Ultrafast Processes in Chemistry
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Module No # 08
Lecture No # 40
SFG and SHG with Ultrafast Pulses

We are in the middle of our discussion of sum frequency generation and second harmonic generation. We have studied the basics leaving out most of the mathematics and most of the physics. So we are trying to develop a user's perspective of this rather complicated subject matter. Now today what we want to discuss is what are the issues that one needs to keep in mind when one wants to do sum frequency generation or second harmonic generation not with regular continuous wave laser light but with ultrafast pulses.

After all the entire course is about ultrafast phenomena and we need to be aware that it is important that we have to take care of certain parameters if you want to do nonlinear spectroscopy or even any non-linear optical process using ultrafast pulses. It is not as if you can take out a nonlinear crystal from anywhere.

Say your millennia is broken the continuous wave that comes for solid state laser may be you have a millennia that are gone bad you take out that sum frequency well nonlinear optical crystal from there and you think that you are going to use femtosecond pulse using the same crystal it will not work. So today we are going to learn why it will not work. And what is it that we need to keep in mind if you are going to do second harmonic generation sum frequency generation so on and so forth using ultra short pulses.

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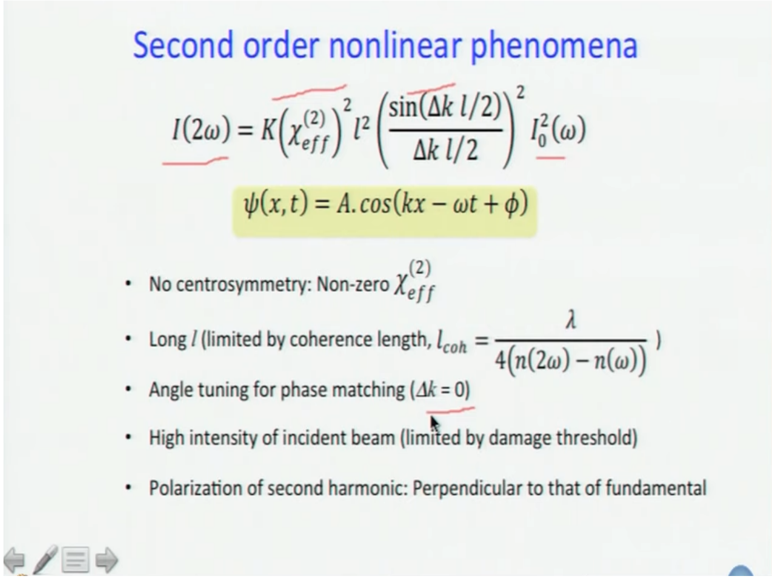

Second order nonlinear phenomena

$$I(2\omega) = K\left(\chi_{eff}^{(2)}\right)^2 l^2 \left(\frac{\sin(\Delta k\, l/2)}{\Delta k\, l/2}\right)^2 I_0^2(\omega)$$

$$\psi(x,t) = A.cos(kx - \omega t + \phi)$$

- No centrosymmetry: Non-zero $\chi_{eff}^{(2)}$
- Long l (limited by coherence length, $l_{coh} = \frac{\lambda}{4(n(2\omega) - n(\omega))}$)
- Angle tuning for phase matching ($\Delta k = 0$)
- High intensity of incident beam (limited by damage threshold)
- Polarization of second harmonic: Perpendicular to that of fundamental

But before that it has we do a quick recap of what we have learnt already. We have learnt that this is the expression for the intensity of second harmonic light. What are the factors there? Of course the second order non-linear susceptibility is one that should be as high as possible and as you have discussed without proving anything that they should be no centro-symmetry this is to be non-zero.

If centro-symmetry is there then in fact this is 0 forgot about having a high value. Secondly, we said that it is better to have a large value of I0 provided I0 is not so large that there is material damage in the crystal. And finally we worked with this term sin delta k l / 2 divided by delta k l / 2 whole square where l is the length of the crystal and delta k is the difference between the k vectors which boils down to difference in momenta of the combining light right.

And of course since sin square theta by theta square it is going to have a maximum at theta equal to 0. So we have come back to this expression shortly. What we said is that first of all l is limited by coherence length. We have seen delta k = 0 by angle tuning we are going to we have discussed it and we will do a quick recap in the next slide. And we have talked some about the polarization of the second harmonic being perpendicular to that of the fundamental.

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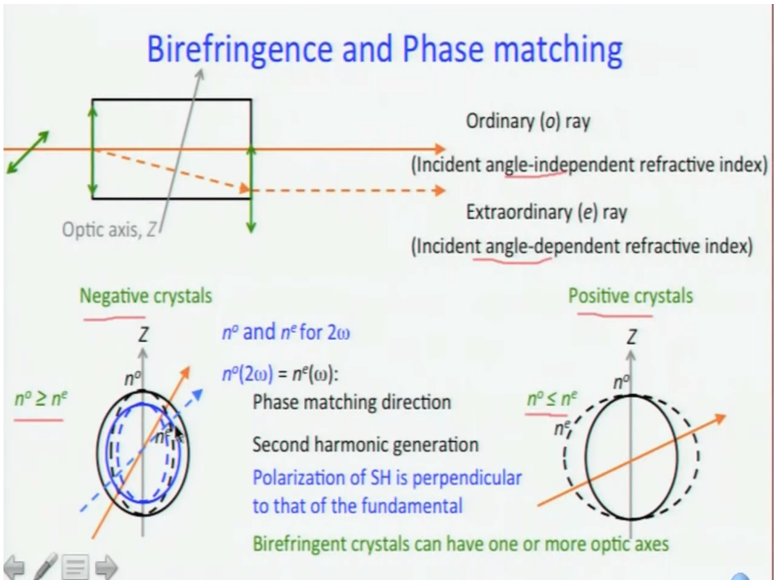

Birefringence and Phase matching

Ordinary (*o*) ray
(Incident angle-independent refractive index)
Extraordinary (*e*) ray
(Incident angle-dependent refractive index)

Optic axis, Z

Negative crystals

$n^o \geq n^e$

n^o and n^e for 2ω

$n^o(2\omega) = n^e(\omega)$:
Phase matching direction

Second harmonic generation

Polarization of SH is perpendicular to that of the fundamental

Positive crystals

$n^o \leq n^e$

Birefringent crystals can have one or more optic axes

And again we are going to do a little more detailed discussion about that. And this is what we are discussed in the previous module in very great detail but once again not a doing any real math. So what we learnt there is that there are 2 things that are important here. It is not only that the nonlinear optical crystal should have a high value of second order nonlinear sustainability but it should also be birefringence.

What is the meaning of birefringence? The meaning of birefringence is that when light enters polarized light it should split into an ordinary ray or o ray with the same polarization and an extra ordinary or e ray with perpendicular polarization. And the advantage of that is that you have crystals in which this refractive index for ordinary and extra ordinary rays are going to be different right. And they are going to be different not only for the fundamental but also for the second harmonic.

So we said that there are 2 kinds of crystal negative crystals for which n0 no the refractive index for the ordinary ray is greater than or equal to that of the extra ordinary ray and positive crystal in which refractive index of the ordinary ray is less than equal to that of the extra ordinary ray. And the other thing that one needs to keep in mind is that for ordinary ray the refractive index is not dependent on the incident angle whereas for the extra ordinary the refractive index is dependent on the incident angle.

The polar plot for the refractive index of ordinary ray is going to be a circle and that for extra ordinary ray it is going to be an ellipse. So for negative crystal this is what the picture going to be the one drawn in black. The circle solid circle is the polar plot for the ordinary ray the dashed ellipse is the polar plot for the extra ordinary ray. So, extra ordinary ray polar plot is contain completely within the polar plot for the refractive index of ordinary ray.

In positive crystals it is the other way around because here no is less than equal to ne whereas no is greater than equal to ne alright. And then we said that lets us consider the situation where the refractive index is less for the second harmonic compared to the fundamental then you get a similar set of circle and ellipse for the second harmonic but they are going to smaller in size. And then since you have one ellipse, we have a ellipse and we have a circle we see that in this particular angle of the incidence the circle for this second harmonic overlaps with the ellipse for the fundamental.

Which means the refractive index of the extra ordinary ray of the second harmonic is equal to the refractive index of the ordinary ray for the fundamental for that particular angle of incidence. And that is when the refractive index is unmatched. So phase matching is achieved the conservation of the momentum is assured and that is when you get second harmonic generation ok. So this is what we had discussed in the last module. I thought will just recap once again because it is not very easy at least to ask chemistry student to understand maybe.

So is there any question so far? Are we all yes so I think what is saying is that if the refractive index is very small compared of for the second harmonic compared to the ordinary ray? Then maybe there will be not be any overlap. If that is the case there will not be any second harmonic generation. We will not get second harmonic generation in that case. There has to be an overlap otherwise second harmonic generation is not going to happen. It is not enough to take a non centro-symmetric material.

Just because your material is non centro-symmetric does not necessarily mean that it is going to be in a low active ok. So in fact very few examples of material are there where you are going to get second harmonic thus why they are so expensive. It is not easy to make as well ok alright. And then we said that it is possible so what are we doing? What happens when we change the angle of the crystal? Essentially it is difficult to change the angle of the incidence because then the entire optical path will change.

But if we rotate the crystal then we essentially play around with the optic axis of the crystal and there by change the angle of incidence without having to change the direction of the light beam ok there is a trick. So angle tuning that is how it comes and we said that it is possible to have crystals that are not uniaxial but generally nowadays unless you have some very specialized application there plenty of good uniaxial crystal positive or negative crystals which you could use. So generally, one would use uniaxial crystal unless there is some compelling reason to not do so.

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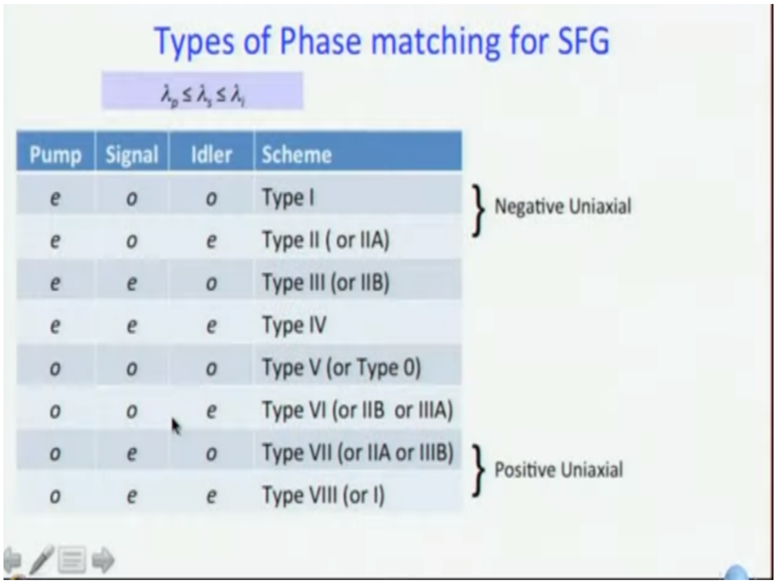

Types of Phase matching for SFG

$\lambda_p \le \lambda_s \le \lambda_i$

Pump	Signal	Idler	Scheme
e	o	o	Type I
e	o	e	Type II (or IIA)
e	e	o	Type III (or IIB)
e	e	e	Type IV
o	o	o	Type V (or Type 0)
o	o	e	Type VI (or IIB or IIIA)
o	e	o	Type VII (or IIA or IIIB)
o	e	e	Type VIII (or I)

Negative Uniaxial

Positive Uniaxial

And now I want to show you this table that you can actually find in Wikipedia. There are other ways of representing the same thing, but I like this table particularly because it introduces the terms that we are going to use in the next module when we talk about optical parametric generation and application. It introduces the terms pump, signal and idler. And well why pump, why signal, why idler the reason is historic.

They used like that it is like a SPDF or orbitals. Why are they called SPDF and not ABCD what is S what is P? Remember we digress a little bit sharp, principle, diffuse something like that right. So those are ancient term these people are completely forgotten the relevance of. So here also more for historic reasons what we say is that this is basically a 3 color process right. We are talking about sum frequency generation special case of which is second harmonic generation right.

So we can say omega 1 omega 2 omega 3 right. So what we are saying is the out of this 3 kinds of light the one with the smallest wavelength is called pump. The smallest wave length is called lambda p for pump. The one with the largest wavelength longest wavelength is called the idler ok. It is nothing to do with laziness or activeness of the light. It is a name what it means is idler means out of 3 beams that are there idler is the one with the longest wavelength that is smallest energy.

And the intermediate one is called lambda s for signal ok. So please remember this highest energy is pump, intermediate energy signal, lowest energy idler ok. And also please do not miss the less than equal to signs sometimes it is possible that say idler and signal might have the same values. In whatever we have discussed so far it is not very logical to say that pump and signal will have the same value.

But idler and signal have a same value we have encountered that already is not it. When does idler and signal have the same wavelength? In case of second harmonic generation lambda = lambda s right? So that is all that it is. Please remember this lambda p less than equal to lambda s less than equal to lambda i that is all. Now the crystals are classified into type 1, type 2 sometimes they are classified as type 3, type 4, type 5, type 6 some so on and so forth depending on the re relative polarization of signal, idler and pump.

In our case please do not forget in the discussion so far pump is what is being produced ok right. What is the meaning of pump? In the discussion we have had so far. Pump means sum frequency or second harmonic right that is being produced. So what this means is that if you have an a signal with a well 0 degrees polarization and idler with 0 degree polarization they are going to give you the sum frequency which will have polarization at 90 degrees ok 0 and 90 are written as o and e respectively ok.

So as far as sum frequency of second harmonic generation is concerned if you have a same polarization of the combining light the 2 combining lights degenerate on or non-degenerate then we have already discussed the case where you are going to have perpendicular polarization of a light coming out the sum frequency or the second harmonic. So that is called o o e kind of phase matching.

Please do not get confused here the problem is since I have written pump first you have to read from right hand side to left hand side opposite. So type 1 phase matching is also called o o e phase matching meaning 2 light beams of 0 degree polarization are going to combine to give you sum frequency of 90 degree polarization. Of course, you might as well call it e e o means the same. In fact you see o o e is called type 1, e e o is also called type 1.

Only if you want to differentiate between the polarization of the incoming light whether you want to specify that it is horizontal or it is vertical then you call this type 1 and you call this type 8 ok. And the discussion that we have had so far is actually of type 1 phase matching right. And will you agree with me if I say that when we talk about second harmonic generation then it is going to type 1.

I will clarify the state little more little maybe expand the statement little more shortly but in the discussion we have had so far we agree with second harmonic generation unless you separate the beams rotate the polarization of one for some reason the light that goes on goes in it has the same polarization right. You are mixing light with itself the input light with itself. So that is why if it is o then o o e is what you will get. If it is e then e e o is what you will get.

But there is another kind of polarization type 4 and type 5. Type 5 is also called type 0. Where you have e e e o o o that means there is no change in polarization. When will that happen? When will no change in polarization happen? When a circle overlaps with the circle. A rectangle overlaps your sorry not rectangle a ellipse overlaps with o ellipse right. Right or wrong why did we get o o e earlier? Because the refractive index polar plot for refractive index of the o ray of the fundamental sorry e ray of the fundamental overlapped with the polar plot of the o ray of the second harmonic ok.

Now relative sizes can be different right depending on which material it is. Depending on that it is possible that one rectangle one ellipse will cut another ellipse ok. Then you get e e o kind of thing. And then if you mix 2 kind 2 different lights now if it is 2 different is it can be omega 1 + omega 1. But suppose you have taken that light and you have rotated the polarization by 90 degrees and combining. Then you are going to have o e then if it is type 3 or IIB you will get e polarization if it is type 6 of IIB or IIIB you will get o polarization ok. So there can be many combinations depending on what kind of whether the crystal is positive or negative and what kind of crystal it is?

There is compendium of which crystalize of this type in this book that we are studying you can look it up okay. But it is important to know this because polarization does have an important role to play in any nonlinear optical application that you want to work with okay right. So these o o e or e o e this you get for negative crystals and this are usually obtained for positive crystal. This way you can look at many different combination.

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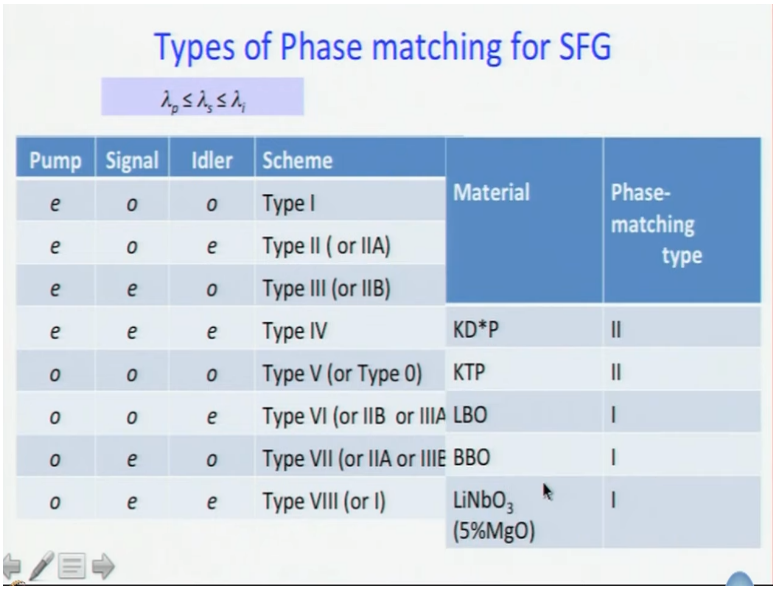

Types of Phase matching for SFG

$\lambda_p \le \lambda_s \le \lambda_i$

Pump	Signal	Idler	Scheme	Material	Phase-matching type
e	o	o	Type I		
e	o	e	Type II (or IIA)		
e	e	o	Type III (or IIB)		
e	e	e	Type IV	KD*P	II
o	o	o	Type V (or Type 0)	KTP	II
o	o	e	Type VI (or IIB or IIIA	LBO	I
o	e	o	Type VII (or IIA or IIIE	BBO	I
o	e	e	Type VIII (or I)	LiNbO$_3$ (5%MgO)	I

Now let me show you some example so this are some example KD star P what is that? What is KDP? What is KTP? Homework I will not tell you. You have to find out the only thing I will tell you is star means deuterium instead of hydrogen. But please find out what is KDP and what is KTP what is LBO BBO perhaps you know beta barium borate, but you should know what this means and what is this LiNbO3? Lithium niobite right lithium niobite.

So these are all different kinds of phase matching crystal. Last 3 are type 1 first 2 are type 2 okay. These are example that other examples as well. And the question is which of this will you use? Will you use type 1 nor type 2? As you see what some other parameters are there that become more important than type 1 or type 2 when we want to talk about using ultrafast pulses okay.

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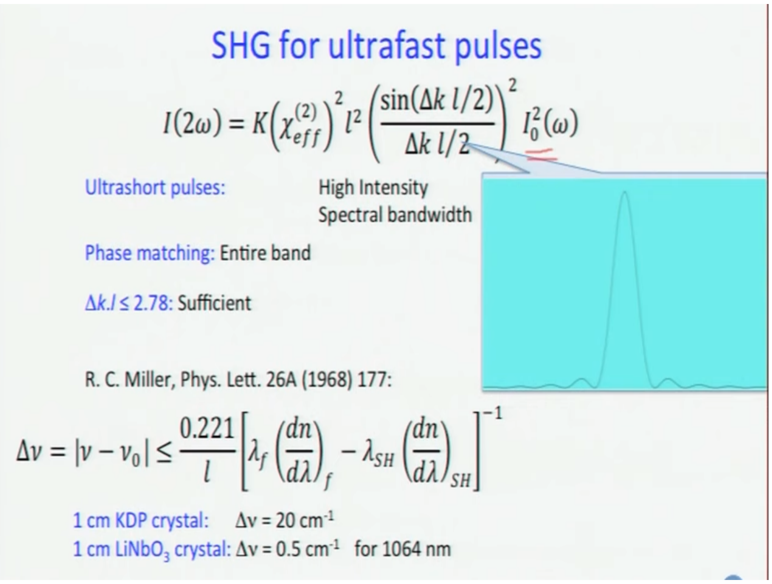

SHG for ultrafast pulses

$$I(2\omega) = K\left(\chi^{(2)}_{eff}\right)^2 l^2 \left(\frac{\sin(\Delta k\, l/2)}{\Delta k\, l/2}\right)^2 I_0^2(\omega)$$

Ultrashort pulses: High Intensity
Spectral bandwidth

Phase matching: Entire band

$\Delta k.l \le 2.78$: Sufficient

R. C. Miller, Phys. Lett. 26A (1968) 177:

$$\Delta\nu = |\nu - \nu_0| \le \frac{0.221}{l}\left[\lambda_f\left(\frac{dn}{d\lambda}\right)_f - \lambda_{SH}\left(\frac{dn}{d\lambda}\right)_{SH}\right]^{-1}$$

1 cm KDP crystal: $\Delta\nu = 20\ \text{cm}^{-1}$
1 cm $LiNbO_3$ crystal: $\Delta\nu = 0.5\ \text{cm}^{-1}$ for 1064 nm

So to understand that once again let us go back to this expression that we had written a little earlier. Which parts of these this expression are going to be helped by ultra-short pulses and which facts are going to be made more difficult? First of all we all have we have discussed earlier that ultra-short pulses has high intensity that is one feature. Second feature is that it has a spectral bandwidth is that good or is that bad?

High intensity is good is not it because here you have this factor of I0. So laser pulse if you use ultra-short pulses then at least this I0 square is going to be high anyway and we know why? We have discussed that already. Now spectral bandwidth is good or is it bad? We have telling you it is bad. Why it is bad? What is the discussion we have had so far? We said remember the k vectors this k is written here.

So the entire discussion was based on the fact that you have to have an exact phase matching that is delta k has to be equal to 0. Now what do you have in a pulse light? Is it monochromatic it is not. What does it mean? It has many color many different what we called plane waves. A plane wave is essentially a monochromatic wave where you have these parallel planes that define different amplitudes different phases ok.

So this is not a plane wave. We will discuss may be in the next module what it is? But this is the problem. How are we going to achieve delta k = 0 when there are so many case? You get the problem. It is a problem ok. So the problem is that you have to somehow achieve phase matching for the entire band. How will you do it? Well nature gives us a way out fortunately and from this expression can you tell me what the way out is? What is the natural way out natural that word is a hint?

If I want to plot this function I2 omega what will I get? Will I get a delta function? Then what is the factor that yes what is the important factor in this discussion sin square theta by theta square. That has some finite width is not it? Remember in our discussion of line width and all Sin square theta / theta square is the minimum line width that has to be there. Even if you have 2 specific states and that is what give you natural line width with spectral lines.

So this is the plot really you remember. So thing is this here at this point sin square theta / theta square = 0. But you do have a width alright. So even this is not exactly 0 so if you consider the width of this function and all it turns out that it is sufficient you can manage to get phase matching provided delta k into l is less that equal to 2.78 ok no the this 2.78 just comes from you know numerical solution of this problem.

I cannot write a formula and say that this is why it is 2.78 difficult to do that right. But if you look at the pulses it turns out that you are ok provided delta k into l is less that equal to 2.78 ok. Now what is the meaning of delta k once again? Delta k means basically difference between the a k vectors right. So if you have many k vectors you will have several delta k values within this limit.

So here if you read this ancient paper you will see that ok. What does each k characterize? It characterizes 1 particular plane wave right. That particular plane wave will also characterize by a characteristic frequency. So what this paper does from 1968 is that it starts from this delta k dot l less that equal to 2.78 and works out the expression for delta Nu. Where Nu is something we understand better and Nu is something that we work with little better.

We will not do the derivation I will just show you the expression. Delta Nu where delta Nu is Nu - Nu 0. What is Nu 0 the central frequency. So delta Nu - Nu 0 is only half of the band right. So Nu - N0 has to be less than equal to 0.221 / l multiplied by lambda f dn d lambda f, f stand for fundamental minus lambda second harmonic dn d lambda second harmonic reciprocal of that. What is dn d lambda? What is n here? Refractive index right and we know that refractive index is a function of frequency.

dn d lambda is the rate of change of wavelength with respect to sorry rate of change of refractive index with respective to wavelength that is all ok gradient ok. So this is what it is? So now from here if you know which fundamental wavelength you are dealing with and dn d lambda for fundamental as well as second harmonic can be known experimentally. From a for a the material and I hope you understand that dn d lambda for fundamental or dn d lambda of second harmonic is going to depend solely on the material that you are using ok.

And it is not very difficult to work you take a thin slices of the material see how much of change and refractive index is there and you can work it out. So from there for a 1 centimeter KDP crystal it turns out that delta Nu is 20 cm inverse whereas for 1-centimeter lithium niobite crystal delta Nu is only 0.5 centimeter inverse. But then I cannot just stop here I have to say which wavelength it is?

It will depend on lambda fundamental lambda second harmonic also. So the wavelength that we are working with is 1064 nanometer. What is the claim to frame of 1064 nanometer? 1064 nanometer is the magic number what is it? Yes is the fundamental emission of Nd YAG right the one of the most popularly widely use laser 1064 nanometer you will recognize the second harmonic better 532 nanometer. So if I want to convert 1064 nanometer to 532 nanometer which material would be better. If I am using a pulse should it be KDP should it be lithium niobite. Let us close this module on this note we will come back in the next module and we will discuss from this point on.