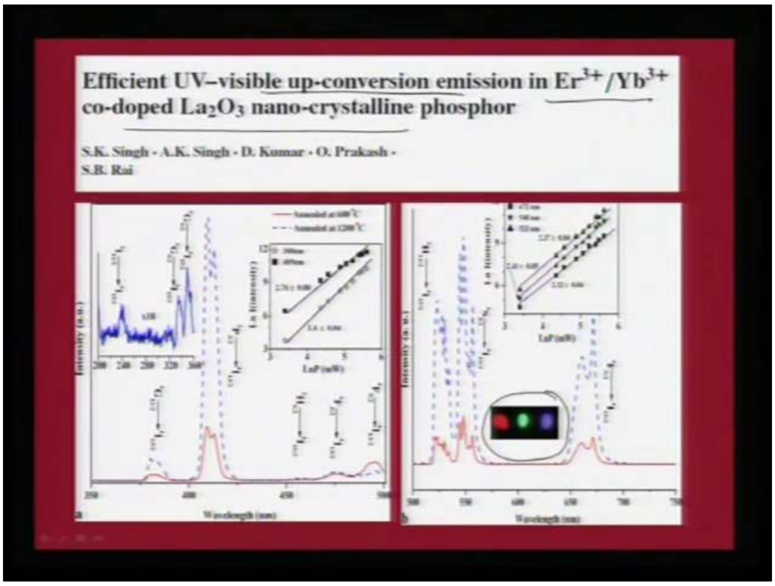

We can also workout for up-conversion phosphors using simple lanthanum oxide, which is doped with erbium and ytterbium. You can see the colour purity that you can get out of such substitution.

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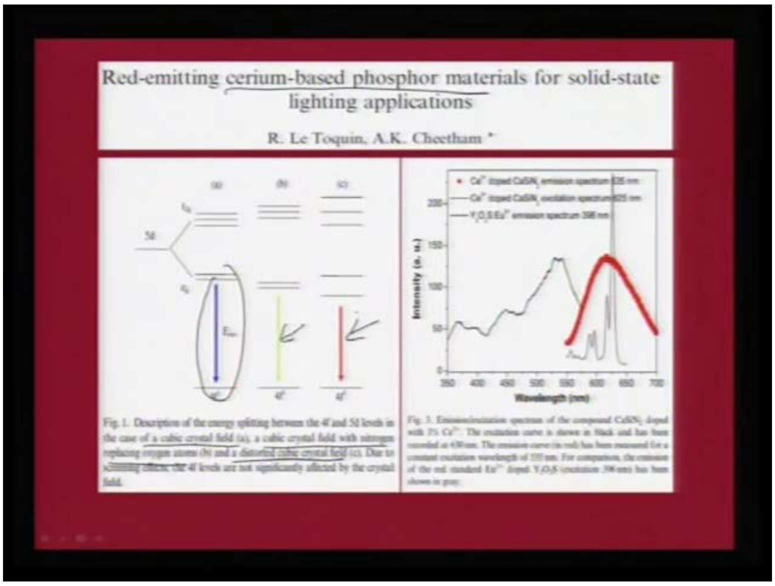

And we can also look for red emitting cerium based phosphors which are reported, and the colour emission in each case will differ depending on the side symmetry for example, in a cubic crystal field you will get for the same doping a blue colour. But, in a distorted cubic lattice you will expect a red light, and suppose you going to add with the nitrogen replacing oxygen atoms, then you can modify the colour emission to green. So, such substitutions are also possible.

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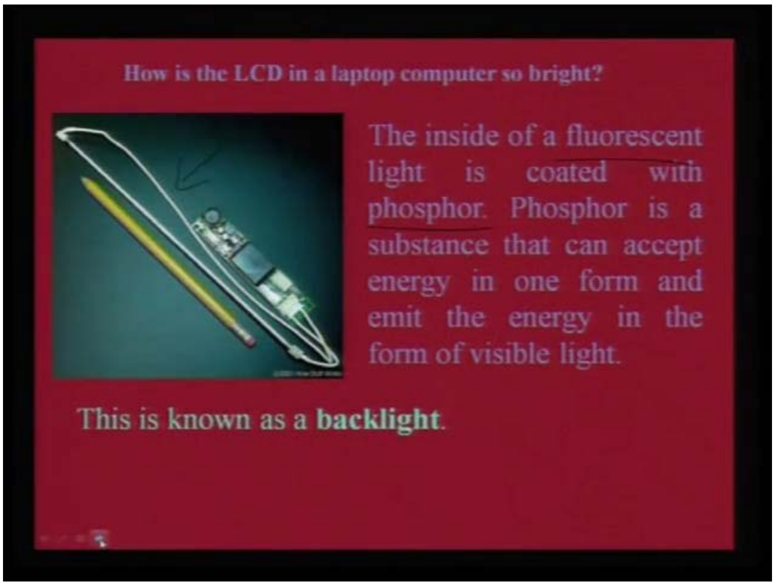

And lastly I would like to leave with one more thought that LCD, whenever we handle LCD laptop, computers which we normally use. The colour emission or the bright colour that comes out is actually because of the phosphors, and you have a very sleek fluorescent lamp like this, and this pencil is kept therefore comparison. So, it is as small as that, and this can bring out the white light emission that is needed for LCD displays. So, apart from the liquid crystal panel that you have, the background emission is actually moderated by these phosphors, which are coated in this fluorescent tube.

So, the range of applications of this phosphors are not limited only to CRT, but to a variety of other display materials, and as you would see it is just a simple doping in a host matrix which brings about all these fascinations. So, here the chemistry become very important, chemistry in terms of the choice of dopant, and the chemistry of up-conversion comes into picture. Then the chemistry of controlling the size comes into picture, the chemistry of pigmentation to improve the contrast comes into picture. Therefore, there is plenty of chemistry principles that are involved in this technology, which we need to bear in mind. Therefore, a useful chemist, chemist who understands all this ideas can successfully produce an engineer, a variety of new phosphors for future applications.